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Determination of the Thermodynamic Excess Functions G^E, H^E, and S^E of the Liquid Ternary System AgCl—LiCl—KCl by Means of EMF-Measurements

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By means of EMF-measurements using the formation cell

graphite/Ag/AgCl (l, x_{AgCl})—LiCl (l, x_{LiCl})—KCl x_{KCl})/(Cl_2)graphite

the partial molar excess *Gibbs* energies, G^E_{AgCl}, of silver chloride in the ternary system AgCl—LiCl—KCl were determined over the whole concentration range at five temperatures between 973 K and 1,123 K.

The experimentally determined G^E_{AgCl}-values were fitted using the *Redlich-Kister* equation. From the *Redlich-Kister* parameters and their temperature dependence, obtained by the fitting procedure, the integral and partial molar excess *Gibbs* energies, heats of mixing, and excess entropies were calculated.

The fitting process permits also the calculation of the thermodynamic excess function of the binary system lithium chloride—potassium chloride.

(Keywords: Electromotive force; Lithium chloride; Molten salts; Potassium chloride; Silver chloride; Thermodynamics)

Bestimmung der thermodynamischen Exzeßfunktionen des Systems AgCl—LiCl—KCl *mit Hilfe von EMK-Messungen*

Auf Grund von EMK-Messungen mit Hilfe der Bildungszelle

Graphit/Ag/AgCl (l, x_{AgCl})—LiCl (l, x_{LiCl})—KCl (l, x_{KCl})/(Cl_2)Graphit

wurden die molaren partiellen freien Exzeßenthalpien G^E_{AgCl} von AgCl im gesamten Konzentrationsbereich des Dreistoffsystems AgCl—LiCl—KCl bei fünf Temperaturen zwischen 973 K und 1 123 K bestimmt.

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Die experimentell ermittelten G^E_{AgCl}-Werte wurden mit Hilfe eines *Redlich-Kister*-Ansatzes für thermodynamische Exzeßfunktionen ausgeglichen. Die auf Grund der Ausgleichsrechnung erhaltenen *Redlich-Kister*-Parameter wurden zur Berechnung der molaren freien Exzeßenthalpien G^E, sowie der partiellen molaren freien Exzeßenthalpien der beiden anderen Komponenten Lithiumchlorid und Kaliumchlorid herangezogen. Ferner wurden aus der Temperaturabhängigkeit der *Redlich-Kister*-Parameter die molaren Mischungswärmen und die molaren Exzeßentropien, sowie die entsprechenden partiellen molaren Größen berechnet. Die Ausgleichsrechnung gestattet auch die thermodynamischen Exzeßfunktionen des binären Systems Lithiumchlorid-Kaliumchlorid zu berechnen.

1. Introduction

As a continuation of our studies[1, 2] on the thermodynamic properties of binary and ternary salt mixtures by means of the emf method, we report in the present paper the evaluation of the thermodynamic excess functions of the liquid ternary system AgCl—LiCl—KCl.

In the literature determinations of only the partial molar excess *Gibbs* energies G^E_{AgCl} of AgCl in the eutectic mixture of LiCl and KCl between 673 K and 873 K can be found. The binary systems, which constitute the ternary system, however, are well investigated.

In this paper a complete survey of the molar excess *Gibbs* energies, G^E, the molar heats of mixing, H^E, the molar excess entropies, S^E, as well as of the corresponding partial molar quantities for the ternary system AgCl—LiCl—KCl in the temperature range from 923 K to 1,123 K is presented. The investigations are based on emf measurements using the following formation cell

$$\text{graphite/Ag(s)/liquid AgCl}(x_1)\text{—LiCl}(x_2)\text{—KCl}(x_3)/(\text{Cl}_2)\,\text{graphite}$$

Furthermore, it will also be shown that the thermodynamic mixing functions for the system LiCl—KCl, which is difficult to examine, can be determined from the data obtained for the ternary system.

2. Experimental

The cell for the emf measurements consisted of a dense alumina tube closed on one side, and equipped with an alumina lid, through which the various electrodes, the thermocouple, and the chlorine gas inlet and outlet were introduced. The graphite electrodes were placed in alumina tubes, which served as supports and protection against oxygen attack during the heating and cleaning process.

In order to avoid the influence of exterior electric fields the whole measuring cell was put into an earthed *Faraday* cage.

The measuring cell was heated in a CALOCOAX-oven; this guarantees a constant temperature over the total length of the oven, because of its mode of operation. Basically, the oven consists of a double tube closed on both sides. It contains a small amount of an alkali metal which saturates a porous material. By means of a two-stage heater the metal is evaporated. It then condenses and sets free the heat of evaporation on the inner side of the oven. Afterwards the condensate is transported to the heating zone via the porous structure.

