EMF Study of the Thermodynamics of Liquid K_xKCl_{1-x}

J. Bernard, J. Blessing, J. Schummer, and W. Freyland

Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe, Kaiserstraße 12, 7500 Karlsruhe, Germany

Electrochemistry / Liquids / Thermodynamics

We report EMF-measurements of the metal activity a_K of liquid K_xKCl_{1-x} melts for metal mol fractions $10^{-3} \leq x \leq 0.7$ and temperatures 800°C $\leq T \leq$ 877°C. The composition has been controlled in situ by the Wagner method of coulometric titration. From the activities the partial molar excess free enthalpies and the integral free enthalpy have been determined. They exhibit clear deviations from a simple regular solution description for salt rich solutions. The behaviour of the partial excess entropy of the metal is qualitatively discussed on the basis of localized and spin paired electronic states in nonmetallic solutions. The concentration dependence of a_K in the nonmetallic regime is consistent with the predictions of a simple electronic defect model which considers thermal equilibria mainly between F-centers and aggregated F-centers.

Introduction

A fascinating characteristic of metal-molten salt (M-MX) solutions is the transition from nonmetallic to metallic states which at elevated temperatures may be followed continuously with varying composition [1]. Naturally this electronic transition most strongly manifests in the corresponding change of the electronic structure and properties, respectively – for reviews see e.g. [1–3]. However, its influence on the thermodynamic properties is less well understood.

In dealing with this problem alkalimetal-alkalihalide melts are especially attractive and may be considered as model systems because of their relatively simple microscopic structure. The salt melt is completely dissociated at all temperatures so that the intermolecular interaction is largely determined by Coulomb interactions. In salt rich solutions a strong localization of electrons prevails. For the example of K_xKCl_{1-x} recent spectroscopic studies [4] and quantum molecular dynamics calculations [5, 6] strongly indicate that electronic defects very similar to the crystalline F-center form which aggregate with increasing mol fraction x to form bipolarons and bipolaron aggregates. Metallic characteristics occur at relatively high x-values, for $x \geq 0.2$, if one takes e.g. the Pauli susceptibility of metal as a criterion for nearly free electron behaviour [7]. In metal rich solutions neutron diffraction studies indicate the formation of salt clusters [8].

First thermodynamic investigations of these M-MX melts have been performed by Bredig and coworkers [1] who mainly focused on precise determinations of the phase behaviour. More recently further studies of the thermodynamics have been reported which used different methods such as calorimetry [9], vapour pressure [10] or $pVTx$-measurements [11]. However, in all these investigations the composition has been controlled by weighing the added amount of the components and so only a limited small number of concentrations has been measured. In the present study we have used an EMF-technique to determine the metal activity a_K of K_xKCl_{1-x} at various constant temperatures with precise variation of composition. Emphasis is on this last point which is achieved by coulometric titration i.e. in situ variation of metal amount. In this way we succeeded to control the composition almost continuously from very dilute salt rich to metal rich solutions. The main objective of this work is to test the correlation of the changes in the thermodynamic and electronic properties.

Experimental

The titration technique and the set up of the corresponding EMF-cells used here is very similar to that described previously in the study of dilute Na-NaBr solutions [12]. So we focus in the following only on those changes necessary for adaption to the K-KCl system and, in particular, on a detailed consideration of error sources and their corrections. Otherwise we refer to the above publication [12].

Two different EMF-cells with distinct cathods (working electrode) have been employed:

$$\text{Mo, } Ca_{0.1}Sn_{0.9}(l) \mid CaF_2(s) \mid K_yKF_{1-y}(s), K(v), K_xKCl_{1-x}(l), \text{Mo} \quad (A)$$

$$\text{Mo, } Ca_{0.1}Sn_{0.9}(l) \mid CaF_2(s) \mid K_y(CaF_2 \cdot KF)_{1-y}(s), K(v), K_xKCl_{1-x}(l), \text{Mo} \quad (B)$$

In both cases the Ca-Sn reference electrode had a fixed low Ca-activity of $\sim 10^{-7}$ at 800°C [13] which ensures a negligible electronic transference of the solid electrolyte CaF_2 [14]. The amount of the Ca-Sn alloy has been chosen such that during titration the alloy composition did not change significantly. When current is passed through these cells, K-metal is formed in the solid KF and double salt $CaF_2 \cdot KF$, respectively, which fixes the metal activity a_K at a given EMF according to

$$a_K = \exp\left(\frac{(E-E_0)F}{RT}\right) \quad (1)$$

Here E_0 denotes the EMF at saturation and F is the Faraday constant. The metal dissolved in the solid fluorides equilibrates with K in the vapour phase through which the molten salt is doped. In equilibrium the activity in all three phases is the same. The time for complete equilibration is determined by diffusion in the solid fluorides.

