P11: $p = 2{,}1 \cdot 10^{15}\ \mathrm{cm}^{-3}$,
P14: $p = 7{,}0 \cdot 10^{14}\ \mathrm{cm}^{-3}$,
P16: $p = 5{,}3 \cdot 10^{14}\ \mathrm{cm}^{-3}$.

Zur Untersuchung des Einflusses verschiedener Herstellungsmethoden seien die Proben P11, P12 und P13 verglichen, die alle mit 0,5 At.-% In dotiert sind. P13 aus Sb-Sorte I wie die meisten Proben mit Sb-angereicherter Zone zonengeschmolzen, jedoch ohne Wasserstoff erschmolzen, zeigt keine n-Leitung, sondern p-Leitung im ganzen Temperaturbereich. Die Probe P11, mit angereicherter Zone und mit Wasserstoff hergestellt, zeigt n-Leitung bei Zimmertemperatur und geht zu tiefen Temperaturen hin zum p-Typ über. Die Probe P12 wie P11, jedoch ohne Sb-angereicherte Zone hergestellt, ergibt für 180 °K die höchste gemessene negative Thermokraft von nahezu 1000 μV/Grad (Abb. 2). Zu höheren Temperaturen hin erfolgte infolge einsetzender Eigenleitung ein Abfall der Thermokraft. Für den Abfall und den Nulldurchgang der Thermokraft zu tiefen Temperaturen hin erfolgte für P12 verglichen mit P11 eine Verschiebung zu tieferen Temperaturen, n-Leitung bleibt über einen größeren Temperaturbereich erhalten. Die angereicherte Zone zeigt also danach einen Einfluß auf die Probeneigenschaften. Nach UGAI und Mitarbeitern [24] erhält man beim Ziehen aus Sb-reicher Schmelze Proben mit Sb-Überschuß; es ergaben sich höhere Defektelektronenkonzentrationen.

Der transversale Nernst-Ettingshausen-Effekt zeigt nach Abb. 5 wie bei früher diskutierten Mischkristallen [3, 5] maximale absolute Werte im Gebiet gemischter Leitung, d. h. im Gebiet des Übergangs von n- nach p-Leitung bei tiefen Temperaturen. Ein abermaliges Anwachsen zu großen Werten deutet sich für P12 auf Grund wachsender gemischter Leitung infolge Eigenleitung bei höheren Temperaturen an.

Herrn Prof. Dr. E. JUSTI danken wir für die Möglichkeit zur Durchführung dieser Untersuchungen im Institut für Technische Physik der Technischen Universität Braunschweig, der Deutschen Forschungsgemeinschaft danken wir für Sachbeihilfen.

[24] YA. A. UGAI, E. M. AVERBAKH u. G. S. KRUGLOVA, Sov. Phys. J. **3**, 86 [1965].

Miscibility Gaps in Fused Salts

Note VI. Systems of Lithium Sulphate with Zinc, Cadmium and Lead Bromides

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(Z. Naturforsch. **26 a**, 1322—1328 [1971]; received 20 April 1971)

Demixing phenomena in mixtures containing Li_2SO_4 with $ZnBr_2$, $CdBr_2$ or $PbBr_2$ have been extensively studied. It has been found that the tendency to demix in these systems is greater than in the corresponding systems containing chloride instead of bromide ions.

Moreover, the extension of the miscibility gap in the investigated systems increases when going from Li, Zn/Br, SO_4 to Li, Pb/Br, SO_4 to Cd, Li/Br, SO_4.

This sequence in the tendency to demix is slightly different from that found for the systems containing chlorides.

The analysis of the standard enthalpy variation of the methatetic reaction allows a correct prevision in the sequence of the tendency to demix for the studied systems.

To continue the study of demixing phenomena in systems formed by molten salts [1], the present work analyzes mixtures containing zinc, cadmium and lead bromides along with lithium sulphate. Demixing phenomena in the two reciprocal ternary systems $Li_2SO_4 + MeCl_2$ (Me = Cd and Pb) have been

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[1] Previous papers of this series are in: Z. Naturforsch. **20 a**, 561 [1965]; **21 a**, 595 [1966]; **22 a**, 53 [1967]; **23 a**, 2073 [1968]; **25 a**, 1484 [1970].

