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Volume 33

MOLTEN ALKALI METAL ALKANOATES

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SOLUBILITY DATA SERIES



Editor-in-Chief A.S. KERTES

Volume 33

MOLTEN ALKALI METAL CALKANOATES

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IN MEMORIAM



Dr. Paolo Franzosini, Professor of Physical Chemistry, University of Pavia, Italy, and the Editor of this volume, passed away on January 24, 1986 at the age of 56.

Born in Trecate, near Turin, he received his university education while on a prestigious scholarship at the Collegio Ghislieri of the University of Pavia, graduating with honors in 1952. He then spent two years as a postdoctoral research assistant with Professor Clusius in the Department of Physical Chemistry at the Federal Polytechnic Institute of Zurich. In the years 1955-1960 he served as Assistant Professor at the University of Pavia, and had been promoted to the rank of Associate Professor at the early age of thirty. In 1965 he moved to the University of Camerino as Professor and Chair of Physical Chemistry. In 1968 he was back at his alma mater as Professor of Electrochemistry, and in 1980 as the Chair of Physical Chemistry. In 1979 he served as Visiting Professor at the University of Mogadiscio, Somaliland, and in 1981 at the University of Michigan in Ann Arbor.

In the thirty years of scientific activity, he published over 100 papers, mostly in the field of thermodynamics and thermochemistry of molten salt systems. He made significant contribution to the Atlas of Miscibility Gaps in 1968, and to the Atlas of Phase Diagrams in 1973 on molten salts with organic anions. In 1980 he coedited, with Professor Sanesi, Volume 28 of IUPAC's Chemical Data Series on Thermodynamics and Transport Properties of Organic Salts. In the years 1978-1984 he was member of IUPAC Commission on Thermodynamics. In 1982 he joined the Solubility Data Project and served as the National Representative of Italy to IUPAC's Commission on Solubility Data. At that time he was appointed Editor of the present volume.

He has not seen the completion of this volume. Thanks to the devotion and expertise of his colleagues, Professors Ferloni, Schiraldi and Spinolo of the Department of Physical Chemistry, University of Pavia, this volume, the final major work of Professor Franzosini, was brought to completion.

Paolo was an interesting intellect with a broad European humanitarian culture. He was a Rotarian from an early age, president of the Rotary Club of Pavia, and served in the distinguished position of Rotary District Governor in 1982-3.

Through the generosity of the Franzosini family, it has been possible for the Solubility Data Commission to establish the Paolo Franzosini Endowment Fund, the proceeds of which to assist young scientists in their association with IUPAC's Solubility Data Project.

We are all diminished by his passing.

A.S. Kertes Editor-in-Chief

Jerusalem, March 1988

FOREWORD

If the knowledge is undigested or simply wrong, more is not better

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the Solubility Data Project is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission products from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books and other tabulated and graphical compilations - as they exist today are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, and thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to the advancement of science is at least questionable. Additionally, the change which is ta'ing place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature. Foreword

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the Solubility Data Project is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The Solubility Data Project has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover all relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

- (1) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;
- (ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;
- (iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

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The typical data sheet carries the following information:

- components definition of the system their names, formulas and (i) Chemical Abstracts registry numbers;
- reference to the primary source where the numerical information is (11) reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
- (i1i) experimental variables; (iv) identification of the compiler;
 - (v) experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

- (v1) experimental method used for the generation of data; (vii) type of apparatus and procedure employed;
- (viii) source and purity of materials;
- (ix) estimated error;
 - (x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

PREFACE

1.Phase relationships of alkali alkanoates.

1.1. Solid state transitions of alkali alkanoates.

Most alkali alkanoates (either linear or branched) exhibit polymorphism in the solid state, and the number of phases tends to increase with increasing chain length. However, controversy often exists about the number, nature, and stability range of the polymorphs present in a given salt. Since different hydrates appear as well, "in the literature one may find almost the whole Greek alphabet, primed and unprimed, each notation supposed to define a separate phase. It has been maintained that each such phase is associated with a unique crystal structure, while others have claimed that the different X-ray diffraction patterns do not necessarily represent true crystal structures, but instead are merely associated with different types of disorder of the chains. There is also the additional problem of the descendant phases, i.e., structures that occur at some elevated temperature and remain unaltered at room temperature in a pseudoequilibrium for a long time" (Ref. 1). The present volume discusses solubilities of those linear alkali alkanoates marked with a cross in the scheme below, and, as well, the iso-butanoates and iso-pentanoates of Na and K. No information is available so far on the solubilities of other alkali alkanoates.

- 44 AL an ai 44 AL ai 46 AL an ai 46 AL ai	Numb	oer (of ca	irboi	n ato	ons,	n _C ,			
Cation	1	2	3	4	5	6	7	3	9	18
LI	x	x	x	x						
Na	×	×	x	x	x	x				x
К	x	×	x	x	×	×	×	x	x	
Rb		x								
Cs		x								

In order to obtain a homogeneous picture of the thermal behavior (in terms of phase transformation temperatures and enthalpy changes) of alkali alkanoates, more than 100 linear and branched homologues belonging to the different alkali families have been submitted to DSC analysis during the last few years in the editor's laboratory. The results obtained on heating are thought to offer an acceptable degree of trustworthiness and internal consistency. Therefore, as useful background material for discussion of the solubility curves, the pertinent superambient solid state transition temperature, T_{trs} , are collected in Tables 1 and 2. These temperatures represent first order, or predominantly first order, phase transitions. For completeness, the temperatures of fusion, T_{fus} , and of clearing, T_{clr} , (when they exist) are also listed in Tables 1 and 2. However, the data on sodium octadecanoate (produced in a different laboratory) are listed separately in Table 4.

The following remarks can be made about the precision and accuracy of the data reported in Tables 1, 2.

Precision is not infrequently better than ± 1 K, although becoming poorer in some cases: in particular, very poor reproducibility was obtained for solid state transitions of sodium methanoate and ethanoate.

Accuracy is thought to be often of the same order of magnitude as precision. However, one must consider that DSC is a dynamic method of investigation, and that some solid state transitions of methanoates and ethanoates are characterized (even on heating at a moderate scanning rate) by a remarkable sluggishness. Consequently, in Tables 1, 2 the T_{trs} data for the shortest homologues can be somewhat too high. This disadvantage tends

Preface

to decrease in the next higher homologues, and does not involve fusion and clearing. As an example, high accuracy equilibrium adiabatic calorimetric data, taken very recently by Franzosini et al. (Refs. 8, 9) on sodium methanoate and propanoate, are compared in Table 3 with the previous DSC values. The comparison also includes the enthalpy changes involved.

For sodium octadecanoate, reference will be made to the recent DSC data by Forster et al. (Ref. 10), collected in Table 4.

Table 1 - $T_{clr},\ T_{fus},$ and superambient T_{trs} values determined by DSC for 21 linear alkali alkanoates.

nC	Cation	T _{clr} /K	T _{fus} /κ	τ' _{trs} /κ	τ" _{trs} /κ	T" ^f trs/K	T ^{IV} trs/K	Ref.
1	Li Na K	- - -	546 <u>+1</u> 530.7+0.5 441.9 <u>+</u> 0.5	496+2 502+5 418 <u>+</u> 1	- - -			2 3 3
2	Li Na K Rb Cs	- - - -	557+2 601.3+0.5 578.7+0.5 514+1 463+1	527+15 422.2+0.5 498+1	465 <u>+</u> 3 _ _ _	414 <u>+</u> 10		2 2 2 2 2 2
3	Li Na K	-	606.8+0.5* 562.4+0.5 638.3+0.5	533+2 494+1 352•5+0•5	470.2+0.5			2 2 2
4	Li Na K	- 600.4+0.2 677.3+0.5	591.7+0.5 524.5+0.5 626.1+0.7	508.4+0.5 562.2+0.6	498.3+0.3 540.8+1.1	489.8+0.2 467.2+0.5	450,4+0.5 461,4 <u>+</u> 1.0	2 4 4
5	Na K	631+4 716+2	498 <u>+</u> 2 586.6 <u>+</u> 0.7	- 399.5 <u>+</u> 0.9	-			5 5
6	Na K	639.0+0.5 725.3+0.8	499.6+0.6 531.7 <u>+</u> 0.5	473 <u>+</u> 2	386+2		~ ~	5 5
7	ĸ	722 <u>+</u> 3	571.3 <u>+</u> 0.9	345.4 <u>+</u> 0.6	332.0+0.8			5
8	ĸ	712+2	560.6+0.8	326.6+0.1				6
2	K	707.4 <u>+</u> 0.8	549.1 <u>+</u> 0.8	390.5 <u>+</u> 0.4	367.5 <u>+</u> 0.5	*		6

clr: clearing; fus: fusion; trs: transition * A metastable fusion point was also detected at $T_{fus(m)}/K = 584\pm1$

Table 2 - $T_{clr},\ T_{fus},\$ and superambient T_{trs} values determined by DSC for 4 alkali iso-alkanoates.

nC	Cation	T _{clr} /K	T _{fus} /K	T'trs/K	Ref.
4	Na K	- 625.6 <u>+</u> 0.8	526.9+0.7 553.9+0.5	- 424 <u>+</u> 3	7 7
5	Na K	559 <u>+1</u> 679 <u>+</u> 2	461.5 <u>+</u> 0.6 531 <u>+</u> 3	-	7 7 7

clr: clearing; fus: fusion; trs: transition

nC	Cation	Quantity	Value	liethod	Ref
1	Na	T _{fus} /K T _{trs} /K (Δ _{fus} H _m /R)/K (Δ _{trs} H _m /R)/K	530.46+0.04 530.7+0.5 491.5+1 502+5 2130 (*) (2.06+0.05) 150 (*) (1.41+0.05)	ad.cal. DSC ad.cal. DSC ad.cal. 10 ³ DSC ad.cal. 10 ² DSC	8 3 8 3 8 3 8 3 3
3	Na	T_{fus}/K T_{trs}/K T_{trs}/K $(\Delta_{fus}H_m/R)/K$ $(\Delta_{trs}H_m/R)/K(**)$	561.88 ± 0.03 562.4 ± 0.5 491 ± 1 494 ± 1 467 ± 1 470.2 ± 0.5 1597.3 ± 0.6 (1.61 ± 0.05) (0.91 ± 0.02) (0.89 ± 0.05)	ad.cal. DSC ad.cal. DSC ad.cal. DSC ad.cal. 103 DSC 103 ad.cal. 103 DSC	9 2 9 2 9 2 9 2 9 2 9 2 2 9

Table 3 - Comparison between adiabatic calorimetric and DSC data.

fus: fusion; trs: transition

(*) Single determination.

(**) Cumulative enthalpy change relevant to both solid state transitions.

Table 4 - T_{clr}, T_{fus}, and superambient T_{trs} values determined by DSC for sodium octadecanoate.

	T _{clr} /K	T' _{trs} /K	τ _{fus} /κ	Τ" _{trs} /κ	T"´trs/K	T ^{IV} trs/K	T ^V trs/K	T ^{VI} trs/K
	552.7	547.7	527.2	469/476	448	408	390	368
L.	NI	NI	I S	SN	SpW W	SW	CI	CII

clr: clearing; fus: fusion; trs: transition

L: isotropic liquid; N: neat; SN: subneat; SpW: superwaxy; W: waxy; SW: subwaxy; C: crystal.

1.2. Mesomorphism in alkali alkanoates.

Mesomorphic phases (liquid crystalline, or plastic crystalline, or both) can also form in alkali alkanoates, the stability range of the mesomorphic state being intermediate between those of the "true" crystalline and of the "true" liquid phases. In particular, liquid crystals (likely of the smectic type) form in linear alkanoates, starting with butanoate when the cation is either sodium or potassium, from pentanoate when the cation is rubidium, and from hexanoate when the cation is caesium. No liquid crystals form when the cation is lithium. In long chain homologues (which, however, are of little relevance to the present purposes) plastic crystals form for all alkali cations. (See, e.g., the data reported in Table 4 for sodium octadecanoate.)

Unfortunately, the nomenclature employed by different authors is far from homogeneous. In particular, most Russian investigators call "fusion" the transformation of either a crystalline solid or a liquid crystal into an isotropic liquid which is often misleading in the interpretation of phase diagrams. More reasonably, in non - Russian literature a distinction is usually made between clearing temperature, T_{clr} (i.e., the temperature at which a liquid crystal transforms into an isotropic liquid), and fusion temperature, T_{fus} (i.e., the temperature at which a "true" crystal transforms into either an isotropic liquid or a liquid crystal)(*). Further details on these points are given in Section 2.2.

(*) It might be further considered whether in the sequence (met in several long chain alkali alkanoates): crystal --> plastic crystal(s) --> liquid crystal(s) --> isotropic liquid the term "fusion" should be applied to the first or to the second transformation, but such a discussion would be of little relevance here. In Table 4 the term fusion was applied to the transformation from the (plastic crystalline) subneat to the (liquid crystalline) neat I phase. The literature contains reports on the phase diagrams of 58 binaries (9 with common anion, and 49 with common cation), involving alkali alkanoates which exhibit mesomorphism: they are listed in Table 5 where the component(s) which can exist in the mesomorphic liquid state are underlined.

Unfortunately, information is mostly restricted to the lower boundary of the isotropic liquid field. More details are available only in a limited number of cases among which special interest is to be attached to the following: a) $(C_{4H70_2})K + (C_{4H70_2})Na$, b) $(C_{4H70_2})Li + (C_{4H70_2})Na$, c) $KC_{2H30_2} + KC_{4H70_2}$, d) $NaC_{2H30_2} + NaC_{4H70_2}$, and e) $NaC_{4H70_2} + NaN0_3$, inasmuch as a comparison is here possible between the results obtained by Prisyazhnyi et al. (Refs. 11, 12), who studied the lower boundaries of both the isotropic liquid and the liquid crystal fields, and those obtained by previous authors, who studied only the lower boundary of the isotropic liquid.

Table 5 - Binaries involving at least one alkali alkanoate able to exist in the liquid crystalline state.

Systems with common anion:

1)	~(C4H7O2)2K2	(C4H702)2Mg	2)	~(C4H7O2)K	~(C4H7O2)Na
3)	~(1.C4H7O2)K	(i.C4H702)Na	4)	(C4H7O2)L1	~(C4H7O2)Na
5)	(C4H7O2)2Mg	~(C4H702)2Na2	6)	~(C5H9O2)K	~(C5H9O2)Na
7)	~(1.C5H9O2)K	~(i.C5H902)Na	8)	(C5H9O2)2Mg	~(C5H9O2)2Na2
9)	~(C6H1102)K	$\sim (C_6H_{11}O_2)Na$	-,	· J J-2/2-0	· J J L/L·····L

Systems with common cation:

KC2H3O2	~KC4H702	11)	KC2H3O2	~Ki.C4H7O2
KC2H302	~KC5H902	13)	KC2H302	~Ki.C5H9O2
KC2H3O2	~KC6H1102	15)	~кс4н702	KCNS
~KC4H702	KNO ₂	17)	~кс4н702	KNO3
~K1.C4H702	KNO ₂	19)	~K1.C4H7O2	KN03
~KC5H9O2	KNO2	21)	~кС5Н902	KNO3
~K1.C5H902	KNO ₂	23)	~Ki.C5H9O2	KNO3
~KC6H1102	KN02	25)	~KC7H1302	KNO2
~KC8H1502	KNO ₂	27)	~KC9H1702	KNO ₂
NaCHO2	~NaC4H702	29)	NaCHO ₂	~Nai.C5H902
NaC ₂ H ₃ O ₂	~NaC4H7O2	31)	NaC ₂ H ₃ O ₂	~NaC5H9O2
NaC ₂ H ₃ O ₂	~Nai.C5HgO2	33)	NaC ₂ H ₃ O ₂	~NaC6H11O2
~NaC4H702	Nai.C4H7O2	35)	~NaC4H702	~Nai.C5H9O2
~NaC4H7O2	~NaC6H1102	37)	~NaC4H7O2	NaC7H5O2
~NaC4H7O2	~NaC18H3502	39)	~NaC4H7O2	NaCNS
~NaC4H702	NaNO ₂	41)	~NaC4H7O2	NaNO3
Nai.C4H7O2	~Nai.C5H9O2	43)	Nai.C4H7O2	~NaC6H1102
Nai.C4H702	~NaC18H3502	45)	~NaC5H9O2	NaCNS
~NaC5H9O2	NaNO ₂	47)	~NaC5H9O2	NaNO ₃
~Nai.C5HgO2	~NaC6H1102	49)	~Nai.C5H9O2	NaC7H502
~Nai.C5H902	~NaC18H3502	51)	~Nai.C5H9O2	NaCNS
~Nai.C5H9O2	NaNO ₂	53)	"Nai.C5H9O2	NaNO ₃
~NaC6H1102	NaC7H502	55)	~NaC6H1102	~NaC18H3502
~NaC6H1102	NaCNS	57)	~NaC6H1102	NaN03
NaC7H502	~NaC18H35O2			-
	KC2H302 KC2H302 KC2H302 KC4H702 KC5H902 KC5H902 KC5H902 KC6H1102 KC6H1102 KC6H102 NaC2H302 NaC2H302 NaC2H302 NaC2H702 NaC4H702 NaC4H702 Na1.C4H702 Na1.C4H702 Na1.C4H702 Na1.C5H902 Na2.C6H1102 NaC6H102 NaC7H502	KC2H302 ~KC4H702 KC2H302 ~KC5H902 KC2H302 ~KC6H1102 ~KC4H702 KN02 ~KL.C4H702 KN02 ~KL.C4H702 KN02 ~KC5H902 KN02 ~KC5H902 KN02 ~KC6H1102 KN02 ~KC6H102 KN02 ~KC6H102 KN02 ~KC6H102 KN02 ~KC6H102 KN02 ~NaC4H702 NaC4H702 NaC4H702 Na1.C5H902 ~NaC4H702 NaC6H1102 ~NaC4H702 NaC6H1102 ~NaC4H702 NaC18H3502 ~NaC4H702 NaN02 Nat.C4H702 Nal.C5H902 Nat.C4H702 Nal.C5H902 Nat.C5H902 Nal.C5H902 Nat.C5H902 Nal.C3H3502 ~Nat.SH902 NaN02 ~Nat.SH902 NaN02 ~Nat.SH902 Nal.C7H502 ~Nat.SH902 Nal.C5H902 ~Nat.SH902 Nal.C5H902 ~Nat.SH902 Nac6H1102	KC2H302 ~KC4H702 11) KC2H302 ~KC5H902 13) KC2H302 ~KC6H1102 15) ~KC4H702 KN02 17) ~KL.C4H702 KN02 19) ~KC5H902 KN02 19) ~KC5H902 KN02 21) ~KL.C4H702 KN02 23) ~KC6H1102 KN02 25) ~KC8H1502 KN02 23) NaCH02 ~NaC4H702 31) NaC2H302 ~NaC4H702 31) NaC4H702 NaI.C4H702 37) ~NaC4H702 NaI.C5H902 43) Na1.C4H702 NaI.C5H902 43) Na1.C4H702 NaI.C5H902 45) ~NaC4H702 NaN02 47) Na1.C4H702 <td< td=""><td>KC2H302 ~KC4H702 11) KC2H302 KC2H302 ~KC5H902 13) KC2H302 KC2H302 ~KC6H1102 15) ~KC4H702 KC4H702 KN02 17) ~KC4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC5H902 KN02 21) ~KC5H902 ~KL.C5H902 KN02 23) ~KL.C5H902 ~KC6H1102 KN02 25) ~KC7H1302 ~KC8H1502 KN02 27) ~KC9H1702 NaCH02 ~NaC4H702 31) NaC2H302 NaC2H302 ~NaC4H702 33) NaC2H302 NaC4H702 Na1.C5H902 33) NaC4H702 ~NaC4H702 Na1.C4H702 39) ~NaC4H702 ~NaC4H702 Na02 41) ~NaC4H702 ~NaC4H702 Na02 41) ~NaC4H702 Na1.C4H702 ~NaC18H350</td></td<>	KC2H302 ~KC4H702 11) KC2H302 KC2H302 ~KC5H902 13) KC2H302 KC2H302 ~KC6H1102 15) ~KC4H702 KC4H702 KN02 17) ~KC4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC4H702 KN02 19) ~KL.C4H702 ~KC5H902 KN02 21) ~KC5H902 ~KL.C5H902 KN02 23) ~KL.C5H902 ~KC6H1102 KN02 25) ~KC7H1302 ~KC8H1502 KN02 27) ~KC9H1702 NaCH02 ~NaC4H702 31) NaC2H302 NaC2H302 ~NaC4H702 33) NaC2H302 NaC4H702 Na1.C5H902 33) NaC4H702 ~NaC4H702 Na1.C4H702 39) ~NaC4H702 ~NaC4H702 Na02 41) ~NaC4H702 ~NaC4H702 Na02 41) ~NaC4H702 Na1.C4H702 ~NaC18H350

~ Compounds which form liquid crystals.

In order to improve homogeneity and succinctness in discussing the systems in Table 5, it seemed convenient to present here a selection of model phase diagrams [see Schemes A, \dots , D (*)] to which reference will be made in the subsequent critical evaluations.

(*) Schemes A, ..., D were drawn in the - usually accepted - assumption that any (actually known) transformation

mesomorphic phase <==> isotropic liquid
is first order.







Preface



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It must be noted that in these diagrams the presence of liquid crystals causes the occurrence of invariants to which no official designation has been given so far. Therefore, in order to avoid misunderstandings, throughout the present volume we indicate (provisionally) as M_E an invariant at which liquid crystals, LC (and not an isotropic liquid, IL, as in a common eutectic, E), are in equilibrium with two solids; and, respectively, as M_E an invariant at which an isotropic liquid is in equilibrium with the liquid crystals and one solid phase (and not with two solid phases, as in a common eutectic, E). Here the subscript E is added because the situation of the equilibrium curves involved is similar to that met at a eutectic point.

For situations similar to those met in Schemes B, the subscript P will be used.

By analogy, invariants (met in subsequent Schemes) involving equilibria among two liquid crystalline and one isotropic liquid phase will be indicated as M_E^* and M_P^* , respectively. Finally, invariants involving two liquid crystalline and one solid phase (i.e., exhibiting a situation similar to that met in a monotectic) will be designated as M_M points.

Scheme A.1.

Component 1 can exist as a liquid crystal between $T_{fus}(1)$ and $T_{clr}(1)$. Component 2 melts at $T_{fus}(2)$, and actually cannot exist as a liquid crystal. Components 1, 2 are assumed to be partially miscible in the solid state (*). The binary invariants are an M_E and an M_E point.

Scheme A.2.

This differs from Scheme A.1 in that a maximum, M, is present in the liquid crystal - isotropic liquid equilibrium curves.

Scheme A.3.

This differs from Scheme A.1 in that complete mutual solubility (with a minimum, m) is assumed for components 1, 2 in the solid state.

Scheme B.1.

This differs from Scheme A.1 in that the isotropic liquid - liquid crystal equilibrium curves impinge on the liquidus branch richer in component 1. Accordingly the binary invariants are a eutectic, E, and an M'p point.

Schemes B.2, B.3.

These represent self-explanatory modifications of Scheme B.1.

Scheme C.1.

Both components can exist as liquid crystals between $T_{fus}(1)$ and $T_{clr}(1)$, and between $T_{fus}(2)$ and $T_{clr}(2)$, respectively. Mutual solubility is assumed to be complete in the mesomorphic liquid, and limited in the solid state. The only binary invariant is an M_E point.

Scheme C.2.

This differs from Scheme C.1 in that a limited mutual solubility is assumed for the components in the liquid crystalline state. Besides the M_E point, two more binary invariants exist, i.e., an M_E and an M_M point.

Scheme C.3.

This is a special case (Ref. 13) where four liquid crystal - isotropic liquid diphasic fields ought to be formed, with one maximum, M, and two minima, m_1 and m_2 , respectively.

Scheme D.1.

Component 1 can exist as a liquid crystal between $T_{fus}(1)$ and $T_{c1r}(1)$. Component 2 melts at $T_{fus}(2)$, and cannot exist as a liquid crystal. An intermediate compound $\{(1)_2(2)_3 \text{ in the Scheme; } D: dystectic point]$ is formed, which cannot exist as a liquid crystal. The binary invariants are E, M_E , M_E^* .

(*) Indeed, the complete absence of mutual solubility in the solid state has to be considered an exception rather than the rule.

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Scheme D.2.

This differs from Scheme D.1 in that liquid crystal formation is assumed for both components.

Scheme D.3.

This differs from Scheme D.1 in that the intermediate compound melts yielding a liquid crystalline and an isotropic liquid phase; consequently, an M'p point is formed.

Detailed information (updated 1979) on the phase relationships of alkanoates are given in Chapter 1.2 (Ref. 14) of a volume on thermodynamic and transport properties of organic salts published (1980) as a book project of the IUPAC Commission on Thermodynamics.

2. Some ambiguities met in the current literature.

2.1. Transition and peritectic points in binary systems.

Breaks along a branch of the lower boundary of the isotropic liquid region in a binary (where, for simplicity it is assumed that no mesomorphic phases are involved) can arise from the occurrence of

- (a) polymorphic (first order) transformations in either component (examples are shown in Schemes E.1 - E.3);
- (b) limited mutual solubility of the components in the solid state (an example is shown in Scheme F);
- (c) incongruent fusion of an intermediate compound (an example is shown in Scheme G).
- (i) In Schemes E.1 E.3 component 1 undergoes (at constant pressure) the polymorphic (first order) transformation

$$(1)_{II} \xrightarrow{T_{trs}(1)} (1)_{I}$$

In Scheme E.1, it is further assumed that component 2 (in the solid state) is soluble in neither polymorph of component 1. At $T_T = T_{trs}(1)$, equilibrium exists among solid polymorphs (1)_I and (1)_{II}, and the isotropic liquid of composition x_T :

$$(1)_{II} + (IL)_T \rightleftharpoons (1)_I + (IL)_T \text{ i.e. } (1)_{II} \rightleftharpoons (1)_I$$

Scheme E.2 shows one of the possible situations which can be met when it is assumed that component 2 is soluble only in one polymorph of component 1 [in Scheme E.2: in polymorph (1)_{II} stable at $T \leq T_{trs}(1)$]. At $T_p \neq T_{trs}(1)$ [in Scheme E.2: $T_p > T_{trs}(1)$], equilibrium exists (at constant pressure) among solid polymorph (1)_I, solid solutions S [of composition x_S , and formed with polymorph (1)_{II} and component 2], and isotropic liquid of composition x_p :

$$(1)_{\mathrm{I}} + (\mathrm{IL})_{\mathrm{P}} \rightrightarrows \mathrm{S}$$

Scheme E.3 shows one of the possible situations which can be met when it is assumed that component 2 is soluble in either polymorph of component 1. At T_P , the phases in invariant equilibrium (at constant pressure) are: the isotropic liquid of composition x_P , and two solid solutions of composition x_{S_R} and $x_{S_{C_r}}$, respectively.

In Schemes E, the isotropic liquid of composition either x_T (Scheme E.1), or x_P (Schemes E.2, E.3) is incongruent with respect to the two solid coexisting phases (i.e., the liquid cannot be synthetized from the solids). When in a binary the incongruent liquid is in equilibrium (at constant pressure) with two solids of the same composition [i.e., in Scheme E.1: polymorphs (1)_I and (1)_{II}] the point representing the liquid phase (in Scheme E.1: point T, whose abscissa is x_T) is designated as a transition point.

When in a binary the incongruent liquid is in equilibrium (at constant pressure) with two solids of different composition, Haase and Schoenert (Ref. 15) call the point representing the liquid phase (i.e., in Schemes E.2 and E.3: point P, whose abscissa is x_p) a peritectic point. Haase and Schönert's definition of peritectic



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point is convenient for the present purposes, but less restrictive than other widely used formulations. A detailed discussion is unnecessary here, but if any other formulations are accepted, the various situations should be considered accordingly.

(ii) In Scheme F, components 1 and 2 are assumed to exhibit a limited mutual solubility in the solid state. At the peritectic point, P, the equilibrium is:

 $S_{\alpha} + (IL)_{P} = S_{\beta}$

(iii) Finally, in Scheme G, the intermediate compound $[(1)_2(2)$, in the specific case] is said to melt incongruently at T_P because (at this temperature) the isotropic liquid, (IL)_P, is once more incongruent with respect to both solid phases [i.e., (1)₂(2) and (1)] entering the peritectic equilibrium

$$(1) + (IL)_{p} = (1)_{2}(2)$$

In this case, the invariant, P, is designated either a peritectic point, or transition point of the peritectic type (Ref. 15).

(iv) The situations shown in Schemes E-G, though apparently far different from one another, can be distinguished only with difficulty in the absence of information on the solidus, e.g., on the phase relations of the pure components, the Tammann triangles (examples of with are shown in Scheme G), etc. Unfortunately, a number of authors, who restricted their investigations to the visual polythermal determination of the liquidus, were frequently inclined either to assume a break on a liquidus branch as an evidence for the existence of an incongruently melting compound (correct only in Scheme G), or to identify the temperature at which a break occurs with that at which a pure component undergoes a phase transition (correct only in Scheme E.1).

As a final remark, it can be added that in the Russian literature an invariant point P is indicated only occasionally as a "peritekticheskaya tochka" (i.e., peritectic point), but most often as a "perekhodnaya tochka" which, however, is translated in English issues of the Russian journals as either transition point (a correct, though rather misleading, literal translation), or peritectic point, etc.

2.2. The case of pure components.

This subject was already mentioned in Section 1.2, but it is now thought useful to comment further on one or two specific papers.

(1) Sokolov, in one of his earliest studies (1954; Ref. 16) on alkanoates, reported that crystalline sodium methanoate, ethanoate, and propanoate melted directly into isotropic liquids, whereas several other sodium alkanoates behaved "as if they had two distinct fusion temperatures: the first one relevant to the transformation from the solid crystalline to the liquid crystalline phase, and the second one to that from the liquid crystalline to the isotropic liquid phase"(*). This statement was in agreement with previous findings by a few former authors known to him; see, e.g., Ref. 17.

Despite the correctness of the above assertions, Sokolov then decided unfortunately (Ref. 16) "to assume as the fusion temperature ... of both the pure salts and mixtures thereof the temperature at which the homogeneity of the melt disappeared"(*) (which, however, is correct only in the absence of mesomorphic phases).

This decision caused a misinterpretation of the topology of several among the many systems studied later on by the Smolensk group, as will be seen throughout the volume.

(11) In 1956 Sokolov (Ref. 18) provided information, during the 10th Scientific Conference of the Smolensk Medical Institute, on phase transformations occurring in several alkali alkanoates at T < T_{fus} . Here fusion is obviously to be intended in Sokolov's sense, i.e., either true fusion or clearing. This information - which concerned only temperatures, and not the nature of the transformations - appeared in the Summaries of Papers presented at the Conference. Sokolov's summary could not be directly consulted but, as far as we know, no numerical data were reported on it. None the less, it has been subsequently quoted by the investigators of the Smolensk group as the pertinent primary source. Comparison of such quotations, however, shows inconsistencies,

^{*} Translated from Russian by P. Ferloni, Pavia (Italy).

a few of which are:

- (a) There should be either three transitions of sodium propanoate (at 468, 490, and 560 K, respectively) according to Ref. 19, or four (at 350, 468, 490, and 560 K, respectively) according to Ref. 20.
- (b) There should be either two transitions of potassium n-butanoate (at 463, and 553-558 K, respectively) according to Ref. 21, or three (at 463, 553-558, and 618 K, respectively) according to Ref. 22.
- (c) There should be either two transitions of potassium iso-pentanoate (at 327, and 618 K, respectively) according to Refs. 21, 23, or three (at 473, 493, and 618 K, respectively) according to Ref. 24.

(111) Because divergent opinions have been expressed rather frequently by different authors about the number, nature, and location of phase transformations occurring in alkanoates, each single situation has been critically evaluated throughout the volume. No discussion, on the contrary, has been made of the phase transformations occurring in the inorganic components of the systems, inasmuch as data from various sources proved usually to be either coincident or negligibly different.

3. Tabulation of the systems.

Binaries with common anion have been listed in Part 1 of the volume following the increasing complexity of the anion, and, for a given anion, following the alphabetical order of the cation.

Example:

Component 1	Component 2
(CHO ₂) ₂ Ba (CHO ₂) ₂ Ba	(CHO ₂) ₂ K ₂ (CHO ₂) ₂ Na ₂
(CHO ₂) ₂ Ca	(CHO ₂) ₂ K ₂
(CHO ₂)K	(CHO ₂)Li
(C ₂ H ₃ O ₂) ₂ Cd	(C ₂ H ₃ O ₂)Cs Etc.

Binaries with common cation have been listed in Part 2 of the volume following the alphabetical order of the cation, and, for a given cation, following the self-explanatory scheme reported here.

Component 2
•••
KCHO ₂
KC2H302
KC3H502
KC4H702
K1-C4H702
KC1
Etc.

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Paolo Franzosini

INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

The Solubility Data Project (SDP) has as its aim a comprehensive search of the literature for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled on data sheets in a uniform format. The data for each system are evaluated, and where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

Definitions

A mixture (1, 2) describes a gaseous, liquid, or solid phase containing more than one substance, when the substances are all treated in the same way.

A solution (1, 2) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the solvent, and may itself be a mixture, is treated differently than the other substances, which are called solutes. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a dilute solution.

The solubility of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. Saturated implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the corresponding substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the quantities used as measures of solubility and in the reference states used for definition of activities, activity coefficients and osmotic coefficients.

The qualifying phrase "substance related chemically to B" requires comment. The composition of the saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportion of anhydrous salt in solution, rather than the relative proportions of hydrated salt and water.

Quantities Used as Measures of Solubility

1. Mole fraction of substance B, xB:

 $x_{B} = n_{B} / \sum_{s=1}^{C} n_{s}$ [1]

where $n_{\rm S}$ is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). Mole per cent of B is 100 x_B .

2. Mass fraction of substance B, wg:

$$w_{B} = m_{B}' / \sum_{s=1}^{C} m_{s}'$$
 [2]

where $m_{\rm g}'$ is the mass of substance s. Mass per cent is 100 wg. The equivalent terms weight fraction and weight per cent are not used.

3. Solute mole (mass) fraction of solute B (3, 4):

$$x_{s,B} = m_B / \sum_{g=1}^{C'} m_g = x_B / \sum_{g=1}^{C'} x_g$$
 [3]

$$w_{s,B} = m_{B'} / \sum_{g=1}^{C'} m_{g'} = w_{B} / \sum_{g=1}^{C'} w_{g}$$
 [3a]

where the summation is over the solutes only. For the solvent A, $x_{S,A} = x_A/(1 - x_A)$, $w_{S,A} = w_A/(1 - w_A)$. These quantities are called Jänecke mole (mass) fractions in many papers.

4. Molality of solute B (1, 2) in a solvent A:

 $m_{\rm B} = n_{\rm B}/n_{\rm A} M_{\rm A}$ SI base units: mol kg⁻¹ [4]

where M_A is the molar mass of the solvent.

5. Concentration of solute B (1, 2) in a solution of volume V:

 $c_B = [B] = n_B/V$ SI base units: mol m⁻³ [5]

The symbol c_B is preferred to [B], but both are used. The terms molarity and molar are not used.

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions among these quantities can be carried out using the equations given in Table I-1 following this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

6. Density: $\rho = m/V$ SI base units: kg m⁻³ [6]

7. Relative density: d; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol d_t' will be used for the density of a mixture at t°C, 1 bar divided by the density of water at t'°C, 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)

8. A note on nomenclature. The above definitions use the nomenclature of the IUPAC Green Book (1), in which a solute is called B and a solvent A In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation sheets.

Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-12).

Activity Coefficients (1)

(a) Mixtures. The activity coefficient f_B of a substance B is given

RT ln
$$(f_B x_B) = \mu_B - \mu_B^*$$
 [7]

where μ_B^* is the chemical potential of pure B at the same temperature and pressure. For any substance B in the mixture,

$$\lim_{\mathbf{X}_{\mathbf{B}} \to \mathbf{1}} f_{\mathbf{B}} = \mathbf{1}$$
 [8]

[10]

(b) Solutions.

γB^{®®}

= 1

by

(1) Solute B. The molal activity coefficient γ_B is given by RT $\ln(\gamma_B m_B) = \mu_B - (\mu_B - RT \ln m_B)^{\infty}$ [9]

where the superscript $^{\infty}$ indicates an infinitely dilute solution. For any solute B,

Activity coefficients y_B connected with concentrations c_B , and $f_{X,B}$ (called the rational activity coefficient) connected with mole fractions x_B are defined in analogous ways. The relations among them are (1, 9), where ρ^* is the density of the pure solvent:

$$f_{\rm B} = (1 + M_{\rm A} \sum_{\rm g} m_{\rm g}) \gamma_{\rm B} = [\rho + \sum_{\rm g} (M_{\rm A} - M_{\rm g}) c_{\rm g}] y_{\rm B} / \rho^{\star}$$
[11]

$$\boldsymbol{\gamma}_{B} = (1 - \sum_{s} \boldsymbol{x}_{s}) \boldsymbol{f}_{x,B} = (\rho - \sum_{s} \boldsymbol{M}_{s} \boldsymbol{c}_{s}) \boldsymbol{y}_{B} / \rho^{*}$$
[12]

$$y_{B} = \rho^{*} f_{X,B} [1 + \sum_{a} (M_{s}/M_{A} - 1) x_{B}] / \rho = \rho^{*} (1 + \sum_{a} M_{s} m_{s}) \gamma_{B/\rho}$$
[13]

For an electrolyte solute $B \equiv C_{\nu+}A_{\nu-}$, the activity on the molality scale is replaced by (9)

$$\gamma_{\rm B}m_{\rm B} - \gamma_{\pm}^{\nu}m_{\rm B}^{\nu}Q^{\nu} \qquad [14]$$

where $\nu = \nu_{+} + \nu_{-}$, $Q = (\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}})^{1/\nu}$, and ν_{\pm} is the mean ionic activity coefficient on the molality scale. A similar relation holds for the concentration activity, y_{BCB} . For the mole fractional activity,

$$f_{x,B}x_{B} = Q f_{\pm}^{\nu} x_{\pm}^{\nu}$$
 [15]

where $x_{\pm} = (x_{\pm}x_{\pm})^{1/\nu}$. The quantities x_{\pm} and x_{\pm} are the ionic mole fractions (9), which are

$$x_{+} = \nu_{+}x_{B}/[1 + \sum_{s}(\nu_{s} - 1)x_{s}]; \quad x_{-} = \nu_{-}x_{B}[1 + \sum_{s}(\nu_{s} - 1)x_{s}] \quad [16]$$

where $\nu_{\rm S}$ is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction $x_{\rm S}$. Note that the mole fraction of solvent is now

$$x_{A}' = (1 - \sum_{g} v_{g} x_{g}) / [1 + \sum_{g} (v_{g} - 1) x_{g}]$$
[17]

so that

$$x_A' + \sum_{S} \nu_S x_S = 1$$
 [18]

The relations among the various mean ionic activity coefficients are:

$$f_{\pm} = (1 + M_{A} \sum_{g} \nu_{g} m g) \gamma_{\pm} = [\rho + \sum_{g} (\nu_{g} M_{A} - M_{g}) c_{g}] y_{\pm} / \rho^{*}$$

$$(1 - \sum_{g} \lambda_{g}) c_{g}$$

$$(1 - \sum_{g} \lambda_{g}) c_{g}$$

$$(1 - \sum_{g} \lambda_{g}) c_{g}$$

$$\gamma_{\pm} = \frac{(1 - \sum_{s} x_{s})f_{\pm}}{1 + \sum_{s} (\nu_{s} - 1)x_{s}} = (\rho - \sum_{s} M_{s}c_{s})y_{\pm}/\rho^{*}$$
[20]

$$y_{\pm} = \frac{\rho^{*}[1 + \sum_{g}(M_{g}/M_{A} - 1)x_{g}]f_{\pm}}{\rho[1 + \sum_{g}(\nu_{g} - 1)x_{g}]} = \rho^{*}(1 + \sum_{g}M_{g}m_{g})\gamma_{\pm}/\rho \qquad [21]$$

(11) Solvent, A:

The osmotic coefficient, ϕ , of a solvent A is defined as (1):

$$\rho = (\mu_A^* - \mu_A) / RT M_A \sum_{m_B} m_B \qquad [22]$$

where μ_A^* is the chemical potential of the pure solvent.

The rational osmotic coefficient,
$$\phi_X$$
, is defined as (1):

$$\phi_{X} = (\mu_{A} - \mu_{A}^{*})/RT \ln x_{A} = \phi_{M} \sum_{m_{S}} \ln(1 + M_{A} \sum_{m_{S}})$$
[23]

The activity, a_A , or the activity coefficient, f_A , is sometimes used for the solvent rather than the osmotic coefficient. The activity coefficient is defined relative to pure A, just as for a mixture.

For a mixed solvent, the molar mass in the above equations is replaced by the average molar mass; i.e., for a two-component solvent with components J, K, M_A becomes

$$M_{A} = M_{J} + (M_{K} - M_{J}) x_{V,K}$$
 [24]

where $x_{V,K}$ is the solvent mole fraction of component K.

The osmotic coefficient is related directly to the vapor pressure, p, of a solution in equilibrium with vapor containing A only by (12, p.306):

$$\phi M_{A} \sum \nu_{s} m_{s} = -\ln(p/p_{A}^{*}) + (V_{m,A}^{*} - B_{AA})(p - p_{A}^{*})/RT \qquad [25]$$

where p_A^* , $V_{m,A}^*$ are the vapor pressure and molar volume of pure solvent A, and B_{AA} is the second virial coefficient of the vapor.

The Liquid Phase

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is similar to that of Kirkwood and Oppenheim (7); see also (11, 12). Consider a solid mixture containing c thermodynamic components 1. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{C} x_{i}' (S_{i}' dT - V_{i}' dp + d\mu_{i}') = 0$$
 [26]

A liquid mixture in equilibrium with this solid phase contains c' thermodynamic components 1, where c' > c. The Gibbs-Duhem equation for the liquid mixture is:

$$\sum_{i=1}^{C} x_1 (S_i dT - V_i dp + d\mu_1') + \sum_{i=C+1}^{C'} x_1 (S_i dT - V_i dp + d\mu_1) = 0 \quad [27]$$

Subtract [26] from [27] and use the equation

$$d\mu_1 = (d\mu_1)_{T,p} - S_1 dT + V_1 dp$$
 [28]

and the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_{i=1}^{C} x_{1}(d\mu_{1}')_{T,p} + \sum_{i=C+1}^{C'} x_{1}(d\mu_{1})_{T,p} = 0$$
[29]

The resulting equation is:

$$RT\sum_{i=1}^{C} x_{i}'(dlna_{i})_{T,p} = \sum_{i=1}^{C} x_{i}'(H_{i} - H_{i}')dT/T - \sum_{i=1}^{C} x_{i}'(V_{i} - V_{i}')dp \quad [30]$$

where

$$H_1 - H_1' = T(S_1 - S_1')$$
 [31]

is the enthalpy of transfer of component i from the solid to the liquid phase at a given temperature, pressure and composition, with H_i and S_1 the partial molar enthalpy and entropy of component i.

Use of the equations

$$H_1 - H_1^0 = -RT^2(\partial \ln a_i/\partial T)_{x,p}$$
 [32]

$$V_1 - V_1^0 = RT(\partial \ln a_i / \partial p)_{X,T}$$
[33]

where superscript o indicates an arbitrary reference state gives:

$$RT\sum_{i=1}^{C} x_{i}'dlna_{i} = \sum_{i=1}^{C} x_{i}'(H_{1}^{0} - H_{1}')dT/T - \sum_{i=1}^{C} x_{i}'(V_{1}^{0} - V_{1}')dp \quad [34]$$

where

$$dlna_1 = (dlna_i)_{T,p} + (dlna_i/\partial T)_{X,p} + (dlna_1/\partial p)_{X,T}$$
[35]

The terms involving enthalpies and volumes in the solid phase can be written as:

$$\sum_{i=1}^{C} x_{i}' H_{i}' = H_{s}^{*} \qquad \sum_{i=1}^{C} x_{i}' V_{i}' = V_{s}^{*} \qquad [36]$$

With eqn [36], the final general solubility equation may then be written:

$$R_{1=1}^{C} x_{i}' dlna_{i} = (H_{S}^{*} - \sum_{1=1}^{C} x_{1}' H_{1}^{0}) d(1/T) - (V_{S}^{*} - \sum_{1=1}^{C} x_{1}' V_{1}^{0}) dp/T \quad [37]$$

Note that those components which are not present in both phases do not appear in the solubility equation. However, they do affect the solubility through their effect on the activities of the solutes.

Several applications of eqn [37] (all with pressure held constant) will be discussed below. Other cases will be discussed in individual , evaluations.

(a) Solubility as a function of temperature.

Consider a binary solid compound $A_n B$ in a single solvent A. There is

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no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with c = 2, $x_A' = n/(n + 1)$, $x_B' = 1/(n + 1)$, eqn [37] becomes:

$$dln(a_A^n a_B) = -\Delta H_{AB}^0 d(1/RT)$$
[38]

where

$$\Delta H_{AB}^{0} = nH_{A} + H_{B} - (n+1)H_{S}^{*}$$
[39]

is the molar enthalpy of melting and dissociation of pure solid $A_{n}B$ to form A and B in their reference states. Integration between T and T_{0} , the melting point of the pure binary compound $A_{n}B$, gives:

$$\ln(a_{A}^{n}a_{B}) = \ln(a_{A}^{n}a_{B})_{T=T_{0}} - \int_{T_{0}}^{T} \Delta H_{AB}^{0} d(1/RT)$$
 [40]

(1) Non-electrolytes

In eqn [32], introduce the pure liquids as reference states. Then, using a simple first-order dependence of ΔH_{AB}^* on temperature, and assuming that the activitity coefficients conform to those for a simple mixture (6):

$$RT \ln f_A = wx_B^2 \qquad RT \ln f_B = wx_A^2 \qquad [41]$$

then, if w is independent of temperature, eqn [32] and [33] give:

$$\ln\{x_B(1-x_B)^n\} + \ln\left\{\frac{n^n}{(1+n)^{n+1}}\right\} = G(T)$$
 [42]

where

$$G(T) = -\left\{\frac{\Delta H_{AB}^{*} - T^{*} \Delta C_{p}^{*}}{R}\right\} \left\{\frac{1}{T} - \frac{1}{T^{*}}\right\} + \frac{\Delta C_{p}^{*}}{R} \ln(T/T^{*}) - \frac{w}{R} \left\{\frac{x_{A}^{2} + nx_{B}^{2}}{T} - \frac{n}{(n+1)T^{*}}\right\}$$

$$(43)$$

where ΔC_p^* is the change in molar heat capacity accompanying fusion plus decomposition of the pure compound to pure liquid A and B at temperature T^* , (assumed here to be independent of temperature and composition), and ΔH_{AB}^* is the corresponding change in enthalpy at $T - T^*$. Equation [42] has the general form:

$$\ln\{x_B(1-x_B)^n\} = A_1 + A_2/(T/K) + A_3\ln(T/K) + A_4(x_A^2 + nx_B^2)/(T/K)$$
[44]

If the solid contains only component B, then n = 0 in eqn [42] to [44].

If the infinite dilution reference state is used, then:

RT
$$\ln f_{X,B} = w(x_A^2 - 1)$$
 [45]

and [39] becomes

$$\Delta H_{AB}^{m} = nH_{A}^{*} + H_{B}^{m} - (n+1)H_{S}^{*}$$
[46]

where ΔH_{AB}^{∞} is the enthalpy of melting and dissociation of solid compound $A_{n}B$ to the infinitely dilute reference state of solute B in solvent A; H_{A}^{*} and H_{B}^{∞} are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with ΔH_{AB}^{∞} replacing ΔH_{AB}^{*} , ΔC_{p}^{∞} replacing ΔCp^{*} , and $x_{A}^{2} - 1$ replacing x_{A}^{2} in the last term.

See (5) and (11) for applications of these equations to experimental data.

(11) Electrolytes

(a) Mole fraction scale

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn [34] becomes:

$$\ln\left\{\frac{x_{B}^{\nu}(1-x_{B})^{n}}{(1+(\nu-1)x_{B})^{n+\nu}}\right\} - \ln\left\{\frac{n^{n}}{(n+\nu)^{n+\nu}}\right\} + \ln\left\{\left[\frac{f_{B}}{f_{B}^{\star}}\right]^{\nu}\left[\frac{f_{A}}{f_{A}^{\star}}\right]^{n}\right\}$$
$$- - \left\{\frac{\Delta H_{AB}^{\star} - T^{\star}\Delta C_{P}^{\star}}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^{\star}}\right\} + \frac{\Delta C_{P}^{\star}}{R}\ln(T/T^{\star})$$
[47]

where superscript * indicates the pure salt hydrate. If it is assumed that the activity coefficients follow the same temperature dependence as the right-hand side of eqn [47] (13-16), the thermochemical quantities on the right-hand side of eqn [47] are not rigorous thermodynamic enthalpies and heat capacities, but are apparent quantities only. Data on activity coefficients (9) in concentrated solutions indicate that the terms involving these quantities are not negligible, and their dependence on temperature and composition along the solubility-temperature curve is a subject of current research.

A similar equation (with $\nu = 2$ and without the heat capacity terms or activity coefficients) has been used to fit solubility data for some MOH-H₂O systems, where M is an alkali metal (13); enthalpy values obtained agreed well with known values. The full equation has been deduced by another method in (14) and applied to MCl₂-H₂O systems in (14) and (15). For a summary of the use of equation [47] and similar equations, see (14).

(2) Molality scale

Substitution of the mean activities on the molality scale in eqn [40] gives:

$$\nu \ln \left[\frac{\gamma_{\pm} m_{B}}{\gamma_{\pm} m_{B}^{*}} \right] - \nu (m_{B}/m_{B}^{*} - 1) - \nu \{m_{B}(\phi - 1)/m_{B}^{*} - \phi^{*} + 1\}$$

$$= G(T)$$
[48]

where G(T) is the same as in eqn [47], $m_B^* = 1/nM_A$ is the molality of the anhydrous salt in the pure salt hydrate and γ_{\pm} and ϕ are the mean activity coefficient and the osmotic coefficient, respectively. Use of the osmotic coefficient for the activity of the solvent leads, therefore, to an equation that has a different appearance to [47]; the content is identical. However, while eqn [47] can be used over the whole range of composition ($0 \le x_B \le 1$), the molality in eqn [48] becomes infinite at x_B = 1; use of eqn [48] is therefore confined to solutions sufficiently dilute that the molality is a useful measure of composition. The essentials of eqn [48] were deduced by Williamson (17); however, the form used here appears first in the Solubility Data Series. For typical applications (where activity and osmotic coefficients are not considered explicitly, so that the enthalpies and heat capacities are apparent values, as explained above), see (18).

The above analysis shows clearly that a rational thermodynamic basis exists for functional representation of solubility-temperature curves in two-component systems, but may be difficult to apply because of lack of experimental or theoretical knowledge of activity coefficients and partial molar enthalpies. Other phenomena which are related ultimately to the stoichiometric activity coefficients and which complicate interpretation include ion pairing, formation of complex ions, and hydrolysis. Similar considerations hold for the variation of solubility with pressure, except that the effects are relatively smaller at the pressures used in many investigations of solubility (5).

(b) Solubility as a function of composition.

At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\mu_{A_{n}B} = \mu_{A_{n}B}(sln) = n\mu_{A} + \mu_{B}$$

$$= (n\mu_{A}^{*} + \nu_{+}\mu_{+}^{\infty} + \nu_{-}\mu_{-}^{\infty}) + nRT \ln f_{A}x_{A}$$

$$+ \nu RT \ln (\gamma_{\pm}m_{\pm}Q)$$

for a salt hydrate $A_D B$ which dissociates to water (A), and a salt (B), one mole of which ionizes to give ν_+ cations and ν_- anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, $f_A = x_A = 1$, and the quantity K_B in

$$\Delta G^{\infty} = (\nu_{+}\mu_{+}^{\infty} + \nu_{-}\mu_{-}^{\infty} + n\mu_{A}^{*} - \mu_{AB}^{*})$$

= -RT ln K^{*}

$= -\nu RT \ln(Q\gamma_{\pm}m_B)$

is called the solubility product of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of K_S can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_yA_y \cdot nH_2O$ in the presence of other solutes is given by eqn [50] as

$$\nu \ln\{m_{\rm H}/m_{\rm H}(0)\} = -\nu \ln\{\gamma_{\rm H}/\gamma_{\rm H}(0)\} - n \ln\{a_{\rm A}/a_{\rm A}(0)\}$$
[51]

where a_A is the activity of water in the saturated solution, m_B is the molality of the salt in the saturated solution, and (0) indicates absence of other solutes. Similar considerations hold for non-electrolytes.

Consideration of complex mixed ligand equilibria in the solution phase are also frequently of importance in the interpretation of solubility equilibria. For nomenclature connected with these equilibria (and solubility equilibria as well), see (19, 20).

The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a nonstoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. See (21) for the modern formulation of the effect of particle size on solubility. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (22), is often used to investigate the composition of solid phases in equilibrium with salt solutions. This method has been reviewed in (23), where [see also (24)] least-squares methods for evaluating the composition of the solid phase from wet residue data (or initial composition data) and solubilities are described. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A brief description of the data sheets has been given in the FOREWORD; additional explanation is given below.

Guide to the Compilations

The format used for the compilations is, for the most part, selfexplanatory. The details presented below are those which are not found in the FOREWORD or which are not self-evident.

Components. Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (25) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

- (a) saturating components;
- (b) non-saturating components in alphanumerical order;
- (c) solvents in alphanumerical order.

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The saturating components are arranged in order according to a 18-column periodic table with two additional rows: Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements 3 to 12: transition elements 13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens 18: noble gases Row 1: Ce to Lu Row 2: Th to the end of the known elements, in order of atomic number.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is carefully noted in the text, and CA Registry Numbers are given where available, usually in the critical evaluation. Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the critical evaluation.

Original Measurements. References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts.

Experimental Values. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass per cent for weight per cent; mol dm⁻³ for molar; etc. Both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1983 atomic weights (26).

Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

Method. Source and Purity of Materials. Abbreviations used in Chemical Abstracts are often used here to save space.

Estimated Error. If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and and reporting errors are based on the papers by Ku and Eisenhart (27).

Comments and/or Additional Data. Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References. See the above description for Original Measurements.

Guide to the Evaluations

The evaluator's task is to check whether the compiled data are correct, to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. A brief description of the evaluation sheets is given below.

Components. See the description for the Compilations.

Evaluator. Name and date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator produces text evaluating all the published data for each given system. Thus, in this section the evaluator reviews the merits or shortcomings of the various data. Only published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are considered as tentative if only one set of measurements is

available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1, 28) when the data can be accurately converted.

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Table I-l Quantities Used as Measures of Solubility of Solute B Conversion Table for Multicomponent Systems Containing Solvent A and Solutes s				
	mole fraction ×B =	mass fraction w _B =	molalıty m _B =	concentration cg =
x _B	× _B M	$\frac{M_{B}x_{B}}{A + \sum_{g}(M_{g} - M_{A})x_{g}}$	$\frac{x_{B}}{M_{A}(1 - \sum_{g} x_{g})}$	$\frac{\rho x_B}{M_A + \sum\limits_{g} (M_g - M_A) x_g}$
wB	$\frac{w_{\rm B}/M_{\rm B}}{1/M_{\rm A} + \sum_{\rm g} (1/M_{\rm g})}$	- 1/M _A)w _s w _B	$\frac{w_B}{M_B(1 - \sum_{g} w_g)}$	pwB/MB
mB	$\frac{M_{A}m_{B}}{1 + M_{A}\sum_{g}m_{g}}$	$\frac{M_Bm_B}{1 + \sum_{g}m_gM_g}$	mB	$\frac{\rho m_B}{1 + \sum_{g} M_g m_g}$
c _B	$\frac{M_A c_B}{\rho + \sum\limits_{g} (M_A - M_g)}$	c_s M _B c _B /ρ	<u>c</u> β ρ - Σ ^M gcs	с _В

 ρ = density of solution M_A , M_B , M_S = molar masses of solvent, solute B, other solutes s Formulas are given in forms suitable for rapid computation; all calculations should be made using SI base units.

SYSTEMS WITH COMMON ANION
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Barium methanoate (barium formate); (CHO₂)₂Ba; [541-43-5] Potassium methanoate (potassium formate); (CHO₂)₂K₂; [590-29-4] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	• • • • • • • • • • • • • • • • • • • •
The experimental values are given only in graphical form (see figure). Characteristic point(s): Eutectic, E, at 162.6 ^{O}C and $x_1 = 0.074$ (authors). Peritectic, P, at 192.2 ^{O}C and $x_1 = 0.373$ (authors). Note - The investigation was limited to $x_1 \leq 0.50$ due to thermal instability.	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a provided by	Component 1: K&K material of stated purity \geq 99 %. Component 2: C. Erba RP material of stated purity \geq 99 %.
resistance thermometer, and connected with a L&N Type K-3 potentiometer.	
NOTE:	
The fusion temperature of component 2 read by the compiler on the original plot, i.e., $T_{fus}(2)$ ~ 169 °C (442 K) agrees satisfacto- rily with the value $T_{fug}(2)$ = 441.9±0.5 K reported in Table 1 of the Preface. The authors' assertion that the negative deviation with respect to ideality of the liquidus branch richest in component 2 proves poor miscibility of the solid components in this region is reasonable. No	ESTIMATED ERROR: Temperature: accuracy probably ±0.1 K (compiler). REFERENCES: (1) Braghetti,M.; Leonesi,D.; Franzosini,P. Pio Sci 1968 38 116-118
assumption is made by the authors about the	Ale. Sei. <u>1900</u> , 30, 110-110.

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<pre>COMPONENTS: (1) Barium methanoate (barium formate); (CHO₂)₂Ba; [541-43-5] (2) Sodium methanoate (sodium formate); (CHO₂)₂Na₂; [141-53-7]</pre>	ORIGINAL MEASUREMENTS: Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.	
VARIABLES: Temperature.	PREPARED BY: Baldini, P.	
EXPERIMENTAL VALUES: The experimental values are given only in graphical form (see figure). Characteristic point(s): Eutectic, E, at 224.8 °C and $x_1 = 0.354$ (authors). Peritectic, P, at 242.0 °C and $x_1 = 0.518$ (authors). Note - The investigation was limited to $x_1 \leq 0.55$ due to thermal instability.	u_{250}	
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE: A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	SOURCE AND PURITY OF MATERIALS: Component 1: K&K material of stated purity \geq 99 %. Component 2: C. Erba RP material of stated purity \geq 99 %.	
The fusion temperature of component 2 read by the compiler on the original plot, i.e., $T_{fus}(2)^{\sim} 258 \ ^{\circ}C$ (531 K) agrees satisfacto- rily with the value $T_{fus}(2) = 530.7\pm0.5$ K reported in Table 1 of the Preface. The authors' assertion that the negative deviation with respect to ideality of the liquidus branch richest in component 2 proves poor miscibility of the solid components in this region is reasonable. No assumption is made by the authors about the nature of the peritectic equilibrium.	ESTIMATED ERROR: Temperature: accuracy probably <u>+0.1 K</u> (compiler). REFERENCES: (1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38, 116-118.	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Barium methanoate (barium formate); (CHO₂)₂Ba; [541-43-5] Thallium(I) methanoate (thallous formate); (CHO₂)₂Tl₂; [992-98-3] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure). Characteristic point(s):	105-
Eutectic, E, at 95.4. ^o C and $x_1 = 0.079$ (authors). Note - The investigation was limited to $x_1 \leq 0.09$ due to thermal instability.	0.
	$\begin{array}{c} 95 \\ E \\ 0.95 \\ X_2 \\ 1 \\ (CHO_2)_2 Ba \leftarrow (CHO_2)_2 TI_2 \end{array}$
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial Crystallization temperatures were measured	Component 1: K&K material of stated purity \geq 99 %. Component 2: BDH material of stated purity \geq 99 %.
with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	REFERENCES: (1) Braghetti, M.; Leonesi, D.; Franzosini, P.
NOTE:	(2) Braghetti, M.; Berchiesi, G.; Franzosini, P.
The fusion temperature of component 2 read by the compiler on the original plot, i.e., $T_{fus}(2) \sim 101$ °C (374 K) coincides with the values determined with DSC by Braghetti et al. (Ref. 2), and with DTA by Meisel et al. (Ref. 3), although being 3 K lower than that obtained with hot-stage polarizing microscopy by Baum et al. (Ref. 4).	 Franzosini, P. Ric. Sci. 1969, 39, 576-584. (3) Meisel, T.; Seybold, K.; Halmos, Z.; Roth, J.; Melykuti, C. J. Thermal Anal. 1976, 10, 419-431. (4) Baum, E.; Demus, D.; Sackmann, H. Wiss. Z. Univ. Halle 1970, 19, 37-46.
ESTIMATED ERROR:	
Temperature: accuracy probably +0.1 K (compiler).	

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Calcium methanoate (calcium formate); (CHO₂)₂Ca; [544-17-2] Potassium methanoate (potassium formate); (CHO₂)₂K₂; [590-29-4] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure).	
Characteristic point(s):	190- \
Eutectic, E, at 163.2 $^{\circ}$ C and $x_1 = 0.057$ (authors).	
Note - The investigation was limited to $\mathbf{x}_1 \leq 0.11$ due to thermal instability.	
	E
	$\begin{array}{ccc} 0.9 & X_2 & 1 \\ (CHO_2)_2Ca \leftarrow & (CHO_2)_2K_2 \end{array}$
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured	C. Erba RP materials of stated purity > 99 %.
by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	
NOTE:	
The fusion temperature of component 2 read	ESTIMATED ERROR:
by the compiler on the original plot, i.e., $T_{fug}(2)^{\sim} 169 {}^{\circ}C (442 \text{K})$ agrees satisfacto- rily with the value $T_{fug}(2)^{\sim} 441.9 \pm 0.5 \text{K}$	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
authors' assertion that the negative	REFERENCES:
liquidus branch richer in component 2 proves poor miscibility of the solid components in this region is reasonable.	(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38, 116-118.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Calcium methanoate (calcium formate); (CHO₂)₂Ca; [544-17-2] Sodium methanoate (sodium formate); (CHO₂)₂Na₂; [141-53-7] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure).	
Characteristic point(s):	
Eutectic, E, at 233.4 $^{\circ}$ C and $x_1 = 0.243$ (authors).	250
Note - The investigation was limited to $x_1 \leq 0.27$ due to thermal instability.	230- E
	$0.8 \qquad 1$ (CHO ₂) ₂ Ca \leftarrow (CHO ₂) ₂ Na ₂
	222
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP materials of stated purity > 99 %.
NOTE:	
The fusion temperature of component 2 read	ESTIMATED ERROR:
by the compiler on the original plot, i.e., $T_{fus}(2) \sim 258 \circ C$ (531 K) agrees satisfacto- rily with the value $T_{fus}(2) = 530.7+0.5$ K reported in Table 1 of the preface. The authors assertion that the negative deviation with respect to ideality of the	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
	REFERENCES:
liquidus branch richer in component 2 proves poor miscibility of the solid components in this region is reasonable.	(1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38 , 116-118.



COMPONENTS:	EVALUATOR:
 Potassium methanoate (potassium formate);	Franzosini, P.,
(CHO ₂)K; [590-29-4] Lithium methanoate (lithium formate);	Dipartimento di Chimica Fisica,
(CHO ₂)Li; [556-63-8]	Universita´ di Pavia (ITALY).

This system was studied by Sokolov and Tsindrik (Ref. 1) as a side of the reciprocal ternary K, Li/CHO_2 , NO_3 , and by Pochtakova (Ref. 2) as a side of the ternary CHO_2/K , Li, Na. In both cases, the visual polythermal analysis was employed, and the investigation was restricted to the liquidus.

The obtained results, i.e., formation of a 1:1 congruently melting intermediate compound giving a eutectic with either component, are qualitatively similar. It is, however, to be remarked that no explanation is offered by Pochtakova (Ref. 2, where Ref. 1 is quoted) for the considerable difference between the temperature she found (427 K) for the eutectic at $100x_1$ about 40, and that (413 K) measured previously by Sokolov and Tsindrik (Ref. 1).

The fusion temperatures of the pure components reported in both Ref. 1 and Ref. 2, i.e., $T_{fus}(1)=440$ K, $T_{fus}(2)=546$ K, are in fair agreement with those listed in Table 1 of the Preface (441.9+0.5 K, 546+1 K). On the contrary, poor correspondence exists between solid state transition temperatures quoted in Ref. 1 from Ref. 3 (i.e., 333, 408, and 430 K for component 1; 360, 388, and 505 for component 2) and those listed in Table 1 of the Preface (418+1 K for component 1, and 496+2 K for component 2).

- Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. 1969, 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1969, 14, 302-306.
 Pochtakova, E.I.
- Zh. Neorg. Khim. 1980, 25, 1147-1150; Russ. J. Inorg. Chem. (Engl. Transl.) 1980, 25, 637-639 (*). (3) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); (CHO₂)K; [590-29-4] Lithium methanoate (lithium formate); (CHO₂)Li; [556-63-8] 	Pochtakova, E.I. Zh. Neorg. Khim. <u>1980</u> , 25, 1147-1150; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1980</u> , 25, 637-639 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	
Characteristic point(s):	273
Eutectic, E_1 , at 121 ^o C (author) and $100x_2$ ⁼ 25 (according to Fig. 1 and Fig. 2 of the original paper, erroneously reported as $100x_1$ in the text; compiler). Eutectic, E_2 , at 154 ^o C (author) and $100x_2$ ⁼ 60 (according to Fig. 1 and Fig. 2 of the original paper, erroneously reported as $100x_1$ in the text; compiler).	$ \begin{array}{c} 167 \\ & & & & & & & \\ & & & & & & \\ 0 & & & & & & \\ 0 & & & & & & \\ 0 & & & & & & \\ (CHO_2)K & & & & & \\ \end{array} $
Intermediate compound(s):	
(CHO ₂) ₂ KLi, congruently melting at 163 ^o C (author).	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated. Component 1: t _{fus} (1)/ ⁰ C= 167. Component 2: t _{fus} (2)/ ⁰ C= 273.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Potassium methanoate (potassium formate)	Franzosini, P.,
(CHO ₂)K; [590-29-4] Magnesium methanoate (magnesium formate)	Dipartimento di Chimica Fisica,
(CHO ₂) ₂ Mg; [557-39-1]	Universita [°] di Pavia (ITALY).

The system was studied by Berchiesi et al. (Ref. 1), who indicated component 1 as $(CHO_2)_2K_2$, and by Pochtakova (Ref. 2), who indicated component 1 as $(CHO_2)K$ in Table 6 of her paper, and as $(CHO_2)_2K_2$ in Fig. 2. Inspection of text and figures led both the compiler and evaluator to assume the latter formula as the correct one: consequently, a direct comparison is possible between data from either sources.

Comparison makes apparent that Pochtakova (Ref. 2), who seems not to be aware of Ref. 1, could obtain no evidence for the eutectic due to the fact that she performed no measurements at $0 < 100x_2 \leq 5$, while the eutectic composition (Ref. 1) is $100x_2=1.3$.

It is to be added that: (i) Berchiesi et al.'s fusion temperature of component 1 read by the evaluator on the original plot, i.e., $T_{fus}(1)$ 169 °C (442 K) agrees with the value $T_{fus}(1)$ = 441.9+0.5 K reported in Table 1 of the Preface more satisfactorily than Pochtakova's figure (440 K); (ii) the solid state transition temperatures quoted for component 1 in Ref. 2 from Ref. 3 (i.e., 333, 408, and 430 K) cannot be identified with the relevant data of Table 1 of the Preface, where a single transition is mentioned which occurs at $T_{trs}(1)/K$ = 418+1; and (iii) Pochtakova's points are affected by a scattering noticeably larger than Berchiesi et al.'s.

In conclusion, the evaluator recommends the data by Berchiesi et al. (Ref. 1), although regretting that they are presented only in graphical form, and not supported by any investigation of the solidus.

- (1) Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u>, 50, 1972-1975.
- (2) Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium methanoate (potassium formate); (CHO₂)₂K₂; [590-29-4] (2) Magnesium methanoate (magnesium formate); (CHO₂)₂Mg; [557-39-1] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARTABLES.	PREPARED RY.
lemperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure). Characteristic point(s): Eutectic, E, at 167.4 $^{\circ}$ C and x_2 = 0.013 (authors).	190-
Note - The investigation was limited to $x_1 \ge 0.97$ due to thermal instability.	$ \begin{array}{c} $
AUXILIARY	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	Component 1: C. Erba RP material of stated purity \geq 99 %. Component 2: K&K material of stated purity \geq 99 %.
	ESTIMATED ERROR:
	Temperature: accuracy probably +0.1 K (compiler).
	REFERENCES:
	(1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38 , 116-118.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium methanoate (potassium	Pochtakova, E.I.
(CHO ₂) ₂ K ₂ ; [590-29-4]	Zh. Ubshch. Khim. <u>1974</u> , 44, 241-248.
<pre>(2) Magnesium methanoate (magnesium formate);</pre>	
(CHO ₂) ₂ Mg; [557-39-1]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
· •	
EXPERIMENTAL VALUES:	
$t^{O}C T/K^{a} 100x_{2}$	
167 440 0	م ۱
212 485 7.5	
225 498 10 239 512 12.5	8
243 516 15 257 530 17.5	250
269 542 20 280 552 22 5	
287 560 25	
^a T/K values calculated by the compiler.	200
Note - The system was investigated at	
$0 \le 100 \mathbf{x}_2 \le 25$ due to thermal instability of component 2. No characteristic point was	
observed in the mentioned composition	
region.	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal method, supplemented with differential thermal analysis (no	Materials prepared (Ref. 1) by reacting the proper ("chemically pure") carbonate with a
numerical DTA data, however, are tabulated	slight excess of methanoic acid of
	Component 1 undergoes phase transitions at
	Component 2 undergoes a phase transition
	at $t_{trs}(2)/^{o}C = 140$.
	ECTIVATED EDDOD.
	L SILFAI ED ERROR:
	Compiler).
	REFERENCES:
	(1) Sokolov, N.M.
	Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593. (2) Sokolov, N.M.
	Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
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COMPONENTS:	EVALUATOR:	
 Potassium methanoate (potassium formate); (CHO₂)K; [590-29-4] Sodium methanoate (sodium formate); (CHO₂)Na; [141-53-7] 	Spinolo, G., Dipartimento Universita ² d	di Chimica Fisica, li Pavia (ITALY).
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	l	
CRITICAL EVALUATION:		
The binary CHO_2/K , Na was studied by Dmitrevskaya (as a side system of the reciprocal ternary CHO_2 , NO_3/K , Na; Ref. 1) and by Leonesi et al. (as a side system of the reciprocal ternary CHO_2 , $C1/K$, Na; Ref. 2). In both papers, visual observation was employed, and investigation was restricted to the liquidus; moreover, the latter authors listed only the few numerical data which were relevant to their purposes. The main features of the phase diagrams given in either source exhibit rather close similarities, as shown here:		
	Ref. 1	Ref. 2
$\frac{T_{fus}(1)}{K}$	440	441.9
$T_{fus}(2)/K$:	531	530.7
Intermediate compound (i.c.)	(CHO ₂) ₄ K ₃ Na	$(CHO_2)_4 K_3 Na$
$T_{fus}(i.c.)/K$	-	453.2
Eutectic E ₁ ; T/K:	441	438.2
Eutectic E ₁ ; x ₂ :	0.505	0.495
Eutectic E ₂ ; T/K:	440	436.7
l Eutectic Eo: xo:	0.04	0.043

It is, however, to be stressed that: (i) Dmitrevskaya's liquidus branch rich in component 1 exhibits a maximum (unexplained by the author) at 444 K and $x_1 = 0.98$, whereas Leonesi et al. found a monotonically decreasing trend; and (ii) Dmitrevskaya quotes (from Ref. 3) the occurrence of phase transitions in component 1 (at 333, 408, and 430 K), and in component 2 (at 515 K) which have no correspondence in Table 1 of the Preface.

