Coupled Phase Diagram-Thermodynamic Analysis of the 24 Binary Systems, A_2CO_3-AX and A_2SO_4-AX Where A = Li, Na, K and X = Cl, F, NO_3, OH

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A complete bibliographic search for all thermodynamic and phase diagram data on the 24 binary systems A_2CO_3-AX and A_2SO_4-AX (where A = Li, Na, K and X = F, Cl, OH, NO_3) was carried out. A computer-assisted simultaneous evaluation of all data was performed in order to obtain optimized equations for the thermodynamic properties of the phases. A re-evaluation of the thermodynamic data for several of the pure salts was also carried out. The optimized thermodynamic parameters are reported as well as the phase diagrams calculated from these equations. These are considered to be the best evaluated phase diagrams which can be deduced from the data currently available. Estimated error limits of all binary assessments are given.

Key words: carbonates; halides; hydroxides; molten salts; nitrates; phase diagrams; sulfates; thermodynamic assessments.

Contents

List of Tables

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List of Figures

1. Introduction

Molten salt systems involving alkali carbonates and sulfates are of importance in hot corrosion, in electrochemical cells such as the molten carbonate fuel cell, and in many chemical and metallurgical applications.

The present article reports coupled critical evaluations of phase diagram and thermodynamic data for several binary common-cation systems involving the cations Li^+, Na^+, K^+ and the anions Cl^-, CO_3^{2-}, F^-, NO_3^-, OH^-, SO_4^{2-}. It forms part of a continuing program of critical evaluation of molten salt phase diagram and thermodynamic property data. A analysis of such data for the 70 binary common-ion alkali halide systems was reported previously[1] in this journal.

An extensive literature survey of all available phase diagram and thermodynamic data, some of which are summarized in compendia[2-5], was carried out. We believe that the bibliographic searches are as complete as possible.

In the critical evaluation technique, all available phase diagram and thermodynamic data for a system are simultaneously optimized in order to obtain a set of equations describing the thermodynamic properties of the phases as functions of temperature and composition. These equations for the thermodynamic properties of all known phases are consistent with the measured thermodynamic properties and phase diagrams as well as with established thermodynamic principles and theories of solution behavior. The phase diagram can subsequently be calculated by computer from the thermodynamic equations.

Hence, all the thermodynamic properties as well as the phase diagram can usually be represented and stored by means of a small set of coefficients. Furthermore, the self-consistent analytical representation permits the data to be interpolated and extrapolated. The procedure greatly reduces the amount of data needed to characterize fully a binary system.

With such a technique, the evaluator can therefore test the thermodynamic consistency within and among all reported phase diagram and excess property measurements. Discrepancies among various sets of data can often be resolved in this way, and error limits can more easily be assigned. Unknown or uncertain phase boundaries can often be estimated with good precision and, conversely, some reported phase boundaries can be rejected as being inconsistent with the thermodynamic properties of the system. This results in a much more rigorous and objective assessment of all data than has hitherto been possible.

Of particular importance is the fact that it is often possible to estimate the thermodynamic properties and phase diagrams of ternary and higher-order systems from the assessed parameters for their binary sub-systems. To this end, semi-empirical techniques have been developed based, for example, upon extensions of regular solution theory. The present analysis of the binary systems is thus the first, and most important, step in the development of databases for multicomponent systems.

2. Computer-Coupled Thermodynamic/ Phase Diagram Analysis

2.1. Introduction

A short bibliography on computer-coupled thermodynamic/phase diagram analysis and calculation[6-13] should suffice to orient the reader. The principles of simultaneous least-squares optimization of thermodynamic and phase diagram data are described in Ref. 6. The interactive computer programs which were used in the optimizations and phase diagram calculations are described in Ref. 7. These programs are available "on-line" or on diskette, and further information may be obtained from the authors.

2.2. Thermodynamic Relationships

The reader should refer to the previous work[1] for a complete discussion of the thermodynamic relationships used in a critical evaluation. A resume is given here.

For equilibrium between a solid and a liquid phase in a binary system with components A and B, we may write:

$$RT \ln a_A^{\ell} - RT \ln a_A^{s} = -\Delta_{fus} G_A^{\circ} \tag{1}$$

where a_A^{ℓ} and a_A^{s} are the activities of A on the liquidus (with respect to the liquid standard state) and on the solidus (with respect to the solid standard state) at temperature T. $\Delta_{fus} G_A^{\circ}$ is the Gibbs energy of fusion of A at T and R is the gas constant. A similar equation may be written for component B or for any intermediate compound $A_x B_y$.

The activity of a component A in a phase a may be written as:

$$a_A^{\alpha} = \gamma_A^{\alpha} X_A^{\alpha} \tag{2}$$

where X_A^{α} is the molar fraction of component A in the phase α and γ_A^{α} is the activity coefficient given by:

$$RT \ln \gamma_A^{\alpha} = G_A^{E(\alpha)} = G^{E(\alpha)} + x_B \frac{\partial G^{E(\alpha)}}{\partial X_A} \tag{3}$$

where $G_A^{E(\alpha)}$ is the partial molar excess Gibbs energy of A in α.

For the liquid phase the enthalpy of mixing (H^E) and excess entropy (S^E) may be expanded as polynomials in the equivalent fractions as follows:

$$G^E = H^E - TS^E = X_A G_A^E + X_B G_B^E \tag{4}$$

$$H^E = (q_A X_A + q_B X_B) Y_A Y_B [h_0 + h_1 (Y_B - Y_A) + \ldots + h_n (Y_B - Y_A)^n] \tag{5}$$

$$S^E = (q_A X_A + q_B X_B) Y_A Y_B [s_0 + s_1 (Y_B - Y_A) + \ldots s_n (Y_B - Y_A)^n] \tag{6}$$

where the h_i and s_i are empirical coefficients. The factors q_A and q_B are the number of equivalents per mol of component. For example, $q_{NaCl} = 1$, $q_{K_2SO_4} = 2$. Y_A and Y_B are the equivalent fractions defined as:

$$Y_A = \frac{q_A X_A}{q_A X_A + q_B X_B} = (1 - Y_B) \tag{7}$$

The factor $(q_A X_A + q_B X_B)$ in Eqs. (5, 6) is the number of equivalents per mol of solution.

Although H^E and S^E could also be expressed as polynomials in the mol fractions, X_A and X_B, experience has shown that expansions in terms of the equivalent fractions generally give somewhat better representations with fewer coefficients.

Expressions for the partial properties can be obtained by differentiating Eqs. (5, 6) via Eq. (3) to give:

$$H_A^E = q_A Y_B^2 \sum_{i=0}^{n} h_i [Y_B - Y_A)^i - 2i Y_A (Y_B - Y_A)^{i=1}] \tag{8}$$

$$S_A^E = q_A Y_B^2 \sum_{i=1}^{n} s_i [(Y_B - Y_A)^i - 2i Y_A (Y_B - Y_A)^{i-1}] \tag{9}$$

$$H_B^E = q_B Y_A^2 \sum_{i=-0}^{n} h_i [(Y_B - Y_A)^i + 2i Y_B (Y_B - Y_A)^{i=1}] \tag{10}$$

$$S_B^E = q_B Y_A^2 \sum_{i=0}^{n} s_i [(Y_B - Y_A)^i + 2i Y_B (Y_B - Y_A)^{i=1}] \tag{11}$$

Whence

$$G_A^E = H_A^E - T S_A^E \tag{12}$$

$$G_B^E = H_B^E - T S_B^E \tag{13}$$

The empirical coefficients h_i and s_i are found by the simultaneous optimization of the thermodynamic and phase diagram data. No more than two terms were required in Eqs. (5, 6) for any of the 24 systems in the present study. That is $n = 1$ in Eqs. (5, 6).

Our experience with molten salt solutions has also shown that the enthalpic term H^E in Eq. (4) is generally larger in magnitude than the entropic term TS^E. Hence, if available data are limited, it is a reasonable assumption to set $S^E = 0$ and to assume that G^E is temperature independent.

2.3. Limiting Slope of Liquidus Lines Estimation of Solid Solubility

In some systems, the extent of solid solubility is not known. In such cases , the measured limiting slope of the liquidus line (dX_A^{ℓ}/dT) at $X_A = 1$ (pure A) can permit the extent of solid solubility to be estimated. In the limit at $X_A = 1$, both the liquid and solid phases become Henrian such that $G_A^{E(s)}$ and $G_A^{E(\ell)}$ both approach zero. Similarly, for $X_A \approx 1$, the Gibbs energy of fusion of A is given by $\Delta_{fus} H_A^{\circ} (1 - T/T_{fus}^{\circ}(A))$ where $\Delta_{fus} H_A^{\circ}$ is the enthalpy of fusion of A at its melting point, $T_{fus}^{\circ}(A)$. Differentiation of Eq. (1) in the limit at $X_A = 1$ then gives:

$$dX_A^{\ell}/dT - dX_A^{s}/dT = \Delta_{fus} H_A^{\circ}/R (T_{fus}^{\circ}(A))^2 \quad \text{when } X_A = 1 \tag{14}$$

From the known enthalpy of fusion and the measured limiting liquidus slope, dX^{ℓ}/dT, the limiting solidus slope, dX^{s}/dT, can be calculated. If this is close to zero, then the solid solubility is of limited extent.

2.4. Intermediate Compounds

Some of the systems studied contain intermediate compounds. In no cases have the Gibbs energies of fusion of these compounds been measured. However, once $H^{E(\ell)}$ and $S^{E(\ell)}$ have been determined, the Gibbs energies of fusion of the compounds can be calculated from their measured liquidus lines via Eq. (1) if they are assumed to be stoichiometric compounds. Their Gibbs energies of formation from the pure liquid component salts can then also be calculated as the Gibbs energy of liquid-liquid mixing minus the Gibbs energy of fusion.

2.5. Properties of the Pure Salts

It should be noted that for all 24 binary systems reported here, one consistent set of melting points and transformation points of the pure salts has been adopted. In many reported experimental binary phase diagrams, the melting and transformations points differ significantly from these values. Account was taken of this problem in the evaluations.

The temperatures and Gibbs energies of fusion and transformation of all the pure component salts are listed in Table 1. These are based largely on data from a recent reference[14]. However, several data were revised during the course of the present evaluation. These revisions are discussed in the Appendix.

2.6. Optimization Procedure

The actual steps followed in an optimization vary from system to system. Details are given for each system in section 3. However, some general observations can be enunciated.

In four of the 24 systems, $H^{E(\ell)}$ in the liquid phase has been measured calorimetrically. These data were fitted to one or two-membered series as in Eq. (5). Equation (1) was then used to calculate excess liquid Gibbs energies along the A- and B-liquidus lines. Combining these excess Gibbs energies with the already-fitted calorimetric liquid enthalpies permitted the excess liquid entropy, $S^{E(\ell)}$, to be calculated and then smoothed by representation as a 1- or 2-member polynomial as in Eq. (6).

In those systems for which calorimetric liquid enthalpies were not available, $S^{E(\ell)}$ was set equal to zero, and the values of $G^{E(\ell)} = H^{E(\ell)}$ obtained from the phase diagram were then smoothed by polynomial representation with one or two terms.

2.7. Presentation of Results

The results of the analysis are presented together according to the anion pair of the binary systems. The reported experimental data are summarized in part (a) of the summary table for each group (Tables 2–7) The data are summarized with respect to both the invariants (type, temperature and composition range) and the liquidus data (reference and experimental method used). The abbreviations used are: E = eutectic, P = peritectic, 1:1 = melting point of an intermediate compound of this stoichiometry, TA = thermal analysis, V-P = visual/polythermal method, V = visual method (temperature of first appearance of crystals)

The phase diagrams are shown in Figs. 1–29. Not all reported experimental points are shown on the phase diagram in each case. However, all references found for each system have been included. The optimized coefficients of Eqs. (5, 6) for $H^{E(\ell)}$ and $S^{E(\ell)}$ of the liquid phase are given in Table 8. Calculated Gibbs energies of fusion and formation (from the pure liquids) of the intermediate compounds are listed in Table 9. The phase diagrams shown were calculated from these equations and are considered to be the "best" evaluated diagrams which can be deduced from the data currently available. Phase boundaries indicated by dashed lines are considered to be less accurately known.

In part (b) of the summary tables (Tables 2–7), the calculated invariants are identified by type, composition and temperature. In the "Comments" column, information is provided concerning the data used in the optimization, along with other pertinent remarks on the recommended phase diagram. The last column, "Accuracy," reports our estimate of the accuracy which should be attached to each recommended phase diagram.

3. The Evaluations

A) Systems A_2CO_3-AF (Figs. 1–3) where A = Li, Na, K:

In all these systems the limiting liquidus slopes confirm the absence of solid solubility. This was confirmed by X-ray diffraction[15] of the pure salts. None of the excess enthalpies of the liquid phases have been measured. The reported liquidus data were reproduced well with the assumption of regular solution expressions for H^E with $S^E = 0$. A summary of reported and evaluated data for these systems appears in Table 2.

For the K_2CO_3-KF system, Schmitz-Dumont and Heckmann[15] reported only a small phase diagram with smoothed curves and no data points. Amadori's tabulated data[18] were therefore used in the optimization. There is a congruently melting compound $KF\cdot K_2CO_3$ (684 °C $< T_{fus} <$ 688 °C) reported by most of the authors[15,17,18,22]; Schmitz-Dumont and Heckmann[15] verified the composition by X-ray diffraction. The optimization gave the thermodynamic properties for the compound $KF\cdot K_2CO_3$ listed in Table 9.

The calculated liquidus curves fall within 10 °C of experimental data in these three systems.

TABLE 1. Thermodynamic properties of the pure salts (see Appendix)
$\Delta_{fus}G°$ or $\Delta_{trs}G° = a + bT + cT^2 + dT \ln T + e/T$ J mol^{-1}

Salt		T_{fus} or T_{trs} (°C)	aX10^{-3}	b	cX10^3	d	eX10^{-5}
LiF	s→ℓ	848	14.518	128.535	8.709	−21.494	−2.65
NaF	s→ℓ	996	10.847	156.584	4.950	−23.978	−1.07
KF	s→ℓ	857	13.763	127.035	7.211	−20.962	
LiCl	s→ℓ	610	4.420	197.318	16.435	−31.966	
NaCl	s→ℓ	801	7.735	202.091	11.925	−31.824	
KCl	s→ℓ	771	4.755	215.399	12.734	−33.581	1.82
$LiNO_3$	s→ℓ	255	25.563	−48.415			
$NaNO_3$	s→ℓ	310	15.177	−26.033			
KNO_3	α→β	130	5.110	−12.680			
	β→ℓ	337	10.129	−16.605			
LiOH	s→ℓ	477	20.962	−27.949			
NaOH	α→β	297	6.360	11.158			
	β→ℓ	320	6.360	−10.725			
KOH	α→β	249	6.339	−12.144			
	β→ℓ	404	9.372	−13.843			
Li_2SO_4	α→β	578	25.650	−30.141			
	β→ℓ	860	8.990	− 7.935			
Na_2SO_4	s→ℓ	884	23.012	−19.889			
K_2SO_4	α→β	583	8.954	−10.460			
	β→ℓ	1069	36.819	−27.436			
Li_2CO_3	α→β	410	2.238	− 3.277			
	β→ℓ	730	44.769	−44.635			
Na_2CO_3	α→β	359	0.368	− 0.582			
	β→τ	485	2.536	− 3.346			
	τ→ℓ	858	29.665	−26.229			
K_2CO_3	α→β	422	0.230	− 0.331			
	β→ℓ	901	27.614	−23.51			

B) Systems AF-A_2SO_4 (Figs. 4–6) where A = Li, Na, K:

The excess enthalpy of these systems has been measured by direct calorimetry, and sometimes also by solid-liquid mixing experiments[33]. The results obtained by direct calorimetry[25] were considered to be more accurate and were used in every case. There are two congruently melting compounds, NaF·Na_2SO_4 and KF·K_2SO_4. A summary of reported and evaluated data appears in Table 3.