 © VCH Verlagsgesellschaft mbH, W-6940 Weinheim, 1993 *0005-9021/93/0202-0177 $ 10.00+.25/0*

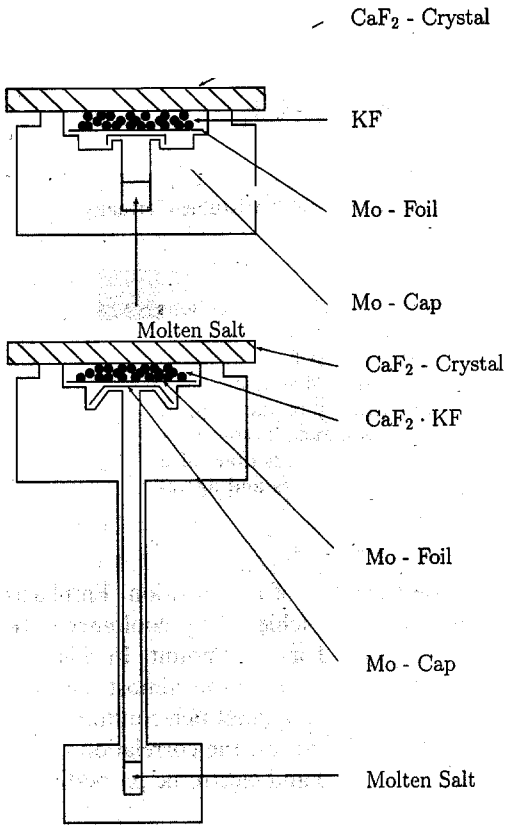

Fig. 1
Different constructions of the working electrode of the EMF-cell. Upper part: homogeneous temperature profile along electrode; lower part: compartment for solid fluoride is separated from the molten salt compartment by a thin walled Mo-capillary along which a definite temperature profile is applied with the molten salt at a lower temperature to reduce salt mixing (see text)

The main drawback of this technique is a possible mixing of the salts through the vapour phase which both influences the activity measurement and the determination of the metal concentration in the molten salt. The vapour pressure of the pure salts near their respective melting points is of the order of 10^{-3} bar. The partial pressure of the alkali metal varies from $< 10^{-3}$ bar to ~ 1 bar going from salt to metal rich solutions. Taking this into account complex transport reactions through the vapour phase have to be envisaged which may cause severe trouble. In order to exclude or reduce this influence we have worked with two different constructions of the working electrode which are presented in Fig. 1. In both cases the solid fluoride is pressed against the CaF_2 single crystal and is separated from the molten KCl by a tightly fitting Mo-cap. We have tested both pure KF and the double salt $CaF_2 \cdot KF$, the latter having a clearly reduced KF partial pressure. In the arrangement of the upper part of Fig. 1 the whole EMF-cell has been kept at a constant homogeneous temperature. However, with this set up we could not prevent that in the majority of experiments a significant mixing of the salts took place during the measurement. In order to avoid this we have tried a second construction as shown in the lower part of Fig. 1. Here the compartment of the solid fluoride is separated by a Mo-capillary of about 3 cm length from the molten salt and a temperature gradient of about 15 to 20 K has been applied along the capillary the molten salt being at the lower temperature. With this modification better reproducibility of the EMF measurements has been achieved over long periods of 1 to 2 days. A typical example of raw data of the EMF as a function of the titrated charge Q, obtained with this cell at 798°C of the melt is plotted in Fig. 2.

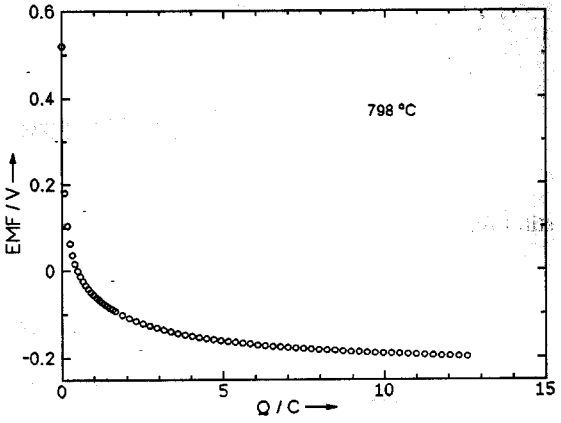

Fig. 2
Typical raw data of EMF vs titrated charge Q for a sample of liquid KCl of 62 mg

In all the measurements of the EMF a complete equilibrium could not be awaited because of the slow solid state diffusion. Instead the following criterion was applied: if the EMF did not change by more than 1 mV/2 min the voltage was recorded and the next titration step started. This has been automatically controlled and recorded by a personal computer.

For the absolute determination of the metal activity two contributions are important. According to Eq. (1) the E_0-value is essential which has been calibrated in different ways: titration of the double salt alone to saturation, measurement of the solid fluoride equilibrated with liquid K in place of KCl, and replacement of the molten salt by a molten alloy $K_{0.4}Bi_{0.6}$ with known EMF vs pure K [15, 16]. From these calibrations an E_0 of $CaF_2 \cdot KF$ at 800°C has been found of E_0 (800°C) = −0.233 V with a temperature coefficient of $\partial E^0/\partial T = -8.1 \cdot 10^{-5} VK^{-1}$. For pure KF the same E_0 has been taken yielding good agreement of a_K with separate results from vapour pressure measurements [17].

With applying a defined temperature gradient to the working electrode − Fig. 1, lower part − an additional correction has to be considered. Inside the working electrode compartment a constant partial pressure of potassium, p_K, is assumed, whereas the activities $a_K(T)$ at the top (KF and $CaF_2 \cdot KF$, respectively) and bottom (KCl) end should be different. Yet the activity is defined through the vapour pressure by:

$$a_K(T) = p_K(T)/p_K^0(T \quad (2)$$

with $p_K^0(T)$ being the vapour pressure of pure potassium. Thus to obtain the metal activity for the molten salt temperature, T_{KCl}, we have to correct the activity measured for the fluoride, T_{KF}, by:

$$a_K(T_{KCl}) = a_K(T_{KF}) \cdot p_K^0(T_{KF})/p_K^0(T_{KCl}) \quad (3)$$

For pure K the vapour pressures have been taken from literature [18].