Due to these reasons, and to the higher accuracy to be attributed to the findings by Leonesi et al., the evaluator is inclined to recommend the data listed above under the heading "Ref. 2".

It is finally to be added that previous cryometric work had allowed Leonesi et al. (Ref. 4) to infer, on the basis of the well known equation

$$\lim_{m \to 0} \frac{(\Delta T/m)}{K} = 1 - \rho_0$$

(K: cryometric constant of component 1, used as the solvent; ΔT : experimental freezing point depression; m: molality of component 2, used as the solute), a limiting value ρ_0 about 0.17 for the ratio between the solute concentrations in the solid and liquid phases at equilibrium.

- (1) Dmitrevskaya, O.I.
 Zh. Obshch. Khim. 1958, 28, 299-304 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 295-300.
- (2) Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u>, 25a, 52-55.
- (3) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
 (4) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P.
- Ric. Sci. <u>1968</u>, 38, 702-705.



COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium methanoate (potassium formate):	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P.
(CHO ₂)K; [590-29-4]	Z. Naturforsch. 1970, 25a, 52-55.
(2) Sodium methanoate (sodium formate); (CHO ₂)Na; [141-53-7]	
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VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Eutectic, E_1 , at 165.0 °C and 100 x_1 = 50.5	
Eutectic, E_2 , at 163.5 °C and $100x_1 = 95.7$	
(authors).	
Intermediate compound(s):	
$(CHO_2)_{4}K_{3}Na$, congruently melting at 180.0 C (authors)	
100.0 C (authors).	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an	C. Erba RP materials, dried by heating
inert atmosphere, and allowing one to observe the system visually, was employed	under vacuum. Component 1: $t_{c_{inc}}(1)/{}^{\circ}C= 168.7.$
(for details, see Ref. 1). The initial	Component 2: $t_{fus}^{IUS}(2)/^{\circ}C= 257.5$.
with a Chromel-Alumel thermocouple checked	
by comparison with a certified Pt resistance thermometer, and connected with	
a L&N Type K-3 potentiometer.	
	ESTIMATED ERROR:
	Temperature: accuracy probably +0.1 K.
	REFERENCES:
	(1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38, 116-118.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); (CHO₂)₂K₂; [590-29-4] Strontium methanoate (strontium formate); (CHO₂)₂Sr; [592-89-2] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure).	

Characteristic point(s):

Eutectic, E, at 153.2 $^{\circ}$ C and x_2 = 0.150 (authors). Peritectic, P, at 170.8 $^{\circ}$ C and x_2 = 0.327 (authors).

Note - The investigation was limited to $\mathbf{x}_1 \geq 0.60$ due to thermal instability.



AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer. NOTE:	Component 1: C. Erba RP material of stated purity ≥ 99 %. Component 2: K&K material of stated purity ≥ 99 %.
The fusion temperature of component 1 read by the compiler on the original plot, i.e., $T_{fus}(1)$ ~ 169 °C (442 K) agrees satisfacto- rily with the value $T_{fus}(1)$ = 441.9+0.5 K	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
reported in Table 1 of the Preface. The authors' assertion that the negative deviation with respect to ideality of the liquidus branch richest in component 2 proves poor miscibility of the solid components in this region is reasonable. No assumption is made by the authors about the nature of the peritectic equilibrium.	REFERENCES: (1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38, 116-118.

COMPONENTS	ORTCINAL MEASUREMENTS.
Unit of Minib.	
(1) Lithium methanoate (lithium formate); (CHO ₂)Li: [556-63-8]	Tsindrik, N.M. Zh. Obshch. Khim. 1958, 28 , 830-834.
(2) Sodium methanoate (sodium formate);	20, 050 054.
(CHO ₂)Na; [141-53-7]	
VARIABLES:	PREPARED BY:
Tomo ana tumo	Poldini D
Temperature.	balulni, r.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁	
258 531 0	· ↓
250 523 5 242 515 10	÷
232 505 15	
224 497 20 214 487 25	250 -
204 477 30	× ,
194 467 35	
176 449 45	
170 443 50	
184 457 60	
196 469 65	~~~~~
208 481 70	m m
232 505 80	
[.] ^a T/K values calculated by the compiler.	0 50 100× ₁ 100 (CHO ₂)Na (CHO ₂)Li
Characteristic point(s):	2 2
Minimum, m, at 170 °C and $100x_2 = 50$ (author).	
Note - The system was investigated at $0 < 100$	x, < 80.
	ΝΡΟDΜΑΦΤΟΝ
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures	Materials of analytical purity
thermocouple.	of lithium methanoate: 273; author).
NOTE:	
The fusion temperatures of both components.	
$T_{fus}(1) = 546$ K and $T_{fus}(2) = 531$ K, are in	
excellent agreement with the corresponding values listed in Table 1 of the Preface.	
The abscissa of point m, $100x_2 = 50$,	
coincides with that found by Pochtakova (Ref. 1), whereas its ordinate, 443 K, is	ESTIMATED ERROR:
somewhat lower than Pochtakova's value,	
1.e., 449 K.	(compiler).
	REFERENCES:
	(1) Pochtakova, E.I.
	Zh. Neorg. Khim. 1980, 25, 1147-1150; Russ I. Inorg (hom (Engl. Trend))
	<u>1980</u> , 25, 637-639 (*).
	1

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium methanoate (lithium formate); (CHO₂)Li; [556-63-8] Sodium methanoate (sodium formate); (CHO₂)Na; [141-53-7] 	Pochtakova, E.I. Zh. Neorg. Khim. <u>1980</u> , 25, 1147-1150; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1980</u> , 25, 637-639 (*).
	DDEDADEN BV.
VARIADLES:	Related DI:
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	[]
Characteristic point(s):	258 00 0 0 273
Continuous series of solid solutions with a minimum, m, at 176 °C (according to Fig. 1 and Fig. 2 of the original paper, erroneously reported as 716 in the text; compiler) and $100x_2 \approx 50$ (author).	C 100 100X ₂ 0 (CHO ₂) Na (CHO ₂) Li
AUXILIARY 1	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated. Component 1: $t_{fug}(1)/^{\circ}C=273$.
NOTE:	Component 2: $t_{fus}^{lus}(2)/^{o}C=258$.
The fusion temperatures of both components, $T_{fus}(1) = 546$ K and $T_{fus}(2) = 531$ K, are in excellent agreement with the corresponding values listed in Table 1 of the Preface. The abscissa of point m, $100x_2 = 50$, coincides with that found by Tsindrik (Ref. 1), whereas its ordinate, 449 K, is scomewhat hicker then Tsindrik's unlike	
i.e., 443 K.	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	(1) Tsindrik, N.M. Zh. Obshch. Khim. <u>1958</u> , 28, 830-834.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Magnesium methanoate (magnesium formate); (CHO₂)₂Mg; [557-39-1] Sodium methanoate (sodium formate); 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
(CHO ₂) ₂ Na ₂ ; [141-53-7]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{1}$	J
258 531 0 257 530 2.5 256 529 5 255 528 7.5 251 524 10 253 526 15 253 526 17.5 252 525 20 257 530 22.5 267 540 25 282 555 27.5 300 573 30 a T/K values calculated by the compiler. Note - The system was investigated at $0 \leq component 1$. Eutectic, E, at 252 °C and $100x_1 = 21$ (author)	$100x_1 \leq 30 \text{ due to thermal instability of }$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method. NOTE: Concerning component 2, it can be remarked that the fusion temperature given by the author, $T_{fus}(2) = 531$ K, is in excellent agreement with the value listed in Table 1 of the Preface, i.e., 530.7 ± 0.5 K, whereas the value quoted from Ref. 2 for the solid state transition temperature, $T_{trs}(2) = 515$ K, is noticeably higher than that reported in the Table, i.e., 502 ± 5 K. It can be added that Berchiesi et al. (Ref. 3) asserted they could not investigate this binary due to thermal instability of the mixtures of any composition.	Materials prepared by reacting the proper ("chemically pure") carbonate with a slight excess of methanoic acid of analytical purity (Ref. 1). Component 1 undergoes a phase transition at $t_{trs}(1)/{}^{0}C=140$. Component 2 undergoes a phase transition at $t_{trs}(2)/{}^{0}C=242$ (Ref. 2). ESTIMATED ERROR: Temperature: accuracy probably ± 2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24 , 1581-1593. (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
	 (3) Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u>, 50, 1972-1975.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Magnesium methanoate (magnesium formate); (CHO₂)₂Mg; [557-39-1] Thallium(I) methanoate (thallous formate); (CHO₂)₂Tl₂; [992-98-3] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	
EXPERIMENTAL VALUES:		
The experimental values are given only in graphical form (see figure).	150-	
Characteristic point(s): Minimum, m, at 97.0 ^o C and $\mathbf{x}_1 = 0.030$ (authors). Note - The investigation was limited to $\mathbf{x}_1 \leq 0.06$ due to thermal instability.		
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured	Component 1: K&K material of stated purity > 99 %. Component 2: BDH material of stated purity > 99 %.	
with a Chromel-Alumel thermocouple checked by comparison with a certified Pt	ESTIMATED ERROR:	
resistance thermometer, and connected with a L&N Type K-3 potentiometer.	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).	
NOTE:	REFERENCES:	
The fusion temperature of component 2 read by the compiler on the original plot, i.e., $T_{fus}(2)^{\sim}$ 101 °C (374 K) coincides with the values determined with DSC by Braghetti et al. (Ref. 2), and with DTA by Meisel et al. (Ref. 3), although being 3 K lower than that obtained with hot-stage polarizing microscopy by Baum et al. (Ref. 4). Solid solutions ought to form.	 Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118. Braghetti, M.; Berchiesi, G.; Franzosini, P. Ric. Sci. 1969, 39, 576-584. Meisel, T.; Seybold, K.; Halmos, Z.; Roth, J.; Melykuti, C. J. Thermal Anal. 1976, 10, 419-431. Baum, E.; Demus, D.; Sackmann, H. Wiss. Z. Univ. Halle 1970, 19, 37-46. 	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); (CHO₂)₂Na₂; [141-53-7] Strontium methanoate (strontium formate); (CHO₂)₂Sr; [592-89-2] 	Berchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G. Can. J. Chem. <u>1972</u> , 50, 1972-1975.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure). Characteristic point(s):	$ \begin{array}{c} 260\\ 0\\ 220\\ 0\\ (CHO_2)_2Na_2 \end{array} (CHO_2)_2Sr $
Eutectic, E, at 235.4 ^o C and x_2 = 0.246 (authonormal Note - The investigation was limited to $x_1 \ge$	ors). 0.70 due to thermal instability.
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	Component 1: C. Erba RP material of stated purity ≥ 99 %. Component 2: K&K material of stated purity ≥ 99 %.
NOTE:	
The fusion temperature of component 1 read by the compiler on the original plot, i.e., $T_{fus}(1)^{\sim} 258 \ ^{\circ}C$ (531 K) satisfactorily agrees with the value (530.7+0.5 K) reported in Table 1 of the Preface. The authors assertion that the negative deviation with respect to ideality of the liquidus branch richer in component 2 proves poor miscibility of the solid components in this region is reasonable.	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
	REFERENCES: (1) Braghetti,M.; Leonesi,D.; Franzosini,P. Ric. Sci. <u>1968</u> , 38 , 116-118.
	l

COMPONENTS.	ORTGINAL MEASUREMENTS:
(1) Strontium methanoate (strontium formate);	perchiesi, G.; Cingolani, A.; Leonesi, D.; Piantoni, G.
(CHO ₂) ₂ Sr; [592-89-2] (2) Thallium(I) methanoate (thallous	Can. J. Chem. <u>1972</u> , 50, 1972-1975.
formate); (CHO_{-}) $\pi 1 + [002-08-3]$	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The experimental values are given only in graphical form (see figure).	
Characteristic point(s):	$(CHO_2)_2$ Sr \leftarrow $(CHO_2)_2$ TI ₂
Eutectic, E, at 96.8 $^{\circ}$ C and $x_1 = 0.051$ (authors).	
Note - The investigation was limited to $\mathbf{x}_1 \leq 0.07$ due to thermal instability.	
AUXILIARY	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an	Component 1: K&K material of stated purity
inert atmosphere, and allowing one to observe the system visually, was employed	> 99 %.
(for details, see Ref. 1). The initial	≥ 99 %.
with a Chromel-Alumel thermocouple checked	REFERENCES:
by comparison with a certified Pt resistance thermometer, and connected with	(1) Braghetti, M.; Leonesi, D.;
a L&N Type K-3 potentiometer.	Franzosini, P. Bic. Sci. 1968 38, 116-118.
NOTE:	(2) Braghetti, M.; Berchiesi, G.;
The fusion temperature of component 2 read by the compiler on the original plot, i.e., $T_{fus}(2)^{-1} 101$ °C (374 K) coincides with the values determined with DSC by Braghetti et al. (Ref. 2), and with DTA by Meisel et al. (Ref. 3), although being 3 K lower than that obtained with hot-stage polarizing microscopy by Baum et al. (Ref. 4).	 Franzosini, P. Ric. Sci. <u>1969</u>, 39, 576-584. (3) Meisel, T.; Seybold, K.; Halmos, Z.; Roth, J.; Melykuti, C. J. Thermal Anal. <u>1976</u>, 10, 419-431. (4) Baum, E.; Demus, D.; Sackmann, H. Wiss. Z. Univ. Halle <u>1970</u>, 19, 37-46.
ESTIMATED ERROR:	
Temperature: accuracy probably <u>+0.1 K</u> (compiler).	

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] 	Nadirov, E.G.; Bakeev, M.I. Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR 1974, 25, 129-141.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	ب_
t/ ^o C T/K ^a 100x ₂	Ź.
228 501 40 242 515 45 249 522 50	250 - 250 -
256 ^p 529 58 257 530 60 247 520 65	
235 508 70 221 494 75	
196 469 80 167 440 85	200
174 447 90 178 451 95	
181 454 100	Ö E
a T/K values calculated by the compiler. b 456 $^{\circ}$ C in the original table (compiler).	└─────└─ [│] 0 50 100×₂ 100 (C_H_0_)_Cd (C_H_0_)Cs
Characteristic point(s): Eutectic, E, at 167 °C (164 °C according to Fig. 9 of the original paper; compiler) and $100x_2=$ 85 (authors).	
Intermediate compound(s): $(C_2H_3O_2)_7Cd_2Cs_3$, congruently melting at 257 ^O C (255 ^O C, thermographic analysis), and exhibiting a polymorphic transition (at 130 ^O C, thermographic analysis; 133 ^O C, conductometry).	
Note - The system was investigated at 40 \leq 10	$0x_2 \leq 100.$
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple and a PP potentiometer. Additional investigations were performed by means of thermographical analysis, electrical conductometry, and X-ray diffractometry.	Not stated.
NOTE:	
The occurrence of the intermediate compound is supported by X-ray diffractometry, and seems reliable. According to the authors,	
this compound has a density of 2.472 g cm ⁻³ . Although the $T_{fus}(2)$ value (454 K) given in this paper is lower than the corresponding one from Table 1 of the Preface, i.e., 463 K the correspondent to the the	ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler).
diagram should be considered as substantially correct.	REFERENCES:

COMPONENTS:	EVALUATOR:
 Cadmium ethanoate (cadmium acetate);	Schiraldi, A.,
(C ₂ H ₃ O ₂) ₂ Cd; [543-90-8] Potassium ethanoate (potassium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)K; [127-08-2]	Universita´ di Pavia (ITALY).

This system was studied by Lehrman and Schweitzer (Ref. 1), Il'yasov (Ref. 2), Pavlov and Golubkova (Ref. 3), and Nadirov and Bakeev (Ref. 4), with significantly discrepant results.

Lehrman and Schweitzer (Ref. 1), and Pavlov and Goblubkova (Ref. 3) claim the existence of three congruently melting intermediate compounds, and four eutectics; however, both the coordinates of the eutectics, and the compositions and the fusion temperatures of the intermediate compounds given in either paper do not allow one to reconcile the phase diagram proposed in Ref. 1 with that reported in Ref. 3.

According to Il'yasov (Ref. 2), a single eutectic should exist [at 505 K (232 °C) and $100x_2^{=}$ 75] within the composition range he investigated, viz., $0 \leq 100x_1 \leq 43$ (the corresponding compositions given in the original paper refer to equivalent fractions of potassium ethanoate).

Finally, according to Nadirov and Bakeev (Ref. 4), a eutectic at either 461, or 469, or 476 K (188, 196, 203 °C, respectively) dependently on the method employed for the determination, and $100x_2 = 54$, and an intermediate compound, $(C_2H_3O_2)_8CdK_6$, incongruently melting at either 518, or 524, or 526 K (245C, 251C, 253 °C, respectively) dependently on the method employed for the determination, are the characteristic features of the system.

The general disagreement existing among the above mentioned authors seems not to be attributed to differences in the purity of the alkanoates they employed, although this factor might play some role in the case of Lehrman and Schweitzer (Ref. 1), inasmuch as they report a fusion temperature of component 2, $T_{fus}(2) = 565 \text{ K}$ (292 °C), which is significantly lower than the generally accepted value of about 579 K (578.7±0.5 K, in Table 1 of the Preface).

Indeed, it seems more likely that the formation of complex ions in the melt (Ref. 4) might affect the results obtained with techniques (e.g., the visual polythermal method) implying the observation of the system during cooling. Should these complex ions be sufficiently stable, the actual liquidus might be different as a consequence of largely different cooling rates.

Taking into account this possibility, the evaluator is inclined to consider as more reliable the phase diagram suggested by Nadirov and Bakeev (Ref. 4), as it is supported by results obtained with several investigation methods, including X-ray diffractometry which was employed to confirm the existence of the intermediate compound $(C_{2H_3O_2})_8$ CdK₆.

Some doubt, however, might subsist about the interpretation of the slope variation Nadirov and Bakeev (Ref. 4) observed in the plot electric conductivity vs. T, as due to an allotropic transition of potassium ethanoate at 467 K (194 $^{\rm O}$ C). According to Table 1 of the Preface, inter alia, a solid state transition in this salt is to be expected only at T_{trs}(2)= 422.2+0.5 K.

- (1) Lehrman, A.; Schweitzer, D.
- J. Phys. Chem. 1954, 58, 383-384.
- (2) Il'yasov, I.I.
 Zh. Obshch. Khim, 1962, 32, 347-349.
 (3) Pavlov, V.L.; Golubkova, V.V.
- Vestn. Kiev. Politekh. Inst. Ser. Khim. Mashinostr. Tekhnol. 1969, No. 6, 76-79. (4) Nadirov, E.G.; Bakeev, M.I.
 - Tr. Khim.-Metall. Inst. Akad. Nauk. Kaz. SSR 1974, 25, 129-141.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] (2) Potassium ethanoate (potassium acetate); acetate); (C₂H₃O₂)K; [127-08-2] 	Lehrman, A.; Schweitzer, D. J. Phys. Chem. <u>1954</u> , 58, 383-384.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁	v
292 565 0.0 289 562 10.0 246 519 20.0 183 ^b 456 20.0 195 468 30.0 202 475 33.3 196 469 35.0 188 ^b 461 35.0 203 476 38.0 213 486 40.0 217 490 41.0 221 494 42.86 216 489 44.44 206 479 48.0 210 483 50.0 205 478 52.0 202 475 55.0 187 ^b 460 55.0 190 463 60.0 220 493 70.0 a T/K values calculated by the compiler. b Eutectic temperatures (filled circles in the characteristic point(s): Eutectic, E ₁ , at 187 °C (authors) and 100x ₂ = Eutectic, E ₂ , at 201 °C (authors) and 100x ₂ = Eutectic, E ₄ , at 183 °C (authors) and	41 (compiler). 41 (compiler). 54 (compiler). 64 (compiler). (authors). (authors).
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A molten salt bath was employed to melt the mixtures placed in a 2.5x20 cm Pyrex tube. The beginning of crystallization (under stirring and by seeding) was observed visually and the corresponding temperature	Component 1: "C.P." material added with a few drops of glacial ethanoic acid and dried in an oven at 140 °C. Component 2: "Analytical Reagent" material dried at 140 °C for one week.
was measured with a potentiometer (16 mV full scale) and a Copper-Constantane thermocouple (whose emf could be read to ± 0.02 mV), calibrated at the boiling points of water and benzophenone, and at the	ESTIMATED ERROR: Temperature: accuracy probably <u>+0.5 K</u> (compiler).
fusion points of tin and potassium nitrate.	

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] Potassium ethanoate (potassium constate); 	ll'yasov, I.I. Zh. Obshch. Khim. <u>1962</u> , 32, 347-349.
(C ₂ H ₃ O ₂) ₂ K ₂ ; [127-08-2]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{\circ}C$ T/K^{a} $100x_{1}$	······
306 579 0 203 576 5	
292 565 15	
285 558 20 277 550 25	
263 536 30	· \
248 521 35 232 505 40	280 - 280 -
235 508 45	
237 510 50	٩
242 515 60	
a w/v walues calculated by the second law	
1/K values calculated by the compiler.	240 -
	E
	$(C_2H_3O_2)_2K_2$ $(C_2H_3O_2)_2Cd$
Characteristic point(s):	
Eutectic, E, at 232 °C and $100 \pi_2$ = 60 (auth	or).
Note - The system was investigated at 0 \leq 100	$\mathbf{x}_1 \leq 60.$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:					ORIGINAL MEASUREMENTS:	
 Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] 					Pavlov, V.L.; Golubkova, V.V. Vestn. Kiev. Politekh. Inst. Ser. Khim. Mashinostr. Tekhnol. <u>1969</u> , No. 6, 76-79.	
VARIABL	ES:					PREPARED BY:
Tempera	ture.					Baldini, P.
EXPERIM	ENTAL	VALUES:			·	
t/°C	t/K ^a	100 x 1	t/ ^o C	T/K ^a	100 x₁	
300	573	5.0	152	425	49.9	
298	571	7.1	176	449	55.0	+
290	563	9.9	178	451	55.2	300 -
278	551	11.9	150 ^b	423	55.2	2
268	541	15.0	160	433	60.1	4
264	537	17.0	148 ^b	421	60.1	250 - 1
166 ^b	439	17.0	160	433	60.2	230 8 8
232	505	20.1	148 ^b	421	60.2	
166 ^D	439	20.1	192	465	65.1	
220	493	22.1	150	423	65.1	200 - 8 -
1660	439	22.1	198	471	66.9	163 / 1
164	437	25.0	220	493	69./	
170	439	25.1	150	493	70.1	150 - E,
200	473	3/ 0	262	42J 515	75 5	E ₂ E ₃
148b	475	34.9	242	511	77.0	
188	461	37.5	230	505	80.0	
178	451	39.9	230	503	82.0	0 50 100 _m 100
148 ^b	421	39.9	240	513	85.0	
164	437	45.1	242	515	85.3	
172	445	46.9	248	521	95.1	
188	461	49.9				
<pre>a T/K values calculated by the compiler. b Eutectic temperatures. Characteristic point(s): Eutectic, E₁, at 166 °C and 100x₁= 24 (authors). Eutectic, E₂, at 148 °C and 100x₁= 42 (authors). Eutectic, E₃, at 150 °C and 100x₁= 58 (authors). Eutectic, E₄, at 230 °C and 100x₁= 82 (authors). Intermediate compound(s): (C₂H₃O₂)₄CdK₂, congruently melting at 200 °C (authors). (C₂H₃O₂)₃CdK, congruently melting at 188 °C (authors). (C₂H₃O₂)₇Cd₃K, congruently melting at 242 °C (authors).</pre>						
AUXILIARY INFORMATION						
METHOD/	APPARA	TUS/PROCED	URE:			SOURCE AND PURITY OF MATERIALS:
						· - · · · · · · · · · · · · · · · · · ·
Visual polythermal method and time- temperature curves. Mixtures prepared in a glove-box.				and repared	Component 1 of analytical purity, dehydrated ($T_{fus}(1)=257-258^{\circ}C$, 530-531 K). Component 2 of analytical purity, heated at 110-140 $^{\circ}C$ to constant mass ($T_{fus}(2)=306-$	
ESTIMATED ERROR: 308					308°C, 579-581 K).	
Temperature: accuracy probably +2 K						

(compiler).

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] 	Nadirov, E.G.; Bakeev, M.I. Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR 1974, 25, 129-141.			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES:				
t/ ^o C T/K ^a 100x ₂	ل المسلم ا			
239 512 25 222 495 40 213 486 45 205 478 50 203 476 54 231 504 60 245 518 65 248 521 70 250 523 75 252 525 80 257 530 85 282 555 90 306 579 100 ^a T/K values calculated by the compiler.	$ \begin{array}{c} $			
Characteristic point(s):				
Eutectic, E, at 203 °C (visual polythermal method, initial crystallization), or 196 °C (thermographical analysis, fusion temperature), or 188 °C (conductometry, fusion temperature), and $100x_2$ = 54 (authors). Peritectic, P, at 253 °C (visual polythermal method), or 245 °C (thermographical analysis), or 251°C (conductometry, Fig.3 of the original paper), erroneously reported				
as $215 - 0$ in the text (compiler), and $100 \mathbf{x}_2^{\sim} 84$ (compiler).				
Note 1 - The system has been investigated at	$25 < 100x_2 < 100.$			
Note 2 - At about 194 ^o C abrupt changes (to be related to a polymorphic transition; authors) occur in the electrical conductivity of the mixtures with $100x_2$ = 85, 90, 95.				
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple and a PP potentiometer. Additional investigations have been performed by means of thermographical analysis, electrical conductometry, and X-ray diffractometry.	Not stated. ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler).			

COMPONENTS:	EVALUATOR:
 (1) Cadmium ethanoate (cadmium acetate);	Schiraldi, A.,
(C ₂ H ₃ O ₂) ₂ Cd; [543-90-8] (2) Sodium ethanoate (sodium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Na; [127-09-3]	Universita´ di Pavia (ITALY).

This system was studied by I1'yasov (Ref. 1), and Pavlov and Golubkova (Ref. 2). The former author claims the diagram to be of the simple eutectic type, with the invariant at 528 K (255 °C) and $100x_2$ = 68 (the eutectic composition is given in Ref. 1 as $100x_2$ = 52 since it refers to the equivalent fraction of component 2), whereas Pavlov and Golubkova suggest the existence of the intermediate compound $(C_2H_3O_2)_4$ CdNa₂, congruently melting at 527 K (254 °C), and, accordingly, of two eutectics, E_1 , E_2 , occurring at 496 K (223 °C) and $100x_2$ = 75, and at 507 K (234 °C) and $100x_2$ = 58, respectively.

Although the experimental data by Pavlov and Golubkova seem more detailed than those by Il'yasov, the evaluator has no arguments to definitely prefer the diagram shown in Ref. 2, ruling out that of Ref. 1.

As a comment, one may notice that the fusion temperature of the intermediate compound given in Ref. 2 is close to that of the eutectic reported in Ref. 1. This might suggest undercooling of Pavlov and Golubkova's samples. In any case, the existence of the intermediate compound suggested by the latter authors should be confirmed with X-ray diffractometry.

It is finally to be added that the fusion temperature of component 2 by Il'yasov (601 K) meets that listed in Table 1 of the Preface (601.3 ± 0.5 K), whereas the value by Pavlov and Golubkova (595 K) is significantly lower.

- (1) I1'yasov, I.I.
 Zh. Obshch. Khim. <u>1962</u>, 32, 347-349.
- Pavlov, V.L.; Golubkova, V.V.
 Vestn. Kiev. Politekh. Inst. Ser. Khim. Mashinostr. Tekhnol. 1969, No. 6, 76-79.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)₂Na₂; [127-09-3] 	Il [*] yasov, I.I. Zh. Obshch. Khim. <u>1962</u> , 32, 347-349.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁	ب []
328 601 0 318 591 10 315 588 15 309 582 20 297 570 30 287 560 35 277 550 40 261 534 45 259 532 50 264 537 55 267 540 60 267 540 65 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 255 °C and $100x_2$ = 52 (auth Note - The system was investigated at 0 \leq 100	$300 - 40 + 100 \times 1000 \times 100 $
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated.
	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES:
	1



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Cadmium ethanoate (cadmium acetate); (C₂H₃O₂)₂Cd; [543-90-8] Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Nadirov, E.G.; Bakeev, M.I. Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR 1974, 25, 129-141.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
236 509 40 233 506 50 231 504 60 228 501 65 217 490 70 215 488 75 206 479 80 192 465 84.1 179 452 86 198 471 87 214 487 90 231 504 95 237 510 100 ^a T/K values calculated by the compiler. Characteristic point: Eutectic, E, at 179 °C (visual polythermal method, initial crystallization), or 145 °C (fusion temperature by thermographical analysis), or 169 °C (fusion temperature by conductometry), and $100x_2$ = 86 (authors). Intermediate compound: $(C_2H_3O_2)_4CdRb_2$, polythermal method), 192 °C (thermographical	incongruently melting at 219 °C (visual analysis), or 206 °C (conductometry).
Note - The system has been investigated at 40	$\leq 100 \mathbf{x}_2 \leq 100.$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple and a PP potentiometer. Additional investigations were performed by means of thermographical analysis and electrical conductometry.	Not stated.
NOTE:	
The occurrence of intermediate compounds in the binaries $C_{2H_3O_2}/Cd$, K and $C_{2H_3O_2}/Cd$, Cs was claimed by the same authors in the same paper, and supported with X-ray diffraction patterns: for the present system, on the contrary, no analogous evidence was given. Moreover, the exceedingly large differences among the eutectic temperatures obtained with different techniques is to be stressed.	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES:

COMPONENTS:	EVALUATOR:
 (1) Cesium ethanoate (cesium acetate)	Schiraldi, A.,
(C ₂ H ₃ O ₂)Cs; [3396-11-0] (2) Potassium ethanoate (potassium acetate)	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)K; [127-08-2]	Universita´ di Pavia (ITALY).

Results on this binary have been repeatedly reported by Diogenov et al. (Refs. 1-3) as a part of their investigations on ternary and reciprocal ternary systems. These authors, who carried out visual polythermal observations on the liquidus, define the system as of the eutectic type with the invariant at either 405 K (132 °C; Ref. 1), or 403 K (130 °C; Ref. 2), or 413 K (140 °C; Ref. 3), and $100x_2 = 28.5$. It is not clear whether the different eutectic temperatures given in Refs. 1-3 come from different sets of measurements or depend on adjustments suggested by the general topology of the particular ternary studied in each paper. A knee in the liquidus branch richer in component 1 (Ref. 1) has been interpreted by these authors as due to a phase transition occurring in this salt at 447 K (174 °C). Diogenov et al. also claimed in a previous paper (Ref. 4) the occurrence in component 2 of a phase transition at 565-566 K (292-293 °C).

The DTA investigations by Storonkin et al. (Ref. 5) give further support to the fact that the system is of the eutectic type although the temperature (412 K) and composition $(100x_2 = 32)$ of the invariant have been singled out by extrapolation of the two liquidus branches. According to Fig. 3 of the original paper (Ref. 5), the authors assume that the eutectic equilibrium covers the composition range from $100x_2 = 0$ to $100x_2 = 100$. They do not mention, however, the occurrence of any allotropic transition in either component: according to Table 1 this ought to be correct for what concerns component 1, whereas component 2 ought to undergo a phase transition at 422.2+0.5 K.

Storonkin et al. (Ref. 5) ascribe the differences between their and Diogenov et al.'s diagram to the higher purity of the salts they employed: indeed, the fusion temperature they report for component 1 $[T_{fus}(1)/K = 467]$ is much closer to that listed in Table 1 of the Parface (46211) and the fusion temperature they are the fusion temperature the salts they are the salts the salts they are the salts they are the salts they are the salts they are the salts the salts they are the salts the salts the salts they are the salts the of the Preface (463+1) than that given by Diogenov et al. (453).

As a conclusion, the following remarks should be taken into account.

(1) The phase transition temperature reported for cesium ethanoate by Diogenov et al. seems to be unreliable.

(ii) The phase transition temperature reported for potassium ethanoate in Ref. 4 (565-566 K) seems also to be unreliable, as it cannot be identified with any transition temperature found by other investigators (Ref. 6).

(iii) The eutectic temperature reported by Storonkin et al., viz., 412 K, seems satisfactorily supported by their DTA results, as well as the trend of the liquidus branch richer in cesium ethanoate. On the contrary, there is some doubt about the reliability of the other liquidus branch which, according to these authors, does not show any "knee" to be possibly matched with the expected (see above) phase transition of potassium ethanoate. Consequently, the eutectic composition (attained by extrapolation of the liquidus branches) cannot be considered more reliable than that reported by Diogenov.

(iv) Finally, the complete immiscibility in the solid state should be more carefully verified, e.g., by further DTA or DSC investigations extended to extreme compositions.

- (1) Nurminskii, N.N. and Diogenov, G.G.; Zh. Neorg. Khim. <u>1960</u>, 5, 2084-2087; Russ. J.
- Inorg. Chem. (Engl. Transl.) 1960, 5, 1011-1013 (*). (2) Diogenov, G.G. and Sergeeva, G.S.; Zh. Neorg. Khim. 1965, 10, 292-294; Russ. J. Inorg. Chem. (Engl. Transl.) 1965, 10, 153-154 (*).
- (3) Diogenov, G.G. and Morgen, L.T.; Fiz.-Khim. Issled. Rasplavov Solei, Irkutsk 1975, 59-61.
- (4) Diogenov, G.G.; Nurminskii, N.N. and Gimel'shtein, V.G.; Zh. Neorg. Khim. 1957, 2, 1596-1600; Russ. J. Inorg. Chem. (Engl. Transl.) 1957, 2(7), 237-245.
- (5) Storonkin, A.V.; Vasil'kova, I.V. and Tarasov, A.A.; Vestn. Leningr. Univ., Fiz., Khim. 1977, (4), 80-85.
- (6) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.; Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford 1980, 29-115.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] 	Diogenov, G.G.; Sergeeva, G.S. Zh. Neorg. Khim. 1965, 10, 292-294; Russ. J. Inorg. Chem. (Engl. Transl.) 1965, 10, 153-154 (*).
VARIABLES:	PREPARED BY:
	Baldini. P.
EXPERIMENTAL VALUES:	
The authors refer to Ref. 1 for the experimentation of the experimentation of the temperature.	mental values, although giving a different
Characteristic point(s):	
Eutectic, E, at 130 °C and $100x_2$ = 28.5 (authors	ors).
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method. Temperatures measured with a Chromel-Alumel thermocouple.	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C= 180$ (Fig. 1 of the original paper). Component 2: $t_{fus}(2)/{}^{\circ}C= 310$ (Fig. 1).
	Tug(), i i i i i i i i i i i i i i i i i i i
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:
	(1) Nurminskii, N.N.; Diogenov, G.G. Zh. Neorg. Khim. 1960, 5, 2084-2087; Russ. J. Inorg. Chem., (Engl. Transl.) 1960, 5, 1011-1013.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] 	Diogenov, G.G.; Morgen, L.T. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 59-61.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The authors refer to Ref. 1 for the experimentation of the experimentation of the temperature.	ental values, although giving a different
Characteristic point(s):	
Eutectic, E, at 140 °C and 100 \mathbf{x}_1 = 71.5 (authors	ors).
	· · · · · ·
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method. Temperatures measured with a Chromel-Alumel thermocouple and a millivoltmeter.	Not stated. Component 1: t _{fus} (1)/ ⁰ C= 187 (Fig. 1 of the original paper).
	Component 2: $t_{fus}(2)/C=308$ (Fig. 1).
	COLINALED EKKUK:
	compiler).
	REFERENCES:
	 (1) Nurminskii, N.N.; Diogenov, G.G. Zh. Neorg. Khim. <u>1960</u>, 5, 2084-2087; Russ. J. Inorg. Chem., (Engl. Transl.) 1960, 5, 1011-1013.
COMPONENTS:	ORIGINAL MEASUREMENTS:
--	---
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] 	Storonkin, A.V.; Vasil [*] kova, I.V.; Tarasov, A.A. Vestn. Leningr. Univ., Fiz., Khim. <u>1977</u> , (4), 80-85.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.

EXPERIMENTAL VALUES:

Data reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 412 K and $100x_1 = 68$ (authors).



AUXILIARY INFORMATION SOURCE AND PURITY OF MATERIALS: METHOD/APPARATUS/PROCEDURE: DTA and "contact polythermal method" under Component 1 synthetized from Cs_2CO_3 and polarized light. IR spectra were also used ethanoic acid (T_{fus}(1)/K= 467; authors). Component 2 of analytical pur: to state the existence of intermediate Component 2 of analytical purity recrystallized twice from water and dried compound(s). under vacuum ($T_{fus}(2)/K = 584$; authors). The purity of both components was checked by thermographical analysis. The mixtures were prepared in a glove box. ESTIMATED ERROR: Temperature: probably +2 K accuracy (compiler). **REFERENCES:**

COMPONENTS:	EVALUATOR:
 (1) Cesium ethanoate (cesium acetate);	Franzosini, P.,
(C ₂ H ₃ O ₂)Cs; [3396-11-0] (2) Lithium ethanoate (lithium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Li; [546-89-4]	Universita´ di Pavia (ITALY).

This binary was first studied as a side of the ternary $C_{2H_3O_2}/Cs$, Li, Rb (Ref. 1), and re-determined by the same group ten years later (Ref. 2). Due to more accurate experimental methods (DTA and X-ray diffractometry) employed in the latter paper (Ref. 2), the phase diagram therein shown seems much more reliable than the previous one (Ref. 1).

Accordingly, the system is to be considered as characterized (Ref. 2) by the occurrence of a single intermediate compound, $(C_{2}H_{3}O_{2})_{3}CsLi_{2}$, congruently melting at 563 K (290 °C), and by two eutectics, at 420 K (147 °C) and $100x_{1}$ = 77, and at 520 K (247 °C) and $100x_{1}$ = 12, respectively.

The main difference of this phase diagram with respect to that presented in the previous work (Ref. 1) is the lack of a further intermediate compound, $(C_{2H_3O_2})_2C_{SLi}$ (incongruently melting). Consequently to this lack, however, a large part of the phase diagram of the ternary $C_{2H_3O_2}/C_S$, Li, Rb (Ref. 1) ought to be redrawn, which, at the present time has not been done, at least as far as the evaluator knows.

The fusion temperatures of component 1 and component 2 as given in Refs. 1, 2 (458-459 K, and 561-563 K, respectively) are not far from those listed in Table 1 of the Preface (463+1 K, and 557+2 K, respectively). Moreover, no mention is made of the occurrence of phase transitions in either component, which is again in agreement with Table 1 of the Preface, although in disagreement with the fact that in other papers by the same group (see, e.g., Ref. 3) component 1 is described as undergoing a phase transition at 477 K (174 $^{\circ}$ C).

- (1) Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. <u>1964</u>, 9, 482-487; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1964</u>, 9(2), 265-267.
- (2) Sarapulova, I.F.; Kashcheev, G.N.; Diogenov, G.G. Nekotorye Vopr. Khimii Rasplavlen. Solei i Produktov Destrusktii Sapropelitov, Irkutsk <u>1974</u>, 3-10.
- (3) Nurminskii, N.N.; Diogenov, G.G.
 Zh. Neorg. Khim. 1960, 5, 2084-2087; Russ. J. Inorg. Chem. (Engl. Transl.) 1960, 5, 1011-1013 (*).

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] 	Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. <u>1964</u> , 9, 482-487; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1964</u> , 9(2), 265-267 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
185 458 0 247 520 44.0 182 455 2.5 261 534 47.0 175 448 7.0 271 544 50.0 163 436 12.5 282 555 55.0 147 420 19.5 288 561 59.5 140 413 24.5 292 565 64.5 160 433 26.5 292 565 70.0 170 443 27.5 283 556 75.5 184 457 29.5 270 543 81.5 196 469 32.0 250 523 86.5 208 481 34.0 250 523 90.0 219 492 36.5 267 540 93.0 230 503 40.0 279 552 96.5 232 505 42.0 290 563 100.0 238 511 43.5 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E_1 , at 135 °C and $100x_1 = 76$ (auth Peritectic, P , at 233 °C and $100x_1 = 12$ (author Intermediate compound(s): $(C_2H_3O_2)_2CsLi$, incongruently melting. $(C_2H_3O_2)_3CsLi_2$, congruently melting at 293 °	ors). hors). C (according to the text and Fig. 2 of the
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method. Temperatures measured by means of a Chromel-Alumel thermocouple.	Not stated.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Lithium ethanoate (lithium acetate); (C₂H₃O₂)L1; [546-89-4] 	Sarapulova, I.F.; Kashcheev, G.N.; Diogenov, G.G. Nekotorye Vopr. Khimii Rasplavlen. Solei i Produktov Destruktsii Sapropelitov, Irkutsk, <u>1974</u> , 3-10.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{1} t/^{o}C T/K^{a} 100x_{1}$	
288 561 0 275 ^{bc} 548 50 284 ^{bc} 557 0 147 ^{bd} 420 50 253 526 10 247 520 55 252 ^{bc} 525 10 147 ^{bd} 420 55 247 ^{be} 520 10 182 455 70 268 541 20 172 ^{bc} 445 70 267 ^{bc} 540 20 148 ^{bd} 421 70 247 ^{be} 520 20 147 420 80 283 556 25 147 ^{bd} 420 80 283 ^{bc} 556 25 156 ^{bc} 429 85 246 ^{be} 519 25 147 ^{bd} 420 85 293 566 33 186 459 100 290 ^{bc} 563 33 185 ^{bc} 458 100 273 546 50 35 ^f 308 100 ^a T/K values calculated by the compiler. ^b Differential thermal analysis (filled circl c Initial fusion. ^d Eutectic stop (E ₁). ^e Eutectic stop (E ₂). ^f Solid state transition. Characteristic points: Eutectic, E ₁ , at 147 0 Eutectic, E ₂ , at 247 0	es C and $100x_1 = 77.0$ (authors). C and $100x_1 = 12.0$ (authors). ently melting at 293 °C (290 °C by DTA).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A thermographical analysis was performed with a Kurnakov pyrometer mod. 1959 (reference material: Al_2O_3). Only heating traces (at the heating rate of 5-6 °C/min) were recorded due to the tendency of the melts to undercool. Supplementary visual polythermal observations are also tabulated. X-ray diffraction patterns were used to obtain information on the intermediate compound.	Not stated. Component 1 undergoes a phase transition at t _{trs} (1)/ ⁰ C = 35.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:	
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).	
CRITICAL EVALUATION:	L	
This binary was first investigated as a side of the ternary $C_{2H_3O_2}/Cs$, Na, Rb by Diogenov and Sarapulova (Ref. 1), who reported a eutectic at 388 K (115 °C) and $100x_1 = 68$, on the basis of visual polythermal observations.		
The liquidus by these authors shows a knee at about 585 K and $100x_1$ about 5, which might be identified with the phase transition of $(C_2H_3O_2)$ Na reported by Diogenov at 596 K (323 °C; Ref. 2), and by Gimel'shtein and Diogenov at 583-584 K (310-311 °C; Ref. 3). However, such figures do not meet any of the high temperature T_{trs} values by other authors (Ref. 4), which range between 511-513 and 527+15 K.		
Substantially analogous results, including the knee (for which no explanation is offered), have been reported also by Storonkin et al. (Ref. 5) for the liquidus branch richer in component 2. The other branch by these authors, however, lies significantly above the corresponding curve by Diogenov and Sarapulova: the difference has been attributed by Storonkin et al. to the higher purity of the cesium ethanoate they employed. According to the latter authors (Ref. 5), who carried out DTA determinations through		
most of the composition range, the eutectic temperature is 392 K, and the eutectic composition (which was obtained by extrapolation, due to the tendency to undercool of the melts of composition close to x_E) is $100x_1 = 64$.		
In the opinion of the evaluator, the followin	g points should be remarked.	
(1) Neither Ref. 1 nor Ref. 5 report the phase transition of sodium ethanoate observed by other authors (Ref. 4) at 510-530 K, i.e., well above the eutectic temperature of the binary.		
(11) No comment is explicitely made in either work on the apparent knee of the liquidus branch richer in component 2.		
(iii) No experimental support is given to rule out the occurrence of solid solutions in the regions of the phase diagram close to the pure components.		
 (iv) The phase transition of cesium ethan (Ref. 6) at 447 K is neither confirmed nor (Ref. 1) by the same group. 	oate observed by Nurminskii and Diogenov mentioned in the present investigation	
Accordingly, it seems justified to cast some doubts about the reliability of the upper part of the liquidus branch richer in component 2, whereas the eutectic temperature $(390+2 \text{ K})$ and composition $(100x_2 = 66+2)$ seem satisfactorily supported by the data available.		
REFERENCES:		
 Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. <u>1964</u>, 9, 1499-1502; 9,814-816. Diogenov, G.G. 	Russ. J. Inorg. Chem. (Engl. Transl.) 1964,	
Zh. Neorg. Khim. <u>1956</u> , 1(4), 799-805; 1(4), 199-205.	Russ. J. Inorg. Chem. (Engl. Transl.) 1956,	
 (3) Gimel'shtein, V.G.; Diogenov, G.G. Zh. Neorg. Khim. <u>1958</u>, 3, 1644-49; 3(7), 230-236. 	Russ. J. Inorg. Chem. (Engl. Transl.) 1958,	
(4) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Thermal Properties, in Thermodynamic a IUPAC Chemical Data Series No. 28 (Franz Press, Oxford, <u>1980</u> , 29-115.	Franzosini, P. nd Transport Properties of Organic Salts, osini, P.; Sanesi, M.; Editors), Pergamon	
(5) Storonkin, A.V.; Vasil'kova, I.V. and Tar Vestn. Leningr. Univ., Fiz., Khim. <u>1977</u> ,	asov, A.A. (4), 80-85.	

 ⁽⁶⁾ Nurminskii, N.N. and Diogenov, G.G.
 Zh. Neorg. Khim. <u>1960</u>, Z, 2084-2087; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1960</u>, 5, 1011-1013.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Storonkin, A.V.; Vasil'kova, I.V.; Tarasov, A.A. Vestn. Leningr. Univ., Fiz., Khim. 1977, (4), 80-85.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
	•

EXPERIMENTAL VALUES:

Data presented only in graphical form (see figure).



Characteristic point(s):

Eutectic, E, at 392 K and $100x_1 = 64$ (authors).

Note - Undercooling does not allow one to draw the liquidus with accuracy at compositions close to the eutectic.

AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
DTA and "contact polythermal method" under polarized light. IR spectra were also used to state the existence of intermediate compound(s).	Component 1 synthetized from Cs_2CO_3 and ethanoic acid $(T_{fus}(1)/K=467; authors)$. Component 2 of analytical purity recrystallized twice from water and dried under vacuum $(T_{fus}(2)/K=607; authors)$. The purity of both components was checked by thermographical analysis. The mixtures were prepared in a glove box.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 (1) Cesium ethanoate (cesium acetate);	Schiraldi, A.,
(C ₂ H ₃ O ₂)Cs; [3396-11-0] (2) Rubidium ethanoate (rubidium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Rb; [563-67-7]	Universita´ di Pavia (ITALY).

This binary was studied as a side of the ternary $C_{2H_3O_2/Cs}$, Na, Rb (Ref. 1), and of the reciprocal ternary Cs, $Rb/C_{2H_3O_2}$, NO₂ (Ref. 2), respectively.

Both papers give substantially analogous results, i.e., a liquidus with a minimum at 446 K (173 °C) and $100x_1 = 72$ (Ref. 1), and at 445 K (172 °C) and $100x_1 = 71$ (Ref. 2), respectively. It is, however, not clear whether the slight differences in the coordinates of the minimum as given in Ref. 1 and Ref. 2, respectively, come from different sets of determinations, or from a suitable adjustment improving the overall presentation of the ternary involved. It is also to be remarked that, although coming from the same group, a significant difference exists between the $T_{\rm fus}(2)$ values given in Ref. 1 (453.2 K) and Ref. 2 (460 K), the corresponding value given in Table 1 being 463±1 K.

Moreover, in neither paper the phase transition of rubidium ethanoate, occurring at either 489-493 K (Ref. 3), or 498<u>+</u>1 (Preface, Table 1) is explicitely mentioned, although, e.g., it might reasonably justify the knee observed at about 498 K (Ref. 1) in the liquidus branch richer in component 2.

The inspection of the liquidus of both ternaries mentioned above strongly supports the occurrence of solid solutions in the $C_{2H_3}O_2/Cs$, Rb side binary. However, the limits of the T, \mathbf{x}_2 field covered in the binary by these solutions seem poorly defined, in particular for what concerns the compositions close to pure component 2, and for temperatures close to the transition temperature of this salt. Thence, in the evaluator's opinion, an investigation of the solidus would be desirable, in order to attain more satisfactory information about these points.

- (1) Diogenov, G.G.; Sarapulova, I.F.
 Zh. Neorg. Khim. <u>1964</u>, 9, 1499-1502; Russ. J. Inorg. Chem. (Engl. Transl.)<u>1964</u>, 9, 814-816.
- (2) Diogenov, G.G.; Morgen, L.T. Fiz.-Khim. issled. Rasplavov Solei, Irkutsk, 1975, 62-64.
- (3) Gimel'shtein, V.G.; Diogenov, G.G.
 Zh. Neorg. Khim. 1958, 3, 1644-1649; Russ. J. Inorg. Chem. (Engl. Transl.) 1958, 3(7), 230-236.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. <u>1964</u> , 9, 1499-1502 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1964</u> , 9, 814-816.
VARIABLES:	PREPARED BY:
Temperature.	Baldini. P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100 x ₁	U []
240.0 ^b 513.2 0 232.5 505.7 3.5 226.5 499.7 5.3 224.4 497.6 8.5 223.0 496.2 14.0 216.5 489.7 21.0 208.0 481.2 27.5 202.0 475.2 33.5 197.0 470.2 40.0 190.0 463.2 47.2 185.0 458.2 53.5 180.0 453.2 60.0 175.0 448.2 66.5 172.5 445.7 71.7 173.7 446.9 77.0 175.0 448.2 82.5 177.5 450.7 87.5 179.0 452.2 93.0 180.0 453.2 100.0 ^a T/K values calculated by the compiler. ^b 238 in Fig. 1 of the original paper (compiled)	$\frac{1}{180} - \frac{1}{(C_2H_3O_2)Rb} - \frac{100x_1}{(C_2H_3O_2)C_5}$
Continuous series of solid solutions with a (authors).	minimum, m, at 173 ^o C and 100x ₁ about 72
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple.	"Chemically pure" materials, recrystallized twice and dehydrated by prolonged heating (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 (1) Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. 1964, 9, 1292-1294; Russ. J. Inorg. Chem. (Engl. Transl.) 1964, 9, 704-706.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Diogenov, G.G.; Morgen, L.T. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 62-64.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Continuous series of solid solutions with a about 71 (compiler).	minimum, m, at 172 °C (authors) and $100x_1$
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermo couple.	Not stated. Component 1: $t_{fus}(1)/^{\circ}C \approx 187$. Component 2: $t_{fus}(2)/^{\circ}C = 238$.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	<u> </u>

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); (C₂H₃O₂)Cs; [3396-11-0] (2) Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] 	Pavlov, V.L.; Golubkova, V.V. Visn. Kiiv. Univ., Ser. Khim., Kiev, 1972, No. 13, 28-30.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	250 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 -
Characteristic point(s):	
Eutectic, E_1 , at 140 °C and 100 x_2 = 20 (authors). Eutectic, E_2 , at 104 °C and 100 x_2 = 45 (authors).	
Note - Glasses form at $50 \leq 100 \mathbf{x}_2 \leq 60$.	
Intermediate compound(s):	
$(C_2H_3O_2)_4Cs_2Zn$, congruently melting at 190 °(; (authors).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The visual polythermal method as well as time-temperature curves were employed. The temperatures were measured with a Chromel-Alumel thermocouple checked at the freezing temperatures of Zn, $K_2Cr_2O_7$, Cd, Sn, and benzoic acid.	Component 1: obtained by reacting Cs_2CO_3 and ethanoic acid, and kept in a dessiccator in the presence of P_2O_5 until constant mass. Component 2: $(C_2H_3O_2)_2Zn.2H_2O$ of analytical purity dried to constant mass at 110 °C.
The formation of glasses in this system	
seems likely. Accordingly, one should expect marked undercooling over a large composition range which would make the results of visual polythermal observations less reliable than usual. The lack of any further experimental evidence (e.g., from X-ray diffractometry) justifies casting doubts about the actual existence of the intermediate compound(s).	ESTIMATED ERROR: Temperature: accuracy probably <u>+2 K</u> (compiler). REFERENCES:

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Spinolo, G.,
(C ₂ H ₃ O ₂)K; [127-08-2] Lithium ethanoate (lithium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Li; [546-89-4]	Universita [~] di Pavia (ITALY).

The system potassium ethanoate - lithium ethanoate was investigated by Diogenov (visual polythermal analysis, 1956: Pochtakova (visual polythermal Ref. 1), analysis, 1965; Ref. 2), Sokolov and (visual polythermal analysis, Tsindrik supplemented with DTA, 1969; Ref. 3), and Gimel'shtein (DTA, supplemented with X-ray 1970, 1971; patterns, Refs. 4, 5, respectively).

Phase transitions are reported at 571 K (298 °C) by Diogenov (Ref. 1), at 331 and 428 K (58 and 155 °C, respectively) by Sokolov (Ref. 6, quoted in Refs. 2, 3), and at 428 K (155 °C) by Gimel'shtein (Ref. 5) for component 1; at 540 K (267 °C) by Diogenov (Ref. 1), and at 405 K (132 °C) by Gimel'shtein (Ref. 5) for component 2. In Table 1 of the Preface mention is made of a transition at 422.2+0.5 K for component 1, whereas no transition is reported for component 2.



Diogenov (Ref. 1) investigated the binary concerned here as a side system of the ternary $C_{2H_3O_2/K}$, Li, Na, and claimed the existence of two congruently melting intermediate compounds, i.e., $(C_{2H_3O_2})_2$ KLi and $(C_{2H_3O_2})_3$ KLi₂, respectively. The existence of the former, inferred by Diogenov from discontinuities observed in the liquidus of the binary itself and of two internal cuts of the ternary, was denied by all subsequent authors. In particular, no evidence of the existence of a crystallization field attributable to a 1:1 compound was found either by Pochtakova (Ref. 2) in her re-investigation of the ternary $C_{2}H_{3}O_{2}/K$, Li, Na, or by Sokolov and Tsindrik (Ref. 3), and Gimel'shtein (Ref. 4) in their studies of the topology of the reciprocal ternary K, $Li/C_{2H_3O_2}$, NO₃. The thermographical traces recorded by Gimel'shtein (and detailed in Ref. 5) support satisfactorily the assertion that in the mixtures of potassium and lithium ethanoates only the intermediate compound $(C_{2H_3O_2})_3 KLi_2$ does form, which melts congruently at 547+2 K (Refs. 2, 4, 5), and gives eutectics with each of the component salts.

In the figure, the visual data by Pochtakova (Ref. 2) are plotted, along with the thermographical ones obtained by Gimel'shtein (Ref. 5) to give a comprehensive and reasonably reliable representation of the liquidus, solidus, and subsolidus. The main discrepancies between the two authors occur in the fusion temperatures of the pure components:

T_{fus}(1)/K= 575, 585 (Refs. 2, 5, respectively);

 $T_{fus}(1)/K=557$, 565 (Refs. 2, 5, respectively). The more correct probably are those reported in Ref. 2, which are closer to $T_{fus}(1)/K=578.7\pm0.5$, and $T_{fus}(2)/K=557\pm2$, reported in Table 1 of the Preface. These discrepancies, however, do not affect substantially the overall features of the phase diagram.

- (1) Diogenov, G.G.; Zh. Neorg. Khim. <u>1956</u>, 1, 2551-2555 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1956</u>, 1(11), 122-126.
- (2) Pochtakova, E.I.; Zh. Neorg. Khim. <u>1965</u>, 10, 2333-2338 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1965</u>, 10, 1268-1271.
 (3) Sokolov, N.M.; Tsindrik, N.M.; Zh. Neorg. Khim. <u>1969</u>, 14, 584-590 (*); Russ. J. Inorg. Chem., (Engl. Transl.) <u>1969</u>, 14, 302-306.
 (4) Gimel shtein, V.G.
- Symposium, "Fiziko-Khimicheskii Analiz Solevykh Sistem", Irkutsk, 1970, 39-45. (5) Gimel'shtein, V.G.
- Tr. Irkutsk. Politekh. Inst. 1971, No. 66, 80-100.
- (6) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] 	Diogenov, G.G. Zh. Neorg. Khim. 1956, 1, 2551-2555 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1956, 1(11), 122-126.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	v
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \sum_{j=0}^{2} \sum_{k=1}^{300} \sum_{j=1}^{300} \sum_{k=1}^{300} \sum_{j=1}^{300} \sum$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple.	"Chemically pure" materials, recrystallized twice and dehydrated by prolonged heating. Components 1 and 2 undergo phase transitions at $t_{trs}(1)/^{0}C=298$ and $t_{trs}(2)/^{0}C=267$, respectively, according to Fig. 1 of the original paper (compiler).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:



COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Lithium ethanoate (lithium acetate); (C₂H₃O₂)L1; [546-89-4] 	Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. <u>1969</u> , 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1969</u> , 14, 302-306.
VARIABLES:	PREPARED BY:
Temperature	Baldini. P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure). Characteristic point(s): Eutectic, E_1 , at 197 °C and $100x_1 = 62$ (author Eutectic, E_2 , at 234 °C and $100x_1 = 13$ (author Intermediate compound(s):	$(C_{2}H_{3}O_{2})K = (C_{2}H_{3}O_{2})L_{1}$
(C ₂ H ₃ O ₂) ₃ KL1 ₂ , congruently melting (authors).	
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method, supplemented with differential thermal analysis.	Commercial materials recrystallized. Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C=58$, 155 (Ref. 1) and melts at $t_{fus}(1)/^{\circ}C=301$. Component 2 melts at $t_{fus}(2)/^{\circ}C=284$.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Lithium ethanoate (lithium acetate); (C₂H₃O₂)L1; [546-89-4] 	Gimel'shtein, V.G. Symposium, ["] Fiziko-Khimicheskii Analiz Solevykh Sistem", Irkutsk, <u>1970</u> , 39-45.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Eutectic, E_1 , at 197 ^O C and $100x_2 = 37.5$ (author). Eutectic, E_2 , at 234 ^O C and $100x_2 = 87$ (author).	
Intermediate compound(s):	
$(C_{2H_{3}O_{2}})_{3}$ KLi ₂ , congruently melting at 275 °C, and undergoing a phase transition at 65 °C (author).	
AUXILIARY I	NFORMATION
METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
Thermographical analysis.	Not stated
Thermographical analysis.	Component 2 undergoes a phase transition at $t_{trs}(2)/^{o}C= 132$.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Lithium ethanoate (lithium acetate); (C₂H₃O₂)L1; [546-89-4] 	Gimel'shtein, V.G. Tr. Irkutsk. Politekh. Inst. <u>1971</u> , No. 66, 80-100.
VARIARI FS.	PREPARED BY.
VARIADLES:	FRIERED DI.
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
312 585 0 260 533 55.0	I Contraction of the second
155 428 0 197 470 55.0	1
260 533 20.0 64 337 55.0	
196 469 20.0 260 533 75.0	
157 430 20.0 234 507 75.0 65 338 20.0 132 405 75.0	
225 498 42.5 66 339 75.0	
198 471 42.5 275 548 95.0	
155 428 42.5 236 509 95.0	
65 338 42.5 132 405 95.0	
250 523 50.0 292 565 100	
197 470 50.0 132 405 100	
^a T/K values calculated by the compiler.	
The meaning of the data listed in the table	becomes apparent by observing the figure
reported in the critical evaluation.	
Characteristic point(s): Eutectic, E_1 , at 197 °C and $100x_2$ = 37.5 (auth Eutectic, E_2 , at 237 °C (234 °C according to	or). Fig. 4) and 100x ₂ = 87.0 (author).
Intermediate compound: (C ₂ H ₃ O ₂) ₃ KLi ₂ , congruently melting at 275 ^O C at 65 ^O C (author).	(author), and undergoing a phase transition
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Differential thereal evaluate (value a	Nat about a
derivatograph with automatic recording of	Not stated. Component 1 molts at to $(1)/^{0}C = 312$ (310
the heating curves) and room temperature X-	according to Fig. 4 of the original paper:
ray diffractometry (using a URS-501M	compiler), and undergoes a phase transition
apparatus) were employed.	at $t_{trs}(1)/^{o}C= 155$.
NOTE:	Component 2 melts at $t_{fus}(2)/^{o}C= 292$ (291 according to Fig. 4 of the original paper;
m1 14 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	compiler), and undergoes a phase transition
The coordinates of the characteristic	at $t_{trs}(2)/C= 132$.
basis of his own DTA measurements, and of	
previous literature data (Refs. 1. 2). X-	
ray patterns were taken at $100x_2 = 45$, 70.	ESTIMATED ERROR:
2	
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	(1) Pochtakova, E.I.
	Zh. Neorg. Khim. 1965, 10, 2333-2338.
	(2) Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. 1969, 14, 584-590.



COMPONENTS:	EVALUATOR:	
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Franzosini, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).	
	<u> </u>	
CRITICAL EVALUATION:		
This system has been the most widely studied the different authors are summarized hereafte	during the last 70 years. The opinions by r.	
(1) <u>Baskov</u> (<u>1915</u> ; Ref. 1). $T_{fus}(1) = 568.2 \text{ K}$ (295.0 °C); $T_{fus}(2) = 593.2 \text{ K}$ (320.0 °C); continuous series of solid solutions with a minimum, m, at 496.2 K (223.0 °C) and $100x_2 = 46$ (method: thermal analysis; liquidus and solidus investigated).		
(2) Bergman; Evdokimova (1956; Ref. 2). $T_{fus}(1) = 575 \text{ K} (302 ^{\circ}\text{C}); T_{fus}(2) = 599 \text{ K} (326 ^{\circ}\text{C}); T_{trs}(2) = 527 \text{ K} (254 ^{\circ}\text{C});$ eutectic, E, at 497 K (224 $^{\circ}\text{C}$) and $100x_2 = 45$ (method: visual polythermal analysis, supplemented with three DTA records; liquidus and solidus investigated).		
(3) <u>Diogenov; Erlykov (1958;</u> Ref. 3). $T_{fus}(1) = 583.5 \text{ K} (310.5 ^{\circ}\text{C});$ $T_{trs}(1) = 569 \text{ K} (296 ^{\circ}\text{C});$ $T_{fus}(2) = 610 \text{ K} (337 ^{\circ}\text{C});$ $T_{trs}(2) = 599 \text{ K} (326 ^{\circ}\text{C});$ continuous series of solid solutions with a minimum, m, at 501 K (228 ^{\circ}\text{C}) and 100x_2 = 45 (method: visual polythermal analysis; liquidus only investigated).		
(4) <u>Golubeva; Bergman; Grigor'eva</u> (1958; Ref. Intermediate compound (C ₂ H ₃ O ₂) ₃ K ₂ Na, incong visual polythermal analysis).	4). ruently melting at 513 K (240 ^o C) (method:	
(5) <u>Sokolov; Pochtakova</u> (<u>1958</u> ; Ref. 5). $T_{fus}(1) = 574 \text{ K} (301 ^{\circ}\text{C}); T_{fus}(2) = 604 \text{ K} (331 ^{\circ}\text{C}); the authors from Ref. 2]; eutectic, E1, at E2, at 508 K (235 °C) and 100x_2 = 46.5; congruently melting at 514 K (241 °C) (methodonly investigated).$	^o C); $[T_{trs} (2)= 527 \text{ K} (254 ^{\text{O}C});$ quoted by 513 K (240 $^{\text{O}C}$) and 100 $x_2=$ 38.5; eutectic, intermediate compound, (C ₂ H ₃ O ₂) ₅ K ₃ Na ₂ , d: visual polythermal analysis; liquidus	
(6) <u>Nesterova; Bergman</u> (1960; Ref. 6). $T_{fus}(1) = 579 \text{ K} (306 ^{\circ}\text{C}); T_{fus}(2) = 601 \text{ K} (328 100 \text{ m}_2 = 36.5; eutectic, E, at 505 \text{ K} (232 (C_2H_3O_2)_3K_2Na, incongruently melting (method: investigated).$	^o C); peritectic, P, at 511 K (238 ^o C) and ^o C) and $100x_2 = 50$; intermediate compound, visual polythermal analysis; liquidus only	
(7) <u>Il'yasov; Bergman (1960;</u> Ref. 7). $T_{fus}(1) = 579 \text{ K} (306 ^{\circ}\text{C}); T_{fus}(2) = 601 \text{ K} (328)$ $256 ^{\circ}\text{C}$) and $100x_2 = 35;$ eutectic, E, at 5 compound, $(C_2H_3O_2)_3K_2N_4$, incongruently mel liquidus only investigated).	^o C); peritectic, P, at 523-529 K (250- 13 K (240 ^o C) and $100x_2$ = 50; intermediate ting (method: visual polythermal analysis;	
(8) <u>Diogenov; Sarapulova</u> (<u>1964;</u> Ref. 8). $T_{fus}(1) = 583 \text{ K (310 °C);}$ $T_{fus}(2) = 608 K (333 (composition not reported); eutectic, E2, at intermediate compound, (C2H3O2)5K3Na2, cong analysis).$	5 ^O C); eutectic, E ₁ , at 513 K (240 ^O C) 508 K (235 ^O C) (composition not reported); ruently melting (method: visual polythermal	
(9) Sokolov; Pochtakova (1967; Ref. 9). $T_{fus}(1) = 575 \text{ K} (302 ^{\circ}\text{C}); T_{fus}(2) = 604 \text{ K} (331 ^{\circ}\text{C}); solid state transitions at 428 and 331 \text{ K} (155 and 58 ^{\circ}\text{C}) for component 1, at 511, 403, 391, and 331 \text{ K} (238, 130, 118, and 58 ^{\circ}\text{C}) for component 2; eutectic, E1, at 513 \text{ K} (240 ^{\circ}\text{C}) and 100x_2 = 38.5; eutectic, E2, at 506 K (233 ^{\circ}\text{C}) and 100x_2 = 46.5; intermediate compound, (C_2H_3O_2)_5K_3Na_2, congruently melting at 513-514 K (240-241 ^{\circ}\text{C}) (method: thermographical analysis, supplemented with visual polythermal measurements and microscopic observations in polarized light).$		
(10) <u>Diogenov; Chumakova</u> (<u>1975;</u> Ref. 10). $T_{fus}(1) = 575 K (302 °C);$ $T_{fus}(2) = 599 K (32)$ (composition not reported); eutectic, E, at intermediate compound, (C ₂ H ₃ O ₂) ₅ K ₃ Na ₂ , incong analysis).	6 ^o C); peritectic, P, at 513 K (240 ^o C) 510 K (237 ^o C) (composition not reported); ruently melting (method: visual polythermal	

COMPONENT	S:		EVALUATOR:		
(1) Potas (C ₂ H ₃ (2) Sodiu (C ₂ H ₃)	sium ethanoate (potassin O ₂)K; [127-08-2] m ethanoate (sodium ace O ₂)Na; [127-09-3]	um acetate); tate);	Franzosini, Dipartimento Universita	P., di Chimica di Pavia (I'	Fisica, TALY).
CRITICAL	EVALUATION (cont.d):		<u> </u>		
(11) <u>Storonkin; Vasil'kova; Tarasov</u> (1977; Ref. 11). $T_{fus}(1) = 584 \text{ K}$ (311 °C); $T_{fus}(2) = 607 \text{ K}$ (334 °C); eutectic, E, at 511 K (238 °C) and 100x ₂ = 46 (method: differential thermal analysis and "contact polythermal method" under polarized light, supplemented with IR spectroscopy).					
Informati conflicti state tra	on from different so ng, possibly due – into nsitions are characteri:	ources on t er alia — to zed by a rema	he thermophy hygroscopicit rkable sluggi	sics of b y, and to shness.	oth components is the fact that solid
$T_{fus}(1)$ values ranging between 565 and 584 K, and $T_{fug}(2)$ values ranging between 592 and 610 K can be found in the literature (Ref. 12). The DSC data from Preface Table 1, i.e., $T_{fus}(1) = 578.7\pm0.5$ K and $T_{fug}(2) = 601.3\pm0.5$ K, are thought to be reasonably trustworthy, being supported by independent cryometric measurements by the same group (Ref. 12). Concerning in particular the T_{fus} data given in Refs. 1-11, the following remarks can be made. Poor reliability seems to be attached to the fusion temperatures from Refs. 1, 3, 8, 10, 11. Indeed: (i) Baskov (Ref. 1), who studied the system in 1915, might have not had at disposal high purity samples, thus obtaining too low T_{fus} values $[T_{fus}(1) = 568.2$ K; $T_{fug}(2) = 593.2$ K]; (11) Diogenov et al.'s figures $[T_{fug}(1) = 568.5$ K (1958; Ref. 3), 583 K (1964; Ref. 8), and 575 K (1975; Ref. 10); $T_{fug}(2) = 610$ K (1958; Ref. 3), 508 K (1964; Ref. 8), and 599 K (1975; Ref. 10)] look as doubtful, due to excessive fluctuation; (111) Storonkin et al.'s figures $[T_{fus}(1) = 584$ K; $T_{fug}(2) = 607$ K (1977; Ref. 11)] seem also to be doubtful and for the same reason, inasmuch as in previous papers Storonkin, Vasil'kova, and Potemin (1974; Ref. 13) gave $T_{fus}(2) = 604$ K. Instead, the agreement with T_{fus} data from Preface Table 1 is satisfactory for the most recent figures by Bergman et al. (Refs. 6, 7), and still acceptable for those by Sokolov and Pochtakova (Refs. 5, 9).					
 Salt	T _{trs} /K	Method	Year	Ref.	
с ₂ н ₃ 0 ₂ к	428, 331 565-566 569 423 (503, 433, 353) 428, about 348 422.2+0.5 413-423	Vis. pol. Vis. pol. Vis. pol. Dilat.,DTA 	1956 1957 1958 1966 1966 1972 1975 1975	15 16 3 17 18 19 Preface, T 20	 able 1
C ₂ H ₃ O ₂ Na	527 596 511-513, 403, 391, 331 599 583-584 527+15, 465+3, 414+10 337	Vis. pol. Vis. pol. Vis. pol. Vis. pol. Vis. pol. DSC DTA	1956 1956 1958 1958 1958 1975 1975	2 21 15 3 22 Preface, T 23	able 1
Vis. pol.: visual polythermal analysis; Dilat.: dilatometry; (): provisional data.					
Potassium ethanoate was submitted to X-ray investigation by Hatibarua and Parry					

Potassium ethanoate was submitted to X-ray investigation by Hatibarua and Parry (Ref. 19), who obtained evidence for a monoclinic -> monoclinic transformation at about 348 K, and for a monoclinic -> orthorhombic transformation at 428 K. Allowance being made for some fluctuations in the T_{trs} values, it can be asserted that the occurrence of the former transition is supported by Sokolov's (Ref. 15), and Hazlewood et al.'s (Ref. 18) findings, while on the occurrence of the latter transition all the authors concerned agree, but for Diogenov et al. (Refs. 3, 16). These, in turn, are alone in claiming that component l undergoes a transformation at a temperature as high as 560-570 K: the evaluator, however, is inclined to think that the existence of the latter

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Franzosini, P.,
(C ₂ H ₃ O ₂)K; [127-08-2] Sodium ethanoate (sodium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Na; [127-09-3]	Universita' di Pavia (ITALY).

