of the adducts showed that most of them decompose on heating. To evaluate the relative strengths of arsenic–nitrogen bonds, it was necessary to assume that the molar enthalpy of sublimation of each adduct was equal to the enthalpy of vaporization of 1 mol of ligand (*34*, *35*). Standard enthalpies of sublimation of several adducts (that could be measured) and its respective ligands, confirmed our assumption (*36*–*38*). For adducts of the same stoichiometry, $\bar{D}$(As–N) values also follow the sequence py < β-mpy < γ-mpy. $\Delta_r H^\ominus$(g) and $\bar{D}$(As–N) values are listed in Table V.

Comparison of the same base with different acids gives the acidity order $AsCl_3 > AsI_3$ as is expected from the electronegativity values of chloride and iodine atoms.

In synthesis, the $\Delta_r H^\ominus$ and other parameters data indicate that the As–N bond is stronger as we go in the sequence py < β-mpy < γ-mpy. The substitution of one hydrogen in the pyridine ring by the electronic donator methyl group causes the increase of the electronic density in the aromatic ring and consequently the electronic density on the nitrogen atom. It is then expected that the electronic density available for bonding is higher in β-mpy and γ-mpy than in py. The order observed between β-mpy and γ-mpy is due to the stronger inductive effect of the *p*-methyl than the *m*-methyl group.

On the other hand, for a given ligand, the stronger bond is formed with the stronger acid as is also shown by the data on the $\Delta_r H^\ominus$ and other parameters.

Registry No. Py, 110-86-1; β-mpy, 108-99-6; γ-mpy, 108-89-4; $AsCl_3 \cdot py$, 112070-05-0; $AsCl_3 \cdot \beta$-mpy, 112087-35-1; $AsCl_3 \cdot \gamma$-mpy, 112070-10-7; $2AsBr_3 \cdot 3py$, 112070-08-3; $AsBr_3 \cdot 3\beta$-mpy, 112070-07-2; $AsBr_3 \cdot 2\gamma$-mpy, 112070-06-1; $AsI_3 \cdot 2py$, 94503-44-3; $AsI_3 \cdot \beta$-mpy, 112070-09-4; $AsI_3 \cdot \gamma$-mpy, 112070-11-8; $AsCl_3$, 7784-34-1; $AsBr_3$, 7784-33-0; AsI_3, 7784-45-4.

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Solid–Liquid Equilibria in the Reciprocal Ternary System K,Li/S,CO_3

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The solid–liquid equilibria in the molten salt system K,Li/S,CO_3 were studied as a function of composition and temperature. The lowest freezing–melting mixture of the reciprocal ternary system lies within the region bordered by the following selected four points: $X_{K_2S} = 0.20$, $X_{K_2CO_3} = 0.40$, $X_{Li_2CO_3} = 0.40$; $X_{K_2S} = 0.20$, $X_{K_2CO_3} = 0.32$, $X_{Li_2CO_3} = 0.48$; $X_{K_2S} = 0.12$, $X_{K_2CO_3} = 0.45$, $X_{Li_2CO_3} = 0.43$; and $X_{K_2S} = 0.09$, $X_{K_2CO_3} = 0.32$, $X_{Li_2CO_3} = 0.59$ at 485 °C. The precision of the liquidus temperatures is ±10 °C.

Introduction

Data concerning phase diagrams of reciprocal ternary systems, mixtures containing two cations and two anions, have received attention in recent years. Among the different measurements, those on solid–liquid equilibria are particularly important for use in fuel cells. Solid–liquid (SL) equilibria are reported, relative to the reciprocal ternary system K,Li/S,CO_3. To our knowledge, no data for this system have been previously reported, except liquidus data concerning the binary system (K,Li/CO_3), which have been measured by Janz and Lorenz (*1*).