The concentration scale of dissolved metal in molten salt is given by the measured charge Q. However, from the total titrated Q those parts which correspond to dissolved metal in the fluoride and to metal in the vapour phase have to be subtracted. The first contribution has been calibrated in a separate experiment on the fluorides alone at corresponding temperatures, the second has been estimated from the known volume of the working electrode and the vapour pressure of pure K from literature [18]. Fig. 3 gives an overview how these different parts contribute in the various ranges of EMF or activity, respectively. From this it is immediately apparent that the absolute accuracy of the concentration is poor at low Q and corresponding low $x (x \leq 0.01)$, improving with increasing x. A typical value for the maximum absolute error in x is $\Delta x = 0.005$

which is roughly constant over the whole concentration range studied, i.e. $10^{-3} \leq x \leq 0.7$.

The error analysis in the activity determination has to distinguish between the two methods employed. With the working electrode at constant temperature the main error contributions are due to uncertainties in the temperature measurement (±4 K), the error of the E_0-value (±1 mV) and a small constant offset of the EMF from the value at complete equilibration in the solid fluoride. Without mixing of the salts these contributions amount to an absolute maximum error of the activity of ±3% estimated at $x = 0.1$ and ±2% at $x = 0.7$. With applying a temperature gradient to the working electrode the absolute error is increased mainly due to the uncertainty in the absolute temperature. The corresponding error bars are indicated in Fig.4 of the following chapter. For further details of the corresponding error analysis see references [19, 20].

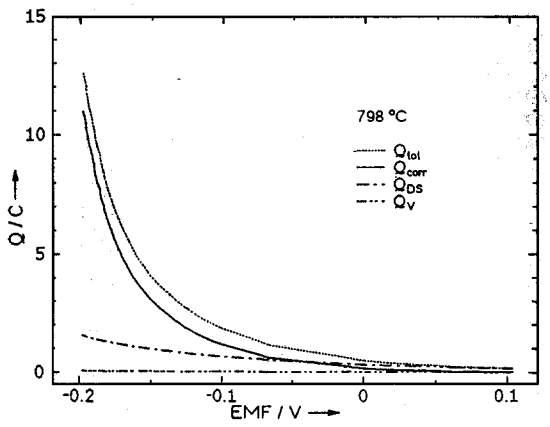

Fig. 3
Comparison of the different corrections contributing to the total measured charge Q_{tot} of the example of Fig. 2; Q_v = correction for K in vapour phase; Q_{DS} = correction for K dissolved in solid double salt; Q_{corr} = finally corrected charge corresponding to K in molten KCl

Results

In Fig.4 metal activities of K_xKCl_{1-x} at 798°C and 800°C, respectively, are compared. The two data sets stem from separate experiments with different working electrodes. That at 798°C belongs to measurements with the temperature gradient working electrode, that at 800°C has been obtained at homogeneous temperature. Obviously there is a roughly constant offset in a_K of about 0.04. However, within the errors of a_K and x_K the agreement is satisfactory and the reproducibility of the relative change $a_K(x_K)$ is good.

Figs.5 and 6 give the corresponding results at various temperatures for distinct composition ranges together with the comparison with literature data obtained from vapour pressure measurement [10, 17]. Altogether the absolute agreement with the literature data is good. The numerical values of the activity measurements are summarized in Tables1 and 2.

Discussion

In the following we will concentrate on the characteristic changes of the thermodynamic properties with composition in relation to the electronic behaviour in salt rich solutions. We will also briefly discuss the thermodynamics in the intermediate range around the consolute point of liquid-liquid demixing.

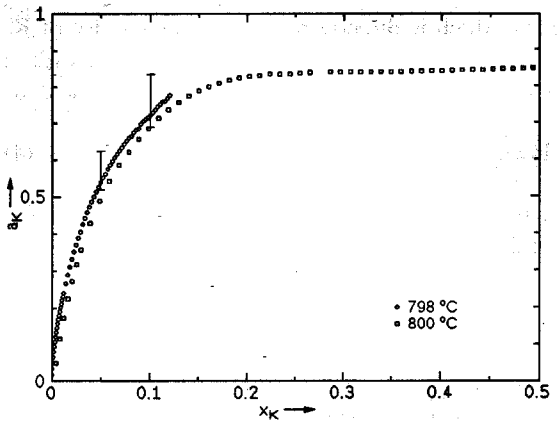

Fig. 4
Comparison of the activity results of K_xKCl_{1-x} as a function of x_K as measured with the different EMK cells of Fig. 1. The error bars correspond to the measurements with the temperature gradient arrangement and present the maximum absolute error

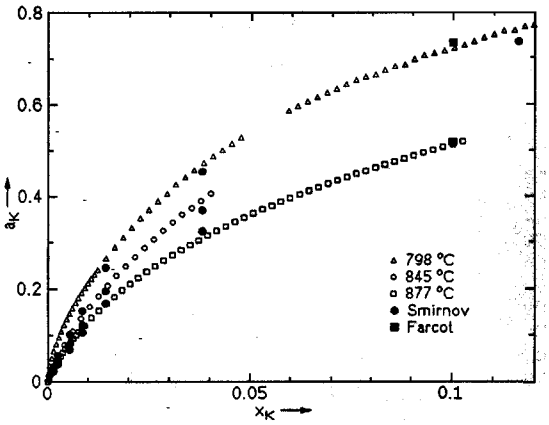

Fig. 5
Activity results of K_xKCl_{1-x} vs x_K at various temperatures in comparison with literature data; measurements performed with the cell in Fig. 1, lower part