CRITICAL EVALUATION (cont.d):

transformation is quite doubtful.

The number and location of solid state transitions in sodium ethanoate is still an open question, and the pertinent data are the most uncertain among those listed in Preface Table 1. It can only be said that the occurrence of a transition at 510-530 K seems to be reasonably supported (Refs. 2, 15, and Preface Table 1), whereas insufficient experimental evidence has been provided so far for the remaining transitions, including that reported by Diogenov et al. (Refs. 21, 3, 22) at 580-600 K.

Concerning the topology of the phase diagram, the evaluator is inclined not to take into account the findings by: (1) Baskov (Ref. 1), because reasonable doubts exist - as said above - about the purity of the salts he could have at disposal in 1915; (11) Diogenov et al. (Refs. 3, 8, 10), for both the above made remarks on the phase transformation temperatures they report, and their conflicting assertions on the phase relations (continuous series of solid solutions in Ref. 3; congruently melting intermediate compound in Ref. 8; incongruently melting intermediate compound in Ref. 10).

Storonkin et al. (Ref. 11) quoted in their paper Refs. 1-5, 7, 8, and - inter alia - asserted correctly that it is hard to state the composition of an incongruently melting intermediate compound on the only basis of visual observations carried out on the liquidus. They asserted also that: (i) due to undercooling of the molten mixtures of composition $50 \leq 100x_1 \leq 60$, no reliable information could be drawn from their liquidus on the formation of any intermediate compound; and (ii) their supplementary IR measurements gave no evidence of the existence of such compounds. Accordingly, they claimed the occurrence of a eutectic as the only invariant, and singled out its composition $(100x_2 = 46)$ by extrapolation of the part of the liquidus branches they were able to investigate. Storonkin et al. (Ref. 11), however, employed salts on the purity of which doubts - as said above - are not unreasonable, and were not aware of the more recent paper by Sokolov and Pochtakova (Ref. 9).

Bergman et al. in their oldest paper (Ref. 2) claimed the existence of a eutectic, but subsequently changed their mind (Refs. 4, 6, 7), and asserted that the incongruently melting compound $(C_{2H_3O_2})_{3K_2Na}$ was formed. It can be observed that the fusion temperatures of the pure components given in their most recent paper (Ref. 7), i.e., $T_{fus}(1)/K=579$ and $T_{fus}(2)/K=601$, are in excellent agreement with the corresponding values listed in Table 1 of the Preface $(578.7\pm0.5 \text{ K}, \text{ and } 601.3\pm0.5 \text{ K}, \text{ respectively})$, and that they make no mention of difficulties in measuring the liquidus. The composition they stated for the intermediate compound, however, was not supported by any investigation of the solidus, and poor reliability is to be attached to the peritectic temperature they suggested (511 K in Ref. 6; 523-529 K in Ref. 7).

Finally, Sokolov and Pochtakova (Refs. 5, 9) in their more recent paper (Ref. 9) employed thermographical analysis to support the assertion already made in Ref. 5 that the intermediate compound $(C_2H_3O_2)_5K_3Na_2$ is formed in the binary. They too seem not to have met special difficulties in measuring the liquidus.

In conclusion, the evaluator is inclined to think that:

- in the composition range $40 \le 100 \mathbf{x}_2 \le 100$ a eutectic exists at 508+3 K and $100 \mathbf{x}_2 = 48 \pm 2$;

- an intermediate compound is likely formed: it ought to have composition $(C_2H_3O_2)_5K_3Na_2$, and melt congruently (thus giving origin to a second eutectic in the composition range $0 \le 100x_2 \le 40$);

- limited mutual solubility exists on both sides of the diagram;

The second conclusion is based on Sokolov and Pochtakova's (Refs. 5, 9) information, which seems the most reliable at disposal so far, although being not fully free from criticisms (see, e.g., the above made remarks on the solid state transformations occurring in pure components).

The last assertion is supported by the findings of Sokolov and Pochtakova (Ref. 9), and Storonkin et al. (Ref. 11). Moreover, Braghetti et al. (Ref. 24) found for sodium

COMPONENTS:	EVALUATOR:		
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Franzosini, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).		
CRITTCAL EVALUATION (cont d).	l		
CRITICAL EVALUATION (CONE.d):			
	limiting value		
$ \lim_{m \to 0} (\Delta T/m) = 14.6 \text{ K molality}^{-1} $			
(ΔT : experimental freezing point depression; m: molality of the solute), whereas the cryometric constant of potassium ethanoate is 18.0+0.3 K molality ⁻¹ (Ref. 24).			
REFERENCES:			
 Baskov, A.; Zh. Russk. FizKhim. Obshch Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Ob 27 296-314. 	n. <u>1915</u> , 47, 1533-1535. Schei i Neorg. Khim. Akad. Nauk SSSR <u>1956</u> ,		
(3) Diogenov, G.G.; Erlykov, A.M.	- m-1-1		
(4) Golubeva, M.S.; Bergman, A.G.; Grigor'ev	a. 1ekno1. <u>1936</u> , No. 5, 413-416. a. E.A.		
Uch. Zap. Rostovskna-Donu Gos. Univ. 1 (5) Sokolov, N.M.; Pochtakova, E.I. Zh. Obsi	<u>958,</u> 41, 145-154. ich. Khim. <u>1958</u> , 28, 1397-1404.		
 (6) Nesterova, A.K.; Bergman, A.G. Zh. Obshch. Khim. 1960, 30, 317-320; Ru 	uss. J. Gen. Chem., Engl. Transl., 1960, 30,		
339-342 (*). (7) Il'yasov, I.I.; Bergman, A.G.			
Zh. Obshch. Khim. 1960, 30, 355-358. (8) Diogenov, G.G.; Sarapulova, I.F.			
Zh. Neorg. Khim. 1964, 9, 1292-1294 1964, 9, 704-706.	(*); Russ. J. Inorg. Chem., Engl. Transl.,		
 (9) Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1967, 37, 1420-1422. 			
(10) Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplayov Solei. Irku	itak. 1975. 7-12.		
(11) Storonkin, A.V.; Vasil'kova, I.V.; Taras	ov, A.A.		
(12) Sanesi, M.; Cingolani, A.; Tonelli, P.L.	; Franzosini, P.		
Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon			
Press, Oxford, <u>1980</u> , 29-115. (13) Storonkin, A.V.; Vasil'kova, I.V.; Potem	Press, Oxford, <u>1980</u> , 29-115. 3) Storonkin, A.V.; Vasil'kova, I.V.; Potemin. S.S.		
Vestn. Leningr. Univ., Fiz., Khim. 1974((14) Potemin, S.S.: Tarasov, A.A.: Panin, O.B	16), 73-76.		
Vestn. Leningr. Univ., Fiz., Khim. 1973(Vestn. Leningr. Univ., Fiz., Khim. <u>1973</u> (1), 86-89.		
Tezisy Dokl. Nauch. Konf. S.M.I. 1956, a	s quoted in Ref. 9.		
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Trans. Faraday Soc. <u>1966</u> , 62, 3101-3113. (19) Hatibarua, J.R.; Parry, G.S.			
Acta Cryst. <u>1972</u> , B28, 3099-3100. (20) Poppl, L.			
Proc. Eur. Symp. Thermal Anal., 1st, <u>197</u> (21) Diogenov, G.G.	<u>6, 237–240.</u>		
Zh. Neorg. Khim. <u>1956</u> , 1, 799-805; 1(4), 199-205.	Russ. J. Inorg. Chem. (Engl. Transl.) 1956,		
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3 (7), 230-236.	Auss. J. Inorg. Chem. (Engl. Transl.) 1938,		
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(24) Braghetti, M.; Leonesi, D.; Franzosini, Ric. Sci. <u>1968</u> , 38, 116-118.	P.		

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Baskov, A. Zh. Russk. FizKhim. Obshch. 1915, 47, 1533-1535.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C^{a}$ T/K^{b} $t/^{o}C^{c}$ T/K^{b} 100 x_{2}	
<pre>295.0 568.2 295.0 568.2 0.0 288.0^d 561.2 263.5 536.7 12.0 260.0 533.2 250.0 523.2 24.0 237.0 510.2 228.5 501.7 37.5 231.0 504.2 223.5 496.7 40.5 223.0 496.2 223.0 496.2 46.5 232.0 505.2 52.0 253.0^e 526.2 240.5 513.7 58.5 271.5 544.7 256.5 529.7 66.5 293.0 566.2 277.2 550.4 78.0 307.5 580.7 295.0 568.2 87.5 320.0 593.2 320.0 593.2 100.0 a Starting of crystallization. b T/K values calculated by the compiler. c End of crystallization. d 238.0 in the original text (correction compatible with Fig. 1 of the text; c compiler). e 233.0 in the original text (correction compatible with Fig. 1 of the text; c compiler). Characteristic point(s): Minimum, m, at 233 °C (author), or 223 °C</pre>	C (compiler), and 100 x ₂ = 46; none of the
cooling curves shows a eutectic stop (author	• NFORMATION
	SOURCE AND DUDITY OF MATERIALS.
MEINOD/AFFARATUS/FROCEDURE:	SOURCE AND FURITI OF MATERIALS:
Thermal analysis.	Materials dehydrated by heating, then cooled in a dessiccator before use.
	ESTIMATED ERROR: Temperature: accuracy not evaluable (complian).
	REFERENCES:

<u> </u>	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{0}C T/K^{a} 100x_{2} t^{0}C T/K^{a} 100x_{2}$	المحمد المحم
302 575 0.0 238 511 52.3 298 571 2.4 249 522 58.4 296 569 4.6 256 529 61.3 293 566 7.9 265 538 64.0 288 561 11.8 268 541 66.1 280 553 15.5 274 547 68.0 274 547 18.8 277 550 69.9 267 540 23.0 281 554 71.9 256 529 28.1 285 558 73.7 245 518 33.0 290 563 75.7 242 515 34.9 294 567 77.3 238 511 37.2 295 568 79.4 233 506 39.3 298 571 81.0 231 504 41.8 302 575 83.0 227 500 44.2 309 582 86.0 227 500 44.2 309 582 86.0 231 504 49.4 326 599 100 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 224 °C and $100x_2$ = 45 (authors Note - DTA heating traces were recorded respectively) previously melted and cooled of temperature.). on three mixtures $(100x_2=5, 20, 80, quickly, in order to confirm the eutectic$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method: the temperatures of starting crystallization were measured with a Nichrome-Constantane thermocouple and a millivoltmeter (17 mV full-scale).	"Chemically pure" $(C_2H_3O_2)K$ and $(C_2H_3O_2)Na\cdot 3H_2O$ were dried to constant mass. Component 2 undergoes a phase transition at $t_{trs}(2)/^{O}C=254$.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. <u>1958</u> , No. 3, 413-416.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{0}C$ T/K^{a} 100 x_{1} $t^{0}C$ T/K^{a} 100 x_{1}	
337 610 0 229 502 52.0 336 609 1.2 228 501 52.7 332 605 3.3 229.5 502.5 55.5 326 599 4.5 231.5 504.5 57.5 326 599 7.5 235 508 60.0 321 594 10.5 237.5 510.5 62.0 316 589 13.7 242 515 64.0 310 583 17.0 250 523 68.5 305 578 19.9 254 527 70.0 296 569 23.2 264 537 75.0 289 562 26.0 274 547 80.0 282 555 28.5 282 555 84.5 274 547 31.0 284 557 85.5 266 539 37.3 292 568 89.5 250 523 40.6 295 568 91.7	$\begin{array}{c} \begin{array}{c} \begin{array}{c} & \\ & \\ & \\ \end{array} \\ 300 \\ \\ \\ 250 \\ \\ \\ \end{array} \\ \\ 250 \\ \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $
AUXILIARY I	• NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated. Component 1 undergoes a phase transition at $t_{trs}(1)/^{O}C=296$. Component 2 undergoes a phase transition at $t_{trs}(2)/^{O}C=326$.
	ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

······	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Golubeva, M.S.; Bergman, A.G.; Grigor'eva, E.A. Uch. Zap. Rostovskna-Donu Gos. Univ. 1958, 41, 145-154.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
-	
EXPERIMENTAL VALUES:	
Intermediate compound(s):	
$(C_{2}H_{3}O_{2})_{3}K_{2}Na$, melting with decomposition at	240 ^o C (authors).
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a Chromel-Alumel thermocouple.	Materials of analytical purity recrystallized twice, and dehydrated before use.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES :

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. <u>1958</u> , 28, 1397-1404.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₁ t/°C T/K ^a 100x ₁ 331 604 0 38 511 55 322 595 5 238 511 57.5 315 588 10 241 514 60 307 580 15 240 513 61.5 299 572 20 242 515 62.5 291 564 25 246 519 65 282 555 30 251 524 67.5 273 546 35 255 528 70 264 537 40 263 536 75 258 531 42.5 272 545 80 254 527 45 282 555 85 247 520 47.5 290 563 90 244 517 50 298 571 95 238 511 52.5 301 574 100 235 508 53.5 ^a T/K values calculated by the compiler. Characteristic point(s): Peritectic, P, (eutectic in the compiler's op Eutectic, E, at 235 °C and $100x_1 = 53.5$ (autho Intermediate compound(s):	$\int_{1}^{4} \int_{0}^{4} \int_{0$
	, completion,
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE: Visual polythermal method.	SOURCE AND PURITY OF MATERIALS: "Chemically pure" materials were employed. Component 2 undergoes a phase transition at t _{trs} (2)/°C= 254 (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2 K</u> (compiler).
	REFERENCES: (1) Bergman, A.G.; Evdokimova, K.A.
	296-314.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Nesterova, A.K.; Bergman, A.G. Zh. Obshch. Khim. <u>1960</u> , 30 , 317-320; Russ. J. Gen. Chem. (Engl. Transl.), <u>1960</u> , 30, 339-342 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
306 579 0 290 563 5 283 556 10 276 549 15 267 540 20 259 532 25 250 523 30 241 514 35 237 510 40 235 508 45 232 505 50 243 516 55 253 526 60 263 536 65 273 546 70 ^a T/K values calculated by the compiler. Characteristic point(s): Peritectic, P, at 238 °C and $100x_2$ = 36.5 (authors) Intermediate compound(s): ($C_2H_3O_2$) $_3K_2Na$, melting with decomposition (authors)	$\sum_{k=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{j=1}^{n} \sum_{j$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method; temperatures measured with a thermometer (accuracy: +0.5 °C). A glycerol bath was employed.	"Chemically pure", recrystallized materials were used. Component 2: t _{fus} (2)/ ^O C= 328 (Fig. 2 of the original paper).
	ESTIMATED ERROR:
	Temperature: accuracy <u>+</u> 0.5 K (authors).
	REFERENCES:



1			
COMPONENTS:	ORIGINAL MEASUREMENTS:		
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Diogenov, G.G.; Sarapulova, I.F. Zh. Neorg. Khim. <u>1964</u> , 9, 1292-1294 (*); Russ. J. Inorg. Chem. (Engl. Transl.), <u>1964</u> , 9, 704-706.		
VARIABLES:	PREPARED BY:		
Temperature.	Baldini, P.		
EXPERIMENTAL VALUES:			
Characteristic point(s): Eutectic, E_1 , at 240 °C; composition not stated (authors). Eutectic, E_2 , at 235 °C; composition not stated (authors).			
(CoHeOr)-KeNar (congruently melting compiler			
AUXILIARY INFORMATION			
ME THOD/AP PARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal method; temperature measured with a Chromel-Alumel thermocouple.	"Chemically pure" materials, recrystallized twice and dehydrated by prolonged heating at about 300 °C were employed. Component 1: $t_{fus}(1)/°C= 310$. Component 2: $t_{fus}(2)/°C= 335$ (authors).		
	ESTIMATED ERROR:		
	Not evaluable (compiler).		
	REFERENCES:		

<pre>COMPONENTS: (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3]</pre>				ssium ac	ORIGINAL MEASUREMENTS: Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. <u>1967</u> , 37, 1420-1422.	
VARIABLES:					PREPARED BY:	
Tempera	iture.					Baldini, P.
EXPERIM	IENTAL V	ALUES:				
t/°C	t/K ^a	100 x 1	t/°C	T/K ^a	100 x 1	
318b 310 ^c 60 ^g 95 ^h 308b 233 ^d 60 ^g 278b 233 ^d 120 ^f 58 ^g 248 ^b 238 ^d 120 ^f 233 ^d 196 ^e 117 ^f 60 ^g 240 ^b 240 ^b 233 ^d 196 ^e 117 ^f 60 ^g 240 ^b 240 ^b 233 ^d 196 ^e 117 ^f 240 ^g 240 ^b 240 ^b 24	 591 583 333 368 581 506 333 551 506 393 331 521 511 463 393 506 506 506 506 506 506 506 506 469 390 333 513 513 471 	10 10 10 15 15 30 30 30 30 50 50 50 50 50 50 53.5 53.5	120 ^f 60 ^g 233 ^d 118 ^f 60 ^g 246 ^b 246 ^b 122 ^f 268 ^b 240 ^c 120 ^f 286 ^c 120 ^f 286 ^c 120 ^f 286 ^c 120 ^f 300 ^c 142 ^f 60 ^g 142 ^f 187 ^h	393 333 506 391 333 519 513 471 395 541 513 393 333 559 543 393 333 559 543 393 333 477 573 573 415 333 460	60 61.5 61.5 61.5 65 65 65 75 75 75 75 75 75 75 85 85 85 85 85 85 85 95 95 95 95	$ \begin{array}{c} $
 T/K values calculated by the compiler. Temperatures of starting crystallization (authors). Temperatures of ending crystallization (authors). Eutectic temperatures (authors). Solid-solid transition of the intermediate compound (authors). Interaction of the intermediate compound with the solid solution rich in component 1 (authors). Reaction 2[(C₂H₃O₂)₃K₂Na] = (C₂H₃O₂)₅K₃Na + (C₂H₃O₂)K (authors). Limits of the solid solution regions (authors). 						
Characteristic point(s): Eutectic, E_1 , at 240 °C and $100x_1 = 61.5$ (compiler). Eutectic, E_2 , at 233 °C and $100x_1 = 53.5$ (compiler). Intermediate compound: $(C_{2H_3O_2})_{5K_3Na_2}$ congruently melting at 240 °C (compiler), or 241 °C according to the figure of the original paper.						
	AUXILIARY INFORMATION				FORMATION	
METHOD/	METHOD/APPARATUS/PROCEDURE: S				SOURCE AND PURITY OF MATERIALS:	
Thermographical analysis (with recording of the heating traces), supplemented with (not detailed) visual polythermal measurements, and microscopic observations on solid (previously melted) samples in polarized light.		ing of h (not ments, solid arized	"Chemically pure" materials employed. Component 1 melts at 302 °C and undergoes phase transitions at $t_{trs}(1)/°C= 58$, 155 (Ref. 1). Component 2 melts at 331 °C and undergoes phase transitions at $t_{trs}(2)/°C= 58$, 118, 130, 238 (Ref. 1).			
ESTIMATI	ED ERROI	R :				REFERENCES:
Temperat (compile	ture: er).	accuracy	y pro	bably	<u>+</u> 2 К	(1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>

	I
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] (2) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 7-12.
	DEEDADED BY.
	Politici D
Temperature.	
EXPERIMENTAL VALUES:	
Eutectic, E, at 238 ^o C; composition not stated (authors). Peritectic, P, at 240 ^o C; composition not stated (authors).	
Intermediate compound(s):	
(C ₂ H ₃ O ₂) ₅ K ₃ Na ₂ , incongruently melting (author	· ·s)•
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C= 302$. Component 2: $t_{fus}(2)/{}^{\circ}C= 326$ (Fig. 1 of the original paper).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES :

•

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Storonkin, A.V.; Vasil [*] kova, I.V.; Tarasov, A.A. Vestn. Leningr. Univ., Fiz., Khim. <u>1977</u> , (4), 80-85.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	

EXPERIMENTAL VALUES:

Data presented in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 511 K and $100x_1 = 54$ (authors), singled out by extrapolation.



AUXILIARY I	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
DTA and "contact polythermal method" under polarized light. IR spectra were used to deny the existence of any intermediate compound.	Both components of analytical purity recrystallized twice from water and dried under vacuum (T _{fus} /K= 584 and 607, respectively, authors). The purity of both components was checked with thermographical analysis. The mixtures were prepared in a glove box.		
	ESTIMATED ERROR:		
	Temperature: accuracy probably +2 K (compiler).		
	REFERENCES:		

	· · · · · · · · · · · · · · · · · · ·		
COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Lead ethanoate (lead acetate); (C₂H₃O₂)₂Pb; [15347-57-6] 	Lehrman, A.; Leifer, E. J. Amer. Chem. Soc. <u>1938</u> , 60, 142-144.		
VARIABLES:	PREPARED BY:		
Temperature.	Baldini, P.		
EXPERIMENTAL VALUES:			
$t/^{o}C T/K^{a} 100 x_{2} t/^{o}C T/K^{a} 100$	x ₂ + x		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			
AUXILIARY I	NFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
The mixtures $(20-35 \text{ g})$ were weighed into 2.5x20 cm Pyrex tubes, then suspended in a bath of the molten eutectic of Ca, K, Li nitrates. When necessary to prevent decomposition, two drops of glacial ethanoic acid were added. Due to the tendency to supercool, it was preferred to take the temperatures of complete melting. Cooling curves were used to obtain a few eutectic temperatures. Temperatures were measured mainly with a Copper-Constantane thermocouple (checked at the boiling point of water, and at the melting points of Sn, KNO_3 , and of the Sn-Pb eutectic mixture). In a few cases a mercury thermometer was employed.	Component 1: material of "chemically pure" grade, recrystallized from distilled water, then dried in an oven at 100 °C for one week, and at 140 °C for six hours before weighing. Component 2: material of "chemically pure" grade, recrystallized from distilled water acidified with ethanoic acid, then dried at 100 °C. ESTIMATED ERROR: Temperature: accuracy ±0.5 K (authors).		
NOTE: It can be remarked that the fusion	REFERENCES: (1) Sanesi, M.; Cingolani, A.; Tonelli, P.L.: Franzosini P.		
temperature of component 1 found by Lehrman and Leifer does not agree with recent literature data which range mostly between 574 and 584 K (Ref. 1).	Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u> , 29-115.		

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Spinolo, G.,
(C ₂ H ₃ O ₂)K; [127-08-2] Rubidium ethanoate (rubidium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂)Rb; [563-67-7]	Universita ⁻ di Pavia (ITALY).

This binary was first studied with the visual polythermal method by Diogenov and Sarapulova (Ref. 1). Subsequently, Sarapulova et al. (Ref. 2) carried out a thermographical analysis of the system, supplemented with a few visual observations, and X-ray diffractograms recorded on the pure components and five (previously melted) intermediate mixtures.

Only minor differences occur between the liquidus curves by either source. The fusion temperatures of the pure components, i.e., $T_{fus}(1) = 583$ K (Refs. 1, 2), and $T_{fus}(2) = 509$ K (visual; Refs. 1, 2) or 511 K (thermographical; Ref. 2) are acceptable, although somewhat lower than the corresponding values listed in Table 1 of the Preface, i.e., $T_{fus}(1) = 578.7 \pm 0.5$ K, and $T_{fus}(2) = 514 \pm 1$ K. Poorer agreement, on the contrary, exists between the solid state transition temperatures reported in Ref. 2 (i.e., 327 K and 428 K for component 1, and 488 K for component 2), and those listed in Table 1 of the Preface (i.e., 422.2\pm 0.5 K for component 1, and 498\pm 1 K for component 2).

On the basis of the X-ray patterns mentioned above, Sarapulova et al. (Ref. 2) assert that complete miscibility exists even at room temperature, although giving no information about the phase of component 1 they assume to be involved in these solid solutions.

In the evaluator's opinion, doubts are to be cast about the solid state transition at 327 K in component 1. Should it actually exist, the lower part of the diagram shown in Ref. 2 would require completion, whereas, in its absence, the picture of the phase relations would be substantially correct.

- (1) Diogenov, G.G.; Sarapulova, I.F.
 Zh. Neorg. Khim. 1964, 9, 1292-1294 (*); Russ. J. Inorg. Chem. (Engl. Transl.), 1964, 9, 704-706.
- (2) Sarapulova, I.F.; Kashcheev, G.N.; Diogenov, G.G. Nekotorye Vopr. Khimii Rasplavlen. Solei i Produktov Destruktsii Sapropelitov, Irkutsk, 1974, 3-10.




COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); (C₂H₃O₂)K; [127-08-2] Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] 	Nadirov, E.G.; Bakeev, M.I. Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR 1974, 25, 115-128.
VARIABLES:	PREPARED BY:
Temperature	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{o}C$ T/K^{a} 100 x_{1} $t^{o}C$ T/K^{a} 100 x_{1}	
236 509 0 229 502 60 222 495 10 236 509 65.5 201 474 20 238 511 70 169 442 30 241 514 75 188 461 35 245 518 80 209 482 40 247 520 85 213 486 45 263 536 90 217 490 50 292 565 94.6 219 492 52 306 579 100 222 495 55 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 169 °C and $100x_1 = 30$. Peritectic, P, at 248 °C (visual polythermal $100x_1 = 88$ (according to Fig. 6 of the original Intermediate compound(s): $(C_2H_3O_2)_{10}K_8Zn$, incongruently melting (it conductometry).	$\frac{1}{280}$ $\frac{280}{200}$ $\frac{200}{(C_2H_3O_2)_2Z_n}$ $\frac{1}{(C_2H_3O_2)_2Z_n}$ $\frac{1}{(C_2H_3O_2)_K}$ $\frac{1}{(C_$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis supplemented with conductometry and occasionally with X- ray investigations. Temperatures of initial crystallization measured with a thermocouple.	Component 1: material recrystallized three times and dried at 110-120 °C. Component 2: (C ₂ H ₃ O ₂) ₂ Zn.2H ₂ O of analytical purity, recrystallized twice and dried at 140 °C.
It can be observed that the fusion temperature of component 1 reported by Nadirov and Bakeev (579 K) is in fair agreement with the corresponding value listed in Table 1 of the Preaface (578.7±0.5 K), whereas the fusion temperature of component 2 (509 K) is noticeably lower than other recent data by different investigators (Ref. 1).	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES: (1) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford 1980, 29-115.

COMPONENTS:

 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4]
 Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was investigated by Diogenov (Ref. 1), by Pochtakova (Ref. 2), and again by Diogenov and Chumakova (Ref. 3) with substantially discrepant conclusions.

Diogenov, in his earlier paper (Ref. 1), claimed the existence of: (i) eutectic, E_1 , occurring at 499-500 K (226-227 °C), and (likely) $100x_1$ = 81.5 (the latter figure being quoted in Ref. 4, which is a later paper by the same author); (ii) eutectic, E_2 , occurring at 433 K (160 °C) and $100x_1$ = 57; and (iii) the intermediate compound $(C_2H_3O_2)_5Li_4Na$, congruently melting at 500 K (227 °C).

These results, however, were not confirmed in Ref. 3, where Diogenov and Chumakova reported approximately the same coordinates for E_1 , viz., 492-494 K (219-221 °C) and 100x₁ about 78, but completely different fusion temperature for E_2 , viz., either 486 K (213 °C; Fig. 2 of the original paper), or 449 K (176 °C; Fig. 4 of the original paper). Moreover they suggested for the intermediate compound a new formula, i.e., $(C_2H_3O_2)_4Li_3Na$.

Finally, it is to be noted that the fusion temperatures given in Refs. 1, 3 for component 2 differ by 11 K, and the phase transitions reported in Ref. 1, i.e., $T_{trs}(1)=530 \text{ K} (257 \text{ }^{\circ}\text{C})$, and $T_{trs}(2)=596 \text{ K} (323 \text{ }^{\circ}\text{C})$, do not meet any value of Table 1 of the Preface.

In conclusion, the poor reproducibility of the results by Diogenov's group does not allow one to take them into consideration for assessing the actual diagram of this system.

Conversely, Pochtakova's data (Ref. 2) seem more reliable, although among the phase transition temperatures of component 2 quoted by the author from Ref. 5, i.e., 331, 391, 403, and 511 K (58, 118, 130, and 238 $^{\circ}$ C, respectively), only two can be identified with those listed in Preface, Table 1. This disagreement, however, does not seem, in the evaluator's opinion, to involve heavily the reliability of the liquidus, due also to the fact that the fusion temperatures of both pure components (604 K for component 2, and 557 K for component 1, respectively) are close to those reported in Preface, Table 1 (601.3+0.5 and 557+2 K, respectively).

Accordingly, the phase diagram by Pochtakov can be accepted with some confidence: in particular, the composition of the congruently melting intermediate compound, i.e., $(C_2H_3O_2)_5Li_3Na_2$, seems satisfactorily defined by the dome exhibited by the liquidus.

- (1) Diogenov, G.G.
 Zh. Neorg. Khim. 1956, 1, 799-805(*); Russ. J. Inorg. Chem. (Engl. Transl.) 1956, 1 (4), 199-205.
- (2) Pochtakova, E.I.
 Zh. Neorg. Khim. 1965, 10, 1333-2338 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1965, 10, 1268-1271.
- (3) Diogenov, G.G.; Chumakova, V.P. Fiz.-Khim. Issled. Rasplavov Solei. Irkutsk. <u>1975</u>, 7-12.
- (4) Diogenov, G.G.
 Zh. Neorg. Khim. 1956, 1, 2551-2555; Russ. J. Inorg. Chem. (Engl.Transl.) 1956, 1 (11), 122-126 (*).
- (5) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.



COMPONENTS:						ORIGINAL MEASUREMENTS:
 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 					ate); 2);	Pochtakova, E.I. Zh. Neorg. Khim. <u>1965</u> , 10, 2333-2338 (*); Russ. J. Inorg. Chem., Engl. Transl., <u>1965</u> , 10, 1268-1271.
VARIAB	BLES:					PREPARED BY:
Temper	ature					Baldini, P.
EXPERI	MENTAL	VALUES:				4
t/°C	T/K ^a	100x1	t/ ^o C	T/K ^a	100 x 1	
331 322 314 301 289 277 265 251 236 219 213 219 222 a T/K Charac Eutect Eutect Interm (C ₂ H ₃ O	$\begin{array}{c} 604\\ 595\\ 587\\ 574\\ 562\\ 550\\ 538\\ 524\\ 509\\ 492\\ 486\\ 492\\ 495\\ values\\ teristi\\ ic, E_1,\\ ic, E_2,\\ ediate\\ 2)5Li_3N\end{array}$	0 5 10 15 20 25 30 35 40 45 47.5 50 52.5 calculate c point(s at 219 at 213 ° compound(a ₂ , congr	224 227 224 223 222 229 234 241 259 273 284 d by the): C and 10 C and 10 s): uently r	$\begin{array}{c} 497\\ 500\\ 497\\ 496\\ 495\\ 502\\ 507\\ 514\\ 532\\ 546\\ 557\\ e \ comp1\\ 00x_1 = \ 6\\ 00x_1 = \ 4\\ melting \end{array}$	57.5 60 62.5 65 70 72.5 75 80 90 95 100 1er. 9 (author 7.5 (author 7.5 (author) 42.5 75 80 90 95 100	C (author).
AUXILIARY I					XILIARY I	NFORMATION
METHOD	/APPARA	TUS/PROCE	DURE:			SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.						Not stated. Component 2 undergoes phase transitions at t _{trs} (2)/ ^o C= 58, 118, 130, 238 (Ref. 1).
						ESTIMATED ERROR:
						Temperature: accuracy probably <u>+</u> 2 K (compiler).
						REFERENCES:
						<pre>(1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.</pre>

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] 	Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 7-12.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
Eutectic, E_1 , at 219 °C (Fig. 2 of the original paper) or 221 °C (Fig. 4); composition not stated (100x ₁ about 78 in compiler's graphical estimation from Fig. 4). Eutectic, E_2 , at 213 °C (Fig. 2 of the original paper) or 176 °C (Fig. 4); composition not stated (100x ₁ about 54 in compiler's graphical estimation from Fig. 4).	
Intermediate compound(s):	
$(C_2H_3O_2)_4Li_3Na$, congruently melting at 226 °C (authors).	
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal method.	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C = 291$ (Fig. 3 of the original paper). Component 2: $t_{fug}(2)/{}^{\circ}C = 326$ (Fig. 1 of the original paper).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

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 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4]
 Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7]

EVALUATOR:

Schiraldi, A., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied twice by Diogenov's group, as a side of the ternary $C_{2H_3O_2}/Cs$, Li, Rb (Ref. 1), and as a side of the reciprocal ternary $C_{2H_3O_2}$, NO₃/Li, Rb (Ref. 2), respectively.

In both papers two eutectics are reported, viz., E_1 at 509 K (236 °C), and either $100x_1 = 88.5$ (Ref. 1), or $100x_1 = 88$ (Ref. 2), and E_2 at either 449 K (176 °C; Ref. 1), or 460 K (187 °C; Ref. 2), and $100x_1 = 26$.

In Ref. 1, however, Diogenov and Sarapulova report two intermediate compounds, i.e., $(C_2H_3O_2)_5Li_2Rb_3$ and $(C_2H_3O_2)_5Li_3Rb_2$ [congruently melting at 518 K (245 °C) and 582 K (309 °C), respectively], and consequently a third invariant, whilst Diogenov et al. report in Ref. 2 a single intermediate compound, $(C_2H_3O_2)_3Li_2Rb$ [congruently melting at 573 K (300 °C)].

Due to the detailed experimental evidence (obtained, inter alia, with X-ray diffractometry) given in Ref. 2, the evaluator thinks that the existence of the latter compound should be considered as reasonably assessed. On the contrary, the existence of both $(C_2H_3O_2)_5Li_2Rb_3$ and $(C_2H_3O_2)_5Li_3Rb_2$ does not seem adequately supported.

It is to be noticed that some discrepancies exist between the phase transition temperatures reported in Ref. 2 and those given in Table 1 of the Preface, viz., $T_{fus}(1)=564$ K (291 °C), to be identified with 557+2 K, $T_{trs}(1)=405$ K (132 °C), with no correspondence, $T_{fus}(2)=509$ K (236 °C), to be identified with 514+1 K, and $T_{trs}(2)=479$ K (206 °C), to be identified with 498+1 K. These discrepancies, however, do not imply significant changes in the liquidus by Diogenov et al. (Ref. 2): the evaluator is consequently inclined to consider the presentation by these authors as sufficiently reliable.

- (1) Diogenov, G.G.; Sarapulova, I.F.
 Zh. Neorg. Khim. <u>1964</u>, 9(2), 482-487; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1964</u>, 9, 265-267 (*).
- (2) Diogenov, G.G.; Erlykov, A.M.; Gimel'shtein, V.G.
 Zh. Neorg. Khim. 1974, 19, 1955-1960; Russ. J. Inorg. Chem. (Engl. Transl.) 1974, 19, 1069-1073 (*).

COMPONENTS:					ORIGINAL MEASUREMENTS:	
<pre>(1) Lithium ethanoate (lithium acetate);</pre>					Diogenov, G.G.; Sarapulova, I.F.	
<pre>(C₂H₃O₂)L1; [546-89-4] (2) Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7]</pre>					Zh. Neorg. Khim. <u>1964</u> , 9(2), 482-487; Russ. J. Inorg. Chem., Engl. Transl., <u>1964</u> , 9, 265-267 (*).	
VARIABLES:						
Tomporaturo					PREPARED BY:	
						Baldini, P.
EXPERIM	IENTAL V	ALUES:				
t/oC	T/K ^a	100 x 1	t/oC	T/K ^a	100 x	1 ي
240	513	0	283	556	47.0	t,
234	507	3.5	288	561	48.5	-000
225	490 780	8.3	299	577	55 0	300 - 6 2 -
213	486	14.0	309	582	60.0	
208	481	16.5	309	582	64.0	$\left \begin{array}{c} \phi \\ \phi \end{array} \right\rangle \left\langle \phi \\ \phi $
203	476	18.5	307	580	67.5	¢ š8
195	468	21.0	298	571	74.0	250는 먼 \& -
187	460	23.0	289	562	78.0	
181	454	24.5	267	540	83.5	
203	430	20.5	227	515	88.0	
207	480	29.5	241	514	89.5	
213	486	30.5	246	519	90.5	6
224	497	32.0	258	531	92.0	E ₂
236	509	34.0	265	538	93.0	
242	523	37.5	2/2	545 555	94.5	0 50 100×, 100
273	555	44.5	290	563	100.0	(C_H_O_)R6 (C_H_O_)L;
^a T/K values calculated by the compiler.					232 232	
Charact	eristic	point(s):	Eutecti	lc, E ₁ ,	at 236	$^{\circ}$ C and 100x1= 88.5 (authors).
_			Eutecti	ic, E ₂ ,	at 176	$^{\circ}$ C and $100x_1 = 26$ (authors).
Interme	ediate c	ompound(s)	сс ₂ н ₃ 02 (с ₂ н ₃ 02	2)5L12Rb 2)5L13Rb	3, mel 2, con	ting at 245 °C (authors). gruently melting at 309 °C (authors).
AUXILIARY I					NFORMATION	
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:	
Visual	polyth	ermal anal	ysis. 1	Cemperat	ures	Not stated.
thermod	ouple.	Ltin a	om	.omer Ar	.ume 1	
					į	
					ESTIMATED ERROR:	
					Temperature: accuracy probably <u>+2</u> K (compiler).	
						REFERENCES:

ł.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Diogenov, G.G.; Erlykov, A.M.; Gimel´shtein, V.G. Zh. Neorg. Khim. 1974, 19, 1955-1960; Russ. J. Inorg. Chem., Engl. Transl., 1974, 19, 1069-1073 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	a solo

250 C_{2} C_{2} $C_{$

Characteristic point(s):

Eutectic, E_1 , at 236 ^oC and $100x_2=12$ (authors). Eutectic, E_2 , at 187 ^oC and $100x_2=74$ (authors).

Intermediate compound(s):

 $({\rm C_{2}H_{3}O_{2}})_{3}{\rm Li}_{2}{\rm Rb},$ congruently melting at 300 $^{\rm O}{\rm C}$ (authors).

AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The data were obtained by visual polythermal and thermographical analysis (empty and filled circles in the figure, respectively), supplemented with a few X- ray diffraction patterns.	Not stated. Component 1 melts at 291 ^o C and undergoes a phase transition at 132 ^o C. Component 2 melts at 236 ^o C and undergoes a phase transition at 206 ^o C.
	ESTIMATED ERROR:
	Temperature: precision probably ± 2 K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Lithium ethanoate (lithium acetate); (C₂H₃O₂)Li; [546-89-4] Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] 	Pavlov, V.L.; Golubkova, V.V. Visn. Kiiv. Univ., Ser. Khim., Kiev, <u>1972</u> , No. 13, 28-30.			
VARIABLES:	PREPARED BY:			
m				
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES:	I			
The results are reported only in graphical form (see figure).	275			
	175			
Characteristic point(s):	0 100 X ₂ 100			
Eutectic, E, at 220 °C and $100x_2$ = 75 (authors). $(C_2H_3O_2)Li$ $(C_2H_3O_2)_2Zn$			
Note - Glasses form at $15 \leq 100 \mathbf{x}_2 \leq 30$.				
Intermediate compound(s):				
$(C_{2H_{3}O_{2}})_{3}$ LiZn, congruently melting at 265 °C $(C_{2H_{3}O_{2}})_{5}$ LiZn ₂ , incongruently melting at 240	(authors). ^O C (authors).			
AUXILIARY I	NFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis as well as time-temperature curves were employed. The temperatures were measured with a Chromel-Alumel thermocouple checked at the freezing temperatures of Zn, $K_2Cr_2O_7$, Cd, Sn, and benzoic acid.	Component 1: either $(C_2H_3O_2)Li.2H_2O$ of analytical purity, or material obtained by reacting Li_2CO_3 and ethanoic acid; both materials dehydrated in an oven at 105- 110 °C. Component 2: $(C_2H_3O_2)_2Zn.2H_2O$ of analytical purity dried to constant mass at 110 °C.			
NOIE:				
The formation of glasses in this system is reasonable. Accordingly, one should expect a marked tendency of the molten mixtures to supercool, which might cause the polythermal observations to be less reliable than usual.	ESTIMATED ERROR: Temperature: accuracy probably +2 K			
	REFERENCES:			

COMPONENTS:	EVALUATOR:
 Magnesium ethanoate (magnesium acetate);	Schiraldi, A.,
(C ₂ H ₃ O ₂) ₂ Mg; [142-72-3] Sodium ethanoate (sodium acetate);	Dipartimento di Chimica Fisica,
(C ₂ H ₃ O ₂) ₂ Na ₂ ; [127-09-3]	Universita´ di Pavia (ITALY).

This system has been investigated only by Pochtakova (Ref. 1) who reports the results of visual polythermal observations supplemented with DTA investigations, both in numerical and graphical form.

The trend of the accessible part of the liquidus ($0 \leq 100x_1 \leq 70$) has been interpreted by the author as follows: the occurrence of the intermediate compound $(C_2H_3O_2)_4MgNa_2$, congruently melting at 533 K (260 °C), splits the diagram into two eutectic subsystems whose invariants are E₁, at 529 K (256 °C) and $100x_2$ = 40.0, and E₂, at 528 K (255 °C) and $100x_2$ = 57.5. The author suggests also that the intermediate compound undergoes an alpha-beta transition at 493 K (220 °C), and a lattice readjustment of the beta form at 373 K (100 °C).

For an evaluation of the reliability of the above conclusions, the following discrepancies between the text or tables and the original plot must be mentioned.

(1) In the experimental section of the paper two solid-solid transitions are reported for component 1 at 425 K (152 $^{\circ}$ C) and 449 K (176 $^{\circ}$ C), respectively, whilst the corresponding figures on the plot are 425 K (152 $^{\circ}$ C) and 445 K (172 $^{\circ}$ C).

(ii) The table summarizing the visual polythermal data reports two temperature values at $100x_1 = 50$, the first of which - possibly due to a misprint - probably corresponds to $100x_1 = 30$.

(iii) The table collecting the DTA results reports, at $100x_1 = 60$, five temperature values, one of which (236 O C) is neither included in the phase diagram nor otherwise discussed in the text.

(iv) No DTA evidence for the lattice readjustment at 373 K is provided at the composition of the intermediate compound.

(v) DTA measurements carried out at $100x_2 > 50$ did not allow the author to obtain evidence for either the transition of the intermediate compound at 493 K, or the lattice readjustment at 373 K.

(vi) DTA measurements carried out on the mixtures did not allow the author to obtain evidence for the solid state transitions of the pure components. It is however to be stressed that the transition temperatures of sodium ethanoate are quoted by the author from Ref. 2.

In conclusion the upper part of the phase diagram given in the paper seems to be supported adequately by the experimental results, whereas the system is still to be considered as largely unexplored below the eutectic lines.

- (1) Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u>, 44, 241-248.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauchn. Konf. S.M.I. <u>1956</u>.

COMPON	ENTS:		ORIGINAL MEASUREMENTS:
<pre>(1) Magnesium ethanoate (magnesium acetate); (CoHaOa)aMg; [142-72-3]</pre>		ethanoate (magnesium	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
(2) So (C	$2^{H_{3}O_{2}}/2^{M_{3}O_{2}}/2^{M_{3}O_{2}}/2^{N_{3}O_{2}}/2^{N_{3}O_{2}}$	anoate (sodium acetate); la2; [127-09-3]	
VARIAB	LES:		PREPARED BY:
Temper	ature.		Baldini, P.
EXPERI	MENTAL V	ALUES:	
t/ ^o C	T/K ^a	100x ₁	
331 329 326 324 320 321bc 255bd 313 310 306 297 290 288 284 275 269 261 255 255bc 255bc 255bc 255bc 255bc 255bc 255bc 255bc 255bc 256 257 260bc 259 258 260bc 259 258 260bc 259 258 260bc 258 257 258bc 258b	604 602 599 597 593 594 528 586 583 570 563 561 557 548 528 528 528 528 528 528 528 528 528 52	0 2.5 5 7.5 10 10 10 15 17.5 20 25 27.5 30 ¹ 32.5 35 37.5 40 42.5 42.5 42.5 42.5 42.5 42.5 45 47.5 50 50 50 50 50 50 50 50 55 56.5 57.5 60 60 60 60 60 60 60 60 60 60	es in the figure).
g Second transition of the system. h Third transition of the system.			
$\frac{1}{1}$ 50 in the original text (corrected by the compiler).			
component 1.			

1	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Magnesium ethanoate (magnesium acetate); (C₂H₃O₂)₂Mg; [142-72-3] Sodium ethanoate (sodium acetate); (C₂H₃O₂)₂Na₂; [127-09-3] 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES: (continued)	+
Characteristic point(s):	
Eutectic, E_1 , at 256 ^o C (extrapolated, (differential thermal analysis), and $100x_1 = 0$	visual polythermal analysis), or 258 ^o C 60 (author).
Eutectic, E_2 , at 255 °C and 100 x_1 = 42.5 (aut)	nor).
Intermediate compound(s):	
$(C_{2}H_{3}O_{2})_{4}MgNa_{2}$, congruently melting at 260 °C	C (author).
AUXILIARY I	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis, supplemented with differential thermal analysis.	Component 1: prepared (Ref. 1) by reacting the ("chemically pure") carbonate with a slight excess of ethanoic acid of analytical purity [phase transitions at $t_{trs}(1)/^{O}C=152$, 176]. Component 2: "chemically pure" material recrystallized and dried at 200 ^{O}C to constant mass [phase transitions at $t_{trs}(2)/^{O}C=238-240$, 130, 118, 58, Ref. 2].
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593 Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS:	EVALUATOR:
 Sodium ethanoate (sodium acetate);	Schiraldi, A.,
(C ₂ H ₃ O ₂)Na; [127-09-3] Rubidium ethanoate (rubidium acetate);	Dipartimento di Chimica Fisica
(C ₂ H ₃ O ₂)Rb; [563-67-7]	Universita ⁻ di Pavia (ITALY).

This system was studied twice in Gimel'shtein's laboratory [Ref. 1: visual polythermal analysis (empty circles in the figure); Ref. 2: DTA (filled circles in the figure)] with substantially analogous results for the liquidus: an intermediate compound, $(C_2H_3O_2)_4NaRb_3$, congruently melting at 452-453 K (179 °C, Ref. 1; 180 °C, Ref. 2), forms eutectics with both pure components, at 418-419 K (145-146 °C) and 100x1= 38-38.5, and at 451-453 K (178-180 °C) and 100 x_1 = 23.5, respectively.

Discrepancies, however, exist between Ref.s 1 and 2 about the phase transition temperatures of the pure components.

As for component 1, Gimel'shtein and Diogenov (Ref. 1) report $T_{trg}(1)$ = 583-584 K (310-311 °C), while Gimel'shtein (Ref. 2) gives $T_{trs}(1)$ = 543 K (270 °C). The former figure exceeds largely the highest $T_{trs}(1)$ value listed in Table 1 of the Preface, viz., 527+15 K, while the latter one lies just above the upper uncertainty limit of Table 1 value.

As for component 2, 493 K (220 $^{\circ}$ C) and 479 K (206 $^{\circ}$ C) are reported in Ref. 1 and Ref. 2, respectively, as the transition temperature: the former value is close to, while the latter one is significantly lower than that listed in Table 1 of the Preface, viz., 498<u>+</u>1 K.

X-ray diffractometric results were claimed (Ref. 2) to support the existence of the intermediate compound, and to suggest that this should decompose into a solid solution just below 383 K (110 $^{\circ}$ C). The second assertion, however, does not seem convincing, inasmuch as it would imply a change in the solid from a state of miscibility at lower temperatures into a state of immiscibility at higher temperatures.

Finally, the assumption of the congruent fusion of the intermediate compound does not seem adequately supported: the shape of the liquidus could as well suggest the occurrence of a peritectic equilibrium, e.g., in connection with the incongruent fusion of the compound.

REFERENCES:



(2) Gimel'shtein, G.G.; Tr. Irkutsk. Politech. Inst. 1971, No. 66, 80-100.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Gimel'shtein, V.G.; Diogenov, G.G. Zh. Neorg. Khim. 1958, 3, 1644-1649 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1958, 3 (7), 230-237.
VARIABLES:	PREPARED BY:
Temperature	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} = 100x_{1} t/^{o}C T/K^{a} = 100x_{1}$	
236 509 0 195 468 47	
222 495 5 216 489 52 218 491 9 234 507 57	300 - B-
210 483 14.5 248 521 62	کر
198 471 18.5 260 533 67	ا کر ا
186 459 22 271 544 72	
175 448 28 299 572 87	
166 439 31.7 308 581 93	
161 434 33.5 311 584 95.5	
145 418 38 315 588 96.5	
	Esq.
" T/K values calculated by the compiler.	
Characteristic point(s):	Δ Ε1,
$^{\text{Lutectic}}$, $^{\text{L}}_{1}$, at 145 °C (according to Fig.	0 50 $100x_1$ 100
according to Fig. 1 of the original paper,	
and not at 179 °C as reported in the text;	
compiler) and $100x_1 = 38$ (authors).	\sim 2 of the original paper, or at 179 °C
according to Fig. 1 of the original paper; co	mpiler) and $100x_1$ about 23.5 (compiler).
Intermediate compound(s):	
(C ₂ H ₃ O ₂) ₄ NaRb ₃ , congruently melting at 180 °C	(authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Temperatures	Not stated.
measured with a Chromel-Alumel thermocouple	Component 1 undergoes a phase transition at
being hyproscopic, the method of additions	t _{trs} (1)/°C ⁼ 311 (310 °C according to Fig. 2)
with determination of the sample mass by	Component 2 undergoes a phase transition at
difference was employed in order to avoid	$t_{trs}(2)/^{o}C=220.$
hydration.	
	ESTIMATED ERROR:
	BILLING MUNIC
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

/	· · · · · · · · · · · · · · · · · · ·
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] Rubidium ethanoate (rubidium acetate); (C₂H₃O₂)Rb; [563-67-7] 	Gimel'shtein, V.G. Tr. Irkutsk. Politekh. Inst. <u>1971</u> , No. 66, 80-100.
	PREDAREN RY.
	Paldini D
	Jaiumi, 1.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
328 601 0 108 381 70.0	
270 543 0 197 470 85.0	
271 544 15.0 110 383 85.0	
148 421 15.0 218 491 95.0	
205 478 50.0 206 479 95.0	
146 419 50.0 178 451 95.0	
110 383 50.0 235 508 100	
144 417 70.0 206 479 100	
^a T /K values calculated by the compiler.	
Characteristic point(s):	
Eutectic, E_1 , at 178 $^{\circ}C$ and $100x_1 = 23.5$ (auth	or).
Eutectic, E_2 , at 146 °C and 100 x_1 38.5 (auth	or).
Intermediate compound(s):	
$(C_{2H_{3}O_{2}})_{4}$ NaRb ₃ , congruently (compiler) mel transformation at 110 °C (author).	ting at 179 ^O C (author), and undergoing a
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Differential thermal analysis (using a derivatograph with automatic recording of the heating curves) and room temperature X- ray diffractometry (using a URS-501M apparatus) were employed.	Not stated. Component 1 melts at $t_{fus}(1)/{}^{o}C= 328$ (327 according to Fig. 7 of the original paper; compiler), and undergoes a phase transition at $t_{trs}(1)/{}^{o}C= 270$. Component 2 melts at $t_{fus}(2)/{}^{o}C= 235$ (236 according to Fig. 7 of the original paper; compiler), and undergoes a phase transition
NOTE - 1	at $t_{trs}(2)/^{o}C= 206$.
The meaning of the data listed in the table becomes apparent by observing the figure	FORTMATED EDDOD.
reported in the critical evaluation.	ESTIMIED ERROR:
NOTE - 2	Temperature: accuracy probably <u>+2</u> K (compiler).
The coordinates of the characteristic points were stated by the author on the basis of his own DTA measurements, and of previous literature data (Ref. 1). X-ray	REFERENCES: (1) Gimel'shtein, V.G.; Diogenov, G.G.
patterns were taken at 100x ₁ = 27.5.	Zh. Neorg. Khim. <u>1958</u> , 3, 1644-1649.
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Сомра	NENTS	•
COLLE	JUCNIO	

EVALUATOR:

 Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3]
 Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] Schiraldi, A., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Lehrman and Skell (Ref. 1), Pavlov and Golubkova (Ref. 2), and Nadirov and Bakeev (Ref. 3).

A qualitative agreement exists between Refs. 1 and 2, as both of them report a phase diagram characterized by two eutectics, E_1 and E_2 , and the congruently melting intermediate compound $(C_{2H_3O_2})_{4Na_2Zn}$. Differences between these papers concern the coordinates of the eutectics: according to Ref. 1, E_1 should occur at 491-493 K (218-220 °C) and 100x₂ about 28, and E_2 at 548.5-551.8 K (175.3-178.6 °C) and 100x₂ about 54, whereas, according to Ref. 2, the invariants should be at 473 K (200 °C) and 100x₂= 25, and at 413 K (140 °C) and 100x₂= 50, respectively.

The phase diagram suggested in Ref. 3 shows in turn: (i) a single eutectic at either 415, or 421 K (either 142, or 148 °C, according to visual polythermal and conductometric investigations, respectively) and $100x_2 = 57$; (ii) a peritectic at either 480, or 477, or 484 K (either 207, or 204, or 211 °C, according to visual polythermal, conductometric, and thermographical results, respectively), and, possibly, $100x_2 = 33.3$; and (iii) the intermediate compound $(C_2H_3O_2)_4Na_2Zn$ reported here as incongruently melting.

In the evaluator's opinion, the discrepancies among the diagrams suggested by the different authors should be attributed mainly to different degrees of accuracy in the determination of the actual liquidus temperatures. In this connection, it is important to stress that Lehrman and Skell observed a tendency of the melts to supercool and, in particular, found at temperatures below 483 K extremely viscous melts "so that great difficulty was experienced in obtaining crystallization and reproducible melting points" (Ref. 1). Consequently, in the case of the present binary, poorly reliable results can be reasonably expected both by techniques implying observations performed on cooling (as visual polythermal analysis), and by techniques (as conductometry) implying observations performed on heating at constant rate. Accordingly, the diagrams by Pavlov and Golubkova (based only on visual polythermal observations), and by Nadirov and Bakeev (based mainly on visual polythermal and conductometric investigations) probably suffer from limited accuracy.

In conclusion, the evaluator is inclined to consider as more reliable the findings by Lehrman and Skell (who employed very small heating rates), viz.: (i) the presence of the intermediate compound $(C_2H_3O_2)_4Na_2Zn$, congruently melting at about 500 K; and (ii) the occurrence of two eutectics, E_1 at about 490 K and $100x_2$ about 28, and E_2 at about 550 K and $100x_2$ about 54.

- (1) Lehrman, A.; Skell, P.
 J. Am. Chem. Soc. <u>1939</u>, 61, 3340-3342.
- (2) Pavlov, V.L.; Golubkova, V.V.
 Visn. Kiiv. Univ., Ser. Khim., Kiev, 1972, No. 13, 28-30.
- (3) Nadirov, E.G.; Bakeev, M.I. Tr. Khim.-Hetall. Inst. Akad. Nauk Kaz. SSR <u>1974</u>, 25, 115-128.

1	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium ethanoate (sodium acetate); (C₂H₃O₂)Na; [127-09-3] (2) Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] 	Lehrman, A.; Skell, P. J. Amer. Chem. Soc. <u>1939</u> , 61, 3340-3342.
VARIABLES:	PREPARED BY:
m	
Temperature	Baldini, P.
EXPERIMENTAL VALUES:	
t/°C T/K ^a $100x_2$ t/°C T/K ^a $100x_2$ 328.3 601.5 0 203.9 477.1 46.0 313.4 586.6 10.1 198.0 471.2 48.0 277.5 550.7 20.0 194.6 467.8 49.0 261.4 534.6 22.6 192.5 465.7 50.0 233.2 506.4 26.5 189.1 462.3 51.0 218.0 ^b 491.2 26.5 183.0 456.2 52.0 223.3 496.5 28.0 178.6 ^c 451.8 52.0 220.0 ^b 493.2 28.0 180.9 454.1 55.0 225.7 498.9 30.0 175.3 ^c 448.5 55.0 227.2 500.4 33.3 197.8 471.0 60.0 227.1 500.3 33.3 212.5 485.7 66.7 227.1 500.3 33.3 212.5 485.7 66.7 220.2 493.4 40.0 242.4 515.6 100.0 a T/K values calculated by the compiler. ^b Eutectic stop (E ₁); filled circles in the fill the formula of th	Figure. $C_2H_3O_2N_6 \qquad (C_2H_3O_2)N_6 \qquad (C_2H_3O_2)_2Z_1$ $C_2H_3O_2N_6 \qquad (C_2H_3O_2)_2Z_1$ $C_2H_3O_2N_6 \qquad (C_2H_3O_2)_2Z_1$ $C_3C_2C_3C_3C_3C_3C_3C_3C_3C_3C_3C_3C_3C_3C_3C$
AUXILIARY 1	NFURMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The salts, contained into 2.5x20 cm Pyrex tube and added with 5 drops of glacial ethanoic acid, were heated in bath formed with the eutectic mixture of calcium, potassium, and lithium nitrates. The temperature of disappearance of the last crystal as the mixture was heated under stirring was measured with Copper- Constantane thermocouple and potentiometer. The fusion temperatures tabulated come from three or more determinations ranging within 1 K. The eutectic stops relevant to E_1 were measured by means of time - temperature cooling curves.	Materials of not stated source, recrystallized from dilute ethanoic acid, and dehydrated according to Ref. 1. ESTIMATED ERROR: Temperature: accuracy <u>+</u> 0.5 K (compiler).
	REFERENCES: (1) Davidson, A.W.; McAllister J. Amer. Chem. Soc. <u>1930</u> , 52, 519-527.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium ethanoate (sodium acetate); $(C_2H_3O_2)Na; [127-09-3]$ (2) Zinc ethanoate (zinc acetate); $(C_2H_3O_2)_2Zn; [557-34-6]$	Pavlov, V.L.; Golubkova, V.V. Visn. Kiiv. Univ., Ser. Khim., Kiev, <u>1972</u> , No. 13, 28-30.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
275 - 275	$\frac{1}{C_2}$ $\frac{1}{C_2H_3O_2}$ $\frac{1}{C_2H_3O_2}$ $\frac{1}{C_2H_3O_2}$ $\frac{1}{C_2H_3O_2}$ $\frac{1}{C_2H_3O_2}$
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis as well as time-temperature curves were employed. The temperatures were measured with a Chromel-Alumel thermocouple checked at the freezing temperatures of Zn, $K_2Cr_2O_7$, Cd, Sn, and benzoic acid.	Component 1: (C ₂ H ₃ O ₂)Na.3H ₂ O of analytical purity recrystallized from water and dried in an oven at 110-120 °C to constant mass. Component 2: (C ₂ H ₃ O ₂) ₂ Zn.2H ₂ O of analytical purity dried to constant mass at 110 °C.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:	
	Neddrey E.C. & Beleast M.T.	
$(C_{2H_2O_2})$ Na; [127-09-3]	Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR	
(2) Zinc ethanoate (zinc acetate);	<u>1974</u> , 25 , 115-128.	
$(C_{2H_{3}O_{2}})_{2Zn}; [557-34-6]$		
VARIABLES:	PREPARED BY:	
Tomporature	Baldini P	
	baldini, i.	
EXPERIMENTAL VALUES:		
$t/^{\circ}C$ T/K^{a} 100 x_{1}	ų [
236 509 0	÷ ÷	
229 502 10	300 - 0 -	
217 490 20		
174 447 35		
165 438 40	9	
142 415 43		
177 450 50	γ_{α} β	
189 462 55		
206 479 66.7		
214 487 70	à ở	
234 507 75		
261 534 80	V I	
279 552 85	E	
298 5/1 90	0 50 100 <i>×</i> , 100	
332 605 100		
a T/K values calculated by the compiler.		
Characteristic point(a):		
Eutectic, E, at either 142 ^o C (visual poly	thermal analysis), or	
148 °C (conductometry), and $100x_1 = 43$.		
Peritectic, P, at either 207 °C (visual poly	thermal analysis), or	
204 °C (conductometry), or 211 °C (thermogra	phical analysis), and	
the coordinates of the peritectic might	be $206 {}^{\circ}\text{C}$ (visual	
polythermal analysis; tabulated value) and 1	$00x_1 = 66.7$].	
Intermediate compound(s):		
(C ₂ H ₃ O ₂),Na ₂ Zn, incongruently melting.		
(-2-3-2/4-02-0, 1000-00001, molling.		
AUXILIARY INFORMATION		
METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis supplemented	Component 1: "chemically pure" hydrated	
thermographical	$U_2H_3U_2Na$ recrystallized twice and dried at	
Temperatures of initial crystallization	analytical purity, recrystallized twice and	
measured with a thermocouple.	dried at 140 °C.	
	ESTIMATED ERROR:	
	Temperature: accuracy probably + 9 V	
	(compiler).	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Lead(II) ethanoate (lead acetate); (C₂H₃O₂)₂Pb; [15347-57-6] (2) Zinc ethanoate (zinc acetate); (C₂H₃O₂)₂Zn; [557-34-6] 	Petersen, J. Z. Elektrochem. <u>1914</u> , 20, 328-332.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	
• • • • • • • • • • • • • • • • • • • •		
EXPERIMENTAL VALUES:		
$220 \int 0 $	$\frac{1}{40}$ $\frac{1}{40}$ $\frac{1}{2}$ (C ₂ H ₃ O ₂) ₂ Z n form (see figure).	
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Mixtures contained in a glass tube and heated in a sulfuric acid bath. NOTE:	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C= 204$. Component 2: $t_{fus}(2)/{}^{\circ}C= 244$.	
$T_{fus}(1)$ and $T_{fus}(2)$ are in reasonable agreement with the data by other authors (Ref. 1). The general features of the diagram seem to be reliable.		
	ESTIMATED ERROR:	
	Temperature: accuracy not evaluable (compiler).	
	REFERENCES: (1) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.; Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u> , 29-115.	

I

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Rubidium ethanoate (rubidium acetate); $(C_2H_3O_2)Rb;$ [563-67-7] (2) Zinc ethanoate (zinc acetate); $(C_2H_3O_2)_2Zn;$ [557-34-6]	Nadirov, E.G.; Bakeev, M.I. Tr. KhimMetall. Inst. Akad. Nauk Kaz. SSR 1974, 25, 115-128.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁	
236 509 0 223 496 10 219 492 15 212 485 20 198 471 30 182 455 35 159 432 40 173 446 45 187 460 50 196 469 55 204 477 60 209 482 65 217 490 70 223 496 75 230 503 80 232 505 85 235 508 90 236 509 93.7 237 510 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at either 159 °C (visual polythand $100x_1 = 40$	hermal analysis), or 163 °C (conductometry),
AUXILIARY 1	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis supplemented with conductometry, and occasionally with thermographical and X-ray investigations. Temperatures of initial crystallization measured with a thermocouple.	Component 1: material recrystallized three times and dried at 110-120 °C. Component 2: (C ₂ H ₃ O ₂) ₂ Zn.2H ₂ O of analytical purity, recrystallized twice and dried at 140 °C.
NOTE 1:	
The mixtures at $55 \leq 100 x_1 \leq 80$ tend to form glasses.	
NOTE 2:	
The $T_{fus}(1)$ and $T_{fus}(2)$ values given here are lower than the corresponding values from Preface 1 [$T_{fus}(1)$ = 514 K] and from Ref. 1 [$T_{fus}(2)$ = 514-533 K], respectively. In Fig. 8 of the original paper the authors report an isothermal line at 404 K (131 °C) which is not discussed in the text. The ability to form glasses might imply poor reliability of the eutectic coordinates; however, the classification of the diagram as of the simple eutectic type might be	ESTIMATED EKKOR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES: (1) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.; Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors),
accepted with some confidence.	Pergamon Press, Oxford, 1980, 29-115.

1	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium propanoate (potassium propionate); (C₃H₅O₂)K; [327-62-8] Lithium propanoate (lithium propionate); (C₃H₅O₂)Li; [6531-45-9] 	Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. <u>1969</u> , 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1969</u> , 14, 302-306.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	[]
Characteristic point(s):	
Eutectic, E_1 , at 291 °C (authors) and $100x_1 = 67.5$ (according to Fig. 1 of the original paper; erroneously reported as 19 in the text; compiler). Eutectic, E_2 , at 279 °C (authors) and $100x_1 = 19$ (according to Fig. 1 of the original paper; erroneously reported as 67.5 in the text; compiler).	$ \begin{array}{c} 3 & G_{3} \\ & G_{3} \\ & G_{3} \\ & G_{3} \\ & H_{5} O_{2} \\ \end{array} \\ & K \\ & (C_{3} H_{5} O_{2}) \\ \end{array} \\ & (C_{3} H_{5} O_{2}) \\ & (C_{3} H$
Intermediate compound(s):	
(C _{3H5O2)2} KLi (probable composition), congruently melting (authors).	
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. NOTE: The fusion temperature of component 2 is about 5 K lower than that listed in	Materials prepared by reacting "chemically pure" carbonates with propanoic acid of analytical purity (Ref. 1). Component 1 undergoes a phase transition at $t_{trs}(1)/^{\circ}C= 68$ (Ref. 2) and melts at $t_{fus}(1)/^{\circ}C= 365$.
Preface, Table 1 (606.8 \pm 0.5 K), whereas $T_{fus}(1)$ meets satisfactorily the value (638.3 \pm 0.5 K) given in the table. The general features of the diagram should be considered with some confidence.	Component 2 undergoes a phase transition at t _{trs} (2)/ ^o C= 265 and melts at t _{fus} (2)/ ^o C= 329.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	 REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593 (this is Ref. 2 in the original paper, not Ref.3 as quoted by the authors). (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium propanoate (potassium propionate); (C₃H₅O₂)₂K₂; [327-62-8] Magnesium propanoate (magnesium propionate); (C₃H₅O₂)₂Mg; [557-27-7] 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	•
$t/^{\circ}C$ T/K ^a 100x ₂ t/ $^{\circ}C$ T/K ^a 100x ₂ 365 638 0 312 585 32.5 358 631 2.5 305 578 35 354 627 5 306 ^{bC} 579 36.5 352 625 7 5 306 ^{bd} 579 26.5	
347 620 10 236 ^{be} 509 36.5 347 620 10 236 ^{be} 509 36.5 345 618 12.5 306 579 37.5 343 616 15 315 588 40 341 614 17.5 320 593 42.5 335 608 20 322 595 45 332 605 22.5 322 ^{bc} 595 45	350
328 601 25 306 ^{baa} 579 45 330 ^{ba} 603 25 235 ^{ba} 508 45 304 ^{bd} 577 25 324 597 47.5 236 ^{ba} 509 25 324 597 50 324 597 27.5 324 597 52.5 318 591 30 324 597 55	250 • •
 a T/K values calculated by the compiler. b Differential thermal analysis (DTA). c Initial crystallization. d Eutectic stop. e First transition of the system. 	0 30 100× ₂ 60 (C ₃ H ₅ O ₂) ₂ K ₂ (C ₃ H ₅ O ₂) ₂ Mg
Characteristic point(s): Eutectic, E, at 306	^o C (DTA), and $100x_2 = 36.5$ (author).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis, supplemented with differential thermal analysis.	Materials prepared (Ref. 1) by reacting the proper ("chemically pure") carbonate with a slight excess of propanoic acid of
REFERENCES:	analytical purity. Component 1 undergoes phase transitions at $t_{res}(1)/{}^{0}C = 68$, 330
 Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. 	(Ref. 2). Component 2 undergoes phase transitions at t _{trs} (2)/ ^O C= 185, 200, 217, 246. NOTES:
(3) Sanesi, M.; Cingolani, A.; Ionelli, P.L.; Franzosini, P.; Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No.28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u> , 29-115.	The system was investigated at $0 \le 100x_2 \le 55$ due to thermal instability of component 2. The fusion temperature of component 1 is in fair agreement with that listed in Preface, Table 1, whereas discrepancies exist for the solid state transition temperatures of
ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler).	the same component. Moreover, it is worth mentioning that Pochtakova's paper is the only source of information (see Ref. 3) for what concerns the solid state transitions of magnesium propanoate.