Experimental Section

Commercially available samples of K_2S, Li_2S, K_2CO_3, and Li_2CO_3 (Alfa) were used for preparation of the binary and ternary mixtures. Particular care was devoted to the purification and drying of the salt components. The K_2S was of 44% nominal purity, the principal impurities being polysulfides as well as hydrates of the polysulfides. The method of purification

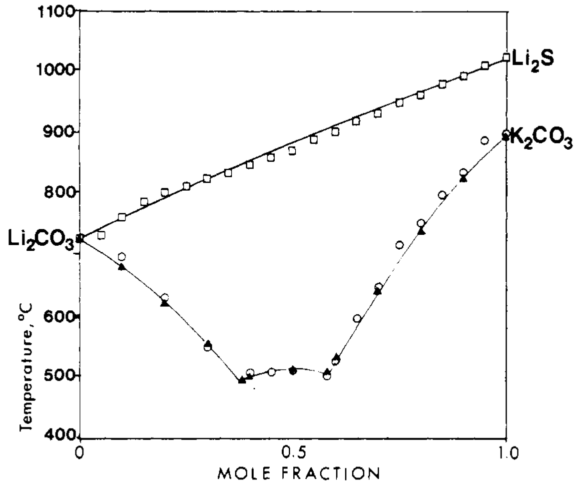

Figure 1. Liquidus temperatures for the binaries ($Li_2S + Li_2CO_3$), ($K_2CO_3 + Li_2CO_3$): □ are experimental data for ($Li_2S + Li_2CO_3$); ○ are experimental data for ($K_2CO_3 + Li_2CO_3$); △ are representative data points for ($K_2CO_3 + Li_2CO_3$) from Janz and Lorenz (*1*).

involved heating the K_2S to temperatures as high as 1000 °C in a hydrogen atmosphere. The hydrates and polysulfides were presumed removed by the bubbled hydrogen upon heating to 1000 °C.

The product of this procedure, taken as pure K_2S, melted at 840 ± 10 °C. Accepted values for the melting point of K_2S range from 835–840 °C (*2*,*4*) to 948 °C (*5*), depending, apparently, on purification technique; the highest value, 948 °C, was arrived at from the K–K_2S system (*5*). Our procedure, starting with sulfur-rich material, yielded a melting point in closer accord with the lower values (*2*–*4*).

The other individual components (of ±99% purity) were dried to constant weight under either an H_2, N_2, CO_2, or argon atmosphere at a maximum furnace temperature of 1000 °C, and stored over $CaSO_4$ in desiccators until used. The high-temperature tubular furnace employed in this study has been described in detail elsewhere (*6*), with the furnace height being shortened. Type K (chromel–alumel) uncalibrated thermocouples were used as the input for a proportional temperature controller (Barber-Coleman Model 122A). The temperature at any point in the furnace could be controlled to 5 °C.

The main experimental technique was visual observation of the liquidus, on both heating and cooling. Some points were checked by using an ac-impedance bridge (*7*) with gold electrodes suspended in the melts. The sulfide–carbonate materials were weighed as quickly as possible in air in milligram amounts in the exact stoichiometries required for the mixtures, and were transferred to a desiccator. All transfers were performed in a dry argon atmosphere, except when transfered from desiccator to the furnace. Possible contamination through trace impurities is minimzed in this preparative method. The samples thus prepared were then conditioned in alumina crucibles under an argon atmosphere, before measurements, by repeated thermal cycling (from 1 to 50 °C/min) through the melting–crystallization range by using the furnace setup. Some reaction was noticed with the alumina during the purification of the potassium sulfide.

The prefused eutectics and selected ternary mixtures were visually observed for the first crystals on freezing or last crystals on melting. The visual method and ac impedance method were used for checking the pure components and the K,Li/CO_3 system; the methods agreed fairly well, to roughly ±10 °C.

The precision limit for the liquidus temperature measurements, based on replicating the main diagonals and four ternary cuts three times each, is at worst ±10 °C. The only seeded samples were the eutectics, identified by Janz and Lorenz, for the K,Li/CO_3 system. All other samples were not observed to undergo supercooling, as the temperatures recorded during the heating/cooling thermal cycling process agree within 10 °C.

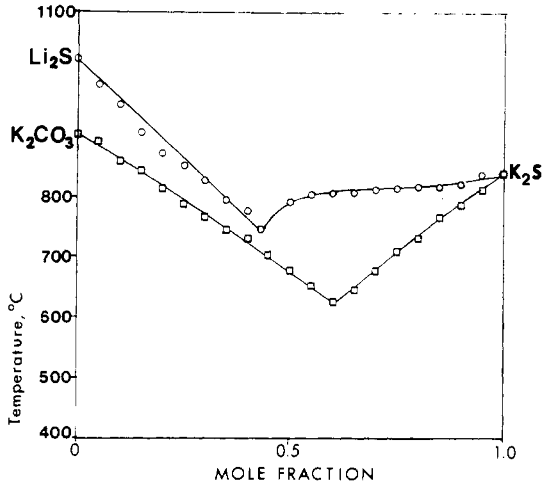

Figure 2. Liquidus temperatures for the binaries: ○, ($K_2S + Li_2S$); □, ($K_2S + K_2CO_3$).