The limiting liquidus slopes at both extremes indicate negligible solid solubility in all systems.

In the system LiF-Li_2SO_4, all the liquidus data points[15,23,25] are concordant within 5°. Since the data of Schmitz-Dumont and Heckmann[15] appeared only on a phase diagram, an optimization was performed on the tabulated[23,25] data.

For the NaF-Na_2SO_4 system, the liquidus data and pure salt melting points of Wolters[27] are lower than those

For the NaF-Na_2SO_4 system, the liquidus data and pure salt melting points of Wolters[27] are lower than those

of other authors[15,25,26,28] which latter are concordant within 10° except near the lower eutectic, where there is greater scatter. The optimization was performed on the more recent data[25,26] which are representative of other work.

A congruently melting compound NaF·Na_2SO_4 is reported[25-30,32]. Reported melting points lie in the range 781–787 °C. The stoichiometry was verified by X-ray diffraction[15]. The optimization gave thermodynamic properties for NaF·Na_2SO_4 which are listed in Table 9.

For the system KF-K_2SO_4, the melting points of the pure salts in Refs. 28 and 34 are up to 10° different from the accepted values of Table 1 and the liquidus curves lie consistently highly than in the more recent studies[25,26] which are in good agreement. The data of Schmitz-Dumont and Heckmann[15] appeared only as smoothed curves on a phase diagram and were omitted in the analysis. The congruently melting compound KF·K_2SO_4 has been reported by references 25, 26, 28, 34. Reported melting points lie in the range 871–886 °C. The compound was studied by optical properties of thin sections, thermal analysis and X-ray diffraction[15,28,34]. The optimization performed on the data of Refs. 25 and 26 gave the thermodynamic properties for $KF \cdot K_2SO_4$ listed in Table 9.

The calculated liquidus curves in all systems lie within 10° of the chosen data.

C) Systems ACl-A_2CO_3 (Figs. 7–9) and ACl-A_2SO_4 (Figs. 10–12) where A = Li, Na, K:

For most of these systems, reported liquidus data are relatively abundant. They are all simple eutectic systems. The fit to the data is generally good. A summary of reported and evaluated data appears in Table 4.

In all these systems, no solid solubility was reported. In some cases the limiting liquidus slopes suggested some solubility. However, this possibility could not be sustained due to errors in the reported melting points of the pure salts and due to lack of supporting data in these and similar systems. Therefore zero solid solubility was assumed in each case. There are no reports of experimental measurement of the excess enthalpy of the liquids.

For the system $NaCl$-Na_2CO_3, the liquidus data points of the oldest work[40] deviate consistently from the later[18,38,41,42,44] and were not considered further. Some inaccuracy in the melting point of pure NaCl Refs. 18 and 44, causes scatter in the experimental data on the NaCl side, but in the rest of the phase diagram agreement is good among the data of Refs. 18, 38, 41, 42, 44, which were all used in the optimization.

For the system KCl-K_2CO_3, the data of Sackur[38,41] are limited to rather dilute solutions only. His data suggest solid solubility on the K_2CO_3 side, but this is contradicted by Amadori's more extensive data[18]. Thus only two data sources[18,47] were used in the optimization.

In the system $NaCl$-Na_2SO_4, the scatter among all experimental liquidus data is as much as 20° over the phase diagram. Most of the data[27,28,38,63,65,69,70,73] are more concordant, while those of Refs. 67 and 71 are respectively high by 15° and 10°. The reported melting point of Na_2SO_4 is higher than the accepted value by 8° in Ref. 73 and 13° in Ref. 65. The liquidus data of Nagornyi and Zimina Ref. 69 are representative of the more concordant data and were used in the calculations.

TABLE 2. Systems A_2CO_3-AF where A = Li, Na, K

(a) Summary of reported data

System (A-B)	Ref.	Invariants and congruent melting points data ranges			Liquidus data
		Type	X_B	°C	Ref. & method
Li_2CO_3-LiF	15–17	E	0.45–0.49	600–608	15(TA) 16(TA)
Na_2CO_3-NaF	15,17–22	E	0.39–0.40	686–700	15(TA) 18(TA)
K_2CO_3-KF	15,17,18, 21.22	E	0.46–0.48	682–688	15(TA) 18(TA)
		E	0.60–0.62	677–682	
		1:1	0.5	684–688	

(b) Summary of evaluated diagram

System (A-B)	Invariants and congruent melting points			Comments	Accuracy °C
	Type	X_B	°C		
Li_2CO_3-LiF	E	0.500	609	All liquidus data[15,16] used in optimization	±10
Na_2CO_3-NaF	E	0.410	694	All liquidus data[15,18] used in optimization	±10
K_2CO_3-KF	E	0.456	687	Data of Ref. 18 optimized	±5
	E	0.602	679		
	1:1	0.5	688		

D) Systems A_2CO_3-AOH (Figs. 13–17) where A = Li, Na, K:

These three systems are simple eutectics. The difference in the melting points of the hydroxides and the carbonates is at least 250°, and so the eutectic is always close to the hydroxide side. A summary of reported and evaluated data is presented in Table 5.

The excess enthalpy of the liquid has not been reported in these systems. The limiting liquidus slopes do not suggest solid solubility.

Perfil'eva and Reshetnikov studied the system Li_2CO_3-LiOH twice[81,82] and their later data[82] are inconsistent with their earlier[81]. The phase diagrams they presented are incoherent and were not considered further in this analysis. The data of the French authors[80] are therefore used in the calculations, although their reported melting point of pure Li_2CO_3 is lower by nearly 20° than the accepted value.

For the system Na_2CO_3-NaOH, the liquidus curves defined by Refs. 80, 84, 86, 87 are reasonably concordant (within 10°) and were used in the present calculations. The data of Ref. 85 were rejected because they were consistently higher than the others. The oldest report[83] shows severely scattered data and refers to a minimum, rather than a eutectic.

There are two groups of liquidus data for the system K_2CO_3-KOH: the first includes data of Khitrov[85] and Michaud[89]. Data in this first group are higher by as much as 50° than those in the second group[80]. It is not evident from simple inspection which data are closer to true behavior. It was possible to fit accurately each group of data. However, when $G^{E(\ell)}$ was set to zero, the calculated liquidus lay between the two groups of experimental points. Thus it was decided that the assumption of an ideal liquid would probably better reflect the excess properties of this phase.

The excess enthalpy of these systems, as obtained by optimization of the phase diagram data, is seen (Table 8) to approach ideality as the cation radius increases.

TABLE 3. Systems AF-A_2SO_4 where A = Li, Na, K

(a). Summary of reported data

System (A-B)	Invariants and congruent melting points data ranges				Liquidus data
	Ref.	Type	X_B	°C	Ref. & method
Li//F,SO_4	15,23–25	E	0.56–0.58	531–535	15(TA) 23(V-P) 25(TA)
Na//F,SO_4	15,22	E	0.36–0.41	772–781	15(TA) 25(TA)
	25–33	E	0.70–0.73	742–750	26(V-P)27(TA)
	1:1	0.5	781–787		28(TA)
K//F,SO_4	15,22,	E	0.58–0.59	864–883	15(TA) 25(TA)
	24 26	E	0.16–0.17	776–788	26(V-P)28(TA)
	28,33–35	1:1	0.5	871–886	34(TA)

(b). Summary of evaluated diagram

System (A-B)	Invariants and congruent melting points			Comments	Accuracy °C
	Type	X_B	°C		
LiF-Li_2SO_4	E	0.587	531	Excess enthalpy of Ref. 25 and liquidus data of Refs. 23 and 25 used in optimization	±5
NaF-Na_2SO_4	E	0.411	779	Excess enthalpy of Ref. 25 and liquidus data of Refs. 25 and 26 used in optimization	±10
	E	0.712	748		
	1:1	0.5	785		
KF-K_2SO_4	E	0.169	779	Excess enthalpy of Ref. 25 and liquidus data of Refs. 25 and 26 used in optimization	±10
	E	0.575	869		
	1:1	0.5	872		

TABLE 4. Systems $ACl-A_2CO_3$ and $ACl-A_2SO_4$ where A = Li, Na, K

(a). Summary of reported data

System		Invariants Data Ranges			Liquidus data
(A-B)	Ref.	Type	X_B	°C	Reference & method
$LiCl-Li_2CO_3$	36, 37	E	0.24–0.28	506–507	37(TA)
$NaCl-Na_2CO_3$	18,20,21, 29,38–45	E	0.41–0.47	632–645	18(TA),38(T),40(V) 41(TA),42(TA), 44(V-P)
$KCl-K_2CO_3$	18,20,21, 38,41, 46–49	E	0.35–0.38	623–636	18(TA),38(TA), 41(TA)47(V-P)
$LiCl-Li_2SO_4$	36,50–63	E	0.35–0.37	476–488	50(V-P),57(V-P), 58(V-P),59(V-P), 60(V-P),61(V-P), 62(V-P),63(TA & V-P),
$NaCl-Na_2SO_4$	27–29,38 39,63–75	E	0.45–0.48	623–634	27(TA),28(T), 38(TA) 63 (V-P),65(TA), 67(TA),69(V-P) 73(TA)
$KCl-K_2SO_4$	28,39,59, 62,65,70, 76–79	E	0.23–0.29	688–694	28(TA),59(V-P) 65(TA),70(V-P) 76(TA),77(TA)

(b). Summary of evaluated diagram

System	Invariants				Accuracy
(A-B)	Type	X_B	°C	Comments	°C
$LiCl-Li_2CO_3$	E	0.262	509	Data of Ref. 37 optimized Calculated liquidus lies within 6° of data	±10
$NaCl-Na_2CO_3$	E	0.448	634	Data of Refs. 18,38,41, 42,44 optimized	±10
$KCl-K_2CO_3$	E	0.366	629	Data of Refs 18 and 47 used in optimization. Calculated liquidus lies within 5° of data	±5
$LiCl-Li_2SO_4$	E	0.368	480	Data of Refs. 50,57–63 used in optimization.	±15 ($X_B > 0.75$)
				Calculated liquidus deviates slightly more on steep side ($X_B > 0.75$)	±10 ($X_B > 0.75$)
$NaCl-Na_2SO_4$	E	0.481	628	Data of Ref. 69 optimized Calculated liquides lies within 5° of data	±5
$KCl-K_2SO_4$	E	0.263	690	All data Refs. 28,59,65, 70,76,77 used in optimization (up to 25° scatter on K_2SO_4 side	±5 (KCl side) ±15 (K_2SO_4 side)

E) Systems AOH-A_2SO_4 (Figs. 18–22) where A-Li, Na, K:

These systems present several difficulties in analysis. There are no phase diagram or thermodynamic data available for LiOH-Li_2SO_4; the stoichiometry of intermediate compounds has been a matter of dispute in NaOH-Na_2SO_4; the few liquidus data for KOH-K_2SO_4 are limited to a small composition interval near the KOH extreme. A summary of reported and evaluated data is given in Table 6.

No excess enthalpy data are available for these systems.

Only a tentative phase diagram can be calculated for the system LiOH-Li_2SO_4, based on critically evaluated data for the analogous common-cation systems NaOH-Na_2SO_4 and KOH-K_2SO_4 studied here. It is possible that the Li system may contain one or more compounds, as do the NaOH-Na_2SO_4 system and the analogous isostructural systems[91,92] MOH-M_2CrO_4 (M = Li, Na, K). For the system NaOH-Na_2SO_4, the data of Ravich and Elenevskaya[96] are up to 25° higher than those of Bergman and Khitrov[93]. In the latest report[97], only the invariants were studied. The rest of the diagram is based on a previous work[96]. The peritectic near 480 °C has been reported by all investigators[93-97], but the stoichiometry of the compound associated with it is not certain. Some authors[94,96,97] studied the compound by thermal analysis and X-ray diffraction and reported the stoichiometry as 2NaOH·$3Na_2SO_4$. They reported a solid phase transition of this compound at 418 °C. Others[93,95] claim the stoichiometry to be 1:1 but with no supporting evidence.

In three works[94,96,97] a second experimental peritectic is given at 316 °C with the compound 2NaOH·Na_2SO_4 assigned to it. Although the presence of 2:3 and 2:1 compounds is possible, the calculated diagram shows only the 1:1 compound. Separate optimizations were performed on the two sets of liquidus data[93,96]. The eutectic calculated from the data of Bergman and Khitrov[93] is closer to the experimental, and so these data were used in the analysis. The optimization gave the thermodynamic properties for the compound NaOH·Na_2SO_4 listed in Table 9.

At those composition extremes where liquidus data were available in these systems, the limiting liquidus slopes did not indicate any solid solubility. Zero solubility was assumed in all systems.

TABLE 5. Systems A_2CO_3-AOH where A = Li, Na, K

(a). Summary of reported data

System (A-B)	Invariants Data Ranges				Liquidus data
	Ref.	Type	x_B	°C	Ref. & method
Li_2CO_3-LiOH	80–82	E	0.82–0.90	419–442	80(TA) 81(TA) 82(TA)
Na_2CO_3-NaOH	80,83–88	E	0.90–0.94	283–292	80(TA), 83(TA) 84(TA), 85 (V-P) 86(TA), 87(TA)
K_2CO_3-KOH	80,82,85,	E	0.90–0.91	360–367	80(TA) 85(V-P) 89,90 89(TA)

(b). Summary of evaluated diagram

Li_2CO_3-LiOH	E	0.822	418	Data of Ref. 80 used in optimization. Calculated liquidus lies within 5° of data	±5
Na_2CO_3-NaOH	E	0.917	285	Data of Refs. 80,84,86,87 used in optimization. Calculated liquidus lies within 10° of data	±10
K_2CO_3-KOH	E	0.907	367	Calculated liquidus offered as best compromise among badly scattered data	±20

F) Systems A_2CO_3-ANO_3 (Figs. 23–25) and ANO_3-A_2SO_4 (Figs. 26–29) where A=Li, Na, K:

In all these systems, the phase diagram data available were always confined to a composition region near the pure nitrate. The difference between the melting points of the nitrate and the other salt can be as high as 700 °C. As a consequence, the phase diagrams are highly asymmetric, and liquidus data are consistently missing at higher temperatures due to decomposition of the mixtures. A summary of reported and evaluated data for these systems appears in Table 7.

It is possible that these six systems contain solid solubility similar to the M_2CO_3-M_2SO_4 (M = Li, Na, K) systems[5]. While the limiting liquidus slopes are consistent with zero solid solubility in the nitrates, there are no data to indicate whether or not there is solid solubility at the other extreme. Zero solubility was assumed at both extremes in the present calculations.

