- (1) Potassium bromide; KBr; [7758-02-3]
- (2) Potassium methanoate (potassium formate); KCHO₂; [590-29-4]

ORIGINAL MEASUREMENTS:

Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. 1970, 25a, 52-55.

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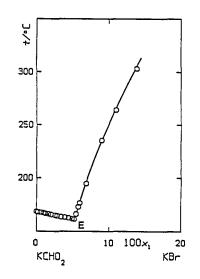
VARIABLES: Temperature.

IABLES: PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x ₁
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
	537.2	10.99
303.1	576.3	13.90



Characteristic point(s): Eutectic, E, at 161.3 °C and $100x_1 = 5.3$ (authors).

AUXILIARY INFORMATION

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.

NOTES:

under vacuum.

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.

C. Erba RP meterials, dried by heating

SOURCE AND PURITY OF MATERIALS:

The system could not be investigated above about $300\,^{\circ}\text{C}$ due to the thermal instability of the methanoate.

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.

ESTIMATED ERROR:

Temperature: accuracy probably $\pm 0.1 \text{ K}$ (compiler).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

a T/K values calculated by the compiler.

- (1) Potassium bromide;
- KBr; [7758-02-3]
- (2) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]

ORIGINAL MEASUREMENTS:

Il'yasov. I.I.; Bergman, A.G.
Zh. Obshch. Khim. 1961, 31, 368-370.

VARIABLES:

Temperature.

PREPARED BY:

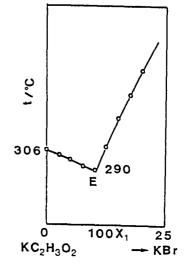
Baldini, P.

EXPERIMENTAL VALUES:

The results are given only in graphical form (see figure). The system was investigated at $0 \le 100x_1 \le 25$.

Characteristic point(s):

Eutectic, E, at 290 $^{\circ}$ C and $100x_1 = 10$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple and a millivoltmeter (Ref. 1).

NOTE:

See the NOTE relevant to the results obtained by Piantoni et al. (Ref. 2) on the same system (next Table).

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1: $t_{fus}(1)/^{o}C=740$. Component 2: $t_{fus}(2)/^{o}C=306$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K.

- (1) Il'yasov, I.I.; Bergman, A.G. Zh. Obshch. Khim. 1960, 30, 355-358.
- (2) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. 1968, 38, 127-132.

- (1) Potassium bromide; KBr; [7758-02-3]
- (2) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P.

Ric. Sci. 1968, 38, 127-132.

VARIABLES:

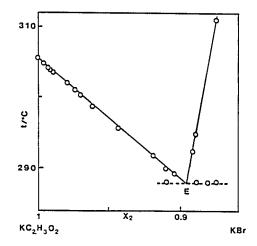
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are given only in graphical form (see figure). The system was investigated at 0 \leq 100 x_1 \leq 13.



Characteristic point(s):

Eutectic, E, at 287.9 °C and $100x_2$ = 89.5 (authors).

AUXILIARY INFORMATION

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.

NOTE:

Higher accuracy, and satisfactory mutual consistency of the results obtained by Piantoni et al. for the three binaries K/C₂H₃O₂, (Br,Cl,I) suggest to prefer here the data by these authors to those by Il'yasov and Bergman (Ref. 2). Increasingly positive deviation from ideality was observed by Piantoni et al. for the liquidus branch richer in the halide when KCl, KBr, and KI were successively taken into account. This is consistent with the (cryometric) limiting values:

[$\lim_{2\to 0} (\Delta T/m_2) = 17.7$, 17.4, and 16.0 K $m_2 \to 0$

molality⁻¹, respectively] previously found by Braghetti et al. (Ref. 1) when the same halides were employed as solutes in molten potassium ethanoate (whose cryometric constant is: $K_1 = 18.0 \pm 0.3$ K molality⁻¹; Ref. 1).

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum (private communication by the authors to the compiler).

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4]
- (2) Potassium ethanoate (potassium acetate);

 $KC_2H_3O_2$; [127-08-2]

PREPARED BY:

Sokolov, N.M.

ORIGINAL MEASUREMENTS:

Zh. Obshch. Khim. 1965, 35, 1897-1902.

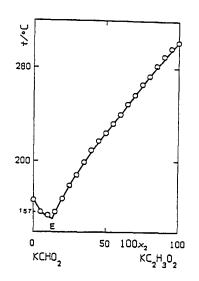
Baldini, P.

VARIABLES:

Temperature.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2
167	440	0
157	430	5
154	427	10
157	430	15
168	441	20
179	452	25
188	461	30
199	472	35
209	482	40
217	490	45
224	497	50
232	505	55
240	513	60
249	522	65
257	530	70
266	539	75
273	546	80
282	555	85
290	563	90
297	570	95
302	575	100



a T/K values calculated by the compiler.

Characteristic point(s): Eutectic, E, at 151 $^{\circ}$ C and $100x_{2}$ = 13 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

The fusion temperatures found by Sokolov are in reasonable agreement with those reported in Preface, Table 1 [$T_{fus}(1)$ = 441.9+0.5 K, and $T_{fus}(2)$ = 578.7+0.5 K]. Disagreement, on the contrary, exists about the number and location of the solid state transitions. As an example, for component 1 Table 1 of the Preface reports a single transition at a temperature (418+1 K)halfway between the highest (430 K) and second highest (408 K) values by Sokolov; the literature unfortunately provides no other data (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

SOURCE AND PURITY OF MATERIALS:

Not stated.

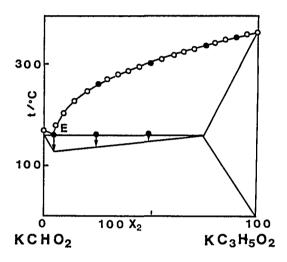
Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C=60, 135, 157 (Ref. 1).$ Component 2 undergoes phase transitions at

 $t_{trs}(2)/^{o}C=58$, 150 [Ref. 1; the figure 150, however, is probably a misprint, because in several other papers the same author, quoting the same source (unavailable to the compiler), reports the figure 155; compiler].

- (1) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (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.

COMPONENTS: (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4] (2) Potassium propanoate (potassium propionate); KC₃H₅O₂ [327-62-8] VARIABLES: PREPARED BY: Baldini, P.

EXPERIMENTAL VALUES:



The results are reported only in graphical form (see figure; empty circles: visual polythermal analysis; filled circles: thermographical analysis).

Characteristic point(s): Eutectic, E, at 160 °C and $100x_2$ = 5 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis supplemented with thermographical analysis.

NOTE:

The fusion temperatures by Sokolov and Minchenko (440 and 638 K for components 1 and 2, respectively) almost coincide with those listed in Preface, Table 1 (respect ively 441.9+0.5 K and 638.3+0.5 K). approximate agreement exists also on the solid state transition of component 2. On the contrary, there in disagreement about solid state transitions of component 1, inasmuch as Table 1 of the Preface reports a single transformation at a temperature halfway between the highest (418+1 K) (430 K) and second highest (408 K) values by Sokolov and Minchenko; the literature, unfortunately, provides no other data (Ref. 3).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

SOURCE AND PURITY OF MATERIALS:

Component 1 (commercial material recrystallized from methanoic acid) melts at $t_{fus}(1)^{/O}C=167$ and undergoes phase transitions at $t_{trs}(1)^{/O}C=60$, 135, 157 (Ref. 1). Component 2 (prepared from propanoic acid and carbonate, Ref.2) melts at 365 ^{O}C and undergoes a phase transition at 68 ^{O}C (Ref. 1).

- (1) Sokolov, N.M.

 Tezisy Dokl. X Nauch. Konf. S.M.I.
 1956,
- (2) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (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, 1980, 29-115.

COMPONENTS:	EVALUATOR:
(1) Potassium methanoate (potassium formate); KCHO ₂ ; [590-29-4] (2) Potassium butanoate (potassium butyrate); KC ₄ H ₇ O ₂ [589-39-9]	Dipartimento di Chimica Fisica,

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 (ii) 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. Obshch. Khim., 1974, 44, 1429-1431.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium methanoate (potassium formate); KCHO ₂ ; [590-29-4] (2) Potassium butanoate (potassium butyrate); KC ₄ H ₇ O ₂ [589-39-9]	Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim., 1974, 44, 1429-1431.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).

Characteristic point(s): Eutectic, E, at 166 °C and $100x_2$ = 0.9 (authors).

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

167, popular and a 100 K C H O 2 K C 4H 7O 2

Component 1: commercial material recrystallized; it melts at 167 $^{\rm O}$ C. Component 2: prepared from n-butanoic acid and the carbonate (Ref. 1); it melts at $\rm t_{fus}(2)/^{\rm O}C=404$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1581-1593.

- Potassium methanoate (potassium formate);
 KCHO₂; [590-29-4]
- (2) Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂ [19455-20-0]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

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 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 [$T_{\rm fus}(2)$ = 553.9+0.5 K] listed in Preface, Table 2. Consequently: (i) the transition temperature at $\overline{621}$ 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 $T_{\rm trs}(2)$ value (424+3 K) listed in Table 2 of the Preface.

- (1) Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim., 1977, 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, 1980, 29-115.

- (1) Potassium methanoate (potassium formate);
 - KCHO₂; [590-29-4]
- (2) Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂ [19455-20-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim., 1977, 47, 740-742.

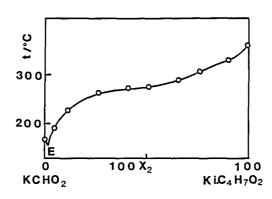
VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:



The results are reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 164 °C and $100x_2 = 1$ (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: commercial material recrystallized from methanoic acid; it melts at $t_{fus}(1)/^{0}c=167$ and undergoes phase transitions at $t_{trs}(1)/^{0}c=60$, 135, 157.

Component 2: prepared from i-butanoic acid and the carbonate (Ref. 1); it melts at $t_{\rm fus}(2)/^{\rm o}{\rm C}$ = 356 and undergoes phase transitions at $t_{\rm trs}(2)/^{\rm o}{\rm C}$ = 208, 273, 348.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

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

- (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4]
- (2) Potassium chloride; KC1; [7447-40-7]

ORIGINAL MEASUREMENTS:

Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. 1970, 25a, 52-55.

VARIABLES:

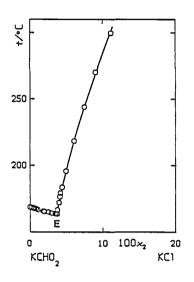
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T /K ^a	100 x 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
165.0	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



aT/K values calculated by the compiler.

Characteristic point(s): Eutectic, E, at 163.5 $^{\circ}\text{C}$ and $100\text{x}_{2}\text{=}$ 3.7 (authors).

AUXILIARY INFORMATION

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.