[2] a) D. S. LESNYKH and A. G. BERGMAN, J. Gen. Chem, USSR **32**, 557 [1953]; b) Uch. Zap. Rostov Univ. **20**, Trudy Khim. Fak. No. 6, 19 [1954].

previously studied by LESNYKH and BERGMAN[2]: no miscibility gap has been found in the system $Li_2SO_4 + ZnCl_2$ (see [3]).

The present research has been undertaken on one hand to compare the results obtained for the systems containing bromides with those reported for the systems containing chlorides, on the other hand to verify the regularities previously found in the effect of the polarizing powers or ionic radii of the ions on the tendency to demix.

Apparatus and Materials

Thermal Stability of $ZnSO_4$, $CdSO_4$ and $PbSO_4$

The apparatus employed and the experimental technique have already been described in previous papers [1]. The salts used were: Li_2SO_4, $PbSO_4$, $CdSO_4$, $CdBr_2$ (C. Erba RP); $ZnBr_2$, $ZnSO_4$, $PbBr_2$ (BDH Analar); LiBr (Merck Ultrapur). These salts have been dried according to the procedures suggested in literature. $ZnBr_2$ has been purified by distillation [4].

First, we had to face the problem of finding the field of thermal stability of the three sulphates $ZnSO_4$. $CdSO_4$, $PbSO_4$. Literature reports contrasting data. For example, according to some authors, $ZnSO_4$ decomposes already at 400 °C, whilst according to others this decomposition begins only at 730 °C [5].

We have studied the thermogravimetric behaviour of the three sulphates using the DuPont de Nemours TGA Mod. 950, set on the maximum sensitivity (5 in./mg) with the heating rate of 10 °C/min. The following information was obtained.

$ZnSO_4$: decomposition begins at about 600 °C, but weight loss does not exceed 1–2% in the temperature range between 600 and 700 °C. Over 700 °C decomposition is very active.

$PbSO_4$: decomposition begins at about 950 °C.

$CdSO_4$: decomposition begins at about 800 °C, but the weight loss does not exceed 2% in the temperature range 800–900 °C.

Results

A. The System Li, Zn/Br, SO_4

Figure 1 shows solid-liquid equilibria (SL) of the four binary systems which are the sides of the composition square. In the same figure the coordinates of the eutectic points are reported. All these mixtures are eutectic-type systems. The slope variation of the liquidus curve at the transition temperature of Li_2SO_4 (see [6]) (576 °C) in the systems containing this salt is well evident. Previous measurements on the binary $Li_2SO_4 + ZnSO_4$ (see [3]) reported a eutectic at 510 °C.

Figure 2 a reports the stable diagonal ($Li_2SO_4 + ZnBr_2$) and the unstable one [$(LiBr)_2 + ZnSO_4$] for this reciprocal ternary system: demixing areas have been shaded.

For the stable diagonal the interpolated compositions (in molecular fractions) at which, by cooling and shaking, demixing takes place are reported in Table 1 along with the corresponding temperatures. The coordinates of the point of maximum (PM) are: $x_{Li_2SO_4} = .50_5$, $t = 816$ °C. Along the stable diagonal the primary crystallization temperature (PCT) increases from 654° to 703 °C while $x_{Li_2SO_4}$ varies from $.07_5$ to $.86_5$.

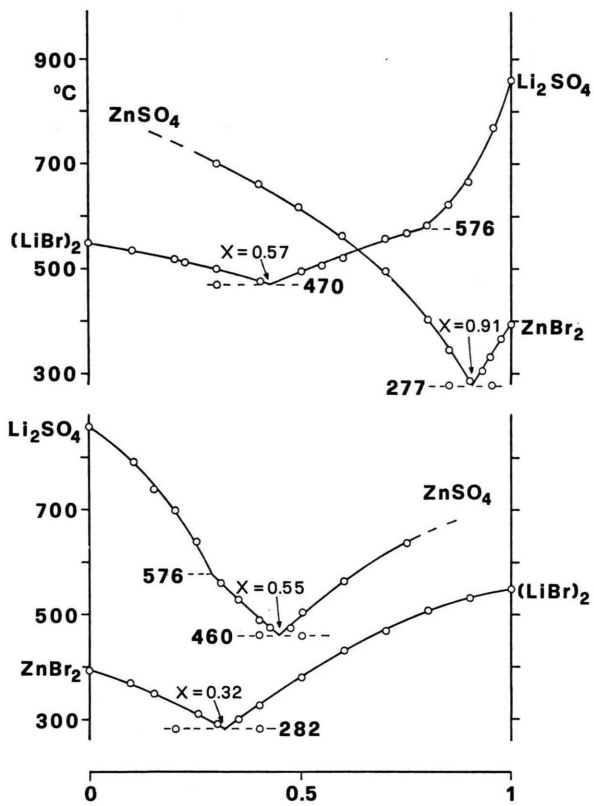

Fig. 1. Phase diagrams for the binary systems forming the sides of the composition square of the reciprocal ternary Li, Zn/Br, SO_4.