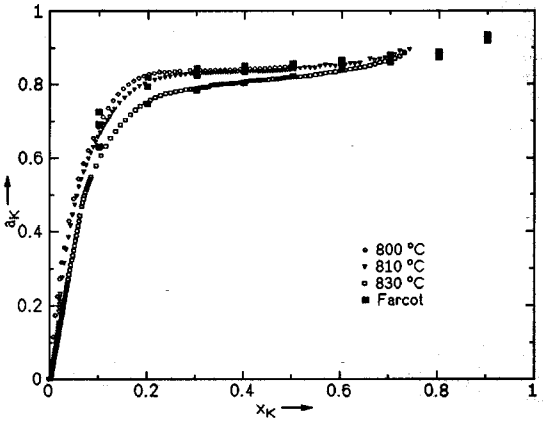

Fig. 6
Same as Fig. 5, but data obtained with the cell shown in Fig. 1, upper part

A quantity which is directly related to the activity of K, a_K, is the partial molar excess free enthalpy, g_K^E, according to:

$$g_K^E = RT\ln a_K - RT\ln x_K \tag{4}$$

From this the partial molar excess free enthalpy of KCl, g_{KCl}^E, is obtained through the Gibbs-Duhem integration:

$$g_{KCl}^E = \frac{x_K}{x_K - 1} g_K^E + \int_0^{x_K} \frac{g_K^E}{(1-x_K)^2} dx_K \tag{5}$$

From Eqs. (4) and (5) one obtains the integral molar excess free enthalpy g^E and the corresponding integral quantity of the mixture g^M. All these quantities are summarized in Fig. 7 for 3 temperatures in the range 800°C ≤ T ≤ 830°C

Table 1
Metal activities a_K as a function of metal mol fraction x_K at various temperatures T of liquid K_xKCl_{1-x} measured with the temperature gradient EMF cell (Fig. 1 lower part)

x_K	a_K	x_K	a_K
	T = 798°C		
0.0000	0.0000	0.0429	0.5002
0.0001	0.0176	0.0452	0.5140
0.0004	0.0347	0.0475	0.5271
0.0009	0.0507	0.0498	0.5401
0.0014	0.0660	0.0521	0.5520
0.0020	0.0807	0.0545	0.5617
0.0026	0.0948	0.0568	0.5751
0.0032	0.1081	0.0592	0.5859
0.0039	0.1214	0.0615	0.5964
0.0046	0.1338	0.0639	0.6062
0.0053	0.1460	0.0663	0.6152
0.0060	0.1577	0.0687	0.6247
0.0068	0.1690	0.0711	0.6333
0.0075	0.1804	0.0735	0.6427
0.0083	0.1911	0.0759	0.6513
0.0091	0.2017	0.0783	0.6599
0.0099	0.2114	0.0808	0.6638
0.0107	0.2218	0.0831	0.6741
0.0115	0.2311	0.0856	0.6819
0.0123	0.2406	0.0881	0.6849
0.0143	0.2659	0.0904	0.6972
0.0164	0.2894	0.0928	0.7055
0.0185	0.3108	0.0953	0.7108
0.0206	0.3317	0.0978	0.7152
0.0228	0.3520	0.1003	0.7218
0.0249	0.3703	0.1027	0.7286
0.0271	0.3887	0.1051	0.7366
0.0294	0.4049	0.1075	0.7450
0.0315	0.4254	0.1100	0.7516
0.0338	0.4420	0.1124	0.7595
0.0360	0.4577	0.1150	0.7604
0.0383	0.4730	0.1175	0.7681
0.0406	0.4870	0.1199	0.7767
	T = 845°C		
0.0000	0.0000	0.0192	0.2486
0.0005	0.0135	0.0215	0.2683
0.0022	0.0474	0.0238	0.2874
0.0040	0.0790	0.0261	0.3060
0.0061	0.1080	0.0284	0.3249
0.0081	0.1352	0.0307	0.3426
0.0103	0.1606	0.0330	0.3600
0.0125	0.1845	0.0354	0.3744
0.0147	0.2071	0.0377	0.3898
0.0169	0.2284	0.0401	0.4056

Table 1 *(Continued)*

x_K	a_K	x_K	a_K
	T = 877°C		
0.0000	0.0000	0.0371	0.3043
0.0003	0.0077	0.0393	0.3148
0.0006	0.0149	0.0415	0.3246
0.0010	0.0226	0.0438	0.3342
0.0015	0.0305	0.0460	0.3438
0.0021	0.0384	0.0482	0.3529
0.0026	0.0464	0.0505	0.3620
0.0032	0.0542	0.0528	0.3708
0.0037	0.0623	0.0551	0.3789
0.0043	0.0701	0.0573	0.3873
0.0049	0.0777	0.0596	0.3954
0.0056	0.0851	0.0620	0.4033
0.0062	0.0923	0.0643	0.4111
0.0069	0.0994	0.0666	0.4185
0.0076	0.1063	0.0690	0.4262
0.0083	0.1131	0.0713	0.4335
0.0090	0.1197	0.0737	0.4405
0.0107	0.1369	0.0760	0.4481
0.0126	0.1528	0.0784	0.4548
0.0144	0.1681	0.0808	0.4613
0.0164	0.1825	0.0831	0.4681
0.0183	0.1968	0.0855	0.4744
0.0203	0.2102	0.0879	0.4806
0.0223	0.2233	0.0903	0.4873
0.0244	0.2362	0.0927	0.4932
0.0265	0.2484	0.0951	0.4991
0.0286	0.2603	0.0975	0.5054
0.0307	0.2720	0.1000	0.5115
0.0328	0.2832	0.1024	0.5179
0.0350	0.2939		