According to the authors, the trend of liquidus branch richer in component l 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 potassium cryometric constant of methanoate was K = 11.5+0.1 K molality⁻¹ and that $\lim_{n \to \infty} (\Delta T/m) = 1\overline{1.6} \text{ K}$ molality⁻¹

 $\ m\to 0$ (ΔT : experimental freezing point depression; m: molality of the solute) when KCl was the solute.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP meterials, dried by heating under vacuum.

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.

The system could not be investigated above $300\,^{\circ}\text{C}$ due to the thermal instability of the methanoate.

ESTIMATED ERROR:

Temperature: accuracy probably ± 0.1 K (compiler).

- (1) Braghetti, M.; Leonesi, D.; Franzosini, P.; Ric. Sci. 1968, 38, 116-118.
- (2) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P. Ric. Sci. 1968, 38, 702-705.

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

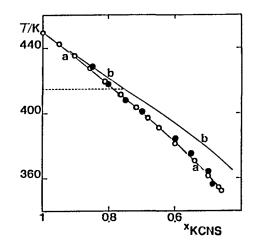
EVALUATOR:

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

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 $T_{\rm trs}$ and $\Delta_{\rm trs}H_{\rm m}$ 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 $T_{fus}(1)$ [440 K (Ref. 1); 441.85 K (Ref. 2)], $T_{fus}(2)$ [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

$$T(2) = \frac{\left[\Delta_{fus}(2)H_{m}/R + \Delta_{trs}(2)H_{m}/R\right] + (A/R)(x_{1})^{2}}{\left[\Delta_{fus}(2)S_{m}/R + \Delta_{trs}(2)S_{m}/R\right] - \ln x_{2}}$$

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: $\Delta_{\text{fus}}(2) H_{\text{m}}/R = 1545 \text{ K}$; $\Delta_{\text{trs}}(2) H_{\text{m}}/R = 186 \text{ K}$ (to be introduced only when $T(2) \leq T_{\text{trs}}$); 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 $T_{\rm trs}(2)/K=415$] a better evidence of the expected change of slope. Accordingly, and taking also into account the poor reliability of the $T_{\rm trs}(1)$ 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.

- (1) Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. 1958, 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. 1949, 17, 254.
- (5) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

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

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.

VARIABLES:

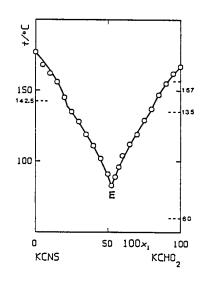
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 1
177	450	0
168	441	5
162	435	10
156	429	15
145	418	20
135	408	25
128	401	30
119	392	35
111	384	40
102	375	45
91	364	50
83	356	52.5
89	362	55
96	369	57.5
104	377	60
112	385	65
119	392	70
129	402	75
137	410	80
147	420	85
155	428	90
162	435	95
167	440	100



Characteristic point(s): Eutectic, E, at 83 °C and $100x_1 = 52.5$ (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: commercial material recrystallized from water; it undergoes phase transitions at $t_{trs}(1)/^{o}C=60$, 135, 157 (Ref. 1). Component 2: commercial material recrystallized from alcohol; it undergoes a phase transition at $t_{\rm trs}(2)/{}^{\rm o}{\rm C}$ = 142.5 (Ref. 2).

ESTIMATED ERROR:

+2 K Temperature: probably accuracy (compiler).

- (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Ravich, M.I.; Ketkovich, V.I.; Rassonskaya, I.S.; Izv. Sektora Fiz.-Khim. Anal. 1949, 17, 254.

a T/K values calculated by the compiler.

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

ORIGINAL MEASUREMENTS:

Berchiesi, G.; Laffitte, M. J. Chim. Phys. 1971, 877-881.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

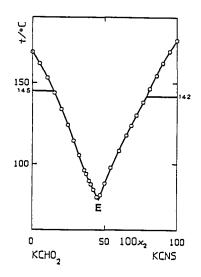
t/ ^o C	T/K ^a	100 x ₂	t/°C	T/K ^a	100 x 2
176.00 169.10 161.98 154.50 138.28 130.28 123.90 117.85 108.22 97.75	449.15 442.25 435.13 427.65 419.65 411.43 403.43 397.05 391.00 381.37 370.90 361.30	100 95.10 90.43 85.79 81.03 76.41 71.76 68.20 64.85 59.85 54.00 50.03	84.25 87.55 89.70 93.88 96.20 105.48 114.40 124.20 133.90 143.92 152.95	357.40 360.70 362.85 367.03 369.35 378.63 387.55 397.35 407.05 417.07 426.10 434.80	42.18 40.52 39.28 37.25 35.88 32.19 28.41 24.37 19.91 15.12 10.16 4.97
	354.18 353.00	46.91 44.45	168.70	441.85	0

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 78.5 °C and $100x_2$ = 46 (compiler).

Note - The data relevant to the liquidus branch richer in component 2 were already published in Ref. 1.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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).

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1 undergoes a phase transition at $T_{\rm trs}(1)/K=$ 418 (Ref. 1). Component 2 undergoes a phase transition at $T_{\rm trs}(2)/K=$ 415 (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably ±0.05 K (compiler).

- (1) Braghetti, M.; Berchiesi, G.; Franzosini, P. Ric. Sci. 1969. 39. 576-584.
- Ric. Sci. 1969, 39, 576-584.

 (2) Braghetti, M.; Leonesi, D.;
 Franzosini, P.
 Ric. Sci. 1968, 38, 116-118.

- (1) Potassium methanoate (potassium formate);
 KCHO: 1590-29-41
- KCHO₂; [590-29-4] (2) Potassium iodide; KI; [7681-11-0]

ORIGINAL MEASUREMENTS:

Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P.

Z. Naturforsch. 1970, 25a, 52-55.

VARIABLES:

Temperature.

PREPARED BY:

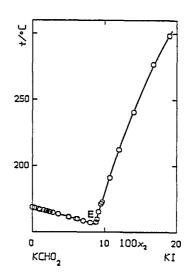
Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/Kª	100 x 2	t/°C	T/Kª	100 x 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 listed numerical values represent a private communication by one of the authors (F., P.) to the compiler.



Note 2 - The system could not be investigated above 300 $^{\rm O}{\rm C}$ due to the thermal instability of the methanoate.

Characteristic point(s): Eutectic, E, at 156.3 $^{\circ}$ C and $100x_{2}$ = 8.7 (authors).

AUXILIARY INFORMATION

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.

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.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum.

ESTIMATED ERROR:

Temperature: accuracy probably ±0.1 K (compiler).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- Potassium methanoate (potassium formate);
 KCHO₂; [590-29-4]
- (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/°C	T/K ^a	100 x 2
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			

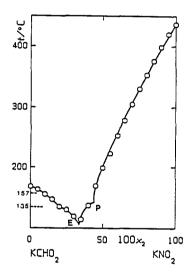
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 107 $^{\rm o}$ C and 100 x_2 = 33.5 (authors). Peritectic, P, at 143 $^{\rm o}$ C and 100 x_2 = 44 (authors).

Intermediate compound(s):

 ${
m K_2CHO_2NO_2}$ (tentative composition; authors) incongruently melting.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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 information from other sources is available. It can be noted, however, that, e.g., the trend of the liquidus branch richer in KCHO₂ of the binary K/CHO₂, NO₃ studied by Berchiesi et al. (Ref. 3) supports Table 1 statement. Moreover, the existence (and composition) of the intermediate compound ought to be more convincingly proved.

SOURCE AND PURITY OF MATERIALS:

Component 1: commercial "chemically pure" material recrystallized from methanoic acid; it undergoes phase transitions at $t_{\rm trs}(1)/^0{\rm C}=$ 60, 135, 157 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{\rm fus}(2)/^0{\rm C}=$ 436 after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^0{\rm C}=$ 45 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.
- (3) Berchiesi, G.; Cingolani, A.; Leonesi, D. Z. Naturforsch. 1970, 25a, 1766-1767.

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

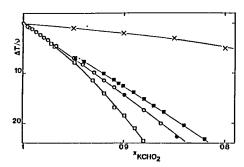
EVALUATOR:

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

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 $100x_2 = 32.5$, 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 incongruently melting intermediate compound [whose composition, argued from auxiliary DSC measurements, should be $K_5(\text{CHO}_2)_4\text{NO}_3$], a peritectic at 399.7 K and $100\text{x}_2=26.2$, and a eutectic at 387 K and $100\text{x}_2=37.9$.



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 $K_1=11.5\pm0.1$ K molality which corresponds to $\Delta_{\text{fus}}(1)\text{H}_{\text{m}}=11.9$ kJ mol (2.84±0.03 kcal mol 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 ; Ref. 4), and with Calvet microcalorimetry by Berchiesi and Laffitte (11.5±0.1 kJ mol ; Ref. 5).

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

[lim
$$(\Delta T/m_2)$$
]/y= 11.5, 11.55, and 11.4 K molality⁻¹ $m_2 \rightarrow 0$

for KNO_3 (y= 1; y: number of cryometrically active foreign species), $LiNO_3$ (y= 2), and $CsNO_3$ (v=2), respectively, which implies that a solubility of these solutes in $KCHO_2$ in the solid state should be either absent, or negligible. The three sets of $(\Delta T/\Sigma)$ 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/CHO₂, NO₃ 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, O.I.; 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. 1968, 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.

COMPONENTS: (1) Potassium methanoate (potassium formate); KCHO₂; [590-29-4] 2) Potassium nitrate; KNO₃; [7757-79-1] VARIABLES: Temperature. CORIGINAL MEASUREMENTS: Dmitrevskaya, O.I. Zh. Obshch. Khim. 1958, 28, 299-304 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 295-300. PREPARED BY: Baldini, P. EXPERIMENTAL VALUES: t/°C T/K^a 100x₂ t/°C T/K^a 100x₂

t/ºc	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100x ₂
167	440	0	161	434	47.5
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			

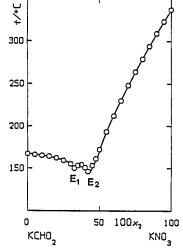
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 150 $^{\rm o}$ C and 100x₁= 67.5 (author). Eutectic, E₂, at 146 $^{\rm o}$ C and 100x₂= 44 (author).

Intermediate compound(s):

K3(CHO2)2NO3, congruently melting (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" materials, recrystallized and dried to constant mass. Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm O}{\rm C}=$ 60, 135, 157 (Ref. 1). Component 2 undergoes phase transitions at $t_{\rm trs}(2)/^{\rm O}{\rm C}=$ 124, 316 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

152 COMPONENTS: ORIGINAL MEASUREMENTS: (1) Potassium methanoate (potassium formate); Berchiesi, G.; Cingolani, A.; Leonesi, D. KCHO₂; [590-29-4] Z. Naturforsch. 1970, 25a, 1766-1767. (2) Potassium nitrate; KNO3; [7757-79-1] VARIABLES: PREPARED BY: Temperature. Baldini, P. EXPERIMENTAL VALUES:

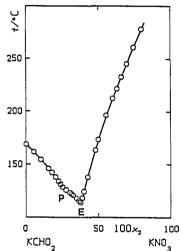
t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
168.7	441.9	0	115.9	389.1	36.5
161.6	434.8	5.3	114.3	387.5	37.6
154.3	427.5	10.2	118.6	391.8	38.8
146.0	419.2	15.5	124.5	397.7	40.0
142.3	415.5	17.9	138.0	411.2	42.6
138.0	411.2	20.4	163.4	436.6	47.9
133.9	407.1	22.5	173.4	446.6	50.0
131.2	404.4	23.8	196.2	469.4	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/°C > 280 could not be taken due to the thermal instability of the melts (authors).