The temperature in the cell was measured with a Ni—NiCr thermocouple situated directly next to the measuring electrode. This thermocouple, together with a second one which was located in the condensation zone of the oven, served also to regulate the temperature. The two heating stages of the oven were arranged such that the heating stage with lower power was controlled by the oven temperature, whilst the heating stage with higher power was regulated by the thermocouple registering the temperature within the measuring cell. Thus the temperature in the cell could be kept constant to ± 1 °C.

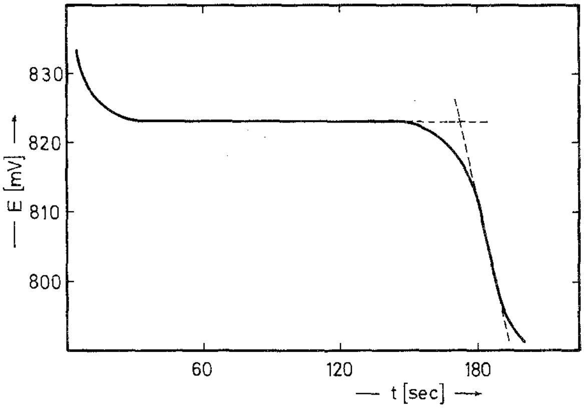

Fig. 1. Dependence of the cell voltage E on time during the dissolution of silver deposited on a graphite electrode. The extrapolated value at the end of the dissolution process gives the emf-value

The partial molar excess *Gibbs* energies can be determined on the basis of emf measurements on the formation cell

Ag (s)/AgCl-*Salt Mixture*/(Cl_2) *Graphite*

In order to obtain reliable and reproducible emf values the normal electrodes in the above-mentioned formation cell were modified in two respects:

1. Instead of compact silver, a graphite rod was used as an electrode because silver dissolves in the presence of chlorine gas in the melt under investigation. Therefore, with silver electrodes, the concentration of AgCl in the electrolyte could not be kept constant. At the graphite rod a small, coulometrically-controlled, amount of silver was deposited. During the subsequent dissolution of the deposited silver the cell voltage is practically constant; it changes by 0.3 mV at the most. At the end of the dissolution process the cell voltage breakes down. The cell voltage, extrapolated to the end of the dissolution curve, was considered to be the emf value. By this procedure, illustrated in Fig. 1, concentration changes can be avoided in the electrolyte.

2. The potential of the bubbling chlorine gas electrode shows small irregular fluctuations. In order to stabilize the potential a quasi-stationary chlorine electrode was used. This was loaded anodically with 20 μA/cm² (geometrical surface) against a coaxially-mounted auxiliary cathode. The chlorine electrode consisted of a dense graphite tube coated with pyrocarbon. The lower end of the tube was closed with a porous plug of coal (LY 300, manufactured by Sigri-Elektrographit, FGR) through which the chlorine gas could diffuse into the melt. This electrode has a constant potential and shows practically no fluctuations.

For the various electrodes, graphite rods (RWO, spectroscopically-pure, fabricated by Ringsdorff, FGR) were used; these were heated for several hours at 1,073 K in dry chlorine gas in order to remove possible surface oxides.

Lithium chloride and potassium chloride (p.a. chemicals of Merck, Darmstadt, FGR) were purified by electrolysis in the measuring cell by applying mutually anodically and cathodically loaded graphite electrodes whilst treating the melt with dry chlorine and hydrogen chloride gas. This procedure is absolutely necessary because even traces of oxygen, which cannot be removed from the melt by hydrogen chloride and chlorine gas alone without accompanying pre-electrolysis, may shift the potential of the chlorine electrode to positive values and hence influence considerably the measured results.

The silver chloride used for the measurements was prepared according to a procedure described by *Derr* et al.[3] and treated and purified according to *Wallace* et al.[4]. The addition of weighed amounts of silver chloride to the electrolyte was accomplished by a sluice whilst flushing with dry chlorine gas. Afterwards, dry hydrogen chloride gas was introduced into the melt for several hours.

Cyclic voltammetry was used to check for the presence of oxygen and water. It is known that traces of oxygen and water, dissolved in the electrolyte, show a distinct cathodic peak in the cyclic voltammograms.

The emf measurements were started only when the oxygen reduction peak in the cathodic sweep had disappeared completely.

3. Method of Evaluation

In the present paper emf measurements were performed on liquid AgCl(1)—LiCl(2)—KCl(3) mixtures along specific concentration paths with a constant ratio of the mole fractions of LiCl and KCl. From the measured reversible cell voltage E of the formation cell, the partial molar excess *Gibbs* energies G^{E}_{AgCl} of silver chloride can be deduced with the help of the following equation:

$$G^{E}_{AgCl} = RT \ln f_{AgCl} = (E_0 - E)nF - RT \ln x_{AgCl} \qquad (1)$$

f_{AgCl}	activity coefficient of AgCl
E_0	standard emf (using pure AgCl as an electrolyte)
x_{AgCl}	mole fraction of AgCl

