

## Solution of Chlorine in NaCl–AlCl<sub>3</sub> and CsCl–AlCl<sub>3</sub> Melts

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The solubility of Cl<sub>2</sub> in molten NaCl–AlCl<sub>3</sub> and CsCl–AlCl<sub>3</sub> mixtures in the composition range 0–60 mol % AlCl<sub>3</sub> has been determined by a manometric technique. This involves keeping the gas volume above the melt constant and to measure the pressure decrease as the gas dissolves in the melt.

No pronounced difference between the solubility of Cl<sub>2</sub> in equimolar NaCl–AlCl<sub>3</sub> and CsCl–AlCl<sub>3</sub> melts was observed. Contrary to the pure alkali chlorides, a decreasing solubility with increasing temperature was found in the AlCl<sub>3</sub>-rich melts.

Positive enthalpies for the constant pressure dissolution process were found both for NaCl ( $\approx 50 \text{ kJ} \cdot \text{mol}^{-1}$ ) and CsCl ( $\approx 2 \text{ kJ} \cdot \text{mol}^{-1}$ ). With increasing AlCl<sub>3</sub> content a gradual decrease towards negative enthalpies ( $\approx -5 \text{ kJ} \cdot \text{mol}^{-1}$ ) was found for both equimolar mixtures. It was concluded that Cl<sub>2</sub> dissolves as Cl<sub>2</sub> molecules and that species as Cl<sub>3</sub><sup>-</sup> or AlCl<sub>3</sub> · nCl<sub>2</sub> are not stable. UV–VIS absorption spectra and Raman spectroscopy confirmed this conclusion.

Chloroaluminate melts are interesting solvents from a fundamental point of view as covalency and basicity can be varied within wide ranges. They have also attracted interest as battery electrolyte, electrolyte for aluminium production and reaction medium for chlorination. With respect to the bath properties chlorine solubility is an important parameter. Stupina *et al.*<sup>1</sup> have measured the solubility of Cl<sub>2</sub> in molten NaAlCl<sub>4</sub>, KAlCl<sub>4</sub> and NaCl–KCl–AlCl<sub>3</sub> melts. The solubility was found to exceed  $10^{-6} \text{ mol} \cdot \text{cm}^{-3}$ . The same was found for equimolar and acidic NaCl–AlCl<sub>3</sub> and CsCl–AlCl<sub>3</sub> mixtures, investigated by Carpio *et al.*<sup>2</sup> and by Wærnes and Østvold,<sup>3</sup> respectively, using a manometric method. Wærnes, Palmisano and Østvold<sup>4</sup> also measured the chlorine solubility in pure molten NaCl and NaCl–CsCl with 65 mol % CsCl. Borisoglebskii, Van Khyng and Vetyukov<sup>5</sup> determined the solubility of chlorine in NaCl–AlCl<sub>3</sub> and NaCl–KCl–AlCl<sub>3</sub> mixtures with AlCl<sub>3</sub> content up to 25 mol %. Increased solubility with increasing AlCl<sub>3</sub> content was observed.

### PRINCIPLES

*Chlorine solubility measurements.* The equilibrium (1) is studied:



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The partial standard Gibbs energy change for this dissolution reaction at constant pressure is given by

$$\Delta\bar{G}_P^0 = \Delta\bar{H}_P^0 - T\Delta\bar{S}_P^0 = -RT \ln K_P \quad (2)$$

where o denotes that  $\text{Cl}_2$  is in its standard state both in the gas and dissolved state.

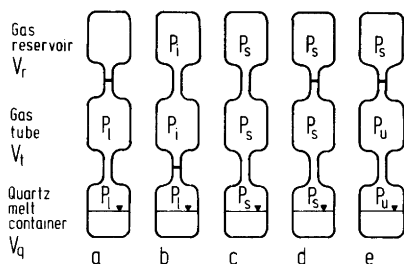
Assuming that Henry's law is valid for the solute and that  $\text{Cl}_2(\text{g})$  obeys the ideal gas law, the equilibrium constant,  $K_P$ , is equal to the inverse Henry's law constant

$$K_P = \frac{c_{\text{Cl}_2}(\text{diss})}{P_{\text{Cl}_2}(\text{g})} = \frac{\Delta n}{V\Delta P_{\text{eq}}} = \frac{\Delta n\rho}{w\Delta P_{\text{eq}}} \quad (3)$$

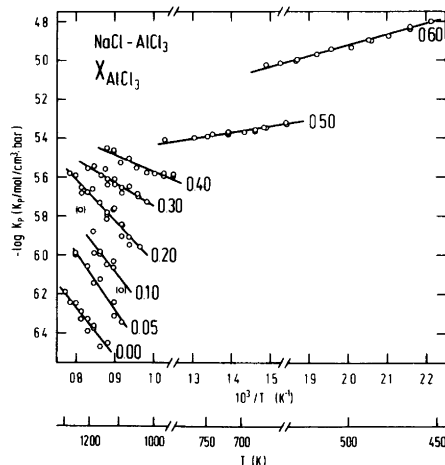
$\Delta n$  is the change in number of moles of  $\text{Cl}_2$  dissolved in the melt associated with a change in the equilibrium pressure of  $\text{Cl}_2$ ,  $\Delta P_{\text{eq}}$ ,  $V$  and  $\rho$  are the volume and the density, respectively, of the melt, and  $w$  the weight of salt. The change in equilibrium pressure was initiated by adding  $\text{Cl}_2(\text{g})$  to the cell using a procedure described in the experimental section.

At the standard chlorine pressure,  $K_P$  is equal to the solubility of chlorine. The partial enthalpy of dissolution is given by the equation

$$\Delta\bar{H}_P^0 = -R \ln K_P / d(1/T) \quad (4)$$



**Fig. 1.** Schematic diagram of the experimental procedure for the solubility measurements of chlorine in molten salts. a, a lower equilibrium pressure,  $P_1$ , is established. Except for a few measurements, a chlorine pressure of  $\approx 1$  bar was maintained above the melts. b, the valve to the melt container is closed and the pressure in the two thermostated volumes is increased to an initial pressure,  $P_i$ . c, then the valve to the melt container is opened and a start pressure,  $P_s$ , is obtained in the gas volumes. d, with the assumption that the pressure  $P_s$  is rapidly established before chlorine dissolves in the melt, the valve to the reservoir is closed. This is done to obtain a large pressure drop reading. e, due to the increased pressure above the melt, chlorine dissolves in the melt until a new upper equilibrium pressure,  $P_u$ , is obtained.