Characteristic point(s): Eutectic, E, at 114 °C and $100x_2=37.9$ (authors). Peritectic, P, at 126.5 °C and $100x_2=26.2$ (authors).

Intermediate compound(s): K₅(CHO₂)₄NO₃, incongruently melting (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual method (for details, see Ref. 1) supplemented with DSC measurements.

SOURCE AND PURITY OF MATERIALS:

C. Erba (Milan, Italy) materials dried before use.

ESTIMATED ERROR:

<u>+0.1</u> K Temperature: accuracy probably (compiler).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium propanoate (potassium propionate);

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1397-1404.

кс₃н₅о₂; [327-62-8]

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

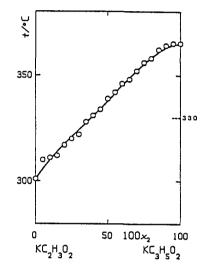
EXPERIMENTAL VALUES:

T/K ^a	100 x 2	t/°C	T/Kª	100 x 2
574	0	342	615	55
583	5			60
584	10	348	621	65
585	15	352	625	70
590	20	356	629	75
593	25	358	631	80
595	30	362	635	85
601	35	364	637	90
604	40	365	638	95
607	45	365	638	100
612	50			
	574 583 584 585 590 593 595 601 604 607	574 0 583 5 584 10 585 15 590 20 593 25 595 30 601 35 604 40 607 45	574 0 342 583 5 346 584 10 348 585 15 352 590 20 356 593 25 358 595 30 362 601 35 364 604 40 365 607 45 365	574 0 342 615 583 5 346 619 584 10 348 621 585 15 352 625 590 20 356 629 593 25 358 631 595 30 362 635 601 35 364 637 604 40 365 638 607 45 365 638

a T/K values calculated by the compiler.

Characteristic point(s):

Continuous series of solid solutions.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

The occurrence of a continuous series of solid solutions in this binary seems likely.

The fusion temperatures of both components [T_{fus}(1)= 574 K, and T_{fus}(2)= 638 K] are in reasonable agreement with the corresponding data listed in Preface, Table 1 (578.7±0.5 K, and 638.3±0.5 K, respectively). Conversely, there is no correspondence between the solid state transition temperature of component 2 quoted from Ref. 1 (603 K) and that of Table 1 (352.5±0.5 K). It is, however, to be noted that in other papers by the same group (see, e.g., Ref. 2) a transition of component 2 - ignored here - is quoted from the same Ref. 1 as occurring at 341 K.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared from commercial propanoic acid (distilled before use) and "chemically pure" potassium carbonate; the recovered solid was recrystallized from n-butanol; it undergoes a phase transition at $t_{\rm trs}(2)/{}^{\rm C}$ C= 330 (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Sokolov, N.M.; Tsindrik, N.M. Zh. Neorg. Khim. 1969, 14, 584-590 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1969, 14, 302-306.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium butanoate (potassium butyrate); KC4H7O2; [589-39-9]

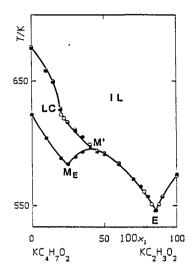
EVALUATOR:

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

CRITICAL EVALUATION:

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 $100x_1$ = 85.5], 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 °C)], and solid state transition at 618 K (345 °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 [$T_{clr}(2)$ = 676 K (403 °C)] and fusion [$T_{fus}(1)$ = 575 K (302 °C); $T_{fus}(2)$ = 623 K (350 °C)] temperatures substantially agree with the corresponding values from Table 1 of the Preface (677.3+0.5; 578.7+0.5, and 626.1+0.7 K, respectively). Prisyazhnyi et al.'s, and Sokolov and Pochtakova'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 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) besides 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 or of the M pype: 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.

- (1) Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. 1960, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 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. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9]

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:

Temperature.

PREPARED BY:

Baldini, P.

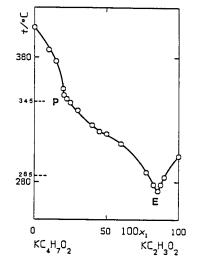
EXPERIMENTAL VALUES:

t/ºC	T/Kª	100 x 1	t/°C	T/K ^a	100×1
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 $^{\circ}$ C and $100x_1 = 85.5$ (authors).



Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction) at 350 $^{\rm O}C$ and $100{\bf x_1}=$ 20.5 (authors).

Intermediate compound(s):

 $K_7C_2H_3O_2(C_4H_7O_2)_6$ (presumable composition; authors) incongruently melting.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material recrystallized; it undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}$ = 58, 155 (Ref. 1). Component 2: prepared by reacting KHCO₃ 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 $t_{\rm trs}(2)/^{\rm C}$ = 190, 285, 345

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(Ref. 1).

- (1) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9]

ORIGINAL MEASUREMENTS:

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:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

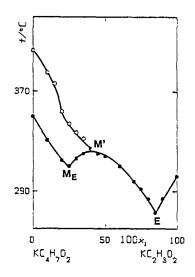
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).

Characteristic point(s):

Invariant point, M_E , at about 310 °C and 100 \mathbf{x}_1 about 25 (compiler). Eutectic, E, at about 273 °C and 100 \mathbf{x}_1 about 85 (compiler). Invariant point, M, at about 323 °C and 100 \mathbf{x}_1 about 40 (compiler).

Intermediate compound(s):

 $K_5(C_2H_3O_2)_2(C_4H_7O_2)_3$, melting at about 323 °C (compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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 Al₂O₃ 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.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: $t_{fus}(1)/^{o}C$ about 302 (compiler). Component 2: $t_{fus}(2)/^{o}C$ about 350; $t_{c1r}(2)/^{o}C$ about 403 (compiler).

ESTIMATED ERROR:

Temperature: accuracy not evaluable (compiler).

(1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]

(2) Potassium iso.butanoate (potassium iso.butyrate); Ki.C₄H₇O₂; [19455-20-0]

EVALUATOR:

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

CRITICAL EVALUATION:

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 $100\mathbf{x}_1$ = 86.5; (ii) a eutectic, E_2 , at 567 K (294 °C) and $100\mathbf{x}_1$ = 32; and (iii) an intermediate compound, $K_5(C_2H_3O_2)_3(\mathbf{i}.C_4H_7O_2)_2$, congruently melting at 578 K (305 °C).

Component 2, however, forms liquid crystals. Therefore the temperature of 633 K (360 °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 [$T_{\rm fus}(2)$ = 553.9±0.5 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 $T_{\rm trs}(2)$ value (424±3 K) listed in Preface, Table 2.

The fusion temperature of component 1, $T_{\rm fus}(1) = 574$ 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. Trans1.)
 1960, 30, 1433-1437.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- Potassium ethanoate (potassium acetate); $KC_2H_3O_2$; [127-08-2]
- (2) Potassium iso.butanoate (potassium iso.butyrate);

K1.C4H702; [19455-20-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1405-1410 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1433-1437.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

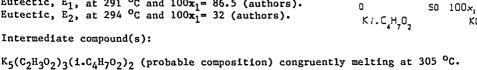
T/K ^a	100x ₁	t/ºC	T/Kª	100 x 1
633	0	304	577	50
625	5	304	577	55
616	10	305	578	60
593	20	302	575	70
583	25	298	571	75
577	27.5	294	567	85
571	30	291	564	86.5
567	32	293	566	87.5
569	32.5	294	567	90
570	35	298	571	95
574	40	301	574	100
	633 625 616 593 583 577 571 567 569 570	633 0 625 5 616 10 593 20 583 25 577 27.5 571 30 567 32 569 32.5 570 35	633 0 304 625 5 304 616 10 305 593 20 302 583 25 298 577 27.5 294 571 30 291 567 32 293 569 32.5 294 570 35 298	633 0 304 577 625 5 304 577 616 10 305 578 593 20 302 575 583 25 298 571 577 27.5 294 567 571 30 291 564 567 32 293 566 569 32.5 294 567 570 35 298 571

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 291 $^{\rm o}$ C and $100{\rm x_1}$ = 86.5 (authors). Eutectic, E₂, at 294 $^{\rm o}$ C and $100{\rm x_1}$ = 32 (authors).

Intermediate compound(s):



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

300

273

Component 1: "chemically pure" material recrystallized. prepared from commercial Component 2: "pure" grade iso butanoic acid, distilled before use, and potassium "chemically pure" hydrogen carbonate (Ref. 1); recrystallized from n-butanol. Component 1 undergoes phase transitions at t_{trs}(1)/°C= 58, 155 (Ref. 2). Component 2 undergoes phase transitions at t_{trs}(2)/°C= 208, 273, 348 (Ref. 2).

100

KC2H302

ESTIMATED ERROR:

probably +2 K Temperature: accuracy (compiler).

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M. Tezisy Dok1. 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).

Potassium ethanoate (potassium acetate);
 KC₂H₃O₂; [127-08-2]

(2) Pořassíum pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1] **EVALUATOR:**

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

CRITICAL EVALUATION:

This system was studied only by Pochtakova (Ref. 1) who claimed the existence of: (i) a eutectic point at 553 K (280 $^{\rm O}$ C) and $100{\rm x_2}$ = 12.5; (ii) a "perekhodnaya tochka" (likely a peritectic) at 607 K (334 $^{\rm O}$ C) and $100{\rm x_2}$ = 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 $T_{\rm clr}(2)$ 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 $_{\rm p}$ point at about 588 K (315 $^{\rm O}{\rm C}$) and $100{\rm x}_2$ 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 $B \cdot 2 \cdot$

- (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: ORIGINAL MEASUREMENTS: (1) Potassium ethanoate (potassium acetate); Pochtakova, E.I. KC₂H₃O₂; [127-08-2] Zh. Obshch. Khim. 1966, 36, 3-8. (2) Potassium pentanoate (potassium valerate); КС₅H₉O₂; [19455-21-1] VARIABLES: PREPARED BY: Temperature. Baldini, P. EXPERIMENTAL VALUES: 2

400

300

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
302	575	0	320	593	45
288	561	5	325	598	47.5
283	556	10	330	603	50
280	553	12.5	334	607	52.5
286	559	15	345	618	55
290	563	17.5	355	628	57.5
295	568	20	364	637	60
302	575	25	381	654	65
308	581	30	409	682	75
313	586	35	418	691	80
315 ^b	588	40	426	699	85
318	591	42.5	444	717	100

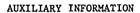
a T/K values calculated by the compiler. b 415 in the original table (compiler).