COMPONENTS:	EVALUATOR:
 Potassium propanoate (potassium propionate);	Franzosini, P.,
(C ₃ H ₅ O ₂)K; [327-62-8] Sodium propanoate (sodium propionate);	Dipartimento di Chimica Fisica,
(C ₃ H ₅ O ₂)Na; [137-40-6]	Universita ⁻ di Pavia (ITALY).

This binary was studied by visual polythermal analysis in Sokolov's laboratory as a side system of two reciprocal ternaries [i.e., K, Na/C₂H₃O₂, C₃H₅O₂ (Ref. 1), and K, Na/C₃H₅O₂, NO₃ (Ref. 2)] with almost identical results.

The occurrence of eutectics at 583-585 K (310-312 °C) and $100x_1 = 66$, and at 560-561 K (287-288 °C) and $100x_1 = 8$ is to be held for certain, as well as the existence of a congruently melting intermediate compound. However, the composition of the latter as claimed by the authors [i.e., $(C_{3H_5O_2})_5K_3Na_2$], although possible, does not seem fully proved due to the fluctuation of the experimental points, and the lack of data other than the visual polythermal ones.

The fusion temperature of component 1 (638 K) is in fair agreement with that (638.3 \pm 0.5 K) listed in Table 1 of the Preface, whereas the fusion temperature of component 2 (571 K) has to be considered as too high, inasmuch as the DSC value given in Table 1 of the Preface, (562.4 \pm 0.2 K) was subsequently confirmed by that obtained with adiabatic calorimetry (561.88 \pm 0.03 K; Table 3).

Rather puzzlingly, for the solid state transition temperature of component 1 far different values are quoted [from the same source (Ref. 3)] in Ref. 1 and Ref. 2, i.e., 603 and 341 K, respectively. Both figures are in turn different from that reported in Table 1 of the Preface (352.5±0.5 K).

Again from Ref. 3, solid state transitions are quoted in both Ref. 1 and Ref. 2 as occurring in component 2 at $T_{trs}(2)/K=350$, 468, 490, and 560. Doubts, however, are to be cast about the existence of the lowest transition as well as of the highest one, inasmuch as DSC provided evidence for the occurrence of only two solid state transformations (at 470.2+0.5 and 494+1 K, respectively; Preface, Table 1) which was subsequently confirmed with adiabatic calorimetry (Preface, Table 3).

- Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. <u>1958</u>, 28, 1397-1404.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. 1958, 28, 2920-2926 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2949-2954.
- (3) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium propanoate (potassium propionate); (C₃H₅O₂)K; [327~62-8] Sodium propanoate (sodium propionate); 	Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1958</u> , 28, 2920-2926 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u> , 28, 2949-2954.
(C _{3H5} O ₂)Na; [137-40-6]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{o}C T/K^{a} 100x_{1} t^{o}C T/K^{a} 100x_{1}$	ų []
298 571 0 318 591 55 292 565 5 319 592 60 287 560 8 314 587 65 294 567 10 310 583 66 303 576 15 316 589 70 307 580 20 322 595 75 310 583 30 340 613 85 315 588 35 351 624 90 316 589 40 358 631 95 317 590 45 365 638 100 317 590 50 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , at 310 °C and 100x1= 66 (authors Eutectic, E ₂ , at 287 °C and 100x1= 8 (authors Intermediate compound(s): (C ₃ H ₅ O ₂) ₅ K ₃ Na ₂ (probable composition), congru	s). $G_{G_{3}H_{5}O_{2}}^{300}$, $G_{G_{3}H_{5}O_{2}}^{0}$, $G_{G_{3}H_{5}O_{2}^{0}}^{0}$, $G_{G_{3}H_{5}O_{2}}^{0}$, $G_{G_{3}H_{5}O_{2}^{0}}^{0}$, $G_{G_{3}H_{5}O_{2}^{0}^{0}^{0}^{0}^{0}^{0}^{0}^{0}^{0}^{0$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Temperature of initial crystallization measured with a Nichrome-Constantane thermocouple checked at the boiling point of water, and at the fusion points of benzoic acid, mannitol, succinic acid, silver nitrate, tin, potassium nitrate, and potassium dichromate. Mixtures melted in a glass tube inserted into a wider tube to ensure uniform heating. Glass fiber stirrer used.	Components prepared by adding a small excess of distilled commercial propanoic acid to a solution of the proper "chemically pure" hydrogen carbonate; the solids recovered after evaporation of the solvent were recrystallized from butanol. Component 1 undergoes a phase transition at $t_{trs}(1)/^{0}C= 68$ (Ref. 1). Component 2 undergoes phase transitions at $t_{trs}(2)/^{0}C= 77$, 195, 217, 287 (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	(1) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .

	······································
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium propanoate (lithium propionate); (C₃H₅O₂)Li; [6531-45-9] Sodium propanoate (sodium propionate); (C₃H₅O₂)Na; [137-40-6] 	Tsindrik, N.M.; Sokolov, N.M. Zh. Obshch. Khim., <u>1958</u> , 28, 1404-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u> , 28, 1462-1467.
VADTADI FC.	PREDADED RV.
Temperature.	baldini, F.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
329 602 0 322 595 5 316 589 10 304 577 15 292 565 20 278 551 25 262 535 30 246 519 35 226 499 40 218 491 42.5 206 479 45 196 469 47.5 194 467 48 198 471 50 204 477 52.5 212 485 55 216 489 57.5 224 497 60 248 521 70 266 539 80 282 555 90 298 571 100 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 194	$^{\circ}$ C and $100x_2 = 48$ (authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis.	Components prepared from propanoic acid and
NOTE:	the proper hydrogen carbonate (Ref. 1), and recrystallized from n-butanol. Component 2 undergoes phase transitions at
The fusion temperature of component 2 (571 K) is to be considered as too high, inasmuch as the DSC value (562.4+0.2 K) given in Preface, Table 1 was subsequently confirmed by that obtained with adiabatic calorimetry (561.88+0.03 K; Preface, Table 3). For the same component, both DSC and adiabatic calorimetry control (Defect	t _{trs} (2)/ ^o C= 77, 195, 217, 287 (Ref. 2).
Table 1 and Table 3, respectively) the	ESTIMATED ERROR:
occurrence of only two (instead of four, as quoted by the authors from Ref. 2) solid state transitions. Nevertheless, the main	Temperature: accuracy probably <u>+</u> 2 K (compiler).
reatures of the diagram are to be looked at with sufficient confidence.	REFERENCES:
	 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

	T						
COMPONENTS:	EVALUATOR:						
 Magnesium propanoate (magnesium propionate); (C₃H₅O₂)₂Mg; [557-27-7] Sodium propanoate (sodium propionate); (C₃H₅O₂)₂Na₂; [137-40-6] 	Franzosini, P., Dipartimento di Chimica Fisica, Universita [~] di Pavia (ITALY).						
CRITICAL EVALUATION:							
This binary was studied by Pochtakova (Ref. 1) both with visual polythermal and DTA investigation. In order to evaluate the trustworthiness of her results, the following points have to be considered.							
(1) The fusion temperature of component 1 (577 K) coincides with the DSC value by Ferloni et al. (Ref. 2).							
(ii) Pochtakova's solid state transition temperatures of the same component (i.e., 458, 473, 490, and 519 K) represent the only source of information on this subject.							
(iii) The fusion temperature of component 2 (571 K) has to be considered as too high, inasmuch as the DSC value (562.440.2 K) given in Preface, Table 1 was subsequently confirmed by that obtained with adiabatic calorimetry (561.8840.03 K; Preface, Table 3).							
(iv) As for the solid state transitions of the same component quoted by Pochtakova from Ref. 3 as occurring at $T_{trs}(2)/K=350$, 468, 490, and 560, heavy doubts are to be cast about the existence of the lowest and highest ones inasmuch as DSC provided evidence for only two solid state transformations (at 470.2+0.5, and 494+1 K, respectively; Preface, Table 1) which was subsequently confirmed with adiabatic calorimetry (Preface, Table 3).							
(v) Indeed, the DTA traces recorded at $100x_1 = 2.5$, 4, 25, and 42.5 seem to be consistent with the existence of only two solid state transitions of component 2; moreover, they support the occurrence of eutectic E_2 , and tend to prove the absence of solid solutions between component 2 and the intermediate compound.							
(vi) The DTA traces recorded at $100\mathbf{x}_1 = 60$, 65, and 75 are somewhat embarrassing because all of them support the occurrence of eutectic \mathbf{E}_1 , but evidence for solid state transitions of component 1 is offered only by the trace taken at $100\mathbf{x}_1 = 60$ for what concerns the transition at 473 K, and by that taken at $100\mathbf{x}_1 = 65$ for what concerns the transition at 458 K.							
(vii) No explanation is given by the author for the discontinuities exhibited at temperatures far above the liquidus by the DTA traces taken at $100x_1 = 60$, and 65.							
In conclusion, the evaluator is inclined to consider as satisfactorily supported by the experimental evidence:							
(i) the occurrence of the congruently melting intermediate compound $(C_{3}H_{5}O_{2})_{4}MgNa_{2}$;							
(ii) the occurrence of eutectics E_1 and E_2 , located as suggested by Pochtakova; and							
(iii) the phase relations relevant to solidus and subsolidus at $0 \le 100x_1 \le 50$ as suggested by Pochtakova.							
On the contrary, the knees occurring in the liquidus branch richest in component 1 as well as in that richest in component 2, the nature of possible transformations occurring in the melt, and the phase relations relevant to solidus and subsolidus at $50 \leq 100x_1 \leq 100$ seem to need further investigation.							
REFERENCES:							
(1) Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248.							
(2) Ferloni, P.; Sanesi, M.; Franzosini, P. Z. Naturforsch. <u>1976</u> , 31a, 679-682.							
(3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .							

COMPONENTS:						ORIGINAL MEASUREMENTS:
 (1) Magnesium propanoate (magnesium propionate); (C₃H₅O₂)₂Mg; [557-27-7] (2) Sodium propanoate (sodium propionate); (C₃H₅O₂)₂Na₂; [137-40-6] 					onate);	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
WADTABI FC.						PREPARED BY.
VARIABLES:						Raldini P.
1emperature.						
EXPERIMENTAL VALUES:						
t/°C	T/K ^a	100 x 1	t/°C	т/к ^а	100 m 1	
298 288 288 ^{bc}	571 561 561	0 2.5 2.5	247 248 244 ^{bc}	520 521 517	47.5 50 50	+ Concernent of point
214 ^{bj}	489 487	2.5	245	518	55	250
288 ^{bc}	561 561	2.5 4	241 240 ^{bc}	514 513	60 60	E ₂ E ₁
216 ^{bj}	489	4	235be	508	60	•
287	560 557	5 10	200 ^{b1} 286 ^{b1}	473 559	60 60	200
281	554	15	246	519	62.5	
274	547 543	20 25	239 235bc	512 508	65 65	150
270 ^{bc}	543	25	235 ^{be}	508	65	
240 ^{bd}	513 469	25 25	185 ^{0g} 284b1	458 557	65 65	
264	537	30	244	517	67.5	
258	531 525	35 37 5	245	518 522	70 75	0 50 100×, 100
247	520	40	250 ^{bc}	523	75	$(C_{3}H_{5}O_{2})_{2}Na_{2}$ $(C_{3}H_{5}O_{2})_{2}Mg$
244	517	42.5	236 ^{be}	509	75	
242 ^{bd}	515	42.5	253	526	80	
193 ^{bh}	466	42.5	285	558	90 100	
246 519 45 304 577 100 a T/K values calculated by the compiler. b c c Initial crystallization. c e Compiler. c					iler.	b Differential thermal analysis. d First eutectic stop. f First transition of the system.
g Second transition of the system.						h Third transition of the system.
Fourth transition of the system.						J Fifth transition of the system.
Sixin transition of the system. Seventh transition of the system (no explanation is offered by the author for the occurrence of this point above the liquidus, compiler).						
Characteristic point(s): Eutectic, E_1 , at 239 °C (235 °C by D.T.A.), and $100x_1 = 65$ (author). Eutectic, E_2 , at 244 °C (242 °C by D.T.A.), and $100x_1 = 42.5$ (author).						
Intermediate compound: (C ₃ H ₅ O ₂) ₄ MgNa ₂ , congruently melting at 248 ^O C (244 ^O C by D.T.A.).						
METHOD	/APPAR	ATUS/PROCI	EDURE:			SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis, supplemented with differential thermal analysis.					lemented	Materials prepared (Ref. 1) by reacting the proper ("chemically pure") carbonate with a slight excess of propagoic acid of
REFERENCES:						analytical purity. Component 1 undergoes phase transitions at
 Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf.S.M.I.1956. 			4, 158 £.S.M.	1-1593. I.1956.	$t_{trs}(1)/^{\circ}C = 185$, 200, 217, 246. Component 2 undergoes phase transitions at $t_{trs}(2)/^{\circ}C = 77$, 195, 217, 287 (Ref. 2).	
-						ESTIMATED ERROR:
						Temperature: precision probably +2 K (compiler).

COMPONENTS:	EVALUATOR:	
 Potassium butanoate (potassium butyrate);	Franzosini, P.,	
(C ₄ H ₇ O ₂) ₂ K ₂ ; [589-39-9] Magnesium butanoate (magnesium butyrate);	Dipartimento di Chimica Fisica,	
(C ₄ H ₇ O ₂) ₂ Mg; [556-45-6]	Universita' di Pavia (ITALY).	

This binary was studied only by Pochtakova (Ref. 1) who, on the basis of her visual polythermal and DTA results, asserted the occurrence of a congruently melting intermediate compound, i.e., $(C_4H_7O_2)_4K_2Mg$, forming (possibly simple) eutectics with either component.

Component 1, however, goes through the liquid crystalline state before transformation into a clear melt. Therefore, the topology of the phase diagram at $0 \le 100x_2 \le 50$ should be described more correctly with reference to Scheme B.1 of the Preface, and an invariant type M'_p (undetected by Pochtakova) should also exist.

The following points are still worth mentioning.

(1) Pochtakova's fusion temperature of component 1 (677 K) coincides with the clearing temperature (677.3+0.5 K) listed in Preface, Table 1 for the same component, whereas her $T_{fus}(2)$ value (575 K) is noticeably higher than data by other authors reported in Ref. 2.

(11) Among the phase transformation temperatures of component 1 quoted in Ref. 1 from Ref. 3 (i.e., 618, 553-558, and 463 K) the first one can be reasonably identified with the fusion temperature (626.1 ± 0.7 K) listed in Preface, Table 1, whereas the second and third ones lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 , and 467.2 ± 0.5 and 461.4 ± 1.0 , respectively) also reported in Table 1 of the Preface.

(iii) No explanation is given by the author for the discontinuities observed at temperatures (643 and 624 K, respectively) far above the liquidus in the DTA traces taken at $100x_2$ = 25 and 50.

(iv) The author's explanation, that the discontinuities observed at temperatures corresponding to the lowest section of the subsolidus might be due to transformation (at about 445 K) of the intermediate compound into a metastable phase turning to stable at 370-400 K, should be more detailed and better supported.

In conclusion it seems to the evaluator that the composition of the intermediate compound, the location of both eutectics, the liquidus dome, and the liquidus branch richest in component 2 are sufficiently well assessed, whereas the remaining part of the diagram needs several refinements to become satisfactory.

- Pochtakova, E.I.
 Zh. Obshch. Khim. <u>1974</u>, 44, 241-248.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPON	ENTS:					ORIGINAL MEASUREMENTS:
(1) Dependent huterster (setter)						
(1) Potassium butanoate (potassium butvrate):						Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248.
(C ₄ H ₇ O ₂) ₂ K ₂ ; [589-39-9]						
(2) Magnesium butanoate (magnesium						
(C ₄ H ₇ O ₂) ₂ Mg; [556-45-6]						
VARIABLES:						PREPARED BY:
Temperature.						Baldini, P.
Temperature.						
EXPERIMENTAL VALUES:						·
t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
404	677	0	318 ^{bc}	591	50	
389	662	5	170^{DD}	443	50	
39260	665	5	354	627 500	50	°c ₆₀ ●
196bi	207	5	300	509	55	350 - 20
272 ^{bj}	545	5	297	570	65	
352 ^{bk}	625	5	306 ^{bc}	579	65	300 300
390 ^{bc}	663	9	238 ^{be}	511	65	کم ہوت - ۲۵ - ۲۰۰۰ - ۲۰
305 ^{bd}	578	9	164^{bh}	445	65	
172 ^{bh}	445	9	283	556	70	
196 ⁰¹	469	9	272	545	72.5	E ₂
277 ^D J	550	9	262	535	75	200
3495	622	10	252	525	//.5	
368	649	15	240 232bc	505	81.5	150 -
359	632	17.5	232 ^{be}	505	81.5	•
361	634	20	122 ^{bf}	395	81.5	•
348	621	25	172 ^{bh}	445	81.5	
342 ^{bc}	575	25	245	518	82.5	
294 ^{Dd}	567	25	252	525	85	
172 ^{bn}	445	25	268	541	90	
194 ⁵¹	467	25	2/300 2220be	540	90	
370	643	25	232	373	90	
322	595	32.5	136 ^{bg}	409	90	
307	580	35	174 ^{bh}	447	90	
302 ^{bc}	575	36	288	561	95	
302 ^{bd}	575	36	284 ^{bc}	557	95	
173 ^{pn}	446	36	230 ^{be}	503	95	
304	577	37.5	105 ⁰¹	378	95	
305	502	40 / =	108.00	441 576	95	
317	590	45 50	502	373	100	
a T /K values calculated by the compiler.						
C Init	erenti ial cr	al therma ystalliza	al analy ation.	sis.		
a Fire	st eute	ctic stop	p.			
f	ond eut	ectic st	op.			
g Firs	st tran	sition of	t the sy	stem.		
h Thi	niu tra nd tran	sition of	JI THE E	stem.		
1 Four	th tra	nsition (of the s	vstem.		
j Fifth transition of the system.						
k Sixt	th tran	sition o	f the sy	stem.		
∫ [⊥] Seve	enth t	ransitio	n of th	ne syst	em (no ex	planation if offered by the author for the
0000	irrence	of this	point a	above t	he liquid	us, compiler).
1						i
[
1						

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium butanoate (potassium buturate):	Pochtakova, E.I. Zh. Obshch. Khim. 1974. 44. 241-248.
$(C_4H_7O_2)_2K_2;$ [589-39-9]	200 Obsilent Alia <u>1974</u> , 44, 241 2401
(2) Magnesium butanoate (magnesium butyrate);	
(C ₄ H ₇ O ₂) ₂ Mg; [556-45-6]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES: (continued)	Letter (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)
Characteristic point(s):	
Eutectic, E_1 , at 300 ^o C (302 ^o C by D.T.A Eutectic, E_2 , at 235 ^o C (232 ^o C by D.T.A), and 100x ₂ = 36.0 (author).), and 100x ₂ = 81.5 (author).
Intermediate compound(s):	
$(C_7H_4O_2)_4K_2Mg$, congruently melting at 31	8 °C.
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Vigual nolythermal analysis, sunnlemented	Materials prepared (Ref. 1) by reacting the
with differential thermal analysis.	proper ("chemically pure") carbonate with a
	analytical purity. Component 1 undergoes
	phase transitions at $t_{trs}(1)/{}^{0}C = 190, 280-$ 285, 345 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	(1) Sokolov, N.M.
	Zn. Ubshch. Khim. <u>1954</u> , 24, 1581-1593. (2) Sokolov, N.M.
	Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	EVALUATOR:
 Potassium butanoate (potassium butyrate);	Franzosini, P.,
(C ₄ H ₇ O ₂)K; [589-39-9] Sodium butanoate (sodium butyrate);	Dipartimento di Chimica Fisica
(C ₄ H ₇ O ₂)Na; [156-54-7]	Universita [°] di Pavia (ITALY).

The visual polythermal method was employed by Sokolov and Pochtakova (Ref. 1), and by Dmitrevskaya (Ref. 2) to study the lower boundary of the isotropic liquid field: according to these authors, continuous series of solid solutions ought to exist.

Both components, however, form liquid crystals. Consequently: (i) the fusion temperatures, $T_{fug}(1)=677 \text{ K} (404 \text{ }^{O}\text{C})$ and $T_{fug}(2)=603 \text{ K} (330 \text{ }^{O}\text{C})$, reported in Refs. 1, 2 should be identified with the clearing temperatures; and (ii) a continuous series of liquid crystal (and not of solid) solutions should be expected.

More recently, Prisyazhnyi et al. (Ref. 3) - to whom Refs. 1, 2 seem to be unknown carried out a derivatographical reinvestigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Their clearing [678 K (405 °C); 595 K (322 °C)] and fusion [628 K (355 °C); 523 K (250 °C)] temperatures substantially agree with the corresponding values from Preface, Table 1 (677.3+0.5, 600.4+0.2, and 626.1+0.7, 524.5+0.5 K, respectively).

Prisyazhnyi et al.'s, and Dmitrevskaya's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals). The complete phase diagram ought to be similar to that reported in Scheme C.1, and the only invariant ought to be classified as an M_E point, at which equilibrium occurs among one liquid crystalline and two solid phases. The statements made in Refs. 1, 2 cannot be considered as correct, whereas Prisyazhnyi et al.'s measurements look as compatible with expectation.

The latter measurements can be further commented as follows: (i) the two-phase region pertinent to the liquid crystal - isotropic liquid equilibria might be so narrow as to prevent observation of two distinct sets of points in this region; (ii) the lack of information about eutectic fusion in the different samples submitted to derivatographical analysis remains, however, rather surprising.

(continued in the next page)



COMPONENTS:	EVALUATOR:
 Potassium butanoate (potassium butyrate);	Franzosini, P.,
(C ₄ H ₇ O ₂)K; [589-39-9] Sodium butanoate (sodium butyrate);	Dipartimento di Chimica Fisica
(C ₄ H ₇ O ₂)Na; [156-54-7]	Universita' di Pavia (ITALY).

CRITICAL EVALUATION: (continued)

Finally, the following two points deserve attention.

(1) Among the phase transformation temperatures of component 1 quoted in Refs. 1, 2 from Ref. 4 (i.e., 618, 553-558, and 463 K) the first one can be reasonably identified with the fusion temperature (626.1 ± 0.7 K) listed in Preface, Table 1, whereas the second and third ones lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 , and 467.2 ± 0.5 and 461.4 ± 1.0 , respectively) also reported in Table 1 of the Preface.

(11) For component 2, Table 1 of the Preface [besides the clearing temperature] provides solid state transitions at 450.4+0.5, 489.8+0.2, 498.3+0.3, and 508.4+0.5, and fusion at 524.5+0.5. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 5). On the other hand, phase transformations are quoted in Refs. 1, 2 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify conveniently the two intermediate transition temperatures from Ref. 4 with the first transition temperature and the fusion temperature from Table 1, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted in Refs. 1, 2.

- (1) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. <u>1958</u>, 28, 1693-1700 (*); Russ. J. Gen. Chem.(Engl. Transl.) <u>1958</u>, 28, 1741-1747.
- (2) Dmitrevskaya, 0.I.
 Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2046-2051.
- (3) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. <u>1983</u>, 49, 659-660.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.
- (5) Schiraldi, A.; Chiodelli, G.
 J. Phys. E: Sci. Instr. <u>1977</u>, 10, 596-599.

COMPONENTS:	ORIGINAL MEASUREMENTS:						
 Potassium butanoate (potassium butyrate); (C₄H₇O₂)K; [589-39-9] Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7] 	Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. <u>1958</u> , 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u> , 28, 1741-1747.						
VARIABLES:	PREPARED BY:						
Temperature.	Baldini, P.						
EXPERIMENTAL VALUES:							
t/ ^o C T/K ^a 100x ₁	ل المعالم معالم م						
<pre>330 603 0 339 612 5 348 621 10 356 629 15 364 637 20 370 643 25 375 648 30 380 653 35 385 658 40 389 662 45 393 666 50 396 669 55 399 672 60 402 675 65 405 678 70 406 679 75 406 679 80 405 678 85 405 678 85 405 678 90 404 677 95 404 677 100 a T/K values calculated by the compiler. Characteristic point(s): Continuous series of</pre>	solid solutions (author).						
AUXILIARY I	NFORMATION						
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:						
Visual polythermal analysis. Temperatures measured with a Nichrome- Constantane thermocouple.	Components synthetized from "chemically pure" potassium and sodium hydrogen carbonates, and n-butanoic acid (Ref. 2, where, however, carbonates instead of hydrogen carbonates are employed; compiler); the salts obtained were recrystallized from n-butanol. Component 1 undergoes phase transitions at $t_{trs}(1)/^{O_{C=}}$ 190, 280-285, 345 (Ref. 2). Component 2 undergoes phase transitions at $t_{trs}(2)/^{O_{C=}}$ 117, 232, 252, 316 (Ref. 2). ESTIMATED ERROR: Temperature: accuracy probably ± 2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593. (2) Sokolov, N.M. Terisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .						


COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium butanoate (potassium butyrate); (C₄H₇O₂)K; [589-39-9] Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7] 	Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. <u>1983</u> , 49, 659-660.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal equilibria). Characteristic point(s): Eutectic, E, at 194 °C and 100x ₁ = 38 (authors).	$ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
AUXILIARY 1	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6 K min ⁻¹ , and using $Al_{2}O_{3}$ as reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase. Supplementary information was obtained by conductometry.	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C$ about 355; $t_{clr}(1)/{}^{\circ}C$ about 405 (compiler). Component 2: $t_{fus}(2)/{}^{\circ}C$ about 250; $t_{clr}(2)/{}^{\circ}C$ about 322 (compiler).
	ESTIMATED ERROR:
	Temperature: accuracy not evaluable (compiler).

EVALUATOR:

Schiraldi, A.,

Dipartimento di Chimica Fisica Universita' di Pavia (ITALY).

COMPONENTS:

 Lithium butanoate (lithium butyrate); (C₄H₇O₂)Li; [21303-03-7]
 Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7]

CRITICAL EVALUATION:

The visual polythermal analysis was employed by Tsindrik and Sokolov (Ref. 1) to study the lower boundary of the isotropic liquid field: according to these authors, a eutectic ought to exist at 495 K (222 $^{\circ}$ C), and $100x_{2}$ = 50.

Component 2, however, forms liquid crystals. Consequently: (i) the fusion temperature, 603 K (330 $^{\circ}$ C) reported in Ref. 1 should be identified with the clearing temperature; (ii) the two branches of the curve refer to equilibria of different kind; and (iii) the intersection of the two branches cannot be classified as a eutectic.

More recently, Prisyazhnyi et al. (Ref. 2) - to whom Ref. 1 seems to be unknown carried out a derivatographical reinvestigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid



the isotropic liquid, and the liquid crystal field. Their clearing $[T_{clr}(2)=595 \text{ K} (322 \ ^{\circ}C)]$ and fusion $[T_{fus}(1)=598 \text{ K} (325 \ ^{\circ}C); T_{fus}(2)=524 \text{ K} (251 \ ^{\circ}C)]$ temperatures substantially agree with the corresponding values from Table 1 of the Preface (600.4+0.2; 591.7+0.5, and 524.5+0.5 K, respectively).

Prisyazhnyi et al.'s, and Tsindrik and Sokolov's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals). Assuming that limited solid solutions are present, the complete phase diagram ought to be similar to that reported in Preface, Scheme A.1. The upper invariant ought to be classified as an $M_{\rm E}$ point, and the lower one as an $M_{\rm E}$ point.

Prisyazhnyi et al.'s measurements look as compatible with expectation, although the lack of information about eutectic fusion in the different samples studied by derivatographical analysis remains rather surprising. Instead, the narrowness of the two-phase region pertinent to the liquid crystal - isotropic liquid equilibria could have prevented the observation of two distinct sets of points in this region.

Finally, the following point requires attention. For component 2, Table 1 of the Preface [besides the $T_{clr}(2)$ value] provides four solid state transitions at 450.4±0.5, 489.8±0.2, 498.3±0.3, and 508.4±0.5 K, and $T_{fus}(2)/K=524.5\pm0.5$. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). On the other hand, phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify conveniently the two intermediate transition temperatures from Ref. 4 with the first solid state transition and fusion temperatures from Table 1 of the Preface, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted in Ref. 1.

- (1) Tsindrik, N.M.; Sokolov, N.M.
 Zh. Obshch. Khim. 1958, 28, 1728-1733 (*); Russ. J.
 1958, 28, 1775-1780.
 (2) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.
- Ukr. Khim. Zh. <u>1983</u>, **49**, 659-660.
- (3) Schiraldi, A.; Chiodelli, G.
 J. Phys. E: Sci. Instr. 1977, 10, 596-599.
 (4) Scholar, N.M.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium butanoate (lithium butyrate); (C₄H₇O₂)Li; [21303-03-7] Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7] 	Tsindrik, N.M.; Sokolov, N.M. Zh. Obshch. Khim. <u>1958</u> , 28, 1728-1733 (*); Russ. J. Gen. Chem. (Engl. transl.) <u>1958</u> , 28, 1775-1780.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	·····
329 602 0 326 599 5 318 591 10 308 581 15 298 571 20 285 558 25 273 546 30 260 533 35 248 521 40 234 507 45 222 495 50 240 513 55 254 527 60 270 543 65 280 553 70 292 565 75 302 575 80 312 585 85 320 593 90 327 600 95 330 603 100 ^a T/K values calculated by the compiler.	$^{\circ}C$ and $100x_2 = 50$ (authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis; temperatures of initial crystallization measured with a Nichrome-Constantane thermocouple and a millivoltmeter.	Both components prepared from "chemically pure" carbonates and n-butanoic acid (Ref. 1); the solids recovered after evaporation were recrystallized from n-butanol. Component 2 undergoes phase transitions at $t_{trs}(2)/^{o}C=117$, 232, 252, 316 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

<u>-</u>	······································
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Lithium butanoate (lithium butyrate); (C₄H₇O₂)Li; [21303-03-7] (2) Sodium butanoate (sodium butyrate); (C₄H₇O₂)Na; [156-54-7] 	Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Ukr. Khim. Zh. <u>1983</u> , 49, 659-660.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES: The results are reported only in graphical form (see figure). Data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria). Characteristic point(s): Eutectic, E, at 188 °C and 100x1 = 41 (authors	
Invariant point, M E, at about 215 °C and 100	x1 about 52 (compiler).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6 K min ⁻¹ , and using Al_{2O_3} as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase. Supplementary information was obtained by conductometry.	Not stated. Component 1: $t_{fus}(1)/{}^{\circ}C$ about 325 (compiler). Component 2: $t_{fus}(2)/{}^{\circ}C$ about 251; $t_{clr}(2)/{}^{\circ}C$ about 322 (compiler).
oblained by conductometry.	ESTIMATED ERROR:
	Temperature: accuracy not evaluable (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Magnesium butanoate (magnesium butyrate); (C₄H₇O₂)₂Mg; [556-45-6] Sodium butanoate (sodium butyrate); (C₄H₇O₂)₂Na₂; [156-54-7] 	Franzosini, P. Dipartimento di Chimica fisica, Universita' di Pavia (ITALY)

This binary was studied only by Pochtakova (Ref. 1) who (on the basis of visual polythermal and DTA results) claimed the occurrence of the congruently melting intermediate compound $(C_{4H_7O_2})_7 M_{52Na_3}$, able to give eutectics with either component.

Component 2, however, goes through the liquid crystalline state before transformation into a clear melt. Therefore the topology of the phase diagram at $0 \leq 100 \mathbf{x}_1 \leq 57$ should be described more correctly with (probable) reference to Preface, Scheme A.I: in this case the invariant ought to be of the M_E' type.

The following points are still worth mentioning.

(1) Pochtakova's fusion temperature of component 1 (575 K) is noticeably higher than data by other authors reported in Ref. 2, whereas her $T_{fus}(2)$ value (603 K) is in reasonable agreement with the clearing temperature (600.4+0.2 K) listed in Preface, Table 1 for component 2.

(ii) Again for component 2, Table 1 of the Preface provides four transition temperatures (450.4+0.5, 489.8+0.2, 498.3+0.3, and 508.4+0.5 K), and $T_{fus}(2)/K=524.5+0.5$. It is to be stressed that these phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). On the other hand, phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identity conveniently the two intermediate transition temperatures from Ref. 4 with the highest solid state transition and fusion, respectively, from Table 1 of the Preface, whereas reasonable doubts can be cast about the actual existence of the highest and lowest transformations quoted by Pochtakova.

(111) In the DTA traces taken at $100x_1 = 10$ and 35, Pochtakova observed discontinuities at 587 and 573 K, and at 528 and 507 K, respectively, which might correspond to the higher (587 and 528 K) and lower (573 and 507 K) boundary of a diphasic region, thus supporting an interpretation of the phase diagram based on Scheme A.1 of the Preface.

(iv) The author's explanation, that the discontinuities observed at temperatures corresponding to the lowest section of the subsolidus might be due to the transformation (at about 435 K) of the intermediate compound into a metastable phase turning to stable at about 410 K, should be more detailed and better supported.

In conclusion, it seems to the evaluator that the existence of an intermediate compound, the location of both eutectics, and the liquidus branch richest in component 1 are sufficiently well assessed, whereas other parts of the diagram need refinements.

- (1) Pochtakova, E.I. Zh. Obshch. Khim. 1974, 44, 241-248.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.
- (3) Schiraldi, A.; Chiodelli, G.
 J. Phys. E: Sci. Instr. <u>1977</u>, 10, 596-599.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

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COMPON	IENTS:					ORIGINAL MEASUREMENTS:
(1) Ma bu (0 (2) So (0	ignesiu tyrate 4H7 ⁰ 2) dium bu 4H7 ⁰ 2)2	n butanoa); Mg; [556 itanoate 2 ^{Na} 2; [15	te (magn -45-6] (sodium 6-54-7]	esium butyra	ate);	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
VARIA	BLES:		~~ <u>~</u>			PREPARED BY:
Temper	ature.					Baldini, P.
EXPERI	MENTAL	VALUES:			· · · · · · · · · · · · · · · · · · ·	<u> </u>
t/ ^o C	T/K ^a	100 x 1				
330 318 305 208bd 248b1 314bj 288 278 268 258 248 255 214bd 234bh 238 220 220bc 216bd 225 bc 216bd 225 bc 216bd 216bd 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 216bd 217bc 21	603 591 578 573 481 521 521 521 521 521 521 521 521 521 52	0 5 10 10 10 10 10 10 15 20 25 30 35 50 50 55 55 60 calculat the Figu stillon of nsition of this this 35 50 50 55 55 60 calculat therma a the figu stillon of nsition of this 35 35 35 35 35 35 35 35 35 35 50 50 50 50 51 50 51 50 51 50 51 50 51 50 51 51 51 51 51 50 51	217 220bc 206be 135bf 215 208bc 208be 140bf 162bg 218 226 234 230bc 205be 126bf 164bg 247 248bc 205be 133bf 158bg 266 275 270bc 202be 138bf 302 ed by th 1 analys refrom re. the sys f the sys of the sys	490 493 479 408 488 481 413 435 491 499 507 503 478 399 437 520 521 477 406 431 539 548 543 475 411 575 e comp is (fi visual tem syst the ove the ove the complete the syst the syst the complete the syst	65 65 65 67.5 69 69 69 70 72.5 75 75 75 75 75 75 75 80 80 80 80 80 80 80 80 80 80 80 80 90 90 90 90 90 90 90 90 90 90 90 90 90	Here in the Figure). tanation if offered by the author for the s, compiler).
(co	ntinued	l in the	next pag	e)		

l			
COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Magnesium butanoate (magnesium	Pochtakova, E.I. Zh. Obabab. Khim. 1974 . 44 . 241-248		
$(C_{4H70_2)_2Mg}; [556-45-6]$	20. Obsileito Killiko 1974, 44, 241-240.		
(2) Sodium butanoate (sodium butyrate); (C ₄ H ₇ O ₂) ₂ Na ₂ ; [156-54-7]			
VARIABLES:	PREPARED BY:		
Temperature.	Baldini, P.		
EXDEDIMENTAL VALUES: (continued)			
LATERIERIAE VALOES. (Concineed)			
Characteristic point(s):			
Eutectic, E_1 , at 210 °C (208 °C by DTA), and Eutectic, E_2 , at 220 °C and 100 x_1 = 45 (author	100 x₁= 69 (author).		
Intermediate compound(s):			
(C ₄ H ₇ O ₂) ₇ Mg ₂ Na ₃ (author), congruently melt Fig. 1, compiler).	ing at 225 ^O C (as reported in Ref. 1,		
AUXTLIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal analysis (empty circles	Materials prepared (Ref. 2) by reacting the		
in the Figure) supplemented with DTA	proper ("chemically pure") carbonate with a		
(filled circles).	analytical purity. Component 2 undergoes		
	phase transitions at t _{trs} (2)/ °C= 117, 232, 252, 316 (Ref. 3).		
	ESTIMATED ERROR:		
	Temperature: accuracy probably +2 K (compiler).		
	REFERENCES:		
	(1) Pochtakova, E.I.		
	Zh. Obshch. Khim. <u>1978</u> , 48, 1212-1214. (2) Sokolov, N.M.		
	Zh. Obshch. Khim. 1954, 24, 1581-1593. (3) Sokolov. N.M.: Tezisy Dokl. X Nauch.		
	Konf. S.M.I. <u>1956</u> .		

COMPONENTS:	EVALUATOR:
 Potassium iso.butanoate (potassium iso.butyrate); (i.C₄H₇O₂)K; [19455-20-0] Sodium iso.butanoate (sodium iso.butyrate); (i.C₄H₇O₂)Na; [996-30-5] 	Schiraldi, A., Dipartimento di Chimica Fisica Universita ⁻ di Pavia (ITALY).

This system was studied only by Sokolov and Pochtakova (Ref. 1) who suggested the phase diagram to be of the eutectic type, the invariant point occurring at 521 K (248 °C) and $100 x_1 = 7.5$.

Component 1, however, forms liquid crystals. Therefore the temperature of 633 K (360 °C) given in Ref. 1 should be identified with the clearing (and not the fusion) temperature of this component, and compared with the $T_{clr}(1)$ value (625.6+0.8 K) reported in Table 2.

For the same component, three phase transition temperatures are quoted in Ref. 1 from Ref. 2, i.e., 621, 546, and 481 K, the second of which can be reasonably identified with the fusion temperature $[T_{fus}(1)=553.9\pm0.5$ K] listed in Preface, Table 2. Consequently: (1) the transition temperature at 621 K (if actually existing) might correspond to some kind of transformation (undetected by DSC, see Preface, Table 2) within the liquid crystal field; and (ii) only the transition at 481 K should correspond to a solid state transformation, although the latter figure is almost 60 K higher than the single $T_{trs}(1)$ value (424+3 K) listed in Table 2 of the Preface.

Concerning component 2, the fusion temperature of 535 K (262 °C; Ref. 1) is in reasonable agreement with that (526.9 ± 0.7 K) reported in Table 2 of the Preface. In this Table, however, no mention is made of other phase transformations, although three solid state transitions are quoted for this component in Ref. 1 (from Ref. 2), at 493, 364, and 340 K (220, 91, and 67 °C), respectively. Duruz et al. (Ref. 3) report in turn: fusion at 527 K (in agreement with the fusion temperature from Table 2), and solid state transitions at 493 K (in agreement with the highest transition temperature from Ref. 2), and at 468 K (a figure which has no correspondence in Ref. 2). Finally, Ferloni et al. (Ref. 4) are inclined to think that Sokolov's transformation at 340 K (Ref. 2) actually represents a transition of a hydrated form of the salt.

In the evaluator's opinion, a re-investigation of the phase relations in solid sodium **iso**.butanoate would be desirable. At any rate, the phase diagram suggested by Sokolov and Pochtakova (Ref. 1) has to be modified (due to the occurrence of liquid crystals in component 1) with reference to Schemes A.1, or A.3, of the Preface according to the kind of solid state miscibility between components, the eutectic point actually being an M'_E point.

- (1) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1971</u>, A 322, 281-299.
- (4) Ferloni, P.; Sanesi, M.; Tonelli, P.L.; Franzosini, P.
 Z. Naturforsch. <u>1978</u>, A 33, 240-242.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium iso.butanoate (potassium iso.butyrate); (i.c₄H₇O₂)K; [19455-20-0] (2) Sodium iso.butanoate (sodium iso.butyrate); (1.c₄H₇O₂)Na; [996-30-5] 	Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1960</u> , 30, 1433-1437.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁	· · · · · · · · · · · · · · · · · · ·
<pre>262 535 0 254 527 5 248 521 7.5 255 528 10 266 539 15 277 550 20 285 558 25 293 566 30 302 575 35 308 581 40 315 588 45 320 593 50 325 598 55 331 604 60 335 608 65 338 611 70 342 615 75 345 618 80 348 621 85 353 626 90 357 630 95 360 633 100</pre>	$^{\circ}$ C and $100x_1 = 7.5$ (authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Both components were prepared from commercial "pure" grade iso.butanoic acid, distilled before use and the proper
<pre>REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156. (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956 (this is Ref. 6 in the original paper, and not Ref. 5 as erroneously quoted in the text; compiler).</pre>	<pre>"chemically pure" hydrogen carbonate (Ref. 1); then recrystallized from n-butanol. Component 1 undergoes phase transitions at t_{trs}(1)/°C= 208, 273, 348 (Ref. 2). Component 2 undergoes phase transitions at t_{trs}(2)/°C= 67, 91, 220 (Ref. 2). ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler).</pre>

COMPONENTS:	EVALUATOR:
 Potassium pentanoate (potassium valerate);	Schiraldi, A.,
(C ₅ H ₉ O ₂)K; [19455-21-1] Sodium pentanoate (sodium valerate);	Dipartimento di Chimica Fisica,
(C ₅ H ₉ O ₂)Na; [6106-41-8]	Universita' di Pavia (ITALY).

This system was studied only by Dmitrevskaya and Sokolov (Ref. 1), who claimed that continuous series of solid solutions exist.

Both components, however, form liquid crystals (see Preface, Table 1). Consequently: (i) the fusion temperatures, $T_{fus}(1) = 717$ K (444 °C) and $T_{fus}(2) = 630$ K (357 °C) given in Ref. 1, are actually to be identified with the clearing temperatures (the corresponding values from Preface, Table 1 being 716+2 K and 631+4 K, respectively); (i1) the transition temperatures $T_{trs}(1) = 580$ K ($\overline{307}$ °C) and $T_{trs}(2) = 489$ K (216 °C) quoted in Ref. 1 from Ref. 2, are in turn to be identified with the actual fusion temperatures (the corresponding values from Table 1 of the Preface being 586.6+0.7 K and 498+2 K, respectively).

Continuous series of liquid crystal (instead of solid) solutions ought to form, and the phase diagram ought to be similar to that shown in Preface, Scheme C.1.

Moreover, the following point deserves attention. For component 2, Table 1 of the Preface reports no solid state transition, whereas Dmitrevskaya and Sokolov quote (again from Ref. 2) $T_{trs}(2)/K=$ 482 and 453. It is, however, to be stressed that the single transition observed (at 479+1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 3) was not more mentioned in a subsequent DSC investigation by the same group (Ref. 4).

In conlusion, due to the lack of information about the boundaries of the mesomorphic liquid field, and to conflicting assertions about solid state transitions, a re-investigation of the system would be desirable.

- Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1965</u>, **35**, 1905-1909.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1971</u>, A322, 281-299.
- (4) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II <u>1972</u>, 1879-1881.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium pentanoate (potassium valerate); (C₅H₉O₂)K; [19455-21-1] Sodium pentanoate (sodium valerate); (C₅H₉O₂)Na; [6106-41-8] 	Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1965</u>, 35, 1905-1909.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
357 630 0 366 639 5 375 648 10 382 655 15 388 661 20 393 666 25 397 670 30 402 675 35 406 679 40 407 680 45 414 687 50 418 691 55 426 699 65 430 703 70 432 705 75 436 709 80	400
 439 712 85 440 713 90 442 715 95 444 717 100 ^aT/K values calculated by the compiler. Characteristic point(s): Continuous series of 	0 50 100×1 100 (C ₅ H ₉ O ₂)Na (C ₅ H ₉ O ₂)K solid solutions.
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Both components prepared from n-pentanoic acid and the proper carbonate (Ref. 1). Component 1 undergoes a phase transition at $t_{trs}(1)/^{\circ}C= 307$ (Ref. 2). Component 2 undergoes phase transitions at $t_{trs}(2)/^{\circ}C= 180$, 209, 216 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593. (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .

COMPONENTS:	EVALUATOR:
 Magnesium pentanoate (magnesium valerate);	Franzosini, P.,
(C ₅ H ₉ O ₂) ₂ Mg; [556-37-6] Sodium pentanoate (sodium valerate);	Dipartimento di Chimica Fisica,
(C ₅ H ₉ O ₂) ₂ Na ₂ ; [6106-41-8]	Universita´ di Pavia (ITALY).

This binary was studied only by Pochtakova (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid region at $0 \leq 100 x_1 \leq 72.5$ (the investigation of mixtures richer in component 1 being prevented by their tendency to form glasses). She claimed the occurrence of an incongruently melting intermediate compound, i.e, $(C_5H_0O_2)_8Mg_3Na_2$, able to give a eutectic with component 2.

The latter component, however, forms liquid crystals. Consequently, the topology of the phase diagram at $0 \leq 100x_1 \leq 55$ could be described more correctly with (possible) reference to Scheme D.1 of the Preface: accordingly, Pochtakova's eutectic ought to be an M'_E point, and an invariant type M_E (undetected by visual polythermal analysis) ought to exist at $100x_1 < 55$.

A few more points are worth mentioning.

(1) Pochtakova's (extrapolated) fusion temperature of component 1 (537 K) seems reasonable, although somewhat higher than the only other value provided by the literature (531 K; Ref. 2), while her $T_{fus}(2)$ value (630 K) agrees fairly with the clearing temperature (631+4 K) listed in Preface, Table 1 for component 2.

(11) For the same component, Table 1 of the Preface provides also a $T_{fus}(2)=498+2$ K, a figure which can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Pochtakova from Ref. 3.

(111) Once more for component 2, Table 1 of the Preface reports no solid state transition, whereas Pochtakova quotes (from Ref. 3) $T_{trs}(2)/K^{=}$ 482 and 453. It is, however, to be stressed that the single transition observed (at 479+1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 4) was not more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

In conlusion, due to the lack of information about the boundaries of the mesomorphic liquid field, and to conflicting assertions about solid state transitions, a re-investigation of the system would be desirable.

- Pochtakova, E.I.
 Zh. Obshch. Khim. 1974, 44, 241-248.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1971</u>, A322, 281-299.
- (5) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II <u>1972</u>, 1879-1881.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Magnesium pentanoate (magnesium valerate); 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1974</u> , 44, 241-248.
<pre>(C₅H₉O₂)₂Mg; [556-37-6] (2) Sodium pentanoate (sodium valerate); (C₅H₉O₂)₂Na₂; [6106-41-8]</pre>	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₁ t/ ^o C T/K ^a 100	Dx₁ Ų
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	5.5 5.5 5.5 5.5 5.5 5.5 5.5 5.5
AUXILIA	RY INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. NOTE: The system was investigated $0 \le 100x_1 \le 72.5$ due to the tendency component 1 to form glasses.	Materials prepared (Ref. 1) by reacting the proper ("chemically pure") carbonate with a slight excess of n-pentanoic acid of analytical purity. Component 1: $t_{fug}/^{O}C$ (extrapolated) at 264. Component 2 undergoes phase transitions at $t_{trs}(2)/^{O}C$ = 180, 209, 216 (Ref. 2).
	ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K
	 (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593. (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	EVALUATOR:
 Potassium iso.pentanoate (potassium iso.valerate);	Schiraldi, A.,
(i.C ₅ H ₉ O ₂)K; [589-46-8] Sodium iso.pentanoate (sodium iso.valerate);	Dipartimento di Chimica Fisica,
(1.C ₅ H ₉ O ₂)Na; [539-66-2]	Universita [~] di Pavia (ITALY).

This system was studied by Pochtakova (Ref. 1), and by Dmitrevskaya and Sokolov (Ref. 2): according to both papers, continuous series of solid solutions ought to be formed.

Both components, however, form liquid crystals (see Preface, Table 2). Consequently the fusion temperatures, $T_{fug}(1) = 669 \text{ K} (396 ^{\circ}\text{C}; \text{ Refs. 1, 2})$, and $T_{fug}(2) = 533 \text{ K} (260 ^{\circ}\text{C}; \text{ Ref. 1})$ or 535 K (262 $^{\circ}\text{C}$; Ref. 2), are actually to be identified with the clearing temperatures, the corresponding values from Table 2 of the Preface being 679+2 K and 559+1 K, respectively. The latter figure is remarkably higher than those given by the Russian authors, although meeting rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

No mention is made in Refs. 1, 2 of the actual fusion of component 1 which occurs at 531+3 K (Table 2): the latter figure is supported by the trend of the thermomagnetical curves plotted by Duruz and Ubbelohde (Ref. 5). As for the other phase transitions of the same component, Pochtakova quotes from Ref. 6 two T_{trs} values, i.e., 327 and 618 K (54 and 345 °C, respectively), for which no comparison is possible with the findings by other investigators, inasmuch as: (i) no transformation is reported in Table 2 as occurring below $T_{fus}(1)=531+3$ K; and (ii) no transformation is reported in Table 2 or in Ref. 5 as occurring within the field of existence of the mesomorphic liquid. It is a bit puzzling the fact that for potassium iso-pentanoate Dmitrevskaya and Sokolov (Ref. 2) quote from the same source (Ref. 6) transitions at 618, 493, and 473 K (ignoring that quoted by Pochtakova at 327 K).

In the case of component 2, the transition at 451 K (178 $^{\circ}$ C; quoted in Refs. 1, 2 from Ref. 5) should be indentified with the actual fusion temperature (the corresponding value from Table 2 of the Preface being 461.5+0.6 K).

Taking into account the above remarks, the upper part of Dmitrevskaya and Sokolov's diagram, Ref. 2, (to be compared with the upper part of Preface, Scheme C.1) supports the idea that continuous series of liquid crystal (instead of solid) solutions do form. Moreover, the left-hand side of the lower part of the same diagram might suggest that, at lower temperatures, solid solutions are also present.

- Pochtakova, E.I. Zh. Obshch. Khim. 1963, 33, 342-347.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. <u>1967</u>, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1967</u>, 37, 2050-2054.
- (3) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A 322, 281-299.
- (5) Duruz, J.J.; Ubbelohde, A.R.
 Proc. R. Soc. London <u>1975</u>, A 342, 39-49.
- (6) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Potassium iso.pentanoate (potassium iso.valerate); (i.C₅H₉O₂)K; [589-46-8] Sodium iso.pentanoate (sodium iso.valerate); (1.C₅H₉O₂)Na; [539-66-2] 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1963</u> , 33, 342-347.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·	
396		
ن ۲ 260 مهمی می		
100 (i.C ₅ H ₀ O ₂)Na	100 X ₂ 0 (i. C ₅ H ₉ O ₂)K	
The results are reported only in graphical form (see figure). Characteristic point(s): Continuous series of solid solutions.		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis.	Both components prepared from commercial iso.pentanoic acid (distilled twice before	
ESTIMATED ERROR:	hydrogen carbonate (Ref. 1, where, however, carbonates instead of hydrogen carbonates	
Temperature: accuracy probably <u>+2</u> K (compiler).	are employed; compiler). Component 1 undergoes phase transitions at t (1)/°C= 54 345 (Ref. 2) and melts at	
REFERENCES:	$t_{fus}(1)/^{o}C=396$. Component 2 undergoes phase transitions at t. (2)/ $^{o}C=152$. 178	
 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. 	(Ref. 2) and melts at $t_{fus}^{crs(2)/oC=260}$.	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Potassium iso.pentanoate (potassium iso.valerate); (1.c₅H₉O₂)K; [589-46-8] (2) Sodium iso.pentanoate (sodium iso.valerate); (1.c₅H₉O₂)Na; [539-66-2] 	Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.	
VARTABLES.	PREPARED BY.	
-		
Temperature.	Baldini, P.	
EXPERIMENTAL VALUES:	<u></u>	
$t/^{\circ}C T/K^{a} 100x_{1}$	ų [
262 535 0	\$	
178 ⁰ 451 0		
320 593 25	350	
300 ^b 573 25		
200 ^b 473 25		
186° 459 25		
340 ^b 613 50	250	
216 ^b 489 50	•	
384 657 75	• 220	
242 ^b 515 75	• • • • • • • • • • • • • • • • • • • •	
396 669 100	178	
345 ^D 618 100	150	
200 ^b 473 100		
a T/K values calculated by the compiler. b Transformation in phase. Characteristic point(s): Continuous series of solid solutions. $0 50 100 \times_1 100 (i.C_5H_9O_2)No (i.C_5H_9O_2)K$		
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Thermographical investigation (heating curves recorded automatically). NOTE: The data tabulated (and plotted in the figure) refer to the thermographical	Both components synthetized from iso.butanoic acid and the proper carbonate (Ref. 2). Component 1 undergoes phase transitions at $t_{trs}(1)/^{O}C= 345$, 220, 200 (Ref. 3). Component 2 undergoes phase transitions at $t_{trs}(2)/^{O}C= 152$, 178 (Ref. 3).	
linvestigation; other points of the liquidus, taken by visual polythermal	ESTIMATED ERROR:	
analysis and consistent with the tabulated ones, are reported only in a graphical form (Fig. 2 of the original paper). For the	Temperature: accuracy probably <u>+2</u> K (compiler).	
paper by Sokolov et al. (Ref. 1) where,	REFERENCES:	
however, the present binary is merely mentioned as a side of a reciprocal ternary.	 Sokolov, N.M.; Tsindrik, N.M.; Dmitrevskaya, O.I. Zh. Obshch. Khim. <u>1961</u>, 31, 1051-1056. Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. 	
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COMPONENTS:	EVALUATOR:
 Potassium hexanoate (potassium caproate);	Schiraldi, A.,
(C ₆ H ₁₁ O ₂)K; [19455-00-6] Sodium hexanoate (sodium caproate);	Dipartimento di Chimica Fisica,
(C ₆ H ₁₁ O ₂)Na; [10051-44-2]	Universita ⁻ di Pavia (ITALY).

This system was studied only by Pochtakova (Ref. 1), who claimed the existence of a continuous series of solid solutions.

Both components, however, form liquid crystals (see Preface, Table 1). Consequently: (1) the fusion temperatures, $T_{fus}(1) = 717.7$ K (444.5 °C) and $T_{fus}(2) = 638$ K (365 °C) given in Ref. 1 are actually to be identified with the clearing temperatures (the corresponding values from Table 1 of the Preface being 725.8+0.8 K and 639.0+0.5 K, respectively); (11) the transition temperatures $T_{trs}(1) = 575$ K (302 °C) and $T_{trs}(2) = 499$ K (226 °C), quoted in Ref. 1 from Ref. 2, are in turn to be identified with the fusion temperatures (the corresponding values from Table 1 of the Preface being 581.7+0.5 K and 499.6+0.6 K).

Finally, the following point deserves attention. Two more transitions are quoted in Ref. 1 from Ref. 2 as occurring in component 2 at 615 K ($342 \, ^{\circ}$ C) and 476 K ($203 \, ^{\circ}$ C), respectively. The latter one corresponds to that reported at 473+2 K in Table 1 of the Preface, whereas no evidence was obtained by subsequent investigators (Ref. 3) for a transition comparable with the former one: should it exist, it might mean that two different mesomorphic phases are present in sodium hexanoate.

As a conclusion, in the evaluator's opinion Pochtakova's data support reasonably the idea that continuous series of liquid crystal (instead of solid) solutions are formed, and the phase diagram ought to be not far from that shown in Preface, Scheme C.l.

- (1) Pochtakova, E.I.
 Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1959, 29, 3149-3154.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.
- (3) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.



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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Cesium ethanoate (cesium acetate); CsC₂H₃O₂; [3396-11-0] (2) Cesium nitrite; CsNO₂; [13454-83-6] 	Diogenov, G.G.; Morgen, L.T. Nekotorye Vopr. Khimii Rasplavlen. Solei i Produktov Destruktsii Sapropelitov, Irkutsk, <u>1974</u> , 32-34.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical for Characteristic point(s): Eutectic, E, at 125 °C and $100x_2= 36$ (au	X_2 100 CsNO ₂ orm (see figure).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis; temperatures measured with a Chromel-Alumel thermocouple and a 15 mV millivoltmeter. Supplementary measurements (filled circles in the figure) were performed by thermographical analysis.	Not stated. Component 1: $t_{fus}(1)/{}^{0}C= 187$ (Fig. 1 of the original paper). Component 2: $t_{fus}(2)/{}^{0}C= 405$ (Fig. 1).
NOTE:	REFERENCES:
Concerning component 1, the value of the fusion temperature by Diogenov and Morgen (460 K) is not far from that (463+1 K) listed in Preface, Table 1. For the same component, Nurminskii and Diogenov reported previously (Ref. 1) a solid state transition at 447 K whose existence, however, was not confirmed by any subsequent investigator (Ref. 2).	 Nurminskii, N.N.; Diogenov, G.G. Zh. Neorg. Khim. <u>1960</u>, 5, 2084-2087; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1960</u>, 5, 1011-1013. Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press. Oxford. 1980.
ESTIMATED ERROR:	29-115.
Temperature: accuracy probably <u>+</u> 2 K (compiler).	

Components:	EVALUATOR:	
 (1) Cesium ethanoate (cesium acetate); CsC₂H₃O₂; [3396-11-0] (2) Cesium nitrate; CsNO₃; [7789-18-6] 	Schiraldi, A. Dipartimento di Chimica fisica, Universita' di Pavia (ITALY)	
CRITICAL EVALUATION:		
This binary was studied with visual polythermal analysis by Nurminskii and Diogenov (as a side of the reciprocal ternary Cs, $K/C_{2H_3O_2}$, NO_3 ; Ref. 1), and by Gimel'shtein and Diogenov (as a side of the reciprocal ternary Cs, $Na/C_{2H_3O_2}$, NO_3 ; Ref. 2), with a substantially similar conclusion: the system is of the eutectic type, the invariant being at either 415 K (142 °C; Ref. 1), or 429 K (156 °C; Ref. 2), and $100x_2=25$ (Refs. 1,2).		
In Ref. 1 the authors claim also the existence of a phase transition of component 1 at 447 K (174 ^o C) whose existence, however, was neither mentioned in Ref. 2, nor confirmed by other investigators (Ref. 3).		
The fusion temperature of component 1 reported in both papers, i.e., 455 K (182 ^O C) represents the third lowest value among those listed in Ref. 3, which range between 453 and 467 K. It seems then likely that some impurity (possibly water) was present in the material used by Diogenov et al.		
In the evaluator's opinion, there is no reason to reject the assertion made in Refs. 1 and 2, that the diagram is of the eutectic type: however, due to the possibly inadequate purity of component 1, and to the large discrepancy in the eutectic temperature, a re- investigation of the system would be highly desirable.		
REFERENCES:		
(1) Nurminskii, N.N.; Diogenov, G.G. Zh. Neorg. Khim. <u>1960</u> , 5, 2084-2087; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1960</u> , 5, 1011-1013(*).		
(2) Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., <u>1966</u> , 27, 69-75.		
(3) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u> , 29-115.		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Cesium ethanoate (cesium acetate); CsC₂H₃O₂; [3396-11-0] (2) Cesium nitrate; CsNO₃; [7789-18-6] 	Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., 1966, 27, 69-75.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	
EXPERIMENTAL VALUES:		
Characteristic point(s): Eutectic, E, at 156 $^{\circ}$ C and 100 x_2 = 25 (authors).		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis. Temperatures measured with a Chromel-Alumel thermocouple and a 17 mV millivoltmeter.	Not stated. Component 1: $t_{fus}(1)/{}^{o}C= 182$ (Fig. 2 of the original paper). Component 2: $t_{fus}(2)/{}^{o}C= 407$ (Fig. 2).	
ESTIMATED ERROR:	REFERENCES:	
Temperature: accuracy probably <u>+</u> 2 K (compiler).		

COMPONENTS:	OPTOINAL MEASUREMENTS.
<pre>(1) Cesium ethanoate (cesium acetate); CsC₂H₃O₂; [3396-11-0] (2) Cesium nitrate; CsNO₃; [7789-18-6]</pre>	Nurminskii, N.N.; Diogenov, G.G. Zh. Neorg. Khim. <u>1960</u> , 5, 2084-2087; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1960</u> , 5, 1011-1013 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
<pre>180 453 0 176 449 2.5 172 445 8.0 164 437 14.0 156 429 19.0 148 421 23.0 147 420 26.0 176 449 31.0 195 468 35.0 211 484 39.0 236 509 45.0 263 536 52.5 284 557 60.0 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 142 °C and 100x2= 25 (authors</pre>	$\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i$
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Temperatures measured with a Chromel-Alumel thermocouple and a 17 mV millivoltmeter.	Not stated. Component 1 undergoes a phase transition at $t_{trs}(1)/{}^{0}C=174$ and melts at $t_{fus}(1)/{}^{0}C$ = 182 (Fig. 1 of the original paper), or 180 (table). Component 2 undergoes a phase transition at $t_{trg}(2)/{}^{0}C=392$ and melts at $t_{fus}(2)/{}^{0}C$ = 407 (Fig. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium bromide; KBr; [7758-02-3] Potassium methanoate (potassium formate); KCHO₂; [590-29-4] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₁	· · · · · · · · · · · · · · · · · · ·
<pre>168.7 441.9 0 168.2 441.4 0.20 167.8 441.0 0.60 167.4 440.6 1.00 166.8 440.0 1.27 166.4 439.6 1.70 165.7 438.9 2.03 165.0 438.2 2.61 164.6 437.8 2.89 163.7 436.9 3.43 163.3 436.5 3.98 162.6 435.8 4.50 161.8 435.0 4.98 161.5 434.7 5.25 166.3 439.5 5.51 173.0 446.2 5.81 176.5 449.7 5.97 194.6 467.8 6.85 235.2 508.4 9.04 264.0 537.2 10.99 303.1 576.3 13.90 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 161.</pre>	3° and $100x_{1} = 5.3$ (authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer. ESTIMATED ERROR:	C. Erba RP meterials, dried by heating under vacuum. NOTES: In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler. The system could not be investigated above
Temperature: accuracy probably +0.1 K	about 300 $^{\circ}$ C due to the thermal instability of the methanoate.
(compiler).	According to the authors, the trend of the liquidus branch richer in component 2 is
REFERENCES: (1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38, 116-118.	ilquidus oranch ficher in component 2 is close to ideal, and the formation of solid solutions in this region ought to be either insignificant, or at least contained within narrow limits.









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COMPONENTS:	EVALUATOR:	
 (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4] (2) Potassium butanoate (potassium butyrate); KC₄H₇O₂ [589-39-9] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).	
	I	
CRITICAL EVALUATION:		
This binary was studied only by Sokolov and Minchenko (Ref. 1), who employed the visual polythermal analysis to outline the lower boundary of the isotropic liquid field, and claimed the existence of a single invariant, i.e., a eutectic at 439 K and $100x_2=0.9$.		
However, taking into account that component 2 forms liquid crystals and that its actual fusion temperature is 626.1 ± 0.7 K (see Preface, Table 1), the topology of the phase diagram ought to be described more correctly with reference to Schemes B.1 or B.2 of the Preface. An invariant type M' _p (undetected by Sokolov and Minchenko) should also exist: accordingly, the main branch of Sokolov and Minchenko's diagram should represent solid-liquid equilibria only at temperatures lower than that corresponding to M' _p .		
It can be further noted that a reasonable agreement exists: (1) between the fusion temperature reported for component 1 in Ref. 1 (440 K) and in Table 1 of the Preface (441.9+0.5 K); and (11) between Sokolov and Minchenko's fusion temperature of component 2 (677 K) and the clearing temperature (677.3+0.5 K) listed in Preface, Table 1 for the same component.		
REFERENCES:		
(1) Sokolov, N.M.; Minchenko, S.P.; Zh. Obshc	h. Khim., <u>1974</u> , 44, 1429-1431.	
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium butanoate (potassium butyrate); KC/H₇O₂ [589-39-9] 	Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim., <u>1974</u> , 44, 1429-1431.	
VARIABLES:	PREPARED BY:	
Temperature.	Baldini. P.	
EXTERIMENTAL VALUES.		
m	8404	
form (see figure).	e S grand and a second	
Characteristic point(s): Eutectic, E, at 166 ^o C and 100x ₂ = 0.9 (authors).	1670,500	
METHOD/APPARATUS/PROCEDURE:	E 0 100X ₂ 100	
Visual polythermal analysis.	КСНО ₂ КС ₄ H ₇ O ₂	
SOURCE AND PURITY OF MATERIALS:		
Component 1: commercial material recrystallized; it melts at 167 °C. Component 2: prepared from n-butanoic acid and the carbonate (Ref. 1); it melts at $t_{fus}(2)/°C=404$.		
ESTIMATED ERROR:		
Temperature: accuracy probably +2 K (compiler).		
REFERENCES:		
(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1581-1593.		

COMPONENTS:	EVALUATOR:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂ [19455-20-0] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This binary was studied only by Sokolov and Minchenko (Ref. 1), who employed the visual polythermal analysis to outline the lower boundary of the isotropic liquid field, and claimed the existence of a single invariant, i.e., a eutectic at 437 K and $100x_2$ = 1.

Component 2, however, forms liquid crystals. Therefore the topology of the phase diagram ought to be described more correctly with reference to Schemes B.1 or B.2 of the Preface, and an invariant type M'_p (undetected by Sokolov and Minchenko) should also exist. Accordingly, the main branch of Sokolov and Minchenko's diagram should represent solid-liquid equilibria only at temperatures lower than that corresponding to M'_p .

It can be further noted that a reasonable agreement exists: (i) between the fusion temperature reported for component 1 in Ref. 1 (440 K) and in Preface, Table 1 (441.9 \pm 0.5 K); and (ii) between Sokolov and Minchenko's fusion temperature of component 2 (629 K) and the clearing temperature (625.6 \pm 0.8 K) listed in Table 2 of the Preface for the same component.

Disagreement, on the contrary, exists about the remaining phase transformations. For component 1, Table 1 of the Preface reports a single solid state transition occurring at a temperature (418+1 K) halfway between the highest (430 K) and second highest (408 K) values by Sokolov and Minchenko; the literature, unfortunately, provides no other data (Ref. 2).

For component 2, three phase transition temperatures are mentioned in Ref. 1, i.e., 621, 546, and 481 K, the second of which can be reasonably identified with the fusion temperature $[T_{fug}(2)=53.9\pm0.5 \text{ K}]$ listed in Preface, Table 2. Consequently: (i) the transition temperature at 621 K (if actually existing) might correspond to some kind of transformation (undetected by DSC, see Preface, Table 2) within the liquid crystal field; and (ii) only the transition at 481 K should correspond to a solid state transformation, although the latter figure is almost 60 K higher than the single $T_{trs}(2)$ value (424+3 K) listed in Table 2 of the Preface.

- (1) Sokolov, N.M.; Minchenko, S.P.
 Zh. Obshch. Khim., <u>1977</u>, 47, 740-742.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium iso.butanoate (potassium iso.butyrate); 	Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim., <u>1977</u> , 47, 740-742.	
K1.C ₄ H ₇ O ₂ [19455-20-0]		
VARIABLES:	PREPARED BY:	
Temperature.	Baldini, P.	
The results are reported only in graphical form (see figure). Characteristic point(s):		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis.	Component 1: commercial material recrystallized from methanoic acid; it melts at t _{fus} (1)/°C= 167 and undergoes phase transitions at t _{trs} (1)/°C= 60, 135, 157. Component 2: prepared from i.butanoic acid and the carbonate (Ref. 1); it melts at t _{fus} (2)/°C= 356 and undergoes phase transitions at t _{trs} (2)/°C= 208, 273, 348. ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium chloride; KC1; [7447-40-7] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
t/ ^o C T/K ^a 100x ₂	
168.7 441.9 0 168.3 441.5 0.20 168.1 441.3 0.43 167.7 440.9 0.60 167.4 440.6 0.84 166.7 439.9 1.06 165.7 438.9 1.83 165.5 438.7 1.98 165.6 438.2 2.55 164.3 437.5 2.95 163.8 437.0 3.46 163.6 436.8 3.67 163.6 436.8 3.75 166.6 439.8 3.78 172.1 445.3 4.02 176.6 449.8 4.16 179.2 452.4 4.22 183.5 456.7 4.45 195.8 469.0 4.96 218.4 491.6 6.09 244.0 517.2 7.50 270.1 543.3 9.02 299.7 572.9 11.16	250 250 200 E 0 10 100×2 20 KCH0 ₂ KC1
AUXILIARY I	NFORMATION
NOTES:	METHOD/APPARATUS/PROCEDURE:
In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler. According to the authors, the trend of the liquidus branch richer in component 1 is close to ideal, and the formation of solid solutions in this region ought to be either insignificant, or at least contained within very narrow limits. Indeed, previous investigations by the same group (Ref. 2) stated that the cryometric constant of potassium methanoate was $K = 11.5+0.1$ K molality ⁻¹ , and that $\lim_{m \to 0} (\Delta T : experimental freezing point de-pression; m: molality of the solute) whenKCl was the solute.$	A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer. The system could not be investigated above 300 °C due to the thermal insta- bility of the methanoate. ESTIMATED ERROR: Temperature: accuracy probably ±0.1 K (compiler).
SOURCE AND FURITY OF MATERIALS: C. Erba RP meterials, dried by heating under vacuum.	 Braghetti, M.; Leonesi, D.; Franzosini, P.; Ric. Sci. <u>1968</u>, 38, 116-118. Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P. Ric. Sci. <u>1968</u>, 38, 702-705.