**Fig. 2.** Solubility of  $\text{Cl}_2$  in  $\text{NaCl}-\text{AlCl}_3$  melts plotted as  $\log K_P$  versus inverse temperature at different molfractions of  $\text{AlCl}_3$ ,  $X_{\text{AlCl}_3}$ .

Let us now consider the dissolution reaction (1) as a two step process as discussed by Blander *et al.*<sup>6</sup> The first step is an expansion of the gas to a concentration equal to the concentration of the gas in the dissolved state and the second step the dissolution at constant concentration. The enthalpy change for the first step is zero since the gas behaves ideally. The Gibbs energy for the total process, eqn. (1), is zero at equilibrium and due to ideal gas and Henry's law behaviour the partial entropy change for the total process at equilibrium is

$$\Delta\bar{S}_p = \Delta\bar{H}_p/T = \Delta\bar{H}_p^0/T \quad (5)$$

$\Delta\bar{S}_p$  involves the trivial entropy change due to the expansion of the gas for which the entropy change is

$$\Delta S' = -R \ln c_{\text{Cl}_2(\text{d})}/c_{\text{Cl}_2(\text{g})} \quad (6)$$

By subtracting eqn. (6) from eqn. (5) we find the partial entropy change for the dissolution process at constant concentration,

$$\Delta\bar{S}_c = \Delta\bar{H}_p^0/T + R \ln c_{\text{Cl}_2(\text{d})}/c_{\text{Cl}_2(\text{g})} \quad (7)$$

## EXPERIMENTAL

*Chemicals.* The purification and quality of salts are described elsewhere.<sup>7,8</sup>

*Solubility measurements.* The solubility of  $\text{Cl}_2$  was determined by a manometric technique. The  $\text{Cl}_2$  pressure was measured with a differential manometer (Model 145-O1, Precision Pressure Gage from Texas Instruments) using a quartz Bourdon capsule as the pressure sensing unit.

The method is comparable to the one described by Carpio *et al.*<sup>2</sup> and Wærnes *et al.*<sup>3,4</sup> but with some improvements.

Contrary to previous investigations, no extra calibration procedure due to the temperature gradient in the neck of the melt container was necessary in this work. The step by step experimental procedure, as schematically outlined and described in Fig. 1, was used to determine the Henry's law constant given in eqn. (3).

In Fig. 1 the solubility apparatus is, for convenience, divided into three parts: the quartz container with the melt, the thermostated pyrex tube connected to the Bourdon tube in the

*Table 1.* The solubility of  $\text{Cl}_2$  in fused  $\text{NaCl}-\text{AlCl}_3$  mixtures expressed as  $\log K_p = a_0 + a_1 \cdot (T/K)^{-1}$ . The values in the parentheses are corrected values obtained as explained in the discussion section. SD: Standard deviation.

$X_{\text{AlCl}_3}$	$a_0$	SD( $a_0$ )	$a_1$	SD( $a_1$ )	SD(log $K_d$ )
0.00	-4.263	0.214	-2508.8	259.2	0.027
0.05	-3.647	0.204	-2927.3	238.7	0.029
	(-3.90)		(-2632)		
0.10	-3.803	0.561	-2535.5	643.9	0.036
0.20	-3.915	0.123	-2120.9	139.3	0.031
0.30	-4.563	0.108	-1185.0	119.4	0.020
0.40	-4.724	0.087	-845.0	89.2	0.019
	(-5.25)		(-306)		
0.05	-5.754	0.028	-271.5	19.7	0.006
0.60	-5.012	0.044	-542.7	22.2	0.010

Table 2. The solubility of Cl<sub>2</sub> in fused CsCl–AlCl<sub>3</sub> mixtures expressed as  $\log K_p = a_0 + a_1 \cdot (T/K)^{-1}$ . The values in the parentheses are corrected values obtained as explained in the discussion section. SD: Standard deviation.

$X_{\text{AlCl}_3}$	$a_0$	SD( $a_0$ )	$a_1$	SD( $a_1$ )	SD(log $K_d$ )
0.00	-5.383	0.045	-114.2	47.8	0.007
0.05	-5.707 (-5.480)	0.032	252.0 (20.1)	31.8	0.006
0.10	-5.559	0.022	123.5	23.3	0.006
0.20	-5.627 (-5.660)	0.020	220.8 (254.6)	20.5	0.005
0.30	-5.717	0.022	315.5	21.4	0.005
0.30	-5.689	0.046	293.6	42.6	0.008
0.40	-5.658	0.023	257.2	21.1	0.009
0.49	-5.669	0.015	267.7	11.5	0.007
0.52	-5.661	0.062	263.3	46.6	0.016

manometer, and the thermostated gas reservoir. The partial gas volumes are then denoted  $V_q$ ,  $V_t$  and  $V_r$ , respectively.

As the valve to the reservoir is closed during the dissolution process (steps d and e in Fig. 1) only the gas volumes  $V_q$  and  $V_t$  are used in the calculation of the amount of dissolved chlorine,  $\Delta n$ . Using the ideal gas law

$$\Delta n = \left[ \frac{P_s \cdot V_t}{R \cdot T_t} + \frac{P_s \cdot V_q}{R \cdot T_q} \right] - \left[ \frac{P_u \cdot V_t}{R \cdot T_t} + \frac{P_u \cdot V_q}{R \cdot T_q} \right] = \frac{1}{R} (P_s - P_u) \left[ \frac{V_t}{T_t} + \frac{V_q}{T_q} \right] \quad (8)$$

where

$\Delta n$  – moles of dissolved chlorine

$P_s, P_u$  – chlorine pressures defined in the text of Fig. 1

$V_t, V_q$  – gas volumes of tube and quartz container, respectively

$T_t, T_q$  – temperature of thermostated gas, and mean temperature in the quartz container gas volume, respectively.

In eqn. (8)  $V_q/T_q$  is not known. This ratio can, however, be eliminated using steps b) and c) in the experimental procedure (Fig. 1), as the total chlorine content in the gas volumes  $V_r$ ,  $V_t$  and  $V_q$  does not vary during this step (b → c). This gives

$$\frac{P_i}{RT_t} (V_r + V_t) + \frac{P_1}{RT_q} \cdot V_q = \frac{P_s}{R} \left[ \frac{V_r + V_t}{T_t} + \frac{V_q}{T_q} \right] \quad (9)$$

Rearranged

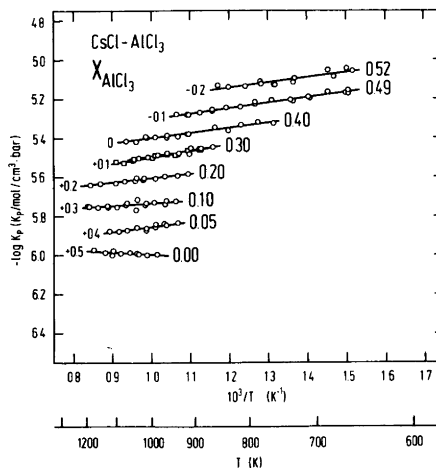
$$\frac{V_q}{T_q} = \frac{P_s - P_i}{P_1 - P_s} \cdot \frac{V_r + V_t}{T_t} \quad (10)$$

In these equations

$V_r$  – gas volume of thermostated reservoir

$P_i, P_1$  – chlorine pressures defined in the text, of Fig. 1.