[3] N. N. EVSEEVA and A. G. BERGMAN, Zhur. Obschei Khim. **21**, 1767 [1951].

[4] T. W. RICHARDS and E. F. ROGERS, Proc. Amer. Acad. **31**, 158 [1895].

[5] P. PASCAL, Nouveau Traitè de Chimie Minerale, Ed. Masson, Paris 1962.

[6] R. RICCARDI and C. SINISTRI, Ric. Sci. **35** (II A), 1026 [1965].

Table 1. Extension of the MG along the stable diagonal $Li_2SO_4+ZnBr_2$.

Temperature (°C)	Demixing extends from	to
720	$x_{Li_2SO_4} = .12$	.84
740	$= .15$	$.81_5$
760	$= .18_5$	.78
780	$= .23_5$	$.73_5$
800	$= .32$	$.66_5$
810	$= .38$	.61
816 (PM)	$= .50_5$	$.50_5$

Along the unstable diagonal, PCT varies from 467 °C ($x_{(LiBr)_2} = .27$) to 590 °C ($x_{(LiBr)_2} = .67_5$) through a maximum at 703 °C ($x_{(LiBr)_2} = .52$). The PM temperature of the liquid-liquid equilibria (LL) on this unstable diagonal coincides with the PM temperature of the stable diagonal.

To fully describe the topology of the reciprocal ternary system, 14 cuts of proper composition have been studied. Figure 3 a shows the projections of these cuts and the temperatures corresponding to significant points of various type. The stratification lens (dashed) impinges over three crystallization fields and occupies 49.6% of the complete map. The main axis of the lens (also dashed) is slightly shifted from the principal diagonal toward the LiBr corner. Along this axis, PCT is constant at 703 ± 1 °C. Figure 3 a also reports, by means of a dash-dotted line, the stability fields of the two phases

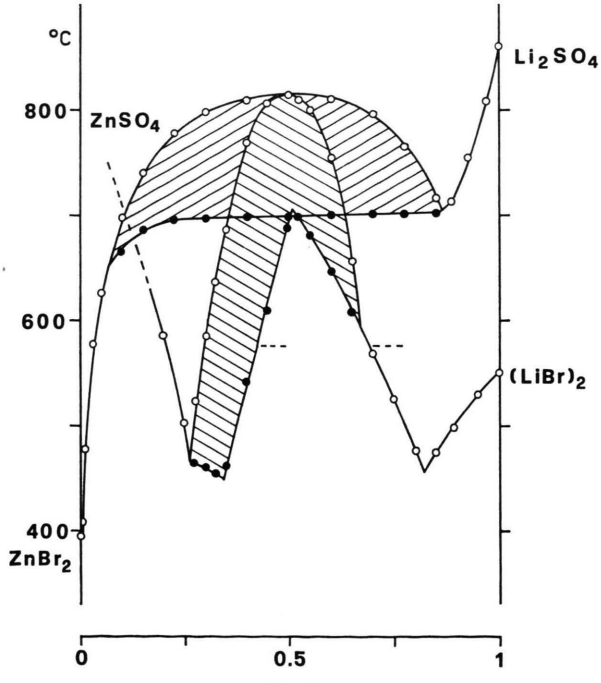

Fig. 2 a. Stable and unstable diagonals of the reciprocal system Li, Zn/Br, SO_4.