The excess enthalpy has been measured only for the system $NaNO_3$-Na_2SO_4[103] in the composition range $0.05 < x_B < 0.08$. Kleppa and Meschel[103] extrapolated from their results the following equation for the enthalpy of mixing:

$$H^E = (-210 \pm 840)\, X_A X_B \text{ J mol}^{-1}. \qquad (15)$$

An optimization with the phase diagram data and Eq. (15) gave improbably large negative entropy terms. Therefore, the equation of Kleppa and Meschel were rejected and phase diagram data and calorimetric measurements were optimized together. The results give an equation for the enthalpy of mixing which is within the error limits of the enthalpy measurements (Table 8).

In the $NaNO_3$-Na_2SO_4 system, the data of Refs. 64 and 98 are consistently lower than those of Ref. 102 by as much as 20°; particularly in the steep part of the liquidus. An optimization on the data of Ref. 102 yielded thermodynamic properties more consistent with the analogous systems studied here.

TABLE 6. Systems AOH-A_2SO_4 where A = Li, Na, K

(a). Summary of reported data

System (A-B)	Invariants Data Ranges				Liquidus data
	Ref.	Type	X_B	°C	Ref. & method
$NaOH$-Na_2SO_4	93–97	E P P	0.04–0.06 0.33–0.36 0.08–0.1	290–293 480–485 316	93(V-P), 96(V-P), 97(TA)
KOH-K_2SO_4	93	E	0.055	370	93(V-P)

(b). Summary of evaluated diagram

System (A-B)	Invariants			Comments	Accuracy °C
	Type	X_B	°C		
$LiOH$-Li_2SO_4	E	0.27	395	Tentative diagram only	
$NaOH$-Na_2SO_4	E P	0.064 0.34	292 470	Data of Ref. 93 used in optimization. Calculated liquidus lies within 10° of data	±10
KOH-K_2SO_4	E	0.056	377	All available data Ref. 93 used in optimization	±10 ($X_B < 0.4$) ±25 ($X_B > 0.4$)

In the KNO_3-K_2SO_4 system, Amadori's data[98] are consistently lower and those of Perman and Howell's[105] but consistently higher (perhaps due to a KNO_3 melting point 3° higher than the accepted value) than the others[103,106]. The few points of Kuz'mina[106] agree with Ref. 102. The data of Bergman and Vaksberg[102] were chosen for the optimization.

In most of these systems, both eutectic and liquidus data were fitted well simultaneously. In those cases (Li_2CO_3-$LiNO_3$ and KNO_3-K_2SO_4) where this was not true, greater weight was given to the liquidus data. This preference resulted in liquid excess properties more in accordance with those observed in the other systems of this group.

All these systems show positive deviations from ideal liquid solution behavior (Table 8).

All six systems were re-evaluated by assuming ideal liquid behavior and solid solubility of the nitrates in the carbonates and sulfates. The solid solutions were assumed to obey Henry's Law. Solid solubilities of the order of 50 mol% were calculated at the eutectic temperatures. However, in order to fit the reported liquidus curves, improbably large entropic terms were required for the Henrian solutions. Most likely there is some solid solubility of the nitrates in the carbonates and sulfates, but not as much as indicated by this analysis. Thus, the real values of G^E for the liquid phase are probably somewhat less positive than the values in Table 8, but the liquids still exhibit positive deviations.

TABLE 7. Systems A_2CO_3-AOH where A = Li, Na, K

(a). Summary of reported data

System (A-B)	Invariants Data Ranges				Liquidus data
	Ref.	Type	X_B	°C	Ref. & method
Li_2CO_3-$LiNO_3$	98	E	0.98	250	98(TA)
Na_2CO_3-$NaNO_3$	98	E	0.98	304	98(TA)
K_2CO_3-KNO_3	98	E	0.96	326	98(TA)
$LiNO_3$-Li_2SO_4	98–100	E	0.01–0.02	245–252	98(TA)
$NaNO_3$-Na_2SO_4	64, 98 100–103	E	0.03–0.05	296–304	64(TA & V-P), 98(V),102(V-P)
KNO_3-K_2SO_4	98,99,102 104–107	E	0.01–0.03	332–338	98(TA),102(V-P) 105(V),106(V-P)

(b). Summary of evaluated diagram

System (A-B)	Invariants			Comments	Accuracy °C
	Type	X_I	°C		
Li_2CO_3-$LiNO_3$	E	0.997	254.6	Data of Ref. 98 optimized	±10 ($X_B > 0.7$) ±20 ($X_B < 0.7$)
Na_2CO_3-$NaNO_3$	E	0.978	306	Data of Ref. 98 optimized	±10 ($X_B > 0.7$) ±20 ($X_B < 0.7$)
K_2CO_3-KNO_3	E	0.964	326	Data of Ref. 98 optimized	±10 ($X_B > 0.7$) ±30 ($X_B < 0.7$)
$LiNO_3$-Li_2SO_4	E	0.015	253.3	Data of Ref. 98 optimized	±10 ($X_B > 0.3$) ±50 ($X_B < 0.3$)
$NaNO_3$-Na_2SO_4	E	0.049	300	Data of Ref. 102 optimized	±10 ($X_B > 0.4$) ±20 ($X_B < 0.4$)
KNO_3-K_2SO_4	E	0.009	334	Data of Ref. 102 optimized	±15 ($X_B > 0.2$) ±50 ($X_B < 0.2$)

TABLE 8. Optimized excess properties of the liquid[a]

$$H^E = Y_A Y_B (h_0 + h_1 (Y_B - Y_A))\ \mathrm{J\ equiv^{-1}}$$

$$S^E = Y_A Y_B (s_0 + s_1 (Y_B - Y_A))\ \mathrm{J\ K^{-1}\ equiv^{-1}}$$

System (A-B)	h_0	h_1	s_0	s_1
Li_2CO_3-LiF	−1477	0	0	0
Na_2CO_3-NaF	−450	0	0	0
K_2CO_3-KF	−1150	0	0	0
LiF-Li_2SO_4[b]	−988	−359	2.352	0
NaF-Na_2SO_4[b]	56	−217	1.214	−2.044
KF-K_2CO_4[b]	−1263	486	1.522	0
LiCl-Li_2CO_3	−1712	0	0	0
NaCl-Na_2CO_3	498	0	0	0
KCl-K_2CO_3	923	1470	0	0
LiCl-Li_2SO_4	280	336	0	0
NaCl-Na_2SO_4	1256	197	0	0
KCl-K_2SO_4	1098	−1038	0	0
Li_2CO_3-LiOH	−4290	−806	0	0
Na_2CO_3-NaOH	−2496	−818	0	0
K_2CO_3-KOH	0	0	0	0
LiOH-Li_2SO_4[c]	−3000 ± 500	0	0	0
NaOH-Na_2SO_4	−3105	0	0	0
KOH-K_2SO_4	−2320	762	0	0
Li_2CO_3-$LiNO_3$	4480	−3263	0	0
Na_2CO_3-$NaNO_3$	3856	−2607	0	0
K_2CO_3-KNO_3	2763	−1557	0	0
$LiNO_3$-Li_2SO_4	6064	4750	0	0
$NaNO_3$-Na_2SO_4	3371	2825	0	0
KNO_3-K_2SO_4	2631	2268	0	0

[a] All coefficients are assumed to be independant of temperature.
[b] Calorimetrically determined excess enthalpy[25].
[c] No data available for this system.

TABLE 9. Calculated Gibbs energies of fusion and of formation (from pure liquid components) of intermediate solid compounds

$$\Delta_{fus}G^\circ = a + bT\,(\mathrm{K})\ \mathrm{J\ mol^{-1}}$$

$$\Delta_f G^\circ = a' + b'T\,(\mathrm{K})\ \mathrm{J\ mol^{-1}}$$

Compound	a	b	a'	b'
$(KF)_{0.5}\,(K_2CO_3)_{0.5}$	18041	−18.760	−18424	12.999
$(NaF)_{0.5}\,(Na_2SO_4)_{0.5}$	21629	−20.432	−21635	14.493
$(KF)_{0.5}\,(K_2SO_4)_{0.5}$	38629	−33.726	−38996	27.457
$(NaOH)_{0.5}\,(Na_2SO_4)_{0.5}$	18323	−24.014	−19358	18.253

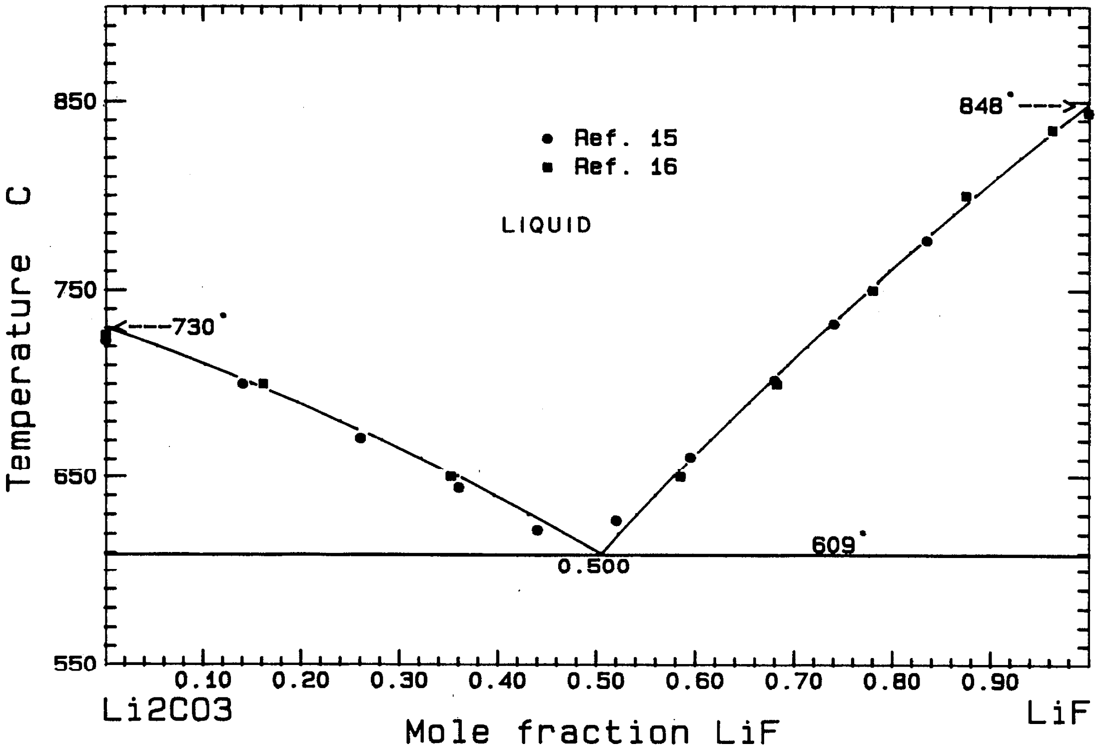

FIG. 1. The system Li_2CO_3-LiF.

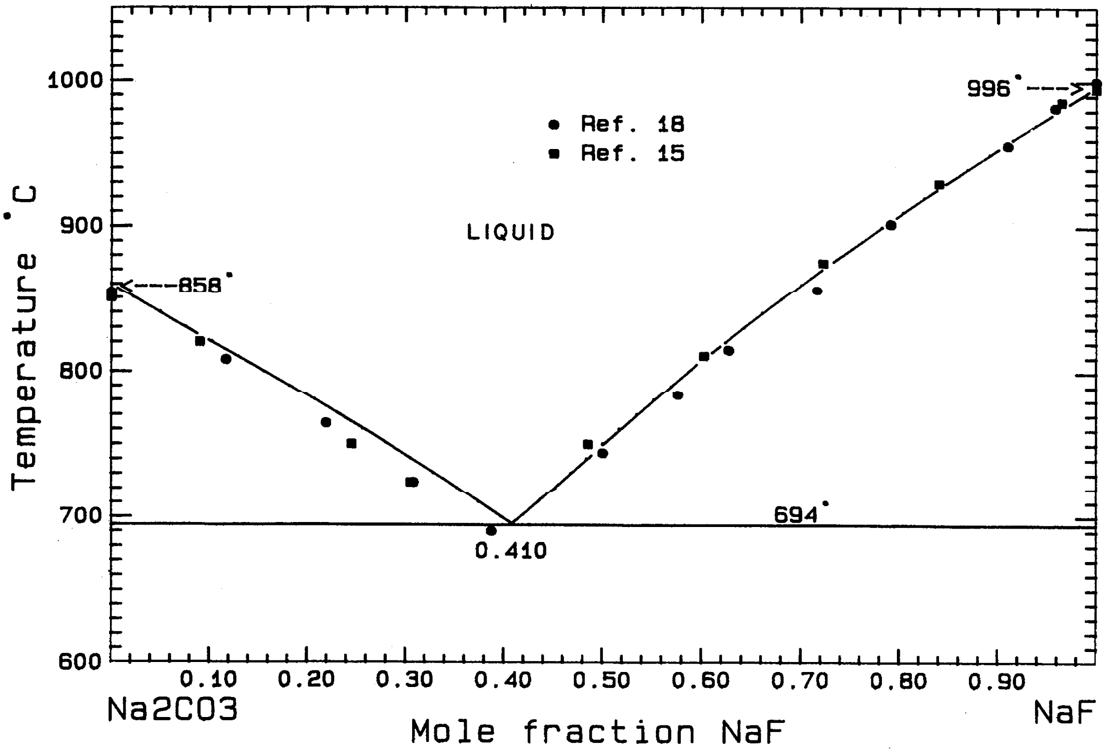

FIG. 2. The system Na_2CO_3-NaF

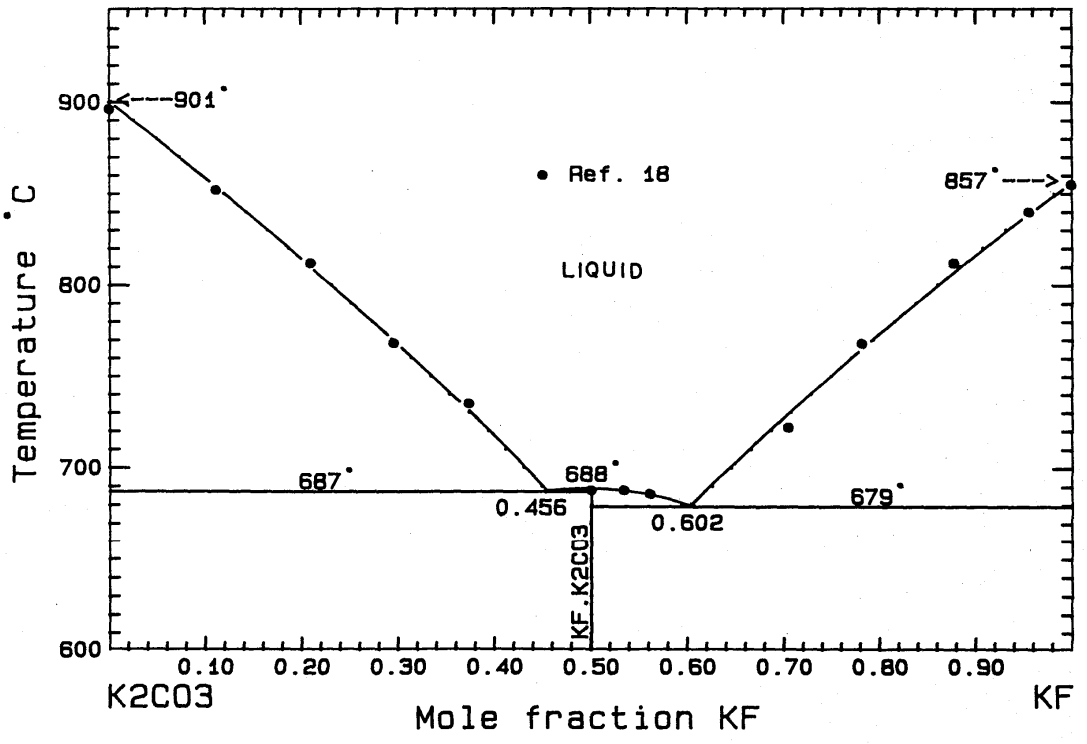

FIG. 3. The System K_2CO_3-KF.