Fig. 3. Solubility of  $\text{Cl}_2$  in  $\text{CsCl}-\text{AlCl}_3$  melts plotted as  $\log K_P$  versus inverse temperature at different molfractions of  $\text{AlCl}_3$ ,  $X_{\text{AlCl}_3}$ . Due to small differences in solubility between different compositions, the lines are shifted relative to the  $\log K_P$  scale with a certain value given at the left side of each line. If the number is +0.5 and the scale reads 6.0 for  $\log K_P$  at a certain  $T$  the real value is 5.5.



If  $V_q/T_q$  as obtained by eqn. (10) is substituted for  $V_q/T_g$  in eqn. (8), and the melt volume is expressed by the density and the weight of the salt,  $K_P$  can be expressed by

$$K_P = \frac{\Delta n/V}{\Delta P} = \frac{\Delta n \rho/w}{P_u - P_l}$$

$$= \frac{\rho}{RTw} \cdot \frac{(P_s - P_u)}{(P_u - P_l)(P_s - P_l)} \left[ (P_l - P_l)V_l + (P_l - P_s)V_r \right] \quad (11)$$

With the density in  $\text{g cm}^{-3}$ , weight of the sample in g, temperature in K, pressure in bar, volumes in  $\text{cm}^3$ , and the gas constant  $R=83.143 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ , the inverse Henry's law constant,  $K_P$ , will have units  $\text{mol cm}^{-3} \text{ bar}^{-1}$ .

**Spectrometry.** The absorption spectra of  $\text{Cl}_2$  were recorded as reported previously.<sup>2,7,8</sup>

The Raman spectra of  $\text{Cl}_2$  in  $\text{CsCl}-\text{AlCl}_3$  melts at  $X_{\text{AlCl}_3} \approx 0.5$  were recorded on a JEOL-400D spectrophotometer. The chloride melts were excited by an argon ion laser at 514.5 nm.

## RESULTS

**Chlorine solubilities.** The solubility of  $\text{Cl}_2$  in  $\text{NaCl}-\text{AlCl}_3$  and  $\text{CsCl}-\text{AlCl}_3$  melts have been determined in the composition range 0–60 mol %  $\text{AlCl}_3$ . The validity of Henry's law was tested by measuring the  $\text{Cl}_2$  solubility at different  $\text{Cl}_2$  pressures as described previously.<sup>3</sup> Results of the present investigation are presented in Figs. 2 and 3 and in Tables 1 and 2.

**Absorption spectra.** Absorption spectra of chlorine in acidic ( $X_{\text{AlCl}_3} > 0.50$ ) and basic  $\text{NaCl}-\text{AlCl}_3$  and  $\text{CsCl}-\text{AlCl}_3$  melts have been recorded. The work has been focused on compositions near the equimolar concentration. Spectra of chlorine in pure molten alkali chlorides have been published by Andresen *et al.*<sup>7,8</sup>

In Figs. 4 and 5 the total absorption spectra, the background spectra and the difference spectra for  $\text{NaCl}-\text{AlCl}_3$  mixtures with 48 and 51 mol %  $\text{AlCl}_3$  are presented. The spectra show an absorption band at approximately 30.3 kK, which is the same wavenumber as observed for absorption in pure chlorine gas. In contrast to the  $\text{NaCl}-\text{AlCl}_3$  system, there

Table 3. Optical density of Cl<sub>2</sub> in chloroaluminate melts. The optical density is defined through the relation  $A = \log I_0/I = \varepsilon cl$  where  $I_0$ ,  $I$  is the intensity of the incident and transmitted light at wavenumber  $\nu$ , respectively,  $\varepsilon$  the molar absorption coefficient at wavenumber  $\nu$ ,  $c$  the concentration of the light-absorbing species and  $l$  the optical path length being 5 mm for all measurements.

Solvent	Com- position (mol %)	Tem- perature (K)	Optical density		Concen- tration $10^6 \cdot c_{Cl_2}$ (mol · cm <sup>-3</sup> )	Absorption coefficient (1 · mol <sup>-1</sup> · cm <sup>-1</sup> )		Optical density of Cl <sub>2</sub>	
			$A_{30.3}$	$A_{30.3}^a$		$\varepsilon_{30.3}$	$\varepsilon_{30.3}^a$	$A_{30.5}(\text{melt})^a$	$A_{30.5}(\text{gas})$
NaCl-AlCl <sub>3</sub>	55-45	735	0.245	0.220	3.113	157.4	141.4	0.081	2.72
NaCl-AlCl <sub>3</sub>		787	0.238	0.216	3.102	153.5	139.3	0.078	2.77
NaCl-AlCl <sub>3</sub>		839	0.234	0.211	3.092	151.4	136.5	0.076	2.78
NaCl-AlCl <sub>3</sub>	52-48	941	0.245	0.207	3.077	159.3	134.6	0.072	2.88
NaCl-AlCl <sub>3</sub>		1048	0.232	0.207	3.064	151.4	135.1	0.068	3.04
NaCl-AlCl <sub>3</sub>		735	0.220	0.209	3.845	114.4	108.7	0.100	2.09
NaCl-AlCl <sub>3</sub>		786	0.207	0.198	3.707	111.7	106.8	0.093	2.13
NaCl-AlCl <sub>3</sub>	50.5-49.5	838	0.193	0.184	3.588	107.6	102.6	0.088	2.09
NaCl-AlCl <sub>3</sub>		944	0.182	0.159	3.394	107.3	93.7	0.079	2.01
NaCl-AlCl <sub>3</sub>		1047	0.179	0.147	3.250	110.1	90.5	0.072	2.04
NaCl-AlCl <sub>3</sub>		573	0.233	0.233	5.147	90.5	90.5	0.150	1.55
NaCl-AlCl <sub>3</sub>	50-50	625	0.210	0.171	4.729	88.8	78.0	0.130	1.62
NaCl-AlCl <sub>3</sub>		680	0.173	0.138	4.386	78.9	70.8	0.120	1.43
NaCl-AlCl <sub>3</sub>		788	0.148	0.138	3.900	75.9	70.8	0.098	1.41
NaCl-AlCl <sub>3</sub>		501	0.346	0.346	6.139	112.7	112.7	0.180	1.92
NaCl-AlCl <sub>3</sub>	NaCl-AlCl <sub>3</sub>	554	0.276	0.276	5.448	101.3	101.3	0.160	1.73
NaCl-AlCl <sub>3</sub>		608	0.210	0.210	4.928	85.2	85.2	0.140	1.50
NaCl-AlCl <sub>3</sub>		708	0.151	0.151	4.262	70.9	70.9	0.110	1.37