Characteristic point(s):

KC₂H₃O₂ KC_EH₉O₂ Eutectic, E, at 280 $^{\circ}$ C and $100x_{2}=12.5$ (author). Characteristic point, P (perekhodnaya tochka in the original text; Introduction), at 334 $^{\circ}$ C and $100x_2=52.5$ (author). the

Intermediate compound(s):

 $K_5(C_2H_3O_2)_2(C_5H_9O_2)_3$ (probable composition), incongruently melting.



METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared from n-pentanoic acid and hydrogen carbonate (Ref. 1, where, however, carbonate instead of hydrogen carbonate was employed). Component 1 undergoes phase transitions at t_{trs}(1)/°C= 58, 155 (Ref. 2). Component 2 undergoes a phase transition at t_{trs}(2)/°C= 307 (Ref. 2).

--- 307

100

50 100x2

ESTIMATED ERROR:

Temperature: +2 K accuracy probably (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

(1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08- 2]

(2) Potassium iso.pentanoate (potassium iso.valerate); Ki.C₅H₉O₂; [589-46-8] **EVALUATOR:**

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

CRITICAL EVALUATION:

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 $100 \text{m}_2 \text{=} 50$; (ii) a peritectic, P, at 543 K (270 $^{\circ}$ C) and $100 \text{m}_2 \text{=} 18.5$; and (iii) an incongruently melting compound, of probable composition $\text{K}_8(\text{C}_2\text{H}_3\text{O}_2)_{7i}.\text{C}_5\text{H}_9\text{O}_2$.

Component 2, however, forms liquid crystals. Therefore the fusion temperature, $T_{fus}(2)=669~K~(396~^{\circ}C)$ 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 $^{\circ}$ C, respectively), no identification is possible with the findings by other investigators, inasmuch as: (1) no transformation is reported in Table 2 as occurring below $T_{fus}(2)$ = 531+3 K; and (11) 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 $^{\rm O}$ C, respectively), the latter figure being in reasonable agreement with the $T^{\prime}_{\rm trs}$ value (422.2+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 $50 \le 100 x_2 \le 100$ 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 ME type should exist.

- (1) Pochtakova, E.I.
 Zh. Obshch. Khim. 1963, 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. 1967, 37, 2160-2166; Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.

- (1) Potassium ethanoate (potassium acetate);
- KC₂H₃O₂; [127-08- 2]
 (2) Potassium iso-pentanoate (potassium iso-valerate);
 K1-C₅H₉O₂; [589-46-8]

ORIGINAL MEASUREMENTS:

Pochtakova, E.I.

Zh. Obshch. Khim. 1963, 33, 342-347.

VARIABLES:

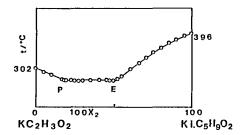
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).



Characteristic point(s):

Eutectic, E, at 269 °C and $100x_2 = 50.0$. Peritectic, P (perekhodnaya tochka in the original text; see the Introduction), at 270 °C and $100x_2 = 18.5$.

Intermediate compound(s):

 $K_8(C_2H_3O_2)_7i \cdot C_5H_9O_2$ (probable composition).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material.
Component 2: prepared from commercial
iso.pentanoic acid (distilled twice before
use) and "chemically pure" hydrogen
carbonate (Ref. 1).

Component 1 undergoes phase transitions at $t_{trs}(1)/^{o}C=58$, 155 (Ref. 2) and melts at $t_{fus}(1)/^{o}C=302$. Component 2 undergoes phase transitions at

Component 2 undergoes phase transitions at $t_{trs}(2)/^{\circ}C=54$, 345 (Ref. 2) and melts at $t_{fus}(2)/^{\circ}C=396$.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium hexanoate (potassium caproate); KC₆H₁₁O₂; [19455-00-6]

EVALUATOR:

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

CRITICAL EVALUATION:

This system was studied only by Pochtakova (Ref. 1) who suggested the existence of: (i) a eutectic, E, at 560 K (287 °C), and $100x_2=11.0$; (ii) a "perekhodnaya tochka" (likely a peritectic) at 592 K (319 °C) and $100x_2=39.0$; and (iii) an incongruently melting intermediate compound, $K_5(C_2H_3O_2)_3(C_6H_{11}O_2)_2$.

Component 2, however, forms liquid crystals. Therefore the fusion temperature, $T_{\rm fus}(2)$ = 717.7 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, $T_{\rm fus}(2)$ = 581.7±0.5 K (Preface, Table 1).

Concerning component 1, fusion occurs at 574 K (301 $^{\rm O}$ C; Ref. 1), and solid state transitions occur at 428 K (155 $^{\rm O}$ C; Ref. 2), and 331 K (58 $^{\rm O}$ C; Ref. 2). Only the former two values, however, find a direct identification with data listed in Table 1 of the Preface, i.e., 578.7 \pm 0.5 K and 422.2 \pm 0.5 K, 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.

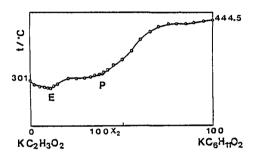
Conversely, if the existence of the compound is not accepted, the phase diagram might be interpreted with reference to Scheme $B \cdot 2 \cdot$

- (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. 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: ORIGINAL MEASUREMENTS: (1) Potassium ethanoate (potassium acetate); Pochtakova, E.I. Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); KC₂H₃O₂; [127-08-2] Russ. J. Gen. Chem. (Engl. Transl.) 1959, (2) Potassium hexanoate (potassium 29, 3149-3154. caproate); $KC_{6}H_{11}O_{2}$; [19455-00-6] VARIABLES: PREPARED BY: Baldini, P. Temperature.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).



Characteristic point(s):

Eutectic, E, at 287 °C and $100x_2=11.0$ (author). Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction), at 319 °C and $100x_2=39.0$.

Intermediate compound(s):

$K_5(C_2H_3O_2)_3(C_6H_{11}O_2)_2$ (approximate composition), incongruently melting. AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE SOURCE AND PURITY OF MATERIALS: "Chemically pure" $\rm KC_2H_3O_2$, and $\rm KC_6H_{11}O_2$ prepared by reacting $\rm K_2CO_3$ with n-hexanoic Visual polythermal analysis. acid (Ref. 1). Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C=58, 155 \text{ (Ref. 2)}.$ Component 2 undergoes a phase transition at t_{trs}(2)/°C= 302 (Ref. 2). ESTIMATED ERROR: +2 K Temperature: accuracy probably (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.

- Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium chloride; KC1; [7447-40-7]

ORIGINAL MEASUREMENTS:

Il'yasov, I.I.; Bergman, A.G.
Zh. Obshch. Khim. 1960, 30, 355-358.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100x ₂
306	579	0
305	578	2.5
304	577	5.0
295	568	10.0
300	573	11.0
328	601	13.0
366 ^b	639	16.0
383 ^c	656	17.5

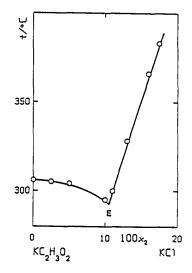
T/K values calculated by the compiler.
 Erroneously reported as 266 in Table 1 of

the original paper (compiler).

c Erroneously reported as 283 in Table 1 of the original paper (compiler).

Characteristic point(s):

Eutectic, E, at 293 °C and $100x_2=10.5$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple and a millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Not stated.

NOTES:

The system was investigated at $0 \le 100 x_2 \le 17.5$ due to thermal instability of component 1.

See also the note relevant to the results obtained by Piantoni et al. (Ref. 1) on the same system (next Table).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. 1968, 38, 127-132.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium chloride; KC1; [7447-40-7]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. 1968, 38, 127-132.

VARTABLES:

Temperature.

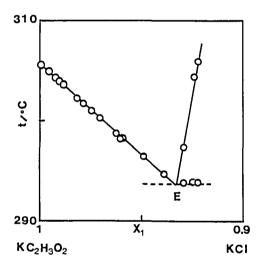
PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are given only in graphical form (see figure). The system was investigated at $0 \le 100x_2 < 8$.

Characteristic point(s): Eutectic, E, at 293.6 °C and $100x_1 = 93.3$ (authors).



AUXILIARY INFORMATION

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 resistan ce thermometer, and connected with a L&N Type K-3 potentiometer.

NOTE:

Higher precision, and satisfactory mutual consistency of the results obtained by Piantoni et al. for the three binaries K/C₂H₃O₂, (Br,Cl,I) suggest to prefer here the data by these authors to those by Il'yasov and Bergman (Ref. 2). Increasingly positive deviation from ideality was observed by Piantoni et al. for the liquidus branch richer in the halide when KC1, KBr, and KI were successively taken into account. This is consistent with the (cryometric) limiting values [1im $(\Delta T/m_2) = 17.7$, 17.4, 16.0 K and $m_2 \rightarrow 0$

molality⁻¹, respectively] previously found by Braghetti et al. (Ref. 1) when the same halides were employed as solutes in molten potassium ethanoate (the cryometric constant of which is: K_1 = 18.0±0.3 K molality⁻¹; Ref. 1).

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum (private communication by the authors to the compiler).

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

- (1) Braghetti, M.; Leonesi, D.; Franzosini, P.
- Ric. Sci. 1968, 38, 116-118. (2) Il'yasov. I.I.; Bergman, A.G.
 - Zh. Obshch. Khim. 1960, 30, 355-358.

(1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]

(2) Potassium thiocyanate; KCNS; [333-20-0]

EVALUATOR

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

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 \pm 0.5 K); and (ii) between Sokolov'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'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: T _{fus} (2)/K:	579 449	575 450
Intermediate compound	K ₃ C ₂ H ₃ O ₂ (CNS) ₂	K ₃ C ₂ H ₃ O ₂ (CNS) ₂
Eutectic E ₁ ; T/K:	405	410-412
Eutectic E ₁ ; 100x ₁ :	42.5	39
Eutectic E2; T/K:	403	408
Eutectic E_2 ; $100x_1$:	27	22.5

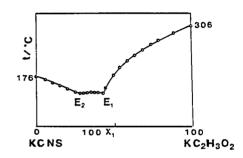
It is, however, to be stressed that Sokolov's graphical presentation of the diagram is somewhat conflicting with the few numerical data reported in the text. Accordingly, the evaluator is inclined to prefer the values listed under the heading "Ref. 1", although regretting that no tabulation of the experimental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

- 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.

COMPONENTS: (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2] (2) Potassium thiocyanate; KCNS; [333-20-0] VARIABLES: Colubeva, 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 (*). PREPARED BY: Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).



Characteristic point(s):

Eutectic, E_1 , at 132 °C and $100x_1 = 42.5$ (authors). Eutectic, E_2 , at 130 °C and $100x_1 = 27$ (authors).