and for $x_K \leq 0.75$. For 798 and 800°C, respectively, both data sets of Fig. 5 and Fig. 6 have been used. As can been seen in e.g. g_K^E, they nicely merge around $x_K \sim 0.1$. The agreement with independent measurements of Smirnov et al. [10] is very good (see Fig. 7). The excess free enthalpy g^E is positive over the whole composition range as expected for solutions with a miscibility gap. It has a maximum of ~5 kJ mol^{-1} near $x_K \sim 0.5$ and decreases symmetrically around this point. The maximum value of 5 kJ mol^{-1} agrees surprisingly well with that of ~4.5 kJ mol^{-1} of the regular solution model taking for the critical temperature the experimental value of T_c = 1063 K [1]. However, on the salt rich side clear deviations from this model are present as is shown in Fig. 8. Here g_K^E for regular solution is given by:

$$g_K^E = \Omega(1-x_K)^2 \tag{6}$$

with Ω = interaction energy, where Ω has been fittet at x_K = 0.5.

Within the interval 800 to 830°C there is only a slight temperature dependence visible in g_K^E below $x_K \leq 0.1$ (Fig. 7). However, the limited number of different temperatures measured and, in particular, the absolute uncertainty of the temperature measurements from separate runs do not allow a quantitative discussion of such quantities as the partial molar excess entropy, $S_K^E = -(\partial g_K^E/\partial T)p,x_K$. Qualitatively we observe a relatively steep incipient decrease of S_K^E below $x_K \leq 0.01$ with $S_K^E(x_K = 0.01) \sim 30$ J mol^{-1} K^{-1}.

Table 2
Metal activities a_K as a function of metal mol fraction x_K at various temperatures T of liquid K_xKCl_{1-x} measured with homogeneous temperature cell (Fig. 1 upper part)

x_K	a_K	x_K	a_K	x_K	a_K
		T = 800°C			
0.0000	0.0000	0.1393	0.7743	0.3275	0.8387
0.0043	0.0494	0.1497	0.7889	0.3380	0.3891
0.0082	0.1155	0.1601	0.8003	0.3484	0.8389
0.0124	0.1736	0.1705	0.8097	0.3588	0.8392
0.0167	0.2247	0.1810	0.8175	0.3692	0.8399
0.0210	0.2725	0.1914	0.8232	0.3796	0.8404
0.0255	0.3169	0.2019	0.8282	0.3900	0.8411
0.0300	0.3569	0.2124	0.8304	0.4004	0.8417
0.0393	0.4298	0.2229	0.3841	0.4108	0.8425
0.0488	0.4891	0.2334	0.8336	0.4211	0.8431
0.0584	0.5428	0.2439	0.8344	0.4315	0.8440
0.0682	0.5863	0.2544	0.8361	0.4418	0.8439
0.0782	0.6219	0.2648	0.8378	0.4522	0.8453
0.0883	0.6555	0.2857	0.8394	0.4625	0.8464
0.0984	0.6848	0.2962	0.8382	0.4728	0.8466
0.1085	0.7129	0.3067	0.8395	0.4832	0.8481
0.1187	0.7366	0.3171	0.8379	0.4935	0.8492
0.1290	0.7570				
		T = 810°C			
0.0000	0.0000	0.0829	0.6147	0.3907	0.8341
0.0010	0.0001	0.0877	0.6308	0.3959	0.8342
0.0020	0.0005	0.0925	0.6444	0.4011	0.8345
0.0029	0.0031	0.0974	0.6576	0.4063	0.8348
0.0037	0.0079	0.1023	0.6697	0.4114	0.8352
0.0046	0.0127	0.1072	0.6816	0.4166	0.8352
0.0053	0.0196	0.1121	0.6932	0.4218	0.8356
0.0061	0.0268	0.1171	0.7033	0.4269	0.8357
0.0068	0.0345	0.1220	0.7127	0.4321	0.8361
0.0076	0.0423	0.1269	0.7255	0.4373	0.8357
0.0084	0.0484	0.1320	0.7342	0.4425	0.8353
0.0091	0.0554	0.1420	0.7511	0.4476	0.8356
0.0099	0.0627	0.1522	0.7646	0.4528	0.8363
0.0107	0.0699	0.1624	0.7759	0.4579	0.8367
0.0114	0.0785	0.1726	0.7865	0.4631	0.8370
0.0122	0.0849	0.1829	0.7957	0.4682	0.8373
0.0130	0.0921	0.1932	0.8023	0.4734	0.8376
0.0137	0.0994	0.2140	0.8120	0.4785	0.8381
0.0145	0.1067	0.2244	0.8160	0.4837	0.8386
0.0152	0.1142	0.2348	0.8191	0.4888	0.8393
0.0160	0.1219	0.2452	0.8218	0.4940	0.8391
0.0167	0.1297	0.2556	0.8246	0.5043	0.8409
0.0175	0.1378	0.2660	0.8263	0.5145	0.8439
0.0183	0.1449	0.2764	0.8275	0.5248	0.8454
0.0190	0.1534	0.2868	0.8295	0.5351	0.8442
0.0190	8.1831	0.2921	0.8292	0.5453	0.8448
0.0197	0.1943	0.2973	0.8292	0.5556	0.8491
0.0204	0.2037	0.3025	0.8295	0.5658	0.8519
0.0211	0.2134	0.3077	0.8298	0.5760	0.8508
0.0218	0.2225	0.3129	0.8308	0.5863	0.8486
0.0225	0.2310	0.3181	0.8305	0.5965	0.8536
0.0262	0.2758	0.3233	0.0311	0.6067	0.8525
0.0300	0.3148	0.3285	0.8315	0.6169	0.8574
0.0340	0.3513	0.3337	0.8320	0.6271	0.8558
0.0380	0.3846	0.3389	0.8321	0.6373	0.8580
0.0422	0.4163	0.3441	0.8326	0.6577	0.8695
0.0464	0.4454	0.3492	0.8328	0.6679	0.8649
0.0508	0.4723	0.3544	0.8333	0.6781	0.8682
0.0552	0.4967	0.3596	0.8335	0.6882	0.8713
0.0596	0.5212	0.3648	0.8331	0.6984	0.8752
0.0642	0.5426	0.3700	0.8332	0.7085	0.8803
0.0688	0.5621	0.3752	0.8332	0.7187	0.8900
0.0734	0.5815	0.3804	0.8336	0.7288	0.8863
0.0781	0.5991	0.3856	0.8339	0.7389	0.8944