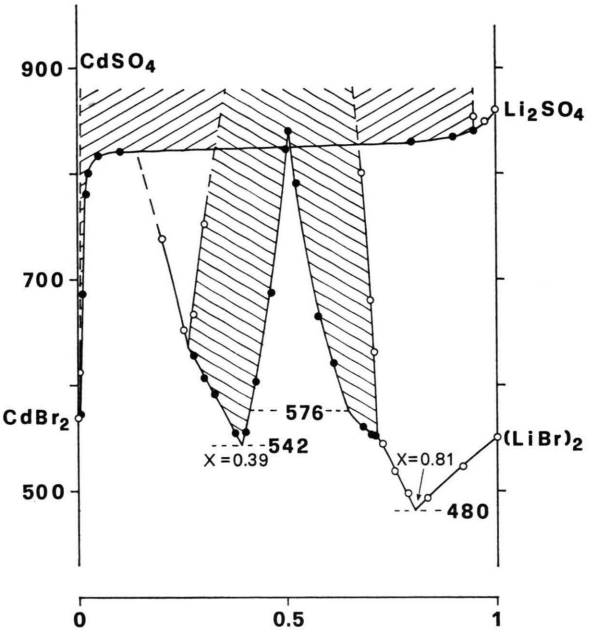

Fig. 2 b. Stable and unstable diagonals of the reciprocal system Cd, Li/Br, SO_4.

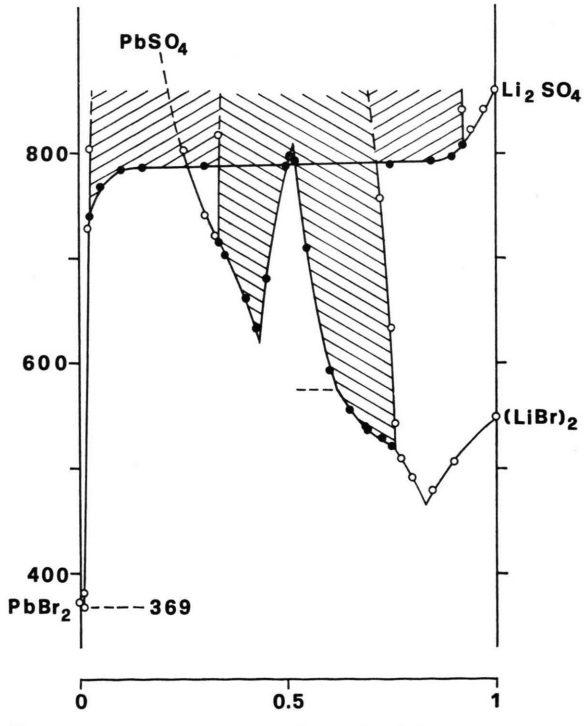

Fig. 2 c. Stable and unstable diagonals of the reciprocal system Li, Pb/Br, SO_4.

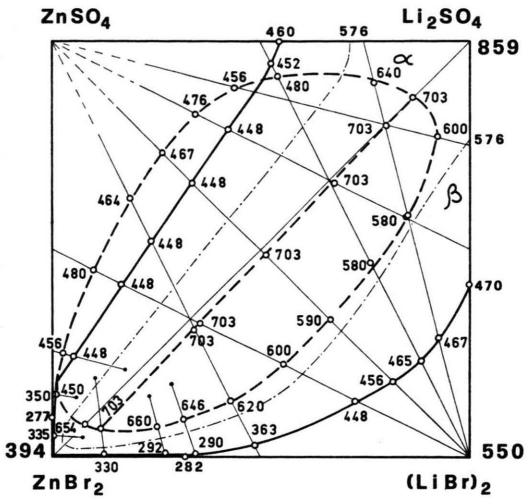

Fig. 3 a. Diagonal and off-diagonal cuts studied in the square of the reciprocal ternary Li, Zn/Br, SO_4.

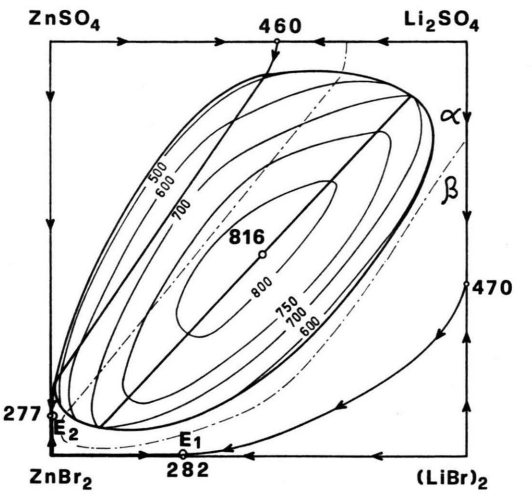

Fig. 3 b. Square of compositions of the reciprocal ternary Li, Zn/Br, SO_4 with the projections of some LL isotherms and the position of the upper critical point.