Intermediate compound(s):

 $K_3C_2H_3O_2(CNS)_2$ congruently melting at 134 °C (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual observation of fusion of the salt mixtures contained in a glass tube surrounded by a wider tube to secure a more uniform heating. Temperatures measured with a Chromel-Alumel thermocouple.

SOURCE AND PURITY OF MATERIALS:

Materials of analytical purity recrystallized twice.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Potassium ethanoate (potassium acetate);
- KC₂H₃O₂; [127-08-2] (2) Potassium thiocyanate; KCNS; [333-20-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1966, 36, 577-582.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

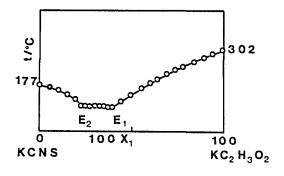
The results are reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E_1 , at 137 °C (text and Fig. 1 of the original paper) or 139 °C (Fig. 2 and Fig. 3) and $100x_1=39$ (author). Eutectic, E_2 , at 135 °C and $100x_1=22.5$ (author).

Intermediate compound(s):

K₃C₂H₃O₂(CNS)₂, congruently melting.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

Curve 1 of Fig. 1 of the original paper, which is reproduced in the figure, is somewhat unsatisfactory inasmuch $\rm E_2$ seems higher than $\rm E_1$ (compiler).

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1 melts at $t_{fus}(1)/^{\circ}C=302$ and undergoes phase transitions at $t_{trs}(1)/^{\circ}C=58$, 155 (Ref. 1). Component 2 melts at $t_{fus}(2)/^{\circ}C=177$ and undergoes a phase transition at $t_{trs}(2)/^{\circ}C=143$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Vrzhesnevskij, I.B. Zh. Russk. Fiz.-Khim. Obshch. 1911, 43, 1368.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium iodide KI; [7681-11-0]

ORIGINAL MEASUREMENTS:

Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. 1958, No. 3, 413-416.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

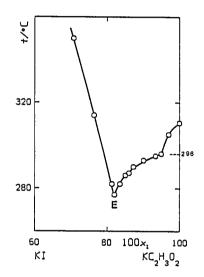
EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 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 $100x_1 = 82.0$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

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).

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1 undergoes a phase transition at t_{trs}(1)/°C= 296.

Component 2 melts at $t_{fus}(2)/{}^{o}C=683$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. 1968, 38, 127-132.

- (1) Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium iodide; KI; [7681-11-0]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci. 1968, 38, 127-132.

VARIABLES:

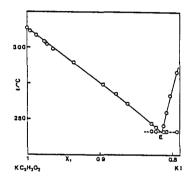
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

The results are given only in graphical form (see figure). The system was investigated only at $0 \le 100x_2 \le 20$.



Characteristic point(s): Eutectic, E, at 276.5 °C and $100x_1 = 81.4$ (authors).

NOTE:

Higher precision, and satisfactory mutual consistency of the results obtained by Pianto ni et al. for the three binaries $K/C_2H_3O_2$, (Br,Cl,I) suggest to prefer here the data by these authors to those by Diogenov and Erlykov (Ref. 2), whose solid state transition of component 1 at 569 K, moreover, was not confirmed in more recent literature (Ref. 3). Increasingly positive deviation from ideality was observed by Piantoni et al. for the liquidus branch richer in the halide when KCl, KBr, and KI were successively taken into account. This is coherent with the (cryometric) limiting values [lim $(\Delta T/m_2)$ = 17.7,

 $m_2 \rightarrow 0$ 17.4, and 16.0 K molality⁻¹, respectively] previously found by Braghetti et al. (Ref. 1) when the same halides were employed as solutes in molten potassium ethanoate (whose cryometric constant is: K_1 = 18.0±0.3 K molality⁻¹; Ref. 1).

AUXILIARY INFORMATION

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:

C. Erba RP materials, dried by heating under vacuum (private communication by the authors to the compiler).

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

- Braghetti, M.; Leonesi, D.; Franzosini, P.
- Ric. Sci. 1968, 38, 116-118. (2) Diogenov, G.G.; Erlykov, A.M.
- Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. 1958, No. 3, 413-416.
- (3) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.
 Thermal Properties, in Thermodynamić and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

(1) Potassium ethanoate (potassium acetate);

KC₂H₃O₂; [127-08-2] (2) Potassum nitrite; KNO₂; [7758-09-0]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

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: (1) 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 (11) between Sokolov and Minich's (Ref. 2) higher transition temperature (428 K), and the single $T_{\rm trs}(1)$ 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 conclusion, 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.

- (1) Potassium ethanoate (potassium acetate); $KC_2H_3O_2$; [127-08-2]
- (2) Potassum nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Bergman, A.G.; Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.

VARIABLES:

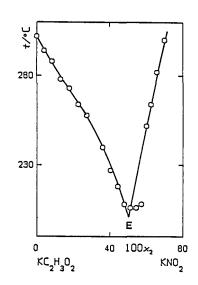
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	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
240	513	36.1
227	500	40.3
218	491	44.3
208	481	47.9
206	479	51.2
206 ^b	479	54.4
208 ^b	481	57.3
252	525	60.1
264	537	62.5
282	555	65.8
300	573	70.0



 $^{
m a}_{
m L}$ 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 $^{\rm o}{\rm C}$ and $100{\rm x}_2$ = 50 (authors).

Note - The system was investigated at $0 \le 100x_2 \le 70$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis: the temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple and a 17 mV full-scale millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Source not stated. Component 2: $t_{fus}(2)/^{\circ}C=440$.

ESTIMATED ERROR:

+2 K Temperature: accuracy probably (compiler).

- Potassium ethanoate (potassium acetate); KC₂H₃O₂; [127-08-2]
- (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A.

Zh. Neorg. Khim. 1961, 6, 2558-2562 (*);
Russ. J. Inorg. Chem. (Engl. Transl.) 1961,
6, 1293-1295.

VARIABLES:

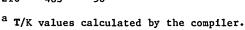
Temperature.

PREPARED BY:

Baldini, P.

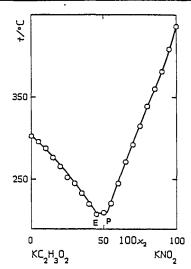
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
302 295	575 568	0 5	221 245	494 518	55 60
287 276 265	560 549 538	10 15 20	271 292	544 565	65 70 75
252 245	525 518	25 30	315 339 360	588 612 633	80 85
233 220	506 493	35 40	381 408	654 681	90 95
208 210	481 483	45 50	436	709	100



Characteristic point(s):

Eutectic, E, at 208 $^{\circ}$ C and $100x_2$ = 45 (compiler). Peritectic, P, at 210 $^{\circ}$ C and $100x_2$ = 52 (compiler).



Note - The assignment of the invariants as reported in Table 2 of the original paper, i.e., E at 210 $^{\circ}$ C and 100 \mathbf{x}_2 = 45, and P at 208 $^{\circ}$ C and 100 \mathbf{x}_2 = 52, is nonsensical and not compatible with the experimental values (compiler).

Intermediate compound(s):

 $K_2C_2H_3O_2NO_2$ (tentative composition; authors) incongruently melting (the tentative composition by the authors is not compatible with the above assignement of the invariants; compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: commercial "chemically pure" material recrystallized from water; it undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}$ = 58, 155 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{\rm fus}(2)/^{\rm C}$ = 436 after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ = 45 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G.
 Izv. Sektora Fiz.-Khim. Anal. 1952, 21,
 178-183.

- (1) Potassium ethanoate (potassium acetate); $KC_2H_3O_2$; [127-08-2]
- (2) Potassium nitrate; KNO3; [7757-79-1]

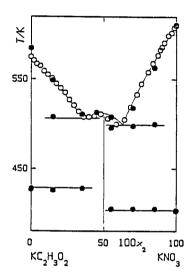
EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied by Bergman and Evdokimova (Ref. 1), Diogenov et al. (Ref. 2), Gimel'shtein (Ref. 3), 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, temperatures from Refs. 1-4 (575, 583, 586, and 575 K, respectively) fluctuate (rather widely) around the $T_{fus}(1)$ (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: (1) 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	Ker. 2	Kei. 3	Ref. 4
507	493	507	507
36	39	35.5	35
495	485	497	497
61.5	61	62.5	62
511	502	511	511
	507 36 495 61.5	507 493 36 39 495 485 61.5 61	507 493 507 36 39 35.5 495 485 497 61.5 61 62.5

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.

- (1) 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.

- (1) Potassium ethanoate (potassium acetate); KC2H3O2; [127-08-2]
- (2) Potassium nitrate; KNO3; [7757-79-1]

ORIGINAL MEASUREMENTS:

Bergman, A.G.; Evdokimova, K.A. Iz. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.

VARIABLES:

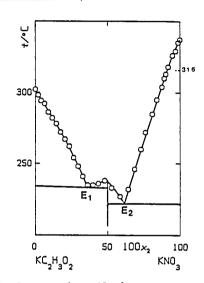
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	T/°C	T/K ^a	100x ₂
302	575	0	233	506	52.7
298	571	2.0	227	500	58.5
294	567	4.0	232	505	64.2
292	565	6.4	246	519	68.5
286	559	9.0	260	533	72.9
282	555	11.7	272	545	76.0
278	551	14.6	285	558	80.7
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	586	90.2
248	521	29.6	318b	591	91.9
241	514	32.8	326°	599	94.8
235	508	36.1	329 ^d	602	97.0
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).

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(s):

 ${\rm K_2C_2H_3O_2NO_3}$, congruently melting at 238 °C (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

polythermal analysis: temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple and a 17 mV full-scale millivoltmeter.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

SOURCE AND PURITY OF MATERIALS:

Source not stated. Component 2: in the temperature field of interest it undergoes a phase transition at $t_{trs}(2)/^{o}C=316-318$ (Ref. 1).

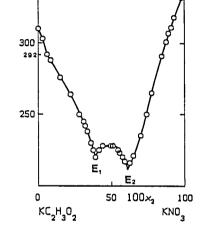
REFERENCES:

(1) Bergman, A.G.; Berul', S.I. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

d Erroneously reported as 229 in table 5 of the original paper (compiler).

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Potassium ethanoate (potassium acetate); Diogenov, G.G.; Nurminskii, N.N.: Gimel'shtein, V.G. Zh. Neorg. Khim. 1957, 2, 1596-1600 (*); KC2H3O2; [127-08-2] (2) Potassium nitrate; KNO₃; [7757-79-1] Russ. J. Inorg. Chem. (Engl. Transl.) 1957, 2(7), 237-245. VARIABLES: PREPARED BY: Temperature. Baldini, P. **EXPERIMENTAL VALUES:**

Į.					
t/ºC	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
310	583	0	225	498	54.5
303	576	3	223	496	55.5
292	565	6	220	493	57.5
288	561	8.5	217	490	59
276	549	15	216	489	62.5
264	537	22	221	494	65
250	523	28	235	508	70
245	518	31	250	523	74
242	515	32	265	538	77.5
238	511	33.5	291	564	84.5
230	503	36	301	574	87.5
225	498	37.5	307	580	89
220	493	39	311	584	91
225	498	41.5	318	591	93
228	501	44	332	605	98
228	501	49.5	337	610	100
228	501	51			



Characteristic point(s): Eutectic, E_1 , at 220 °C and $100x_1$ = 61 (authors). Eutectic, E_2 , at 212 °C and $100x_2$ = 61 (authors).