NaCl-AlCl <sub>3</sub>	49-51	487	0.465	0.460	7.105	130.9	129.5	0.210	2.19
NaCl-AlCl <sub>3</sub>		533	0.383	0.374	6.261	122.4	119.5	0.180	2.08
NaCl-AlCl <sub>3</sub>		581	0.309	0.306	5.605	110.3	109.2	0.160	1.91
NaCl-AlCl <sub>3</sub>	45-55	464	0.776	0.751	6.726	230.7		0.210	3.58
NaCl-AlCl <sub>3</sub>		473	0.750	0.725	6.514	230.3		0.200	3.63
NaCl-AlCl <sub>3</sub>		521	0.594	0.569	5.592	212.4		0.170	3.35
NaCl-AlCl <sub>3</sub>		571	0.470	0.445	4.903	191.7		0.140	3.18
NaCl-AlCl <sub>3</sub>		649	0.281	0.239	4.158	135.2		0.110	2.17
CsCl-AlCl <sub>3</sub>	60-40	827	2.104	4.496	4.420	936.0			
CsCl-AlCl <sub>3</sub>		847	2.113	4.420	4.420	956.0			
CsCl-AlCl <sub>3</sub>		878	2.203	1021.7	4.313	1021.7			
CsCl-AlCl <sub>3</sub>	55-45	856	0.841	389.5	4.319	389.5			
CsCl-AlCl <sub>3</sub>	52-48	708	0.454	182.3	4.981	182.3	145.7	0.130	2.79
CsCl-AlCl <sub>3</sub>		750	0.477	200.5	4.757	200.5	171.1	0.120	3.39
CsCl-AlCl <sub>3</sub>		795	0.461	200.5	4.552	200.5	173.5	0.110	3.59
CsCl-AlCl <sub>3</sub>	51-49	709	0.392	153.7	5.100	153.7	123.5	0.130	2.42
CsCl-AlCl <sub>3</sub>		750	0.385	158.3	4.864	158.3	129.5	0.130	2.42
CsCl-AlCl <sub>3</sub>		795	0.387	166.7	4.644	166.7	139.1	0.120	2.69
CsCl-AlCl <sub>3</sub>	50-50	700	0.335	129.4	5.176	129.4	124.4	0.140	2.30
CsCl-AlCl <sub>3</sub>		752	0.289	118.6	4.872	118.6	115.8	0.130	2.17
CsCl-AlCl <sub>3</sub>		837	0.264	117.7	4.485	117.7	113.3	0.110	2.31
CsCl-AlCl <sub>3</sub>	45-55	662	0.382	0.254	5.660	135.0		0.150	2.55

<sup>a</sup> Corrected values due to absorption overlap.

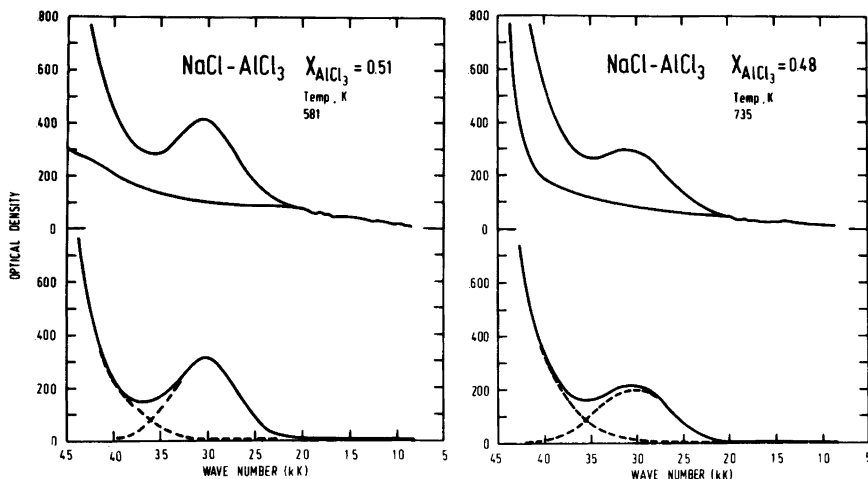


Fig. 4. Absorption spectra of NaCl-AlCl<sub>3</sub> with Cl<sub>2</sub> dissolved.  $P_{\text{Cl}_2} \approx 1$  bar. Upper part: With and without chlorine. Lower part: Difference spectrum. Optical path length: 5.00 mm.

are marked spectral differences between acidic and basic CsCl-AlCl<sub>3</sub> melts. This can be observed in Fig. 5 by comparing the absorption spectra of chlorine in CsCl-AlCl<sub>3</sub> for melts with 49 and 55 mol % AlCl<sub>3</sub>. An additional absorption band is partly overlapping the 30.3 kK band and appears as a shoulder on the strongly increasing charge transfer contour observed for the basic melts. The broken lines in Figs. 4 and 5 indicate how the difference spectrum is resolved into different absorption bands.