COMPONENTS:

 Potassium methanoate (potassium formate); KCHO₂; [590-29-4]
 Potassium thiocyanate; KCNS; [333-20-0]

CRITICAL EVALUATION:

The liquidus of this binary was studied with visual methods by Sokolov and Pochtakova (Ref. 1), and by Berchiesi and Laffitte [Ref. 2, where reference is made to a previous investigation by Braghetti et al. (Ref. 3) for what concerns the branch richer in component 2, and the T_{trs} and $^{\Delta}_{trs}H_m$ values of either components]. According to both papers, a single eutectic exists whose coordinates should be either 356 K and $100x_2$ = 47.5 (Ref. 1), or 351.7 K and $100x_2$ = 46 (Ref. 2).

Substantially agreeing figures are reported for $T_{fug}(1)$ [440 K (Ref. 1); 441.85 K (Ref. 2)], $T_{fug}(2)$ [450 K (Ref. 1); 449.15 K (Ref. 2)], and $T_{trs}(2)$ [415.7 K (Ref. 4, quoted in Ref. 1); 415 K (Ref. 3, quoted in Ref. 2)]. Conversely, disagreement exists about the number and location of the solid state transitions of component 1, which ought to be three (at 430, 408, and 333 K, respectively) according to Ref. 5, quoted in Ref. 1, and only one (at 418 K) according to Ref. 3, quoted in Ref. 2. The latter information, however, ought to be looked at as more trustworthy being based on DSC records.



According once more to Ref. 3, solid solutions ought to be absent (or at least contained within very narrow limits) in the composition range between pure component 2 and the eutectic, as suggested by the DSC traces. The authors could thus employ the well known equation

$$\mathbf{T}(2) = \frac{\left[\Delta_{fus}(2)\mathbf{H}_{m}/\mathbf{R} + \Delta_{trs}(2)\mathbf{H}_{m}/\mathbf{R}\right] + (\mathbf{A}/\mathbf{R})(\mathbf{x}_{1})^{2}}{\left[\Delta_{fus}(2)\mathbf{S}_{m}/\mathbf{R} + \Delta_{trs}(2)\mathbf{S}_{m}/\mathbf{R}\right] - \ln \mathbf{x}_{2}}$$

to calculate the solid-liquid equilibrium temperatures, T(2)/K, relevant to the liquidus branch richer in component 2 (see curve a of Fig. 1), assuming the following numerical values: $\Delta_{fus}(2)H_m/R= 1545$ K; $\Delta_{trs}(2)H_m/R= 186$ K (to be introduced only when T(2) $\leq T_{trs}$); and $A/K= -800/R + (360/R)x_1$ (A/K: empirical factor introduced to take into account the non-ideal behavior of the mixtures; ideality represented by curve b).

In the figure, the filled and empty circles correspond to data from Ref. 1 and Ref. 2, respectively. It is apparent that spreading is larger in the first set than in the second one, which, moreover, gives [at $T_{trs}(2)/K=415$] a better evidence of the expected change of slope. Accordingly, and taking also into account the poor reliability of the $T_{trs}(1)$ values quoted in Ref. 1, the evaluator recommends Berchiesi and Laffitte's presentation (Ref. 2), although regretting that information was not extended to the solidus.

REFERENCES:

- (1) Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. <u>1958</u>, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.
- (2) Berchiesi, G.; Laffitte, M.; J. Chim. Phys. 1971, 877-881.
- (3) Braghetti, M.; Berchiesi, G.; Franzosini, P.; Ric. Sci. 1969, 39, 576-584.
- (4) Ravich, M.I.; Ketkovich, V.I.; Rassonskaya, I.S.; Izv. Sektora Fiz.-Khim. Anal. <u>1949</u>, 17, 254.
- (5) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

EVALUATOR:

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Franzosini, P.,
Dipartimento di Chimica Fisica,
Universita' di Pavia (ITALY).
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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium methanoate (potassium	Sokolov, N.M.; Pochtakova, E.I.
10^{10}	Zn. UDSncn. Knim. 1956, 20, 1391-1397 (*); Russ. I. Con. Chem. (Fngl. Transl.) 1958
(2) Potassium thiocyanate:	28, 1449–1454.
KCNS; [333-20-0]	
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
►/90 m/v8 100-	
t/c $1/k^{-100x_1}$	
177 450 0	
168 441 5	t / •
162 435 10	
135 408 25	
128 401 30	
119 392 35	Q
111 384 40	
83 356 52.5	
89 362 55	
96 369 57.5	l &
104 377 60	E
112 385 65	
129 402 75	
137 410 80	0 50 100× 100
147 420 85	KCNS KCHO
155 428 90	2
167 440 100	
^a T/K values calculated by the compiler.	
Characteristic point(s): Eutectic, E, at 83 °C and $100x_{1} = 52.5$ (authors).	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated.
	Component 1: commercial material
	recrystallized from water; it undergoes
	phase transitions at $t_{trs}(1)/C = 60$, 135,
	Component 2: commercial material
	recrystallized from alcohol; it undergoes a
	phase transition at $t_{trs}(2)/^{o}C= 142.5$ (Ref.
	2).
	ESTIMATED ERROR:
	(compiler).
	REFERENCES:
	(1) SOKOLOV, N.M. Teriev Dokl. X Nauch- Konf. S.M.T.
	1956.
	(2) Ravich, M.I.; Ketkovich, V.I.;
	Rassonskaya, I.S.; Izv. Sektora Fiz Khim. Anal. <u>1949</u> , 17, 254.

<pre>COMPONENTS: (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4] (2) Potassium thiocyanate; KCNS; [333-20-0]</pre>	Berchiesi, G.; Laffitte, M. J. Chim. Phys. <u>1971</u> , 877-881.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
	I
EXPERIMENTAL VALUES: $t/^{0}C$ T/K ⁴ 100- $t/^{0}C$ T/K ⁴ 100-	
176.00 449.15 100 84.25 357.40 42.1 169.10 442.25 95.10 87.55 360.70 40.2 161.98 435.13 90.43 89.70 362.85 39.2 154.50 427.65 85.79 93.88 367.03 37.2 146.50 419.65 81.03 96.20 369.35 35.8 138.28 411.43 76.41 105.48 378.63 32.1 130.28 403.43 71.76 114.40 387.55 28.4 123.90 397.05 68.20 124.20 397.35 24.2 117.85 391.00 64.85 133.90 407.05 19.9 108.22 381.37 59.85 143.92 417.07 15.1 97.75 370.90 54.00 152.95 426.10 10.1 88.15 361.30 50.03 161.65 434.80 4.9 81.03 354.18 46.91 168.70 441.85 0 79.85 353.00 44.45 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 78.5 °C and $100\mathbf{x}_2$ = 46 (compil Note - The data relevant to the liquidus branch richer in component 2 were already published in Ref. 1.	$ \begin{array}{c} $
AUXTLTARY_T	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The liquidus was determined with a visual method, (details in Ref. 2), supplemented with DSC measurements. The enthalpy changes (not to be listed here) associated with various thermodynamic processes were measured with differential flux calorimetry (using a modified Tian-Calvet calorimeter).	Not stated. Component 1 undergoes a phase transition at $T_{trs}(1)/K=$ 418 (Ref. 1). Component 2 undergoes a phase transition at $T_{trs}(2)/K=$ 415 (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 0.05 K (compiler).
	REFERENCES:
	 Braghetti, M.; Berchiesi, G.; Franzosini, P. Ric. Sci. 1969, 39, 576-584. Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium iodide; KI; [7681-11-0] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	
168.7 441.9 0 160.0 433.2 6.06 168.2 441.4 0.32 160.0 433.2 6.24 167.5 440.7 0.85 158.5 431.7 7.02 167.0 440.2 1.06 157.2 430.4 8.01 166.5 439.7 1.61 157.6 430.8 8.82 165.9 439.1 1.94 159.7 432.9 8.96 165.9 439.1 2.05 165.5 438.7 9.19 165.5 438.7 2.33 171.3 444.5 9.49 165.3 438.5 2.46 172.6 445.8 9.64 164.7 437.9 2.86 190.8 464.0 10.72 163.7 436.9 3.60 212.0 485.2 11.99 163.6 436.8 3.61 240.6 513.8 14.03 161.6 434.8 5.00 276.7 549.9 16.78 161.3 434.5 5.10 298.3 571.5 18.98 ^a T/K values calculated by the compiler. Note 1 - In the original paper the results were shown in graphical form. The above 1isted numerical values represent a private communication by one of the authors (F., P.) to the compiler. Note 2 - The system could not be investi instability of the methanoate.	$rac{1}{250}$ 250 200 200 $rac{10}{200}$ $rac{10}{100x_2}$ $rac{20}{200}$ $rac{10}{100x_2}$ $rac{20}{10}$ $KCHO_2$ KI R
Characteristic point(s): Eutectic, E, at 156.	$3 {}^{\circ}C$ and $100 x_2 = 8.7$ (authors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP materials, dried by heating under vacuum.
NOTE:	
According to the authors, the trend of the liquidus branch richer in component 2 is close to ideal, and the formation of solid solutions in this region ought to be either insignificant, or at least contained within narrow limits.	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
	REFERENCES: (1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38, 116-118.

i
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium nitrite; KNO₂; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	ب [
168 441 0 223 496 55 163 436 5 253 526 60 155 428 10 278 551 65 147 420 15 305 578 70 135 408 20 330 603 75 130 403 25 353 626 80 119 392 30 376 649 85 114 387 35 399 672 90 137 410 40 420 693 95 169 442 45 436 709 100 199 472 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 107 °C and $100x_2= 33.5$ (autho Peritectic, P, at 143 °C and $100x_2= 44$ (autho Intermediate compound(s): K ₂ CHO ₂ NO ₂ (tentative composition; authors) 1	rs). rs).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. NOTE: Solid state transitions of component 1 should be three (occurring at 430, 408, and 333 K, respectively) according to Ref. 1, and only one (at 418+1 K) according to Table 1 of the Preface. Unfortunately, no	Component 1: commercial "chemically pure" material recrystallized from methanoic acid; it undergoes phase transitions at $t_{trs}(1)/^{o}C=$ 60, 135, 157 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fug}(2)/^{o}C=$ 436 after three recrystalliza tions; it undergoes a phase transition at $t_{trs}(2)/^{o}C=$ 45 (Ref. 2).
information from other sources is available. It can be noted, however, that, e.g., the trend of the liquidus branch richer in KCHO ₂ of the binary K/CHO_2 , NO ₃ studied by Berchiesi et al. (Ref. 3)	ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler).
supports Table 1 statement. Moreover, the existence (and composition) of the intermediate compound ought to be more convincingly proved.	 REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. (2) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. 1952, 21, 178-183. (3) Berchiesi, G.; Cingolani, A.; Leonesi, D. Z. Naturforsch. 1970, 25a, 1766-1767.

EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica,

Universita' di Pavia (ITALY).

COMPONENTS:

(1) Potassium methanoate (potassium formate) KCHO₂; [590-29-4] (2) Potassium nitrate; KNO3; [7757-79-1]

CRITICAL EVALUATION:

This system was studied first (Ref. 1) by Dmitrevskaya who, on the basis of her visual polythermal investigation, claimed the existence of the congruently melting intermediate compound K3(CHO2)2NO3, able to give eutectics with either component, at 423 K and 100x2= 32.5, and 419 K and $100x_2 = 44$, respectively.

Berchiesi et al. (Ref. 2) re-investigated the binary (employing again a visual method) as a side of the ternary K/CHO2, CNS, NO3, found and an incongruently melting intermediate compound [whose composition, argued from auxiliary DSC measurements, should be $K_5(CHO_2)_4NO_3$], a peritectic at 399.7 K and $100x_2 = 26.2$, and a eutectic at 387 K and $100x_2 = 37.9$.



The following considerations can help to evaluate the trustworthiness of these far different results.

Leonesi et al. (Ref. 3) performed cryometric measurements in molten KCHO₂, stating that the cryometric constant was K_1 = 11.5±0.1 K molality⁻¹ which corresponds to $\Delta_{fus}(1)H_m$ = 11.9 kJ mol⁻¹ (2.84+0.03 kcal mol⁻¹ in the original text). The latter value is, in turn, in satisfactory agreement with those subsequently determined with DSC by Braghetti et al. (11.8 kJ mol⁻¹; Ref. 4), and with Calvet microcalorimetry by Berchiesi and Laffitte (11.5±0.1 kJ mol⁻¹; Ref. 5).

In particular, Leonesi et al. (Ref. 3) found limiting values

 $[\lim (\Delta T/m_2)]/v = 11.5$, 11.55, and 11.4 K molality⁻¹ ^m2 →0

for KNO₃ (y = 1; y: number of cryometrically active foreign species), LiNO₃ (y = 2), and $CsNO_3$ (v = 2), respectively, which implies that a solubility of these solutes in KCHO₂ in the solid state should be either absent, or negligible. The three sets of $(\Delta T/\mathcal{P})$ vs. x_1 data from Ref. 3 (KNO₃: empty circles; LiNO₃: empty squares; CsNO₃: filled squares), which exhibit a satisfactory mutual consistency, are compared in the figure with the data taken in K/CHO_2 , NO_3 mixtures rich in component 1 by Berchiesi et al. (filled circles; Ref. 2), and by Dmitrevskaya (crosses; Ref. 1), respectively: it is apparent that the results from Ref. 1 are inconsistent with those from both Ref. 2 and Ref. 3.

Concerning solid state transformations of component 1, three transitions are quoted in Ref. 1 from Ref. 6 as occurring at 333, 408, and 430 K, respectively, whereas a single transition (at 418 ± 1 K) is listed in Table 1 of the Preface. Berchiesi et al. (Ref. 2) make no explicit reference to any transition, but an inspection of their liquidus branch richest in component 1 allows one to observe a single change of slope around 418 K, i.e., in correspondence with the value from Table 1.

In conclusion, in the evaluator's opinion the data by Berchiesi et al. (Ref. 2) are to be recommended, although a better knowledge of the solidus would be desirable.

- (1) Dmitrevskaya, 0.1.; Zh. Obshch. Khim. 1958, 28, 299-304 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 295-300.
- (2) Berchiesi, G.; Cingolani, A.; Leonesi, D. Z. Naturforsch. 1970, 25a, 1766-1767.
- (3) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P.
- Ric. Sci. <u>1968</u>, 38, 702-705. (4) Braghetti, M.; Berchiesi, G.; Franzosini, P.
- Ric. Sci. 1969, 39, 576-584. (5) Berchiesi, G.; Laffitte, M.; J. Chim. Fis. 1971, 877-881.
- (6) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

CONTROLLING .	OPTOTNAL MEASUPEMENTS.
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium nitrate; KNO₃; [7757-79-1] 	Dmitrevskaya, O.I. Zh. Obshch. Khim. <u>1958</u> , 28, 299-304 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u> , 28, 295-300.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
107 440 0 101 434 47.3 166 439 5 172 445 50 165 438 10 193 466 55 164 437 15 212 485 60 162 435 20 230 503 65 159 432 25 248 521 70 155 428 30 264 537 75 150 423 32.5 279 552 80 153 426 35 294 567 85 154 427 37.5 309 582 90 150.5 423.5 40 323 596 95 146 419 42 337 610 100 153 426 45 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , at 150 °C and 100x ₁ = 67.5 (authentic theory of the term of term	$ \begin{array}{c} $
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple.	"Chemically pure" materials, recrystallized and dried to constant mass. Component 1 undergoes phase transitions at $t_{trs}(1)/^{o}C=$ 60, 135, 157 (Ref. 1). Component 2 undergoes phase transitions at $t_{trs}(2)/^{o}C=$ 124, 316 (current literature).
	ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K
	<pre>(compiler). REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.</pre>

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium methanoate (potassium formate); KCHO₂; [590-29-4] Potassium nitrate; KNO₃; [7757-79-1] 	Berchiesi, G.; Cingolani, A.; Leonesi, D. Z. Naturforsch. <u>1970</u> , 25a, 1766-1767.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	ل (المعني ال
168.7 441.9 0 115.9 389.1 36.5 161.6 434.8 5.3 114.3 387.5 37.6 154.3 427.5 10.2 118.6 391.8 38.8 146.0 419.2 15.5 124.5 397.7 40.0 142.3 415.5 17.9 138.0 411.2 42.6 138.0 411.2 20.4 163.4 436.6 47.9 133.9 407.1 22.5 173.4 446.6 50.0 131.2 404.4 23.8 196.2 469.4 55.4 128.5 401.7 25.2 212.5 485.7 60.0 125.9 399.1 27.5 221.6 494.8 63.0 123.3 396.5 30.3 232.9 506.1 66.0 122.2 395.4 31.5 245.5 518.7 69.7 120.9 394.1 32.5 261.0 534.2 74.6 118.1 391.3 35.0 278.1 551.3 80.0 ^a T/K values calculated by the compiler. Note - Measurements at $t/^{\circ}C \ge 280$ could not be taken due to the thermal instability of the melts (authors). Characteristic point(s): Eutectic, E, at 114 °C and 100x2= 37.9 (author Peritectic, P, at 126.5 °C and 100x2= 26.2 Intermediate compound(s):	rs). (authors).
AllyTitAby	•
METHOD / APPARATIIS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS.
Visual method (for details, see Ref. 1) supplemented with DSC measurements.	C. Erba (Milan, Italy) materials dried before use.
	ESTIMATED ERROR: Temperature: accuracy probably <u>+0.1 K</u> (compiler). REFERENCES: (1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38 , 116-118.

						ORTGINAL MEASUREMENTS:
COMPONENTS:						
(1) Potassium ethanoate (potassium acetate); KCoHoOo: [127-08-2]			issium a	acetate);	Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1397-1404.	
(2) Pa	otassiu	propano	ate (pot	assium		
propionate); KC ₂ H ₅ O ₂ ; [327-62-8]						
VARIA	BLES:					PREPARED BY:
Temper	rature.					Baldini, P.
[
EXPERI	IMENTAL	VALUES:				
t/°C	t/K ^a	100 x 2	t/°C	T/K ^a	100 x 2	
301	574	0	342	615	55	U .
310	583	5	346	619	60	+
311	584	10	348	621	65 70	مع المع
312	500	20	356	629	70	350 - 20
320	593	25	358	631	80	
322	595	30	362	635	85	~ ²⁷
328	601	35	364	637	90	کړ
331	604	40	365	638	95	330
334	607	45	365	638	100	6
339	612	50				and a second sec
a T/K	values	calculat	ed by th	ne compi	ller.	000
Chara	standati	la potetí	-) •			3000
Charac	cleristi	te porne(5).			
Contin	nuous se	eries of	solid so	lutions	8.	
1						0 50 $100x_2$ 100
1						KC ₂ H ₃ O ₂ KC ₃ H ₅ O ₂
]						
				A1	IXILIARY I	NFORMATION
			PDUDE			
MEIHOI	J/APPARA	109/PKUC	EDOKE:			SOURCE AND PURITY OF MATERIALS:
Visual	l polyth	nermal an	alysis.			Company 1. "about colly pure" estants1
						Component 1: cnemically pure material. Component 2: prepared from commercial
NOTE:						propanoic acid (distilled before use) and
The d	occurrer	nce of a	continue	us sei	cies of	chemically pure potassium carbonate; the recovered solid was recrystallized from n-
solid	solut	ions in	this	binary	seems	butanol; it undergoes a phase transition at
likely	y .			•		$t_{rm}(2)/^{\circ}C= 330$ (Ref. 1).
The f	fusion t	emperatu	res of t	oth cor	ponents	
[T _{fus} ((1)= 574	K, and	T _{f.v.} (2).	• 638 K	are in	
reason	nable ag	greement	with the	corre	sponding	1
data	listed	l in	Preface,	Tal	ble l	
(578.7	/+0.5 K	-	and _	638.3	э <u>+</u> 0.5 к,	ESTIMATED ERROR:
respec	ctively)	Conv	ersely,	there	is no	
correspondence between the solid state			80110	1 State	Temperature: accuracy probably $\frac{1}{2}$ K	
quoted	1 from	Ref. 1	(603 K)	and i	that of	(combrtcr).
Table 1 (352.5 <u>+</u> 0.5 K). It is, however, to			, howe	ever, to	REFERENCES:	
be noted that in other papers by the same		ne same	(1) Sokolov N M			
group (see, e.g., Ket. 2) a transition of component 2 - ignored here - is quoted from			is quei	ted from	Tezisy Dokl. Y Nauch, Konf. S.W.T. 1956	
the same Ref. 1 as occurring at 341 K.			at 341	K.	(2) Sokolov, N.M.; Tsindrik, N.M.	
					Zh. Neorg. Khim. 1969, 14, 584-590 (*);	
			Russ. J. Inorg. Chem. (Engl. Transl.)			
					1969, 14, 302-306.	

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Franzosini, P.,
KC ₂ H ₃ O ₂ ; [127-08-2] Potassium butanoate (potassium butyrate);	Dipartimento di Chimica Fisica,
KC ₄ H ₇ O ₂ ; [589-39-9]	Universita´ di Pavia (ITALY).

The visual polythermal analysis was employed by Sokolov and Pochtakova (Ref. 1) to study the lower boundary of the isotropic liquid field. According to these authors, an intermediate compound of presumable composition $K_7C_2H_3O_2(C_4H_7O_2)_6$ ought to form, and two invariants, i.e., a eutectic, E [at 546 K (273 °C), and $100x_1=35.5$], and a "perekhodnaya tochka", P [at 623 K (350 °C), and $100x_1=20.5$], ought to exist.

Component 2, however, forms liquid crystals, which causes the statements about the composition of the intermediate compound and the occurrence of the invariant P to become inconsistent, as explained below. Sokolov and Pochtakova's fusion temperature [677 K (404 $^{\circ}$ C)], and solid state transition at 618 K (345 $^{\circ}$ C; quoted from Ref. 2) should be identified with the clearing and fusion temperatures of component 2, respectively.



More recently, Prisyazhnyi et al. (Ref. 3) - to whom Ref. 1 seems to be unknown - carried out a derivatographical re-investigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Their clearing $[T_{clr}(2)=626 \text{ K}(403\ ^{\circ}\text{C})]$ and fusion $[T_{fus}(1)=575\ \text{ K}(302\ ^{\circ}\text{C});$ $T_{fus}(2)=623\ \text{ K}(350\ ^{\circ}\text{C})]$ temperatures substantially agree with the corresponding values from Table 1 of the Preface $(677.3\pm0.5;\ 578.7\pm0.5,\ and\ 626.1\pm0.7\ \text{K},\ respectively).$ Prisyazhnyi et al.'s, and Sokolov and Pochtakova's results (filled and empty circles, respectively) are compared in the figure (LL: isotropic liquid; LC: liquid crystals), an inspection of which allows one to remark that: (i) the correct composition of the intermediate compound ought to be $K_5(C_2H_3O_2)_2(C_4H_7O_2)_3$ (Ref. 3) and not $K_7C_2H_3O_2(C_4H_7O_2)_6$ (Ref. 1); (ii) point P mentioned in Ref. 1 cannot be an invariant, but corresponds merely to an inflection (on the origin of which, however, no sure explanation can be offered by the evaluator) of the pertinent curve; and (iii) hesides the eutectic, E, two more invariants exist, i.e., an H_E point, and an M' point. The abscissa of the latter being known only approximately, it can be hardly decided if this M' point is actually of the M'_E or of the M'_P type: in the former case, the complete phase diagram should be similar to Scheme D.1 of the Preface; in the latter case, to Scheme D.3.

The two-phase region pertinent to the liquid crystal - isotropic liquid equilibria might be so narrow as to have prevented Prisyazhnyi et al. to observe two distinct sets of points in this region, whereas the lack of information about eutectic fusion in the different samples submitted to derivatographical analysis remains rather surprising.

Finally, the following two points require attention.

(i) In Ref. 1 solid state transitions of component 1 are quoted from Ref. 2 as occurring at 428 and 331 K (155 and 58 °C, respectively), whereas mention is made in Preface (Table 1) of a single transition at 422.2 ± 0.5 K.

(ii) Again in Ref. 1 (and from the same source), two more transformation temperatures, i.e., 558 and 463 K, respectively, are quoted for component 2 which lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 K, and 467.2 ± 0.5 and 461.4 ± 1.0 K, respectively) also reported in Table 1 of the Preface.

REFERENCES:

(1) Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. <u>1960</u>, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1960</u>, 30, 1429-1433.

- (2) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.; Zh. Neorg. Khim. <u>1983</u>, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1983</u>, 28, 140-141 (*).

	I
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] (2) Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9] 	Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1429-1433.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
$t^{O}C T/K^{a} 100x_{1} t^{O}C T/K^{a} 100x_{1}$	$\frac{1}{2}$
404 677 0 321 594 45 386 659 10 319 592 50 377 650 15 311 584 60 355 628 20 288 561 77.5 350 623 20.5 278 551 82.5 347 620 22.5 273 546 85.5 344 617 25 278 551 87.5 338 611 30 284 557 90 326 599 40 301 574 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 273 °C and $100x_1 = 85.5$ (authors). Intermediate compound(s): $K_7C_2H_3O_2(C_4H_7O_2)_6$ (presumable composition; au	$\int_{380}^{380} \int_{}^{0} P^{0} + \frac{1}{50} \int_{100x_{1}}^{0} \frac{1}{100} + \frac{1}{50} \int_{100x_{1}}^{0} \frac{1}{100}$
AUXILIARY 1	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: "chemically pure" material recrystallized; it undergoes phase transitions at $t_{trs}(1)/^{\circ}C=58$, 155 (Ref. 1). Component 2: prepared by reacting KHCO ₃ with n-butanoic acid, and recrystallized from n-butanol (Ref. 2, where, however, carbonate instead of hydrogen carbonate was employed; compiler); it undergoes phase transitions at $t_{trs}(2)/^{\circ}C=190$, 285, 345 (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9] 	Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).
VARIABLES:	PREPARED BY:
Temperature.	Baldiní, P.
EXPERIMENTAL VALUES:	· ·
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).	370
Characteristic point(s):	
Invariant point, M'_E , at about 310 °C and 100x ₁ about 25 (compiler). Eutectic, E, at about 273 °C and 100x ₁ about 85 (compiler). Invariant point, M', at about 323 °C and 100x ₁ about 40 (compiler).	290 - M'
Intermediate compound(s):	¥
$K_5(C_2H_3O_2)_2(C_4H_7O_2)_3$, melting at about 323 °C (compiler).	0 50 100×, 100 KC ₄ H ₇ O ₂ KC ₂ H ₃ O ₂
AUXILIARY I	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of $6-8$ K min ⁻¹ , and using Al ₂ O ₃ as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase.	Not stated. Component 1: $t_{fus}(1)/{}^{o}C$ about 302 (compiler). Component 2: $t_{fus}(2)/{}^{o}C$ about 350; $t_{clr}(2)/{}^{o}C$ about 403 (compiler).
	ESTIMATED ERROR:
	Temperature: accuracy not evaluable (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium iso.butanoate (potassium iso.butyrate); Ki-C₄H₇O₂; [19455-20-0] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This system was studied only by Sokolov and Pochtakova (Ref. 1) who claimed the existence of: (i) a eutectic, E_1 , at 564 K (291 °C) and $100x_1 = 86.5$; (ii) a eutectic, E_2 , at 567 K (294 °C) and $100x_1 = 32$; and (iii) an intermediate compound, $K_5(C_2H_3O_2)_3(i.C_4H_7O_2)_2$, congruently melting at 578 K (305 °C).

Component 2, however, forms liquid crystals. Therefore the temperature of 633 K (360 $^{\text{O}}$ C) given in Ref. 1 should be identified with the clearing (and not the fusion) temperature of this component, and compared with the $T_{clr}(2)$ value (625.6+0.8 K) reported in Preface, Table 2.

For the same component, three more phase transition temperatures are quoted in Ref. 1 from Ref. 2, i.e., 621, 546, and 481 K, the second of which can be reasonably identified with the fusion temperature $[T_{fus}(2)=553.9\pm0.5$ K] listed in Table 2 of the Preface. Consequently: (i) the transition temperature at 621 K (if actually existing) might correspond to some kind of transformation (undetected by DSC, see Table 2) within the liquid crystal field; and (ii) only the transition at 481 K should correspond to a solid state transformation, although the latter figure is almost 60 K higher than the single $T_{trs}(2)$ value (424±3 K) listed in Preface, Table 2.

The fusion temperature of component 1, $T_{fus}(1) = 574$ K (301 °C; Ref. 1), and the transition temperature [428 K (155 °C; quoted in Ref. 1 from Ref. 2)] satisfactorily correspond with the values listed in Table 1 of the Preface (578.7+0.5 K, and 422.2+0.5 K, respectively), whereas the other solid-solid transition quoted by the authors from Ref. 2 as occurring at 331 K (58 °C) has no correspondence in Table 1.

In conclusion, the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface. Accordingly, the eutectic E_2 should actually be an M_E point. The existence of the intermediate compound $K_5(C_2H_3O_2)_3(i\cdot C_4H_7O_2)_2$ seems reasonably supported by the available data.

- (1) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.



COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita [°] di Pavia (ITALY).

This system was studied only by Pochtakova (Ref. 1) who claimed the existence of: (i) a eutectic point at 553 K (280 $^{\circ}$ C) and $100x_2$ = 12.5; (ii) a "perekhodnaya tochka" (likely a peritectic) at 607 K (334 $^{\circ}$ C) and $100x_2$ = 52.5; and (iii) an incongruently melting intermediate compound, $K_5(C_2H_3O_2)_2(C_5H_9O_2)_3$.

Component 2, however, forms liquid crystals. Therefore, Pochtakova's fusion temperature, $T_{fus}(2)=717$ K (444 °C), should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being 716+2 K. The phase transition quoted by the author from Ref. 2 as occurring in the same component at 580 K (307 °C; Ref. 2) can be reasonably identified with the actual fusion temperature, the value from Preface, Table 1 being $T_{fus}(2)=586.6+0.7$ K. No mention is made of further transformations, although Table 1 reports a solid state transition at 399.5+0.9 K.

Among the phase transition temperatures mentioned by Pochtakova for component 1, the fusion at 575 K (302 $^{\circ}$ C; Ref. 1), and the solid state transition at 428 K (155 $^{\circ}$ C; quoted from Ref. 2), can be satisfactorily identified with the corresponding values of Table 1 of the Preface, viz., 578.7+0.5 K and 422.2+0.5 K, respectively. On the contrary, the lower solid-solid transition quoted from Ref. 2 as occurring at 331 K (58 $^{\circ}$ C) has no correspondence in Table 1.

In conclusion, it can be asserted that in Pochtakova's phase diagram the branch whose ends are $T_{clr}(2)$ and point P is relevant to isotropic liquid - liquid crystal equilibria, whereas it is hard to decide, on the basis of the available data, whether or not an intermediate compound is formed.

The existence of the intermediate compound might be argued from analogy with the topology of the binary potassium ethanoate -potassium iso.butanoate (Ref. 3) where evidence was obtained for the formation of a 3:2 compound. Accordingly, the phase diagram might be similar to Scheme D.3 of the Preface with an M_p point at about 588 K (315 °C) and 100x₂ about 40. In this case, Pochtakova's P point should be a mere inflection in the relevant branch.

Conversely, if the existence of the compound is not accepted, the phase diagram might be interpreted with reference to Scheme B.2.

- (1) Pochtakova, E.I. Zh. Obshch. Khim. 1966, 36, 3-8.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437.



COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08- 2] Potassium iso.pentanoate (potassium iso.valerate); Ki.c₅H₉O₂; [589-46-8] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita [°] di Pavia (ITALY).

This system was studied only by Pochtakova (Ref. 1), who claimed the existence of: (i) a eutectic, E, at 542 K (269 $^{\circ}$ C) and $100x_2$ = 50; (ii) a peritectic, P, at 543 K (270 $^{\circ}$ C) and $100x_2$ = 18.5; and (iii) an incongruently melting compound, of probable composition $K_8(C_2H_3O_2)_7i.C_5H_9O_2$.

Component 2, however, forms liquid crystals. Therefore the fusion temperature, $T_{fus}(2) = 669$ K (396 °C) reported by the author should be identified with the clearing temperature, the corresponding value from Preface, Table 2 being 679+2 K. No mention is made by the author of the actual fusion which occurs at 531+3 K according to Table 2: the latter figure is supported by the trend of the thermomagnetical curves plotted by Duruz and Ubbelohde (Ref. 2).

As for the other phase transitions quoted by Pochtakova from Ref. 3 at 327 and 618 K (54 and 345 °C, respectively), no identification is possible with the findings by other investigators, inasmuch as: (i) no transformation is reported in Table 2 as occurring below $T_{fug}(2)$ = 531+3 K; and (ii) no transformation is reported in Table 2 or in Ref. 2 as occurring within the field of existence of the mesomorphic liquid. It is a bit puzzling the fact that for potassium iso-pentanoate Dmitrevskaya and Sokolov (Ref. 4) quote from Ref. 3 (unavailable to the evaluator) transitions at 618, 493, and 473 K (ignoring that quoted by Pochtakova at 327 K), and Pochtakova quotes from the same source transitions at 618 and 327 K (ignoring those quoted by Dmitrevskaya and Sokolov at 493 and 473 K).

Component 1, as quoted in Ref. 1 from Ref. 3, undergoes phase transitions at 331 and 428 K (58 and 155 $^{\circ}$ C, respectively), the latter figure being in reasonable agreement with the T[']_{trs} value (422.2<u>+</u>0.5 K) from Table 1 of the Preface.

The available data do not seem sufficient to prove unambiguously the existence of any intermediate compound. Should it exist, the phase relations at $50 \leq 100x_2 \leq 100$ could be reasonably interpreted with reference to Scheme D.1: Pochtakova's eutectic could be actually an M'_E point, and a further invariant of the M_E type should exist.

- (1) Pochtakova, E.I. Zh. Obshch. Khim. <u>1963</u>, 33, 342-347.
- (2) Duruz, J.J.; Ubbelohde, A.R. Proc. Roy. Soc. London 1975, A 342, 39-49.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. <u>1967</u>, 37, 2160-2166; Russ. J. Gen. Chem. (Engl. Transl.) <u>1967</u>, 37, 2050-2054.



COMPONENTS:	EVALUATOR:		
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium hexanoate (potassium caproate); KC₆H₁₁O₂; [19455-00-6] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).		
CRITICAL EVALUATION:			
This system was studied only by Pochtakova (R a eutectic, E, at 560 K (287 °C), and $100x_2$ = a peritectic) at 592 K (319 °C) and $100x_2$ = intermediate compound, $K_5(C_2H_3O_2)_3(C_6H_{11}O_2)_2$.	ef. 1) who suggested the existence of: (i) 11.0; (ii) a "perekhodnaya tochka" (likely 39.0; and (iii) an incongruently melting		
Component 2, however, forms liquid crystals. Therefore the fusion temperature, $T_{fus}(2) = 717.7 \text{ K}$ (444.5 °C; Ref. 1), should be identified with the clearing temperature, the corresponding value from Preface, Table 1 being 725.8±0.8 K. For the same component, the phase transition quoted in Ref. 1 from Ref. 2 as occurring at 575 K (302 °C) can be identified with the actual fusion temperature, $T_{fus}(2) = 581.7\pm0.5 \text{ K}$ (Preface, Table 1).			
Concerning component 1, fusion occurs at transitions occur at 428 K (155 ^O C; Ref. 2), two values, however, find a direct identif Preface, i.e., 578.7 <u>+</u> 0.5 K and 422.2 <u>+</u> 0.5 K, r	574 K (301 ^O C; Ref. 1), and solid state and 331 K (58 ^O C; Ref. 2). Only the former ication with data listed in Table 1 of the respectively.		
In conclusion, it can be asserted that in Pochtakova's phase diagram the branch whose ends are T _{clr} (2) and point P is relevant to isotropic liquid - liquid crystal equilibria, whereas it is hard to decide, on the basis of the available data, whether or not an intermediate compound is formed.			
The existence of the intermediate compound might be argued from analogy with the topology of the binary potassium ethanoate -potassium iso.butanoate (Ref. 3) where evidence was obtained for the formation of a 3:2 compound. Accordingly, the phase diagram might be similar to Scheme D.3 of the Preface. In this case, Pochtakova's P point should be a mere inflection in the relevant branch.			
Conversely, if the existence of the compound is not accepted, the phase diagram might be interpreted with reference to Scheme B.2.			
REFERENCES:			
 (1) Pochtakova, E.I. Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1959, 29, 3149-3154. 			
(2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .			
 (3) Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437. 			



OPTOTNAL WEAGUDEWENTS.
URIGINAL MEASOREMENTS: Il'yasov, I.I.; Bergman, A.G. Zh. Obshch. Khim. <u>1960</u> , 30, 355-358.
PREPARED BY: Baldini, P.
J [
$KC_2H_3O_2$
NFORMATION
SOURCE AND PURITY OF MATERIALS:
Not stated.
ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES: (1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. <u>1968</u> , 38 , 127-132.



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COMPONENTS:	EVALUATOR
(1) Potassium ethanoate (potassium acetate);	Spinolo, G.,
$KC_{2H_{3}O_{2}}; [127-08-2]$	Dipartimento di Chimica Fisica,
(2) Potassium thiocyanate;	Universita' di Pavia (ITALY).
KCNS; [333-20-0]	

The binary $K/C_2H_3O_2$, CNS was studied by Golubeva et al. (Ref. 1), and by Sokolov (Ref. 2). In both papers, the visual polythermal analysis was employed to draw the lower boundary of the isotropic liquid field.

Concerning the thermal behavior of component 1, it can be noted that a reasonable agreement exists: (i) between the fusion temperatures from Refs. 1, 2, and that listed in Table 1 of the Preface (578.7+0.5 K); and (ii) between Sokolov's (Ref. 2) higher transition temperature (428 K), and the single $T_{trs}(1)$ value (422.2+0.5 K) from Table 1. No correspondence with Table 1 can be found for Sokolov's lower transition (331 K). No solid state transformation of this component is mentioned in Ref. 1.

The main features of the phase diagram given in either source exhibit rather close similarities, as shown here:

	Ref. 1	Ref. 2
T _{fus} (1)/K:	579	575
T _{fus} (2)/K:	449	450
Intermediate compound	K3C2H3O2(CNS)2	к ₃ с ₂ н ₃ 0 ₂ (смз) ₂
Eutectic E_1 ; T/K:	405	410-412
Eutectic E_1 ; 100 \mathbf{x}_1 :	42.5	39
Eutectic E_2 ; T/K:	403	408
Eutectic E_2 ; 100 \mathbf{x}_1 :	27	22.5

It is, however, to be stressed that Sokolov's graphical presentation of the diagram is somewhat conflicting with the few numerical data reported in the text. Accordingly, the evaluator is inclined to prefer the values listed under the heading "Ref. 1", although regretting that no tabulation of the experimental points is supplied by the authors.

- (1) Golubeva, M.S.; Aleshkina, N.N.; Bergman, A.G.
 Zh. Neorg. Khim. 1959, 4, 2606-2610; Russ. J. Inorg. Chem. (Engl. Transl.) 1959, 4, 1201-1203 (*).
- (2) Sokolov, N.M.
 Zh. Obshch. Khim. 1966, 36, 577-582.

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COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium thiocyanate; KCNS; [333-20-0] 	Golubeva, M.S.; Aleshkina, N.N.; Bergman, A.G. Zh. Neorg. Khim. <u>1959</u> , 4, 2606-2610; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1959</u> , 4, 1201-1203 (*).			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
	<u> </u>			
EXPERIMENTAL VALUES:	·			
Characteristic point(s):	$ \begin{array}{c} $			
Eutectic, E_1 , at 132 °C and 100 x_1 = 42.5				
(authors). Eutectic, E_2 , at 130 °C and $100x_1 \approx 27$ (authors).				
Intermediate compound(s):				
$K_{3}C_{2}H_{3}O_{2}(CNS)_{2}$ congruently melting at 134 ^o C	(authors).			
AUXILIARI				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual observation of fusion of the salt mixtures contained in a glass tube sur- rounded by a wider tube to secure a more uniform heating. Temperatures measured with a Chromel-Alumel thermocouple.	Materials of analytical purity recrystal- lized twice.			
	ESTIMATED ERROR:			
	compiler).			
	REFERENCES:			



COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] (2) Potassium iodide KI; [7681-11-0] 	Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. <u>1958</u> , No. 3, 413-416.
	DREDARED DV.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	·
$t/^{\circ}C$ T/K^{a} $100x_{1}$	
310.5 583.5 100 305 578 97.0 296 569 94.9 295 568 93.3 293 566 90.0 290 563 87.2 287 560 86.0 286 559 85.0 282 555 83.5 277 550 82.0 282 555 81.3 314 587 76.4 350 623 70.8 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 277 °C and $100x_1 = 82.0$.	280 50 KI KI KC ₂ H ₃ O ₂
	NEODMATTON
	SOURCE AND PURITY OF MATERIALS.
Vigual polythermal applying	Not stored
NOTE.	Component 1 undergoes a phase transition at
The system was investigated at $100 \ge 100 \mathbf{x}_1 \ge 70.8$. See also the Note relevant to the results obtained by Piantoni et al. (Ref. 1) on the same system (next Table).	t _{trs} (1)/°C= 296. Component 2 melts at t _{fus} (2)/ ^o C= 683.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	<pre>(1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. <u>1968</u>, 38, 127-132.</pre>
I <u></u> _	1.



COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Spinolo, G.,
KC ₂ H ₃ O ₂ ; [127-08-2] Potassum nitrite;	Dipartimento di Chimica Fisica,
KNO ₂ ; [7758-09-0]	Universita [°] di Pavia (ITALY).

This binary was studied by Bergman and Evdokimova (Ref. 1), and by Sokolov and Minich (Ref. 2): in both papers, the visual polythermal analysis was employed to draw the lower boundary of the isotropic liquid field.

Concerning the thermal behavior of component 1, it can be noted that a reasonable agreement exists: (i) between the fusion temperature (575 K) from Refs. 1, 2, and that listed in Table 1 of the Preface (578.7 \pm 0.5 K); and (ii) between Sokolov and Minich's (Ref. 2) higher transition temperature (428 K), and the single $T_{trs}(1)$ value (422.2 \pm 0.5 K) from Table 1. No correspondence with Table 1 can be found for Sokolov and Minich's lower transition (331 K). No solid state transformation of this component is mentioned in Ref. 1.

The experimental points from both papers exhibit rather similar trends; a discrepancy, however, exists about interpretation of the results. Indeed, in Sokolov and Minich's opinion (Ref. 2), the system ought to be characterized by a eutectic and a peritectic, and accordingly by the presence of an incongruently melting intermediate compound. Conversely, in Bergman and Evdokimova's opinion (Ref. 1), the system shows a single invariant, i.e., a eutectic at 573 K and $100x_2 = 50$. It is worth mentioning that, in the evaluator's opinion, the existence of a third (intermediate) branch of the liquidus - if any - might be supported rather by the experimental data from Ref. 1 than by those from Ref. 2. Moreover, the composition of the intermediate compound suggested in Ref. 2 is not compatible with Sokolov and Minich's experimental values.

In conlusion, the evaluator is inclined to think that the actual existence of an intermediate compound is poorly supported by the available data, and therefore to prefer the picture of the system drawn in Ref. 1.

- (1) Bergman, A.G.; Evdokimova, K.A.
 Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
- (2) Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassum nitrite; KNO₂; [7758-09-0] 	Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.		
VARIABLES:	PREPARED BY:		
Temperature	Baldini, P.		
EXPERIMENTAL VALUES:			
$t/^{o}C$ T/K^{a} $100x_{2}$ 302 575 0 294 567 4.0 288 561 8.4 278 551 13.0			
273 546 17.8 264 537 22.6 258 531 27.3	da d		
240 513 36.1 227 500 40.3			
218 491 44.3 208 481 47 9	230 - 230 -		
206 479 51.2	كر		
206 ⁵ 479 54.4 208 ^b 481 57.3	da		
252 525 60.1 264 537 62 5	E		
282 555 65.8	0 40 100×2 80		
300 573 70.0	KC2H302 KNO2		
 ^a T/K values calculated by the compiler. ^b Point not considered in Fig. 2 of the original paper in order to draw the fusibility curve (compiler) 			
Characteristic point(s): Eutectic, E, at 200 ^o C and 100 x₂= 50 (authors).		
Note - The system was investigated at $0 \leq 10$	$0x_2 \leq 70.$		
AUXILIARY I	NFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal analysis: the tempe- ratures of initial crystallization were measured with a Nichrome-Constantane ther- mocouple and a 17 mV full-scale milli- voltmeter.	Source not stated. Component 2: t _{fus} (2)/ ^o C= 440.		
	ESTIMATED ERROR:		
	Temperature: accuracy probably +2 K (compiler).		
	REFERENCES:		
	1		

COMPONENTS:		ORTGINAL MEASUREMENTS:
 Potassium ethanoate (po KC₂H₃O₂; [127-08-2] Potassium nitrite; KNO₂; [7758-09-0] 	tassium acetate);	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.
VARIABLES:		PREPARED BY:
Temperature.		Baldini, P.
EXPERIMENTAL VALUES:		
t/°C T/K ^a $100x_2$ t/° 302 575 0 222 295 568 5 244 287 560 10 27 276 549 15 292 265 538 20 311 252 525 25 33 245 518 30 360 233 506 35 38 220 493 40 400 208 481 45 430 210 483 50 ^a T/K values calculated by f Characteristic point(s): Eutectic, E, at 208 °C and Peritectic, P, at 210 °C and Note - The assignement of i.e., E at 210 °C and 100x compatible with the experiment Intermediate compound(s): $K_2C_2H_3O_2NO_2$ (tentative compo- sition by the authors is point of the site of	OC T/K ^a 100 x_2 1 494 55 5 518 60 1 544 65 2 565 70 5 588 75 9 612 80 0 633 85 1 654 90 3 681 95 5 709 100 the compiler. 100 x_2 = 45 (compil 1 100 x_2 = 52 (compil the invariants as 2 45, and P at 2 ental values (comp position; authors) not compatible wit	er). $KC_{2H_{3}O_{2}}$ reported in Table 2 of the original paper, $R = 100 \text{ m}_{2} = 52$, is nonsensical and not iler). incongruently melting (the tentative component of the invariants;
	AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.		Component 1: commercial "chemically pure" material recrystallized from water; it undergoes phase transitions at $t_{trs}(1)^{O}C= 58$, 155 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)^{O}C= 436$ after three recrystalliza tions; it undergoes a phase transition at $t_{trs}(2)^{O}C= 45$ (Ref. 2).
		ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler).
		REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> . (2) Berul ⁻ , S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.

COMPONENTS:	EVALUATOR:
 Potassium ethanoate (potassium acetate);	Spinolo, G.,
KC ₂ H ₃ O ₂ ; [127-08-2] Potassium nitrate;	Dipartimento di Chimica Fisica,
KNO ₃ ; [7757-79-1]	Universita' di Pavia (ITALY).

This binary was studied by Bergman and Evdokimova (Ref. 1), Diogenov et (Ref. 2), Gimel'shtein (Ref. 3), a1. and Diogenov and Chumakova (Ref. 4). In Ref. 3, the automatic record of the heating curves with a DTA device allowed the author to gain a complete picture of the phase diagram in the superambient region, whereas in Refs. 1, 2, and 4 the visual polythermal analysis was employed to draw merely the lower boundary of the isotropic liquid field.

Concerning component 1, the fusion temperatures from Refs. 1-4 (575, 583, 586, and 575 K, respectively) fluctuate (rather widely) around the $T_{fus}(1)$ value (578.7+0.5 K) listed in Preface, Table 1. Moreover, a reasonable agreement exists between the (single) solid state transition temperature reported in Ref. 3 and Table 1 (428 K and 422.2+0.5 K, respectively), whereas, in the evaluator's opinion, poor reliability is to be attached to Diogenov et al.'s (Ref. 2) assertion that a transition occurs at 565 K, because no support to it is provided by the findings of any author foreign to Diogenov's group (Ref. 5).



The main features of the phase diagram reported in Refs. 1-4 appear to be rather similar, so that the following points can be taken as unambiguously stated: (i) a 1:1 intermediate compound is formed; (ii) it melts congruently, and, accordingly, two eutectics separate its crystallization branches from those relevant to the pure components; and (iii) a fair agreement exists among the coordinates of the invariants provided by Refs. 1, 3, and 4 (see below), whereas the temperature values from Ref. 2 appear to be systematically too low.

	Ref. 1	Ref. 2	Ref. 3	Ref. 4
Eutectic E ₁ ; T/K:	507	493	507	507
Eutectic E ₁ ; 100x ₂	: 36	39	35.5	35
Eutectic E ₂ ; T/K:	495	485	497	497
Eutectic E ₂ ; 100x ₂	: 61.5	61	62.5	62
Int. comp.; T _{fus} 7	K: 511	502	511	511

A direct comparison of the visual polythermal (empty circles) and derivatographical (filled circles) data from Refs. 1 and 3, respectively, is made in the figure.

- Bergman, A.G.; Evdokimova, K.A.; Iz. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
- (2) Diogenov, G.G.; Nurminskii, N.N.; Gimel'shtein, V.G.; Zh. Neorg. Khim. 1957, 2, 1596-1600 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1957, 2(7), 237-245.
 (3) Gimel'shtein, V.G.; Tr. Irkutsk. Politekh. Inst. 1971, No. 66, 80-100.
- (4) Diogenov, G.G.; Chumakova, V.P.
- Fiz.-Khim. Issled. Rasplavov Solei, Irkutsk, 1975, 7-12.
 (5) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

COMPON	ENTC.					OPTCINAL MEASUREMENTS.
COMPONENTS:				ORIGINAL MERSOREMENTS.		
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium nitrate; KNO₃; [7757-79-1] 			ium ac	Bergman, A.G.; Evdokimova, K.A. Iz. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.		
			<u></u>			
VARIAE	LES:					PREPARED BY:
Temper	ature.					Baldini, P.
EXPERI	MENTAL	VALUES:			<u> </u>	
t/°C	T/K ^a	100 x 2	т/ ^о с	т/к ^а	100 x 2	
302	575	0	233	506	52.7	÷
298	571	2.0	227	500	58.5	ор 316 С 316
294	567	4.0	232	505	64.2	3009
292	565	6.4	246	519	68.5 72 0	
282	555	9.0 11.7	200	545	76.0	
278	551	14.6	285	558	80.7	\mathbf{S}
272	545	17.5	295	568	83.9	
267	540	20.5	304	577	87.5	
262	535	23.5	310	583	89.1	
254	527	26.5	313 21.9b	586	90.2	<u> </u>
240	514	32.8	326C	591	94.8	E ₁
235	508	36.1	329d	602	97.0	E ₂
235	508	39.8	335	608	98.8	
236	509	43.6	337	610	100	
238	511	48.0				
a T/K values calculated by the compiler. b Erroneously reported as 218 in table 5 of the original paper (compiler). c Erroneously reported as 226 in table 5 of the original paper (compiler). d Erroneously reported as 229 in table 5 of the original paper (compiler).						
Characteristic point(s):						
Eutectic, E_1 , at 234 °C and $100x_1 = 64$ (authors). Eutectic, E_2 , at 222 °C and $100x_2 = 61.5$ (authors).						
Intermediate compound(a):						
~2 ^C 2 ^H 2	^{02^{NO}3,}	congruent	ty meitir	ig at 2	.38 °C (3	autnors).
1						
AUXILIARY INFORMATION			NFORMATION			
METHOD)/APPARA	ATUS/PROCE	DURE:	,		SOURCE AND PURITY OF MATERIALS:
Visual	L po	lythermal	analy	vsis:	the	Source not stated. Component 2: in the
temper	atures	of init	ial cry	vstalli	zation	temperature field of interest it undergoes
were	measure	ed with a	Nichrome	-Const	antane	a phase transition at $t_{trs}(2)/^{\circ}C=316-318$
thermo	couple	and a	i/ mV	full	-scale	(Ket. 1).
L	OITEC	31. •				REFERENCES:
ESTIM	TED ERI	ROR:				
					1	(1) Bergman, A.G.; Berul', S.I.
Temperature: accuracy probably <u>+2</u> K (compiler).			<u>+2</u> K		1zv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.	



COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium nitrate; KNO₃; [7757-79-1] 	Gimel ⁻ shtein, V.G. Tr. Irkutsk. Politekh. Inst. <u>1971</u> , No. 66, 80-100.			
VARIABLES:	PREPARED BY:			
Temperature	Baldini, P.			
EXPERIMENTAL VALUES:				
$t^{o}C T/K^{a} 100x_{2} t^{o}C T/K^{a} 100x_{2}$				
312 585 0 132 405 55.0				
155 428 0 245 518 70.0				
276 549 15.0 225 498 70.0				
153 426 15 0 200 563 95 0				
238 511 35.0 227 500 85.0				
155 428 35.0 132 405 85.0				
240 513 45.0 338 611 100				
235 508 55.0 130 403 100				
223 490 23.0				
^a T /K values calculated by the compiler.				
Characteristic point(s):				
Eutectic, E_1 , at 234 °C and 100 x_2 = 35.5				
(author).				
(author). 12^{-10} , and $10x_2 = 62.5$				
Intermediate compound(s):				
$K_2C_2H_3O_2NO_3$, congruently melting at 238 °C				
(author).				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Differential thermal analysis (using a	Not stated.			
derivatograph with automatic recording of the heating curves) was employed.	Component 1 melts at $t_{fus}(1)/{}^{\circ}C=312$ (310 ${}^{\circ}C$ according to Fig. 13 of the			
NOTE.	original paper; compiler), and undergoes a			
	phase transition at $t_{trs}(1)/C = 155$. Component 2 melts at $t_{e}(2)/C = 338$			
The meaning of the data listed in the table	(337 °C according to Fig. 13 of the			
becomes apparent by observing the figure	original paper; compiler), and undergoes a			
reported in the critical evaluation.	phase transition at $t_{trs}(2)/{}^{o}C \approx 130$.			
ine coordinates of the characteristic				
hasis of his own DTA measurements and of				
previous literature data (Ref. 1).	ESTIMATED ERROR:			
-				
	Temperature: accuracy probably <u>+2</u> K (compiler).			
	REFERENCES:			
	(1) Bergman, A.G.; Evdokimova, K.A.			
	Iz. Sektora FizKhim. Anal., Inst.			
	Obshchei i Neorg. Khim. Akad. Nauk SSSR			
	<u></u>			

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] Potassium nitrate; KNO₃; [7757-79-1] 	Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 7-12.
VARTABLES:	PREPARED BY:
Tomporg fure.	Roldini P.
Temperature.	batulit, t.
EXPERIMENTAL VALUES:	
Eutectic, E ₁ , at 234 ^o C (Fig. 1 of the original paper); composition not stated (100x ₁ about 65 in compiler's graphical estimation). Eutectic, E ₂ , at 224 ^o C (Fig. 1 of the original paper); composition not stated (100x ₁ about 38 in compiler's graphical estimation). Intermediate compound(s): K ₂ C ₂ H ₃ O ₂ NO ₃ , congruently melting at 238 ^o C (Fig. 1 of the original paper).	
AUXILIARY T	
	SOURCE AND DUDITY OF MATERIALS.
Visual polythermal analysis.	Not stated.
	Component 1: t _{fus} (1)/°C= 302; component 2: t _{fus} (2)/°C= 337 (Fig. 1 of the original paper).
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:







COMPONENTS:	EVALUATOR:
 Potassium butanoate (potassium butyrate);	Franzosini, P.,
KC ₄ H ₇ O ₂ ; [589-39-9] Potassium thiocyanate;	Dipartimento di Chimica Fisica,
KCNS; [333-20-0]	Universita [~] di Pavia (ITALY).

This system was studied only by Sokolov and Pochtakova (Ref. 1), who suggested the existence of: (i) an intermediate compound of probable composition $K_7(C_4H_7O_2)_6CNS$; (ii) a "perekhodnaya tochka" (likely a peritectic), P, at 608 K (335 °C) and $100x_1$ = 82; and (iii) a eutectic, E, at 443 K (170 °C) and $100x_1$ = 6.5.

Component 1, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(1) = 677 \text{ K}$ (404 ^OC), reported in Ref. 1 should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(1) = 677.3\pm0.5 \text{ K}$.

For the same component, the phase transition temperatures quoted (from Ref. 2) in Ref. 1, viz., 618 K (345 $^{\circ}$ C), 553-558 K (280-285 $^{\circ}$ C), and 463 K (190 $^{\circ}$ C), might correspond respectively to the fusion temperature (626.1+0.7 K) and to the first and third solid state transition temperatures (562.2+0.6 K, and 467.2+0.5 K) of Table 1 of the Preface. No mention is made by the authors of other phase transitions, although in Table 1 two more $T_{\rm trs}$ values are reported (540.8+1.1 K and 461.4+1.0 K).

The phase diagram as suggested by the authors can be considered as adequate only for the region (rich in component 2) including the eutectic, whereas it does not seem reliable in the remaining part.

In particular:

(i) the "perekhodnaya tochka", P, should rather be an M_P point, at which the equilibria involving the isotropic liquid and the liquid crystals might be those described in Preface, Scheme B.1;

(ii) the available data cannot be considered as sufficient to support the existence of any intermediate compound.

- (1) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

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COMPONENTS: (1) Potassium butanoate (potassium butyrate);				ium but	ORIGINAL MEASUREMENTS:	
KC ₄ H ₇ O ₂ ; [589-39-9] (2) Potassium thiocyanate; KCNS; [333-20-0]					Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.	
VARIABLES:					PREPARED BY:	
Temperature.					Baldini, P.	
EXPERIMENTAL VALUES:					·	
t/°C T/	/K ^a 1	.00 x 1	t/°C	T/K ^a	100 x 1	
177 4	50	0	301	574	65	
176 44	49	2.5 5	310	595	70	کم ا
170 44	43	6.5	327	600	77.5	¢ (
173 44	46	7.5	335	608 608	80 82	d345
204 47	.77	15	337	610	82.5	٩٣٩
215 48	88	20	342	615	85	_ حمر _ 300
232 50	05	30	364	652	90 95	
260 53	33	45	404	677	100	2
a T/K values calculated by the compiler.						
Characteristic point(s):					200 - 200	
Eutectic,	, E, at	170 °C a	and 100x	1= 6.5		E
(authors). 0 50 $100x_1$ 100 Characteristic point, P (perekhodnaya tochka KCNS KC_{470}^{-2} in the original text; see the Introduction), at 335 °C and $100x_1 = 82$.						
Intermediate compound(s):						
$K_7(C_4H_7O_2)_6CNS$ (proposed by the authors).						
AUXILIARY INFORMATION						
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis. Temperatures measured with a Nichrome- Constantane thermocouple.				a Nich	Component 1: synthetized from "chemically pure" potassium hydrogen carbonate and n- butanoic acid (Ref. 1, where, however, carbonates instead of hydrogen carbonates are employed; compiler), and recrystallized from n-butanol; it undergoes phase transitions at $t_{trs}(1)/^{O_{c=}}$ 190, 280-285, 345 (Ref. 2). Component 2: commercial material recrystallized once from water and once from alcohol.	
					ESTIMATED ERROR:	
					Temperature: accuracy probably <u>+</u> 2 K (compiler).	
					REFERENCES:	
					 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. 	
COMPONENTS:	EVALUATOR:					
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 Potassium butanoate (potassium butyrate);	Franzosini, P.,					
KC ₄ H ₇ O ₂ ; [589-39-9] Potassium nitrite;	Dipartimento di Chimica Fisica,					
KNO ₂ ; [7758-09-0]	Universita' di Pavia (ITALY).					

The visual polythermal analysis was employed by Sokolov and Minich (Ref. 1) to study the lower boundary of the isotropic liquid field: they claimed the occurrence of a congruently melting intermediate compound [of tentative composition $K_8(C_4H_7O_2)_5(NO_2)_3$], able to give eutectics with either component.

Component 1, however, forms liquid crystals. Therefore, the phase diagram has to be reinterpreted, possibly with reference to Preface, Scheme D.1. In this case, Sokolov and Minich's eutectic E_1 should be an M'_E point, and a further (still undetected) invariant type M_E ought to exist.

The fusion temperature, $T_{fus}(1) = 677$ K, reported in Ref. 1, should be identified with the clearing temperature of component 1, and agrees fairly with the $T_{c1r}(1)$ value (677.3±0.5 K) listed in Preface, Table 1.

Neither of the phase transformation temperatures, i.e., 553-558 and 463 K, quoted in Ref. 1 from Ref. 2 for the same component correspond to the $T_{fus}(1)$ value (626.1+0.7 K) given in Table 1, inasmuch as they lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2+0.6 and 540.8+1.1 K, and 467.2+0.5 and 461.4+1.0 K, respectively) also reported in Table 1. It is, however, to be noted that in other papers by the same group (see, e.g., Ref. 3) a phase transformation occurring at 618 K, i.e., close to the $T_{fus}(1)$ value of Table 1, is also mentioned.

- (1) Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. <u>1961</u>, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u>, 6, 1293-1295.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9] Potassium nitrite; KNO₂; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	ب (
404 677 0 334 607 55 396 669 5 347 620 60 382 655 10 357 630 65 365 638 15 368 641 70 352 625 20 374 647 75 339 612 25 383 656 80 325 598 30 392 665 85 317 590 35 403 676 90 316 589 40 413 686 95 306 579 45 436 709 100 319 592 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , 315 °C and $100x_2$ = 33.5 (authors) Intermediate compound(s): K ₈ (C ₄ H ₇ O ₂) ₅ (NO ₂) ₃ (tentative composition; compiler).	rs). $rs).$ $rs).$ $rs(t,H)$ $rs($
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: prepared from "chemically pure" KHCO ₃ and the fatty acid, and recrystallized from n-butanol after having been deposited from the aqueous solution and dried; it undergoes phase transitions at $t_{trs}(1)^{0}$ C= 190, 280-285 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)^{0}$ C= 436 after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)^{0}$ C= 45 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:
	 Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. <u>1952</u>, 21, 178-183.

COMPONENTS:	EVALUATOR:
 Potassium butanoate (potassium butyrate);	Schiraldi, A.,
KC ₄ H ₇ O ₂ ; [589-39-9] Potassium nitrate;	Dipartimento di Chimica Fisica,
KNO ₃ ; [7757-79-1]	Universita [~] di Pavia (ITALY).

This system was studied only by Dmitrevskaya (Ref. 1), who, on the basis of her visual polythermal investigation, suggested the phase diagram to be of the eutectic type, the invariant point being at 556 K (283 $^{\circ}$ C) and $100x_{2}$ = 58.

Component 1, however, forms liquid crystals. Therefore, Dmitrevskaya's fusion temperature, $T_{fug}(1) = 677$ K (404 °C), should be identified with the clearing temperature of potassium butanoate, the corresponding value from Preface, Table 1 being $T_{clr}(1) = 677.3\pm0.5$ K.

Accordingly, it seems likely that the actual phase diagram of this system should correspond to Preface, Scheme B.1 or B.2.

Among the phase transformation temperatures of component 1 quoted in Ref. 1 from Ref. 2 (i.e., 618, 553-558, and 463 K) the first one can be reasonably identified with the fusion temperature (626.1 ± 0.7 K) listed in Table 1, whereas the second and third ones lie each halfway between the two pairs of solid state transition temperatures (i.e., 562.2 ± 0.6 and 540.8 ± 1.1 K, and 467.2 ± 0.5 and 461.4 ± 1.0 K, respectively) also reported in Table 1.

- (1) Dmitrevskaya, O.I.
 Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2046-2051.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.



COMPONENTS:	EVALUATOR:
 Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂; [19455-20-0] Potassium nitrite; KNO₂; [7758-09-0] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita [~] di Pavia (ITALY).

The visual polythermal analysis was employed by Sokolov and Minich (Ref. 1) to study the lower boundary of the isotropic liquid field: they claimed the formation of a continuous series of solid solutions with a minimum at 535 K (262 °C) and $100x_2$ = 32.5.

Component 1, however, goes through the liquid crystalline state before to turn into a clear melt. Accordingly, the topology of the system has to be re-interpreted, a possibility (not very convincing, however) being that shown in Preface, Scheme B.3 which is based on the assumption that continuous solutions do form between solid $\rm KNO_2$ and solid Ki.C₄H₇O₂.

Sokolov and Minich's fusion temperature of component 1, i.e., 638 K ($365 \, {}^{\circ}C$), should be identified with the $T_{clr}(1)$ value (625.6 ± 0.8 K) listed in Preface, Table 2. The discrepancy between the two figures is noticeable: in previous papers by Sokolov's group, however, lower values, i.e., 629 K (Ref. 2) and 633 K (Ref. 3), were reported.

It is further to be noted that three phase transition temperatures are quoted in Ref. 1 from Ref. 4 for component 1, i.e., 621, 546, and 481 K, the second of which can be reasonably identified with the fusion temperature $[T_{fus}(1)=553.9\pm0.5 \text{ K}]$ listed in Table 2 of the Preface. Consequently: (1) the transition temperature at 621 K (if actually existing) might correspond to some kind of transformation (undetected by DSC, see Table 2) within the liquid crystal field; and (ii) only the transition at 481 K should correspond to a solid state transformation, although the latter figure is almost 60 K higher than the single $T_{trs}(1)$ value (424±3 K) listed in Table 2.

- (1) Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. <u>1961</u>, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u>, 6, 1293-1295.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1960</u>, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1960</u>, 30, 19-24.
- (3) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437.
- (4) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS					ORTGINAL MEASUREMENTS:	
<pre>(1) Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂; [19455-20-0] (2) Potassium nitrite; KNO₂; [7758-09-0]</pre>					Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.	
VARIA	BLES:					PREPARED BY:
Tempe	rature.					Baldini, P.
					<u></u>	
EXPER	IMENTAL	VALUES:				
t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
365 339	638 612	0 5	333 345	606 618	55 60	
326	599	10	356	629	65	
310 292	583 565	15 20	366 374	639 647	70 75	
276	549	25	381	654	80	ے گرے ۔ - 380
264	537 539	30 35	392 401	665 674	85 90	
283	556	40	415	688	95	348
301	574 592	45 50	436	709	100	γ
а т/к	values	calculate	d by the	compile	er.	
Chara	cteristi	c point(s	:):			
Contra					deb a	273
minim	nuous se um at	262 °C	and solu	100x ₂ =	· 32.5	m
(auth	ors).			4		0 50 100×2 100
AUXILIARY I					NFORMATION	
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:	
Visua:	l polyth	ermal ana	lysis.			Component 1: prepared from "chemically
			• = "			pure" KHCO3 and the fatty acid, and
}						recrystallized from n-butanol after having
						and dried; it undergoes phase transitions
						at t _{trs} (1)/ ^o C= 208, 273, 348 (Ref. 1).
						Component 2: material prepared by reducing potassium nitrate with lead, melting at
1						$t_{fus}(2)/^{\circ}C= 436$ after three recrystalliza
					tions; it undergoes a phase transition at $t_{trs}(2)/^{o}C= 45$ (Ref. 2).	
					ESTIMATED ERROR:	
					Temperature: accuracy probably +2 K	
					(Compiler).	
					AFERENCED;	
					Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.	
						(2) Berul', S.I.; Bergman, A.G.
					1zv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.	

COMPONENTS:	EVALUATOR:
 Potassium iso.butanoate (potassium iso.butyrate); K1.C₄H₇O₂; [19455-20-0] Potassium nitrate; KNO₃; [7757-79-1] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This binary was studied only by Dmitrevskaya and Sokolov (Ref. 1). On the basis of their visual polythermal results, they claimed the existence of: (i) an incongruently melting intermediate compound of supposed composition $K_{2i}.C_4H_7O_2NO_3$; (ii) a "perekhodnaya tochka" (likely a peritectic), P, at 529 K (256 °C) and $100x_2$ 47.5; and (iii) a eutectic at 526 K (253 °C) and $100x_2$ 32.5.

Component 1, however, goes through the liquid crystalline state before to turn into a clear melt. Therefore, the authors' fusion temperature $[T_{fus}(1)=629 \text{ K} (356 \ ^{\text{O}}\text{C})]$ should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{clr}(1)=625.6\pm0.8 \text{ K}$.

Moreover, three phase transition temperatures are quoted in Ref. 1 from Ref. 2 for the same component, i.e., 621, 546, and 481 K, the second of which can be reasonably identified with the fusion temperature $[T_{fus}(1)=553.9\pm0.5 \text{ K}]$ listed in Preface, Table 2. Consequently: (i) the transition temperature at 621 K (if actually existing) might correspond to some kind of transformation (undetected by DSC, see Table 2) within the liquid crystal field; and (ii) only the transition at 481 K should correspond to a solid state transformation, although the latter figure is almost 60 K higher than the single $T_{trs}(1)$ value (424±3 K) listed in Table 2.

In conclusion, the authors' interpretation of the topology of this system is to be modified. In the evaluator's opinion, it seems reasonable to assume that the phase diagram could be similar to that shown in Preface, Scheme D.1, allowance being made for the fact that in the present case the intermediate compound is incongruently (instead of congruently) melting. Dmitrevskaya and Sokolov's eutectic should actually be an M'_E point, and a further invariant, type M_E , ought to exist. At any rate, a re-investigation of the system would be desirable, in order to obtain information on the solidus, and to assess unambiguously the composition of the intermediate compound.