Table 2 *(Continued)*

x_K	a_K	x_K	a_K	x_K	a_K
		T = 830°C			
0.0010	0.0001	0.0525	0.3752	0.3606	0.8008
0.0020	0.0003	0.0543	0.3889	0.3658	0.8010
0.0030	0.0005	0.0560	0.4019	0.3710	0.8012
0.0040	0.0036	0.0578	0.4152	0.3762	0.8202
0.0048	0.0094	0.0596	0.4289	0.3813	0.8027
0.0057	0.0158	0.0614	0.4428	0.3865	0.8036
0.0065	0.0223	0.0650	0.4678	0.3916	0.8044
0.0074	0.0290	0.0668	0.4791	0.3968	0.8056
0.0082	0.0358	0.0687	0.4896	0.4019	0.8075
0.0091	0.0427	0.0705	0.4988	0.4071	0.8089
0.0099	0.0496	0.0724	0.5070	0.4123	0.8092
0.0108	0.0565	0.0744	0.5147	0.4174	0.8094
0.0116	0.0633	0.0763	0.5218	0.4226	0.8099
0.0125	0.0699	0.0782	0.5288	0.4277	0.8106
0.0133	0.0767	0.0801	0.5356	0.4329	0.8111
0.0142	0.0835	0.0821	0.5420	0.4380	0.8117
0.0150	0.0903	0.0840	0.5484	0.4432	0.8122
0.0159	0.0972	0.0938	0.5796	0.4483	0.8128
0.0167	0.1040	0.1037	0.6076	0.4586	0.8140
0.0176	0.1108	0.1136	0.6327	0.4637	0.8146
0.0184	0.1175	0.1236	0.6549	0.4689	0.8151
0.0193	0.1242	0.1337	0.6731	0.4740	0.8157
0.0202	0.1307	0.1438	0.6908	0.4792	0.8175
0.0210	0.1374	0.1540	0.7048	0.4843	0.8181
0.0219	0.1440	0.1642	0.7187	0.4894	0.8186
0.0228	0.1507	0.1744	0.7314	0.4946	0.8189
0.0236	0.1572	0.1847	0.7415	0.5048	0.8192
0.0245	0.1641	0.1950	0.7499	0.5151	0.8204
0.0254	0.1708	0.2053	0.7569	0.5253	0.8216
0.0262	0.1775	0.2157	0.7639	0.5356	0.8227
0.0271	0.1842	0.2260	0.7694	0.5458	0.8252
0.0279	0.1910	0.2364	0.7742	0.5560	0.8274
0.0288	0.1977	0.2467	0.7780	0.5662	0.8300
0.0297	0.2042	0.2571	0.7808	0.5765	0.8319
0.0305	0.2107	0.2675	0.7834	0.5867	0.8336
0.0314	0.2175	0.2778	0.7862	0.5969	0.8360
0.0323	0.2240	0.2882	0.7873	0.6071	0.8387
0.0332	0.2307	0.2934	0.7880	0.6173	0.8411
0.0340	0.2372	0.2986	0.7895	0.6275	0.8435
0.0349	0.2437	0.3037	0.7906	0.6376	0.8452
0.0358	0.2503	0.3089	0.7914	0.6478	0.8480
0.0367	0.2568	0.3141	0.7920	0.6580	0.8514
0.0375	0.2634	0.3193	0.7920	0.6681	0.8552
0.0384	0.2699	0.3245	0.7931	0.6783	0.8587
0.0402	0.2833	0.3296	0.7980	0.6885	0.8624
0.0419	0.2964	0.3348	0.7989	0.6986	0.8651
0.0437	0.3096	0.3399	0.7992	0.6986	0.8637
0.0454	0.3229	0.3451	0.7992	0.7087	0.8691
0.0472	0.3360	0.3503	0.8001	0.7189	0.8756
0.0490	0.3492	0.3555	0.8008	0.7290	0.8852
0.0507	0.3624				