In order to calculate the molar excess *Gibbs* energies, G^{E}, and the partial molar excess *Gibbs* energies, G^{E}_{LiCl} and G^{E}_{KCl}, of the other components lithium chloride and potassium chloride from the known G^{E}_{AgCl} values, the following procedure has been applied:

The measured G^{E}_{AgCl} values can be fitted using an approximate equation for G^{E}, e.g. the *Redlich-Kister* equation[5].

$$G^{E} = \sum_{\substack{i=1 \\ i<j}}^{2} \sum_{j=2}^{3} x_i x_j \left[a_{ij} + b_{ij}(x_i - x_j) + c_{ij}(x_i - x_j)^2 + \ldots\right] + \\ + x_1 x_2 x_3 \left[\alpha + \beta_1 (x_2 - x_3) + \beta_2 (x_1 - x_3)\right] \qquad (2)$$

With the help of the relation

$$G_1^{E} = G^{E} - x_2 \left(\frac{\partial G^{E}}{\partial x_2}\right)_{x_3 = \text{const}} - x_3 \left(\frac{\partial G^{E}}{\partial x_3}\right)_{x_2 = \text{const}} \qquad (3)$$

and the analogous equations for G_2^{E} and G_3^{E} (which can be deduced by cyclic change of the indices) the following expressions for the partial molar excess *Gibbs* energies can be deduced from the *Redlich-Kister* equation.

$$\begin{aligned} G_1^{E} = {} & x_2 (x_2 + x_3) a_{12} + x_3 (x_2 + x_3) a_{13} - x_2 x_3 a_{23} + \\ & + x_2 (3 x_1 x_2 + 2 x_1 x_3 - x_2 x_3 - x_2^2) b_{12} - \\ & - x_3 (-3 x_1 x_2 - 2 x_1 x_2 + x_2 x_3 + x_3^2) b_{13} + \\ & + 2 x_2 x_3 (x_3 - x_2) b_{23} + \\ & + x_2 (x_1 - x_2)(5 x_1 x_2 + 3 x_1 x_3 - x_2 x_3 - x_2^2) c_{12} + \\ & + x_3 (x_3 - x_1)(-5 x_1 x_3 - 3 x_1 x_2 + x_2 x_3 + x_3^2) c_{13} - \\ & - 3 x_2 x_3 (x_3 - x_2)^2 c_{23} + \\ & + x_2 x_3 (x_2 + x_3 - x_1) \alpha + \\ & + x_2 x_3 (x_2 - x_3)(x_2 + x_3 - 2 x_1) \beta_1 - \\ & - x_2 x_3 (x_1^2 + x_3^2 + x_2 x_3 - 2 x_1 x_2 - 4 x_1 x_3) \beta_2 \end{aligned} \qquad (4)$$

$$\begin{aligned} G_2^{E} = {} & x_1 (x_1 + x_3) a_{12} - \\ & - x_1 x_3 a_{13} + \\ & + x_3 (x_1 + x_3) a_{23} + \\ & + x_1 (-3 x_1 x_2 - 2 x_2 x_3 + x_1 x_3 + x_1^2) b_{12} + \\ & + 2 x_1 x_3 (x_3 - x_1) b_{13} + \end{aligned}$$

$$\begin{aligned}
&+ x_3 (2 x_1 x_2 - x_1 x_3 - x_3^2 + 3 x_2 x_3)\, b_{23} + \\
&+ x_1 (x_1 - x_2)(-5 x_1 x_2 - 3 x_2 x_3 + x_1 x_3 + x_1^2)\, c_{12} - \\
&- 3 x_1 x_3 (x_3 - x_1)^2 c_{13} + \\
&+ x_3 (x_2 - x_3)(3 x_1 x_2 + 5 x_2 x_3 - x_1 x_3 - x_3^2)\, c_{23} - \\
&+ x_1 x_3 (x_1 + x_3 - x_2)\, \alpha + \\
&+ x_1 x_3 (2 x_1 x_2 + 4 x_2 x_3 - x_1 x_3 - x_2^2 - x_3^2)\, \beta_1 - \\
&- x_1 x_3 (x_3 - x_1) - x_1 x_3 (x_3 - x_1)(x_1 - 2 x_2 + x_3)\, \beta_2 \qquad (5)
\end{aligned}$$

$$\begin{aligned}
G_3^{\mathrm{E}} = &- x_1 x_2 a_{12} + \\
&+ x_1 (x_1 + x_2)\, a_{13} + \\
&+ x_2 (x_1 + x_2)\, a_{23} - \\
&- 2 x_1 x_2 (x_1 - x_2)\, b_{12} - \\
&- x_1 (-x_1 x_2 + 2 x_2 x_3 + 3 x_1 x_3 - x_1^2)\, b_{13} + \\
&+ x_2 (x_1 x_2 - 3 x_2 x_3 - 2 x_1 x_3 + x_2^2)\, b_{23} - \\
&- 3 x_1 x_2 (x_1 - x_2)^2 c_{12} + \\
&+ x_1 (x_3 - x_1)(-x_1 x_2 + 3 x_2 x_3 + 5 x_1 x_3 - x_1^2)\, c_{13} + \\
&+ x_2 (x_2 - x_3)(x_1 x_2 - 5 x_2 x_3 - 3 x_1 x_3 + x_2^2)\, c_{23} + \\
&+ x_1 x_2 (x_1 + x_2 - x_3)\, \alpha + \\
&+ x_1 x_2 (x_1 x_2 - 4 x_2 x_3 - 2 x_1 x_3 + x_2^2 + x_3^2)\, \beta_1 - \\
&- x_1 x_2 (-x_1 x_2 + 2 x_2 x_3 + 4 x_1 x_3 - x_1^2 - x_3^2)\, \beta_2 \qquad (6)
\end{aligned}$$