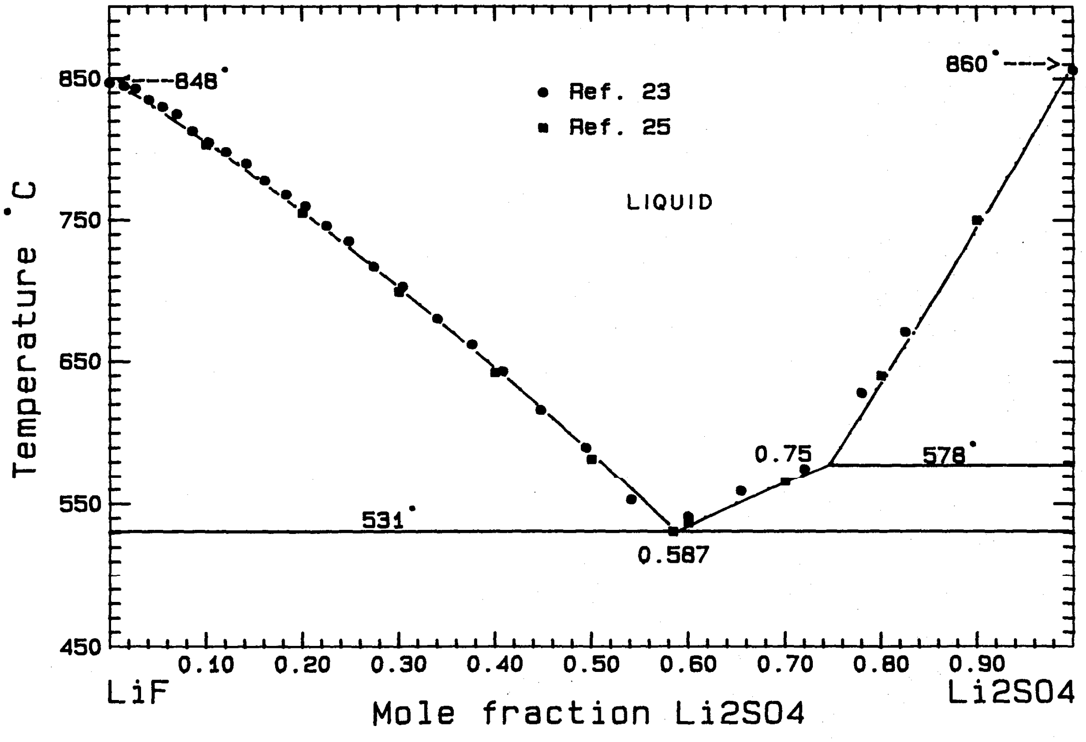

FIG. 4. The system LiF-Li_2SO_4.

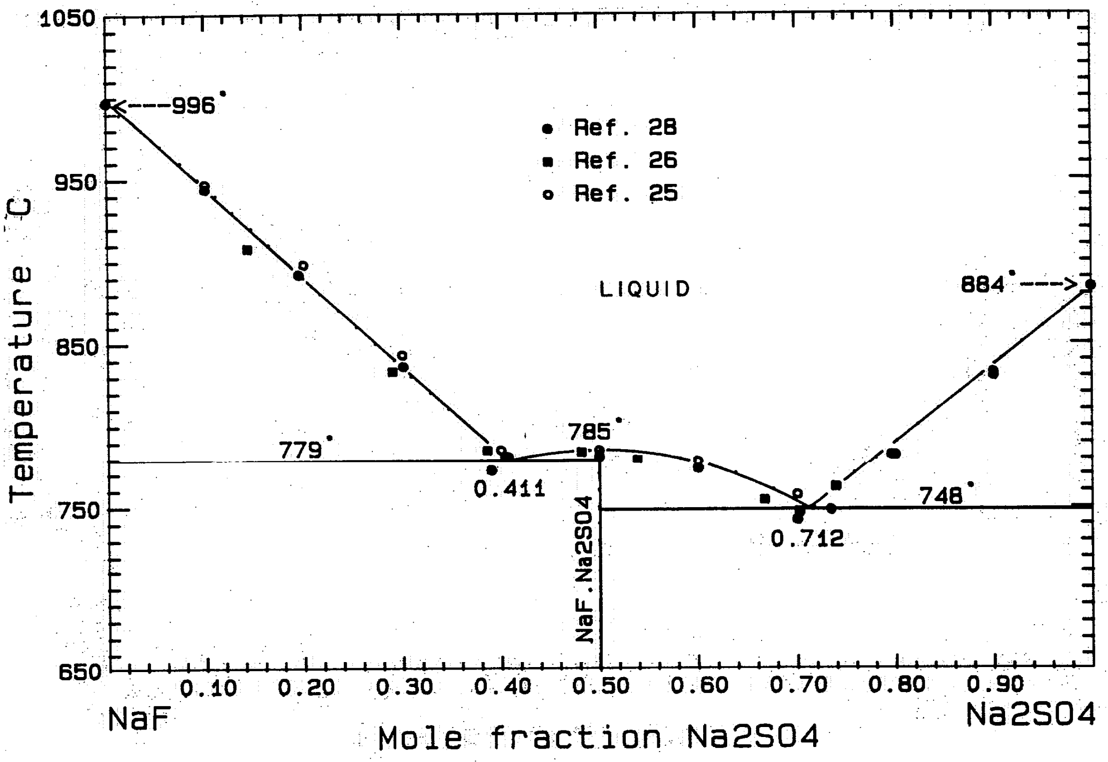

FIG. 5. The system NaF-Na_2SO_4.

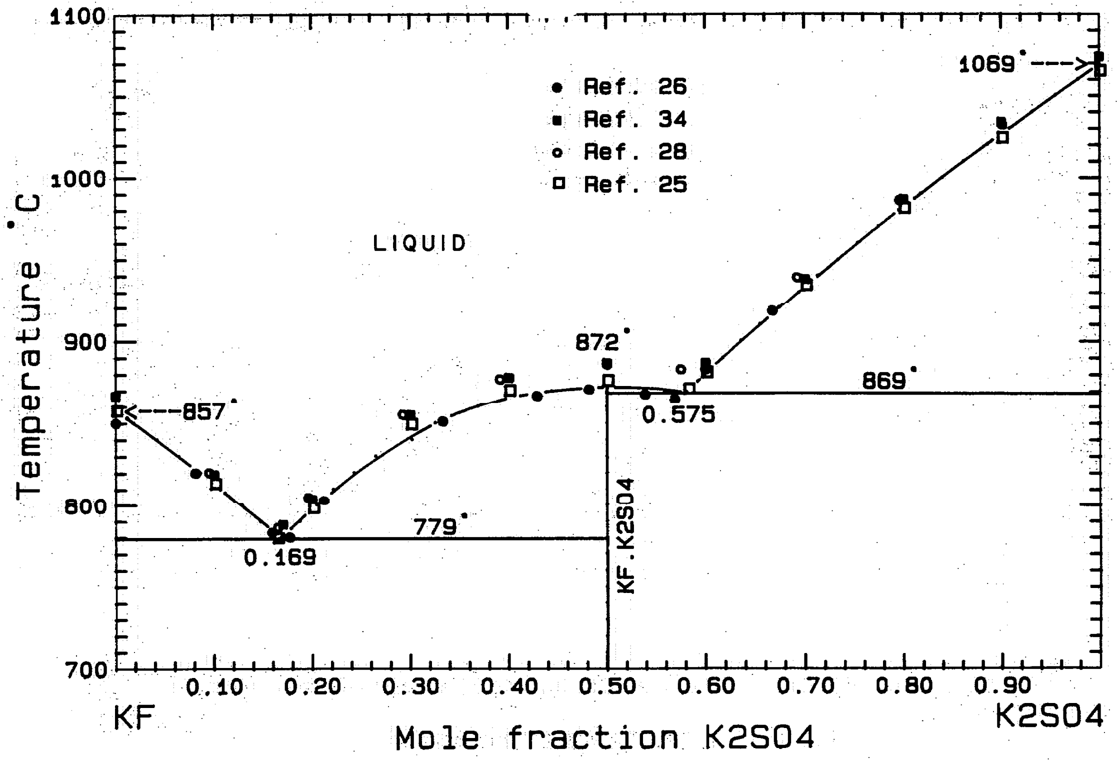

FIG. 6. The system KF-K_2SO_4.

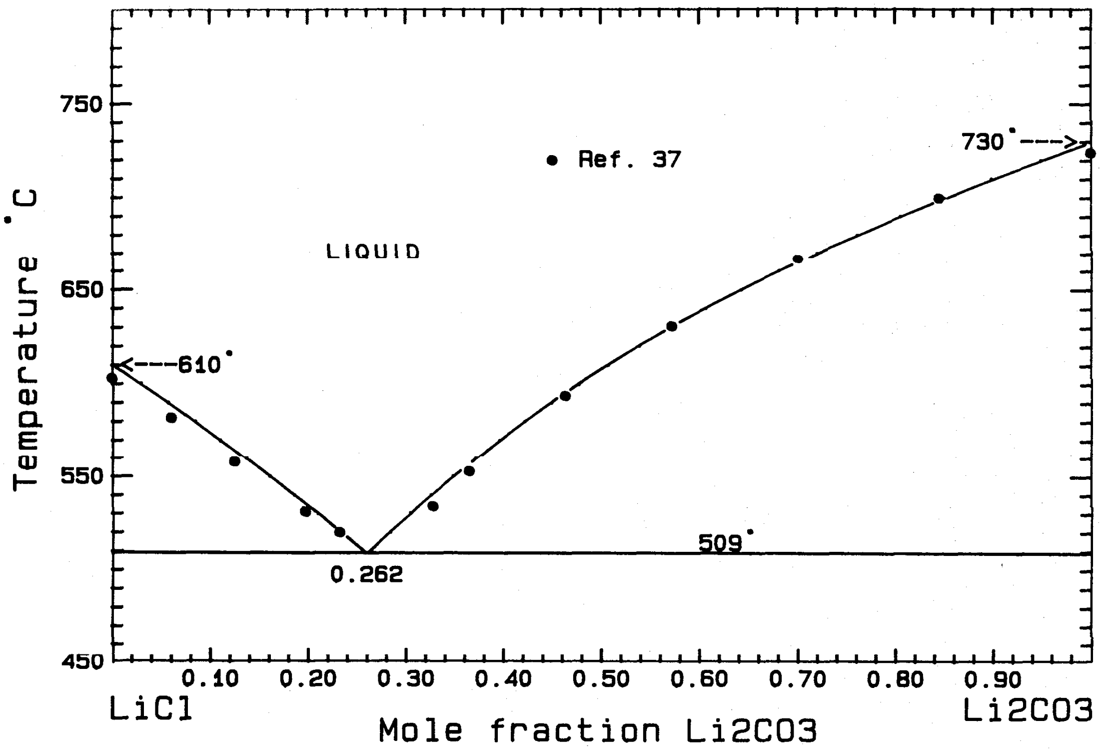

FIG. 7. The system LiCl-Li_2CO_3.

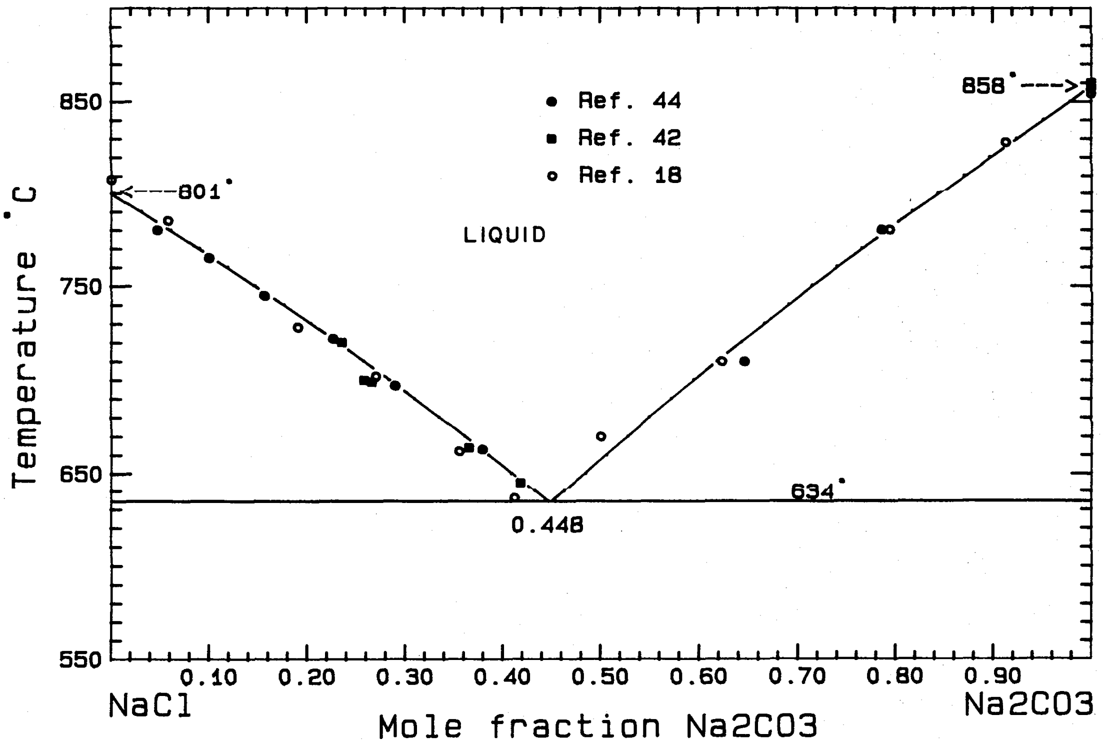

FIG. 8. The system NaCl-Na_2CO_3.