For $x_K > 0.01$ the partial entropy S_K^E decreases more slowly with x_K reaching a value of $S_K^E(x_K = 0.1) \sim 20$ Jmol^{-1} K^{-1}, which is comparable in magnitude with the data of Smirnov et al. [10]. With respect to this trend of S_K^E two points are worth noting. First, in their calorimetric study of liquid Cs_xCsCl_{1-x} Yokokawa, Kleppa and Nachtrieb [9] observe the same trend of $S_{Cs}^E(x_{Cs})$, but the absolute values are smaller by roughly a factor of two. Secondly, with respect to the electronic structure and thermodynamics discussed in more detail below, the following is of interest. In a simple model of the thermodynamics of M-MX solutions Pitzer [21] assumed, that in salt-rich M-MX solutions F-center like states form and that the energy of mixing should be determined by the "conversion of the metal to a hypo-

thetical ionic lattice of positive ions and F-centers". In this model substantial positive excess entropies of mixing are predicted with two main contributions: uncoupling of electron spins yielding a term $R\ln 2$ and reduction of the vibration frequency of surrounding ions in comparison with the pure molten salt. Without knowledge of the frequency change the latter is difficult to quantify, but may be of the order of R. In any case this simple model predicts positive excess entropies in the right order of magnitude. In addition it allows a simple explanation for the observed reduction of S_M^E with increasing x_M. If spin pairing of F-centers to form bipolarons in their singulet state dominates with $x_M > 0.01$, then the term R ln 2 is strongly reduced. This change in the electronic properties is predicted in the quantum molecular dynamics calculations [5, 6] and is directly seen in the behaviour of the static magnetic susceptibility [7].

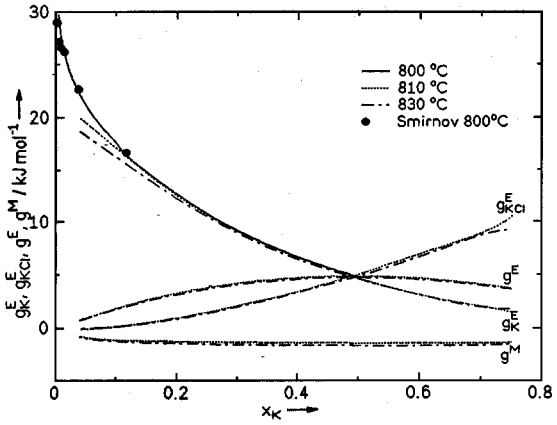

Fig. 7
Partial molar excess free enthalpies, excess free enthalpy and integral free enthalpy of mixing of liquid K_xKCl_{1-x} at different temperatures as a function of composition

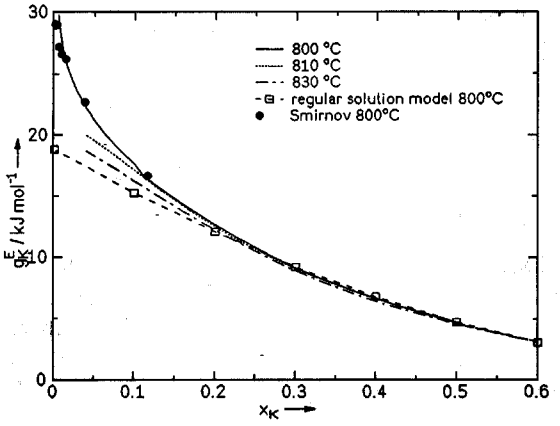

Fig. 8
Comparison of the partial molar free excess enthalpy of K, g_K^E, with the behaviour of the regular solution model

As pointed out already there is a strong similarity between crystalline and molten alkali halides doped with excess metal, especially with respect to their spectroscopic characteristics – see also [4] –. In this context it is of interest how the thermodynamic characteristics as predicted from crystalline defect models compare with the activity results in the corresponding liquid systems. An analogous comparison we have performed recently for very dilute solutions and we would like to refer to this article, especially for the details of the solid state defect model and of the notation [12]. So we concentrate in the following only on the important defect equilibria in solid K_xKCl_{1-x} or $K_{1+\delta}Cl$. The formation of F-centers (V_{Cl}^x) is described by:

$$K + Cl_{Cl}^x \rightleftarrows KCl + V_{Cl}^x \tag{7}$$

With increasing x_K aggregation of F-centes to form n-mers is considered:

$$nV_{Cl}^x \rightleftarrows (V_{Cl})_n^x \tag{8}$$

In addition the ionization of F-centers and n-mers is taken into account:

$$V_{Cl}^x \rightleftarrows V_{Cl}^\bullet + e' \tag{9}$$

$$(V_{Cl})_n^x \rightleftarrows (V_{Cl})_n^\bullet + e'$$

where the electrons e' are assumed to be in conduction band states. Considering these equilibria together with internal equilibria like charge neutrality the following expression for the relation between metal activity and excess metal δ_K is derived:

$$\delta_K = \frac{x_K}{1-x_K} = K_I a_K + nK_{III}(K_I a_K)^n + \frac{K_I K_{II} a_K + nK_{III}K_{IV}(K_I a_K)^n}{(K_I K_{II} a_K + K_{III}K_{IV}(K_I a_K)^n)^{1/2}}$$

It contains the respective equilibrium constants K_I to K_{IV} corresponding to Eq. (7)–(10) and in addition the degree n of n-mers $(V_{Cl})_n^x$. In discussing Eq. (11), which is strictly valid in the solid, it is apparent that with increasing n the concentration dependence of $a_K(x_K)$ gets weaker. In crystalline K_xKCl_{1-x} activity data over a wide composition range as measured here in the liquid are not accessible. Fitting Eq. (11) to the liquid data of Fig. 5 and 6 at 800°C for $0 \leq \delta \leq 0.2$ yields the expected behaviour for varying n according to Eq. (11). This result is plotted in Fig. 9.