The $G_{\mathrm{AgCl}}^{\mathrm{E}}$ values measured at a specific temperature T were then fitted by the help of equation (4). The *Redlich-Kister* parameters thus obtained can be used to calculate G^{E}, G_2^{E} and G_3^{E} for the same temperature by applying equations (2, 5, 6), respectively.

If the molar heats of mixing, H^{E}, and the molar excess entropies, S^{E}, are assumed to be temperature-independent in the temperature range investigated, each *Redlich-Kister* parameter a_{ij}, b_{ij}, c_{ij}, α, β_1, β_2 for G^{E} can be split into two terms according to

$$a_{ij} = a_{ij}^{(h)} - T\, a_{ij}^{(s)}, \qquad (7)$$

where the first term $(a_{ij}^{(h)})$ is a constant and the second term $(a_{ij}^{(s)} T)$ is linearly dependent on the temperature. (The parameters $a_{ij}^{(h)}, \ldots$ and $a_{ij}^{(s)}, \ldots$ are assumed to be temperature independent).

The relations established analogously to the equations (2, 4—6), with the coefficients $a_{ij}^{(h)}, \ldots$ permit the calculation of the molar heats of

Table 1. *Experimentally determined partial molar excess Gibbs energies* G^{E}_{AgCl} *of silver chloride in J mol*$^{-1}$ *in the system* AgCl(x_1)—LiCl(x_2)—KCl(x_3)

x_{AgCl}	x_2/x_3	923 K	973 K	1023 K	1073 K	1123 K
0.05	1:0	8148	8175	8205	8231	8259
0.10		7080	7105	7132	7155	7183
0.20		5349	5373	5393	5417	5437
0.25		4647	4667	4688	4708	4727
0.30		4033	4056	4071	4089	4107
0.40		3013	3028	3047	3059	3073
0.50		2223	2207	2220	2231	2243
0.55		1842	1852	1863	1873	1882
0.60		1520	1528	1537	1545	1554
0.70		952	961	965	970	973
0.80		494	395	503	505	507
0.85		313	316	314	322	323
0.05	3:1	6569	6580	6591	6601	6612
0.10		5804	5816	5829	5841	5853
0.20		4510	4522	4536	4549	4562
0.25		3960	3973	3986	3999	4011
0.30		3465	3476	3489	3501	3514
0.40		2608	2617	2629	2638	2648
0.50		1894	1901	1910	1918	1925
0.55		1581	1588	1595	1602	1608
0.60		1295	1300	1307	1312	1317
0.70		798	802	835	825	813
0.80		409	411	414	402	418
0.85		260	260	260	262	265
0.05	1:1	3808	3709	3733	3756	3779
0.10		3416	3318	3343	3367	3395
0.20		2733	2634	2659	2682	2708
0.25		2404	2335	2357	2379	2403
0.30		2118	2059	2080	2100	2120
0.40		1617	1568	1585	1600	1616
0.50		1187	1149	1160	1171	1181
0.55		991	962	972	980	988
0.60		784	791	798	804	811
0.70		489	493	497	492	504
0.80		259	260	263	262	262
0.85		171	172	176	177	177
0.05	1:3		—587	—534	—480	—431
0.10		569	—517	—465	—414	—352
0.20		—431	—384	—337	—290	—247
0.25		—365	—322	—278	—235	—193
0.30		—301	—263	—224	—186	—148
0.40		—187	—160	—131	—103	—75
0.50		—95	—77	—58	—40	—17
0.55		—58	—44	—29	—15	—2
0.60		—27	—16	—5	5	11
0.70		18	22	28	12	43

Table 1 (continued)

x_{AgCl}	x_2/x_3	923 K	973 K	1023 K	1073 K	1123 K
0.80		41	42	51	52	53
0.85		46	47	51	52	53
0.05	0:1				—6248	—6163
0.10				—5672	—5588	—5504
0.20				—4463	—4388	—4314
0.25			—3981	—3914	—3846	—3779
0.30			—3468	—3402	—3342	—3282
0.40			—2534	—2486	—2442	—2399
0.50			—1744	—1712	—1675	—1656
0.55			—1406	—1378	—1368	—1335
0.60			—1096	—1079	—1064	—1048
0.70			—597	—581	—579	—572
0.80			—240	—233	—231	—228
0.85			—113	—113	—107	—106

mixing and the partial molar heats of mixing of the components. In the same manner the *Redlich-Kister* equations, established with the coefficients $a_{ij}^{(s)}, \ldots$, permit the calculation of the molar excess entropies and the partial molar excess entropies of the components.