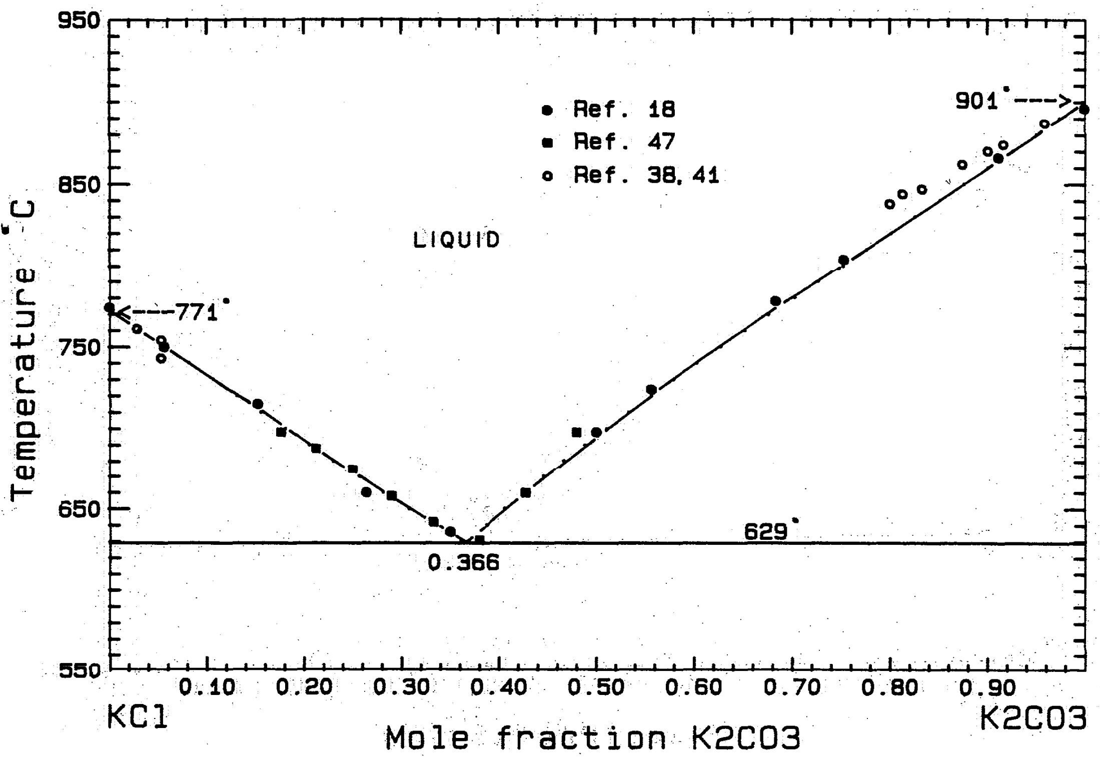

FIG. 9. The system KCl-K_2CO_3.

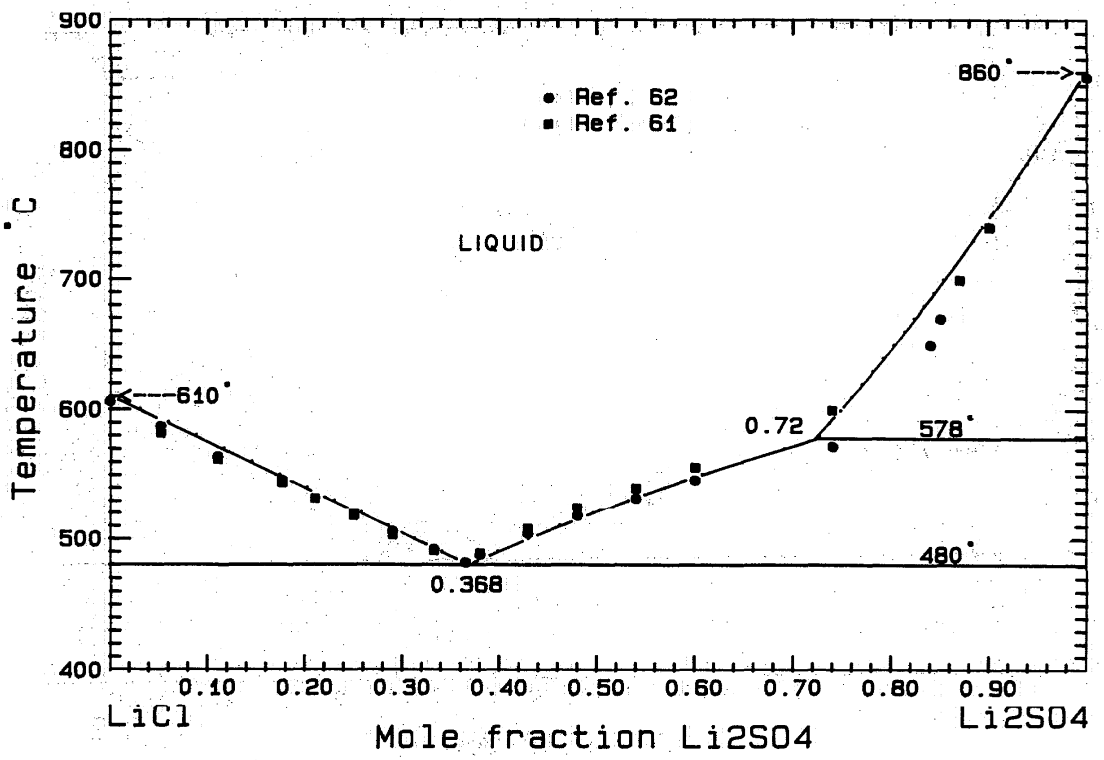

FIG. 10. The system LiCl-Li_2SO_4.

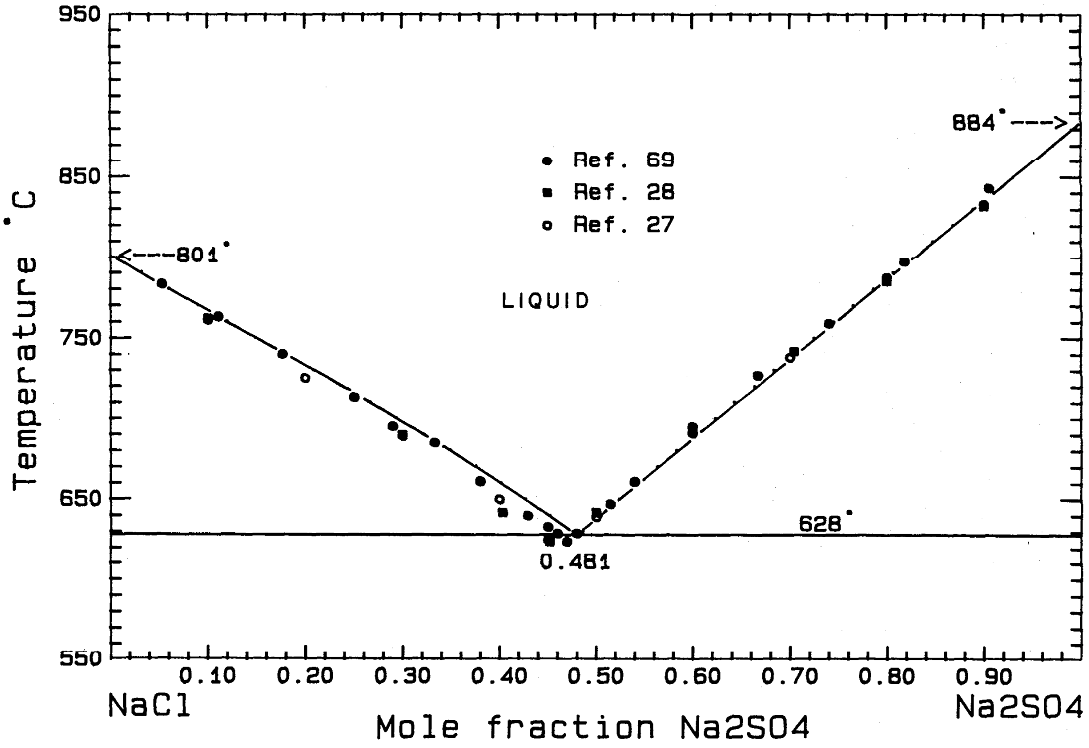

FIG. 11. The system NaCl-Na_2SO_4.

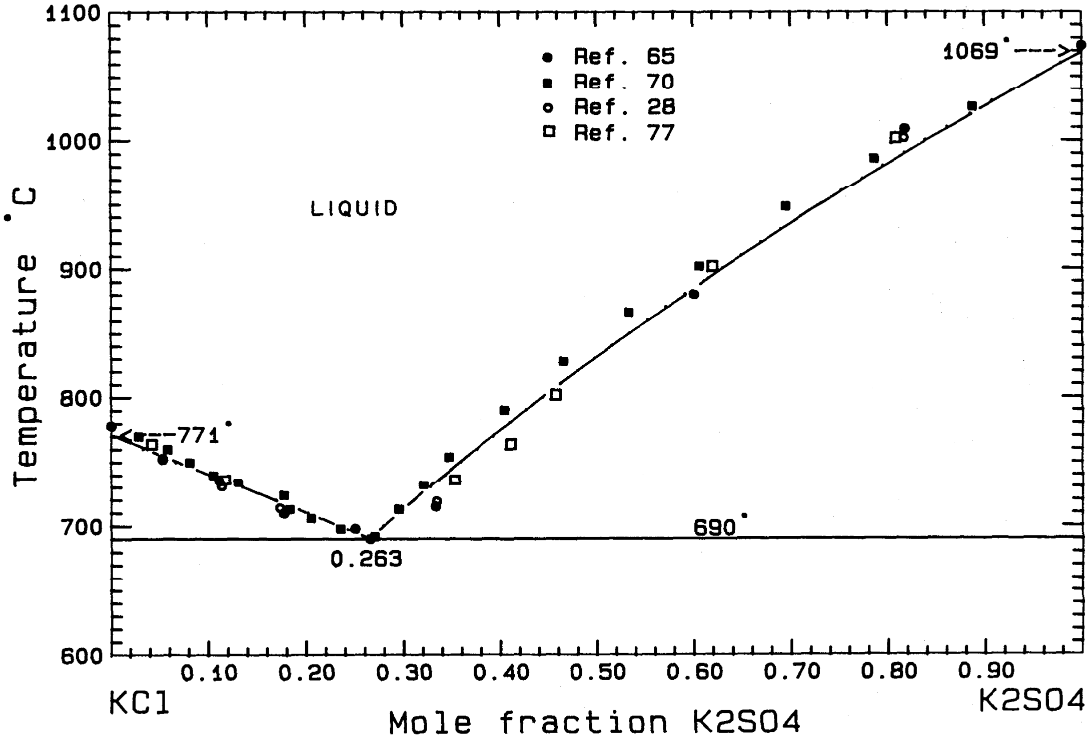

FIG. 12. The system KCl-K_2SO_4.

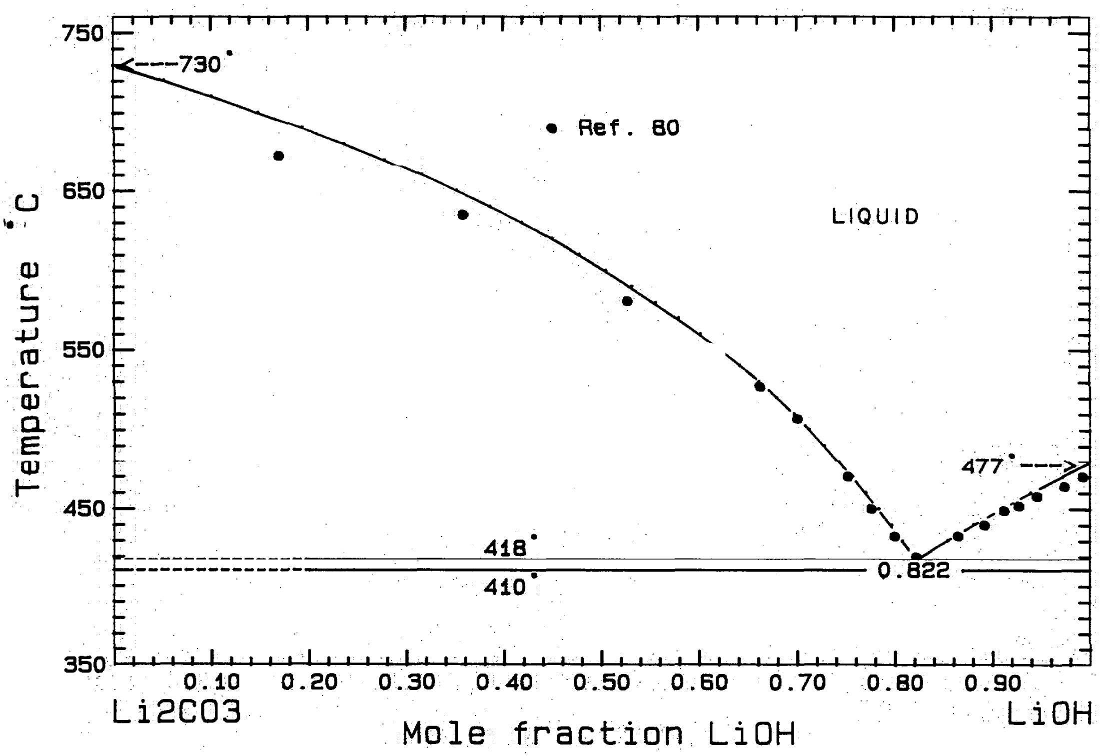

FIG. 13. The system Li_2CO_3-LiOH.

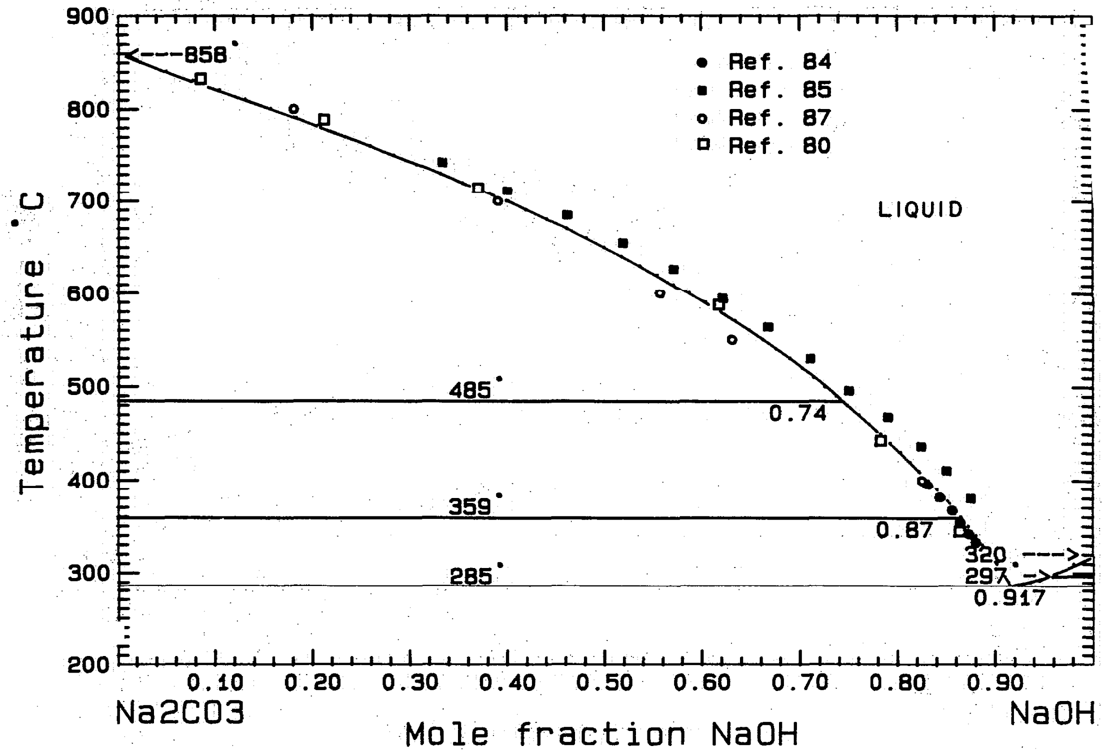

FIG. 14. The system Na_2CO_3-NaOH.