- (1) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1960</u>, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1960</u>, 30, 19-24.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS:					ORIGINAL MEASUREMENTS:	
 (1) Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂; [19455-20-0] (2) Potassium nitrate; KNO₃; [7757-79-1] 					Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 19-24.	
VARIAB	LES:					PREPARED BY:
Temper	ature.					Baldini, P.
EXPERI	MENTAL	VALUES:				
t/ºC	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
356 346 335 321 304 285 253 254 255 255 256 a T/K Charac Eutect (aut) Charac in t at 2 Interm	629 619 608 594 577 558 526 527 528 528.7 529 values of teristic hors). teristic he orig: 56 °C an ediate of	0 5 10 15 20 25 30 32.5 35 40 45 47.5 calculated 1 c point(s): at 253 °C ar c point, 1 inal text; c nd 100x2= 4 compound(s):	258 267 276 286 293 300 308 316 322 330 337 by the o nd 100x ₂ P (perek see the 7.5.	531 540 549 559 566 573 581 589 595 603 610 compile: compile: compile: chodnay; Introdu	50 55 60 65 70 75 80 85 90 95 100 r.	a $K_{i} \in C_{4}H_{7}O_{2}$
K21.C4	H702N03	(supposed o	composit	ion; a	authors) incongruently melting.
				AUXII	LIARY I	NFORMATION
METHOD,	polythe	rus/PROCEDUF	KE: sis.			SOURCE AND PURITY OF MATERIALS: Component 1 synthetized from iso.butanoic acid and K_2CO_3 (Ref. 1). "Chemically pure" component 2 recrystallized. Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C= 208$, 273, 348 (Ref 2). Component 2 undergoes phase transitions at $t_{trs}(2)/^{\circ}C= 124$, 316 (current literature).
						ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593. (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	EVALUATOR:
 Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1] Potassium nitrite; KNO₂; [7758-09-0] 	Schiraldi, A., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

The visual polythermal analysis was employed by Sokolov and Minich (Ref. 1) to study the lower boundary of the isotropic liquid field: they claimed the occurrence of a congruently melting intermediate compound [of tentative composition $K_7(C_5H_9O_2)_4(NO_2)_3$], able to give eutectics with either component.

Component 1, however, forms liquid crystals. Therefore, the phase diagram has to be reinterpreted, possibly with reference to Preface, Scheme D.1. In this case, Sokolov and Minich's eutectic E_1 should be an M'_E point, and a further (still undetected) invariant type M_E ought to exist.

The fusion temperature, $T_{fug}(1)$ = 717 K, reported in Ref. 1, should be identified with the clearing temperature of component 1, and agrees fairly with the $T_{clr}(1)$ value (716+2 K) listed in Preface, Table 1. Moreover, the transition temperature $T_{trs}(1)$ = 580 K (307 °C) quoted in Ref. 1 from Ref. 2 should in turn be identified with the actual fusion temperature, the corresponding value from Table 1 of the Preface being 586.6+0.7 K.

- (1) Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. <u>1961</u>, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u>, 6, 1293-1295.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1] (2) Potassium nitrite; KNO₂; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	· · · ·
t/°C T/K ^a $100x_2$ t/°C T/K ^a $100x_2$ 444 717 0 350 623 55 432 705 5 363 636 60 421 694 10 373 646 65 413 686 15 381 654 70 401 674 20 387 660 75 385 658 25 395 668 80 363 636 30 401 674 85 339 612 35 407 680 90 325 598 40 416 689 95 325 598 45 436 709 100 335 608 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , at 321 °C and $100x_2$ = 37 (author Eutectic, E ₂ , at 323 °C and $100x_2$ = 47 (author Intermediate compound(s): $K_7(C_5H_9O_2)_4(NO_2)_3$ (tentative composition; compiler).	$rs): CC_{SH_9O_2} KNO_2$ authors), congruently melting (at 325 °C;
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: prepared from "chemically pure" KHCO ₃ and the fatty acid, and recrystallized from n-butanol after having been deposited from the aqueous solution and dried; it undergoes a phase transition at $t_{trs}(1)/^{O_{c=}}$ 307 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)/^{O_{c=}}$ 436 after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)/^{O_{c=}}$ 45 (Ref. 2).
	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. (2) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. 1952, 21, 178-183.

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COMPONENTS:	EVALUATOR:			
 Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1] Potassium nitrate; KNO₃; [7757-79-1] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).			
CRITICAL EVALUATION:				
This system was studied only by Dmitrevskaya basis of their visual polythermal observatio type, the invariant being at 583 K (310 ^O C) a	and Sokolov (Ref. 1), who suggested (on the ons) the phase diagram to be of the eutectic and $100x_2^{-4}$ 49.			
Component 1, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(1)=717$ K (444 °C), reported by the authors, should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being 716+2 K.				
For the same component, the phase transition at 580 K (307 $^{\circ}$ C), quoted in Ref. 1 from Ref. 2, can be identified with the actual fusion temperature, $T_{fus}(1)=586.6\pm0.7$ K, reported in Preface, Table 1.				
Accordingly, the available experimental data justify a phase diagram possibly similar to Scheme A.1 in the Preface, the invariant point given in Ref. 1 being consequently an M_E point and not a usual eutectic.				
The slope change apparent in the liquidus b with the occurrence in KNO ₃ of the solid stat the authors.	oranch richer in component 2 is consistent e transition at 589 K (316 ^O C) mentioned by			
REFERENCES:				
(1) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1965</u> , 35 , 1905-1909.				
(2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .				



COMPONENTS:	EVALUATOR:
<pre>(1) Potassium iso.pentanoate (potassium iso.valerate); K1.C5H9O2; [589-46-8] (2) Potassium nitrite; KNO2; [7758-09-0]</pre>	Franzosini, P., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

The visual polythermal analysis was employed by Sokolov and Minich (Ref. 1) to study the lower boundary of the isotropic liquid field: they claimed the formation of a continuous series of solid solutions with a minimum at 562 K (289 °C) and $100x_2$ = 37.5.

Component 1, however, goes through the liquid crystalline state before to turn into a clear melt. Therefore, the fusion temperature, $T_{fus}(1)=669$ K (396 °C), reported by the authors should be identified with the clearing temperature, the corresponding value from Table 2 in the Preface being $T_{clr}(1)=679+2$ K. No mention is made by the authors of the actual fusion which occurs at 531+3 K (Table 2): the latter figure is supported by the trend of the thermomagnetical curves plotted by Duruz and Ubbelohde (Ref. 2). Accordingly, the topology of the system has to be re-interpreted, a possibility (not very convincing, however) being that shown in Preface, Scheme B.3, which is based on the assumption that continuous solutions do form between solid KNO₂ and solid Ki.c₅H₉O₂.

As for the other phase transitions quoted by the authors for the same component from Ref. 3, at 327, and 618 K (54, and 345 $^{\circ}$ C, respectively), no identification is possible with the findings by other investigators, inasmuch as: (1) no transformation is reported in Table 2 of the Preface as occurring below $T_{fus}(1) = 531+3$ K; and (11) no transformation is reported either in Table 2 or in Ref. 2 as occurring within the field of existence of the mesomorphic liquid. It is, however, to be stressed that the transition temperatures mentioned by Sokolov and Minich do not seem to be trustworthy: indeed, it is a bit puzzling the fact that for potassium iso.pentanoate Dmitrevskaya and Sokolov (Ref. 4) quote from Ref. 3 transitions at 618, 493, and 473 K, ignoring that quoted by Sokolov and Minich at 327 K.

- (1) Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. <u>1961</u>, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u>, 6, 1293-1295.
- (2) Duruz, J.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1975</u>, A342, 39-49.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Potassium iso.pentanoate (potassium iso.valerate); Ki.C₅H₉O₂; [589-46-8] (2) Potassium nitrite; KNO₂; [7758-09-0]</pre>	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	V_{+} 380 345 300 0 $K_{i}.C_{s}H_{9}O_{2}$ $K_{1}O_{s}$
AUXILIARY I	NFORMAT ION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: prepared from "chemically pure" $KHCO_3$ and the fatty acid, and recrystallized from n-butanol after having been deposited from the aqueous solution and dried; it undergoes phase transitions at $t_{trg}(1)/^{O_{cm}}$ 54, 345 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)/^{O_{cm}}$ 436 after three recrystalliza tions; it undergoes a phase transition at $t_{trs}(2)/^{O_{cm}}$ 45 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. Berul⁻, S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. <u>1952</u>, 21, 178-183.

I.

COMPONENTS:	EVALUATOR:
 Potassium iso.pentanoate (potassium iso.valerate); Ki.C₅H₉O₂; [589-46-8] Potassium nitrate; KNO₃; [7757-79-1] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This system was studied only by Dmitrevskaya and Sokolov (Ref. 1), who claimed the existence of: (i) a eutectic, E_1 , at 557 K (284 °C) and $100x_2=$ 27.5; (ii) a eutectic, E_2 , at either 553 K (280 °C; according to visual polythermal determinations), or 549 K (276 °C; according to thermographical analysis), and $100x_2=$ 46.0; and (iii) an intermediate compound $K_3(i.C_5H_9O_2)_2NO_3$, congruently melting at 557+2 K (284+2 °C).

Component 1, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(1) = 669 \text{ K}$ (396 °C), reported by the authors should be identified with the clearing temperature, the corresponding value from Preface, Table 2 being $T_{clr}(1) = 679+2$ K. No mention is made by the authors of the actual fusion which occurs at 531+3 K (Table 2): the latter figure is supported by the trend of the thermomagnetical curves plotted by Duruz and Ubbelohde (Ref. 2).

As for the other phase transitions quoted by the authors for component 1 from Ref. 3, at 473, 493, and 618 K (200, 220, and 345 $^{\circ}$ C, respectively), no identification is possible with the findings by other investigators, inasmuch as: (i) no transformation is reported in Table 2 of the Preface as occurring below $T_{fus}(1)=531+3$ K; and (ii) no transformation is reported either in Table 2 or in Ref. 2 as occurring within the field of existence of the mesomorphic liquid. It is, however, to be stressed that the transition temperatures mentioned by Dmitrevskaya and Sokolov do not seem to be trustworthy: indeed, it is a bit puzzling the fact that for potassium iso.pentanoate Dmitrevskaya and Sokolov (Ref. 1) quote from Ref. 3 transitions at 618, 493, and 473 K, whereas, e.g., Pochtakova (Ref. 4) quotes from the same source transitions at 618 and 327 K (ignoring those quoted by Dmitrevskaya and Sokolov at 493 and 473 K).

The interpretation of the phase diagram should be modified in the region rich in component 1. The evaluator is inclined to think that: (i) the transition reported (for component 1) in Ref. 3 at 618 K is erratic; (ii) despite the absence of thermographical evidence for the occurrence of fusion at about 530 K, this part of the diagram ought to be similar to that shown in Preface, Scheme D.1, the eutectic E_1 actually being an M'_E point. Accordingly, a further invariant of the M_E type should exist at lower temperature.

The composition of the intermediate compound could coincide with that suggested by the authors, viz., $100x_2$ = 33.3, and the remaining part of the diagram seems reliable.

- (1) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.
- (2) Duruz, J.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1975</u>, A342, 39-49.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Pochtakova, E.I. Zh. Obshch. Khim. 1963, 33, 342-347.

COMPONENTS:			ORIGINAL MEASUREMENTS:						
(1) Po 1s K1 (2) Po KN	 Potassium iso.pentanoate (potassium iso.valerate); K1.C₅H₉O₂; [589-46-8] Potassium nitrate; KNO₃; [7757-79-1] 			Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.					
VARIA	BLES:					PREPARED BY:			
Temper	ature.					Baldini, P.			
EXPERI	MENTAL	VALUES:				<u></u>	•		·····
t/°C	т/ка	100 x 2	t/ ^o C	T/K ^a	100x ₂	t/ ^o C	T/K ^a	100 x₂	
396	669	0	284	557	27.5	130 ^c	403	60	
396 ^b	669	0	284 ^b	557	27.5	305	578	65	
345 ^c	618	0	284d	557	27.5	308	581	70	
220 ^c	493	Ō	208 ^c	481	27.5	314	587	75	
200 ^c	473	õ	284-5	557.7	30	316 ^b	589	75	
386	659	5	282 ^b	555	30	276 ^d	549	75	
382b	655	5	283	556	40	127 ^C	400	75	
275d	548	5	286 ^b	559	40	317	590	80	
336C	609	5	280 ^d	553	40	323	596	85	
205C	478	5	130 ^C	403	40	328	601	90	
365	638	10	282	555	45	328b	601	90	
344	617	15	280	553	46	275d	548	90	
320	503	20	276 ^b	549	46	130 ^C	403	90	
326b	597	20	276d	540	46	335	608	95	
274d	547	20	126C	300	46	337	610	100	
2/4 208C	/81	20	286	550	50	337b	610	100	
296	569	25	200	567	55	316C	589	100	
302b	575	25	300	573	60	1270	400	100	
278d	551	25	3060	570	60	161	400	100	
2000	473	25	275d	548	60				
^a T/K values calculated by the compiler. ^b Liquidus from thermographical analysis. ^c Transformation in the solid state.									

^d Eutectic temperature.

(continued on next page)



I				
COMPONENTS:	ORIGINAL MEASUREMENTS:			
 (1) Potassium iso.pentanoate (potassium iso.valerate); Ki.C₅H₉O₂; [589-46-8] (2) Potassium nitrate; KNO₃; [7757-79-1] 	Dmitrevskaya, 0.I.; Sokolov, N.M. Zh. Obshch. Khim. <u>1967</u> , 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1967</u> , 37, 2050-2054.			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES: (continued)				
Characteristic point(s):				
Eutectic, E_1 , at 284 ^o C and 100 x_2 = 27.5. Eutectic, E_2 , at 280 ^o C (visual polythermal analysis) or 276 ^o C (thermographical analysis) and 100 x_2 = 46.0.				
Intermediate compound(s):				
$K_3(1.C_5H_9O_2)_2NO_3$ (authors), congruently melti	ing at 284 <u>+</u> 2 ^O C (compiler).			
Note - In the figure the filled circles refer	to thermographical analysis.			
AUXILIARY	INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis supplemented with thermographical analysis (heating curves recorded automatically).	Component 1: synthetized from iso.butanoic acid and the carbonate (Ref. 1). Component 2: "chemically pure" material recrystallized. Component 1 undergoes phase transitions at $t_{trs}(1)/^{O}C=$ 345, 220, 200 (Ref. 2). Component 2 undergoes phase transitions at $t_{trs}(2)/^{O}C=$ 316, 127 (current literature).			
	ESTIMATED ERROR:			
	Temperature: accuracy probably <u>+</u> 2 K (compiler).			
	REFERENCES:			
	(1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.			
	(2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .			

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Potassium hexanoate (potassium caproate); KC₆H₁₁O₂; [19455-00-6] Potassium nitrite; KNO₂; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES:				
t/°C T/K ^a 100 x_2 t/°C T/K ^a 100 x_2 444.4 717.6 0 365 638 55 425 698 5 365 638 60 414 687 10 383 656 65 405 678 15 395 668 70 396 669 20 399 672 75 392 665 25 397 670 80 389 662 30 406 679 85 387 660 35 414 687 90 386 659 40 424 697 95 385 658 45 436 709 100 377 650 50 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , at 356 °C and 100 x_2 = 58 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₂ , at 390 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x_2 = 78.5 (author Eutectic, E ₁ , at 356 °C and 100 x 2 °C and 100 x	rs). hors). uthors) congruently			
meiting (at 399 °C; compiler).				
AUXILIARY I	NFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis.	Component 1: prepared from "chemically			
NOTE: Component 1 forms liquid crystals. Accord- ingly, the fusion temperature reported here, viz., 717.6 K (444.4 °C), should be identified with the clearing temperature (725.8+0.8 K) listed in Preface, Table 1, the actual fusion occurring at $T_{fus}(1)=581.7+0.5$ K (Table 1). The latter figure, in turn, might be identified with the phase transition temperature quoted	pure KHCU ₃ and the fatty acid, and recrystallized from butanol after having been deposited from the aqueous solution and dried; it undergoes a phase transition at $t_{trs}(1)/^{0}C=302$ (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)/^{0}C=436$ after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)/^{0}C=45$ (Ref. 2). ESTIMATED ERROR:			
here from Ref. 1, viz., 575 K (302 °C). The diagram could be re-interpreted with refe- rence to Scheme D.1 of the Preface, the authors' entertic E, being possibly an M'-	Temperature: accuracy probably <u>+</u> 2 K (compiler).			
point.	 REFERENCES: (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. (2) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. 1952, 21, 178-183. 			

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Potassium heptanoate (potassium enanthate); KC₇H₁₃O₂; [16761-12-9] Potassium nitrite; KNO₂; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES:				
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$				
452 725 0 403 676 55 444 717 5 404 677 60 439 712 10 400 673 65 432 705 15 395 668 70 425 698 20 392 665 75 419 692 25 401 674 80 413 686 30 405 678 85 407 680 35 410 683 90 401 674 40 417 690 95 395 668 45 436 709 100 395 668 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E_1 , at 391 °C and 100 x_2 = 47.5 (authors) Eutectic, E_2 , at 389 °C and 100 x_2 = 74 (authors) Intermediate compound(s): $K_5(C_7H_{13}O_2)_2(NO_2)_3$ (tentative composition; compiler).	hors). $KC_7H_{13}O_2$ $KC_7H_{13}O_2$ $KC_7H_{13}O_2$ $KC_7H_{13}O_2$ $KC_7H_{13}O_2$ KO_2			
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis. NOTE: Component 1 forms liquid crystals. Accord- ingly, the fusion temperature reported here, viz., 725 K (452 °C), should be identified with the clearing temperature (722+3 K) listed in Preface, Table 1, the actual fusion occurring at $T_{\rm fun}(1) = 571.3+0.9$ K (Table 1). The diagram	Component 1: prepared from "chemically pure" $KHCO_3$ and the fatty acid, evaporated on a steam-bath, dissolved in ethanol, and precipitated with ether. Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fug}(2)/^{OC}$ = 436 after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)/^{OC}$ = 45 (Ref. 1).			
could be re-interpreted with reference to Scheme D.1, of the Preface, the authors	ESTIMATED ERROR:			
eutectic E_1 possibly being an M_E point.	Temperature: accuracy probably +2 K (compiler).			
	REFERENCES:			
	(1) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.			

COMPONENTS:						ORIGINAL MEASUREMENTS:
<pre>(1) Potassium octanoate (potassium caprylate); KC₈H₁₅O₂; [764-71-6] (2) Potassium nitrite; KNO₂; [7758-09-0]</pre>				sium	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.	
VARIAE	LES:					PREPARED BY:
Temper	ature.					Baldini, P.
EXPERI	MENTAL	VALUES:				
t/°C	T/K ^a	100 x 2	t/ ^o C	t/K ^a	100 x 2	
		•		600		्रेंट
444	/1/	U F	300	639	22	
419	092	5	320	029	00	
396	669	10	345	618	65	ξ Y
368	641	15	360	633	/0	\ 6
347	620	20	373	646	75	400 - \
324	597	25	387	660	80	···· β 7
335	608	30	399	672	85	\ \$
346	619	35	411	684	90	
358	031	40	426	099	95	۲ ا ^م ۱۵ ا
369	642	45 50	436	709	100	
	- •=					
ат/к	values	calculate	d by the	e compil	ler.	
Charac	teristi	c point(s):			Ε,
<pre>Lutectic, E₂, at 344 °C (authors) 100x₂= 64.5 (compiler: the figure 60.5 rep in Table 2 and in Fig. 2 of the original is not consistent with the tabulated data). Intermediate compound(s): K₂C₈H₁₅O₂NO₂ (tentative composition; authors)</pre>					authors) 60.5 rep riginal ed data). authors)	and KC _g H ₁₅ O ₂ KNO ₂ paper congruently melting (at 369 °C; compiler).
AUXILIARY I				AUX	(ILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:	
Visual	polvth	ermal ana	lvsis-			Component 1: prepared from "chemically
visual polythermal analysis. NOTE:						pure" KHCO3 and the fatty acid, evaporated on a steam-bath, dissolved in ethanol, and precipitated with ether. Component 2: material prepared by reducing
Component 1 forms liquid crystals. Accordingly, the fusion temperature reported here, viz., 717 K (444 °C), should be identified with the clearing temperature (712+2 K) listed in Preface, Table 1, the					vstals. erature should erature l, the	potassium nitrate with lead, melting at $t_{fus}(2)/^{\circ}C= 436$ after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)/^{\circ}C= 45$ (Ref. 1).
Tr /1	actual Iusion occurring at			1 1 IIg 		ESTIMATED EDDOD.
The diagram could be re-interpreted with reference to Scheme D.1, the authors' eutectic E, possibly being an Mar point			rpretection the au	i with thors	Temperature: accuracy probably <u>+2</u> K	
al boostory setting an u E borne.						REFERENCES:
						(1) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. 1952, 21,
						178–183.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Potassium nonanoate (potassium pelargonate); KC9H1702; [23282-34-0] Potassium nitrite; KN02; [7758-09-0] 	Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. <u>1961</u> , 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1961</u> , 6, 1293-1295.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.

EXPERIMENTAL VALUES:

t/°C т/к^а $100x_{2}$ 421 694 0 370^b 643 5 370 643 10 ••• 370 643 95 436 709 100

a T/K values calculated by the compiler. b Figure not compatible with curve VI in Fig. 1 of the original paper (compiler).

Characteristic point(s):

Eutectic, E, at $332 \, {}^{\text{O}}\text{C}$ and $100 \mathbf{x}_{2}$ = 6.5 (compiler: the figure 7.5 reported in table 2 of the original paper is not compatible with curve VI in Fig. 1 of the original paper).

Note - Liquid layering occurs at $7.5 \le 100x_2 \le 99$ at $t/^{\circ}C=370$ (see the figure which is a reproduction of curve VI in Fig. 1 of the original paper, and not a plot of the data tabulated; compiler).



prot of the tata tabarates, comparent,				
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis. NOTE: Component 1 forms liquid crystals. Accord- ingly, the fusion temperature reported here, viz., 694 K (421 °C), should be identified with the clearing temperature (707.4+0.8 K) listed in Table 1 of the Preface, the actual fusion occurring at $T_{fug}(1) = 549.1+0.8$ K (Table 1). A possible re-interpretation of the phase diagram might be done with reference to Scheme A.1 of the Preface, modified as shown in Fig. 2, the authors' eutectic being in this	Component 1: prepared from "chemically pure" KHCO ₃ and the fatty acid, evaporated on a steam-bath, dissolved in ethanol, and precipitated with ether. Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)/^{0}C=436$ after three recrystalliza- tions; it undergoes a phase transition at $t_{trs}(2)/^{0}C=45$ (Ref. 1).			
	ESTIMATED ERROR: Temperature: accuracy probably <u>+2 K</u> (compiler).			
case an m E point.	(1) Berul', S.I.; Bergman, A.G. Izv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.			

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Lithium methanoate (lithium formate); LiCHO₂; [556-63-8] (2) Lithium ethanoate (lithium acetate); LiC₂H₃O₂; [546-89-4] 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1975</u> , 45, 503-505.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	
Characteristic point(s):	
Eutectic, E, at 240 °C and $100x_1 = 37.5$ (author).	
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AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated. Component 1 melts at $t_{fus}(1)/^{o}C= 273$. Component 2 melts at $t_{fus}(2)/^{o}C= 284$.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Lithium methanoate (lithium formate); LiCHO₂; [556-63-8] Lithium thiocyanate; LiCNS; [556-65-0] 	Sokolov, N.M.; Dmitrevskaya, O.I. Zh. Neorg. Khim. <u>1969</u> , 14, 286-296 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1969</u> , 14, 148-155.		
VARIABLES:	PREPARED BY:		
Temperature.	Baldini, P.		
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·		
$t^{o}C T/K^{a} 100x_{2} t^{o}C T/K^{a} 100x_{2}$	u [
273 546 0 156 429 48.5 259 532 5 157 430 50 247 520 10 167 440 55 235 508 15 180 453 60 222 495 20 192 465 65 210 483 25 204 477 70 198 471 30 216 489 75 187 460 35 227 500 80 176 449 40 238 511 85 163 436 45 266 539 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 156 °C and $100x_2$ = 48.5 (auth	ors). $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$ $\frac{1}{100}$		
AUXILIARY I	NFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal analysis; solid state transition temperatures drawn from the heating curves obtained with automatic recording.	Not stated. Component 1 undergoes phase transitions at $t_{trs}(1)/{}^{0}C=$ 87, 115, 232. Component 2 undergoes a phase transition at $t_{trs}(2)/{}^{0}C=$ 202.		
NOTE:			
The fusion temperature of component 1 (546 K) coincides with that listed in Preface, Table 1 where, however, a single solid state transformation of the same component is mentioned as occurring at 496+2 K (i.e., some 10 K lower than the highest Sokolov and Dmitrevskaya's transition).	ESTIMATED ERROR: Temperature: accuracy probably <u>+2 K</u> (compiler). REFERENCES:		

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Lithium methanoate (lithium formate); LiCHO₂; [556-63-8] Lithium nitrate; LiNO₃; [7790-69-4] 	Tsindrik, N.M. Zh. Obshch. Khim. <u>1958</u> , 28, 830-834.
VARIABLES:	PREPARED BY:
Temperature.	Baldiní, P.
EXPERIMENTAL VALUES:	
$t^{o}C T/K^{a} 100x_{1} t^{o}C T/K^{a} 100x_{1}$	
256 529 0 180 453 45	
$ \begin{bmatrix} 247 & 520 & 5 & 170 & 443 & 50 \\ 238 & 511 & 10 & 162 & 435 & 55 \end{bmatrix} $	
228 501 15 178 451 60	
220 493 20 194 467 65	
212 485 25 208 481 70	250 %
196 469 35 232 505 80	\mathbf{k}
188 461 40	
^a T/K values calculated by the compiler.	
Characteristic point(s):	200 - 200
Eutectic, E, at 162 ^O C and 100x ₁ = 55 (author).	کر ک
Note – The system was investigated at $0 \le 100 x_1 \le 80$.	, E 0 50 100×1 100 L;N0 L;CH0
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple.	Materials of analytical purity recrystallized twice (extrapolated t _{fus} (1)/ ⁰ C= 273; author).
NOTE:	
The extrapolated T _{fus} (1) reported by the author (546 K) coincides with that listed in Table 1.	
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:



COMPO	NENTS.
COMPU	NEWID:

Lithium ethanoate (lithium acetate); LiC₂H₃O₂; [546-89-4] Lithium nitrate; LiNO₃; [7790-69-4]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was submitted to visual polythermal analysis by Diogenov (Ref. 1) as a side of the reciprocal ternary Li, $Na/C_2H_3O_2$, NO_3 , and by Diogenov et al. (Ref. 2), and Sokolov and Tsindrik (Ref. 3) as a side of the reciprocal ternary K, $Li/C_2H_3O_2$, NO_3 . All investigations were restricted to the liquidus.

The fusion temperature of component 1 given in Refs. 1, 2 (564 K) is 7 K higher than that (557 K) reported both in Ref. 3 and Table 1 of the Preface. Again for component 1, a solid state transformation is mentioned in Refs. 1, 2 as occurring at 536-538 K, whereas, in a subsequent paper by the same group (Ref. 4), a far different temperature (405 K) is reported. No information about the existence of any solid-solid transition in lithium ethanoate is known to the evaluator from any source (included Ref. 3 and Table 1), but Diogenov's group.

The diagrams shown in Refs. 1-3 are qualitatively similar, and characterized by the presence of a single eutectic at $100x_2$ about 51. It is, however, a bit surprising that neither Sokolov and Tsindrik (Ref. 3, where Ref. 1 is quoted), nor Diogenov et al. (Ref. 2, where Ref. 1 is not quoted) have commented on the unusually large discrepancies existing between the eutectic temperatures they found (463 K and 449 K, respectively) and the previous value (418 K) by Diogenov (Ref. 1). These discrepancies might be related to the fact that component 1 tends to form glasses.

At any rate, the evaluator - due to the apparent lack of internal consistency of the measurements by Diogenov's group - is inclined to attach more reliability to the data from Ref. 3, although regretting that they are reported only in graphical form.

- (1) Diogenov, G.G.
 Zh. Neorg. Khim. <u>1956</u>, 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1956</u>, 1 (4), 199-205.
- (2) Diogenov, G.G.; Nurminskii, N.N.; Gimel'shtein, V.G.
 Zh. Neorg. Khim. <u>1957</u>, 2, 1596-1600 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1957</u>, 2(7), 237-245.
- (3) Sokolov, N.M.; Tsindrik, N.M.
 Zh. Neorg. Khim. <u>1969</u>, 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1969</u>, 14, 302-306.
- (4) Diogenov, G.G.; Erlykov, A.M.; Gimel'shtein, V.G.
 Zh. Neorg. Khim. 1974, 19, 1955-1960; Russ. J. Inorg. Chem. (Engl. Transl.) 1974, 19, 1069-1073 (*).

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Lithium ethanoate (lithium acetate); LiC₂H₃O₂; [546-89-4] (2) Lithium nitrate; LiNO₃; [7790-69-4]</pre>	Diogenov, G.G. Zh. Neorg. Khim. 1956, 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1956, 1 (4), 199-205.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t^{o}C T/K^{a} 100x_{1} t^{o}C T/K^{a} 100x_{1}$	
259 532 0 170 443 56 254 527 5 183 456 60 248 521 9 190 463 62.5 241 514 14 206 479 68 234 507 18.5 219 492 72.5 227 500 22.5 233 506 77.5 216 489 27.5 242 515 81 204 477 32 250 523 84.5 188 461 37.5 259 532 90 176 449 41 264 537 92.5 160 433 45 276 549 94 150 423 50 283 556 96 160 433 53 291 564 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 145 °C and $100x_1 = 51$ (author) Note - On the branch richer in component 1 transition of $LiC_2H_3O_2$ (author).	the inflexion at 263 °C indicates a phase
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis.	Not stated.
	ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:



COMPONENTS: (1) Lithium ethanoate (lithium acetate); LiC ₂ H ₃ O ₂ ; [546-89-4] (2) Lithium nitrate; LiNO ₃ ; [7790-69-4]	ORIGINAL MEASUREMENTS: Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. 1969, 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1969, 14, 302-306.
VARIABLES:	PREPARED BY:
Temperature	Baldini, P.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	
Characteristic point(s):	
Eutectic, E, at 190 ^O C (authors) and $100x_2$ about 51 (compiler).	
	284 284 258 E 100X ₂ 100 LIC ₂ H ₃ O ₂ LINO ₃
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis (compiler).	Commercial materials recrystallized (compiler). Component 1: t _{fus} (1)/°C= 284. Component 2: t _{fus} (2)/°C= 258.
	ESTIMATED ERROR: Temperature: accuracy probably +2 K
	REFERENCES:

1						
COMPONENTS:					ORIGINAL MEASUREMENTS:	
(1) Lithium propanoate (lithium propionate);			n propie			
Li	LC3H502;	[6531-45-	-9]			Sokolov, N.M. and Dmitrevskaya, O.I.
(2) Li	thium t	hiocyanate	;			Zh. Neorg. Khim. 1969, 14, 286-296 (*);
	1003; [-	00-00-01				14. 148-155.
[
VARIA	VARIABLES:					PREPARED BY:
Temper	rature.					
EXPERI	IMENTAL	VALUES:		· ···		
t/°C	t/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
329	602	0	196	469	45	
326	599	5	197	470	50	++ \
313	586	10	196	469	55	
294	561	20	210	400	60 65	300 - 2
245	518	25	224	497	70	
220	493	30	237	510	75	
204	477	35	243	516	80	285 9
194	467	37.5	260	533	90	250 -
195	468	40	266	539	100	
а т/к	values	calculated	by the	compile	er.	
Charac	teristi	c point(s)	:			
Eutect	:ic, E ₁ ,	at 194 °C	and 10)0x ₂ = 3:	7.5 (aut	hors). $E_1 \mid E_2$
Eutect	ic, E ₂ ,	at 193 ^O C	and 10	$0x_2^2 = 60$) (autho	rs). $0 50 100 100$
Intern	nediate	compound(s):			L;C ₃ H ₅ O ₂ L;CNS
LigCal	$Li_{2}C_{2}H_{5}O_{2}CNS$ congruently melting at 197 ^o C (authors).					
	52			-		
				AUX	ILIARY I	NFORMATION
METHOI)/APPARA	TUS/PROCED	URE:			SOURCE AND PURITY OF MATERIALS:
Visual	l polyt	hermal ana	lysis;	solid	state	Not stated.
transi	tion t	emperature	s draw	m from	n the	Component 1 undergoes a solid state
heatir	ig cur	ves obtai	ned wit	h auto	omatic	transition at $t_{trs}(1)/{}^{o}C= 265$.
record	ling.					Component 2 undergoes a solid state
						$\frac{1}{1} \frac{1}{1} \frac{1}$
}						
					,	
ļ					1	
]					1	ESTIMATED ERROR:
1					!	(compiler).
1						REFERENCES:
ł						
]						
1						





COMPONENTS: (1) Lithium butanoate (lithium butyrate); LiC(H=00: [21303-03-7]	ORIGINAL MEASUREMENTS:			
(2) Lithium nitrate; LiNO ₃ ; [7790-69-4]	Zh. Obshch. Khim. 1958, 28, 1728-1733 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1775-1780.			
VARIABLES:	PREPARED BY:			
Temperature.	Baldini, P.			
EXPERIMENTAL VALUES:				
$t/^{\circ}C T/K^{a} 100x_{1} t/^{\circ}C T/K^{a} 100x_{1}$	ų [
256 529 0 216 489 45 248 521 5 228 501 50	, Ç			
242 515 10 238 511 55 238 511 12.5 248 521 60				
232 505 15 258 531 65 232 505 17.5 268 541 70	300			
232 505 20 278 551 75 230 503 25 288 561 80	8			
230 503 30 298 571 85 226 499 35 308 581 90	2			
224 497 40 329 602 100 220 493 42.5	250 -			
^a T/K values calculated by the compiler.	Parces of			
Characteristic point(s):	E			
Eutectic, E, at 216 ^o C and $100x_1 = 45$ (authors Peritectic, P, at 232 ^o C and $100x_1 = 15$ (autho), 0 50 100×, 100 rs), LiNO, LiCHO,			
Intermediate compound(s):				
Li ₈ C ₄ H ₇ O ₂ (NO ₃)7 (probable composition; authors), incongruently melting.				
AUXILIARY I	NFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis; temperatures of initial crystallization measured with a Nichrome-Constantane thermocouple and a millivoltmeter.	Component 1: prepared from "chemically pure" carbonate and n-butanoic acid (Ref. 1); the solid recovered after evaporation was recrystallized from n-butanol. Component 2: source not stated			
	ESTIMATED ERKOR:			
	Temperature: accuracy probably +2 K (compiler).			
	REFERENCES:			
	(1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.			

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium bromide; NaBr; [7647-15-6] Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	••••••
t/ ^o c т/K ^a 100ж _l	
257.5 530.7 0 254.5 527.7 2.02 251.8 525.0 3.91 250.4 523.6 4.99 248.8 522.0 6.01 245.7 518.9 8.00 244.2 517.4 8.98 250.9 524.1 10.00 265.1 538.3 11.04 274.0 547.2 11.76 296.1 569.3 13.55 ^a T/K values calculated by the compiler. Note 1 - In the original paper the results were shown in a graphical form. The above listed numerical values represent a personal communication by one of the authors (F., P.) to the compiler. Note 2 - The system could not be investigated above 300 °C due to the thermal instability of the methanoate. Characteristic point(s):	$\frac{1}{2}$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP meterials, dried by heating under vacuum.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
	REFERENCES:
	<pre>(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u>, 38, 116-118.</pre>



COMPONENTS: ORIGINAL MEASUREMENTS: (1) Sodium bromide; Piantoni, G.; Leonesi, D.; Braghetti, M.; NaBr; [7647-15-6] Franzosini, P. (2) Sodium ethanoate (sodium acetate); Ric. Sci., 1968, 38, 127-132. NaC₂H₃O₂; [127-09-3] VARIABLES: PREPARED BY: Temperature. D'Andrea, G. **EXPERIMENTAL VALUES:** t/°C T/K^a 100x2 328.1 601.3 100 330 327.7 600.9 327.1 600.3 326.5 599.7 99.6 98.9 1.℃ 98.2 326.1 599.3 97.8 325.4 97.1 598.6 325.4 598.6 97.1 320 325.4 598.6 97.0 323.0 596.2 94.4 323.1 596.3 94.4 321.0 318.8 594.2 92.2 592.0 89.8 322.3 595.5 88.5 93 100x2 325.9 599.1 88.2 86 100 331.8 605.0 87.6 NaBr NaC,H,O, ^a T/K values calculated by the compiler. Note 1 - In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler. Note 2 - The system was investigated at $0 \le 100x_1 \le 12.5$. Characteristic point(s): Eutectic, E, at 317.9 $^{\circ}$ C and 100 x_2 = 88.9 (authors). AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: A Pyrex device, suitable for work under an inert atmosphere, and allowing one to C. Erba RP materials, dried by heating under vacuum. observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer. NOTE: ESTIMATED ERROR: The authors discuss their own results in Temperature: accuracy probably +0.1 K. comparison with both the expected ideal behaviour of the molten mixtures and the previous data from Ref. 2. Extension of **REFERENCES:** this comparison to the cryometric constant (1) Braghetti, M.; Leonesi, D.; Franzosini, P. at null molality for different solutes in Ric. Sci. 1968, 38, 116-118. (2) Il'yasov. I.I.; Bergman, A.G. molten sodium ethanoate allowed them to argue that sodium bromide and sodium ethanoate show a remarkable tendency to Zh. Obshch. Khim. 1961, 31, 368-370. give mixed crystals.
						······································
COMPONENTS:					ORIGINAL MEASUREMENTS:	
(1) Sodium methanoate (sodium formate):):	Sokolov, N.M.
N N	aCHO ₂ ; [141-53-7]	(Zh. Obshch. Khim. 1954, 24, 1581-1593.
(2) S	odium et	hanoate (sodium ad	etate);	;	
N	aC2H3O2;	[127-09-	•3]			
VARIA	BLES:					PREPARED BY:
Tempe	rature.					Baldini, P.
EXPER	IMENTAL	VALUES:				
t/°C	T/K ^a	100 x 2	t/°C	т/ка	¹⁰⁰ x 2	
258	531	0	296	569	50	
252	525	5	300	573	55	ا ^م مہ
244	517	10	303	5/6	60	
252	525	15	313	586	70	
260	533	20	316	589	75	
267	540	25	320	593	80	۲۵
270	543	30	323	596	85	کم ا
278	557	35 40	326	599	90	ا ا ا ا ا
291	564	45	331	604	100	
а т/к	values	calculate	d by the	compile	er.	
Chara	cteristi	c point(s):			
Futon	tio F	at 242 00	and 100-	10 5	(autho	~
Lucec	μις, Β,	al 242 °C	and IUU	2 10.5	(autho	
AUXILIARY I					NFORMATION	
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:	
Visua Molte	1 polyth	ermal ana	lysis.	and et	irrod	Component 1: prepared by reacting aqueous
Tempe	ratures	measure	d with	a Nic	hrome-	excess of methanoic acid of analytical
Const	antane	thermocou	ple and	a 17 mV	full	purity. The solvent and excess acid were
scale	milli	voltmeter	• The	tempe	rature	removed by heating to 160 °C.
readi	ngs refe	r to the	disappear	ance of	iso-	Component 2: "chemically pure" material.
[trop1	city in	the meit	on coolin	ıg•		
ļ						
					ESTIMATED ERROR:	
						Temperature: scoursey probably +2 K
					(compiler).	
						REFERENCES:
						•
						i

6-1659.		
5-1659.		
)0 H ₅ O ₂		
e proper 258 and Lon at		
$t_{trs}(1)/^{\circ}C= 242$ (Ref. 2). Component 2 melts at $t_{fus}(2)/^{\circ}C= 298$ (according to Fig.s 3, 4, of the original paper; compiler) or 300 (Fig. 1), and undergoes phase transitions at $t_{trs}(2)/^{\circ}C= 195$, 217, 287 (Ref. 2).		
Ly <u>+</u> 2 к		
31-1593.		

COMPONENTS:	EVALUATOR:
 Sodium methanoate (sodium formate);	Franzosini, P.,
NaCHO ₂ ; [141-53-7] Sodium butanoate (sodium butyrate);	Dipartimento di Chimica Fisica,
NaC ₄ H ₇ O ₂ ; [156-54-7]	Universita ⁻ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1), who suggested the existence of: (i) a eutectic, E_1 , at 525 K (252 °C) and $100x_2= 2.5$; (ii) a eutectic, E_2 , at 581 K (308 °C) and $100x_2= 89$; and (iii) an intermediate compound, $Na_2CHO_2C_4H_7O_2$, congruently melting at 614 K (341 °C).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(2) = 603$ K (330 °C; Ref. 1), should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(2) = 600.4\pm0.2$ K. No mention is made by the author of the other phase transitions occurring in component 2, including that corresponding to the actual fusion, viz., $T_{fus}(2) = 524.5\pm0.5$ K (Table 1).

Conversely, the fusion temperature of component 1, $T_{fus}(1)=531$ K (258 °C; Ref. 1), satisfactorily corresponds to the value of Table 1, viz., $T_{fus}(1)=530.7\pm0.5$ K.

In conclusion, Sokolov's assertion of the existence of the congruently melting intermediate compound is a reasonable interpretation of the trend of the available data. In this case, however, the phase diagram could be interpreted with reference to Scheme D.1 of the Preface: in particular, the eutectic E_2 could be actually identified with an M'_E point, Sokolov's diagram likely being similar to that shown in Preface, Scheme D.1.

The unusual size of the dome and the absence of any information about the solidus does not allow one to exclude that Sokolov's points might be at least in part relevant to liquid-liquid instead of solid-liquid equilibria. One might therefore take into account the occurrence of liquid layering as shown in the figure: in particular, the eutectic E_2 could be actually identified with an invariant at which equilibrium occurs among two isotropic liquid and one crystalline liquid phases.

REFERENCES:

(1) Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t^{o} C T/K ^a 100 x_{2} t^{o} C T/K ^a 100 x_{2}	
258 531 0 340 613 55 252 525 2.5 340 613 60 287 560 5 339 612 65 301 574 10 338 611 70 312 585 15 336 609 75 318 591 20 331 604 80 324 597 25 324 597 85 327 600 30 308 581 89 333 606 35 311 584 90 337 610 40 322 595 95 339 612 45 330 603 100 341 614 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E ₁ , at 252 °C and $100x_2= 2.5$ (author). Eutectic, E ₂ , at 308 °C (erroneously reported as 318 °C in the text, compiler) and $100x_2= 89$ (author). Intermediate compound(s): Na ₂ CHO ₂ C ₄ H ₇ O ₂ , congruently melting at	$ \begin{array}{c} $
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Materials prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 ^O C.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 2 4, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 x_{2} $t/^{\circ}C$ T/K^{a} 100 x_{2}	
258 531 0 329 602 55 252 525 1.3 327 600 60 290 563 5 325 598 65 305 578 10 320 593 70 314 587 15 314 587 75 319 592 20 306 579 80 321 594 25 296 569 85 324 597 30 282 555 90 326 599 35 258 531 95 327 600 40 250 523 96.5 329 602 45 260 533 100 330 603 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E_1 , at 252 °C and 100 x_2 = 1.3 (auth Eutectic, E_2 , at 250 °C and 100 x_2 = 96.5 (auth Intermediate compound(s): Na ₂ CHO ₂ 1.C ₄ H ₇ O ₂ , congruently melting at 330 °C	E_{1}^{1}
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling. NOTE:	Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.
As an interpretation alternative to that by	ESTIMATED ERROR:
Sokolov, the large liquidus dome might be due to the occurrence of a miscibility gap in the liquid state.	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

COMPONENTS:

 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
 Sodium iso.pentanoate (sodium iso.valerate); Nai.c₅H_QO₂; [539-66-2]

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed the existence of:

(i) a eutectic, E_1 , at 525 K (252 °C) and $100x_2= 0.75$; (ii) a eutectic, E_2 , at 518 K (245 °C) and $100x_2= 94.5$; and (iii) an intermediate compound, $Na_5(CHO_2)_3(i.C_5H_9O_2)_2$ congruently melting at 593 K (320 °C).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature reported in Ref. 1, $T_{fus}(2) = 535 \text{ K} (262 ^{\circ}\text{C})$ is actually to be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{clr}(2) = 559 \pm 1 \text{ K}$. The remarkable discrepancy between these values might be attributed to the presence of some impurity in Sokolov's sample, inasmuch as the value from Table 2 meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3). According to Table 2, component 2 melts at 461.5\pm0.6 K.

Conversely, the fusion temperature reported in Ref. 1 for component 1, $T_{fus}(1)=531$ K (238 °C) is in satisfactory agreement with the value from Table 1, viz., $T_{fus}(1)=530.7\pm0.5$ K.

In conclusion, Sokolov's assertion of the existence of the congruently melting intermediate compound is a reasonable interpretation of the trend of the available data. In this case, however, the phase diagram should be modified as follows: the eutectic E_2 should be identified with an M_E point, Sokolov's diagram being likely similar to that shown in Scheme D.1.

The unusual size of the dome and the absence of any information about the solidus does not allow one to exclude that Sokolov's points might be at least in part relevant to liquid-liquid instead of solid-liquid equilibria. One might therefore take into account the occurrence of liquid layering as shown in the figure: in particular, the eutectic E_2 could be actually identified with an invariant at which equilibrium occurs among two isotropic liquid and one crystalline liquid phases.

REFERENCES:

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A322, 281-299.



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Franzosini, P.,
Dipartimento di Chimica Fisica,
Universita<sup>°</sup> di Pavia (ITALY).
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COMPONENTS:					ORIGINAL MEASUREMENTS:	
 (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium iso-pentanoate (sodium iso-valerate); Nai-C-H-O-: [539-66-2] 					Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.	
	5902	, [555 00 1	- 1			
VARIABL	ES:					PREPARED BY:
Tempera	ture.					Baldini, P.
EXPERIM	ENTAL V	ALUES:				
t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
258 252 287 300 308 311 314 316 318 320 319 a T/K va Characte Eutectic Eutectic Intermed Na ₅ (CHO ₂	531 525 560 573 581 584 587 593 591 593 592 alues c eristic c, E ₁ , c, E ₂ , ilate c 2)3(1.C	0 0.75 5 10 15 20 25 30 35 40 45 alculated b point(s): at 252 °C a at 245 °C a ompound(s): 5H902)2, co	317 315 312 309 306 301 297 284 265 245 262 y the c nd 1002 nd 1002	590 588 585 582 579 574 570 557 538 518 535 535 compiler $c_2 = 0.75$ $c_2 = 94.5$	50 55 60 65 70 75 80 85 90 94.5 100	or). $ar(x) = \frac{1}{250} + \frac{1}{100} + $
AUXILIARY I						NFORMATION
METHOD/A	PPARAT	US/PROCEDUR	E :			SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.					Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.	
						ESTIMATED ERROR:
						Temperature: accuracy probably +2 K (compiler).
						REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium chloride; NaCl; [7647-14-5] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	+/•C
257.5 530.7 0 256.0 529.2 0.95 254.5 527.7 2.10 253.2 526.4 3.00 251.6 524.8 3.94 250.7 523.9 4.60 249.8 523.0 5.14 252.5 525.7 5.22 259.5 532.7 5.63 260.5 533.7 5.70 266.8 540.0 5.98 275.4 548.6 6.48 286.3 559.5 7.13 293.6 566.8 7.55 298.9 572.1 7.83 ^a T/K values calculated by the compiler. Note 1 - In the original paper the results listed numerical values represent a personal P.) to the compiler. Note 2 - The system could not be invest instability of the methanoate. Characteristic point(s): Eutectic, E, at 249.8 °C and $100x_2 = 5.15$ (aut	were shown in graphical form. The above communication by one of the authors (F., figated above $300 ^{\circ}\text{C}$ due to the thermal
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP materials, dried by heating under vacuum.
NOTE:	
Previous investigations by the same group (Ref. 2) stated that the cryometric constant of sodium methanoate was $K=9.4\pm0.2$ K molality ⁻¹ , and that	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
$\lim_{m \to 0} (\Delta T/m) = 9.6 \text{ K molality}^{-1}$	REFERENCES:
(where ΔT : experimental freezing point de- pression; m: molality of the solute) when NaCl was the solute. Consequently, the solubility of component 2 in component 1 in the solid state ought to be insignificant.	 Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u>, 38, 116-118. Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P. Ric. Sci. 1968, 38, 702-705.

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COMPONENTS:	EVALUATOR:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium thiocyanate; NaCNS; [540-72-7] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita [~] di Pavia (ITALY).

The system sodium methanoate - sodium thiocyanate was investigated by Sokolov, 1954 (Ref. 1), Sokolov and Pochtakova, 1958 (Ref. 2), Cingolani et al., 1971 (Ref. 3), and Storonkin et al., 1974 (Ref. 4).

The liquidus curve drawn on the basis of visual polythermal observations led Sokolov (Ref. 1) to express the opinion that the system was a eutectic one.

Sokolov and Pochtakova (Ref. 2) re-examined the system (as a side of the composition square of the reciprocal ternary K, Na/CHO₂, CNS) using the same method and came to parallel conclusions. It is however to be noted that: (i) differences up to 8 K exist between the fusion temperatures listed in either paper for mixtures of equal composition; and (ii) the coordinates of the eutectic are somewhat different, i.e., 460 K and 100x_2 = 36 according to Ref. 1, and 462 K and 100x_2 = 38 according to Ref. 2.

Cingolani et al. (Ref. 3), not aware of Ref.s 1, 2, found two invariants, viz. a eutectic at 462.7 K and $100x_2$ = 38.0 (in excellent agreement with Ref. 2) and the other one corresponding to the incongruent melting of the intermediate compound Na₅(CHO₂)₄CNS. They supplemented their visual observations (carried out at a cooling rate of about 0.25 K min⁻¹) with DSC analysis, and, in particular, asserted that the composition of the intermediate compound "was confirmed by DSC measurements". They could also observe in the composition triangle of each of the ternaries Na/Br, CHO₂, CNS, Na/CHO₂, CI, CNS, and Na/CHO₂, CNS, I a crystallization region belonging to the binary intermediate compound and covering respectively 0.45, 0.80, and 1.80 % of the liquidus area.

Storonkin et al. (Ref. 4) employed DTA to investigate the ternary Na/CHO₂, CNS, NO₃, and once more found, for the binary system of interest here, just one eutectic at 443 K and $100x_2$ = 36; they also claimed the distribution coefficient of NaCHO₂ in NaCNS to be zero in the thiocyanate crystallization field. They were apparently not aware of Ref. 3.

Because of the better accuracy of the experimental approach, the evaluator is inclined to recommend (among those available so far) the data by Berchiesi et al. (Ref. 3). The fact that Storonkin et al. (Ref. 4), by employing a DTA technique, where not able to detect the intermediate compound still remains surprising. This fact, however, might be explained if the large supercooling effect found by the latter authors in the region of the ternary eutectic could not be prevented in the region of the binary eutectic. Efficient stirring and slow cooling rate have likely allowed Cingolani et al. (Ref. 4) methanoate is even possible, inasmuch as their $T_{fus}(1)/K$ value (528) is some 3 K lower than those reported in Ref.s 1 (531), 2 (531), and 3 (530.65), and in Table 3 [530.46+0.04 (adiabatic calorimetry); 530.7+0.5 (DSC)].

REFERENCES:

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
- (2) Sokolov, N.M.; Pochtakova, E.I.
 Zh. Obshch. Khim. 1958, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.
- (3) Cingolani, A.; Berchiesi, G; Piantoni, G.
 J. Chem. Eng. Data 1971, 16, 464-467.
- (4) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.
 Vestn. Leningr. Univ., Fiz., Khim. <u>1974</u>, (10), 84-88.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium thiocyanate; NaCNS; [540-72-7] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
lemperature.	Baldini, P.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 x_{2} $t/^{\circ}C$ T/K^{a} 100 x_{2}	
258 531 0 212 485 45 250 523 5 232 505 50 241 514 10 244 517 55 233 506 15 256 529 60 213 486 25 267 540 65 202 475 30 284 557 75 190 463 35 302 575 90 187 460 36 311 584 100 197 470 40 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 187 °C and $100x_2$ = 36 (author)	V_{\pm} 300 250 200 U_{\pm} 200 U_{\pm}
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.	Component 1 synthetized from methanoic acid and NaHCO ₃ . Component 2 of analytical purity recrystallized once from water and once from ethanol.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:					ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium thiocyanate; NaCNS; [540-72-7] 					Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.
VARIABLES	:				PREPARED BY:
Temperatu	re.				Baldini, P.
EXPERIMEN	TAL VALUES:				
t/ ^o C T/1	K ^a 100 x 1	t/ ^o C	T/K ^a	100 x 1	
311 58 306 57 298 57 290 56 283 55 269 54 259 53 251 52 237 51 228 50 ^a T/K valu Character: Eutectic,	4 0 9 5 1 10 3 15 6 20 1 25 2 30 2 35 4 40 0 45 1 50 ues calculated istic point(s) E, at 189 °C	210 195 189 195 202 216 225 239 246 256 258 4 by the 0: and 1002	483 468 462 468 475 489 512 519 529 531 compil x ₁ = 62	55 60 62 65 70 75 80 85 90 95 100 er. (authors). $ \frac{1}{270} - \frac{1}{220} -$
AUXILIARY I					NFORMATION
METHOD/APPARATUS/PROCEDURE:					SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.					Component 1: commercial material recrystallized from water; it undergoes a phase transition at t _{trs} (1)/ ⁰ C= 242 (Ref. 1). Component 2: commercial material recrystallized from alcohol.
					ESTIMATED ERROR:
					Temperature: accuracy probably <u>+</u> 2 K (compiler).
					REFERENCES:
					(1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium thiocyanate; NaCNS; [540-72-7] 	Cingolani, A.; Berchiesi, G; Piantoni, G. J. Chem. Eng. Data <u>1971</u> , 16, 464-467.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	· ·
t/°C T/K ^a $100x_2$ t/°C T/K ^a $100x_2$ 257.5 530.7 0 199.5 472.7 30.2 251.0 524.2 4.5 197.0 470.2 32.1 241.0 514.2 10.1 195.0 468.2 34.2 232.5 505.7 14.6 194.0 467.2 34.8 221.0 494.2 20.1 193.0 466.2 35.1 212.0 485.2 23.9 190.5 463.7 37.3 202.5 475.7 27.2 189.5 462.7 38.1 193.0 466.2 38.9 223.5 496.7 50.0 193.0 466.2 39.1 231.0 504.2 53.0 199.0 472.2 41.0 234.5 507.7 54.4 203.5 476.7 42.7 257.0 530.2 65.5 213.0 486.2 45.7 268.5 541.7 72.9 217.0 490.2 47.8 ^a T/K values calculated by the compiler. Note 1 - Measurements at t/°C > 280 not taken due to instability of the melts (authors). Note 2 - Despite the high accuracy of their temperature measurements, the authors chose to tabulate temperatures rounded at 0.5 K	v_{1} v_{2} v
Characteristic point(s): Eutectic, E, at 189.5 °C and $100x_2$ = 38.0 (aut Peritectic, P, at 200.8 °C and $100x_2$ = 28.6 (a Intermediate compound(s): Nac(CHO ₂)/CNS_incongruently melting (authors	hors). uthors).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual method (for details, see Ref. 1). The melts contained in a Pyrex cryostat were cooled at a rate of about 0.25 K/min; the temperatures of initial crystallization were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N potentiometer type K-3. Supplementary DSC measurements were also performed.	Materials of stated purity ≥ 99 % were employed after careful drying.
	ESTIMATED ERROR:
	Temperature: accuracy <u>+</u> 0.05 K (authors).
	REFERENCES:
	(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38 , 116-118.

	1
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium thiocyanate; NaCNS; [540-72-7] 	Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. <u>1974</u> , (10), 84-88.
VARIABLES:	PREPARED BY:
Tomoroturo	Baldini D
	baldini, i.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
255 528 0 235 508 10 210 483 20 182 455 30 186 459 40 215 488 50 240 513 60 259 532 70 280 553 80 295 568 90 308 581 100 ^a T/K values calculated by the compiler. Note - The data tabulated were drawn by the compiler from Fig. 1 of the original paper. Characteristic point(s): Eutectic, E, at 170 °C and $100x_2$ = 36 (authors).	y y y y y y y y
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
DTA. Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules. No other information given.	NaCHO ₂ of analytical purity and "chemically pure" NaCNS, heated 10-15 h at temperatures 50-60 °C below their fusion temperatures, were employed.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium iodide; NaI; [7681-82-5] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. <u>1970</u> , 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini. P.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂ t/°C T/K ^a 100x	2
257.5 530.7 0 243.5 516.7 9. 256.8 530.0 0.42 241.6 514.8 9. 256.3 529.5 0.73 237.7 510.9 12. 255.9 529.1 0.98 234.0 507.2 13. 255.4 528.6 1.34 232.2 505.4 15. 254.7 527.9 1.79 230.0 503.2 15. 254.3 527.5 2.03 236.5 509.7 17. 251.2 524.4 4.02 248.4 521.6 18. 248.3 521.5 6.00 270.9 544.1 20. 244.9 518.1 7.99 306.3 579.5 24. ^a T/K values calculated by the compiler. Note 1 - In the original paper the results were shown in a graphical form. The above listed numerical values represent a personal communication by one of the authors (F., P.) to the compiler. Note 2 - The system could not be investigated above about 300 °C due to the thermal instability of the methanoate. Characteristic point(s): Eutectic, E, at 227.7 °C and $100x_2= 17.25$ (au	00 98 01 99 00 99 99 99 61 260 240 240 0 15 100x ₂ 30 NeCHO ₂ NeI
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP meterials, dried by heating under vacuum.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 0.1 K (compiler).
	REFERENCES:
	<pre>(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u>, 38, 116-118.</pre>

I

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium nitrite; NaNO₂; [7632-00-0] 	Sokolov, N.M. Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.
VARIADLES:	FREFARED DI:
Temperature.	Baldini, P.
EXPERIMENTAL VALUES:	••••••••••••••••••••••••••••••••••••••
$t^{0}C$ T/K^{a} 100 x_{2}	
258 531 0 251 524 5 243 516 10 238 511 15 232 505 20 225 498 25 215 488 30 207 480 35 193 466 40 179 452 45 177 450 50 198 471 55 211 484 60 222 495 65 231 504 70 241 514 75 251 524 80 260 533 85 267 540 90 275 548 95 284 557 100 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 169	$^{\circ}C$ and $100x_2 = 48$ (author).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, $AgNO_3$, Cd, KNO_3 , and $K_2Cr_2O_7$.	"Chemically pure" materials recrystallized from water.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
NOTE:	REFERENCES:
The fusion temperature of component 1 (531 K) is in excellent agreement with the value (530.7+0.5 K) listed in Table 1 of the Preface, where a solid state transition (at 502+5 K), not mentioned by the author, is also reported.	

COMPONENTS:

 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
 Sodium nitrate; NaNO₃; [7631-99-4]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

The system sodium methanoate - sodium nitrate was investigated by Sokolov, 1954 (Ref. 1), Tsindrik, 1958 (Ref. 2), Berchiesi et al., 1972 (Ref. 3), and Storonkin et al., 1974 (Ref. 4).

The liquidus curve drawn on the basis of visual polythermal observations led Sokolov (Ref. 1) to express the opinion that the formation of any intermediate compound was to be excluded, and consequently the system was a eutectic one.

Tsindrik (Ref. 2), who belonged to the same Smolensk Medical Institute (S.M.I.) as Sokolov, re-examined the system (as a side of the composition square of the reciprocal ternary Li, Na/CHO₂, NO₃) using the same method and came to parallel conclusions. Significant discrepancies, however, exist in the trend of the liquidus curves given by either author; and for the coordinates of the eutectic, Tsindrik (Ref. 2) quoted figures (from a paper discussed in 1956 by Sokolov - Ref. 5) which coincide neither with those reported by Sokolov himself in his 1954 paper (Ref. 1) nor with those the evaluator could obtain by plotting Tsindrik's experimental points (Ref. 2).

Berchiesi et al. (Ref. 3), being aware of Sokolov's paper (Ref. 1), found two invariant points: a eutectic and one corresponding to the incongruent melting of the intermediate compound $Na_4(CHO_2)_3NO_3$. They supplemented their visual observations with DSC analysis of four mixtures. In the recorded traces they recognized: for $x_1=0.7926$, "peaks corresponding to the peritectic transition (477 K) and to complete fusion"; for $x_1=0.7312$, "peaks corresponding to the eutectic fusion (464 K), to the peritectic transition (477 K) and to complete fusion"; for $x_1=0.7312$, "peaks corresponding to the eutectic fusion (464 K), to the peritectic transition (477 K) and to complete fusion"; for $x_1=0.6560$, "peaks corresponding to the eutectic fusion and to the peritectic transition"; for $x_1=0.5190$, one "peak corresponding to the eutectic fusion". They could also observe in the composition triangle of the ternary Na/CHO₂, CNS, NO₃ a crystallization region belonging to the binary intermediate compound and covering 5.30 % of the liquidus area.

Storonkin et al. (Ref. 4) employed DTA to investigate the same ternary, and once more found, for the binary system of interest here, just one eutectic although at coordinates different from those reported by Sokolov (Ref. 1) and by Tsindrik (Ref. 2); they also claimed the distribution coefficient of $NaCHO_2$ in $NaNO_3$ to be zero in the nitrate crystallization field. Storonkin et al. (Ref. 4) were apparently aware only of a 1971 paper by Sokolov and Khaitina (Ref. 6), where in turn only Sokolov's 1954 findings (Ref. 1) were quoted.

Finally, it is to be mentioned that the cryometric data of Leonesi et al., 1968 (Ref. 7), proved that the nitrate has no tendency (or at least a negligibly small tendency) to dissolve in the methanoate in the solid state.

In order to evaluate the consistency of the above sets of measurements, the following considerations may be useful.

In any binary system where solid solutions are absent, the branch of the liquidus curve rich in component 1 may often be represented satisfactorily by means of the approximate equation (Ref. 8)

 $T(1) = \{H(1)/R + (A/R)(x_2)^2\} / \{S(1)/R + \ln (x_2)\}$

where A is an empirical constant which of course is zero for ideal systems, and

 $H(1) = \Delta_{fus}(1)H_{m};$ $S(1) = \Delta_{fus}(1)S_{m}.$

When T(1) is between $[T_{fus}(1) \text{ and } T_{trs}(1)]$,

 $\mathbf{H}(1) = \Delta_{fus}(1)\mathbf{H}_{m} + \Delta_{trs}(1)\mathbf{H}_{m}; \qquad S(1) = \Delta_{fus}(1)\mathbf{S}_{m} + \Delta_{trs}(1)\mathbf{S}_{m}.$

Taking now the DSC numerical values listed in Table 3 of the Preface, which concern component 1, i.e. sodium methanoate, one obtains for the ideal behaviour the curve denoted as "ideal" in the Figure of the next page.

EVALUATOR:

Ferloni, P.,

COMPONENTS:

(1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium nitrate; NaNO3; [7631-99-4]

CRITICAL EVALUATION (continued):

For the system K/CHO₂, NO₃ Leonesi et al. (Ref. 7) were able to fit their experimental points fairly well for the branch rich in methanoate, when A/R was assigned the value -175 K. In the present binary, formed with the common cation Na and the same pair of different anions, it seemed not unreasonable to expect analogous behavior. Introducing into Eq. (1) the above $\Delta(1)H_m$ and $\Delta(1)S_m$ values, and again A/R=-175 K, the "real" curve of the Figure is obtained. It can be seen that Berchiesi et al.'s (Ref. 3) points are the closest to whereas progressively this curves, increasing discrepancies are observed for the data of Tsindrik (Ref. 2), Sokolov (Ref. 1), and Storonkin et al. (Ref. 4) (each temperature being corrected in order to make allowance for the differences in the fusion temperatures of the methanoate given by the different authors).

Thus, evaluator is inclined to the recommend (among those available so far) the data by Berchiesi et al. (Ref. 3). The fact that Storonkin et al. (Ref. 4), by employing a DTA technique, where not able to detect the intermediate compound seems rather surprising. This fact, however, might be related to the large supercooling effect found by the latter authors in the region of the ternary eutectic and difficult to prevent also in the region of the binary eutectic. Efficient stirring and slow cooling rate have likely allowed Berchiesi et al. (Ref. 3) to avoid this drawback. The presence of some impurity in Storonkin et al.'s (Ref. 4) methanoate is even possible, inasmuch as their $T_{fus}(1)/K$ value (528) is some 3 K lower than those reported in Ref.s 1 (531), 2 (531), and 3 (530.65), and in Table 3 [530.46+0.04 (adiabatic calorimetry); 530.7+0.5 (DSC)].

REFERENCES:

- (1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Tsindrik, N.M.; Zh. Obshch. Khim. 1958, 28, 830-834.
 (3) Berchiesi, M.A.; Cingolani, A.; Berchiesi, G.; J. Chem. Eng. Data, 1972, 17, 61-64.
 (4) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.
- (5) Sokolov, N.M.; Tezisy Nauch. Konf. S.M.I. 1956a.
- (6) Sokolov, N.M.; Khaitina, M.V.; Zh. Obshch. Khim. 1971, 41, 1417.
- (7) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P.; Ric. Sci. <u>1968</u>, 38, 702.
 (8) Sinistri, C.; Franzosini, P.;Ric. Sci. <u>1963</u>, 33(II-A), 419-430.
 (9) Braghetti, M.; Berchiesi, G.; Franzosini, P.; Ric. Sci. <u>1969</u>, 39, 576.

^a This quotation as given by Tsindrik (Ref. 2) is probaly to be completed as follows: Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. The evaluator did not succeed in obtaining a reprint from the author, but it is highly probable that numerical data are not given in the Tezisy, since such documents usually report only summaries of the discussions held at the pertinent conferences.



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Universita' di Pavia (ITALY).



COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium nitrate; NaNO₃; [7631-99-4] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
258 531 0 252 525 5 242 515 10 232 505 15 214 487 25 206 479 30 198 471 35 192 465 40 188 461 45 186 ^b 459 49 190 463 50 206 479 55 220 493 60 235 508 65 262 535 75 284 557 85 302 575 95 308 581 100 ^a T/K values calculated by the compiler. ^b Eutectic temperature (author). Characteristic point(s): Eutectic, E, at 186 ^o C and 100x ₂ = 49 (author)	v_{1}^{2}
	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.	Component 1 synthetized from methanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]</pre>	Tsindrik, N.M. Zh. Obshch. Khim. <u>1958</u> , 28, 830-834.
NaNo ₂ : $[7631-99-4]$	
3, [
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
	,
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{α} 100 x_2	
258 531 0	
252 525 5	\$ •
236 509 15	
226 499 20 219 492 25	م ³⁰⁰ -
212 485 30	A
204 477 35	المحر
196 469 40 188 461 45	
192 465 50	
210 483 55	کر ہے
226 499 60	
240 513 65	
260 533 75	E
270 543 80	
278 551 85	
298 571 95	0 50 100×2 100
308 581 100	NaCHO ₂ NaNO ₃
^a T/K values calculated by the compiler.	
Characteristic point(s):	
Eutectic, E. at 187 °C and 100 τ = 48 (author	Pof 1)
+ (author;	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; temperatures	Materials of analytical purity twice
measured with a Nichrome-Constantane	recrystallized.
tube, hand-stirred.	transition at t. $(1)/^{\circ}C= 242$ (Ref. 1).
	Component 2 undergoes a solid state
	transition at $t_{trs}(2)/^{o}C=275$ (current
	literature).
	ESTIMATED ERROR:
	····
	(compiler).
	REFERENCES:
	(1) Sokolov, N.M. Tezisy Nauchn. Konf. S.M.I. <u>1956</u> .

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium nitrate; NaNO₃; [7631-99-4] 	Berchiesi,M.A.; Cingolani,A.; Berchiesi,G. J. Chem. Eng. Data, <u>1972</u> , 17, 61-64.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 \mathbf{x}_{2} $t/^{\circ}C$ T/K^{a} 100 \mathbf{x}_{2}	ų –
257.50 530.65 0 205.85 479.00 33.07 249.50 522.65 5.17 204.50 477.65 33.99 242.73 515.88 9.88 203.50 476.65 35.98 237.58 510.73 12.69 202.13 475.28 38.09 234.43 507.58 15.04 201.25 474.40 39.99 231.65 504.80 16.59 199.25 472.40 42.01 229.03 502.18 18.12 195.38 468.53 44.96 226.58 499.73 19.41 193.50 466.65 46.61 223.98 497.13 21.53 195.75 468.90 49.93 221.35 494.50 22.78 200.87 474.02 51.67 219.85 493.00 24.00 208.93 482.08 55.09 217.73 490.88 26.08 220.70 493.85 60.01 215.08 488.23 27.19 243.03 516.18 70.02 213.55 486.70 28.04 263.95 537.10 79.90 213.05 446.20 28.61 284.98 558.13 90.04 210.30 483.45 30.07 306.00 579.15 100.00 207.54 480.69 32.03 a T/K values calculated by the compiler. Characteristic points: Peritectic, P, at 204 Eutectic, E, at 191 °C Intermediate compound: Na4(CH0 ₂) ₃ NO ₃ , incongr	$rac{1}{2}$ $rac{1}{2}$ $rac{1}{2}$ $ ac{1}{2}$ $ ac{1}{2}$ ac
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual method, supplemented by DSC analysis. Salt(s) melted in a Pyrex device (1) put into a furnace whose temperature was controlled by means of a Chromel-Alumel thermocouple connected with a L&N CAT control unit. Temperature of the melt measured with a second thermocouple checked by comparison with a certified Pt resistance thermometer, and a L&N K-5 potentiometer. Stirring by a Chemap Mod.E-1 Vibro-mixer.	C.Erba (Milano,Italy) NaCHO ₂ and NaNO ₃ of stated purity not less than 99% were used after thorough dehydration.
	ESTIMATED ERROR:
	Temperature: accuracy <u>+</u> 0.03 K (authors).
	REFERENCES:
	(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. <u>1968</u> , 38, 116-118.
<pre>213.05 493.00 24.00 208.93 482.08 55.09 217.73 490.88 26.08 220.70 493.85 60.01 213.05 486.23 27.19 243.03 516.18 70.02 213.05 486.20 28.61 284.98 558.13 90.04 210.30 483.45 30.07 306.00 579.15 100.00 207.54 480.69 32.03 a T/K values calculated by the compiler. Characteristic points: Peritectic, P, at 204 C Eutectic, E, at 191 °C Intermediate compound: Na4(CHO₂)₃NO₃, incongru- AUXILLARY II METHOD/APPARATUS/PROCEDURE: Visual method, supplemented by DSC analysis. Salt(s) melted in a Pyrex device (1) put into a furnace whose temperature was controlled by means of a Chromel-Alumel thermocouple connected with a L&N CAT control unit. Temperature of the melt measured with a second thermocouple checked by comparison with a certified Pt resistance thermometer, and a L&N K-5 potentiometer. Stirring by a Chemap Mod.E-1 Vibro-mixer.</pre>	200 - E B C and 100x2= 34.4 (authors). and 100x2= 48.1 (authors). and 100x2= 48.1 (authors). uently melting (authors). NFORMATION SOURCE AND PURITY OF MATERIALS: C.Erba (Milano,Italy) NaCHO2 and NaNO3 of stated purity not less than 99% were used after thorough dehydration. ESTIMATED ERROR: Temperature: accuracy ±0.03 K (authors). REFERENCES: (1) Braghetti,M.; Leonesi,D.; Franzosini,P Ric. Sci. <u>1968</u> , 38, 116-118.