4. Results and Discussion

The emf values of the formation cell

graphite/Ag(s)/liquid AgCl(x_1)—LiCl(x_2)—KCl(x_3)/(Cl_2) graphite

were determined at five temperatures (between 923 K and 1,123 K) and at five constant ratios of the mole fractions of LiCl and KCl for various mole fractions of AgCl, listed in Table 1. Care had to be taken at high potassium chloride concentrations and low temperatures, because of the precipitation of potassium chloride.

From the emf values of the various measurements the partial molar excess *Gibbs* energies G_{AgCl}^{E} of silver chloride were calculated and are presented in Table 1. (The entries represent mean values of several measurements). Further evaluation was made as described above, whereby the G_{AgCl}^{E}-values obtained at all concentrations and temperatures form the basis of the fitting process for the determination of the temperature-independent *Redlich-Kister* parameters $a_{ij}^{(h)}$, $b_{ij}^{(h)}, c_{ij}^{(h)}, \alpha^{(h)}, \beta_1^{(h)}, \beta_2^{(h)}$ and $a_{ij}^{(s)}, b_{ij}^{(s)}, c_{ij}^{(s)}, \alpha^{(s)}, \beta_1^{(s)}, \beta_2^{(s)}$.

The Binary Systems AgCl(1)—LiCl(2) *and* AgCl(1)—KCl(3)

Much experimental research on the two binary systems silver chloride—lithium chloride and silver chloride—potassium chloride has been reported in literature. In these papers mostly the partial molar excess *Gibbs* energies G^{E}_{AgCl} of silver chloride were determined from emf measurements. Occasionally, activity coefficients were determined from the corresponding phase diagrams. Furthermore, calorimetric measurements were performed. Details of the two border systems AgCl—LiCl and AgCl—KCl were described in earlier papers[1, 2] dealing with this research programme.

Table 2. *Redlich-Kister parameters for the molar heats of mixing* H^{E} *in* $J\ mol^{-1}$ *and for the molar excess entropies* S^{E} *in* $J\ mol^{-1}\ K^{-1}$, *obtained by fitting the data of the binary system* AgCl(1)—KCl(3)

$a_{13}^{(h)} = -9314$	$b_{13}^{(h)} = 54$	$c_{13}^{(h)} = 626$
$a_{13}^{(s)} = -2.2087$	$b_{13}^{(s)} = 0.0504$	$c_{13}^{(s)} = 0.6362$

The *Redlich-Kister* parameters obtained in this paper (Tab. 2) for the system AgCl—LiCl differ slightly from those given by *Vytlacil*[1]. The reason for this difference is that the parameters of the present study are based on the fit of the data of the ternary system (including the binary system AgCl—LiCl), whereas the parameters reported by *Vytlacil* are based on the measurements of the binary system AgCl—LiCl alone, and should therefore be more reliable. The difference in the molar heats of mixing, H^{E}, amounts to 40 J mol^{-1} at most. The H^{E} function of this paper is slightly more asymmetric than that given by *Vytlacil*. Analogous behaviour is found with the molar excess entropy. The S^{E}-value at $x_{AgCl} = 0.5$ of the present paper is about 0.045 J mol^{-1} K^{-1} more negative compared with the value obtained from the data of the binary system. The G^{E} values agree generally within 10 J mol^{-1}.

A fitting procedure based on the data of the binary system AgCl—KCl alone yields the *Redlich-Kister* parameters given in Table 2.

As in the case of the system AgCl—LiCl these parameters should be more reliable than those based on the fit of the data of the ternary system, which are listed in Table 3. However the difference of these two sets of parameters is very small. The H^{E} values agree to within 4 J mol^{-1} and the S^{E} values agree to within 0.003 J mol^{-1} K^{-1}.

The agreement between these two sets of parameters indicates that the measurements at different concentrations are consistent.

The Binary System LiCl(2)—KCl(3)

The determination of the partial molar excess *Gibbs* energies G^E_{AgCl} of silver chloride in the ternary system, especially at small concentrations of silver chloride, permits also the calculation of the thermodynamic excess functions of the binary system LiCl—KCl; these are normally difficult to evaluate. This is accomplished by the fitting of the G^E_{AgCl} values of the ternary system, which yields also *Redlich-Kister* parameters for the binary system LiCl—KCl.