The total absorption at 30.3 kK is presented for all measurements in Table 3. The resolved absorption at 30.3 kK is presented for experiments with partly overlapping bands. To perform this resolution it is assumed that the absorption at the low wavenumber side of

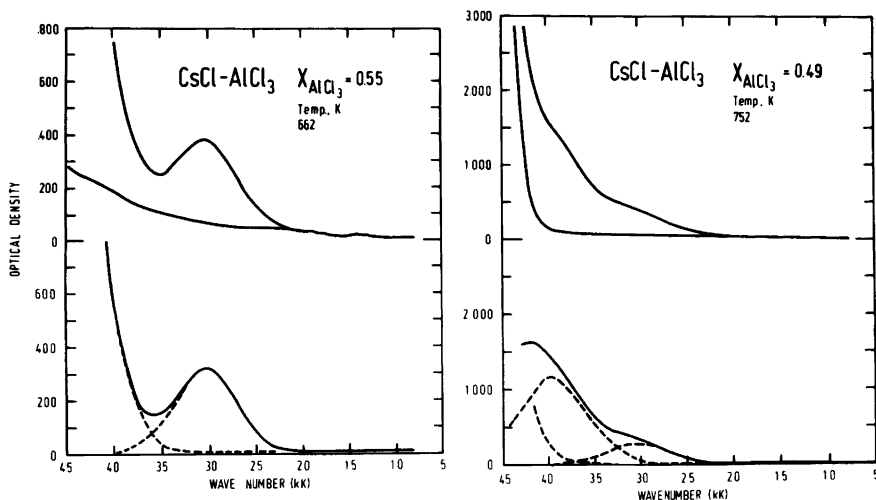


Fig. 5. Absorption spectra of CsCl-AlCl<sub>3</sub> melts with Cl<sub>2</sub> dissolved.  $P_{\text{Cl}_2} \approx 1$  bar. Upper part: With and without chlorine. Lower part: Difference spectrum. Optical path length: 5.00 mm.



the spectrum solely belongs to this band and A symmetrical band at 30.3 kK band may then be constructed. Resolution has not been performed for spectra recorded with high CsCl concentrations since the charge transfer overlap for these melts is so pronounced that resolution is uncertain.

In Table 3 several other parameters are presented in addition to the chlorine absorptions. First, the absorption coefficients calculated with chlorine concentrations obtained from the solubility measurements ( $P_{\text{Cl}_2}=1$  bar) are presented. For comparison, the absorption by pure chlorine gas at the same concentration as in the saturated melts is included in the table. Also the ratio between the dissolved gas single band absorption at 30.3 kK and the pure chlorine gas absorption at 30.5 kK is given. The absorption of chlorine gas is calculated from the data of Jacobs and Giedt<sup>9</sup> with a formula first presented by Sulzer and Wieland.<sup>10</sup> The data of Jacobs and Giedt<sup>9</sup> are chosen as they correspond reasonably well with data obtained by Andresen and Skjølvold<sup>11</sup> and Seery and Britton.<sup>12</sup> Compared with the data of Gibson and Bayliss,<sup>13</sup> the later investigations report slightly higher values for the chlorine molar absorption coefficient.

**Raman spectra.** In the composition range 45 to 55 mol %  $\text{AlCl}_3$ , a limited number of  $\text{CsCl}-\text{AlCl}_3$  mixtures with and without chlorine additions have been examined by Raman spectroscopy.<sup>14</sup> The pure  $\text{CsCl}-\text{AlCl}_3$  melts have been investigated by Rytter *et al.*<sup>15</sup> and only the wavenumber region where new features are observed is presented. The spectra of basic and acidic melts are presented in Fig. 6. The chlorine pressure above these melts is in the range 8–12 bar. For basic as well as acidic melts with dissolved chlorine a weak, polarized shoulder is observed on the high frequency side of the  $\nu_3$  vibration frequency of  $\text{AlCl}_4^-$ . Additional spectra with chlorine pressures in the range 1–2 bar show the same features as those presented here.<sup>16</sup>

## DISCUSSION

**Experimental accuracy.** The relative error in the determination of  $K_P$  as determined from estimated errors in the experimental parameters is  $\pm 5\%$ .<sup>13</sup> The main contribution to this

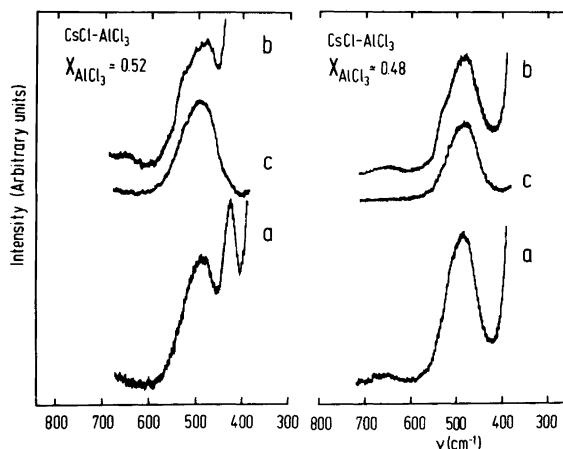


Fig. 6. Raman spectra of acidic and basic  $\text{CsCl}-\text{AlCl}_3$  melts at approximately 400 °C. Excitation line: 514.5 nm.  $P_{\text{Cl}_2} \approx 8-10$  bar. a, melt without  $\text{Cl}_2$  (unpolarized). b, melt with  $\text{Cl}_2$  (unpolarized). c, melt with  $\text{Cl}_2$  (polarized).

error comes from the uncertainty in the determination of the upper equilibrium pressure. This uncertainty is unique as it contributes 5–10 times more to the total error than the random errors introduced via the other parameters.<sup>16</sup> Due to a relatively large temperature gradient  $1\text{ }^{\circ}\text{C cm}^{-1}$  across the cell, the melt temperature can be determined only with a precision of  $\pm 5\text{ }^{\circ}\text{C}$ . This gradient is necessary to obtain quick dissolution of the gas, but will introduce an error in a temperature dependent solubility as for the NaCl-rich melts.

The absorption spectra were recorded with a pressure of  $\text{Cl}_2$  of  $1\text{ bar} \pm 0.07\text{ bar}$ . The loss of salt from the experimental cell containing  $\approx 1\text{ cm}^3$  of melt was too small to be detected in most of the observed spectra. However, at the highest temperatures  $\approx 650\text{ }^{\circ}\text{C}$  and with  $X_{\text{AlCl}_3} = 0.55$  some change in the spectra with time could be observed.

*Chlorine solubility.* The logarithm of the solubility, expressed as the inverse Henry's law constant,  $K_P$ , may be fitted to linear equations of the inverse melt temperature,  $T$ , according to eqn. (12).

$$\log K_P = a_0 + a_1(T/K)^{-1} \quad (12)$$

The coefficients  $a_0$  and  $a_1$  (Tables 1 and 2) are plotted as function of mole fraction  $\text{AlCl}_3$  in Fig. 7. Except for two compositions in each of the NaCl– $\text{AlCl}_3$  and CsCl– $\text{AlCl}_3$  systems,  $a_0$  and  $a_1$  vary continuously with the change in composition. As  $a_0$  is the intercept on the  $\log K_P$  axis for  $T^{-1} \rightarrow 0$ ,  $a_0$  is sensitive to uncertainties in the temperature dependence of the solubility. It is believed that the discontinuity in the  $a_0$  values at 5 and 40 mol %  $\text{AlCl}_3$  in NaCl and at 5 and, possibly, 20 mol %  $\text{AlCl}_3$  in CsCl are due to erroneous temperature dependence of the experimental  $K_P$  values. The  $a_0$  values are, hence, corrected according to the curves given in Fig. 7. To perform a check on the magnitude of the solubilities for those experiments with corrected  $a_0$  values, the experimental solubilities were fitted to a line passing through the corrected point. The value thus obtained for the slope,  $a_1$ , matched