(1) Sodium methanoate (sodium formate);	OKIGINAL MEASUKEMENTS:
NaCHO ₂ ; [141-53-7] (2) Sodium nitrate:	Storonkin, A.V.; Vasil'kova, I.V.; Potemin.S.S.
NaNO ₃ ; [7631-99-4]	Vestn. Leningr. Univ., Fiz., Khim. 1974,
	(10), 84-88.
VARIABLES:	
m	PREPARED BY:
lemperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
255 528 0	· ·
232 505 10 218 491 20	+
202 475 30	300 - 2
190 463 50	
215 488 60	<u>م</u>
234 507 70 252 525 80	250 250
276 549 90	
306 579 100	
^a T/K values calculated by the compiler.	200 - 200 -
Note - The data tabulated were drawn by the compiler from Fig. 1 of the original paper.	E
Characteristic point(s):	$0 50 100 \times 100$
Eutectic, E, at 176 °C and 100 x_2 = 44 (authors). NaCHO ₂ NaNO ₃
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Dut Thomson trittle showson des	
Salt(s) sealed under vacuum in Pyrex	pure" NaNO ₃ , heated 10-15 h at temperatures
ampoules. No other information given.	50-60 ^o C below their fusion temperatures, were employed.
	"Cit cmpic/cut
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
I	1

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Sodium ethanoate (sodium acetate); 	Sokolov, N.M.; Pochtakova, E.I.	
$NaC_{2H_3O_2}$; [127-09-3]	Zh. Obshch. Khim. 1958, 28, 1397-1404.	
NaC ₂ H _c O ₂ : $[137-40-6]$		
3-3-27 (
VARIABLES:	PREPARED BY:	
Temperature.	D'Andrea, G.	
•	-	
EXPERIMENTAL VALUES:		
t/ ^o C T/K ^a 100 x ₂		
331 604 0	ų – – – – – – – – – – – – – – – – – – –	
326 599 5 222 505 10	Ž	
314 587 15		
311 584 20	330%	
307 580 25 303 576 30	2	
301 574 35	9	
298 571 40	<u>م</u>	
299 572 50	De la companya de la comp	
299 572 55	a l	
298 571 60 297 570 65	300	
296 569 70	مصمح	
295 568 75	Ĕ	
293 566 90		
291 564 95	0 50 100×2 100	
295 568 97.5 298 571 100	NaC ₂ H ₃ O ₂ NaC ₃ H ₅ O ₂	
a T/V volume coloulated by the compiler		
The values calculated by the compiler.		
Characteristic point(s): Eutectic, E, at 291	^o C and $100x_2 = 95$ (authors).	
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis.	Component 1: "chemically pure" material; it	
•	undergoes a phase transition at	
NOTE:	t _{trs} (1)/°C= 254 (Ref.1). Component 2: prepared from commercial	
	propanoic acid (distilled before use) and	
The fusion and solid state transition	"chemically pure" sodium carbonate; the	
and 527 K, respectively) agree reasonably	butanol; it undergoes phase transitions at	
with the $T_{fus}(1)$ and $T'_{trs}(1)$ values	t _{trs} (2)/ ^o C= 77, 195, 217, 287 (Ref. 2).	
(601.3+0.5 and 52/+15 K, respectively)		
Concerning component 2, the fusion		
temperature (571 K) looks, on the contrary,	ESTIMATED ERROR:	
to be cast about the reliability of the	Temperature: accuracy probably +2 K	
lowest (350 K) and highest (560 K)	(compiler).	
author from Ref. 2, inasmuch as both DSC	REFERENCES:	
(Table 1) and adiabatic calorimetry (Table 3) proved the occurrence of solid	(1) Bergman, A.G. · Evdokimovo K A	
state transformations only at 491-494 and	Izv. Sektora FizKhim. Anal. 1956, 27,	
467-470 K, respectively.	296-314.	
	Konf. S.M.I. 1956.	
	—	

COMPONENTS	•	
OOUT ON DITTO		

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]

The visual polythermal method was employed by Sokolov (Ref. 1) to study the lower boundary of the isotropic liquid field: the results were subsequently reviewed by Sokolov and Pochtakova (Ref. 2). According to these authors, the [congruently melting at 546 K (273 °C)] intermediate compound Na₅(C₂H₃O₂)₃(C₄H₇O₂)₂ is formed, and two invariants exist, i.e., a eutectic E₁ [at 539 K (266 °C), and $100x_2$ = 33.5], and a eutectic E₂ [at 523 K (250 °C), and $100x_2$ = 691. to these authors, the [congruently melting $100x_2 = 69$].

Component 2, however, forms liquid crystals. Accordingly, the fusion temperature, T_{fus}(2)= 603 K (330 °C), reported in Refs. 1, 2 should be identified with the clearing temperature, $T_{clr}(2)$, of component 2, the corresponding value from Table 1 of the Preface being 600.4+0.2 K.

For the same component, Table 1 of the Preface [besides the $T_{clr}(2)$ value] provides the values 450.4 ± 0.5 , 489.8 ± 0.2 ,

498.3+0.3, and 508.4+0.5 K respectively, for $\overline{T^{1v}}_{trs}(2)$ to $\overline{T^{1}}_{trs}(2)$, and $T_{fus}(2)/K=524.5+0.5$. These phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). Phase transformations are quoted in Ref. 2 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to compare the two intermediate transition temperatures from Ref. 4 with $T^1_{trs}(2)$ and $T_{fus}(2)$ from Table 1 of the Preface. Reasonable doubts can be cast, on the contrary, about the actual existence of Ref. 4 highest and lowest transformations (the former - if present - ought to represent the transformation from one liquid crystalline phase into another).

More recently, Prisyazhnyi et al. (Ref. 5) - to whom Refs. 1, 2 seem to be unknown - carried out a derivatographical re-investigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Their clearing $[T_{clr}(2)=598 \text{ K} (325 \text{ }^{\circ}\text{C})]$ and fusion $[T_{fus}(1)=603 \text{ K} (330 \text{ }^{\circ}\text{C});$ $T_{fus}(2)=527 \text{ K} (254 \text{ }^{\circ}\text{C})]$ temperatures substantially agree with those from Table 1 of the Preface; moreover, it is to be stressed that they do not mention any transition intermediate between T_{clr}(2) and T_{fus}(2). Prisyazhnyi et al.'s, and Sokolov's results (filled and empty circles,

respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals), an inspection of which allows one to state that: (i) the invariant at about $100x_2 = 70$ is actually an M_E point, and (ii) a further characteristic point exists (at about $100x_2 = 80$) which escaped Sokolov's attention, and is probably a minimum, m, in a series of solid solutions. Prisyazhnyi et al.'s results suggest at $0 \leq 100x_1 \leq 60$ a behavior similar to that shown in Scheme A.3 of the Preface.

The two two-phase regions pertinent to the liquid crystal - isotropic liquid equilibria, and to solid solutions formation, respectively, might be so narrow as to have prevented Prisyazhnyi et al. to observe two distinct sets of points in each of these regions, whereas one cannot explain the lack of information by the same authors about eutectic fusion at $60 \leq 100 \mathbf{x}_1 \leq 100$.

REFERENCES:

- Sokolov, N.M.; Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.
 Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. <u>1960</u>, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1429-1433.
- (3) Schiraldi, A.; Chiodelli, G.; J. Phys. E: Sci. Instr. 1977, 10, 596-599.
- (4) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
 (5) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.; Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).



I	<u> </u>					
COMPONENTS:				ORIGINAL MEASUREMENTS:		
(1) Sodium ethanoate (sodium acetate);			etate);	Sokolov, N.M.		
Na Na	^{аС2H3O2} ;	[127-09-	-3]			Zh. Obshch. Khim. 1954, 24, 1581-1593.
(2) SC Na	alum bu aC ₄ H ₇ O ₂ :	156-54	(sodium du -7]	tyrate);	
Į						
VARIA	BLES:					PREPARED BY:
Temper	rature.					D'Andrea, G.
EXPERI	MENTAL	VALUES:				
+/%	T/Va	100-	+ / ⁰ C	т/ка	100-	
	1/1	10012	1/0	17 K	10022	· · [
331	604 592	0	268	541 538	50 55	
309	582	10	260	533	60	Ň d
299	572	15	254	527	65	
290	563	20	250	523	69 70	300 - 5
274	547	30	266	539	75	
266	539	33.5	281	554	80	
268	541 546	35	312	585 597	90 05	Solon /
270	543	45	330	603	100	Ĕ ₁ ^v v _v J
a T/K	va1100	calculate	ad hy the	compile	r.	
1 1/1	VALUES	Carcurate	eu by che	compire		-
Charac	teristi	c point(s	s):			
Eutect	:ic, E _l ,	at 266 9	C and 100	x ₂ = 33.	5 (auth	or).
Eutect	:ic, E ₂ ,	at 250 °	^o C and 100	x ₂ ≈ 69	(author). 0 50 100×2 100
Intermediate compound:						
$Na_5(C_2H_2O_2)_2(C_2H_7O_2)_2$ congruently melting at			lv melt	273 °C.		
						
AUXILIARY 1			AUXI	NFORMATION		
METHOD/APPARATUS/PROCEDURE:				SOURCE AND PURITY OF MATERIALS:		
Visual	L 001	ythermal	analvs	is.	Melts	Component 1: "chemically pure" material.
contai	lned in	a glas	ss tube a	nd sti	rred.	Component 2: prepared by reacting aqueous
Temper	atures	measured	d with a	Nich	rome-	("chemically pure") Na ₂ CO ₃ with a slight
consta scale	ncane milli	voltmeter	uple and a r. The	temper	IUII ature	excess of n-butanoic acid of analytical purity. The solvent and excess acid were
readin	ngs refe	r to the	disappear	ance of	iso-	removed by heating to 160 °C.
tropic	ity in	the melt	on coolin	g•		
ļ						
					ESTIMATED ERROR:	
						Temperature: accuracy probably +2 K
						(compiler).
						REFERENCES:
1						
1						

<pre>COMPONENTS: (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]</pre>	ORIGINAL MEASUREMENTS: Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1429-1433.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES: Characteristic point(s): Eutectic, E ₁ , at 266 $^{\circ}$ C and $100x_2$ = 33.5 (auth Eutectic, E ₂ , at 250 $^{\circ}$ C and $100x_2$ = 69 (author Intermediate compound(s): Na ₅ (C ₂ H ₃ O ₂) ₃ (C ₄ H ₇ O ₂) ₂ , congruently melting at	nors). rs). = 273 °C.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: "chemically pure" material recrystallized; it undergoes a phase transition at $t_{trg}(1)/^{\circ}C=254$ (Ref. 1), and melts at $t_{fug}(1)/^{\circ}C=331$. Component 2: prepared by reacting NaHCO ₃ with n-butanoic acid, and recrystallized from n-butanol (Ref. 2, where, however, carbonate insted of hydrogen carbonate was employed; compiler); it undergoes phase transitions at $t_{trg}(2)/^{\circ}C=117$, 232, 252, 316 (Ref. 3), and melts at $t_{fug}(2)/^{\circ}C=330$. ESTIMATED ERROR:
REFERENCES :	Temperature: accuracy probably +9 K
 Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal. <u>1956</u>, 27 296-314. Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. 	(compiler).

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]</pre>	Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler from Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).	
Characteristic point(s): Eutectic, E, at about 268 °C and $100x_1$ about Minimum, m, at about 245 °C and $100x_1$ about 2 Invariant point, M' _E , at about 250 °C and 100 Intermediate compound(s): Na ₅ (C ₂ H ₃ O ₂) ₃ (C ₄ H ₇ O ₂) ₂ , congruently melting at	NaC ₄ H ₇ O ₂ NaC ₂ H ₃ O ₂ 65 (compiler). (compiler). NaC ₄ H ₇ O ₂ NaC ₂ H ₃ O ₂ NaC ₄ H ₇ O ₂ NaC ₂ H ₃ O ₂ (compiler). (about 273 ^O C (compiler).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6-8 K min ⁻¹ , and using $Al_{2}O_{3}$ as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase.	Not stated. Component 1: $t_{fus}(1)/{}^{o}C$ about 329 (compiler). Component 2: $t_{fus}(2)/{}^{o}C$ about 254; $t_{clr}(2)/{}^{o}C$ about 325 (compiler).
	ESTIMATED ERROR:
	Temperature: accuracy not evaluable (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium iso-butanoate (sodium iso-butyrate); Nai-C₄H₇O₂; [996-30-5] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
<pre>331 604 0 323 596 5 314 587 10 305 578 15 297 570 20 288 561 25 277 550 30 265 538 35 254 527 40 242 515 45 230 503 50 218 491 55 208 481 58 215 488 60 226 499 65 236 509 70 242 515 75 246 519 80 250 523 85 254 527 90 257 530 95 260 533 100 a T/K values calculated by the compiler. Characteristic point: Eutectic, E, at 208 °C</pre>	and $100x_2 = 58$ (author).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of iso.butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:	
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).	
CRITICAL EVALUATION:		
This system was studied only by Pochtakova (Ref. 1), who claimed the existence of: (1) a eutectic, E_1 , at 537 K (264 $^{\circ}$ C) and $100x_2$ = 31.5; (11) a eutectic, E_2 , at 526 K (253 $^{\circ}$ C) and $100x_2$ = 54; and (111) an intermediate compound, $Na_3(C_2H_3O_2)_2C_5H_9O_2$, congruently melting at 541 K (268 $^{\circ}$ C).		
Component 2, however, forms liquid crystals. Therefore, the fusion temperature reported in Ref. 1, $T_{fug}(2) = 630$ K (357 °C), has to be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(2) = 631+4$ K. This Table provides also $T_{fug}(2) = 498+2$ K, a figure which can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Pochtakova from Ref. 2. For the same component, Table 1 of the Preface reports no solid state transition, whereas Pochtakova quotes (from Ref. 2) $T_{trs}(2)/K = 482$ and 453. It is, however, to be stressed that the single transition		
observed (at 479+1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 3) was no		

Concerning component 1, the fusion temperature, $T_{fus}(1) = 604 \text{ K} (331 \text{ }^{\circ}\text{C}; \text{ Ref. 1})$, is reasonably identified with the corresponding value from Table 1 of the Preface, viz., $601.3\pm0.5 \text{ K}$. Allowance being made for the remarkable discrepancy, one might also connect the phase transition quoted from Ref. 2 and occurring at 511 K (238 $^{\circ}\text{C}$) with that at 527±15 K reported in Table 1 of the Preface. No reasonable correspondence, however, can be hazarded between the other T_{trs} values quoted from Ref. 2 [viz., 403 K (130 $^{\circ}\text{C}$), 391 K (118 $^{\circ}\text{C}$), and 331 K (58 $^{\circ}\text{C}$)] and the superambient T_{trs} 's given in Table 1.

more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

On the basis of the available data, the phase diagram of this system could be supposed to be similar to that shown in Scheme D.1 of the Preface, Pochtakova's eutectic E_2 being intended as an M'_E point.

REFERENCES:

- (1) Pochtakova, E.I. Zh. Obshch. Khim. <u>1966</u>, 36, 3-8.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A322, 281-299.
- (4) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II <u>1972</u>, 1879-1881.



COM	DON	E MTC	
GUPL	EON	LIN LO	

 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
 Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Sokolov (Ref. 1), and by Pochtakova (Ref. 2) who reviewed Sokolov's results. Both of them suggested the phase diagram to be of the eutectic type, with the invariant point at either 429 K (156 °C) and $100x_2$ = 73 (Ref. 1), or 433 K (160 °C) and $100x_2$ = 80.0 (Ref. 2).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(2)=535$ K (262 °C; Ref. 1) or 533 K (260 °C; Ref. 2), should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{clr}(2)=559\pm1$ K. The remarkable discrepancy between the latter value and the former ones might be attributed to some impurity in the samples of the Russian authors, inasmuch as the value from Table 2 meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

For the same component, Pochtakova quotes from Ref. 5 two phase transition temperatures, viz., 451 K (178 °C), and 425 K (152 °C). The higher one can be reasonably identified with the actual fusion temperature, and compared with the value $T_{fus}(2)=461.5\pm0.6$ K reported in Table 2 of the Preface, whereas the lower one has no correspondence in the same Table.

Both authors report $T_{fus}(1) = 604$ K (331 °C; Ref.s 1, 2), which may be satisfactorily identified with the value from Table 1 of the Preface, viz., 601.3 ± 0.5 K. Allowance being made for the discrepancy, one might also connect the phase transition quoted (by Pochtakova) from Ref. 5 as occurring at 511 K (238 °C), with that at 527\pm15 K reported in Table 1. No reasonable correspondence, however, can be hazarded between the other T_{trs} values quoted by Pochtakova from Ref. 5 [viz., 403 K (130 °C), 391 K (118 °C), and 331 K (58 °C)] and the superambient T_{trs} 's given in Table 1.

Taking into account the available experimental data, one may suggest that the phase diagram of this system should not be far from those shown either in Scheme A.1, or in Scheme A.3 of the Preface, the eutectic being actually intended as an M_{E} point.

REFERENCES:

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.
- (2) Pochtakova, E.I.
 Zh. Obshch. Khim. <u>1963</u>, 33, 342-347.
- (3) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A 322, 281-299.
- (5) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS	OPTOTNAL MEASUREMENTS.
<pre>(1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium iso.pentanoate (sodium iso.valerate);</pre>	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
Na1. $C_5H_9O_2$; [539-66-2]	
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2}$	
331 604 0 320 593 5 311 584 10 304 577 15 295 568 20 287 560 25 280 553 30 269 542 35 260 533 40 248 521 45 232 505 50 215 488 55 199 472 60 184 457 65 166 439 70 156 429 73 163 436 75 185 458 80 207 480 85 228 501 90 247 520 95 262 535 100 a T/K values calculated by the compiler.	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE: Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	SOURCE AND FURITY OF MATERIALS: Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of iso.pentanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.
	ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler).
	KEFEKENCES:



COMPONENTS:	EVALUATOR:
 Sodium ethanoate (sodium acetate);	Ferloni, P.,
NaC ₂ H ₃ O ₂ ; [127-09-3] Sodium hexanoate (sodium caproate);	Dipartimento di Chimica Fisica,
NaC ₆ H ₁₁ O ₂ ; [10051-44-2]	Universita ⁻ di Pavia (ITALY).

This system was studied by Sokolov (Ref. 1), and by Pochtakova (Ref. 2). The former author claims the existence of two eutectics $[E_1, \text{ at } 541 \text{ K} (268 ^{\circ}\text{C}) \text{ and } 100x_2= 34.5; E_2, \text{ at } 533 \text{ K} (260 ^{\circ}\text{C}) \text{ and } 100x_2= 49.5], \text{ and of the intermediate compound Na}_8(C_2H_3O_2)_5(C_6H_{11}O_2)_3$, which congruently melts at 543 K (270 $^{\circ}\text{C}$). The latter author claims in turn the existence of a eutectic [at 546 K (273 $^{\circ}\text{C}$) and $100x_2= 48.5$], the incongruently melting compound Na}_5(C_2H_3O_2)_4C_6H_{11}O_2, and a "perekhodnaya tochka" [at 550 K (277 $^{\circ}\text{C}$) and $100x_2= 34.0$].

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(2) = 638 \text{ K} (365 ^{\circ}\text{C}; \text{Ref.s 1, 2})$, should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(2) = 639.0 \pm 0.5 \text{ K}$. The transition temperature $T_{trs}(2) = 499 \text{ K} (226 ^{\circ}\text{C})$ quoted by Pochtakova from Ref. 3 has in turn to be intended as the fusion temperature, the corresponding value from Table 1 being 499.6 + 0.6 K.

The following point also deserves attention. Two more transitions are quoted in Ref. 2 from Ref. 3 as occurring in component 2 at 615 K ($342 \, {}^{\rm O}$ C) and 476 K ($203 \, {}^{\rm O}$ C), respectively. The latter agrees with that reported at 473+2 K in Table 1, whereas no evidence was obtained by subsequent investigators (Ref. 4) for a transition comparable with the former one: should it exist, it might mean that two different mesomorphic phases are present in sodium hexanoate.

As for component 1, Sokolov and Pochtakova report $T_{fus}(1) = 603 \text{ K} (330 \text{ }^{\circ}\text{C})$ and 604 K (331 $^{\circ}\text{C}$), respectively, i.e., values which favorably meet that from Table 1 (601.3±0.5 K). For the same component, Pochtakova quotes from Ref. 3 a few other phase transition temperatures, viz., 511 K (238 $^{\circ}\text{C}$), 403 K (130 $^{\circ}\text{C}$), 391 K (118 $^{\circ}\text{C}$), and 331 K (58 $^{\circ}\text{C}$), of which only the first one finds some correspondence with one of the T_{trs} values from Table 1, i.e., T_{trs}^{-} 527±15 K.

In conclusion, either author's suggestions for the phase diagram require modifications. Indeed, the invariant occurring at 533 K and $100\mathbf{x}_2$ = 49.5 (Ref. 1), or at 546 K and $100\mathbf{x}_2$ = 48.5 (Ref. 2), should likely be identified with an M_E^{-} point, the actual coordinates of which, however, should be verified with better accuracy. Moreover, the composition of the intermediate compound and the nature of the second invariant are not sufficiently supported by the available data, and need as well a further investigation, e.g., by DSC or DTA.

REFERENCES:

(1)	Sokolov, N.M.	•				
	Zh. Obshch. I	Khim.	1954,	24,	1581-1593.	
(2)	Pochtakova, 1	E.I.				

Pergamon Press, Oxford, 1980, 29-115.

- Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1959, 29, 3149-3154.
- (3) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. (4) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors),

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t^{\circ}C$ T/K ^a 100x ₂ t/°C T/K ^a 100x ₂	
331 604 0 260 533 49.5 321 594 5 265 538 50 312 585 10 300 573 55 304 577 15 321 594 60 296 569 20 332 605 65 288 561 25 342 615 70 279 552 30 349 622 75 268 541 34.5 353 626 80 269 542 35 360 633 90 269 542 40 363 636 95 265 538 45 365 638 100 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E_1 , at 268 °C and $100x_2$ = 34.5 (auth Eutectic, E_2 , at 260 °C and $100x_2$ = 49.5 (auth Intermediate compound(s): Nac(CalleO2)c(Ccll+02)c (author), congruently	or). $r = 1 \text{ ting at } 270^{\circ}\text{C} \text{ (complicit)}.$
	ΝΕΩΡΜΑΤΤΩΝ
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of n-hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

1	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 	Pochtakova, E.I. Zh. Obshch. Khim. <u>1959</u> , 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1959</u> , 29, 3149-3154.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure).	
Characteristic point(s):	
Eutectic, E at 273 °C and 100x ₂ = 48.5 (author). Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction), at 277 °C and 100x ₂ = 34.0.	
Intermediate compound:	
$Na_5(C_2H_3O_2)_4C_6H_{11}O_2$ incongruently melting. (the composition is approximate).	
	0
	2 218
	P E
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	"Chemically pure" $NaC_2H_3O_2$ and $NaC_6H_{11}O_2$ prepared by reacting Na_2CO_3 with n-hexanoic acid (Ref. 1). Component 1 undergoes phase transitions at $t_{trs}(1)/^{o}C=$ 58, 118, 130, 238 (Ref. 2). Component 2 undergoes phase transitions at $t_{trs}(2)/^{o}C=$ 203, 226, 342 (Ref. 2).
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium benzoate; NaC₇H₅O₂; [532-32-1] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100 x₂	· · · · · · · · · · · · · · · · · · ·
<pre>331 604 0 315 588 2.6 350 623 5 380 653 10 400 673 15 411 684 20 421 694 25 428 701 30 431 704 33 465 738 100 ^a T/K values calculated by the compiler.</pre>	$\begin{array}{c} & & \\$
Eutectic. E. at 315 °C and 100 x_{0} = 2.6 (author).
Note - The system was investigated at $0 \le 10$ benzoate.	$0\mathbf{x}_2 \leq 33$ due to thermal instability of the
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter . The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	"Chemically pure" materials.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	1
<u></u>	1
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium chloride; NaCl; [7647-14-5] 	Il [*] yasov, I.I.; Bergman, A.G. Zh. Obshch. Khim. <u>1960</u> , 30, 355-358.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
328 601 0 328 601 2.5 328 601 5.0 328 601 7.0 328 601 10.0 368 641 12.5 398 671 15.0 427 700 17.5 ^a T/K values calculated by the compiler.	400 350 0 10 100x ₂ 20 NaC H 0 NaC H 0
Characteristic point(s):	
Eutectic, E. at 328 $^{\circ}$ C and 100x ₀ = 10 (authors	
Note - The system was investigated at $0 \leq component 1$.	$100x_2 \leq 17.5$ due to thermal instability of
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple and a millivoltmeter.	Not stated.
NOTE: See the NOTE relevant to the investigation by Piantoni et al. (Ref. 1) on the same system (next Table).	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES: (1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., <u>1968</u> , 38 , 127-132.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium chloride; NaCl; [7647-14-5] 	Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., <u>1968</u> , 38, 127-132.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{1} t/^{o}C T/K^{a} 100x_{1}$	
328.1 601.3 100 323.9 597.1 97.2 327.4 600.6 99.5 323.4 596.6 97.1 327.0 600.2 99.3 323.7 596.9 97.0 326.5 599.7 98.9 323.8 597.0 96.9 326.1 599.3 98.7 322.0 595.2 96.0 326.0 599.2 98.5 322.1 595.3 95.7 325.9 599.1 98.5 321.4 594.6 95.2 325.4 598.6 98.3 321.2 594.4 95.0 325.3 598.5 98.1 327.4 600.6 94.0 325.0 598.2 97.9 332.5 605.7 93.9 324.8 598.0 97.8 338.9 612.1 93.6 a T/K values calculated by the compiler. The system was investigated at $0 \le 100x_2 \le 6$. Characteristic point(s): Eutectic, E, at 320.1 ^o C and $100x_1 = 94.3$ (aut Note - In the original paper the results w listed numerical values represent a private c to the compiler.	330 - 4 $330 - 4$ $320 - 4$ $320 - 4$ 92 92 95 $NaCl NaC2H3O2 hors). ere shown in graphical form. The above ommunication by one of the authors (F., P.)$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP materials, dried by heating under vacuum.
NOTE:	ESTIMATED ERROR:
The authors discuss their own results in comparison with both the expected ideal	Temperature: accuracy probably <u>+</u> 0.1 K.
penaviour of the molten mixtures and the previous data from Ref. 1. They observed that the liquidus branch richard a calum	REFERENCES:
chloride is not far from ideality.	(1) Il'yasov. I.I.; Bergman, A.G. Zh. Obshch. Khim. <u>1960</u> , 30 , 355-358.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium thiocyanate; NaCNS; [540-72-7] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
<pre>331 604 0 326 599 5 320 593 10 313 586 15 302 575 25 295 568 30 287 560 35 278 551 40 268 541 45 256 529 50 244 517 54.5 245 518 55 258 531 60 266 539 65 282 555 75 302 575 90 311 584 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 244 °C and 100x₂= 54.5 (authors)</pre>	r).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter (17 mV full scale) with mirror reading.	Component 1 synthetized from ethanoic acid and NaHCO3. Component 2 of analytical purity recrystallized once from water and once from ethanol.
NOTE:	ESTIMATED ERROR:
See the NOTE attached to the investigation by Storonkin et al. (Ref.1) on the same system.	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	 (1) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Sodium ethanoate (sodium acetate);	Golubeva, M.S.; Aleshkina, N.N.; Bergman,	
$NaC_{2}H_{3}O_{2}; [127-09-3]$	A.G. Zh. Neorg Khim. 1959 & 2606-2610, Pugg.	
NaCNS; [540-72-7]	J. Inorg. Chem., Engl. Transl., <u>1959</u> , 4,	
	1201-1203 (*).	
VARIABLES:	PREPARED BY:	
Temperature.	D'Andrea, G.	
EXPERIMENTAL VALUES:		
The results are reported only in graphical form (see figure).		
<u>ں</u>		
308	326	
	N N N	
E		
0 100	X ₁ 100	
NaCNS	$NaC_2H_3O_2$	
Characteristic point(s):		
Eutectic, E, at 236 °C and $100x_1 = 44.5$ (authorized)	ors).	
AUXILIARY INFORMATION		
	SOURCE AND DURITY OF MATERIALS.	
MINOD/ MINKATOS/TROOLDOKE.	SUBRE AND FORTH OF MATERIALS.	
Visual observation of fusion of the salt	Materials of analytical purity twice	
surrounded by a wider tube to secure a more	recrystallized.	
uniform heating. Temperatures measured with		
a chromel-Alumei thermocouple.		
NOTE:	ESTIMATED ERROR:	
See the NOTE attached to the investigation by Storonkin et al. (Ref.1) on the same	Temperature: accuracy probably +2 K (compiler).	
abrem (see fortowing TADIG).	REFERENCES :	
	(1) Storonkin, A.V.: Vasil'kova, T.V.:	
	Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. <u>1974</u> , (16), 73-76.	

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium ethanoate (sodium acetate);	Storonkin, A.V.; Vasil'kova, I.V.; Potemin,
$\begin{bmatrix} \text{NaC}_{2H_3U_2}; [127-09-3] \\ (2) \text{ Sodium thiographic:} \end{bmatrix}$	S.S. Vesta Leningr, Univ. Fiz. Khim, 1974
NaCNS; [540-72-7]	(16), 73-76.
	DEPAREN BY.
VARIABLES:	FREFARED DI:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 π_{2}	
328 601 0	
314 587 10	
298 571 20	Ŕ
264 537 40	
245 518 50	300 - 7
260 533 70	
278 551 80	_ کر ``
293 566 90 308 581 100	
a T/K values calculated by the compiler.	250
Note - The tabulated data ware drawn by the	
compiler from Fig. 1 of the original paper.	E
	2'3'2
Characteristic point(s).	
Eutectic, E, at 234 $^{\circ}$ C and $100x_2 = 55$ (authors	()•
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Salt(s) sealed under vacuum in Pyrex	"chemically pure" NaCNS, heated 10-15 h at
ampoules.	temperatures 50-60 ^o C below their fusion
No other information given.	temperatures, were employed.
NOTE:	ESTIMATED ERROR:
This binary was also submitted to viewal	Temperature: accuracy probably +2 K
polythermal analysis by Sokolov (Ref. 1),	(compiler).
and Golubeva et al. (Ref. 2). The eutectic	
$(100x_{7}=55)$ fairly agrees with those	(1) Sokolov. N.M.
reported both in Ref. 1 (54.5) and Ref. 2	Zh. Obshch. Khim. 1954, 24, 1150-1156.
(55.5). Sokolov's eutectic temperature	(2) Golubeva, M.S.; Aleshkina, N.N.; Bergman A.G.;
higher than those given both by Storonkin	Zh. Neorg. Khim. 1959, 4, 2606-2610;
et al. (507 K) and Golubeva et al. (509 K; Ref. 2).	Russ. J. Inorg. Chem. (Engl. Transl.)
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium iodide; NaI; [7681-82-5] 	Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. <u>1958</u> , No. 3, 413-416.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₁	
337 610 100	
336 609 97.9	
326 599 92.1	þ.
324 597 87.5	250
320 593 84.5	350 - 7
311 584 77.8	
312 585 76.3	الممر ا
326 599 74.2	
360 633 68.3	
^a T/K values calculated by the compiler.	310
	E
	50 80 100 H
	•••
Note - The system was investigated at $100 \ge 1$	$00x_1 \ge 68.3.$
Characteristic point(s):	
Eutectic, E, at 310 °C and $100x_2 = 23$.	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated.
	Component 1 undergoes a phase transition at
	$t_{trs}(1)/^{\circ}C = 32b$. Component 2 melts at t_{c} (1)/ $^{\circ}C = 670$.
	fus(1)/ o of ot
1	<u></u>
NOTE:	ESTIMATED ERROR:
See the NOTE relevant to the investigation by Piantoni et al. (Ref. 1) on the same	Temperature: accuracy probably <u>+</u> 2 K (compiler).
system.	REFERENCES:
	 (1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., <u>1968</u>, 38, 127-132.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium iodide; NaI; [7681-82-5] 	Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., <u>1968</u> , 38 , 127-132.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{1} t/^{\circ}C T/K^{a} 100x_{1}$	
328.1601.3100315.3588.587.0327.7600.999.6313.6586.885.2327.0600.298.9312.6585.884.2326.4599.698.4311.1584.382.6325.8599.097.8310.2583.481.8325.2598.497.3309.8583.081.4324.9598.197.0308.2581.479.7325.0598.296.9306.5579.778.5324.8598.096.9306.1579.377.5323.6596.895.5307.4580.676.1322.1595.393.8311.8585.075.7318.9592.190.4318.4591.675.0aT/K values calculated by the compiler.Note 1 - In the original paper the resultswere shown in graphical form. The above1isted numerical values represent a privatecommunication by one of the authors (F., P.) to the compiler.Note 2 - The system was investigated at $0 \leq 100x_2 \leq 25.$	$ \frac{1}{320} + \frac{1}{100} + 1$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.	C. Erba RP materials, dried by heating under vacuum.
NOTE:	ESTIMATED ERROR:
The authors discuss their own results in comparison with both the expected ideal behaviour of the molten mixtures and the	Temperature: accuracy probably <u>+</u> 0.1 K.
previous data from Kef.s I and 2. They observed that the liquidus branch richer in sodium iodide is not far from ideality.	 KEFERENCES: (1) Il'yasov. I.I.; Bergman, A.G. Zh. Obshch. Khim. 1961, 31, 368-370. (2) Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. 1 Khim. Tekhnol. <u>1958</u>, No. 3, 413-416.

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COMPONENTS: (1) Sodium ethanoate (sodium acetate); NaC ₂ H ₃ O ₂ ; [127-09-3] (2) Sodium nitrite; NaNO ₂ ; [7632-00-0]	ORIGINAL MEASUREMENTS: Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
$t/^{\circ}C$ T/K^{a} 100 x_{1}	
278 551 0	
275 548 4.6	÷ d
259 532 15.5	
247 520 23.0	
237 510 28.1	270 - 2
228 501 33.0	
236 509 37.2	
240 513 39.3	
258 531 46.9	
265 538 49.4	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
276 549 55.0	220 F E -
287 560 61.3	
297 570 68.0	L1
^a T/K values calculated by the compiler.	$\begin{array}{cccc} 0 & 40 & 100 \times_1 & 80 \\ NaNO_2 & NaC_2H_3O_2 \end{array}$
Characteristic point(s):	
Eutectic, E, at 224 ^o C and $100x_1 = 34$ (authors).
Note - The system was investigated at 0 \leq 100	$\mathbf{x}_1 \leq 68.$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual notythermal analysis, the	Component 1: "chemically ours"
temperatures of initial crystallization	NaC ₂ H ₂ O ₂ .3H ₂ O dried to constant mass; it
were measured with a Nichrome-Constantane	undergoes a phase transition at
thermocouple and a 17 mV full-scale	$t_{rrs}(1)/C = 254$ and fusion at $t_{fus}(1)/C = 254$
millivoitmeter.	Component 2: source not stated.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
NOTE :	REFERENCES:
Concerning component 1. the fusion (599 K)	(1) Sokolov, N.M.
and solid state transition (527 K)	Zh. Obshch. Khim. 1957,27, 840-844(*);
temperatures can be identified respectively with the T_{-} (1) (601 340 5 %) and T_{-} (1)	Russ. J. Gen. Chem. (Engl. Transl.)
(527+15 K) values listed in Preface. Table	(2) Sokolov, N.M.: Tsindrik. N.M.:
1. The coordinates of the eutectic (497 K	Khaitina, M.V.
and $100x_2 = 66$) are in reasonable agreement	Zh. Neorg. Khim. 1970, 15, 852-855;
with those reported by both Sokolov (500- 501 K) and $100x_0 = 65$: Ref. 1), and Sokolov	Kuss. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).
et al. (499 K) and 100x2= 65; Ref. 2).	
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrite; NaNO₂; [7632-00-0] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1957</u> , 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1957</u> , 27, 917-920.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
<pre>331 604 0 327 600 5 322 595 10 315 588 15 306 579 20 299 572 25 292 565 30 285 558 35 279 552 40 269 542 45 259 532 50 248 521 55 237 510 60 228 501 65 237 510 70 243 516 75 249 522 80 258 531 85 266 539 90 275 548 95 284 557 100 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 227 228 °C (according to the above tabulated data</pre>	$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, $AgNO_3$, Cd, KNO_3 , and $K_2Cr_2O_7$.	"Chemically pure" materials recrystallized from water. ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler).
NOTE: The fusion temperature (604 K) of component 1 can be identified with the $T_{fus}(1)$ value (601.3+0.5 K) listed in Preface, Table 1. The coordinates of the eutectic (500-501 K and $100x_2$ = 65) are in reasonable agreement with those reported by both Bergman and Evdokimova (497 K and $100x_2$ = 66; Ref. 1), and by Sokolov et al. (499 K and $100x_2$ = 65; Ref. 2).	 REFERENCES: (1) Bergman, A.G. Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956,27,296-314. (2) Sokolov, N.M.; Tsindrik, N.M.; Khaitina, M.V.; Zh. Neorg. Khim. 1970, 15, 852-855; Russ. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrite; NaNO₂; [7632-00-0] 	Sokolov, N.M.; Tsindrik, N.M.; Khaitina, M.V. Zh. Neorg. Khim. 1970, 15, 852-855; Russ. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).
VARIABLES: Temperature.	PREPARED BY:
	D'Andrea, G.
EXPERIMENTAL VALUES: The results are given only in graphical form (see figure).	
Characteristic point(s):	I
Eutectic, E, at 226 $^{\circ}$ C and $100x_2 = 65$ (authors).	t/.c
formed as far as 100x ₂ = 15.	³³⁰
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis supplemented with differential thermal analysis. ESTIMATED ERROR: Temperature: accuracy probably <u>+2</u> K (compiler). NOTE:	Not stated. Component 1 undergoes phase transitions at $t_{trs}(1)/{}^{o}C= 58$, 118, 180, 288 (Ref. 1; the figures 180, 288 are most probably misprints, inasmuch as the same authors quoting the same source report 130, 238 in several other papers; compiler). Component 2 undergoes a phase transition at $t_{trs}(2)/{}^{o}C= 170$ (Ref. 2).
Concerning component 1: (1) the fusion temperature (603 K) can be identified with the $T_{fus}(1)$ value (601.3+0.5 K) listed in Preface Table 1; and (11) among the solid state transition temperatures (331, 391, 403, and 511 K) quoted by the authors from Ref. 1, only the third and fourth ones find some correspondence in the T_{trs} values listed in Table 1. The coordinates of the	 REFERENCES: (1) Sokolov, N.M.; Tezisy Dokl. X Nauch- Konf. S.M.I. 1956. (2) Bergman, A.G.; Berul', S.I.; Izv. Sektora FizKhim.Anal.1958,21,178-183. (3) Bergman, A.G. Evdokimova, K.A.; Izv. Sektora FizKhim. Anal., Inst.

COMPONENTS:	EVALUATOR:
 Sodium ethanoate (sodium acetate);	Ferloni, P.,
NaC ₂ H ₃ O ₂ ; [127-09-3] Sodium nitrate;	Dipartimento di Chimica Fisica,
NaNO ₃ ; [7631-99-4]	Universita ⁻ di Pavia (ITALY).

The system $Na/C_2H_3O_2$, NO_3 was studied by Sokolov (Ref. 1), Bergman and Evdokimova (as a side of the reciprocal ternary K, $Na/C_2H_3O_2$, NO_3 ; Ref. 2), Diogenov (as a side of the reciprocal ternary Li, $Na/C_2H_3O_2$, NO_3 ; Ref. 2), Gimel'shtein and Diogenov (as a side of the reciprocal ternary Cs, $Na/C_2H_3O_2$, NO_3 ; Ref. 4), Storonkin et al. (as a side of the ternary $Na/C_2H_3O_2$, CNS, NO_3 ; Ref. 5), and Diogenov and Chumakova (as a side of the reciprocal ternary K, $Na/C_2H_3O_2$, NO_3 ; Ref. 6). The visual polythermal analysis, and DTA were employed in Ref.s 1-4 and 6, and in Ref. 5, respectively; moreover, in Ref. 4, X-ray diffraction patterns were taken on some compositions.

The fusion temperature of component 1 should be 604, 599, 610, 600, 601, and 599 K according to Ref.s 1,2,3,4,5, and 6, respectively, the corresponding value listed in Preface, Table 1 being 601.3 ± 0.5 K. For the same component, a solid state transition is reported by Ref.s 2, 3, and 4. The transition temperatures given by Ref.s 2 and 4 (527 and 543 K, respectively) can be identified with the $T_{trs}(1)$ value (527±15 K) listed in Table 1 of the Preface, whereas no reliability is to be attached to Diogenov's figures (596 K; Ref.3) which has no correspondence in Table 1, and, moreover, was not confirmed in subsequent investigations by the same group (Ref. 4).

Diogenov (Ref. 3) claimed the existence of two intermediate compounds, i.e.: (1) Na₃ $(C_2H_3O_2)_2NO_3$, incongruently melting, with a peritectic at 539 K and $100x_2$ ⁼ 38.5; and (11) Na₅ $C_2H_3O_2(NO_3)_4$, congruently melting, with a distectic at 545 K. In the evaluator's opinion, however, the discontinuities Diogenov (Ref. 3) found on either branch of his liquidus are relevant rather to the occurrence of solid state transitions in either component, than to the formation of any intermediate compound. In fact, in their reinvestigations of the binary Na/C₂H₃O₂, NO₃ neither Gimel'shtein and Diogenov (who supplemented their visual observations with some X-ray diffraction patterns; Ref. 4), nor Diogenov and Chumakova (Ref. 6) could confirm Diogenov's former point.

Therefore, the system can be safely classified as of the eutectic type, with the invariant at 494+4 K and $100x_2$ at about 58.

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
- Bergman, A.G.; Evdokimova, K.A.
 Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
- (3) Diogenov, G.G.
 Zh. Neorg. Khim. <u>1956</u>, 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1956</u>, 1 (4), 199-205.
- (4) Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., <u>1966</u>, 27, 69-75.
- (5) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. <u>1974</u>, (16), 73-76.
- (6) Diogenov, G.G.; Chumakova, V.P. Fiz.-Khim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u>, 7-12.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); 	
$NaC_{2H_{3}O_{2}}$; [127-09-3]	Sokolov, N.M.
NaNo ₂ : $[7631-99-4]$	ZII. Obsilett. KIIM. <u>1994</u> , 24, 1190–1190.
57	
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
	· · · · · · · · · · · · · · · · · · ·
EXPERIMENTAL VALUES:	
$t/C T/K^{\alpha} 100x_2$	
331 604 0	پ [
328 601 5 324 597 10	
318 591 15	
304 577 25	
296 569 30 286 550 35	300 - 8 7-1
276 549 40	
263 536 45	
247 520 50	
224 497 58	
231 504 60	
242 515 65	ξ
284 557 85	8
304 577 95	E
308 581 100	L
^a T/K values calculated by the compiler.	$\begin{array}{cccc} 0 & 50 & 100 \\ \text{NaCH} & 0 & \text{NaNO} \end{array}$
Characteristic point(s):	2 3 2 3
Eutectic, E, at 224 °C and $100x_2$ 58 (author)	•
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1 synthetized from ethanoic acid
Salt(s) melted in a test tube. Temperature	and NaHCO3. Commercial component 2 further
measured with a Nichrome-Constantane	purified by the author according to Laiti.
mirror reading to 17 mV.	
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	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrate; NaNO₃; [7631-99-4] 	Bergman, A.G.; Evdokimova, K.A. Izv. Sektora FizKhim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	+
$t/^{\circ}C$ T/K ^a 100x ₂ $t/^{\circ}C$ T/K ^a 100x ₂	
326 599 0 235 508 62.3 323 596 3.3 248 521 67.1 317 590 8.0 258 531 71.2 312 585 11.9 264 537 74.7 308 581 16.2 271 544 76.8 300 573 20.7 276 549 79.6 293 566 25.2 281 554 82.4 285 558 29.8 287 560 85.2 279 552 34.2 293 566 88.0 268 541 39.1 298 571 90.4 258 531 44.0 303 576 94.3 241 514 50.7 304 577 97.0 226 499 56.8 308 581 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 222 °C and $100x_2$ 58 (authors)	$s). \qquad 0 \qquad 50 100 \\ NaC_2H_3O_2 \qquad NaNO_3$
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis: the temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple and a 17 mV full-scale millivoltmeter.	Component 1: "chemically pure" NaC ₂ H ₃ O ₂ .3H ₂ O dried to constant mass; it undergoes a phase transition at $t_{trs}(1)/^{0}C= 254$. Component 2: source not stated; it undergoes a phase transition at $t_{trs}(2)/^{0}C= 275$ (Ref. 1).
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	(1) Bergman, A.G.; Berul', S.I. Izv. Sektora FizKhim. Anal. <u>1952</u> , 21, 178-183.

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium nitrate; NaNO₃; [7631-99-4] 	Diogenov, G.G. Zh. Neorg. Khim. <u>1956</u> , 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1956</u> , 1 (4), 199-205.			
VARIABLES:	PREPARED BY:			
Temperature	D'Andrea G.			
EXPERIMENTAL VALUES:				
t/°C T/K ^a 100x ₂ t/°C T/K ^a 100x ₂				
337 610 0 235 508 62 323 596 3 243 516 65.2 321 594 7 245 518 66 319 592 8.5 255 528 69.7 312 585 14.5 257 530 70.5 306 579 19 266 539 75.5 297 570 25 270 543 78.4 292 565 27 272 543 80 287 560 29.5 270 543 81.5 270 543 36.5 278 551 85.1 263 536 44.5 290 563 90 257 530 48 294 567 91.5 253 526 50 299 572 94.5 240 513 55 304 577 96.7 230 503 59.5 3 3 308 581 100 <t< td=""><td>$\frac{1}{250} - \frac{1}{100} + \frac{1}$</td></t<>	$\frac{1}{250} - \frac{1}{100} + \frac{1}$			
Peritectic, P, at 266 °C (author) and $100x_2 = 38.5$ (compiler). Eutectic, E ₁ , at 225 °C and $100x_2 = 57.5$ (author).				
Eutectic, E_2 , at about 268 °C and 100 \mathbf{x}_2 about 82.5 (compiler).				
Na ₃ (C ₂ H ₃ O ₂) ₂ NO ₃ , incongruently melting (author).				
Na ₅ C_{2} H ₃ O_{2} (NO ₃) ₄ , congruently metting at 2,	2° (autnor).			
transition of $NaC_2H_3O_2$.	an inflexion at 525 C corresponds to a phase			
AUXILIAR	INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis.	Not stated.			
	ESTIMATED ERROR:			
	Temperature: accuracy probably +2 K (compiler).			

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrate; NaNO₃; [7631-99-4] 	Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., 1966, 27, 69-75.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
327 600 0 320 593 6.5	
315 588 11.5	* L
307 580 18.3	
299 572 23.5	
287 560 30.0	300 - S 21
277 550 34.3	
266 539 39.5	
257 530 46.2	270
247 520 51.5	
235 508 56.4	
$\begin{bmatrix} 230 & 503 & 60.2 \\ 0.12 & 514 & 64.7 \end{bmatrix}$	
241 514 64.7	$\mathbf{b}^{\mathbf{p}}$
255 526 70.0	R I
284 557 87.0	E
293 566 90.7	
303 576 96.4	
308 581 100	0 50 $100x_2$ 100
^a T/K values calculated by the compiler.	NaC ₂ H ₃ O ₂ NaNO ₃
Characteristic point(s):	
Eutectic, E, at 225 ^o C and $100x_2$ = 58 (authors	.).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
	Note of the later
Visual polythermal analysis supplemented	Not stated.
measured with a Chromel-Alumel thermocouple	t. $(1)/^{\circ}C= 270$.
and a 17 mV millivoltmeter.	Component 2 undergoes a phase transition at
	$t_{trs}(2)/^{\circ}C=275.$
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrate; NaNO₃; [7631-99-4] 	Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
$t/^{O}C$ T/K^{a} $100x_{2}$ $t/^{O}C$ T/K^{a} $100x_{2}$ 328 601 0 224 497 60 314 587 10 242 515 70 300 573 20 261 534 80 284 557 30 281 554 90 259 532 40 306 579 100	300 - 0 0
$a_{\rm T/V}$ values calculated by the compiler	250 -
Note - The tabulated data were drawn by the compiler from Fig. 1 of the original paper.	E
Characteristic point(s):	0 50 100×2 100
Eutectic, E, at 218 ^o C and $100x_2$ = 56 (authors	3). NaC ₂ H ₃ O ₂ NaNO ₃
AUXILIARY II	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
DTA. Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules. No other information given.	NaC ₂ H ₃ O ₂ of analytical purity and "chemically pure" NaNO ₃ , heated 10-15 h at temperatures 50-60 ^O C below their fusion temperatures, were employed.
ESTIMATED ERROR:	REFERENCES:
Temperature: accuracy probably <u>+</u> 2 K (compiler).	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] Sodium nitrate; NaNO₃; [7631-99-4] 	Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplavov Solei, Irkutsk, <u>1975</u> , 7-12.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
Eutectic, E, at 222 ^O C (Fig. 1 of the orig about 43 in compiler's graphical estimation)	ginal paper); composition not stated $(100x_1)$
AUXILIARY I	VFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated. Component 1: $t_{fug}(1)/^{\circ}C= 326;$
ESTIMATED ERROR:	original paper).
Temperature: accuracy probably <u>+</u> 2 K (compiler).	REFERENCES:

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COMPONENTS:	ORTGINAL MEASUREMENTS:	
<pre>(1) Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6] (2) Sodium thiocyanate; NaCNS; [540-72-7]</pre>	Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.	
	DEPADED RV.	
VARIABLES:	FREFARED DI:	
Temperature.	D Andrea, G.	
EXPERIMENTAL VALUES:		
t/ ^o C T/K ^a 100x ₂		
298 571 0 292 565 5	۷	
289 562 10	+	
287 560 15		
282 555 25	A A	
276 549 35	3002	
273 546 40	Bara por	
270 543 45		
258 531 54	John Land	
261 534 55	250 - Ĕ _	
269 542 60		
285 558 75		
298 571 90		
311 584 100		
^a T/K values calculated by the compiler.	0 50 100×2 100	
Characteristic point(s):	NaC ₃ H ₅ O ₂ NaCNS	
Establish E at 258 9 C and 100m = 54 (author)		
Euclectic, E, at 250 \circ and 100x ₂ \rightarrow (author)	•	
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis.	Component 1 synthetized from propanoic acid	
measured with a Nichrome-Constantane	purity recrystallized once from water and	
thermocouple and a millivoltmeter with	once from ethanol.	
mirror reading to 17 mV.		
	ESTIMATED ERROR:	
NOTE:		
See the NOTE relevant to the investigation	(compiler).	
by Storonkin et al. (Ref. 1) on the same system.	REFERENCES:	
	(1) Stowarking A W . Washing T .	
	Potemin, S.S.	
	Vestn. Leningr. Univ., Fiz., Khim. 1974. (10). 84-88.	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6] Sodium thiocyanate; NaCNS; [540-72-7] 	Storonkin, A.V.; Vasil [*] kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. <u>1974</u> , (10), 84-88.	
VARIABLES:	PREPARED BY:	
Temperature.	D'Andrea, G.	
	······	
EXPERIMENTAL VALUES:		
t/ ^o c T/K ^a 100x ₂		
290 563 0 284 557 10 278 551 20 272 545 30 264 537 40 252 525 50 259 532 60 273 546 70 285 558 80 295 568 90 308 581 100 ^a T/K values calculated by the compiler. Note - The tabulated data were drawn by the compiler from Fig. 3 of the original paper. Characteristic point(s): Eutectic, E, at 249 °C and $100x_2= 54$ (author	s).	
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
DTA. Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules. No other information given.	$NaC_{3}H_{5}O_{2}$ prepared from propanoic acid and NaOH, and "chemically pure" NaCNS, heated 10-15 h at temperatures 50-60 °C below their fusion temperatures, were employed.	
NOTE:		
Concerning component 1, the fusion temperature (563 K) fairly agrees with the values listed in Preface, Tables 1 and 3 [562.4+0.5 K (DSC) and 561.88+0.03 K		
(adiabatic calorimetry) respectively], whereas the figure by Sokolov (571; Ref. 1) seems somewhat too high. An approximately	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K	
equal difference exists also between Storonkin et al.'s and Sokolov's eutectic	(compiler).	
temperatures (522 and 531 K, respectively). The temperature values measured by Storonkin et al.are likely more reliable.	REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24 , 1150-1156.	



COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6] (2) Sodium nitrate; NaNO₃; [7631-99-4] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
298 571 0 264 537 50 294 567 5 258 531 55 291 564 10 255 528 56.5 287 560 15 261 534 60 282 555 25 270 543 65 280 553 30 280 553 75 276 549 35 290 563 85 273 546 40 301 574 95 269 542 45 308 581 100	₩ ¥ 300 ⁴ ⁴ ³⁰⁰ ⁴ ⁶ ⁶ ⁶ ⁶ ⁶ ⁶ ⁶ ⁶
" 1/K Values calculated by the compiler.	250 - E 0 50 $100 \times_2$ 100 NaC ₃ H ₅ O ₂ NaNO ₃
Characteristic point(s): Eutectic, E, at 255 ^o C and 100x ₂ = 56.5 (autho	pr).
AUXILIARY	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.	Component 1 synthetized from propanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.
NOTE: The fusion temperature of component 1 (571 K) is somewhat too high: both DSC and adiabatic calorimetry provide a value close to 562 K (see Preface, Table 3).	ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.

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COMPONENTS:	EVALUATOR:	
 (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita [°] di Pavia (ITALY).	
CRITICAL EVALUATION:		
The system was studied only by Sokolov (continuous series of solid solutions, with a	Ref. 1), who claimed the existence of a minimum at 494 K and $100x_2=72.5$.	
Component 1, however, forms liquid cryst $T_{clr}(1)/K=600.4+0.2$ and $T_{fug}(1)/K=524.5+$ Consequently: (1) Sokolov's fusion temperidentified with the clearing temperature; (should refer to the formation of liquid cr solutions (true liquidus). Besides the min its coordinates are hard to detect on the b diagram should be not too different from that	als in a stability field ranging between 0.5 (according to Preface, Table 1). rature of component 1 (603 K) should be ii) at low values of 100x ₂ , Sokolov's points ystals (pseudo-liquidus), and not of solid imum, m, an M point should exist (although asis of the available data, and the phase t shown in Scheme B.3 of the Preface.	
REFERENCES		
(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 2	4, 1581-1593.	
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium iso.butanoate (sodium iso.butyrate); Na1.C₄H₇O₂; [996-30-5] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.	
VARIABLES:	PREPARED BY:	
Temperature.	D'Andrea, G.	
EXPERIMENTAL VALUES:		
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	ų į	
330 603 0 235 508 55 317 590 5 229 502 60 306 579 10 224 497 65 297 570 15 222 495 70 287 560 20 221 494 72.5 279 552 25 222 495 75 270 543 30 225 498 80 264 537 35 228 501 85 257 530 40 235 508 90 250 523 45 248 521 95 242 515 50 260 533 100 a T/K values calculated by the compiler. Characterietic point(p)	300 - 000	
Characteristic point(s):	$0 50 100 \times 100$	
minimum, m, at 221 °C and $100x_2 = 72.5$ (author).	NoC ₄ H ₇ O ₂ No <i>i</i> ,C ₄ H ₇ O ₂	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature	Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.	
readings refer to the disappearance of iso- tropicity in the melt on cooling.	ESTIMATED ERROR:	
	Temperature: accuracy probably +2 K (compiler).	

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COMPONENTS:	EVALUATOR:
 Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita [°] di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1), who suggests a eutectic phase diagram, the invariant point being at 530 K (257 $^{\circ}$ C) and 100x₂ =90.5. Both components, however, form liquid crystals.

Therefore, the fusion temperatures, $T_{fus}(1)=603 \text{ K} (330 \text{ }^{\circ}\text{C})$ and $T_{fus}(2)=535 \text{ K} (262 \text{ }^{\circ}\text{C})$, should be identified with the clearing temperatures, the corresponding values from Tables 1, 2 of the Preface being $T_{clr}(1)=600.4\pm0.2$ K, and $T_{clr}(2)=559\pm1$ K, respectively. The discrepancy between the values concerning component 2 might be attributed to some impurity of Sokolov's samples, inasmuch as the value from Preface (Table 2) meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2) and by Duruz et al. (553 K; Ref. 3). No mention is made by the author of other phase transitions occurring in either component, including those corresponding to the actual fusion, which should be $T_{fus}(1)=524\pm0.5$ K (Preface, Table 1) and $T_{fus}(2)=461.5\pm0.5$ K (Table 2).

Accordingly, the phase diagram of the system should be modified. The available data do not allow one to rule out neither of the following possibilities: (i) the eutectic point should be identified with a minimum point in a continuous series of liquid crystal solutions; (ii) the eutectic point should be identified with an M'_E point, at which the isotropic liquid should be in equilibrium with two liquid crystal solutions of different composition (Preface, Scheme C.3, Fig. 3.3).

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>19</u>54, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A322, 281-299.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
<pre>330 603 0 287 560 55 326 599 5 284 557 60 323 596 10 281 554 65 320 593 15 277 550 70 316 589 20 273 546 75 312 585 25 269 542 80 308 581 30 263 536 85 305 578 35 258 531 90 300 573 40 257 530 90.5 295 568 45 263 536 95 292 565 50 262 535 100 ^a T/K values calculated by the compiler.</pre>	$r_{\rm c}^{\rm v}$ and $100x_{2}$ = 90.5 (author).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Materials prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).

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COMPONENTS: (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] EVALUATOR: Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed the existence of two eutectics [E₁, at 590 K (317 °C) and $100x_2$ = 22.5; E₂, at 590 K (317 °C) and $100x_2$ = 27.5], and of the intermediate compound Na₄(C₄H₇O₂)₃C₆H₁₁O₂, congruently melting at 594 K (321 °C).

Both components, however, form liquid crystals. Therefore, Sokolov's fusion temperatures, $T_{fus}(1)=603$ K (330 °C) and $T_{fus}(2)=638$ K (365 °C), should be identified with clearing temperatures, the corresponding values from Preface, Table 1 being $T_{clr}(1)=600.4\pm0.2$ K and $T_{clr}(2)=639.0\pm0.5$ K, respectively.

No mention is made by the author of other phase transitions of either component, including those corresponding to their actual fusions, which ought to occur at $T_{fus}(1) = 524.5\pm0.5$ K and $T_{fus}(2) = 499.6\pm0.6$ K, respectively (see Table 1).

Concerning the phase diagram, the available data suggest the following interpretations as possible. If the maximum at 594 K (321 °C) and $100x_2$ = 25 does exist, Sokolov's eutectics could be identified with either M'_E points at the opposite sides of the distectic pertinent to a congruently melting intermediate compound (Preface, Scheme D.2), or m points in a situation similar to that shown in Scheme C.3. Conversely, if the occurrence of the maximum is considered as insufficiently proved, one might think of the existence of either an M''_E point (with limited series of liquid crystal solutions on both sides; Scheme C.2), or a (single) minimum in a continuous series of liquid crystal solutions.

REFERENCES:

(1) Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.

COMPONENTS:						ORIGINAL MEASUREMENTS:
 (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 		te); te);	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.			
VARIABLES:			PREPARED BY:			
Temperature.					D'Andrea, G.	
EXPERIMENTAL VALUES:						
t/°C	t/K ^a	100 ± 2	t/ ^o C	T/K ^a	100 x 2	u [
220	603	0	33/	607	50	· · · · ·
220	601	5	340	613	55	+
320	507	10	3/3	616	60	
324	502	15	245	617	65	
320	593	15	344	600	70	
318	591	20	349	022	70	<u>مہ</u>
31/	590	22.5	353	020	75	360 - 000-
321	594	25	356	629	80	
31/	590	27.5	359	632	85	
319	592	30	360	633	90	apo l
323	596	35	363	636	95	
326	599	40	365	638	100	
331	604	45				<u>کم ک</u>
^a T/K Chara	values o acteristi	calculate	d by the s):	compi	ler.	$E_1 E_2$
Eutectic, E_1 , at 317 °C and $100x_2 = 22.5$ (author). Eutectic, E_2 , at 317 °C and $100x_2 = 27.5$ (author).			nor). $C = 50 \ 100 \times_2 \ 100$ nor). $NaC_4H_7O_2 = NaC_5H_{11}O_2$			
Intermediate compound(s):						
Na ₄ (C ₄ H ₇ O ₂) ₃ C ₆ H ₁₁ O ₂ [erroneously indicated as compiler], congruently melting at 321 °C.		ed as $Na_5(C_4H_7O_2)_4C_6H_{11}O_2$ in the text,				
			. <u>.</u>			
				A1	JXILIARY 1	INFORMATION
METHO	D/APPARA	TUS/PROC	EDURE:			SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.			ss tul a Ni a 17 r temp arance ing.	be and Ichrome- NV full Derature of iso-	Materials prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.	
						ESIMATED EKKUK:
					Temperature: precision probably +2 K (compiler).	
						REFERENCES:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] Sodium benzoate; NaC₇H₅O₂; [532-32-1] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/°C T/K ^a 100x ₂	
330 603 0 330 603 0.13 349 622 5 361 634 10 370 643 15 378 651 20 386 659 25 394 667 30 401 674 35 408 681 40 415 688 45 421 694 50 427 700 55 434 707 60 463 736 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 330 °C and $100x_2$ = 0.13 (authors) Note - The system was investigated at 0 ≤ 100x ₂ ≤ 60 due to thermal instability of the butanoate.	r).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of n-butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.
NOTE:	ESTIMATED ERROR:
Component 1 forms liquid crystals. Therefore Sokolov's fusion temperature,	Temperature: accuracy probably <u>+</u> 2 K (compiler).
$f_{\text{fug}}(1) = 003$ K, should be identified with the clearing temperature, the corresponding value in Table 1 of the Preface being 600.4 ± 0.2 K. It is hard to infer the topology of the system from the available data: indeed, the phase diagram might be similar to that shown in Preface, Scheme A.1, but other possibilities remain open.	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium butanoate (sodium butyrate);	Spinolo, G.,
NaC ₄ H ₇ O ₂ ; [156-54-7] Sodium octadecanoate (sodium stearate);	Dipartimento di Chimica Fisica,
NaC ₁₈ H ₃₅ O ₂ ; [822-16-2]	Universita' di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(C_4H_7O_2)_3(C_{18}H_{35}O_2)_2$ [congruently melting at 663 K (390 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 521 K (248 °C) and $100x_2$ = 15, and a "perekhodnaya tochka" at 582 K (309 °C) and $100x_2$ = 96.5.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Preface, Table 1), and two for component 2 (see Table 4 of the Preface). Sokolov's fusion temperatures, $T_{fus}(1) = 603 \text{ K} (330 \text{ }^{\circ}\text{C})$, and $T_{fus}(2) = 581 \text{ K} (308 \text{ }^{\circ}\text{C})$, consequently should be identified with the clearing temperatures, the corresponding values from Tables 1 and 4 being 600.4+0.2 and 552.7 K, respectively.

Since the complete topology of the binary can hardly be interpreted from the available data, it is more realistic to list here the few points which, in the evaluator's opinion, seem to be sufficiently reliable.

(i) At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 663 K and $100x_2 = 40$.

(ii) Accordingly, the left hand section $(0 \le 100x_2 \le 40)$ of the phase diagram might be interpreted with reference to Preface, Scheme C.2: in this case, Sokolov's eutectic should be identified with an M'_E point.

Conversely, no definite interpretation of the phase diagram at high $100x_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100x_2 = 96.5$) from the trend of his experimental data which does not support unambiguously any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4 of the Preface.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C T/K^{a} 100x_{2} t/^{\circ}C T/K^{a} 100x_{2}$	
330 603 0 376 649 60 289 562 5 370 643 65 261 534 10 364 637 70 248 521 15 358 631 75 277 550 20 350 623 80 317 590 25 340 613 85 351 624 30 330 603 90 379 652 35 314 587 95 389 662 45 312 585 98.5 386 659 50 308 581 100 380 653 55 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 248 °C and 100 x_2 = 15 (author). Characteristic point, P ("perekhodnaya tochka" in the original text; see the	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
Introduction), at 309 °C and $100x_2$ 96.5 (author).	
Intermediate compound(s):	
Na ₅ (C ₄ H ₇ O ₂) ₃ (C ₁₈ H ₃₅ O ₂) ₂ , congruently melting	at 390 °C.
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of n-butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.
	ESTIMATED ERROR:
	Temperature: precision probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium butanoate (sodium butyrate);	Spinolo, G.,
NaC ₄ H ₇ O ₂ ; [156-54-7] Sodium thiocyanate;	Dipartimento di Chimica Fisica,
NaCNS; [540-72-7]	Universita ⁻ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1), who restricted his visual polythermal investigation to the lower boundary of the isotropic liquid field. He asserted the existence of the intermediate compound $Na_4(C_4H_7O_2)_3CNS$, which melts incongruently at 541 K (268 °C), and of a eutectic at 535 K (262 °C) and $100x_2$ = 48.5.

Component 1, however, forms liquid crystals, which are stable between $T_{fus}(1)=524.5+0.5$ K and $T_{clr}(1)=600.4+0.2$ (see Preface, Table 1). Sokolov's fusion temperature (603 K) consequently should be identified with the clearing temperature, whereas the T_{trs} value (525 K), reported by the same author in a subsequent paper (Ref. 2), is in close agreement with the fusion temperature given in Table 1.

In the evaluator's opinion, Sokolov's findings are not sufficient to prove unambiguously the existence of the intermediate compound. Consequently, more than one interpretation can be given for the topology of this binary.

Indeed, if the compound does exist:

(i) the phase diagram could be similar to that shown in Preface, Scheme D.3, (ii) Sokolov's "Perekhodnaya tochka" should to be identified with an M_p point; and (iii) the occurrence of a (so far undetected) M_E point is required.

If, on the contrary, one assumes that the intermediate coumpound does not exist, Sokolov's invariant at 541 K and $100x_2$ = 31.5 might be connected with the fusion of component 1 in the way shown in Scheme B.2 of the Preface.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

I	
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium thiocyanate; NaCNS; [540-72-7] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 x_{2} $t/^{\circ}C$ T/K^{a} 100 x_{2}	
330 603 0 263 536 45 328 601 5 262 535 48 5	v
324 597 10 269 542 50	- Γ ['] Δ
316 589 15 280 553 55	
291 564 25 287 560 60	
275 548 30 290 563 65	
268 541 31.5 298 571 75 266 539 35 307 577 90	
264 537 40 311 584 100	ا کر ہ
^a T/K values calculated by the compiler.	
Characteristic point(s):	Pood
Eutectic, E, at 262 $^{\circ}$ C and 100 x_2 = 48.5 (author).	250 - E
Invariant point, P ("perekhodnava tochka" in	
the original text, see the Introduction), at	
268 °C and $100x_2 = 31.5$ (author).	0 50 $100x_2$ 100
Intermediate compound(s):	
authorized and a second s	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1 synthetized from n-butanoic
Salt(s) melted in a test tube. Temperature	acid and NaHCO3.
measured with a Nichrome-Constantane	Component 2 of analytical purity
mirror reading to 17 mV.	from ethanol.
1	
	ESTIMATED ERROR:
	Temperature: prostaton
	(compiler),
1	REFERENCES:
1	

COMPONENTS:	EVALUATOR:
 Sodium butanoate (sodium butyrate);	Spinolo, G.,
NaC ₄ H ₇ O ₂ ; [156-54-7] Sodium nitrite;	Dipartimento di Chimica Fisica,
NaNO ₂ ; [7632-00-0]	Universita ⁻ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1) who restricted his polythermal investigation to the lower boundary of the isotropic liquid field. He claimed that an intermediate compound, i.e., $Na_4(C_4H_7O_2)_3NO_2$, exists which forms eutectics with either pure component at 590 K (317 °C) and $100x_2 = 17.5$, and at 347 K (274 °C) and $100x_2 = 96$, respectively.

No data on the solidus are available, and consequently the existence of the intermediate compound is not fully proved. Nevertheless, the evaluator is inclined to accept - at least in part - Sokolov's interpretation of the topology of the system.

It must, however, be specified that, due to the fact that component 1 forms liquid crystals stable between 524.5 \pm 0.5 K and 600.4 \pm 0.2 K (see Preface, Table 1), (1) the first eutectic at 590 K ought to be identified with an M^{*}_E point; and (11) a further (so far undetected) invariant, presumably an M^{*}_E point, should exist.

In conclusion, the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface.

REFERENCES:

(1) Sokolov, N.M.
 Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] Sodium nitrite; NaNO₂; [7632-00-0] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1957</u> , 27, 840-844 (*); Russ. J. Gen. Chem., Engl. Transl., <u>1957</u> , 27, 917-920.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	
330 603 0 312 585 55 328 601 5 309 582 60 325 598 10 306 579 65 320 593 15 304 577 70 320 593 20 300 573 75 324 597 25 296 569 80 323 596 30 291 564 85 322 595 35 285 558 90 320 593 40 276 549 95 316 589 45 284 557 100 314 587 50 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E_1 , at 317 °C and 100 \mathbf{x}_2 = 17.5 (auth Eutectic, E_2 , at 274 °C and 100 \mathbf{x}_2 = 96 (author Note - The coordinates of the second eutecti 2 of the original paper; they cannot, however tabulated data; compiler). Intermediate compound(s): Na ₄ (C ₄ H ₇ O ₂) ₃ NO ₂ congruently melting at 324 °C	$\frac{1}{320} - \frac{1}{E_1} - \frac{1}{E_2} - \frac{1}$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, $AgNO_3$, Cd, KNO_3 , and $K_2Cr_2O_7$.	Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial n-butanoic acid distilled before use (Ref. 1); the salt recovered was recrystallized from n-butanol. Component 2: "chemically pure" material recrystallized from water.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	(1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.