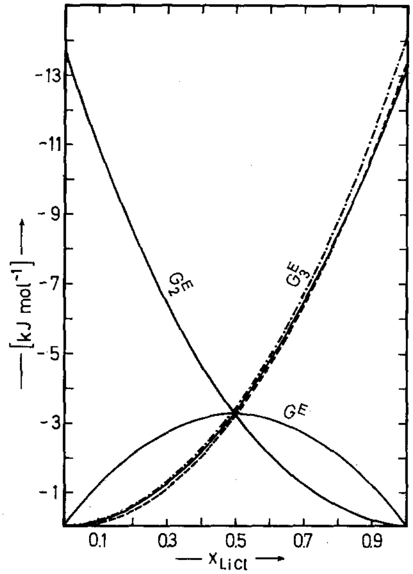

Fig. 2. Partial and integral molar excess *Gibbs* energies of the binary system LiCl(2)—KCl(3). ——— this paper, 1,073 K, —·— this paper, extrapolated to 800 K, — — G^E_{AgCl}, calculated from the liquidus curve by *Lumsden*[5] (applies to a temperature range about 800 K)

The molar *Gibbs* excess energies obtained in this study are negative over the whole range of concentration with a minimum value of —3,310 J mol^{-1} at 1,073 K and $x_{KCl} = 0.5$. The *Redlich-Kister* parameter b_{23} is very small compared with the other two coefficients (a_{23} and c_{23}), indicating that the asymmetry of the system is negligibly small.

In the literature there exist values for the partial molar excess *Gibbs* energies of this system, calculated by *Lumsden*[6] from the phase diagram, which has been investigated by *Aukrust*[7]. The partial molar excess *Gibbs* energy of potassium chloride as calculated from its liquidus curve can be represented by the equation

$$G^{E}_{KCl} = -13{,}390\ x^2_{LiCl}\ [\mathrm{J\ mol^{-1}}],$$

which applies to a temperature range around 800 K. This equation fits

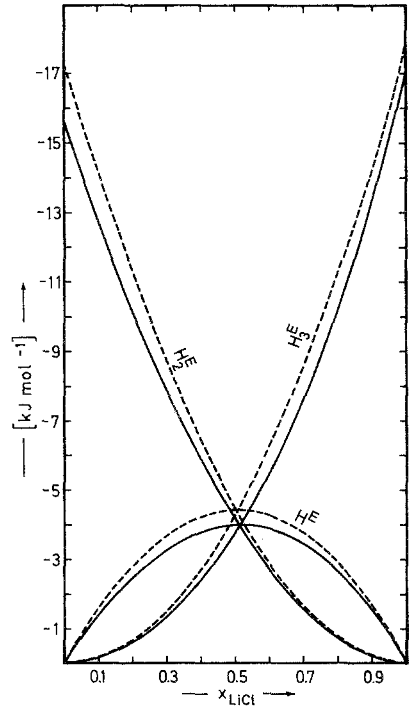

Fig. 3. Partial and integral molar heats of mixing. ——— this paper, 1,073 K, — — *Hersh* and *Kleppa*, 1,013 K

all experimental values obtained from the phase diagram within a range of about 400 J mol^{-1} (between the highest and lowest temperature). Since regular-solution behaviour is assumed, a corresponding equation can be applied to the partial molar excess *Gibbs* energies of LiCl.

In Fig. 2 the data for the partial molar excess *Gibbs* energies for the system LiCl—KCl, obtained in the present study (at 1,073 K), are contrasted with those of *Lumsden* (corresponding to a temperature range about 800 K). By taking into account the temperature dependence of the partial molar excess *Gibbs* energies, the results obtained in the present paper seem to be more negative.

The heats of mixing H^E obtained in the present study correspond to a mean temperature of 1,073 K and are displayed in Fig. 3. From this Figure it can be seen that the heats of mixing are strongly negative in the whole concentration range and exhibit a minimum of $-4{,}050\,\mathrm{J\,mol^{-1}}$ at $x_{\mathrm{LiCl}} = 0.52$. For comparison the heats of mixing determined calorimetrically by *Hersh* and *Kleppa*[8] at 1,013 K are also shown. The measurements of these authors can be represented by the equation

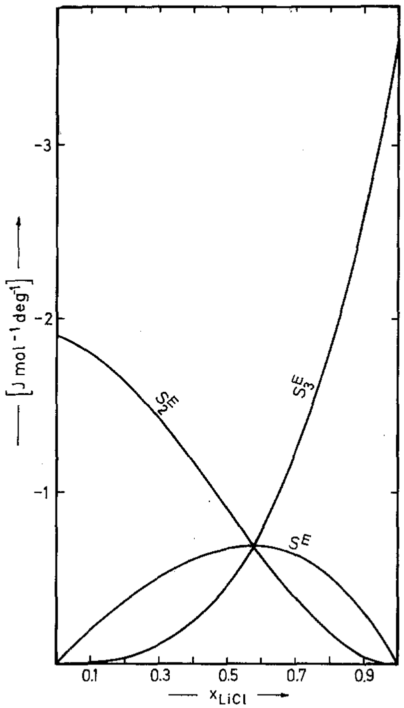

Fig. 4. Partial and integral molar excess entropies at 1,073 K

$$H^E = x_2 x_3 (a + b x_2) = x_2 x_3 (17{,}580 + 377 x_2) \quad [\mathrm{J\,mol^{-1}}],$$

which leads to the following relations for the partial molar heats of mixing

$$H_2^E = x_3^2 (a + 2 b x_2) \text{ and } H_3^E = x_2^2 [a + b (x_2 - x_3)].$$

Table 3 a. *Redlich-Kister-parameters in J mol^{-1} for the molar excess Gibbs energies* G^E