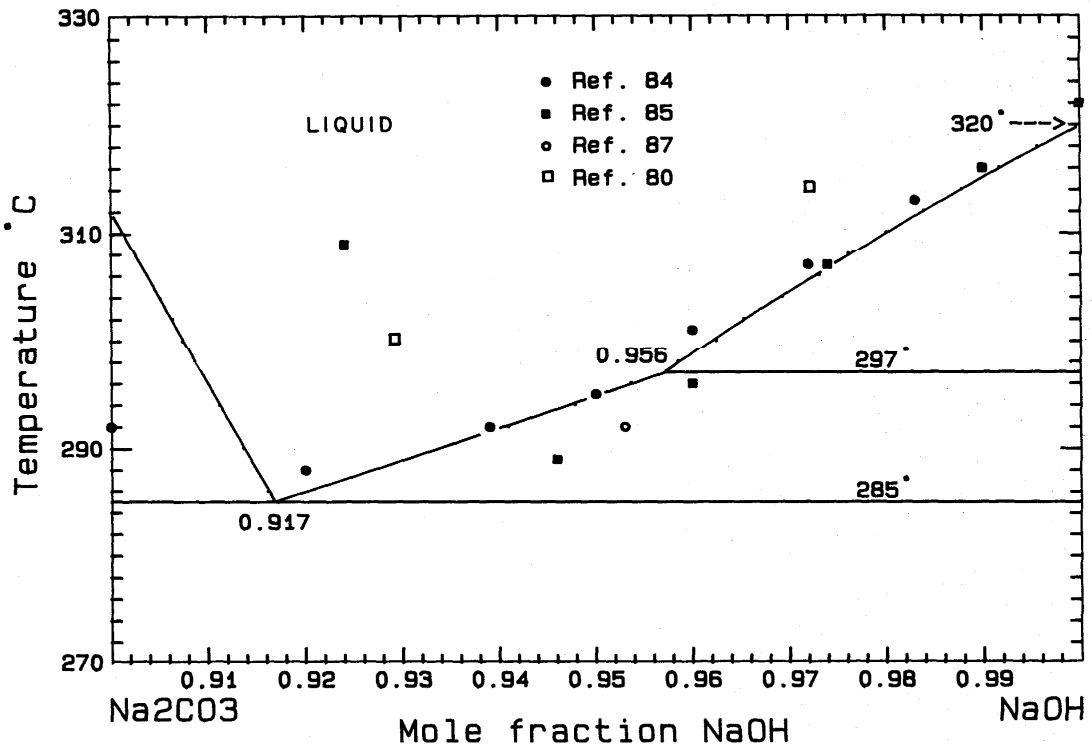

FIG. 15. The system Ha_2CO_3-NaOH enlarged.

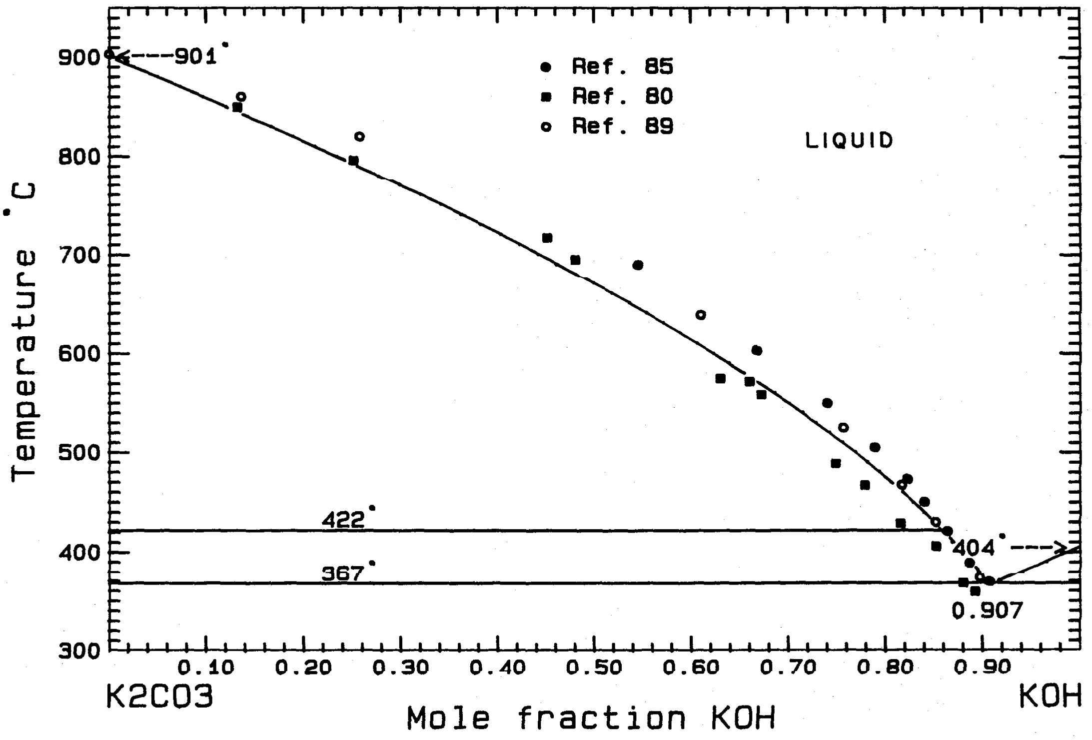

FIG. 16. The system K_2CO_3-KOH.

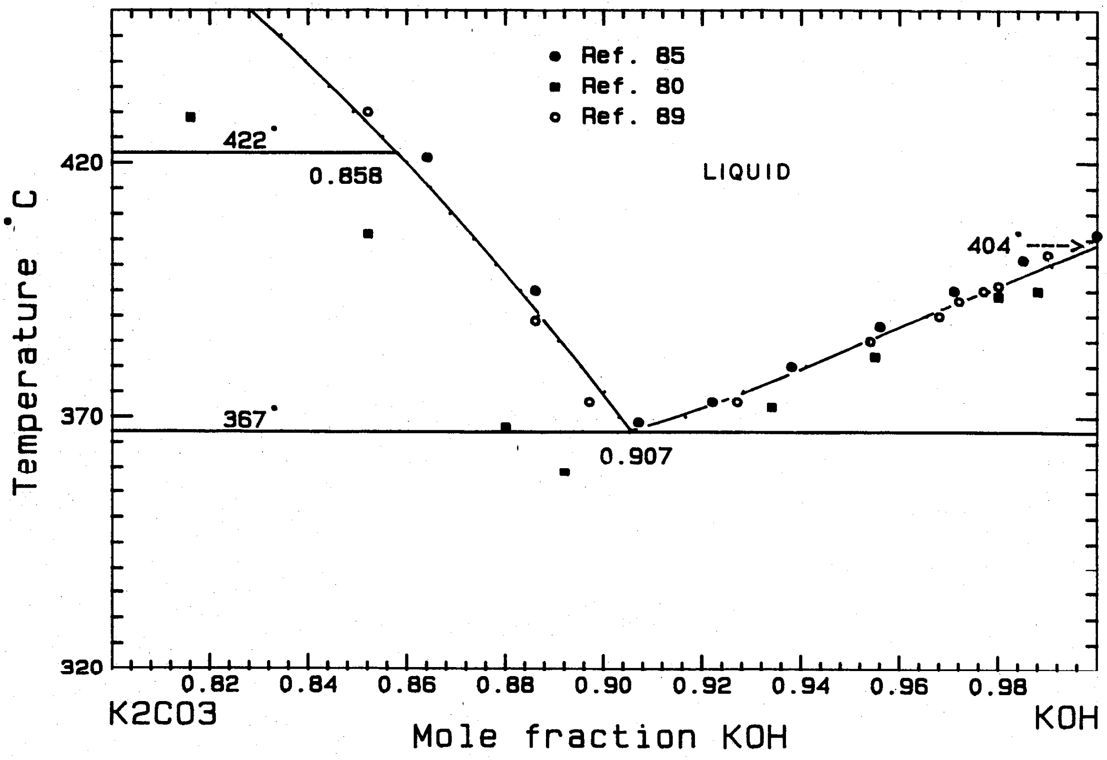

FIG. 17. The system K_2CO_3-KOH enlarged.

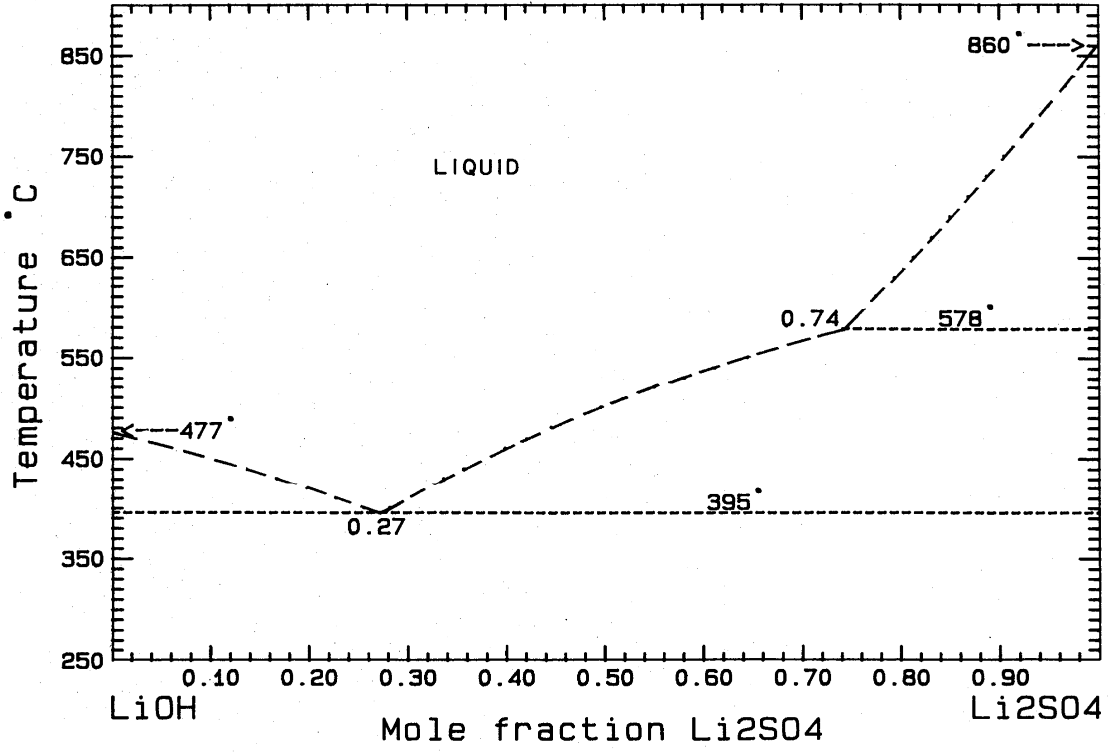

FIG. 18. The system LiOH-Li_2SO_4.

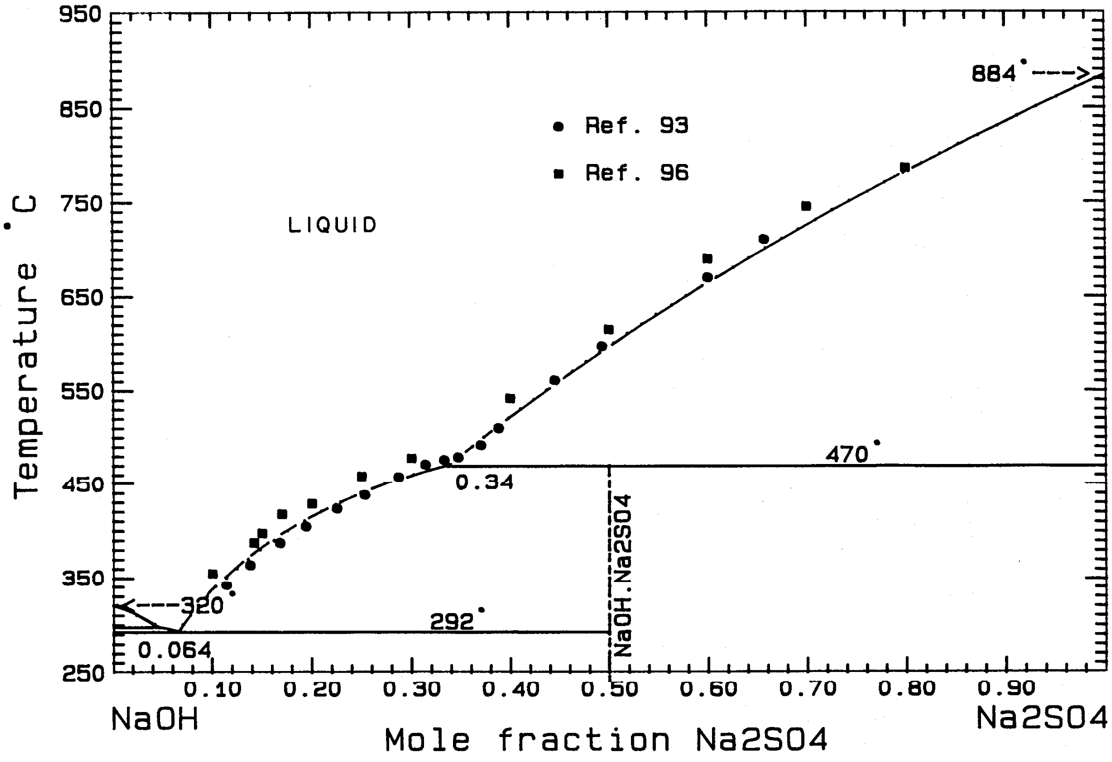

FIG. 19. The system NaOH-Na_2SO_4.