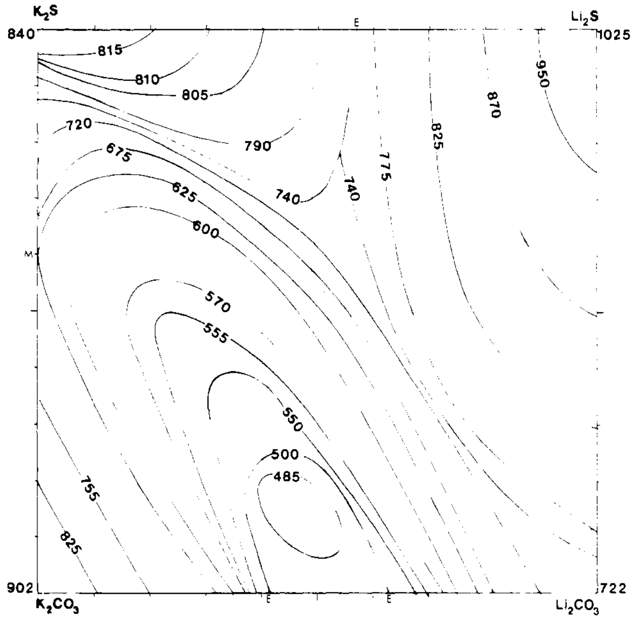

Figure 3. Polythermal projection, reciprocal ternary: $(K,Li)_2/S,CO_3$ E, eutectic; M, minimum-melting mixture. Note: Congruently melting $(Li/K)_2CO_3$ at ~510 °C (*1*) is not shown.

Results and Discussion

General features of the binary and ternary solid–liquid equilibrium are qualitatively confirmed, with the phase diagram being comprised of 995 liquidus temperature points of various binary and ternary compositions.

Figures 1 and 2 report the SL equilibria temperatures of the four binaries K,Li/S, K/S,CO_3, Li/S,CO_3, and K,Li/CO_3 which represent the four sides of the composition square, listed below:

$K_2S + Li_2S$: eutectic at $X_{K_2S} = 0.43$ and 745 °C;

$K_2S + K_2CO_3$: eutectic at $X_{K_2S} = 0.60$ and 625 °C;

$Li_2S + Li_2CO_3$: a continuously melting–freezing curve with the sole solids being the pure salt components;

$K_2CO_3 + Li_2CO_3$: eutectics at $X_{Li_2CO_3} = 0.62$ and 492 °C; and $X_{Li_2CO_3} = 0.42$ and 503 °C. The experimentally determined K,Li/CO_3 binary liquidus temperatures compare favorably with those of Janz and Lorenz (*1*), with the maximum difference being 13 °C. They however, observed a congruently melting 1:1 compound, which we were not able to confirm.

The general topology of the reciprocal ternary system is shown in Figure 3, which represents the four binary liquidus data

Table I. Liquidus Temperatures (°C) in the System K,Li/S,CO_3[a]

Stable Diagonal: $K_2S + Li_2CO_3$

X_{K_2S}	T, °C	X_{K_2S}	T, °C	X_{K_2S}	T, °C
0.000	722	0.400	665	0.800	710
0.100	730	0.500	625	0.900	800
0.200	730	0.600	615	1.000	840
0.300	695	0.700	635		

Unstable Diagonal $Li_2S + K_2CO_3$

X_{Li_2S}	T, °C	X_{Li_2S}	T, °C	X_{Li_2S}	T, °C
0.000	902	0.400	550	0.800	860
0.100	800	0.500	625	0.900	950
0.200	615	0.600	750	1.000	1025
0.300	550	0.700	810		