	T [K] 923	973	1023	1073	1123
a_{12}	8437	8472	8507	8541	8575
a_{13}	−7278	−7167	−7056	−6946	−6835
a_{23}	−13652	−13516	−13379	−13243	−13107
b_{12}	154	160	168	175	183
b_{13}	5	3	2	0	−2
b_{23}	64	108	152	169	240
c_{12}	1048	1049	1050	1051	1053
c_{13}	37	6	−25	−57	−88
c_{23}	−213	−210	−206	−203	−199
α	203	163	123	83	43
β_1	−519	−514	−510	−505	−500
β_2	549	583	618	653	687

Table 3 b. *Redlich-Kister-parameters in J mol^{-1} for the molar heats of mixing* H^E

$a_{12}^{(h)} = 7802$	$b_{12}^{(h)} = 21$	$c_{12}^{(h)} = 1024$	$\alpha^{(h)} = 937$
$a_{13}^{(h)} = -9323$	$b_{13}^{(h)} = 40$	$c_{13}^{(h)} = 614$	$\beta_1^{(h)} = -603$
$a_{23}^{(h)} = -16172$	$b_{23}^{(h)} = -749$	$c_{23}^{(h)} = -275$	$\beta_2^{(h)} = -90$

Table 3 c. *Redlich-Kister-parameters in J mol^{-1} K^{-1} for the molar excess entropies* S^E

$a_{12}^{(s)} = -0.6887$	$b_{12}^{(s)} = -0.1437$	$c_{12}^{(s)} = -0.0248$	$\alpha^{(s)} = 0.7961$
$a_{13}^{(s)} = -2.2164$	$b_{13}^{(s)} = 0.0378$	$c_{13}^{(s)} = 0.6255$	$\beta_1^{(s)} = -0.0912$
$a_{23}^{(s)} = -2.7300$	$b_{23}^{(s)} = -0.8811$	$c_{23}^{(s)} = -0.0675$	$\beta_2^{(s)} = -0.6917$

The largest difference in H^E between these two investigations amounts to about 400 J mol^{-1}.

Considering the fact that the values for the heats of mixing obtained in the present investigation are not results from direct measurements in the binary system, but from a fit of the temperature dependence of the partial molar excess *Gibbs* energies of silver chloride in the ternary system, the agreement is suprisingly good.

The molar excess entropies S^E, displayed in Fig. 4 are also negative. The minimum value, with a mole fraction $x_{LiCl} = 0.58$, is -0.68 J mole^{-1} K^{-1}.

The Ternary System AgCl(1)—LiCl(2)—KCl(3)

The fitting procedure based on the *Redlich-Kister* equation, considering all measured G^{E}_{AgCl} values which result from all concentrations and temperatures investigated, results in the *Redlich-Kister* parameters shown in Table 3. Part a of the Table shows the *Redlich-Kister* parameters a_{ij}, b_{ij}, c_{ij}, α, β_1, β_2 for the molar excess *Gibbs* energy for the five temperatures examined, whereas part b of the table gives the parameters $a_{ij}^{(h)}$, $b_{ij}^{(h)}$, $c_{ij}^{(h)}$, $\alpha^{(h)}$, $\beta_1^{(h)}$, $\beta_2^{(h)}$, for the molar heats of mixing, and part c the parameters $a_{ij}^{(s)}$, $b_{ij}^{(s)}$, $c_{ij}^{(s)}$, $\alpha^{(s)}$, $\beta_1^{(s)}$, $\beta_2^{(s)}$, for the molar excess entropies. With the help of these parameters the thermodynamic excess functions mentioned can be calculated for any concentration in the temperature range from 923 K to 1,123 K.

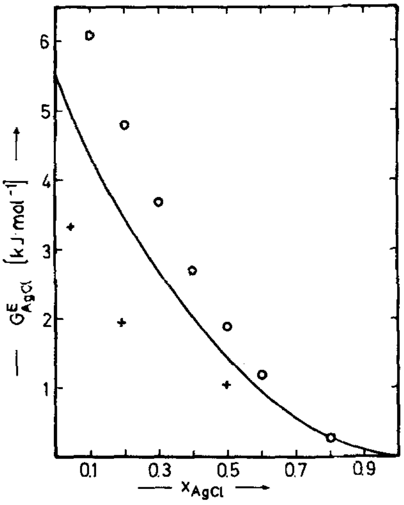

Fig. 5. Partial molar excess *Gibbs* energies G^{E}_{AgCl} of silver chloride along the section $x_{LiCl}/x_{KCl} = 0.579/0.471$ in the ternary system. ——— this paper, extrapolated to 850 K, ○ ○ ○ *Takahashi*[8], 873 K, + + + *Yang* and *Hudson*[9], 823 K

It was found that a satisfactory fit with the help of the *Redlich-Kister* equation can only be achieved, if the ternary parameters α, β_1 and β_2 are also included.