<pre>(1) Sodium butanoate (sodium butyrate); Fer NaC₄H₇O₂; [156-54-7] Dir (2) Sodium nitrate; Uni NaNO₃; [7631-99-4]</pre>	Yerloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

The visual polythermal method was employed by Dmitrevskaya (Ref. 1) [see also Sokolov, (Ref. 2)] to study the lower boundary of the isotropic liquid field: according to this author, an incongruently melting intermediate compound of probable composition Na₄(C₄H₇O₂)₃NO₃ is formed, and two invariants exist, i.e., a eutectic, E [at 540 K (267 °C), and 100x₂= 50], and a "perekhodnaya tochka", P [at 549 K (276 °C), and 100x₂= 27].

Component 1, however, forms liquid crystals. Accordingly, the fusion temperature, $T_{fug}(1) = 603 \text{ K} (330 \text{ }^{\circ}\text{C})$, reported in Ref. 1 should be identified with the clearing temperature, $T_{clr}(1)$, of component 1, the corresponding value from Preface, Table 1 being $600.4\pm0.2 \text{ K}$.



For the same component, Table 1 of the Preface [besides the $T_{clr}(1)$ value] provides four solid state transitions (at 450.4+0.5, 489.8+0.2, 498.3+0.3, and 508.4+0.5) and $T_{fus}(1)/K=524.5+0.5$. These phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). Phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify the two intermediate transition temperatures from Ref. 4 with the first $T_{trs}(2)$ and $T_{fus}(2)$ from Table 1. Reasonable doubts can be raised, on the contrary, about the actual existence of Ref. 4 highest transition (which - if present - should represent the transformations.

More recently, Prisyazhnyi et al. (Ref. 5) - to whom Refs. 1, 2 seem to be unknown - carried out a derivatographical re-investigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Concerning component 1, their clearing $[T_{clr}(1)=599 \text{ K} (326 \text{ }^{\circ}\text{C})]$ and fusion $[T_{fus}(1)=526 \text{ K} (253 \text{ }^{\circ}\text{C})]$ temperatures substantially agree with those from Table 1 of the Preface; it is moreover to be stressed that they do not mention any transition intermediate between $T_{clr}(1)$ and $T_{fus}(1)$.

Prisyazhnyi et al.'s, and Dmitrevskaya's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals), an inspection of which allows one to make the following remarks. An invariant exists, which escaped Dmitrevskaya's attention, and is reasonably to be classified as an M_E point. Moreover, the invariant at about $100x_2^{-2}$ 25 is actually an M' point: its abscissa being known only approximately, it can hardly be decided if it is of the M'_E or of the M'_P type: in the former case, the complete phase diagram should be similar to Scheme D.1 of the Preface; in the latter one, to Scheme D.3.

The two-phase region pertinent to the liquid crystal - isotropic liquid equilibria might be so narrow as to have prevented Prisyazhnyi et al. to observe two distinct sets of points in this region, whereas the lack of information by the same authors about eutectic fusion in the differrent samples studied by derivatographical analysis remains rather surprising.

REFERENCES:

 (1) Dmitrevskaya, O.I.; Zh. Obshch. Khim. <u>1958</u>, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u>, 28, 2046-2051.
 (2) Sokolov, N.M.; Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
 (3) Schiraldi, A.; Chiodelli, G.; J. Phys. E: Sci. Instr. <u>1977</u>, 10, 596-599.
 (4) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.
 (5) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.; Zh. Neorg. Khim. <u>1983</u>, 28, 253-255.

COMPONENTS	ODICINAL MEASUDEMENTS.
<pre>(1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] (2) Sodium nitrate; NaNO₃; [7631-99-4]</pre>	Dmitrevskaya, O.I. Zh. Obshch. Khim. <u>1958</u> , 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1958</u> , 28, 2046-2051.
VARIABLES:	PREPARED BY:
	D'Allurea, 0.
EXPERIMENTAL VALUES:	
$t/^{\circ}C$ T/K^{a} 100 x_{2} $t/^{\circ}C$ T/K^{a} 100 x_{2}	,,
<pre>330^b 603 0 276^b 549 55 329^b 602 5 283^b 556 60 325^b 598 10 288^b 561 65 315^b 588 15 292^b 565 70 283^b 556 25 296^b 569 75 276^b 549 27 297 570 80 274^b 547 30 298^b 571 85 273^b 546 35 300 573 90 271^b 544 40 304^c 577 95 268^b 541 45 308^b 581 100 267^b 540 50 ^a T/K values calculated by the compiler. ^b Value already reported in a previous paper by Sokolov (Ref. 1); the compiler preferred to employ the values tabulated by Dmitrevskaya which are more complete. ^c 302 in Sokolov's paper (Ref. 1). Characteristic point(s): Eutectic, E, at 267 °C and 100x₂= 50 (author) Characteristic point, P ("perekhodnaya too text; see the Introduction), at 276 °C and 10 Intermediate compound(s):</pre>	ha" in the original $0x_2^m 27$ (author).
Probably Na ₄ (C ₄ H ₇ O ₂) ₃ NO ₃ , incongruently melti	ng (author).
	SOURCE AND PURTTY OF MATERIALS.
Visual polythermal analysis. Temperatures measured with a Nichrome- Constantane thermocouple.	Component 1 synthetized from "chemically pure" sodium hydrogen carbonate and n- butanoic acid that first had been distilled twice. "Chemically pure" component 2 recrystallized and dried to constant mass. Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C=117$, 232, 252, 316 (Ref. 2). Component 2 undergoes a phase transition at $t_{trs}(2)/^{\circ}C=270$ (current literature).
	ESTIMATED ERROR:
	(compiler).
	REFERENCES:
	 Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156. Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] Sodium nitrate; NaNO₃; [7631-99-4] 	Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria). Characteristic point(s): Invariant point, M _E , at about 244 °C and 100x ₂ about 5 (compiler). Eutectic, E, at about 267 °C and 100x ₂ about 50 (compiler). Invariant point, M', at about 276 °C and 100x ₂ about 25 (compiler). Intermediate compound(s): Na ₄ (C ₄ H ₇ O ₂) ₃ NO ₃ , melting at about 276 °C	$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6-8 K min ⁻¹ , and using $Al_{2}O_{3}$ as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to de- tect the transformation points from the liquid crystalline into the isotropic li- quid phase.	Not stated. Component 1: $t_{fus}(1)/{}^{o}C$ about 253; $t_{clr}(1)/{}^{o}C$ about 326 (compiler). Component 2: $t_{fus}(2)/{}^{o}C$ about 308 (compiler).
	ESTIMATED ERROR:
	Temperature: accuracy is not evaluable (compiler).
	Temperature: accuracy is not evaluable (compiler). REFERENCES:
	Temperature: accuracy is not evaluable (compiler). REFERENCES:
	Temperature: accuracy is not evaluable (compiler). REFERENCES:

COMPONENTS:	EVALUATOR:	
 Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).	
CRITICAL EVALUATION:		
This system was studied only by Sokolov (continuous series of solid solutions, with a	Ref. 1), who claimed the existence of a minimum at $461-462$ K and $100x_2=50$.	
The fusion temperature of component 1 (533 K) is not far from that reported in Preface, Table 2 (526.9 ± 0.7 K).		
Component 2, however, forms liquid crystals in a stability field ranging between $T_{clr}(2)/K=559\pm1$ and $T_{fus}(2)/K=461.5\pm0.6$ (according to Table 2).		
Consequently, Sokolov's fusion temperature of component 2 should reasonably be identified as the clearing temperature of this component. Its value, i.e., 535 K, is remarkably lower than that listed in Table 2, i.e., 559+1 K: the latter figure, however, meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3), so that the discrepancy might be attributed to insufficient purity of Sokolov's sample (indeed, due to the - usually small - value of the enthalpy change associated with clearing, a small amount of impurities is often sufficient to cause a dramatic drop of the clearing temperature).		
Many of Sokolov's points should represent isotropic liquid - liquid crystal, rather than isotropic liquid - solid equilibria.		
Details of the phase diagram, however, are hard to be inferred from the available data.		
REFERENCES		
(1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24 , 1581-1593.		
(2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature <u>1970</u> , 228, 50-52.		
(3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u> , A322, 281-299.		


COMPONENTS:	EVALUATOR:
 Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1) who restricted his visual polythermal investigations to the lower boundary of the isotropic liquid field; and claimed the existence of a single eutectic at 433 K (160 $^{\circ}$ C) and 100x₂= 23.5:

Component 2, however, forms liquid crystals which are stable between 639.0 ± 0.5 K and 499.6 ± 0.6 K (see Preface, Table 1). Consequently, the fusion temperature 638 K ($365^{\circ}\overline{C}$; Ref. 1) should be identified with the clearing temperature, and Sokolov's outline of the phase diagram is incomplete. In particular, at least two invariants should exist, although the available data do not allow one to state with certainty their nature.

The following hypotheses can be tentatively suggested.

(i) Sokolov's invariant should be considered as an M_E point; a second one (an M_E point so far undetected) should exist at a lower temperature and at a higher x_2 value.

(ii) Sokolov's invariant is actually a eutectic, E, and a second invariant (an M'_P point so far undetected) should exist at higher temperature and at a higher x_2 value.

If hypothesis (1) is the correct one, the phase diagram ought to be similar to that shown in Scheme A.2 of the Preface.

However, taking into account that $T_{fus}(2)$ (499.6+0.6 K; Table 1 of the Preface) is significantly higher than the fusion temperature of Sokolov's invariant, and that the enthalpy change pertinent to fusion is usually much larger than that pertinent to clearing, the evaluator is inclined to prefer hypothesis (ii). Reference should be therefore made to Preface, Scheme B.1 or B.2.

REFERENCES:

Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.

COMBO	MENTEC .					ODICINAL MEASUDEMENTS.
COMPONENTS:					ORIGINAL PERSOREPENIS;	
 Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 					e);	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARTA	BIES.					DREDARED RV.
Tempe	rature.					D'Andrea, G.
EXPER	IMENTAL	VALUES:				
t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2	
260	533 510	0	205	478 493	50 55	
218	491	10	235	508	60	
195	468	15	252	525	65 70	3330
160	448 433	20	270	543 563	70	
161	434	25	329	602	85	300
168	441	30	345	618	90	8
182	440	40	365	638	100	
191	464	45				
8					_	
- T/K	values	calculate	ed by the	e compi.	ler.	
Chara	cteristi	lc point(s):			F
Eutec	tic, E,	at 160 °	C and 100	0x ₂ = 23	.5 (autho	$0 = 50 \ 100 \times_2 \ 100$
					$Na_{i}C_{4}H_{7}O_{2}$ $NaC_{6}H_{11}O_{2}$	
AUXILIARY I					XILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:						SOURCE AND PURITY OF MATERIALS:
Visua	1 polytł	nermal and	alysis.			Materials prepared by reacting aqueous
Melts	contai	ined in a	glass tu	ibe and	stir-	("chemically pure") Na ₂ CO ₃ with a slight
Tempe	ratures	measur	ed with	a Ni	chrome-	purity. The solvent and excess acid were
Const	antane	thermoco	uple and	a 17 m	V full	removed by heating to 160 °C.
scale	milli nac mofe	voltmete:	r. The	temp	erature	
tropi	ngs rere city in	the melt	on cooli	irance ding.	or 180-	
·	•			U		
1						
						ESTIMATED ERROR:
					Temperature: accuracy is probably +2 K	
						(compiler).
					REFERENCES:	

COMPONENTS:					ORIGINAL MEASUREMENTS:	
<pre>(1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]</pre>				lium		Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
(2) Sodium beñzoate; NaC ₇ H ₅ O ₂ ; [532-32-1]						
VARIAE	BLES:					PREPARED BY:
Temper	ature.					D'Andrea, G.
EXPERI	MENTAL	VALUES:				
t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2	
260	533	0	335	608	40	J ~
228	501	3.5	344	617 628	45	450 -
255	529	10	367	640	55	
272	545	15	379	652	60	and the second se
288	561	20	389	662	65	200
301	574	25	399	672	70	
312	585 595	30	408 463	736	100	350
a T/K	values	calculat	ed by th	ne comp	iler.	and
Charac	teristi	lc point(s):			2 ²
Eutect	ic, E,	at 228 °	C and 10)0x ₂ = 3	.5 (author	·)· 250 f -
Note - The system was investigated at $0 \le 100 \mathbf{x}_2 \le 80$ due to thermal instability		ated at tability	E 0 50 100×2 100			
or ene	. 100000	-cunoucci				Nor.C ₄ H ₇ O ₂ NoC ₇ H ₅ O ₂
AUXILIARY IN				A	JXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:						SOURCE AND PURITY OF MATERIALS:
Visual	. polyth	nermal an	alysis.			Component 1: prepared by reacting aqueous
Melts	conta	ined in	a gla	iss tu	be and	("chemically pure") Na ₂ CO ₃ with a slight
Stirre	d.	mo 9 011 7 0	d with	a N	chrome-	excess of 180. butanoic acid of analytical purity. The solvent and excess acid were
Consta	intane	thermoco	uple and	la 17 1	nV full	removed by heating to 160 °C.
scale	milli	voltmete	r. The	e tem	perature	Component 2: "chemically pure" material.
readin	igs refe	er to the	disappe	arance	of iso-	
tropic	ity in	the melt	on cool	ing.		
						ESTIMATED ERROR:
						Temperature: accuracy is probably <u>+2</u> K (compiler).
						REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium iso.butanoate (sodium iso.butyrate); NaiC₄H₇O₂; [996-30-5] Sodium octadecanoate (sodium stearate); 	Ferloni, P., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).
NaC ₁₈ H ₃₅ O ₂ ; [822-16-2]	

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(i \cdot C_4H_7O_2)_2(C_{18}H_{35}O_2)_3$ [congruently melting at 596 K (323 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 435 K (162 °C) and $100x_2$ = 25.5, and a "perekhodnaya tochka" at 584 K (311 °C) and $100x_2$ = 94.5.

Component 2, however, forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2)=581$ K (308 °C), should be identified with the clearing temperature and compared with the $T_{clr}(2)$ value reported in Preface, Table 4 (552.7 K). Conversely, Sokolov's $T_{fus}(1)$ [533 K (260 °C)] seems sufficiently reliable, being not far from the value (526.9±0.7 K) reported in Table 2 of the Preface.

In the evaluator's opinion, the phase diagram at $0 \leq 100x_2 \leq 60$ is to be reconsidered, e.g., with reference to Preface, Scheme A.2: Sokolov's eutectic could be an M'_E point, whereas the maximum at $100x_2$ = 60 could represent an azeotrope.

On the contrary, no definite interpretation of the phase diagram at high $100x_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100x_2 = 94.5$) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4 of the Preface.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.			
VARIABLES:	PREPARED BY:			
Temperature.	D'Andrea, G.			
EXPERIMENTAL VALUES:				
t/ ^o C T/K ^a 100x ₂ t/ ^o C T/K ^a 100x ₂				
260 533 0 319 592 50 240 513 5 321 594 55 215 488 10 323 596 60 196 469 15 322 595 65 177 450 20 321 594 70 163 436 25 320 593 75 162 435 25.5 317 590 85 217 490 30 314 587 90 260 533 35 311 584 94.5 291 564 40 312 585 97.5 309 582 45 308 581 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 162 °C and $100x_2$ = 25.5 (author). Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 311 °C (author) and $100x_2$ = 94.5 (erroneously reported as 312 °C and $100x_2$ = 97.5 in the text, compiler). Intermediate compound(s): Na5(i.C4H702)2(C18H3502)3, congruently melting at 323 °C.	$ \begin{array}{c} $			
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of iso.butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.			
	ESTIMATED ERROR:			
	Temperature: accuracy probably <u>+</u> 2 K (compiler).			
	REFERENCES:			

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium iso.butanoate (sodium	Sokolov, N.M.
<pre>iso.butyrate);</pre>	Zh. Obshch. Khim. 1954, 24, 1150-1156.
Na1. $C_4H_7O_2$; [996-30-5] (2) Sodium thiocyapate:	
NaCNS; [540-72-7]	
VARIABLES:	PREPARED BY:
	Diandres C
Temperature.	D'Andrea, G.
	L
$t/^{\circ}C$ T/K^{a} 100 x_{2}	
260 533 0	
247 520 5	<u>}</u>
237 510 10	
221 494 25	
214 487 27.4	300
221 494 30	300
240 213 35	<u>م</u> مہ
266 539 45	202
274 547 50	
280 553 55	250 4 7
295 568 75	
300 573 90	49
311 584 100	8
a T/K values calculated by the compiler.	
Characteristic point(s):	0 50 100×2 100 Na , , C ₄ H ₇ O ₂ NaCNS
Eutectic, E, at 214 °C (compiler; er-	
roneously reported as 240 °C in table 3 of the original paper) and $100x_{c} = 27.4$	
(author).	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Vioual polythermal analysis.	Component 1 synthetized from iso butenoic
Salt(s) melted in a test tube. Temperature	acid and NaHCO2.
measured with a Nichrome-Constantane	Component 2 of analytical purity
thermocouple and a millivoltmeter with	recrystallized once from water and once
mirror full scale 1/ mv.	from ethanol.
	1
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS :	ORIGINAL MEASUREMENTS:
 (1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] (2) Sodium nitrite; NaNO₂; [7632-00-0] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1957</u> , 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1957</u> , 27, 917-920.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
260 533 0 253 526 5 253 526 10 265 538 15 271 544 20 275 548 25 277 550 30 279 552 40 279 552 40 279 552 45 278 551 50 278 551 55 278 551 60 277 550 65 276 549 70 275 548 75 276 549 70 275 548 75 276 549 80 277 550 85 279 552 90 280 553 95 284 557 100 ^a T/K values calculated by the compiler. Characteristic point(s):	$ \begin{array}{c} $
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, $AgNO_3$, Cd, KNO_3 , and $K_2Cr_2O_7$.	Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial iso.butanoic acid distilled before use (Ref. 1); the salt recovered was recrystallized from n-butanol. Component 2: "chemically pure" material recrystallized from water.
NOTE:	ESTIMATED ERROR:
The author does not comment on the minimum at 548 K and $100x_2 = 75$. A possible explanation might be that liquid layering occurs: in this case, the points at $25 \leq 100x_2 \leq 75$ should represent liquid- liquid instead of solid-liquid equilibria, the monotectic temperature being 548 K. It is worth mentioning that stratification was	Temperature: accuracy probably +2 K (compiler). REFERENCES: (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
reported by the same author in the same paper for the binary $Na/i.C_5H_9O_2$, NO_2 .	

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] Sodium nitrate; NaNO₃; [7631-99-4] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t^{0}C T/K^{a} 100x_{2}$	
260 533 0 248 521 5	↓
242 515 10	
233 506 30	کم - soo
244 517 35	
258 531 40	~~~~~
274 547 50	
276 549 55	
280 553 60	
288 561 75	
292 565 85	l V
300 573 95	Ĕ
308 381 100	L
^a T/K values calculated by the compiler.	0 50 100×2 100 Na , . C ₄ H ₇ O2 NaNO3
Characteristic point(s):	
Eutectic, E, at 219 °C and $100x_2$ = 25 (author)	•
-	
AUXILIARY 1	INFORMATION
	SOURCE AND PURITY OF MATERIALS:
METHOD/APPARATUS/PROCEDURE:	Component 1 contracting from the butancia
Visual polythermal analysis.	acid and NaHCO3. Commercial component 2
Salt(s) melted in a test tube. Temperature	further purified by the author according to
measured with a Nichrome-Constantane thermocouple and a millivoltmeter with	Lalt1.
mirror reading to 17 mV.	
	ESTIMATED ERROR.
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

	······································
COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Sodium iso.butanoate (sodium</pre>	Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 19-24.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
Characteristic point(s):	
The paper reports - inter alia - on a refiner by one of the authors (Ref. 1). According to of the eutectic are:	ment of the title binary, previously studied the present investigation, the coordinates
Eutectic, E, at 220 $^{\circ}$ C and $100x_2 = 25$ (authors).	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1 synthetized from iso. butanoic acid and Na ₂ CO ₃ (Ref. 2). "Chemically pure"
NOTE:	component 2 recrystallized. Component 1 undergoes phase transitions at
Concerning component 1, no mention is made in Table 2 of solid state phase	<pre>t_{trs}(1)/°C= 67, 91, 220 (Ref. 3). Component 2 undergoes a phase transition at t_{trs}(2)/°C= 270 (current literature).</pre>
are quoted by the authors (from Ref. 3), at 493 , 364 and 340 K (220 at 493	ESTIMATED ERROR:
respectively. Duruz et al. (Ref. 4) report in turn $T_{exp}^{(1)}(1) = 493$ K (in agreement with	(compiler).
the highest transition temperature from Ref. 3), and $T_{trs}^{*}(1)= 468$ K (a figure	REFERENCES: (1) Sokolov, N.M.
which has no correspondence in Ref. 3). Finally, Ferloni et al. (Ref. 5) are	Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156. (2) Sokolov, N.M.
inclined to think that Sokolov's transformation at 340 K (Ref. 3) actually represents a transition of a hydrated form of the salt.	 Zn. UDSncn. Knim. <u>1954</u>, 24, 1581-1593. (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>. (4) DUTUZ, Juli: Michels, B.L., Ubbalobdo
ve end bart.	A.R. Proc. Roy. Soc. London 1971. A 322.
	281-299. (5) Ferloni, P.; Sanesi, M.; Tonelli, P.L.;
	Franzosini, P. Z. Naturforsch. <u>1978</u> , A 33, 240-242.

COMPONENTS:	EVALUATOR:
 Sodium pentanoate (sodium valerate);	Spinolo, G.,
NaC ₅ H ₉ O ₂ ; [6106-41-8] Sodium thiocyanate;	Dipartimento di Chimica Fisica,
NaCNS; [540-72-7]	Universita ⁻ di Pavia (ITALY) .

This system was studied by Sokolov (Ref. 1) and by Sokolov and Khaitina (Ref. 2): in both papers the visual polythermal investigation was restricted to the lower boundary of the isotropic liquid field. The authors claimed the existence of a 1:1 intermediate compound which melts congruently at 564 K (291 °C; Ref. 1), and forms eutectics with either pure component, at eutectics at 562 K (289 °C) and $100x_2$ = 46, and at 560 K (287 °C) and $100x_2$ = 56.5 or 55, respectively.

Component 1, however, forms liquid crystals, which are stable between 498 ± 2 K and 631 ± 4 K (Preface, Table 1). The latter value fairly agrees with the fusion temperature (630 K) given in Ref. 1 and 2; the former can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Ref. 2 from Ref. 3. Once more for component 1, Table 1 reports no solid state transition, whereas Sokolov and Khaitina quote (from Ref. 3) $T_{trs}(2)/K=482$ and 453. It is, however, to be stressed that the single transition observed (at 479\pm1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 4) was not more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

In the evaluator's opinion, therefore, i) the invariant at 562 K (289 °C) and $100x_2$ = 46 should be identified with an M^{*}_E point, ii) a (so far undetected) M_E invariant should exist within the composition range between M^{*}_E and pure component 1, and iii) the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface, but for the fact that the liquid crystal-isotropic liquid diphasic field exhibits a maximum.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.; Khaitina, M.V. Zh. Obshch. Khim. <u>1972</u>, 42, 2121-2123.
- (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London <u>1971</u>, A322, 281-299.
- (5) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II <u>1972</u>, 1879-1881.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium pentanoate (sodium valerate):	Sokolov, N.M.
$NaC_5H_9O_2$; [6106-41-8]	Zh. Obshch. Khim. 1954, 24, 1150-1156.
(2) Sodium thiocyanate;	
NaCNS; [540-/2-/]	
VARIABLES:	PREPARED BY:
Temperature.	D Andrea, G.
EXPERIMENTAL VALUES:	• · · · · · · · · · · · · · · · · · · ·
$t/^{\circ}C$ T/K^{a} 100 x_{2} $t/^{\circ}C$ T/K^{a} 100 x_{2}	
	ų []
357 630 0 289 562 46 370 643 5 291 564 50	2
378 651 10 288 561 55	2
375 648 15 287 560 56.5	γ
356 629 25 290 563 60	
344 617 30 293 566 65	³⁵⁰ - 2 - 1
331 604 35 297 570 75	
316 589 40 302 575 90	٩
230 303 43 311 384 100	, b
^a T/K values calculated by the compiler.	300 -
Characteristic point(s):	
Eutectic, E_1 , at 289 ^o C and $100x_2 = 46$	
(author).	
Eutectic, E_2 , at 287 °C and $100x_2 = 56.5$	
(auchor).	0 50 100×2 100
Intermediate compound(s):	NaC ₅ H ₉ O ₂ NaCNS
$Na_2C_5H_9O_2CNS$, congruently melting at 291 ^o C	
(author).	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND FURITY OF MATERIALS:
Visual polythermal analysis.	Component 1 synthetized from n-pentanoic
Salt(s) melted in a test tube. Temperature	acid and NaHCO3. Component 2 of analytical
measured with a Nichrome-Constantane	purity recrystallized once from water and
thermocouple and a millivoltmeter with	once from ethanol.
mirror reading to 1/ mv.	
	ESTIMATED ERROR:
	(compiler).
	REFERENCES:

······	I
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8] (2) Sodium thiocyanate; NaCNS; [540-72-7] 	Sokolov, N.M.; Khaitina, M.V. Zh. Obshch. Khim. <u>1972</u> , 42, 2121-2123.
VARIABLES:	PREPARED BY:
Temperature	D'Andres G.
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Eutectic, E_1 , at 289 °C and $100x_2$ about 46 (estimated by the compiler from Fig. 1 of the original paper). Eutectic, E_2 , at 287 °C and $100x_2$ about 55 (estimated by the compiler from Fig. 1 of the original paper).	
Intermediate compound(s):	
Na ₂ C ₅ H ₉ O ₂ CNS, congruently melting.	
AUXILIARY 1	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated. Component 1 undergoes phase transitions at $t_{trs}(1)/^{o}C= 180$, 209, 216 (Ref. 1) and melts at $t_{fus}(1)/^{o}C= 356$. Component 2 melts at $t_{fus}(2)/^{o}C= 311$.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:
	(1) Sokolov, N.M.
	Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

COMPONENTS:	EVALUATOR:
 Sodium pentanoate (sodium valerate);	Ferloni, P.,
NaC ₅ H ₉ O ₂ ; [6106-41-8] Sodium nitrite;	Dipartimento di Chimica Fisica,
NaNO ₂ ; [7632-00-0]	Universita ⁻ di Pavia (ITALY).

This binary was studied only by Sokolov (Ref. 1) who, on the basis of his visual polythermal observations, claimed the phase diagram to be of the eutectic type, the invariant occuring at 555 K (282 °C) and $100x_1 = 0.04$. This investigation was restricted to the range $0 \leq 100x_1 \leq 55$, because of decomposition of mixtures richer in component 1.

Component 1, however, forms liquid crystals. Thence, Sokolov's $T_{fus}(1)$ [i.e., 610 K (357°C)] should be identified with a clearing temperature, and compared with the value $T_{clr}(1)$ = 631<u>+4</u> K reported in Preface, Table 1.

The topology of the phase diagram has therefore to be reconsidered with reference to Preface, Schemes A, among which, however, the available data, unfortunately, do not allow one to make a definite choice.

Anyway, Sokolov's invariant should be an M_E point and not a conventional eutectic.

 ⁽¹⁾ Sokolov, N.M.
 Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

COMPONENTS :	ORTGINAL MEASUREMENTS.
<pre>(1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8] (2) Sodium nitrite; NaNO₂; [7632-00-0]</pre>	Sokolov, N.M. Zh. Obshch. Khim. <u>1957</u> , 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) <u>1957</u> , 27, 917-920.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
323 596 45 323 596 50 323 596 55 323 596 60 323 596 65 323 596 70 323 596 75 323 596 75 323 596 85 321 594 90 319 592 95 284 557 100 ^a T/K values calculated by the compiler. Note - The system was investigated at $0 \le 100x_1 \le 55$ since further increase in component 1 content causes decomposition of the mixtures. Characteristic point(s): Eutectic, E, at 282 °C and 100x_1 = 0.04 (both paper, cannot be drawn from the tabulated dat composition is erroneously reported as $100x_2$ =	figures, listed in table 2 of the original a; moreover, in the same table the eutectic 0.04; compiler).
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS.
Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO ₃ , Cd, KNO ₃ , and $K_2Cr_2O_7$.	Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial pentanoic acid distilled before use (Ref. 1); the salt recovered was re- crystallized from n-butanol; $t_{fus}(1)/^{\circ}C= 357$. Component 2: "chemically pure" material recrystallized from water.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:
	(1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.

COMPONENTS:	EVALUATOR:
 Sodium pentanoate (sodium valerate);	Spinolo, G.,
NaC ₅ H ₉ O ₂ ; [6106-41-8] Sodium nitrate;	Dipartimento di Chimica Fisica,
NaNO ₃ ; [7631-99-4]	Universita ⁻ di Pavia (ITALY).

This system was studied by Sokolov (Ref. 1), and by Sokolov and Khaitina (Ref. 2). In both cases, the visual polythermal analysis was employed to detect the lower boundary of the isotropic liquid field. Accordingly, the authors claimed that a 1:1 intermediate compound forms, which melts congruently at 568 K (295 °C), and gives eutectics with either component. Concerning the precise location of these invariants, some values given in the text of the original papers should be corrected with a closer inspection of the pertinent figures. The correct values seem therefore to be T= 564 K (291 °C) and $100x_2$ = 40.5 (Ref. 2), and T= 554 K (281 °C) and $100x_2$ = 58.5, respectively.

Component 1, however, forms liquid crystals, which are stable between 498 ± 2 K and 631 ± 4 K (Preface, Table 1). The latter value fairly agrees with the fusion temperature (630 K) given in Ref. 1 and 2; the former can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Ref. 3. Once more for component 1, Table 1 reports no solid state transition, whereas Sokolov quotes (Ref. 3) $T_{trs}(1)/K$ - 482 and 453. It is, however, to be stressed that the single transition observed (at 479\pm1 K) with DTA in sodium mpentanoate by Duruz et al. (Ref. 4) was no more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

Taking into account the above remaks, the eutectic at 564 K (291°C) and $100x_2 = 40.4$ ought to be an M_E^* point, and the occurrence of a further invariant (so far undetected and probably an M_E^* point) is to be expected. The phase diagram could be similar to that shown in Scheme D.l of the Preface, but for the fact that the liquid crystal-isotropic liquid field is splitted into two parts by a maximum.

REFERENCES:

(1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1150-1156
 (2) Sokolov, N.M., Vholtzing, M.V.

- (2) Sokolov, N.M.; Khaltina, M.V. Zh. Obshch. Khim. <u>1972</u>, 42, 2121-2123
 (3) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R.
- Proc. Roy. Soc. London 1971, A322, 281-299.
- (5) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II 1972, 1879-1881.

 Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8] Sodium nitrate; NaNO₃; [7631-99-4] 					Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.		
VARIA	BLES:					PREPARED BY:	
Tempe	rature.					D'Andrea, G.	
EXPER	IMENTAL	VALUES:					
t/ ^o C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2		
357 366 372 369 350 336 291 294 a T/K b 299 the cc origin the cc origin Charac	630 639 645 642 623 609 593 569 564 567 values 5 in the ompiler nal pape in the compiler nal pape	0 5 10 15 25 30 35 40 40.5 45 calculate e original on the baser. original on the baser. ic point(s	295 288 281 ^c 285 293 298 300 305 308 ed by the 1 table, asis of I table, asis of I	568 561 554 558 566 571 573 578 581 corre corre corre correc correc cig. 2	50 55 58.5 60 65 75 85 95 100 ler. cted by of the ted by of the	V V 350 300 E_1 E_2 0 S_0 S_0 S_1 S_2	
Eutec Eutec	tic, ^E 1 tic, ^E 2	, at 291 ⁰ , at 281 ⁰	^o C and 10 ^o C and 10	$00x_2 = 4$ $00x_2 = 5$	0.5 (aut) 8.5 (aut)	lor). lor).	
Inter		compound	(8):	-			
Na ₂ C ₅ I	H902N03	, congrue	ntly melt	ing at	295 ^o c ((compiler).	
				AU	XILIARY	INFORMATION	
METHO	D/APPAR	ATUS/PROCI	EDURE :			SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with					Component 1 synthetized from n-pent acid and NaHCO ₃ . Commercial compone further purified by the author accordi Laiti.		

COMPONENTS:

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.	Component 1 synthetized from n-pentanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
······································	

ORIGINAL MEASUREMENTS:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8] (2) Sodium nitrate; NaNO₃; [7631-99-4] 	Sokolov, N.M.; Khaitina, M.V. Zh. Obshch. Khim. <u>1972</u> , 42, 2121-2123.
VARTABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
	· · · · · · · · · · · · · · · · · · ·
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Eutectic, E_1 , at 291 ^o C and 100 x_2 about 40.5 (estimated by the compiler from Fig. 1 of the original paper). Eutectic, E_2 , at 281 ^o C and 100 x_2 about 58.5 (estimated by the compiler from Fig. 1 of the original paper).	
Intermediate compound(s):	
Na ₂ C ₅ H ₉ O ₂ NO ₃ , congruently melting.	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Not stated. Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C= 180$, 209, 216 (Ref. 1) and melts at $t_{fus}(1)/^{\circ}C= 356$. Component 2 undergoes a phase transition at $t_{trs}(2)/^{\circ}C= 275$ (current literature value), and melts at $t_{fus}(2)/^{\circ}C= 308$.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:
	(1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u> .

COMPONENTS:	EVALUATOR:
 Sodium iso.pentanoate (sodium iso.valerate); Nai.c₅H₉O₂; [539-66-2] Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1), who claimed that a continuous series of solid solutions is formed, with a minimum, m, at 512 K (239 $^{\circ}$ C), and 100 x_2 = 20.

Both components, however, form liquid crystals (see Preface, Tables 2, 1). Therefore, Sokolov's fusion temperatures, $T_{fus}(1)/K=535$ (262 °C) and $T_{fus}(2)/K=638$ (365 °C), should be identified with clearing temperatures, the corresponding data from Tables 2 and 1 being 559 ± 1 K and 639.0 ± 0.5 K, respectively.

Concerning component 1, the remarkable discrepancy might be attributed to insufficient purity of Sokolov's sample, inasmuch as the value from Table 2 (559+1) meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3). Indeed, due to the - usually small - value of the enthalpy change associated with clearing, very small amounts of impurities are often sufficient to cause a dramatic drop of the clearing temperature.

A continuous series of liquid crystal (instead of solid) solutions should form, and the complete phase diagram should be similar to that shown in Scheme C.l of the Preface, with a common minimum of the curves limiting the isotropic liquid - liquid crystal diphasic field.

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1581-1593. (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J.
- Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

COM	ONENTS .					OPTOTNAL MEASUDEMENTS.
						ORIGINAL PERSONEPENIS:
(1) Sodium iso.pentanoate (sodium iso.valerate):			sodium		Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.	
	Na1.C ₅ H ₉ O ₂ ; [539-66-2]					
	NaC ₆ H ₁₁ O	exanoate 2; [1005	[soalu	I capro	ate);	
1				_		
VARI	[ABLES:					PREPARED BY:
Temp	perature.					D'Andrea, G.
L						
EXPE	RIMENTAL	VALUES:				
t/°0	C T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2	
262	535	0	283	556	55	
255	528	5	291	564	60	+
247	520	10	296	569	65	Ŕ
243	516	15	304	577	70	350 - 2-
239	512	20	313	586	75	فر
242	515	25	322	595	80	45
248	521	30	331	604	85	
250	529	35	341	614	90	_ کم _ 300
203	546	40	354	627	100	ا ^{لل} مر
277	550	50	202	050	100	
	550	20				
а т/	'K values	calcula	ted by i	the com	piler.	250 - ² 50
Char	acterist:	ic point	(s):			m
		re porne	(0).			
Cont	inuous se	eries of	solid a	olutio	ns with a	1
mini	mum, m	, at	239 ^o C	and	100 x₂= 20	0 50 100×, 100
(aut	hor).					Na/.C_H_O_ NaC_H_O
						592 6112
1						
						······································
AUXILIARY					AUXILIARY :	INFORMATION
METHOD/APPARATUS/PROCEDURE:						SOURCE AND PURITY OF MATERIALS:
Vien	ເສ] ກວງປະເ	lermal a	nalvoia			Materials prepared by reacting aquoous
Me1+	s cont	ined f	n a ol	lass ti	ube and	("chemically pure") NacCo with a alight
stir	red.					excess of either iso pentanoic or n-
Temp	eratures	measur	ed with	ıal	Nichrome-	hexanoic acid of analytical purity. The
Cons	tantane	thermoc	ouple an	nd a 17	mV full	solvent and excess acid were removed by
scal	e milli	lvoltmet	er. Th	ne ter	nperature	heating to 160 °C.
read	lings refe	er to th	e disapp	earance	e of iso-	
trop	icity in	the mel	t on coo	oling.		
						ESTIMATED ERROR:
ļ						Temperatura: contraturation (0.1)
						(compiler).
						REFERENCES :
						1
						-

COMPONENTS:	EVALUATOR:
 Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] Sodium benzoate; NaC₇H₅O₂; [532-32-1] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita [~] di Pavia (ITALY) .

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal analysis to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 534 K (261 $^{\circ}$ C) and 100 x_2 = 3.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 461.5±0.6 K; Preface, Table 2] before being transformed in a clear melt. Therefore, Sokolov's fusion temperature, (535 K) should be identified with the clearing temperature, the corresponding value from Table 2 being 559±1 K. The latter figure is remarkably higher than that given by Ref. 1, and it agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Thus, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.1 of the Preface, and Sokolov's eutectic should be identified with an M'_E point.

- Sokolov, N.M.
 Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A322, 281-299.

I 	
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium iso .pentanoate	Sokolov, N.M.
(sodium iso.valerate);	Zh. Obshch. Khim. 1954, 24, 1581-1593.
Na1. $C_{5}H_{9}O_{2}$; [539-66-2]	
NaC ₇ H _c O ₂ ; [532-32-1]	
/ 5 2/ •	
VARIABLES:	PREPARED BY:
Temporature	DiAndrea C
remperature.	D'Allurea, G.
EXPERIMENTAL VALUES:	
$t/C T/K^{\alpha} 100 \mathbf{x}_2$	
262 535 0	
	ا م ا ⁺
298 571 10	
317 590 15	`۲
337 610 20	
349 622 25	
379 652 35	٢
389 662 40	
396 669 45	d ^D
401 674 50	
	300 - 2
421 694 65	
426 699 70	d 1
463 736 100	^Ф Е
a T/K values calculated by the compiler.	0 50 100×2 100
	$Na_{1}C_{5}H_{9}O_{2}$ $NaC_{7}H_{5}O_{2}$
characteristic point(s):	
Eutectic, E, at 261 ^o C and $100x_2 = 3$ (author).	
Note - The system was investigated at	
$0 \le 100 \mathbf{x}_2 \le 70$ due to thermal instability	
of the iso-pentanoate.	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1: prepared by reacting aqueous
Melts contained in a glass tube and	("chemically pure") Na ₂ CO ₃ with a slight
stirred.	excess of iso.pentanoic acid of analytical
Temperatures measured with a Nichrome-	purity. The solvent and excess acid were removed by besting to 160 °C.
scale millivoltmeter. The temperature	Component 2: "chemically pure" material.
readings refer to the disappearance of iso-	
tropicity in the melt on cooling.	
	ESITUALED EKKUK:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_3(i.C_5H_9O_2)(C_{18}H_{35}O_2)_2$ [congruently melting at 596 K (323 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 413 K (140 °C) and $100x_2 = 17.3$, and a "perekhodnaya tochka" at 582 K (309 °C) and $100x_2 = 93.5$.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Preface, Table 2), and two for component 2 (see Preface, Table 4). Therefore, Sokolov's fusion temperatures, $T_{fus}(1) = 535 \text{ K} (262 \text{ }^{\circ}\text{C})$, and $T_{fus}(2) = 581 \text{ K} (308 \text{ }^{\circ}\text{C})$, should be identified with clearing temperatures, the corresponding values from Tables 2 and 4 being 559+1 and 552.7 K, respectively.

At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 596 K and $100x_2$ = 70. Accordingly, the left hand section ($0 \leq 100x_2 \leq 70$) of the phase diagram might be interpreted with reference to Scheme C.2 of the Preface: in this case, Sokolov's eutectic should be intended as an M^{*}_E point, allowance being made for the fact that Sokolov's "fusion" temperature of component 1 is 24 K lower than the relevant T_{clr} value listed in Table 2, i.e., 559+1 K. It is, however, to be stressed that the latter figure agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

Conversely, no definite interpretation of the phase diagram at high $100x_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100x_2$ 93.5) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1581-1593.
 (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.
- (3) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970,228, 50-52.
- Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R.
 Proc. R. Soc. London <u>1971</u>, A 322, 281-299.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	
262 535 0 305 578 55 201 474 5 315 588 60 167 440 10 322 595 65 147 420 15 323 596 70 140 413 17.3 321 594 75 162 435 20 318 591 85 225 498 30 314 587 90 247 520 35 309 582 93.5 266 539 40 312 585 95 282 555 45 308 581 100 295 568 50 a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 140 °C and $100x_2 = 17.3$ (author). Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 309 °C (author) and $100x_2 = 93.5$ (erroneously reported as 92 in the text, compiler). Intermediate compound(s):	$ \begin{array}{c} $
$Na_3i \cdot C_5H_9O_2(C_{18}H_{35}O_2)_2$, congruently melting a	t 323 °C (compiler).
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of iso -pentanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+</u> 2 K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] Sodium thiocyanate; NaCNS; [540-72-7] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 523 K (250 $^{\circ}$ C) and $100x_2$ = 32.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 461.5+0.6 K; Preface, Table 2] before turning into a clear melt. Sokolov's fusion temperature (535 K) consequently should be identified with the clearing temperature, the corresponding value from Table 2 being 559+1 K. The latter figure is remarkably higher that that given by Ref. 1, altough meeting rather satisfactorily those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2. of the Preface. Accordingly, Sokolov's eutectic should be identified with an M_E point.

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>,A322, 281-299.

	r
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Colling too postancity (solding	Coholon N.V.
(1) Sodium 180.pentanoate (sodium	50K010V, N.M. Zh. Obshch. Khim. 1954 24 1150-1156
Na1.CcHoOo: [539-66-2]	
(2) Sodium thiocyanate;	
NaCNS; [540-72-7]	
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	L
$t/^{\circ}C$ T/K^{a} 100x	
	[
262 535 0 277 550 5	₹
	+-
288 561 15	
270 543 25	
256 529 30	300 - 200 -
250 523 32	89 2 ⁰
200 233 32 272 545 40	$ \boldsymbol{\varsigma} \setminus \boldsymbol{\gamma} $
285 558 45	V A A I
291 564 50	9 \set
297 570 55	250 - 겉 -
300 573 60	F
305 578 75	
306 579 90	
311 584 100	
T/K values calculated by the compiler.	
Characteristic point(s):	5 9 2
Eutectic, E, at 250 °C and $100x_2$ 32 (author)	•
1	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis.	Component 1 synthetized from iso.pentanoic
Salt(s) melted in a test tube. Temperature	acid and NaHCO3.
measured with a Nichrome-Constantane	Component 2 of analytical purity
thermocouple and a millivoltmeter with	recrystallized once from water and once
mirror reading to 1/ mV.	rrom etnanol.
	ESTIMATED ERROR:
	remperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] Sodium nitrite; NaNO₂; [7632-00-0] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 542 K (269 $^{\circ}$ C) and $100x_2$ = 21.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 461.5+0.6 K; Preface, Table 2] before turning into a clear melt. Sokolov's fusion temperature (535 K) consequently should be identified with the clearing temperature, the corresponding value from Table 2 being 559+1 K. The latter figure is remarkably higher that that given by Ref. 1, although meeting rather satisfactorily those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Allowance being made for the fact that a liquid-liquid miscibility gap impinges on the liquidus branch richer in the higher melting component (NaNO₂), the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, and Sokolov's eutectic ought to be identified with an M'_E point.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971,A322, 281-299.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium iso.pentanoate (sodium	Sokolov, N.M.
130.valerate); Na1.C ₅ H ₀ O ₂ ; [539-66-2]	Zn. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957,
(2) Sodium nitrite;	27, 917-920.
$NaNO_2; [7632-00-0]$	
VARIABLES:	PREPARED BY:
Tomo o no humo	Détadance C
Temperature.	D'Aldrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
262 535 0	
278 551 10	
276 549 15	
270 543 20 272 545 25	P
273 546 30	280 -
274 547 40	
275 548 45 277 550 50	
278 551 55	E
279 552 60 282 555 65	250 -
a T/K values calculated by the compiler.	
Note - Liquid Layering occurs at $66 \leq 100x_2 \leq 98.4$ (author).	0 35 100×2 70 Na / . C_H_O_ NaNO_
Characteristic point(s):	394 2
Eutectic, E, at 269 ^O C and 100x ₂ = 21 (author)	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis; salt mixtures	Component 1: prepared from "chemically
wider tube) and stirred with a glass	in the reference quoted by the author;
stirrer. The temperatures of initial	compiler), and commercial iso.pentanoic
Nichrome-Constantane thermocouple checked	acid distilled before use (Ref. 1); the recovered salt was recrystallized from n-
at the fusion points of water, benzoic	butanol.
$K_{2}Cr_{2}O_{7}$.	recrystallized from water; $t_{fur}(2)/{}^{\circ}C= 284$.
	200
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K
	(Compiler).
	(1) SOKOLOV, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.

COMPONENTS:	EVALUATOR:
 Sodium iso-pentanoate (sodium iso.valerate) Nai.C₅H₉O₂; [539-66-2] Sodium nitrate; NaNO₃; [7631-99-4] 	Ferloni, P., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).

This binary was studied by visual polythermal and thermographical analysis by Sokolov (Ref. 1), and Dmitrevkaya and Sokolov (Ref. 2), respectively, with substantially analogous results. The phase diagram was claimed by these authors to be of the cutectic type with the invariant at either 527 K (254 °C) and $100x_1$ = 31 (Ref. 1), or 526 K (253 °C) and $100x_1$ = 31.5 (Ref. 2).

Component 1, however, forms liquid crystals. Consequently, the fusion temperature, $T_{fus}(1)=535$ K (262°C; Ref.s 1, 2) should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being 559±1 K. The latter figure is remarkably higher than that by the above mentioned investigators, and agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

For the same component: (i) the transition at 451 K (178 $^{\circ}$ C) quoted in Ref. 2 from Ref. 5 should be identified with the actual fusion temperature, the corresponding value from Table 2 being 461.5+0.6 K, whereas (ii) the transition at 425 K (152 $^{\circ}$ C) also quoted in Ref. 2 from Ref. 5 has no correspondence in Table 2.

Thus the whole phase diagram should be re-interpreted, e.g., with reference to Scheme A.2 of the Preface. In particular, the invariant at 526 K and $100x_1$ = 31.5 should be an M_E^{-} point and not a conventional eutectic.

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1150-1156.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M.
 Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.
- (3) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature <u>1970</u>, 228, 50-52.
- (4) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.
- (5) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. <u>1956</u>.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] (2) Sodium nitrate; NaNO₃; [7631-99-4]</pre>	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o C T/K ^a 100x ₂	
262 535 0 273 546 5 280 553 10 280 553 15 265 538 25 257 530 30 254 527 31.2 260 533 35 272 545 40 282 555 45 288 561 50 294 567 55 299 572 60 302 575 65 304 577 75 306 579 85 307 580 95 308 581 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 254 °C and $100x_2$ = 31 (author)	$\frac{1}{250} + \frac{1}{100} + \frac{1}$
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.	Component 1 synthetized from iso .pentanoic acid and NaHCO ₃ . Commercial component 2 further purified by the author according to Laiti.
	ESTIMATED ERROR: Temperature: accuracy probably +2 K (compiler).
	KEFEKENCES:



COMPONENTS:

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    Sodium hexanoate (sodium caproate);
NaC<sub>6</sub>H<sub>11</sub>O<sub>2</sub>; [10051-44-2]
    Sodium benzoate;
NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub>; [532-32-1]
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CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a "perekhodnaya tochka" (P) at 644 K ($371 \, {}^{\rm O}$ C) and $100x_2$ = 13.

Component 1, however, forms liquid crystals [above $T_{fug}(1)$ = 499.6+0.6 K; Table 1 of the Preface] before turning into a clear melt. Sokolov's fusion temperature (638 K) should be consequently identified with the clearing temperature, the corresponding value from Table 1 being 639.0+0.5 K.

Sokolov's P point at $100x_2=13$ corresponds to a slightly marked minimum of the data listed in Ref. 1: the experimental temperature values at $5 \le 100x_2 \le 15$ actually range between 642 and 647 K, i.e. approximately within the accuracy limits estimated by the compiler.

If the temperature differences between the maximum at 646 K (and $100x_2=10$) and the P point at 644 K is thought to be meaningful, the phase diagram could be interpreted with reference to Scheme A.2 of the Preface: accordingly, Sokolov's invariant should be identified with an M'_E point).

If, on the contrary, the above mentioned temperature difference is thought to be meaningless, reference can be made to the front figure, where Sokolov's data are reported. In this case a peritectic equilibrium should exist (at about 644 K) among a liquid crystal, an isotropic liquid and a solid crystal. Accordingly, Sokolov's P point should be identified with an M'_P point, and a further invariant should exist, e.g. an M_E at $T \leq T_{fus}(1)$.

REFERENCES:

Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.



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Spinolo, G.,
Dipartimento di Chimica Fisica,
Universita' di Pavia (ITALY).
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] Sodium benzoate; NaC₇H₅O₂; [532-32-1] 	Sokolov, N.M. · Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARTABLES:	PREPARED BY:
-	
Temperature.	D Andrea, G.
EXPERIMENTAL VALUES:	
t/ ^o c T/K ^a 100x ₂	· []
<pre>365 638 0 369 642 5 373 646 10 371 644 13 374 647 15 380 653 20 396 669 35 400 673 40 463 736 100 ^a T/K values calculated by the compiler.</pre>	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ $
Note - The system was investigated between $0 \le 100x_2 \le 40$ due to thermal instability of the hexanoate.	
AUXILIARY I	NFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.
	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 Sodium hexanoate (sodium caproate);	Ferloni, P.,
Na C ₆ H ₁₁ O ₂ ; [10051-44-2] Sodium octadecanoate (sodium stearate);	Dipartimento di Chimica Fisica,
Na C ₁₈ H ₃₅ O ₂ ; [822-16-2]	Universita' di Pavia (ITALY).

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(C_6H_{11}O_2)_2(C_{18}H_{35}O_2)_3$ [congruently melting at 602 K (329 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 512 K (239 °C) and $100x_2$ = 17.5, and a "perekhodnaya tochka" at 587 K (314 °C) and $100x_2$ = 94.5.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Table 1 of the Preface), and two for component 2 (see Table 4 of the Preface). Sokolov's fusion temperatures, $T_{fus}(1)$ = 638 K (365 °C), and $T_{fus}(2)$ = 581 K (308 °C), are consequently to be identified with the clearing temperatures, the corresponding values from Tables 1 and 4 being 639.0±0.5 and 552.7 K, respectively.

Since the complete topology of the binary can hardly be interpreted from the data available, it is more realistic to list here the few points which, in the evaluator's opinion, seem to be sufficiently reliable.

(i) At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 602 K and $100x_2$ = 60.

(ii) Accordingly, the left hand section ($0 \leq 100x_2 \leq 60$) of the phase diagram might be interpreted with reference to Scheme C.2 of the Preface: in this case, Sokolov's eutectic should be intended as an M_E^{*} point.

Conversely, no definite interpretation of the phase diagram at high $100x_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100x_2 = 94.5$) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

- Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
 Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic
- Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors) Pergamon Press, Oxford, <u>1980</u>, 29-115.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	
365 638 0 326 599 55 320 593 5 329 602 60 272 545 10 328 601 65 242 515 15 327 600 70 239 512 17.5 326 599 75 248 521 20 324 597 80 264 537 25 321 594 85 280 553 30 319 592 90 293 566 35 314 587 94.5 305 578 40 316 589 95 313 586 45 308 581 100 320 593 50 ^a T/K values calculated by the compiler. Characteristic point(s): Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 314 °C and $100x_2= 94.5$ (author). Eutectic, E, at 239 °C and $100x_2= 17.5$ (author) Intermediate compound(s): Na ₅ (C _c H ₁₀ O ₂) ₂ (C ₁₈ H ₃₅ O ₂) ₃ (author),	rec > 1
congruently melting at 329 °C (compiler).	
AUXILIARY 1	
METHOD/APPARATUS/PROCEDURE: Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome- Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of iso- tropicity in the melt on cooling.	Source and PORITY OF MATERIALS: Component 1: prepared by reacting aqueous ("chemically pure") Na ₂ CO ₃ with a slight excess of n-hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.
	ESTIMATED ERROR:
	Temperature: accuracy probably +2 K (compiler).
	REFERENCES:

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COMPONENTS:	EVALUATOR:
 Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] Sodium thiocyanate; NaCNS; [540-72-7] 	Spinolo, G., Dipartimento di Chimica Fisica, Universita ⁻ di Pavia (ITALY).
CRITICAL EVALUATION:	

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 568 K (295 $^{\circ}$ C) and $100x_2$ = 63.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 499.6±0.6 K; Preface, Table 1] before turning into a clear welt. Sokolov's fusion temperature (638 K) is consequently to be identified with the clearing temperature, the corresponding value from Table 1 being 639.0±0.5 K.

Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, and Sokolov's eutectic ought to be intended as an M'_E point.

REFERENCES:

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2] Sodium thiocyanate; NaCNS; [540-72-7] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1150-1156.
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
EXPERIMENTAL VALUES:	
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2}$	·
365 638 0 330 603 50 383 656 5 316 589 55 397 670 10 305 578 60 399 672 15 295 568 63 386 659 25 297 570 65 377 650 30 304 577 75 366 639 35 307 580 90 352 625 40 311 584 100 342 615 45 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 295 °C and $100x_2= 63$ (autho	$\frac{400}{350} - \frac{1}{100} - \frac{1}{100} + $
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17	Component 1 synthetized from n-hexanoic acid and NaHCO ₃ . Component 2 of analytical purity recrystallized once from water and once from ethanol.
mv.	ESTIMATED ERROR:
	Temperature: accuracy probably <u>+2</u> K (compiler).
COMPONENTS:	EVALUATOR:
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 Sodium hexanoate (sodium caproate);	Ferloni, P.,
NaC ₆ H ₁₁ O ₂ ; [10051-44-2] Sodium nitrate;	Dipartimento di Chimica Fisica,
NaNO ₃ ; [7631-99-4]	Universita ⁻ di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 560 K (287 $^{\circ}$ C) and $100x_2$ = 56.5, and the occurrence of liquid layering at 576 K (302 $^{\circ}$ C) and $100x_2$ > 60.

Component 1, however, forms liquid crystals [at $T_{fus}(1) = 499.6\pm0.6$ K; Preface, Table 1] before turning into a clear melt. Sokolov's fusion temperature (638 K) is consequently to be identified with the clearing temperature, the corresponding value from Table 1 being 639.0\pm0.5 K. Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, allowance being made for the fact that a liquid-liquid miscibility gap impinges on the liquidus branch richer in the higher melting component (NaNO₃). Consequently, Sokolov's eutectic should be an M'_E point.

REFERENCES:

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Sodium bexanoate (sodium caproate):	Sokolov N.N.		
NaC ₆ H ₁ , O ₂ : [10051-44-2]	Zh. Obshch. Khim. 1954, 24, 1150-1156.		
(2) Sodium nitrate;	,,		
NaNO ₃ ; [7631-99-4]			
VARIABLES:	PREPARED BI:		
Temperature.	D'Andrea, G.		
EXPERIMENTAL VALUES:			
	y , , , , , , , , , , , , , , , , , , ,		
$t^{0}C T/K^{\alpha} 100x_{2}$	$\hat{\tau}$		
365 638 0			
376 649 5	Ĭ \z		
383 656 10	350 -		
385 658 15			
375 648 25	4		
357 630 35	ζ.		
342 615 40	300 - \@		
326 599 45	χ I		
313 586 50	Ĕ		
296 569 55			
287 560 56.5			
300 573 59			
302 373 60			
^a T/K values calculated by the compiler.	6 11 2 3		
Characteristic point(s): Eutectic, E, at 287	^o C and $100x_2 = 56.5$ (author).		
AUXILIARY I	NFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS.		
Visual polythermal analysis. Salt(s) melted	Component 1 synthetized from n-hexanoic		
in a test tube. Temperature measured with a	acid and NaHCO3. Commercial component 2		
Nichrome-Constantane thermocouple and a	further purified by the author according to		
mV.	44111.		
	ESTIMATED ERROR:		
NOTE:			
	Temperature: accuracy probably +2 K		
At $100x_2 > 60$, liquid layering occurs.	(compiler).		

COMPONENTS:	EVALUATOR:
 Sodium benzoate;	Ferloni, P.
NaC ₇ H ₅ O ₂ ; [532-32-1] Sodium octadecanoate (sodium stearate);	Dipartimento di Chimica Fisica.
NaC ₁₈ H ₃₅ O ₂ ; [822-16-2]	Universita´ di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1) who reported a phase diagram of the eutectic type with the invariant at 574 K (301 $^{\circ}$ C) and 100x₁= 1.3.

Component 2, however, forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2) = 581$ K (308 °C), should be intended as a clearing temperature and compared with the $T_{clr}(2)$ value reported in Table 4 (552.7 K). It is to be stressed that Sokolov's "fusion" temperature looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

The whole phase diagram is therefore to be reconsidered.

REFERENCES:

- (1) Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u>, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u>, 29-115.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Sodium benzoate; NaC_{7H5}O₂; [532-32-1] Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2] 	Sokolov, N.M. Zh. Obshch. Khim. <u>1954</u> , 24, 1581-1593.	
VARIABLES:	PREPARED BY:	
Tamparatura	D'Androa C	
iemperature.	D'Allurea, U.	
EXPERIMENTAL VALUES:		
t/ ^o C T/K ^a 100x ₁		
308 581 0 301 574 1.3 310 583 5 321 594 10 332 605 15 344 617 20 353 626 24 362 635 30 369 642 35 376 649 40 384 657 45 390 663 50 396 669 55 463 736 100 ^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 301 °C and $100x_1 = 1.3$ (author Note - The system was investigated at 0 ≤ 10 octadecanoate.	$\begin{array}{c} & & \\$	
AUXILIARY I	NFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Visual polythermal analysis. Malte con	"Chemically nure" materials	
tained in a glass tube and stirred.	CHEMICALLY PURE MATERIALS.	
Constantane thermocouple and a 17 mV full		
scale millivoltmeter. The temperature readings refer to the disappearance of iso-	compiler).	
tropicity in the melt on cooling.	REFERENCES:	
	(1) Sanesi, M.; Cingolani, A.; Tonelli,	
Component 2 forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2)$ = 581 K (308 °C), should be intended as a clearing temperature and compared with the $T_{c1r}(2)$ value (552.7 K) reported on Preface, Table 4. It is to be stressed that Sokolov's "fusion" temperature looks as fully unreliable, being 18 K higher than the second highest T_{c1r} value determined during the last 30 years (Ref. 1), and 28 K higher than the clearing temperature listed in Table 4. The whole phase diagram is therefore to be reconsidered.	P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, <u>1980</u> , 29-115.	

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COMPONENTS:

(1) Rubidium ethanoate (rubidium acetate); RbC₂H₃O₂; [563-67-7] (2) Rubidium nitrate; RbNO3; [13126-12-0]

CRITICAL EVALUATION:

This binary was studied for the first time by Gimel'shtein and Diogenov (Ref. 1) who reported the lower boundary of the isotropic liquid region in the reciprocal ternary $Na, Rb/C_2H_3O_2, NO_3$ on the basis of visual polythermal observations. They claimed the existence of the intermediate compound $Rb_3(C_2H_3O_2)_2NO_3$ (congruently melting at 475 K [202 °C]) and of two eutectics, E_1 , at 471 K (198 °C) and $100x_1 = 81.5$, and E_2 , at 454 K (181 °C) and $100x_1 = 25.5$ $100x_1 = 35.5$.

In a subsequent paper on the reciprocal ternary $C_{s,Rb}/C_{2}H_{3}O_{2}$, NO₃ (Ref. 2), the same Authors reported refined values of the coordinates of the second eutectic (467 K $[194 ^{\circ}C]$ and $100x_1 = 33$), obtained with the same experimental approach. The new data suggest that those reported in Ref. 1 should be affected by a systematic error (as high as 13 K) in the composition range $20 \le 100 x_1 \le 50$.



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Dipartimento di Chimica Fisica,
Universita' di Pavia (ITALY).
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The system was once more investigated by Gimel'shtein (Ref. 3) who directly measured with D.T.A. the temperatures of the characteristic points previously inferred by the shape of the liquidus. Besides a substantial agreement with the findings of Ref. 2, he reported two more solid state transitions of pure $RbNO_3$, at 437 and 505 K. Moreover, the existence of an intermediate compound was more reliably proved by a comparison of the X-ray powder pattern of an intermediate mixture, which showed diffraction lines not pertinent to either pure component.

Finally, the composition of the compound was adjusted by Diogenov, Erlykov and Gimel shtein (Ref. 4) during an investigation of the reciprocal ternary L1,Rb/C2H3O2,NO3 with coupled visual polythermal and thermographical analysis. According to this paper, the compound has a 1:1 composition and congruently melts at 476 K (203 $^{\circ}$ C) and the eutectics are at 467 K (194 °C) and $100x_1 = 33.5$ and at 471 K (198 °C) and $100x_1 = 82$, respectively.

In spite of the lack of any comment by the Authors on their previous results, the evaluator is inclined to recommend the last interpretation as the more reliable. The figure reports phase boundaries drawn accordingly. On the same figure, the two sets of experimental data, available in numerical form (the visual polythermal data from Ref. 1 and the thermographical data from Ref. 3), have also been plotted as open and full circles, respectively. As a further remark, the melting and transition points of component 1 reported on Ref.s 1-4 reasonably match the most recent literature data: $T_{fus}(1) = 510$, 515, 514, 514, 509; $T_{trs}(1) = 498$ (Ref. 5). For what concerns the phase transitions of component 2, reference can be made to the recent work by Kennedy et al. (Ref. 6 and the bibliography therein quoted).

REFERENCES:

- (1) Gimel'shtein, V.G.; Diogenov, G.G.; Zh. Neorg. Khim. 1958, 3, 1644-1649 (*); Russ.
- (1) Ginel siteli, V.G., Diogenov, G.G., and Keorge Knill, 1990, 3, 1044-1049 (*); Russ.
 J. Inorg. Chem. (Engl. Transl.) 1958, 3 (7), 230-237.
 (2) Diogenov, G.G.; Gimel'shtein, V.G.; Zh. Neorg. Khim. 1966, 11, 207-209 (*); Russ.
 J. Inorg. Chem. (Engl. Transl.) 1966, 11, 113-114.
 (3) Gimel'shtein, V.G.; Tr. Irkutsk. Politekh. Inst. 1971, No. 66, 80-100.
- (4) Diogenov, G.G.; Erlykov, A.M.; Gimel shtein, V.G.; Zh. Neorg. Khim. 1974, 19, 1955-1960; Russ. J. Inorg. Chem. (Engl. Transl.) <u>1974</u>, **19**, 1069-1073 (*). (5) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.; Thermal Properties, in
- Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115. (6) Kennedy, S.W.; Kriven, W.M.; J. Mater. Sci. 1976, 11, 1767-1769.

COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Rubidium ethanoate (rubidium acetate); RbC₂H₃O₂; [563-67-7] Rubidium nitrate; RbNO₃; [13126-12-0] 	Gimel'shtein, V.G.; Diogenov, G.G. Zh. Neorg. Khim. <u>1958</u> , 3, 1644-1649 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1958</u> , 3 (7), 230-237.		
VARIABLES:	PREPARED BY:		
Temperature	D'Andrea, G.		
EXPERIMENTAL VALUES:	······································		
$t/^{\circ}C T/K^{a} = 100x_{1} t/^{\circ}C T/K^{a} = 100x_{1} t/^{\circ}$	$C T/K^{a} = 100x_{1} t/^{o}C T/K^{a} = 100x_{1}$		
317 590 0 212 485 22 201 300 573 3 205 478 25 201 280 553 6 194 467 30.2 202 260 533 10.5 183 456 35 202 244 517 14.3 190 463 41 202 226 499 18.5 198 471 54 201	474 59 202 475 82.5 474 62.5 209 482 86 475 66 213 486 89.5 475 69 224 497 94.5 475 72.5 236 509 100 474 77.5 474 77.5		
^a T/K values calculated by the compiler.			
Characteristic point(s): Eutectic, E ₁ , at 198 Eutectic, E ₂ , at 181	$^{\circ}$ C and 100x ₁ = 81.5 (authors). $^{\circ}$ C and 100x ₁ = 35.5 (authors).		
Intermediate compound: Rb ₃ (C ₂ H ₃ O ₂) ₂ NO ₃ , com	agruently melting at 202 $^{ m OC}$ (authors).		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal method. Temperatures measured with a Chromel-Alumel thermocouple and a 17-mV-range millivoltmeter. Mixtures being hygroscopic, the method of additions	Not stated. Component 1 undergoes a phase transition at $t/^{\circ}C=216$. Component 2 undergoes phase transitions at $t/^{\circ}C=210$, 290.		
difference was employed in order to avoid	ESTIMATED ERROR:		
nyuration.	Temperature: accuracy probably <u>+</u> 2 K (compiler).		
COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Rubidium ethanoate (rubidium acetate); RbC₂H₃O₂; [563-67-7] Rubidium nitrate; RbNO₃; [13126-12-0] 	Diogenov, G.G.; Gimel'shtein, V.G. Zh. Neorg. Khim. <u>1966</u> , 11, 207-209 (*); Russ. J. Inorg. Chem. (Engl. Transl.) <u>1966</u> , 11, 113-114.		
VARIABLES:	PREPARED BY:		
Temperature	D'Andrea, G.		
EXPERIMENTAL VALUES:			
The paper reports - inter alia - on a refinement of the title binary, previously studied by the same authors (Ref. 1). According to the present investigation, the coordinates of the second eutectic are:			
Eutectic, E_2 , at 194 °C and 100 $x_1 = 33$ (authorse	ors).		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Visual polythermal method. Temperatures measured with a Chromel-Alumel	Not stated.		
thermocouple.	REFERENCES:		
ESTIMATED ERROR: Temperature: accuracy probably <u>+</u> 2 K (compiler).	 (1) Gimel'shtein, V.G.; Diogenov, G.G. Zh. Neorg. Khim. <u>1958</u>, 3, 1644-1649 (*); Russ. J. Inorg. Chem. (Engl. Transl.), 1958, 3 (7), 230-237. 		

COMPONENTS:	ORIGINAL MEASUREMENTS:		
 (1) Rubidium ethanoate (rubidium acetate); RbC₂H₃O₂; [563-67-7] (2) Rubidium nitrate; RbNO₃; [13126-12-0] 	Gimel'shtein, V.G. Tr. Irkutsk. Politekh. Inst. <u>1971</u> , No. 66, 80-100.		
VARIABLES:	PREPARED BY:		
Temperature.	D'Andrea, G.		
EXPERIMENTAL VALUES:			
$t/^{o}C T/K^{a} 100x_{2} t/^{o}C T/K^{a} 100x_{2} t$	$/^{o}C T/K^{a} = 100 x_{2} t/^{o}C T/K^{a} = 100 x_{2}$		
235 508 0 202 475 55.0 195 468 80.0 164 437 90.0 206 479 0 193 466 55.0 164 437 80.0 315 588 100 222 495 5.0 164 437 55.0 260 533 90.0 285 558 100 207 480 5.0 200 473 70.0 232 505 90.0 232 505 100 198 471 5.0 192 465 70.0 216 489 90.0 216 489 100 205 478 15.0 165 438 70.0 194 467 90.0 164 437 100 205 478 25.0 220 493 80.0 ^a T/K values calculated by the compiler. The meaning of the data listed in the table becomes apparent by observing the figure reported in the critical evaluation. Characteristic point(s): Eutectic, E_1 , at 198 °C (composition not reported) (author). Eutectic, E_2 , at 194 °C (composition not reported) (author). Intermediate compound(s): Rb ₃ (C ₂ H ₃ O ₂) ₂ NO ₃ , congruently melting at 202 °C (author), and undergoing a phase transition at 65 °C (author).			
AUXILIARY I	NFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Differential thermal analysis (using a derivatograph with automatic recording of the heating curves) and room temperature X-ray diffractometry (using a URS-501M apparatus) were employed. X-ray patterns were taken at $100x_2 = 40$.	Not stated. Component 1 melts at $t_{fus}/^{o}C= 235$, and undergoes a phase transition at $t/^{o}C= 206$. Component 2 melts at $t_{fus}/^{o}C= 315$, and undergoes phase transitions at $t/^{o}C= 164$, 216, 232, 285.		
	ESTIMATED ERROR:		
	Temperature: accuracy probably <u>+</u> 2 K (compiler).		
	REFERENCES:		

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Rubidium ethanoate (rubidium acetate); RbC ₂ H ₂ O ₂ ; [563-67-7]	Diogenov, G.G.; Erlykov, A.M.; Gimel'shtein, V.G.
(2) Rubidium nitrate; RbNO.: [13126-12-0]	Zh. Neorg. Khim. 1974, 19, 1955-1960; Russ.
	1069-1073 (*).
VARIABLES:	PREPARED BY:
Temperature.	D'Andrea, G.
-	
EXPERIMENTAL VALUES:	
Characteristic point(s):	
Eutectic, E_1 , at 198 °C and $100x_2$ 18 (author Eutectic, E_2 , at 194 °C and $100x_2$ 66.5 (author	s). Nors).
Intermediate compound(s):	
$Rb_2C_2H_3O_2NO_3$, congruently melting at 203 ^o C (authors).
	NFORMATION
METHOD / APPARATUS / PROCEDURE .	
The data were obtained by viewal	Not stated. Component 1 undergoes a phase
polythermal and thermographic methods,	transition at $t/^{\circ}C= 206$ and melts at $t = 100000000000000000000000000000000000$
patterns.	Component 2 melts at t _{fus} / ^o C= 317.
	Collinaled Error:
	(compiler).
	REFERENCES:

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