(α and β) of Li_2SO_4. Figure 3 b reports the projections of a certain number of LL isotherms. The upper critical point of the reciprocal ternary system can thus be estimated at $t = 816$ °C, $x_{(LiBr)_2} = .52$ and $x_{ZnSO_4} = .48$.

The ternary eutectics E_1 and E_2 are very close to the binary eutectics in the systems $ZnBr_2 + (LiBr)_2$ and $ZnSO_4 + ZnBr_2$.

The general topology of the system agrees with the triangulation rule.

B. The System Cd, Li/Br, SO_4

SL and LL equilibria concerning the stable ($Li_2SO_4 + CdBr_2$) and unstable [$(LiBr)_2 + CdSO_4$] diagonals of this system are reported in Fig. 2 b.

Along the stable diagonal PCT increases from about 570 °C to 841 °C, while $x_{Li_2SO_4}$ varies from about $.00_5$ to .95. Owing to the thermal instability of the melts in the high temperature range it was not possible to detect completely the LL equilibria.

Along the unstable diagonal PCT varies from 634 °C ($x_{(LiBr)_2} = .26_5$) to 552 °C ($x_{(LiBr)_2} = .71_5$) through a maximum at 841 °C ($x_{(LiBr)_2} = .51$). Figure 2 b also reports the coordinates of the two eutectic points and those of the α-β transition of Li_2SO_4.

No measurements has been made within the composition square for this system.

C. The System Li, Pb/Br, SO_4

The SL equilibria relative to the binary systems which are the sides of the composition square are

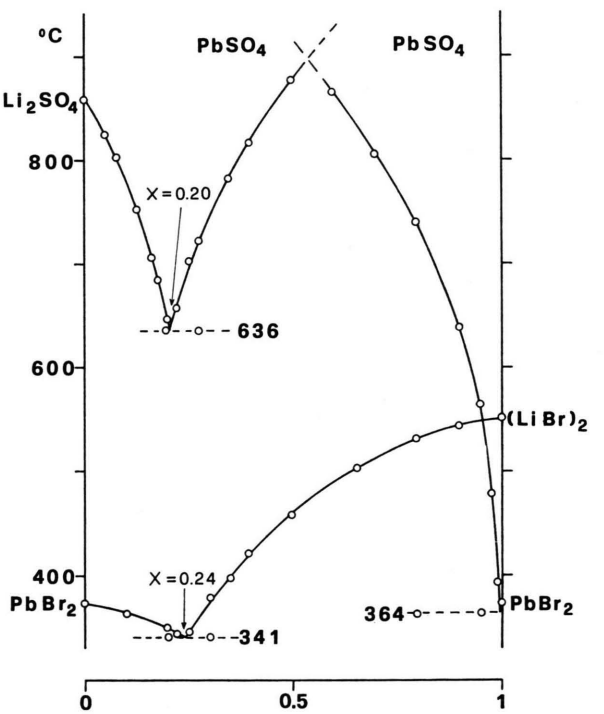

Fig. 4. Phase diagrams for three binary systems forming sides of the composition square of the reciprocal ternary Li, Pb/Br, SO_4.

[7] A. G. Bergman, E. L. Bakumskaya, and V. V. Keropyan, Russ. J. Inorg. Chem. 316 [1962].

[8] A. G. Bergman and Yu. I. Andryushchenko, Russ. J. Inorg. Chem. 882 [1963].

reported in Fig. 4. The system $Li_2SO_4 + (LiBr)_2$ is shown in Fig. 1. The coordinates of the eutectic points are also reported in these figures.

Also in this case the four mixtures which are the sides of the composition square are eutectic-type systems.

Russian authors [7] have recently reported for the system $PbSO_4 + Li_2SO_4$ results in good agreement with those of Fig. 4. For the system $PbBr_2 + (LiBr)_2$ BERGMAN and ANDRYUSHCHENKO [8] report a eutectic at $t = 322$ °C and $x_{(LiBr)_2} = .11_7$.

Figure 2 c shows the SL and LL equilibria relative to the stable and unstable diagonals of this system.

Along the stable diagonal $(Li_2SO_4 + PbBr_2)$ PCT regularly increases from 730 °C ($x_{Li_2SO_4} = .02_5$) to 808 °C ($x_{Li_2SO_4} = .93_5$).