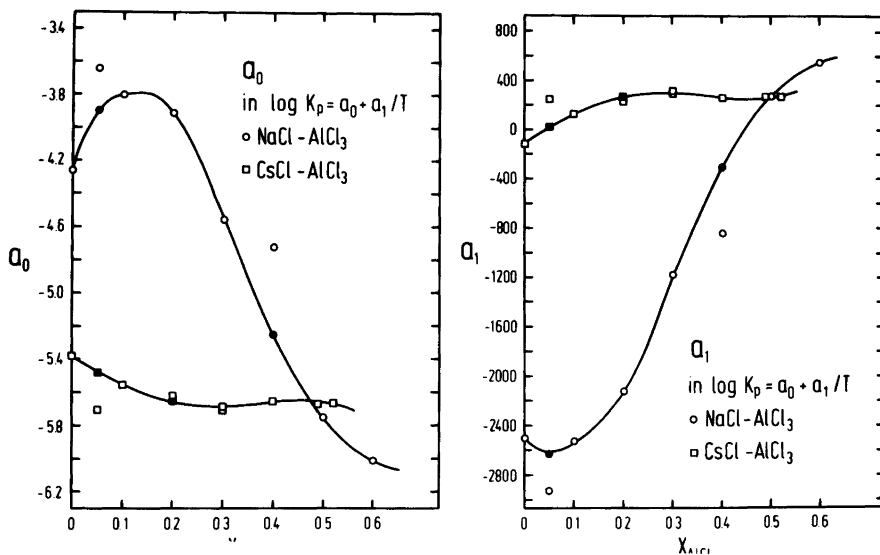


Fig. 7. Composition dependence of  $a_0$  and  $a_1$  (eqn. (12)) for the NaCl– $\text{AlCl}_3$ (O) and CsCl– $\text{AlCl}_3$ (□) systems. Filled symbols are corrected values.

perfectly the continuous change in  $a_1$  as function of composition. The corrected values are used in the thermodynamic calculations.

The thermodynamic quantities are calculated according to the constant concentration dissolution method presented earlier. The chosen standard states are pure gas at pressure  $P^\circ=1$  bar and dissolved gas at concentration  $C_a^\circ=1$  mol cm<sup>-3</sup>. The standard partial enthalpy,  $\Delta H_p^\circ$ , and entropy,  $\Delta S_p^\circ$ , of dissolving 1 mol cm<sup>-3</sup> gas at 1 bar are directly related to the slope and intercept of the plot of  $\log K_p$  versus  $T^{-1}$ .

$$\Delta \bar{H}_p^\circ = a_1 \cdot R \ln 10 \quad (13)$$

$$\Delta \bar{S}_p^\circ = -a_0 \cdot R \ln 10 \quad (14)$$

The calculated  $\Delta \bar{H}_p^\circ$  and  $\Delta \bar{S}_p^\circ$  for each measured composition is presented in Table 4. The quoted uncertainties are calculated from the standard deviations in the coefficients  $a_0$  and  $a_1$  as presented in Tables 1 and 2. Also presented in Table 4 is the entropy of the constant pressure dissolution,  $\Delta \bar{S}_p$  [eqn. (5)], and the entropy of the constant concentration dissolution,  $\Delta \bar{S}_c$  [eqn. (7)]. As these two values are temperature dependent, a standard temperature of 1000 K is adopted although this is in some cases below the melting point or outside the experimental range.

*Enthalpy of dissolution.* The partial standard enthalpy of chlorine dissolution at constant pressure,  $\Delta \bar{H}_p^\circ$ , shown an almost continuous change from positive values for the pure alkali chlorides towards negative values with increasing AlCl<sub>3</sub> content. The most pronounced feature is, however, the large endothermic dissolution in NaCl compared to CsCl. In the equimolar mixtures, NaAlCl<sub>4</sub> and CsAlCl<sub>4</sub>, equal exothermic enthalpies of chlorine dissolution are observed.

The dissolution process, eqn. (1), may be divided into a condensation and a mixing process. As the enthalpy of condensation will be the same at constant temperature and concentration of dissolved gas, the differences observed between the NaCl and CsCl systems must be due to a large endothermic enthalpy of mixing for Cl<sub>2</sub> with the NaCl rich NaCl–AlCl<sub>3</sub> systems. The difference  $\Delta \bar{H}_p^\circ(\text{NaCl–AlCl}_3) - \Delta \bar{H}_p^\circ(\text{CsCl–AlCl}_3)$  are about 50 kJ/mol for  $0 < X_{\text{AlCl}_3} < 0.20$  and it then drops to zero for  $X_{\text{AlCl}_3} = 0.50$ . Since

$$\Delta \bar{H}_p^\circ = -\Delta H_{\text{vap}}^\circ + \Delta \bar{H}_{\text{Cl}_2}^{\text{mix}} \quad (15)$$

this difference is equal to the difference in the partial enthalpy of mixing of Cl<sub>2</sub> in the two systems. Hence, considerably more energy is required to introduce Cl<sub>2</sub> molecules into liquid NaCl than CsCl.

Apparently, the difference in the Cl<sub>2</sub> partial enthalpy of mixing (or dissolution) in NaCl compared to CsCl can partly be explained by the difference in melt structure. The higher charge density of the Na<sup>+</sup> ions compared to the Cs<sup>+</sup> ions will make the melt structure less open in NaCl, and more energy is consequently needed to introduce Cl<sub>2</sub> molecules into NaCl compared to CsCl melts. The polarizable Cs<sup>+</sup> ion may also more easily rearrange its electron distribution to accommodate a neutral molecule in its vicinity. The observed enthalpy change with increasing AlCl<sub>3</sub> content is interpreted as a larger structural change in the NaCl–AlCl<sub>3</sub> system than in the CsCl–AlCl<sub>3</sub> system. The equal dissolution enthalpies for  $X_{\text{AlCl}_3} = 0.50$  indicate minor cation interactions with Cl<sub>2</sub> in these melts.

Table 4. Thermodynamic quantities for the dissolution of  $\text{Cl}_2$  in  $\text{NaCl}-\text{AlCl}_3$  and  $\text{CsCl}-\text{AlCl}_3$  melts.  $\Delta\bar{H}_P$ ,  $\Delta\bar{S}_P$  and  $K_P$  are calculated at 1000 K.