Intermediate compound(s):

K₂C₂H₃O₂NO₃, congruently melting at 229 °C (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Visual polythermal analysis. Source not stated. Component 1 undergoes a phase transition at $t_{trs}(1)/^{\circ}C=292$. ESTIMATED ERROR: Temperature: probably +2 K accuracy (compiler). REFERENCES:

^a T/K values calculated by the compiler.

(1) Potassium ethanoate (potassium acetate); KC₂H₂O₂; [127-08-2]

(2) Potassium nitrate; KNO3; [7757-79-1] ORIGINAL MEASUREMENTS:

Gimel'shtein, V.G.

Tr. Irkutsk. Politekh. Inst. 1971, No. 66, 80-100.

VARIABLES:

PREPARED BY:

Temperature

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/Kª	100 x 2
312	585	0	132	405	55.0
155	428	0	245	518	70.0
276	549	15.0	225	498	70.0
235	508	15.0	132	405	70.0
153	426	15.0	290	563	85.0
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	496	55.0			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 234 °C and $100x_2=35.5$ (author). Eutectic, E_2 , at 224 °C, and $10x_2=62.5$ (author).

Intermediate compound(s):

 $\rm K_2C_2H_3O_2NO_3$, congruently melting at 238 $^{\rm OC}$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Differential thermal analysis (using a derivatograph with automatic recording of the heating curves) was employed.

NOTE:

The meaning of the data listed in the table becomes apparent by observing the figure reported in the critical evaluation. 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).

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1 melts at $t_{fus}(1)/^{o}C=312$ (310 °C according to Fig. 13 of the original paper; compiler), and undergoes a phase transition at $t_{trs}(1)/^{o}C=155$. Component 2 melts at $t_{fus}(2)/^{o}C=338$ (337 °C according to Fig. 13 of the original paper; compiler), and undergoes a phase transition at $t_{trs}(2)/^{o}C=130$.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

REFERENCES:

(1) Bergman, A.G.; Evdokimova, K.A. Iz. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.

Systems with Common Cation 179 COMPONENTS: ORIGINAL MEASUREMENTS: Diogenov, G.G.; Chumakova, V.P. (1) Potassium ethanoate (potassium acetate); $KC_2H_3O_2$; [127-08-2] Fiz.-Khim. Issled. Rasplavov Solei, Irkutsk, 1975, 7-12. (2) Potassium nitrate; KNO₃; [7757-79-1] VARIABLES: PREPARED BY: Temperature. Baldini, P. **EXPERIMENTAL VALUES:** Eutectic, E₁, at 234 $^{\rm o}$ C (Fig. 1 of the original paper); composition not stated (100 \mathbf{x}_1 about 65 in compiler's graphical estimation). Eutectic, $\rm E_2$, at 224 $^{\rm O}{\rm C}$ (Fig. 1 of the original paper); composition not stated (100x1 about 38 in compiler's graphical estimation). Intermediate compound(s): $\rm K_2C_2H_3O_2NO_3$, congruently melting at 238 $^{\rm O}C$ (Fig. 1 of the original paper). AUXILIARY INFORMATION

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METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:					
Visual polythermal analysis.	Not stated. Component 1: $t_{fus}(1)/^{o}C=302$; component 2: $t_{fus}(2)/^{o}C=337$ (Fig. 1 of the original paper).					
	ESTIMATED ERROR:					
	Temperature: accuracy probably +2 K (compiler).					
	REFERENCES:					
	1					

- Potassium propanoate (potassium propionate);
- KC₃H₅O₂; [327-62-8] (2) Potassium thiocyanate; KCNS; [333-20-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1966, 36, 577-582.

VARIABLES:

Temperature.

PREPARED BY:

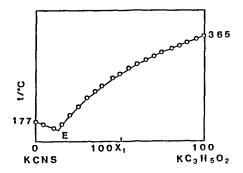
Baldini, P.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 157 °C and $100x_1 = 14$ (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

A substantial agreement exists between the solid state transition and fusion temperatures reported by Sokolov [341 (instead of 350) and 638 K, respectively] for component 1, and those listed in Table 1 of the Preface (352.5+0.5 and 638.3+0.5 K, respectively).

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1 melts at $t_{fus}(1)/^{\circ}C=365$, and undergoes a phase transition at $t_{trs}(1)/^{\circ}C=77$ (Ref. 1; in the compiler's opinion the correct figure ought to be 68, as quoted in several papers by the same author from the same source; according to Ref. 1, 77 °C is the temperature at which a transition occurs in NaC₃H₅O₂). Component 2 melts at $t_{fus}(2)/^{\circ}C=177$ and undergoes a phase transition at $t_{trs}(2)/^{\circ}C=143$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Vrzhesnevskij, I.B. Zh. Russk. Fiz.-Khim. Obshch. 1911, 43, 1368.

- (1) Potassium propanoate (potassium propionate); KC₃H₅O₂; [327-62-8]
- (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

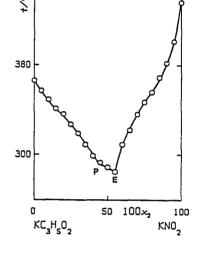
EXPERIMENTAL VALUES:

t/ºC	T/Kª	100x ₂	t/ ^o C	T/K ^a	100 x 2
366 357 349 341 336 327 319 309 299	639 630 622 614 609 600 592 582 572	0 5 10 15 20 25 30 35	285 309 322 336 347 356 369 382 401	558 582 595 609 620 629 642 655 674	55 60 65 70 75 80 85 90
293 289	566 562	45 50	436	709	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at either 285 °C (according to the tabulated data; compiler), or 283 °C (according to table 2 of the original paper; authors), and 100x₂= 55 (authors). Peritectic, P, at 292 °C (figure in poor agreement with the tabulated data; compiler), and 100x₂= 44 (authors).



Intermediate compound(s):

 $K_5(C_3H_5O_2)_3(NO_2)_2$ (tentative composition; authors) incongruently melting.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

A substantial agreement exists between the solid state transition and fusion temperatures reported by Sokolov and Minich (341 and 639 K, respectively) for component 1, and those listed in Table 1 (352.5+0.5 and 638.3+0.5 K, respectively). The actual existence (and composition) of the intermediate compound ought to be more convincingly proved.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" $\rm KHCO_3$ 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 $\rm t_{trs}(1)/^{O}C=68$ (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $\rm t_{fus}(2)/^{O}C=436$ after three recrystallizations; it undergoes a phase transition at $\rm t_{trs}(2)/^{O}C=45$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
 (2) Berul', S.I.; Bergman, A.G.
 Izv. Sektora Fiz.-Khim. Anal. 1952, 21,
 178-183.

- (1) Potassium propanoate (potassium propionate);
- KC₃H₅O₂; [327-62-8] (2) Potassium nitrate; KNO₃; [7757-79-1]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1958, 28, 2920-2926 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2949-2954.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

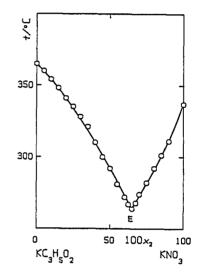
EXPERIMENTAL VALUES:

t/ºC	T/Kª	100 x 2	t/ ^o C	T/K ^a	100 x 2
365	638	0	281	554	55
360	633	5	272	545	60
354	627	10	267	540	62.5
348	621	15	264	537	65
341	614	20	268	541	67.5
335	608	25	274	547	70
328	601	30	282	555	75
321	594	35	292	565	80
310	583	40	301	574	85
300	573	45	311	584	90
292	565	50	337	610	100
1					

 $^{\rm a}$ T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 264 $^{\circ}$ C and $100x_2$ = 65 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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.

NOTE:

A substantial agreement exists between the solid state transition and fusion temperatures reported by Dmitrevskaya and Sokolov (341 and 638 K, respectively) for component 1, and those listed in Preface, Table 1 (352.5+0.5 and 638.3+0.5 K, respectively).

SOURCE AND PURITY OF MATERIALS:

Component 1 prepared by adding a small excess of distilled commercial propanoic acid to a solution of the "chemically pure" hydrogen carbonate; the solid recovered after evaporation of the solvent was recrystallized from n-butanol. Component 2: "chemically pure" material recrystallized. Component 1 undergoes a phase transition at $t_{\rm trs}(1)/{}^{\rm C}$ = 68 (Ref. 1). Component 2 undergoes phase transitions at $t_{\rm trs}(2)/{}^{\rm C}$ = 124, 316 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9]
- (2) Potassium thiocyanate; KCNS; [333-20-0]

EVALUATOR:

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

CRITICAL EVALUATION:

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, $T_{\rm fus}(1)$ = 677 K (404 $^{\rm O}$ C), reported in Ref. 1 should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{\rm clr}(1)$ = 677.3±0.5 K.

For the same component, the phase transition temperatures quoted (from Ref. 2) in Ref. 1, viz., 618 K (345 °C), 553-558 K (280-285 °C), and 463 K (190 °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 \mathbf{T}_{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.

- (1) Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9]
- (2) Potassium thiocyanate; KCNS; [333-20-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1693-1700 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1741-1747.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 1	t/°C	T/K ^a	100 x 1
177 176 174 170 173 183	450 449 447 443 446 456	0 2.5 5 6.5 7.5	301 310 322 327 335 335	574 583 595 600 608 608	65 70 75 77.5 80 82
204 215 224 232 260 278	477 488 497 505 533 551	15 20 25 30 45	337 342 364 379 404	610 615 637 652 677	82.5 85 90 95 100

a T/K values calculated by the compiler.

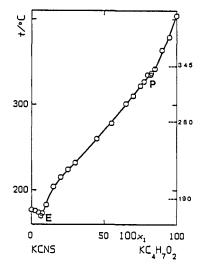
Characteristic point(s):

Eutectic, E, at 170 °C and $100x_1 = 6.5$ (authors).

Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction), at 335 °C and 100x₁= 82.

Intermediate compound(s):

 $K_7(C_4H_7O_2)_6CNS$ (proposed by the authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

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)/OC= 190, 280-285, 345 (Ref. 2). Component 2: commercial material recrystallized once from water and once from alcohol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (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: (1) Potassium butanoate (potassium butyrate); Franzosini, P., KC4H7O2; [589-39-9] (2) Potassium nitrite; Universita di Pavia (ITALY).

CRITICAL EVALUATION:

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 \mathbf{E}_1 should be an M' $_{\mathbf{E}}$ point, and a further (still undetected) invariant type $\mathbf{M}_{\mathbf{E}}$ 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 $T_{clr}(1)$ 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 $T_{\rm fus}(1)$ 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 $T_{\rm fus}(1)$ value of Table 1, is also mentioned.