Also in this case it was not possible to detect completely the MG.

Along the unstable diagonal $[(LiBr)_2 + PbSO_4]$ PCT varies from 710 °C ($x_{(LiBr)_2} = .38_5$) to 518 °C ($x_{(LiBr)_2} = .76_5$) through a maximum at 808 °C ($x_{(LiBr)_2} = .52$).

Figure 5 shows the projections of the 14 examined cuts and the temperatures corresponding to significant points of various type. The stratification lens (dashed) impinges over three crystallization fields and occupies 57.0% of the area of the composition square. Its main axis (also dashed) is shifted from the principal diagonal toward the LiBr corner. Along this axis PCT is constant at 808 ± 1 °C. In the same figure is also indicated, by a dash-dotted line, the solid phase transition of Li_2SO_4. Finally the details relative to the ternary eutectics E_1 and E_2 are blown up in the two circles near the composition square. Their coordinates are: for E_1: $t =$ 322 °C, $x_{PbBr_2} = .73_5$, $x_{(LiBr)_2} = .26$, $x_{Li_2SO_4} = .00_5$; for E_2: $t = 362$ °C, $x_{PbBr_2} = .96$, $x_{PbSO_4} = .03_5$, $x_{Li_2SO_4} = .00_5$.

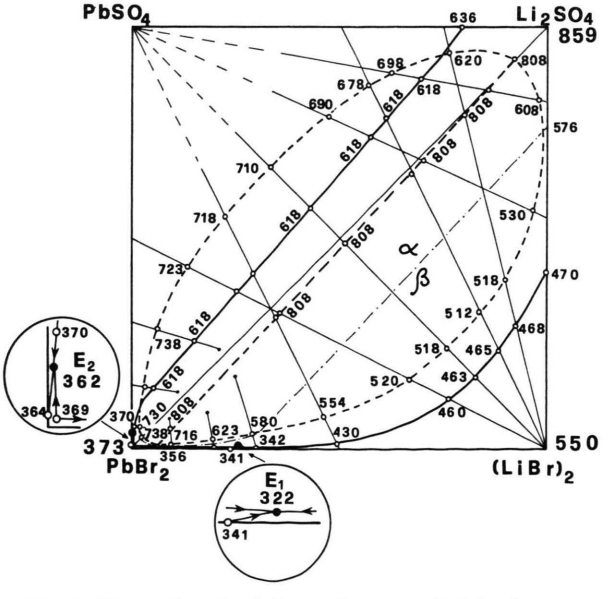

Fig. 5. Diagonal and off-diagonal cuts studied in the square of the reciprocal ternary Li, Pb/Br, SO_4.

The general topology of this system agrees with the triangulation rule.

Discussion

In comparison with the corresponding systems containing chlorides, the two ternary reciprocal systems Li, Pb/Br, SO_4 and Cd, Li/Br, SO_4 clearly show a higher tendency to demix. In fact, for the system Li, Pb/Cl, SO_4 LESNYKH and BERGMAN [2b] report a constant monotectic temperature along the stable diagonal at 650 °C and a width of the gap from 7 to 88 mole-% of Li_2SO_4. These data can be compared with our results for the mixture $Li_2SO_4 + PbBr_2$ (PCT varying from 730° to 808 °C; width of the gap at 808 °C from 3 to 93.5 mole-% of Li_2SO_4). The area of the stratification lens varies from 43.5 to 57.0% of the square on going from the system containing $PbCl_2$ to the one containing $PbBr_2$.

Similar considerations can be made for the two stable diagonals $CdCl_2 + Li_2SO_4$ and $CdBr_2 + Li_2SO_4$. For the former LESNYKH and BERGMAN [2a] report a constant monotectic temperature at 650 °C and a width of the gap from 8 to 80 mole-% of Li_2SO_4. For the latter we found a PCT varying from 570° to 841 °C and a width of the gap at 841 °C going from 0.5 to 95 mole-% of Li_2SO_4. No quantitative comparison can be made for the system containing $ZnBr_2$ owing to the fact that, the corresponding system containing $ZnCl_2$ shows no MG but only a tendency to demix [3]. A summary of the characteristics of the systems containing $Li_2SO_4 + MeX_2$ (Me = Zn, Cd, Pb; X = Cl, Br) is shown in Table 2.