Solvent	Com- position (mol %)	Temp. range (K)	Fitted values	$\Delta\bar{H}_P \pm \text{SD}$ Eqn. (13) (kJ · mol <sup>-1</sup> )	$\Delta\bar{S}_P \pm \text{SD}$ Eqn. (14) (J · mol <sup>-1</sup> · K <sup>-1</sup> )	$\Delta\bar{S}_P$ Eqn. (5) (J · mol <sup>-1</sup> · K <sup>-1</sup> )	$\Delta\bar{S}_c$ Eqn. (7) (J · mol <sup>-1</sup> · K <sup>-1</sup> )	$K_P \cdot 10^7$ Eqn. (3) (mol · cm <sup>-3</sup> · bar <sup>-1</sup> )
NaCl	100	1100–1300	11	48.0 ± 5.0	-81.6 ± 4.1	48	13	1.7
NaCl–AlCl <sub>3</sub>	95–5	1075–1275	9	50.4 ± 4.6	-74.7 ± 3.8	50	20	2.9
NaCl–AlCl <sub>3</sub>	90–10	1100–1200	8	48.5 ± 12.3	-72.8 ± 10.7	49	21	4.6
NaCl–AlCl <sub>3</sub>	80–20	1000–1300	19	40.6 ± 2.7	-75.0 ± 2.3	41	19	9.2
NaCl–AlCl <sub>3</sub>	70–30	1000–1225	14	22.7 ± 2.3	-87.4 ± 2.1	23	7	18
NaCl–AlCl <sub>3</sub>	60–40	950–1150	13	5.9 ± 1.7	-100.5 ± 1.7	6	-6	28
NaCl–AlCl <sub>3</sub>	50–50	625–825	14	-5.2 ± 0.4	-110.2 ± 0.6	-5	-16	33
NaCl–AlCl <sub>3</sub>	40–60	450–575	13	-10.4 ± 0.4	-115.1 ± 0.8	-10	-21	34
CsCl	100	975–1175	10	2.2 ± 0.9	-103.1 ± 0.9	2	-9	32
CsCl–AlCl <sub>3</sub>	95–5	925–1125	11	0.4 ± 0.6	-104.9 ± 0.6	0	-11	35
CsCl–AlCl <sub>3</sub>	90–10	925–1200	14	-2.4 ± 0.4	-106.4 ± 0.4	-2	-12	37
CsCl–AlCl <sub>3</sub>	80–20	900–1200	13	-4.8 ± 0.4	-108.4 ± 0.4	-5	-14	39
CsCl–AlCl <sub>3</sub>	70–30	875–1100	12	-6.0 ± 0.4	-109.4 ± 0.4	-6	-15	40
CsCl–AlCl <sub>3</sub>	70–30	850–1025	10	-5.6 ± 0.8	-108.9 ± 0.9	-5	-15	40
CsCl–AlCl <sub>3</sub>	60–40	750–1075	15	-4.9 ± 0.4	-108.3 ± 0.4	-5	-14	40
CsCl–AlCl <sub>3</sub>	51–49	650–950	19	-5.1 ± 0.2	-108.5 ± 0.3	-5	-14	40
CsCl–AlCl <sub>3</sub>	48–52	650–875	12	-5.0 ± 0.9	-108.4 ± 1.2	-5	-14	40

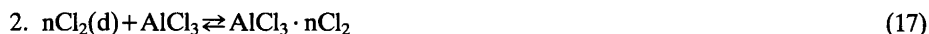
*Entropy of dissolution.* The partial standard entropy of chlorine dissolution,  $\Delta\bar{S}_p^\circ$ , is expected to be negative, since the gas concentration at 1 bar is considerably lower than the hypothetical  $1 \text{ mol} \cdot \text{cm}^{-3}$  standard state concentration in solution. Except for the basic NaCl–AlCl<sub>3</sub> melts, fairly equal entropies ( $-100$  to  $-110 \text{ J mol}^{-1}\text{K}^{-1}$ ) are obtained.

The partial chlorine entropy of dissolution at constant pressure,  $\Delta\bar{S}_p$ , gives the difference between the entropy of the dissolved gas at the solubility concentration and the entropy of the gas at 1 bar. Under otherwise equal conditions for the dissolved Cl<sub>2</sub>, this entropy difference will increase with decreasing solubility, that is, with decreasing chlorine concentration in the melt relative to the concentration in the gas phase. The gas phase concentration at 1000 K is  $1.2 \cdot 10^{-5} \text{ mol cm}^{-3}$  and the dissolved Cl<sub>2</sub> concentration, as presented in Table 4, is always lower. Thus, one might expect the partial entropy of dissolution,  $\Delta\bar{S}_p$ , to be positive. This is, however, only obtained in basic NaCl–AlCl<sub>3</sub> melts and pure molten CsCl where the lowest solubilities are found. A possible explanation may be that the entropy of the dissolved gas is reduced due to restrictions imposed by the melt environment. As a reduction of the translational entropy is anticipated in the solution, the total entropy change by dissolving chlorine in the melt may well be negative.

The entropy change for the constant concentration dissolution of chlorine,  $\Delta S_c$ , is also presented in Table 4. As the gas is assumed to be ideal and Henry's law is found to be valid, the entropy value is independent of the actual chlorine concentration. At equal chlorine concentrations in the melt and the gas phase, a reduction in the partial entropy of chlorine in the melt compared to the gas phase is expected as discussed above resulting in a negative  $\Delta S_c$  for the majority of the mixtures investigated. This is not obtained for basic NaCl–AlCl<sub>3</sub> melts and indicates a different dissolution mechanism in these melts. Some factors than can contribute to an increased entropy of Cl<sub>2</sub> are:

- associations of Cl<sub>2</sub> with ions in the melt resulting in new species and increasing configurational entropy,
- weakening of the bonds in Cl<sub>2</sub> resulting in an increased vibrational energy.

Several dissolution mechanisms have been proposed for chlorine dissolution in chloride melts. We will only mention those which we find most reasonable:



The first mechanism was suggested already in 1958 by Greenberg and Sundheim<sup>17</sup> and was based on spectroscopic measurements. This mechanism has been adopted by Kowalski and Harrington<sup>18</sup> to explain the observed chlorine solubility and results from radioisotopic exchange measurements in KCl–PbCl<sub>2</sub> melts. Van Norman and Tivers<sup>19</sup> explained diffusion and solubility measurements in eutectic LiCl–KCl and pure PbCl<sub>2</sub> melts by this reaction.