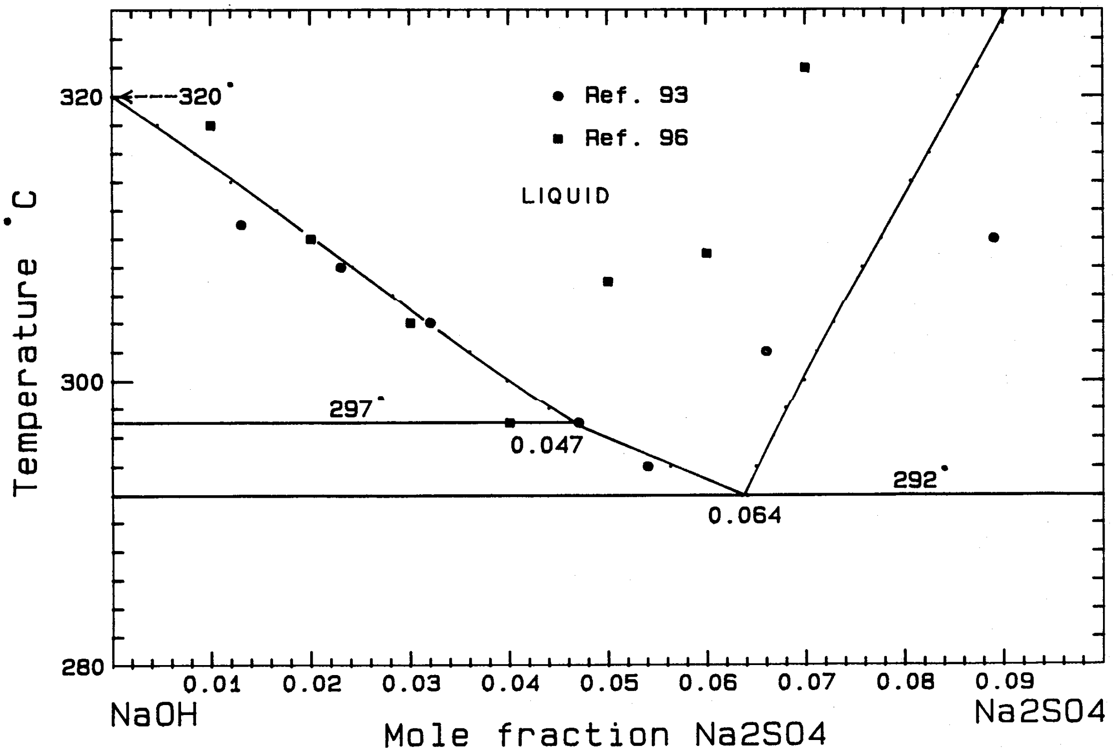

FIG. 20. The system NaOH-Na_2SO_4 enlarged.

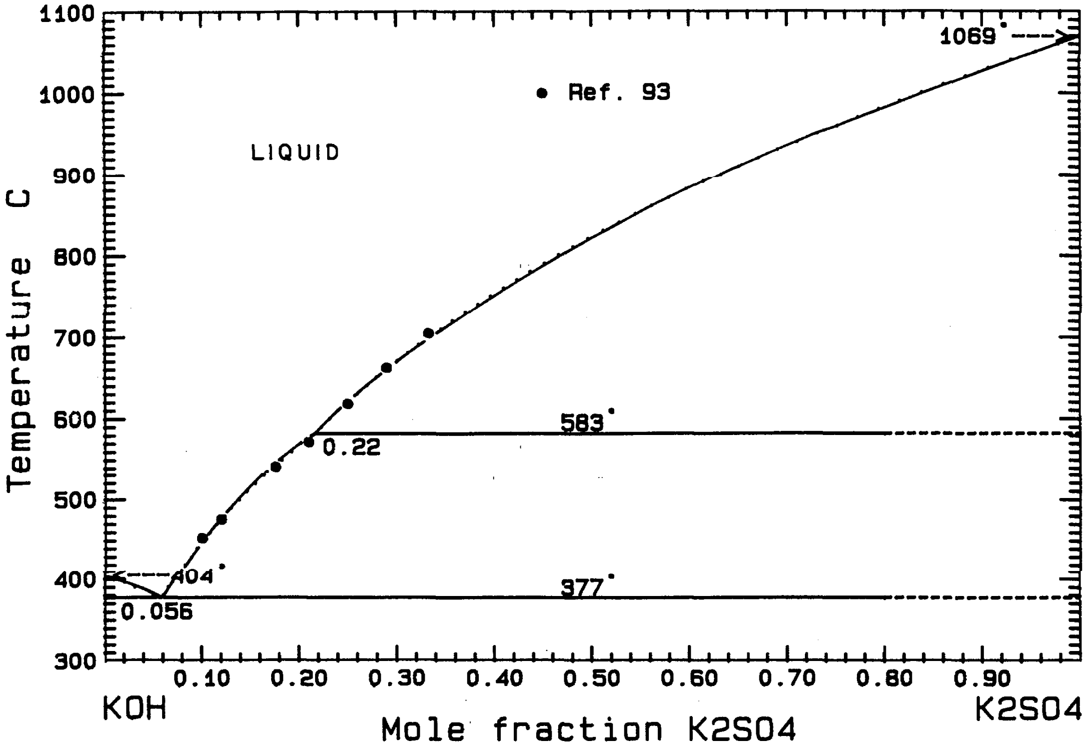

FIG. 21. The system KOH-K_2SO_4.

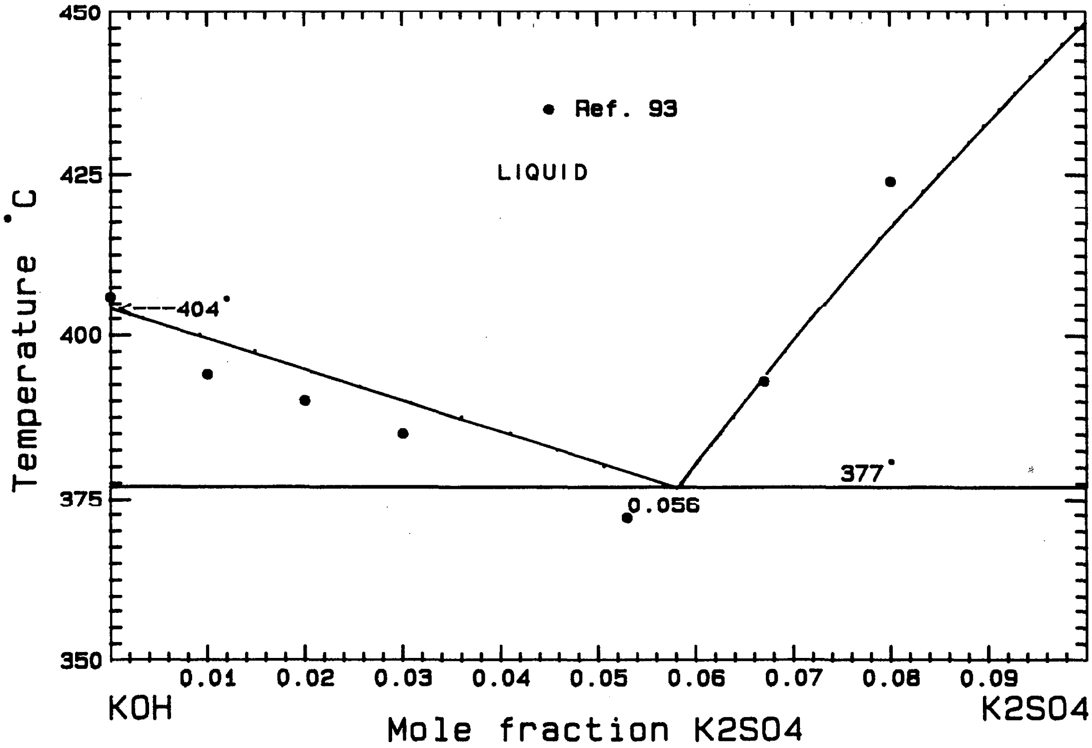

FIG. 22. The system KOH-K_2SO_4 enlarged.

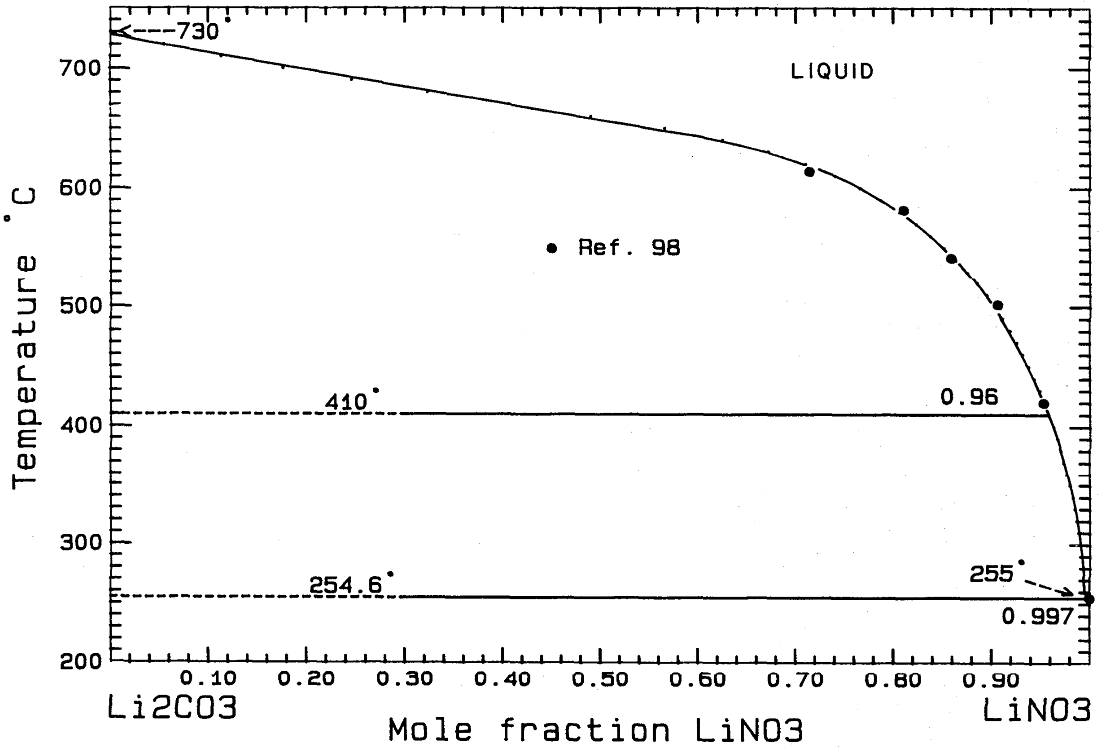

FIG. 23. The system Li_2CO_3-$LiNO_3$.

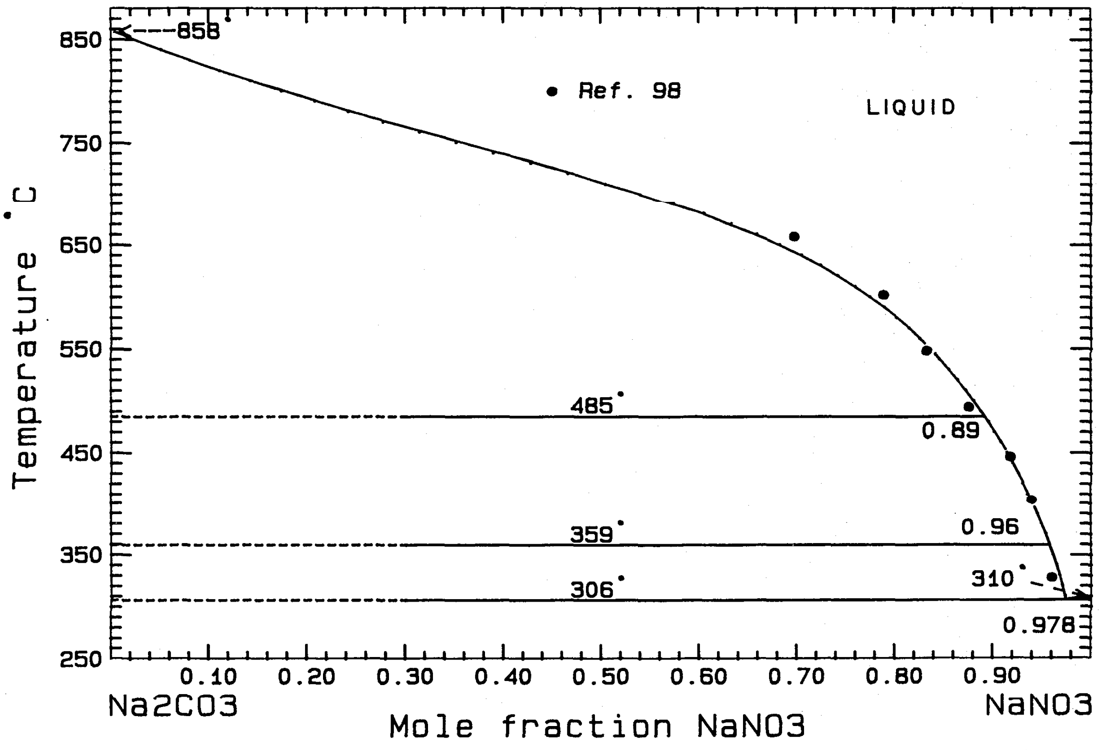

FIG. 24. The system Na_2CO_3-$NaNO_3$.

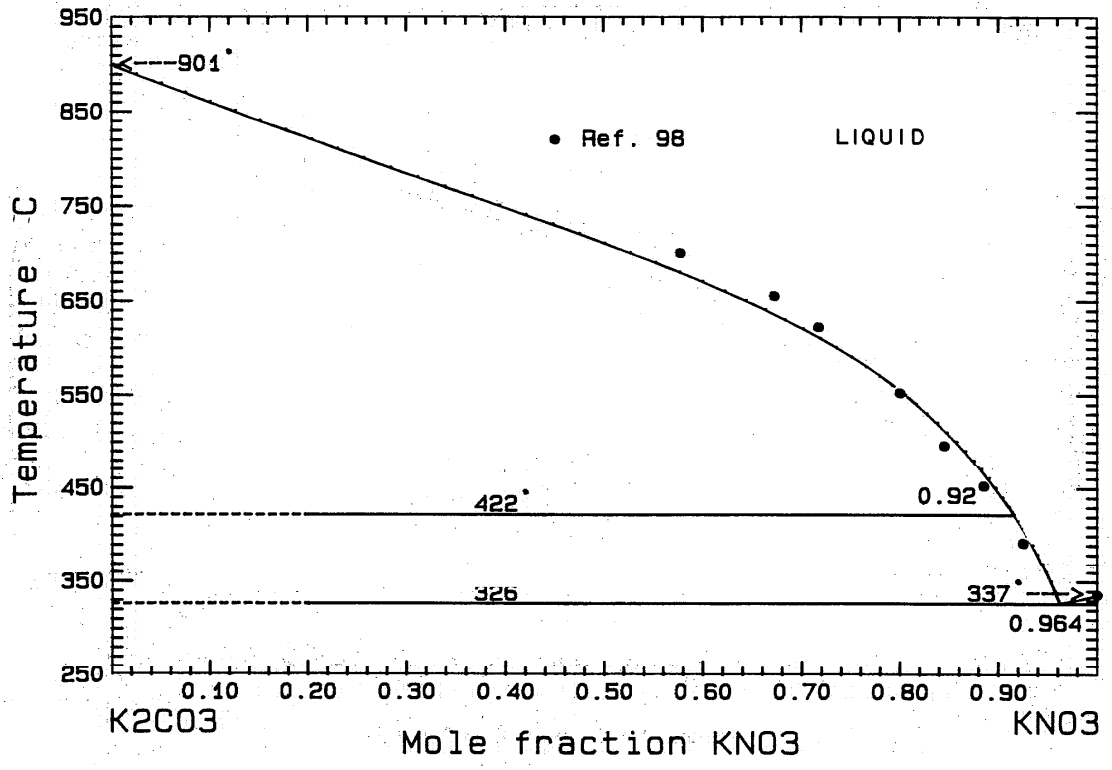

FIG. 25. The system K_2CO_3-KNO_3.