All these considerations agree with what we previously found [1] and in particular with the rule that taking into account a pair of salts of which the first is mainly ionic and the second partially covalent, the tendency to demix increases going from the chloride to the bromide to the iodide of the covalent salt.

Table 2. Characteristics of the MG in the systems: $Li_2SO_4+MeX_2$ (Me=Zn, Cd, Pb; X=Cl, Br). The extension of the MG along the stable and unstable diagonals is in molecular fraction units; the area of the stratification lens is in % of the composition square; ΔH^0_{298} is in kcal/mole.

System	Stable diagonal PCT	Stable diagonal Highest extension of MG	Unstable diagonal Highest extension of MG	Area of the stratification lens	ΔH^0_{298}
Li, Zn/Cl, SO_4	—	—	—	No MG	— 12.9
Li, Zn/Br, SO_4	650—703	0.79	0.41	49.6%	— 19.7
Cd, Li/Cl, SO_4	650 const.	0.72	0.27	29.3%	— 19.1
Cd, Li/Br, SO_4	570—841	0.94	0.45	66.0% *	— 29.2
Li, Pb/Cl, SO_4	650 const.	0.81	0.36	43.5%	— 14.0
Li, Pb/Br, SO_4	730—808	0.91	0.38	57.0%	— 22.1

* Estimated value.

It is very interesting at this point to make a comparison within the three systems studied in this paper. This can be done taking into account, for example, the stable diagonals reported in Fig. 2 or the general characteristics reported in Table 2.

Taking into account Fig. 2 or Table 2 it is possible to state that, in the three studied systems the tendency to demix is

$$\text{Cd-system} > \text{Pb-system} > \text{Zn-system}. \qquad (1)$$

From a thermodynamic point of view, sequence (1) can be easily understood if one takes into account the methatetic reaction:

$$2\,LiBr + MeSO_4 \rightarrow MeBr_2 + Li_2SO_4 \qquad (2)$$
$$(Me = Zn, Cd, Pb).$$

The values of ΔG for this reaction (at the demixing temperature) express in quantitative terms the concept of "tendency to demix".

Owing to lack of data for the free energy at the desired temperature, it is only possible [1] to calculate the value ΔH^0_{298} of reaction (2). Through the data available in literature [9], the following values have been calculated (also reported in Table 2):

$$2\,LiBr + CdSO_4 \rightarrow CdBr_2 + Li_2SO_4,$$
$$\Delta H^0_{298} = -29.2 \text{ kcal/mole},$$
$$2\,LiBr + PbSO_4 \rightarrow PbBr_2 + Li_2SO_4,$$
$$\Delta H^0_{298} = -22.1 \text{ kcal/mole},$$
$$2\,LiBr + ZnSO_4 \rightarrow ZnBr_2 + Li_2SO_4,$$
$$\Delta H^0_{298} = -19.7 \text{ kcal/mole}.$$

The magnitude of these values is in agreement with the sequence (1) of the tendency to demix experimentally found in the systems investigated in the present paper.

As regards systems containing chlorides (see Table 2) the experimental data give the following sequence in the tendency to demix:

$$\text{Pb-system} > \text{Cd-system} > \text{Zn-system}. \qquad (3)$$

It is interesting to observe that in comparison to sequence (1), valid for the Br-systems, sequence (3), valid for Cl-systems, is different only for the inversion between the Cd- and the Pb-systems. The prevision, based on ΔH^0_{298} values, seems in this case not valid (see Table 2).

For what regards the characteristics of the ions present in the systems, it is possible to state that, generally, the tendency to demix will depend mainly on the charge and the dimension of the ions [10] and on the degree of covalency of the components of the methatetic reaction (2).

Unfortunately, the situation is complicated by the fact that the mentioned factors are constantly superimposed to each other and also by the fact that it is difficult to-day to evaluate quantitatively the degree of covalency of a molten salt.

We hope that further study on other systems will enable us to point out sequences type (1) and (3) in order to confirm the importance of some physicochemical properties of the ions.

[9] "Selected Values of Chemical Thermodynamic Properties", Circular NBS 500, Washington, D.C. 1962.

[10] The ionic radii are: $Li^+=.60$; $Zn^{++}=.74$; $Cd^{++}=.97$; $Pb^{++}=1.20$; $Cl^-=1.81$; $Br^-=1.95$ Å (L. PAULING, The Nature of the Chemical Bond, Cornell Univ. Press 1960).