Activities of silver chloride in the eutectic molten salt mixture of lithium chloride and potassium chloride ($x_{LiCl} = 0.579$) have been determined by *Takahashi*[9] and *Yang* and *Hudson*[10].

A comparison of the G^{E}_{AgCl} values obtained by these authors with the results of the present study at a ratio of the mole fractions

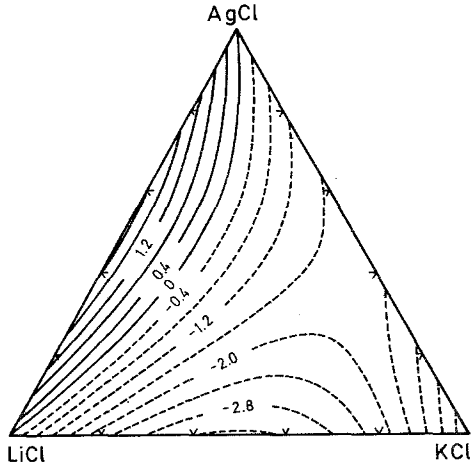

Fig. 6

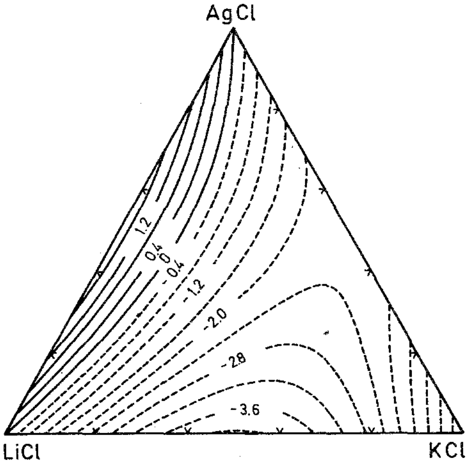

Fig. 7

Fig. 6. Lines of constant molar excess *Gibbs* energy G^E in kJ mol^{-1} in the ternary system AgCl—LiCl—KCl at 1,073 K

Fig. 7. Lines of constant molar heats of mixing H^E in kJ mol^{-1} in the ternary system AgCl—LiCl—KCl at 1,073 K

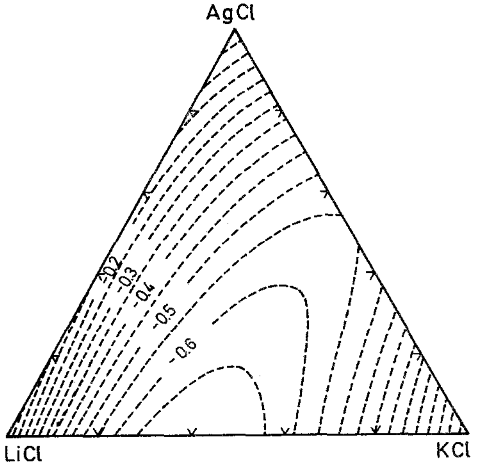

Fig. 8. Lines of constant molar excess entropy S^E in J mol^{-1} K^{-1} in the ternary system AgCl—LiCl—KCl at 1,073 K

$x_{LiCl}/x_{KCl} = 0.579/0.421$ is only possible in a very limited way since the highest temperatures obtained by the above-mentioned authors are 50 and 100 K lower in temperature, respectively, than the lowest temperature investigated in this study. In Fig. 5 the data of the present paper, extrapolated to 850 K, are compared with the values of *Takahashi*[9] and *Yang* and *Hudson*[10] for 873 K and 824 K, respectively. For the total concentration range, the G^E_{AgCl} values of *Takahashi* are higher, whereas those found by *Yang* and *Hudson* are smaller than the values obtained in the present paper. At $x_{AgCl} = 0.2$ the results of these authors differ by 1,500 J mol^{-1} from the present ones. These differences cannot be explained by the temperature dependence of the G^E_{AgCl} values.

The calculated thermodynamic excess functions, G^E, H^E and S^E are displayed in Figs. 6, 7, and 8 in form of *iso*-G^E, *iso*-H^E, and *iso*-S^E plots. It should be noted that the zero line for G^E and H^E are similar in shape but do not coincide. Since the quantities, G^E, H^E, and S^E do not, in general, vanish simultaneously there exists no concentrations for which the mixtures exhibit strictly-ideal behaviour. However, in the vicinity of the zero line of G^E the deviations from ideal behaviour are small.

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