X_{Li_2S}	T, °C	X_{Li_2S}	T, °C	X_{Li_2S}	T, °C
Cut a: Li_2S + {K_2S-K_2CO_3(0.2)}					
0.000	725	0.400	800	0.800	870
0.100	695	0.500	785	0.900	950
0.200	790	0.600	775	1.000	1025
0.300	800	0.700	820		
Cut b: Li_2S + {K_2S-K_2CO_3(0.5)}					
0.000	625	0.400	725	0.800	870
0.100	590	0.500	740	0.900	945
0.200	585	0.600	765	1.000	1025
0.300	600	0.700	820		
Cut c: Li_2S + {Li_2CO_3-K_2CO_3(0.5)}					
0.000	510	0.400	770	0.800	920
0.100	490	0.500	800	0.900	975
0.200	565	0.600	840	1.000	1025
0.300	645	0.700	870		
Cut d: Li_2S + {Li_2CO_3-K_2CO_3(0.2)}					
0.000	640	0.400	830	0.800	955
0.100	685	0.500	855	0.900	1000
0.200	750	0.600	880	1.000	1025
0.300	795	0.700	905		

$X_{K_2CO_3}$	T, °C	$X_{K_2CO_3}$	T, °C	$X_{K_2CO_3}$	T, °C
Cut e: K_2CO_3 + {K_2S-Li_2S(0.2)}					
0.000	815	0.400	585	0.800	770
0.100	805	0.500	585	0.900	840
0.200	680	0.600	620	1.000	902
0.300	610	0.700	725		
Cut f: K_2CO_3 + {K_2S-Li_2S(0.5)}					
0.000	790	0.400	585	0.800	730
0.100	795	0.500	555	0.900	820
0.200	790	0.600	565	1.000	902
0.300	675	0.700	600		
Cut g: K_2CO_3 + {Li_2CO_3-Li_2S(0.5)}					
0.000	875	0.400	610	0.800	650
0.100	840	0.500	525	0.900	790
0.200	810	0.600	485	1.000	902
0.300	745	0.700	565		
Cut h: K_2CO_3 + {Li_2CO_3-Li_2S(0.2)}					
0.000	805	0.400	550	0.800	735
0.100	770	0.500	500	0.900	810
0.200	700	0.600	520	1.000	902
0.300	615	0.700	600		

[a] The X values are mole fractions.

Table II

T, K	$-\Delta G_f°$, kJ/mol				$-\Delta G_R°$[a]
	Li_2CO_3	Li_2S	K_2CO_3	K_2S	
800	1322.5	516.6	1312.6	527.3	20.6
1000	1370.6	545.8	1375.4	567.8	17.2

[a] Reaction 1.

and the projections of the 96 liquidus ternary cuts along with the temperatures of the corresponding eutectics.

Table I reports the SL equilibria temperatures along the two diagonals and the eight selected off-diagonal cuts in a manner similar to that of Flor et al. (*8*). Data for the 96 liquidus cuts across the field of the ternary are summarized in Figure 3 and are represented by isotherms. The $K_2S + Li_2CO_3$ axis coincides with the stable diagonal (*9*) which was calculated (see Appendix) from available Gibbs free energy data from Barin and Knacke (*10*). The lowest freezing-melting mixture of the reciprocal ternary system lies within the region bordered by the following selected four points, as shown in Figure 3: X_{K_2S} = 0.20, $X_{K_2CO_3}$ = 0.40, $X_{Li_2CO_3}$ = 0.40; X_{K_2S} = 0.20, $X_{K_2CO_3}$ = 0.21, $X_{Li_2CO_3}$ = 0.48; X_{K_2S} = 0.12, $X_{K_2CO_3}$ = 0.45, $X_{Li_2CO_3}$ = 0.43; and X_{K_2S} = 0.09, $X_{K_2CO_3}$ = 0.32, $X_{Li_2CO_3}$ = 0.59 at 485 °C.

The reciprocai ternary diagram, Figure 3, with the stable diagonal along the $K_2S + Li_2CO_3$ axis meets the criteria for these systems as described by Ricci (*11*). The high reactivity and thermal instability of molten alkali metal carbonates and sulfides undoubtedly contribute to uncertainties in published data for these salts. The results presented here indicate the complexity of these mitures and demonstrate the need for further refinement.

Appendix

The stable diagonal was calculated for the metathetic reaction

$$Li_2S + K_2CO_3 = K_2S + Li_2CO_3 \qquad (1)$$

by using Gibbs free energy data from Barin and Knacke (*6*). The free energy data and the calculations are summarized in Table II. Based on the calculated $\Delta G°$ values, the methathetic reaction goes from left to right, resulting in the $K_2S + Li_2CO_3$ stable pair.

Registry No. Li_2S, 12136-58-2; Li_2CO_3, 554-13-2; K_2S, 1312-73-8; K_2CO_3, 584-08-7.

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