- (1) Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 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.

- (1) Potassium butanoate (potassium butyrate);
 KC.H-O.: [589-39-9]
- KC₄H₇O₂; [589-39-9]
 (2) Potassium nitrite;
 KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

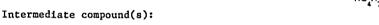
EXPERIMENTAL VALUES:

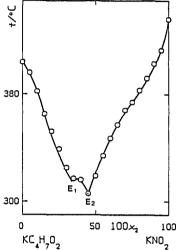
t/ºC	T/K ^a	100 x 2	t/ºC	T/K ^a	100 x 2
404	677	0	334	607	55
396	669	5	347	620	60
382	655	10	357	630	65
365	638	15	368	641	70
352	625	20	374	647	75
339	612	25	383	656	80
325	598	30	392	665	85
317	590	35	403	676	90
316	589	40	413	686	95
306	579	45	436	709	100
319	592	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , 315 °C and $100x_2$ = 33.5 (authors). Eutectic, E_2 , 306 °C and $100x_2$ = 45 (authors).





 $K_8(C_4H_7O_2)_5(NO_2)_3$ (tentative composition; authors) congruently melting (at 317 $^{\rm O}C_7$); compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

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 $t_{\rm trs}(1)/^{\rm OC}=190$, 280-285 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{\rm fus}(2)/^{\rm OC}=436$ after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm OC}=45$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G.
 Izv. Sektora Fiz.-Khim. Anal. 1952, 21,
 178-183.

- (1) Potassium butanoate (potassium butyrate); KC₄H₇O₂; [589-39-9]
- (2) Potassium nitrate; KNO₃; [7757-79-1]

EVALUATOR:

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

CRITICAL EVALUATION:

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 $^{\rm O}$ C), should be identified with the clearing temperature of potassium butanoate, the corresponding value from Preface, Table 1 being $T_{\rm clr}(1)$ = 677.3±0.5 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. 1956.

- Potassium butanoate (potassium butyrate);
- KC₄H₇O₂; [589-39-9] (2) Potassium nitrate; KNO₃; [7757-79-1]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, 0.1. Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2046-2051.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

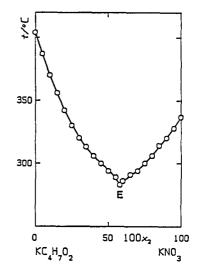
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 _{x2}	t/°C	T/K ^a	100 x 2
404	677	0	289	562	55
387	660	5	283	556	58
370	643	10	286	559	60
356	629	15	291	564	65
342	615	20	294	567	70
330	603	25	300	573	75
320	593	30	306	579	80
313	586	35	314	587	85
306	579	40	320	593	90
300	573	45	328	601	95
294	567	50	337	610	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 283 $^{\circ}$ C and $100x_2 = 58$ (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from "chemically pure" potassium hydrogen carbonate and n-butanoic acid twice distilled. "Chemically pure" component 2 recrystallized and dried to constant mass.

Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}$ = 190, 280-285, 345 (Ref. 1). Component 2 undergoes phase transitions at $t_{\rm trs}(2)/^{\rm C}$ = 124, 316 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Potassium iso.butanoate (potassium
 iso.butyrate);
 Ki.C₄H₇O₂; [19455-20-0]
- (2) Potassium nitrite; KNO₂; [7758-09-0]

EVALUATOR:

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

CRITICAL EVALUATION:

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 $^{\circ}$ C) and 100 x_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 KNO_2 and solid $\text{Ki.C}_4\text{H}_7\text{O}_2$.

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 [$T_{fus}(1) = 553.9 \pm 0.5$ 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 $T_{trs}(1)$ value (424+3 K) listed in Table 2.

- Sokolov, N.M.; Minich, M.A.
 Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 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. 1956.

- (1) Potassium iso.butanoate (potassium iso.butyrate);
- Ki.C₄H₇O₂; [19455-20-0] (2) Potassium nitrite;

KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

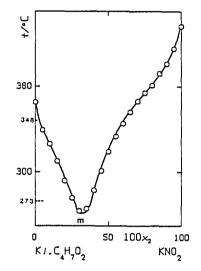
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
365	638	0	333	606	55
339	612	5	345	618	60
326	599	10	356	629	65
310	583	15	366	639	70
292	565	20	374	647	75
276	549	25	381	654	80
264	537	30	392	665	85
266	539	35	401	674	90
283	556	40	415	688	95
301	574	45	436	709	100
319	592	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Continuous series of solid solutions with a minimum at 262 $^{\rm o}{\rm C}$ and 100x2= 32.5 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" KHCO3 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)/°C= 208, 273, 348 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at t_{fus}(2)/°C= 436 after three recrystalliza tions; it undergoes a phase transition at $t_{trs}(2)/^{\circ}C = 45 \text{ (Ref. 2)}.$

ESTIMATED ERROR:

+2 K Temperature: accuracy probably (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

(1) Potassium iso.butanoate (potassium
iso.butyrate);
Ki.C₄H₇O₂; [19455-20-0]

(2) Potassium nitrate; KNO3; [7757-79-1]

EVALUATOR:

Spinolo, G.,

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

CRITICAL EVALUATION:

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 K (356 O C)] should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{clr}(1)$ = 625.6±0.8 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 [$T_{\rm fus}(1)$ = 553.9±0.5 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 $T_{\rm trs}(1)$ 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 ME, 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. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 19-24.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Potassium iso.butanoate (potassium
 iso.butyrate);
- Ki.C₄H₇O₂; [19455-20-0] (2) Potassium nitrate; KNO₃; [7757-79-1]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 19-24.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/ ^o C	T/K ^a	100 x 2
356	629	0	258	531	50
346	619	5	267	540	55
335	608	10	276	549	60
321	594	15	286	559	65
304	577	20	293	566	70
285	558	25	300	573	75
263	536	30	308	581	80
253	526	32.5	316	589	85
254	527	35	322	595	90
255	528	40	330	603	95
255.5	528.7	45	337	610	100
256	529	47.5			

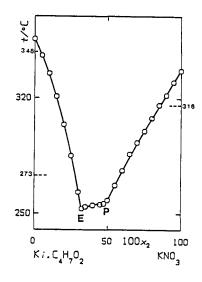
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 253 $^{\circ}$ C and $100x_{2}=32.5$ (authors).

Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction), at 256 $^{\rm OC}$ and $100{\bf x}_{2}$ = 47.5.

 $K_{2}i.C_{4}H_{7}O_{2}NO_{3}$ (supposed composition; authors) incongruently melting.



Intermediate compound(s):

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.butanoic acid and K₂CO₃ (Ref. 1). "Chemically pure" component 2 recrystallized.

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= 124, 316 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

(1) Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1]

(2) Potassium nitrite; KNO₂; [7758-09-0]

EVALUATOR:

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

CRITICAL EVALUATION:

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, $T_{fus}(1)=717$ K, reported in Ref. 1, should be identified with the clearing temperature of component 1, and agrees fairly with the $T_{c1r}(1)$ 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. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

(1) Potassium pentanoate (potassium valerate);

KC₅H₉O₂; [19455-21-1] (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

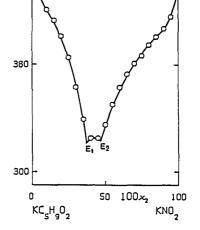
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100x ₂	t/°C	T/Kª	100 x 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 (authors). Eutectic, E_2 , at 323 °C and $100x_2$ = 47 (authors).



Intermediate compound(s):

 $K_7(C_5H_9O_2)_4(NO_2)_3$ (tentative composition; authors), congruently melting (at 325 $^{\rm o}$ C; compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

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 $t_{\rm trs}(1)/^{\rm C}c=307$ (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{\rm fus}(2)/^{\rm C}c=436$ after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}c=45$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
- Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
 (2) Berul', S.I.; Bergman, A.G.
 Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

(1) Potassium pentanoate (potassium valerate); KC₅H₉O₂; [19455-21-1]

(2) Potassium nitrate; KNO₃; [7757-79-1]

EVALUATOR:

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

CRITICAL EVALUATION:

This system was studied only by Dmitrevskaya and Sokolov (Ref. 1), who suggested (on the basis of their visual polythermal observations) the phase diagram to be of the eutectic type, the invariant being at 583 K (310 $^{\circ}$ C) and $100x_{2}=49$.

Component 1, however, forms liquid crystals. Therefore, the fusion temperature, $T_{\rm fus}(1)$ = 717 K (444 $^{\rm O}$ 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 $^{\rm o}$ C), quoted in Ref. 1 from Ref. 2, can be identified with the actual fusion temperature, ${\rm T_{fus}(1)=586.6\pm0.7~K,}$ 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 branch richer in component 2 is consistent with the occurrence in KNO_3 of the solid state transition at 589 K (316 $^{\rm O}$ C) mentioned by the authors.

- (1) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1965, 35, 1905-1909.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Potassium pentanoate (potassium valerate);
- KC_{5H9}O₂; [19455-21-1]
 (2) Potassium nitrate;
 KNO₃; [7757-79-1]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1965, 35, 1905-1909.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

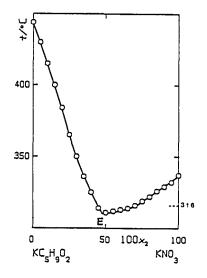
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100x ₂
444	717	0	312	585	55
430	703	5	313	586	60
415	688	10	314	587	65
400	673	15	316	589	70
384	657	20	319	592	75
365	638	25	322	595	80
350	623	30	326	599	85
336	609	35	329	602	90
325	598	40	332	605	95
314	587	45	337	610	100
311	584	50			

^aT/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 310 °C and $100x_2 = 49$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from n-pentanoic acid and the carbonate (Ref. 1); it undergoes a phase transition at $t_{trs}(1)/^{o}C=307$ (Ref. 2).

Component 2: "chemically pure" material recrystallized; it undergoes phase transitions at $t_{trs}(2)/{}^{o}C=124$, 316 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

EVALUATOR:

(1) Potassium iso.pentanoate (potassium iso.valerate);
Ki.C-H.Oo: [589-46-8]

Ki.C₅H₉O₂; [589-46-8] (2) Potassium nitrite; KNO₂; [7758-09-0] Franzosini, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

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 ($289 \text{ }^{\circ}\text{C}$) 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, $T_{\rm fus}(1)$ = 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 $T_{\rm clr}(1)$ = 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 (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 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. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.
- (2) Duruz, J.J.; Ubbelohde, A.R. Proc. Roy. Soc. London 1975, 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.