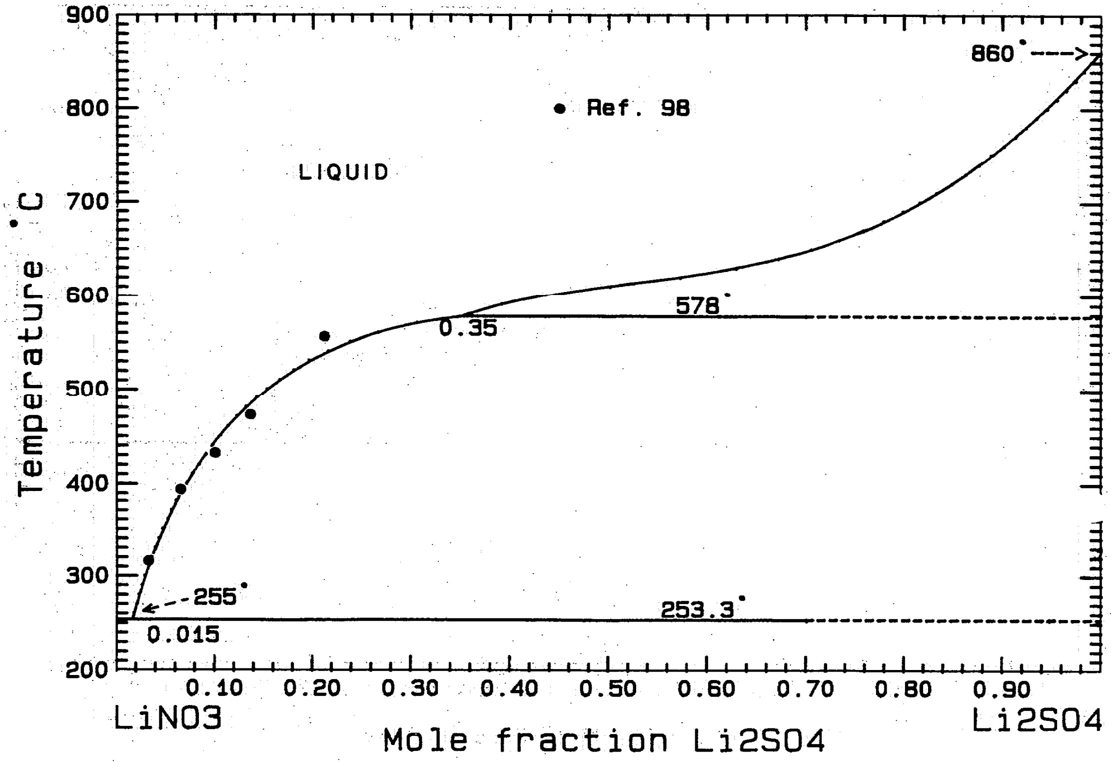

FIG. 26. The system $LiNO_3$-Li_2SO_4.

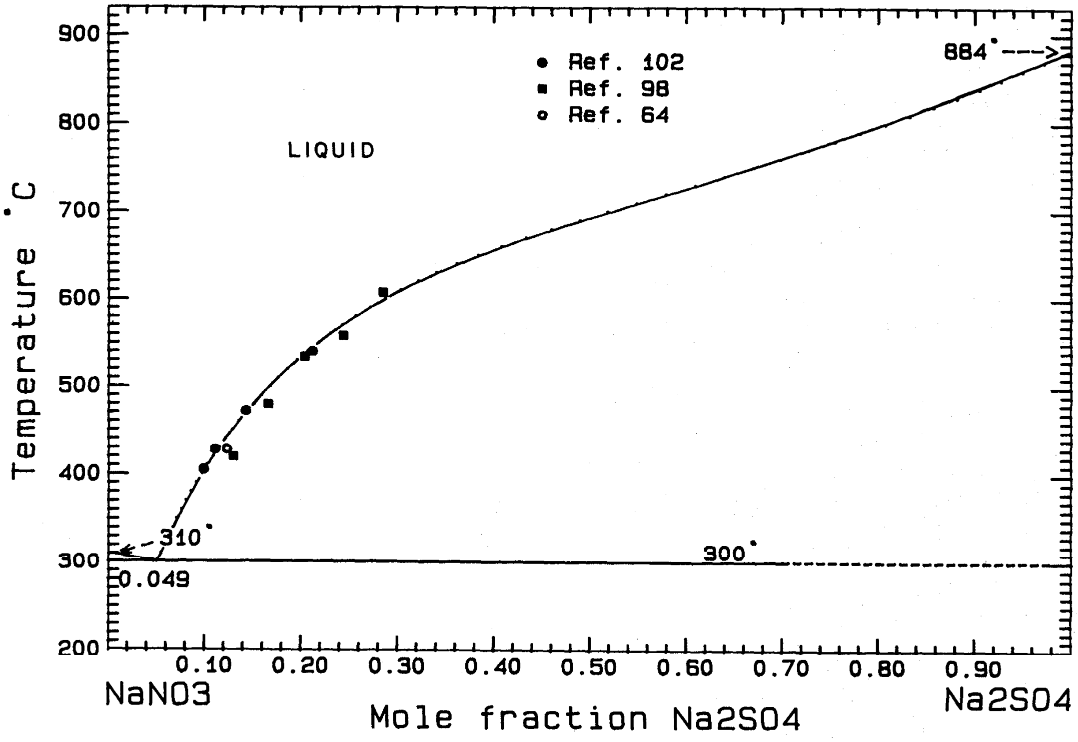

FIG. 27. The system $NaNO_3$-Na_2SO_4.

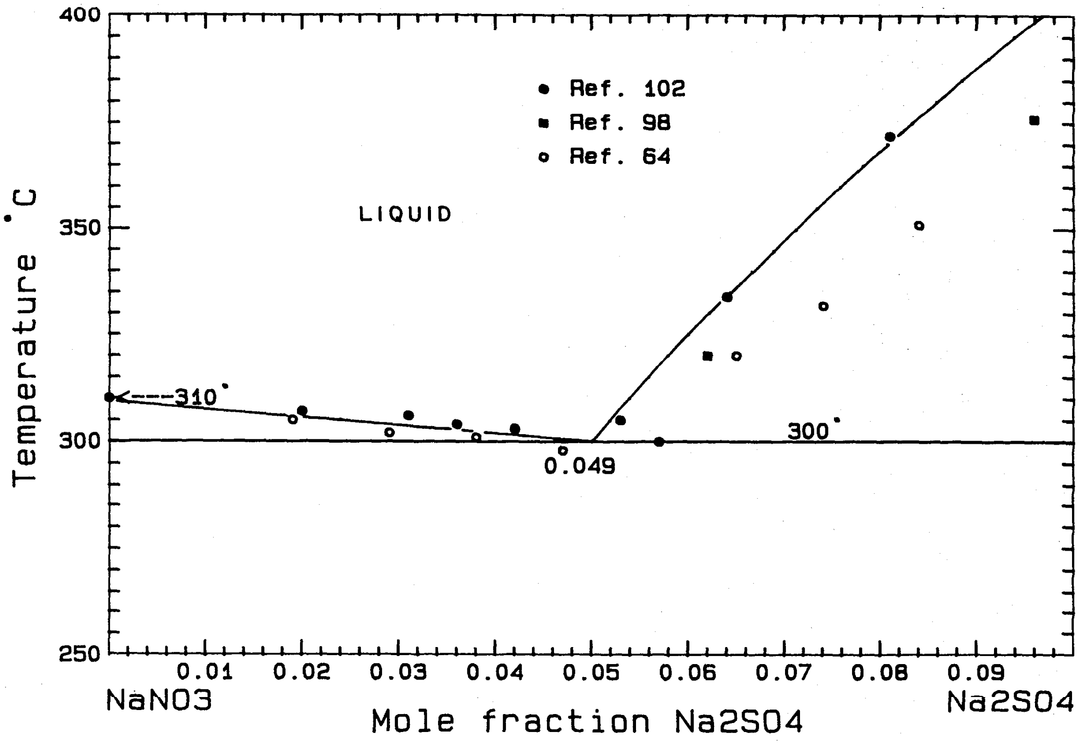

FIG. 28. The system $NaNO_3$-Na_2SO_4 enlarged.

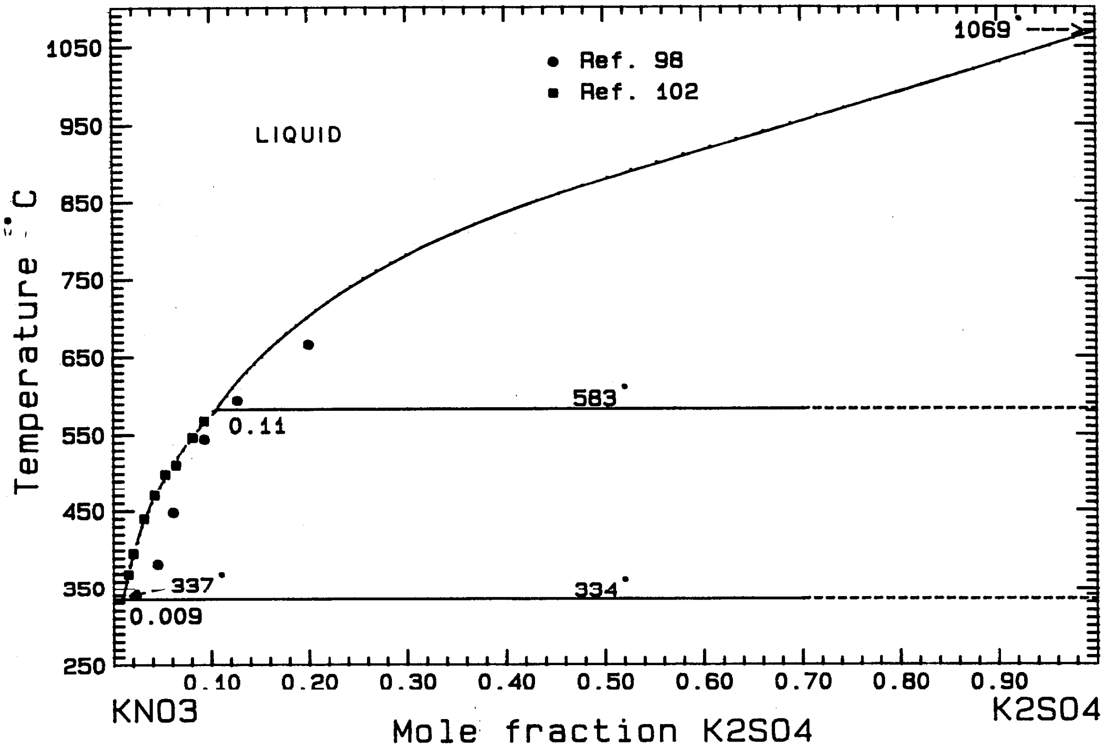

FIG. 29. The system KNO_3-K_2SO_4.

4. Appendix. Thermodynamic Properties of the Pure Salts

Unless stated below, properties have been taken from Ref. 14.

$LiNO_3$

Reference 14 contains no data for this compound. A survey of binary phase diagrams containing $LiNO_3$ in two large compilations[2,5] revealed reported melting points in the range 244–270 °C; more careful work on the pure salt[108-111] indicated 253–255 °C. The value 255 °C was chosen for the present work. Calorimetric determinations of the enthalpy of fusion[109-113] indicated values between 24 940 and 26 740 J mol^{-1}; a mean value of 25563 J mol^{-1} is used here.

$NaNO_3$

Based on the following studies[108,109,115,116], the value of 310 °C was chosen for the melting point of $NaNO_3$. For the enthalpy of fusion, calorimetrically determined values communicated both before[109-112,117,118,121,122] and after[114,119,120] the appearance of Ref. 14 suggest a slightly higher value of 15 177 J mol^{-1} used in this work.

KNO_3

Based on the following studies[109,114,115,123], the value of 337 °C was chosen for the melting point of KNO_3. Calorimetrically determined enthalpies of fusion[109,111,112,114,116,121] vary between 9205 and 10 753 J mol^{-1}, and a slightly higher value of 10129 J mol^{-1}, was used in the present work. Rather large uncertainty limits must be assigned to this value.

Li_2CO_3

The reported polymorphism of Li_2CO_3, as determined by thermal analysis, includes a number of apparent transition temperatures, although investigators do not agree on their status. Reisman[124] discovered that some are spurious, due to impurities (LiOH, Li_2O) introduced by decomposition or the presence of water. The analysis should therefore be done under a dry CO_2 atmosphere[124,125]. Only the transition at 410 °C is retained here, and the enthalpy of transition from Ref. 14 has been used. Based on the data of Ref. 126, the melting point was chosen as 730 °C. The most recently determined enthalpy of fusion, 73 400 J mol^{-1}(126), is not consistent with the same authors(126) phase diagram data for Li_2CO_3-Li_2SO_4, and so the value from Ref. 14, 44770 J mol^{-1} [14,125] was used instead.

Na_2CO_3

The same confusion concerning apparent phase transitions in Li_2CO_3, described above, applies to Na_2CO_3[127]. For present purposes, two transition temperatures were retained: 359 °C and 485 °C, after Janz and Perano[128]. These temperatures are within 5° of other independent measurements[127,129–131]. The enthalpies of transition were taken also from Ref. 128. A melting point of 858 °C has been chosen, based on the data of Ref. 125.

K_2CO_3

The same confusion concerning apparent phase transitions in Li_2CO_3, described above, applies to K_2CO_3[124]. For present purposes, one phase transition at 422 °C[124,128,130] was retained. Although this transition has been called second order[132,133] with zero enthalpy, the volume and crystal structure change, and its manifestation in a phase diagram clearly indicates otherwise. The enthalpy of transformation reported by Janz and Perano[128] is used.

LiOH

The melting point given in Ref. 14 is 471 °C. In a survey of phase diagram data of binary systems involving LiOH[2,5], the reported melting points lie in the range 462–477 °C with most being greater than 473 °C. The value of 477 °C was chosen as representative.

NaOH

The transition temperature given in Ref. 14 is 295 °C. In a survey of phase diagram data of binary systems involving NaOH[2,5], the reported transition temperatures lie in range 294–300 °C. The value of 297 °C was chosen as representative.

KOH

The melting point given in Ref. 14 is 400 °C. In a survey of phase diagram data of binary systems involving KOH[2,5], the reported melting points lie in the range 360–410 °C, with most being greater than 400 °C. The value 404 °C was chosen as representative.

Li_2SO_4

Although Ref. 14 lists the phase transition temperature as 586 °C, careful work on the pure salt[120,126,134–138,141] as well as values reported in binary phase diagram data[2,5] indicate a temperature in the range 572–579 °C. In the present work, 578 °C was adopted. Calorimetric determinations of the enthalpy of transition[120,126,134,135,139,141] indicate values between 24 200 and 28 880 J mol^{-1}. A slightly revised enthalpy of 25 650 J mol^{-1} is used here. The melting point was taken to be 860 °C[126,140]. The enthalpy of fusion quoted in Ref. 14 is 13 800 J mol^{-1}, but three independent determinations, 8990 J mol^{-1} [126] was most consistent with all the binary phase diagrams containing Li_2SO_4 which were critically evaluated in the present work. The value of Dissanayake and Mellander[126] was therefore retained in this work.

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