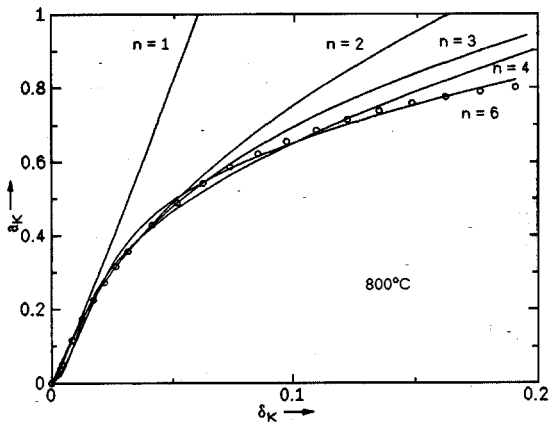

Fig. 9
Fit of the activity results of K_xKCl_{1-x} at 800 °C in the nonmetallic regime ($x_K < 0.2$) with the thermodynamic defect model; n denotes the number of aggregated F-centers

What can we learn from these fits of the thermodynamic model? Of course, it does not contain any information on changes in the density of states or the mechanism which controls the nonmetal-metal transition. It is an electronic defect model and emphasizes the particle or defect point of view. However, it clearly indicates that the concentration dependence of $a_K(x_K)$ cannot be explained with F-center defects alone over a wider range of x_K, but only in the dilute limit. With increasing x_K towards the nonmetal-metal transition a progressive aggregation of F-centers gives the correct $a_K(x_K)$ dependence as expected from the solid state defect thermodynamic model. In the context of the above statement the numbers n have no physical significance. But they indicate the trend of aggregation of localized states with x_K. Exactly in this respect the interpretation of the thermodynamics by the defect model is of interest. It directly links with the behaviour of the partial molar entropy as discussed above.

We are indebted to H. Heyer for his help in starting the first experiment. Financial support of this work by the DFG and in part by the Sonderforschungsbereich 195 "Lokalisierung von Elektronen in makroskopischen und mikroskopischen Systemen" of the DFG is gratefully acknowledged.

References

[1] M. A. Bredig, in: Molten Salt Chemistry, ed. M. Blander, Interscience, New York 1964.
[2] W. W. Warren, Jr., The Metallic and Nonmetallic States of Matter, ed. P. P. Edwards and C. N. R. Rao, Taylor and Francis, London 1985.
[3] W. Freyland, J. Non-Crystalline Solids *117/118*, 613 (1990).
[4] Th. Schindelbeck, D. Nattland, and W. Freyland, J. Physique IV, Colloque C5 *1*, 155 (1991).
[5] M. Parrinello and A. Rahman, J. Chem. Phys. *80*, 860 (1984).
[6] E. S. Fois, A. Selloni, M. Parrinello, and R. Car, J. Phys. Chem. *92*, 3268 (1988).
[7] N. Nicoloso and W. Freyland, Z. Phys. Chemie, Neue Folge *135*, 39 (1983).
[8] P. Chieux, J. F. Jal, L. Hily, J. Dupuy, F. Leclercq, and P. Damay, J. Physique IV, Colloque C5 *1*, 3 (1991).
[9] H. Yokokawa, O. J. Kleppa, and N. H. Nachtrieb, J. Chem. Phys. *71*, 4099 (1979) and J. Chem. Phys. *76*, 5574 (1982).
[10] M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta, *26*, 1275 (1981).
[11] K. Garbade and W. Freyland, Ber. Bunsenges. Phys. Chem. *92*, 1131 (1988).
[12] J. J. Egan and W. Freyland, Ber. Bunsenges. Phys. Chem. *89*, 381 (1985).
[13] J. Delcet, A. Delgado-Brune, and J. J. Egan, in: Calculations of Phase Diagrams and Thermochemistry of Alloys, p.275, The Metallurgical Society of AIME, Warendale, PA 1979.
[14] J. Delcet, R. Heus, and J. J. Egan, J. Electrochem. Soc.: Solid State Sci. Technol. *125*, 755 (1978).
[15]A. Petric, A. D. Pelton, and M. S. Saboungi, J. Phys. F: Met. Phys. *18*, 1473 (1988).
[16] J. J. Egan, in: High Temperature Sci. *19*, 111 (1985).
[17] A. Farcot, PHD Thesis, University Marseille 1984.
[18] P. Y. Achener et al., Thermophysical and Heat Properties of Alkali Metals, AGN-Report No. 8195, San Remo, California 1968.
[19] J. Schummer, Diplomarbeit, Universität Karlsruhe 1990.
[20] J. Blessing, Diplomarbeit, Universität Karlsruhe 1992.
[21] K. S. Pitzer, J. Am. Chem. Soc. *84*, 2025 (1962).
[22] D. Nattland, Th. Rauch, and W. Freyland, J. Chem. Phys., submitted (1992).

(Received: September 22th, 1992 E 8156
final version: November 5th, 1992)