The second model was presented by Stupina *et al.*<sup>1</sup> to explain the solubility of Cl<sub>2</sub> in sodium and potassium tetrachloroaluminates. This mechanism was also used by Borisoglebskii *et al.*<sup>5,20</sup> to explain the solubility and observed decrease in the diffusion coefficient for Cl<sub>2</sub> with increasing AlCl<sub>3</sub> content in chloroaluminate mixtures. New data, however, on the variation of the diffusion constant of dissolved Cl<sub>2</sub>,  $D_{\text{Cl}_2}$ , with increasing AlCl<sub>3</sub> content in chloroaluminate melts indicate an increase rather than a decrease of  $D_{\text{Cl}_2}$ .<sup>3</sup>

The present set of experimental data does not give substantial support to any of the proposed dissolution mechanisms. The solubility of chlorine should, according to both

models, change considerably at  $X_{\text{AlCl}_3}=0.5$  due to the change in the  $\text{AlCl}_3$  or  $\text{MCl}$  activity at this composition. This is, however, not the case, Figs. 2 and 3. Neither does the Raman spectra exhibit any spectrum changes around  $X_{\text{AlCl}_3}=0.5$ , Fig. 6.

In the melt an absorption band appears very close to the location of the band for gaseous chlorine, 30.3 kK versus 30.5 kK. No profound changes in the absorption band of chlorine dissolved in  $\text{NaCl}-\text{AlCl}_3$  melts are observed around  $X_{\text{NaCl}}=0.5$ , Fig. 4. We hence conclude that chlorine dissolves as  $\text{Cl}_2$  in the melts.

There are, however, some small noteworthy changes. The 30.3 kK band is stronger in the melt than in the gas (Table 3) and it has minimum strength at  $X_{\text{AlCl}_3}=0.50$ . The higher molar absorptivity and the minimum at  $X_{\text{AlCl}_3}=0.50$  might be understood as due to polarization of the  $\text{Cl}_2$  molecule, the melt  $\text{Al}_2\text{Cl}_6$  being the most inert in this respect.

The origin of the band at approximately 40 kK for  $\text{CsCl}-\text{AlCl}_3$  melts is at present not known. Several alternatives exist, including complexed  $\text{Cl}_2$  species or perturbed  $\text{Cl}_2$  molecules where forbidden transitions become allowed. Another possibility is a transition from an ionic excited state to a lower lying state of covalent character as observed for the laser induced emission of  $\text{Cl}_2^{21,22}$  at 258 nm (38.8 kK). As this band is visible only for  $\text{CsCl}$  melts, it may be attributed to effects due to the cation. Either the same condition does not exist in  $\text{NaCl}$  melts or an analogous band in  $\text{NaCl}$  is shifted towards shorter wavelengths and, hence, totally shielded by the charge transfer rise.

*Comparison with published data. Gas solubilities in molten salts.* Field<sup>23</sup> has reviewed the literature on gas solubility in molten salts up to 1973. The results may roughly be classified in three categories according to the values of the enthalpy of dissolution,  $\Delta\bar{H}_p^\circ$ , and the entropy of constant concentration dissolution,  $\Delta\bar{S}_c$ ,

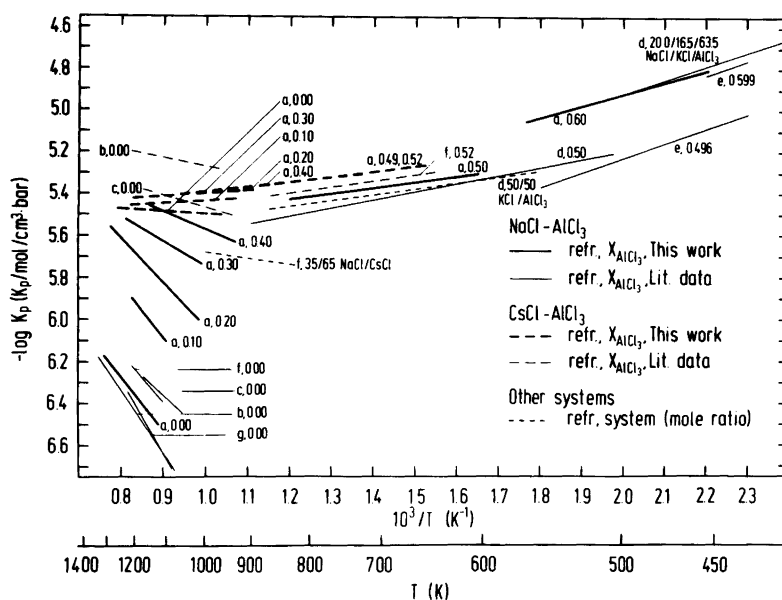


Fig. 8. Solubility of  $\text{Cl}_2$  in different chloride melts expressed as  $\log K_p$  versus inverse melt temperature. The reference letters a-g are: a, this work. b, Ryabukhin and Bekun.<sup>24</sup> c, Andresen *et al.*<sup>7,8</sup> d, Stupina *et al.*<sup>1</sup> e, Carpio *et al.*<sup>2</sup> f, Wærnes *et al.*<sup>3,4</sup> g, Borisoglebskii *et al.*<sup>5</sup>

- “non-reactive” systems with  $\Delta\bar{H}_p^\circ > 0$  and  $\Delta\bar{S}_c < 0$
- “reactive” systems with  $\Delta\bar{H}_p^\circ < 0$  and  $\Delta\bar{S}_c < 0$
- “anomalous” systems with  $\Delta\bar{H}_p^\circ > 0$  and  $\Delta\bar{S}_c > 0$

Chlorine in alkali chlorides, except for CsCl, are found to belong to the “anomalous” systems<sup>4,5,7,8,24</sup> as are Cl<sub>2</sub> in basic chloroaluminate melts<sup>5</sup> and in PbCl<sub>2</sub>–KCl melts rich in PbCl<sub>2</sub>.<sup>18</sup> Binary chloroaluminate melts containing CsCl and AlCl<sub>3</sub>-rich NaCl–AlCl<sub>3</sub> melts belong to the “reactive” systems. However, a distinction between a “non-reactive”, “anomalous”, or “reactive” system seems dubious when the dissolution enthalpy is close to zero.

In Fig. 8 a summary of solubility data of chlorine in some chlorine melts are given. As can be observed only the data for NaCl and the NaCl-rich NaCl–AlCl<sub>3</sub> melts deviate significantly from the other chlorides investigated. The reason for this may be found in the very large positive enthalpy of dissolution for Cl<sub>2</sub> in NaCl-rich melts, Table 4.

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