- (1) Potassium iso-pentanoate (potassium
 iso-valerate);
 Ki-C₅H₉O₂; [589-46-8]
- (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

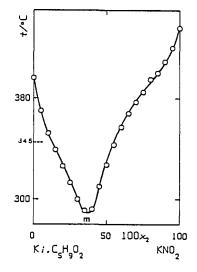
EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/ ^o C	T/K ^a	100 x 2
396	669	0	343	616	55
370	643	5	357	630	60
352	625	10	368	641	65
339	612	15	377	650	70
326	599	20	385	658	75
313	586	25	395	668	80
300	573	30	400	673	85
291	564	35	409	682	90
292	565	40	420	693	95
310	583	45	436	709	100
327	600	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Continuous series of solid solutions with a minimum at 289 $^{\circ}$ C (erroneously reported as 389 both in Fig. 2 of the original paper and in the text; compiler) and $100x_2=37.5$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

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 $t_{\rm trs}(1)/^{\rm C}$ c= 54, 345 (Ref. 1). Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{\rm fus}(2)/^{\rm C}$ c= 436 after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ c= 45 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G.
 Izv. Sektora Fiz.-Khim. Anal. 1952, 21,
 178-183.

- (1) Potassium iso.pentanoate (potassium
 iso.valerate);
 Ki.C₅H₉O₂; [589-46-8]
- (2) Potassium nitrate; KNO3; [7757-79-1]

EVALUATOR:

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

CRITICAL EVALUATION:

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 $100\mathbf{x}_2$ = 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 $100\mathbf{x}_2$ = 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, $T_{fus}(1) = 669 \text{ K } (396 ^{\text{O}}\text{C})$, reported by the authors should be identified with the clearing temperature, the corresponding value from Preface, Table 2 being $T_{c1r}(1) = 679+2 \text{ K}$. No mention is made by the authors of the actual fusion which occurs at $531+3 \text{ K } (\overline{\text{Table 2}})$: 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 $T_{\rm fus}(1)$ = 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.

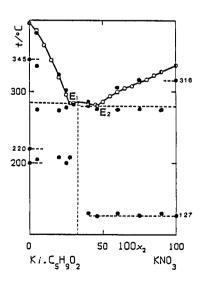
- (1) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.
- (2) Duruz, J.J.; Ubbelohde, A.R. Proc. Roy. Soc. London 1975, A342, 39-49.
- (3) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Pochtakova, E.I.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

COMPONENTS: ORIGINAL MEASUREMENTS: Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); (1) Potassium iso.pentanoate (potassium iso.valerate); Ki.C₅H₉O₂; [589-46-8] (2) Potassium nitrate; Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054. KNO3; [7757-79-1] VARIABLES: PREPARED BY: Temperature. Baldini, P. EVDEDIMENTAL MALIEC

	EXPERI	IMENTAL	VALUES:						
	t/ºC	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100x ₂	t/°C	T/Kª	100 x 2
	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	284 ^d	557	27.5	308	581	70
	220 ^c	493	0	208 ^c	481	27.5	314	587	75
	200 ^c	473	0	284.5	557.7	30	316 ^b	589	75
	386	659	5	282 ^b	555	30	276 ^d	549	75
	382 ^b	655	5	283	556	40	127 ^c	400	75
I	275 ^d	548	5	286 ^b	559	40	317	590	80
	336 ^c	609	5	280 ^đ	553	40	323	596	85
I	205 ^c	478	5	130 ^c	403	40	328	601	90
	365	638	10	282	555	45	328 ^b	601	90
ļ	344	617	15	280	553	46	275 ^d	548	90
I	320	593	20	276 ^b	549	46	130 ^c	403	90
	324 ^b	597	20	276 ^d	549	46	335	608	95
	274 ^d	547	20	126 ^c	399	46	337	610	100
	208 ^C	481	20	286	559	50	337 ^b	610	100
l	296	569	25	294	567	55	316 ^c	589	100
	302b	575	25	300	573	60	127 ^c	400	100
	278 ^d	551	25	306 ^b	579	60			
Į	200 ^C	473	25	275 ^d	548	60			

 $[\]overset{a}{\cdot}$ T/K values calculated by the compiler.

(continued on next page)



b Liquidus from thermographical analysis.

c Transformation in the solid state. d Eutectic temperature.

COMPONENTS: (1) Potassium iso.pentanoate (potassium iso.valerate); Ki.C5HgO2; [589-46-8] (2) Potassium nitrate; KNO3; [7757-79-1] VARIABLES: Temperature. CRIGINAL MEASUREMENTS: Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054. PREPARED BY: Baldini, P.

EXPERIMENTAL VALUES: (continued)

Characteristic point(s):

Eutectic, E_1 , at 284 °C and $100x_2=27.5$. Eutectic, E_2 , at 280 °C (visual polythermal analysis) or 276 °C (thermographical analysis) and $100x_2=46.0$.

Intermediate compound(s):

 $K_3(i.C_5H_9O_2)_2NO_3$ (authors), congruently melting at 284 ± 2 °C (compiler).

Note - In the figure the filled circles refer to thermographical analysis.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis supplemented with thermographical analysis (heating curves recorded automatically).

SOURCE AND PURITY OF MATERIALS:

Component 1: synthetized from iso.butanoic acid and the carbonate (Ref. 1).
Component 2: "chemically pure" material recrystallized.
Component 1 undergoes phase transitions at ttrs(1)/°C= 345, 220, 200 (Ref. 2).
Component 2 undergoes phase transitions at ttrs(2)/°C= 316, 127 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

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

(1) Potassium hexanoate (potassium caproate);

KC₆H₁₁O₂; [19455-00-6] (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/Kª	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			

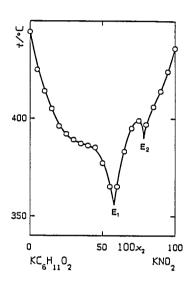
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 356 °C and $100x_2$ = 58 (authors). Eutectic, E_2 , at 390 °C and $100x_2$ = 78.5 (authors).

Intermediate compound(s):

 $^{K_4C_6H_{11}O_2(NO_2)_3}$ (tentative composition; authors) congruently melting (at 399 $^{\rm OC};$ compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

Component 1 forms liquid crystals. Accordingly, the fusion temperature reported here, viz., 717.6 K (444.4 $^{\circ}$ C), should be identified with the clearing temperature (725.8+0.8 K) listed in Preface, Table 1, the actual fusion occurring at $T_{\rm fus}(1) = 581.7 \pm 0.5$ K (Table 1). The latter figure, in turn, might be identified with the phase transition temperature quoted here from Ref. 1, viz., 575 K (302 $^{\circ}$ C). The diagram could be re-interpreted with reference to Scheme D.1 of the Preface, the authors eutectic E_1 being possibly an M_E point.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" KHCO $_3$ and the fatty acid, and recrystallized from butanol after having been deposited from the aqueous solution and dried; it undergoes a phase transition at $t_{\rm trs}(1)/{}^{\rm C}$ C= 302 (Ref. 1).

Component 2: material prepared by reducing potassium nitrate with lead, melting at $t_{fus}(2)/^{\circ}C=436$ after three recrystallizations; it undergoes a phase transition at $t_{trs}(2)/^{\circ}C=45$ (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (2) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

COMPONENTS: ORIGINAL MEASUREMENTS: Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); (1) Potassium (potassium heptanoate enanthate); $KC_7H_{13}O_2$; [16761-12-9] Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295. (2) Potassium nitrite; KNO₂; [7758-09-0] VARIABLES: PREPARED BY: Baldini, P. Temperature.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 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			

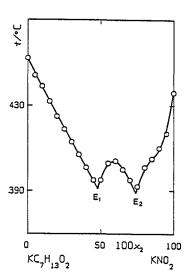
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 391 $^{\rm o}{\rm C}$ and $100{\rm m_{2}}$ = 47.5 (authors). Eutectic, E_2 , at 389 $^{\rm o}{\rm C}$ and $100{\rm m_{2}}$ = 74 (authors).

Intermediate compound(s):

 ${
m K_5(C_7H_{13}O_2)_2(NO_2)_3}$ (tentative composition; authors) congruently melting (at 404 $^{\rm O}{\rm C}$; compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

Component 1 forms liquid crystals. Accordingly, the fusion temperature reported here, viz., 725 K (452 $^{\rm O}$ C), should be identified with the clearing temperature (722+3 K) listed in Preface, Table 1, the actual fusion occurring at T_{fus}(1)= 571.3+0.9 K (Table 1). The diagram could be re-interpreted with reference to Scheme D.1, of the Preface, the authors eutectic E₁ possibly being an M'_E point.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" ${\rm KHCO}_3$ 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 $t_{\rm fus}(2)/^{\rm C}$ = 436 after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ = 45 (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

- Potassium octanoate (potassium caprylate);
- KC₈H₁₅O₂; [764-71-6] (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

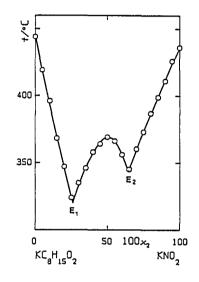
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
444	717	0	366	639	55
419	692	5	356	629	60
396	669	10	345	618	65
368	641	15	360	633	70
347	620	20	373	646	75
324	597	25	387	660	80
335	608	30	399	672	85
346	619	35	411	684	90
358	631	40	426	699	95
364	637	45	436	709	100
369	642	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 320 °C and $100x_2$ = 26 (authors). Eutectic, E_2 , at 344 °C (authors) and $100x_2$ = 64.5 (compiler: the figure 60.5 reported in Table 2 and in Fig. 2 of the original paper is not consistent with the tabulated data).



Intermediate compound(s):

 $^{\rm K}_{\rm 2}C_{\rm 8}H_{\rm 15}O_{\rm 2}NO_{\rm 2}$ (tentative composition; authors) congruently melting (at 369 $^{\rm o}C$; compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

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 actual fusion occurring at $T_{fus}(1) = 560.6 \pm 0.8$ K (Preface, Table 1). The diagram could be re-interpreted with reference to Scheme D.1, the authors' eutectic E₁ possibly being an M'_E point.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" KHCO₃ 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 $t_{\rm fus}(2)/^{\rm C}$ = 436 after three recrystallizations; it undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ = 45 (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably <u>+2</u> K (compiler).

REFERENCES:

(1) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

- Potassium nonanoate (potassium pelargonate);
- KC₉H₁₇O₂; [23282-34-0] (2) Potassium nitrite;
- (2) Potassium nitrite; KNO₂; [7758-09-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minich, M.A. Zh. Neorg. Khim. 1961, 6, 2558-2562 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 1293-1295.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

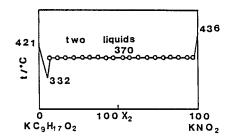
t/°C	T/K ^a	100x ₂
421	694	0
370 ^b	643	5
370	643	10
370 436	643 709	95 100

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 $^{\circ}$ C and 100m₂= 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).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

Component 1 forms liquid crystals. Accordingly, 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 $T_{\rm fus}(1)=549.1\pm0.8$ 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 case an M'E point.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" KHCO₃ 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 $t_{fus}(2)/^{O}C=436$ after three recrystallizations; it undergoes a phase transition at $t_{trs}(2)/^{O}C=45$ (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Berul', S.I.; Bergman, A.G. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.