Densities of Molten Mixtures of KCl and $AlCl_3$

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Densities of molten mixtures of KCl and $AlCl_3$ have been determined over a wide temperature and compositional range. An empirical equation $\rho = f(X,T)$ has been obtained from the data.

THE densities of some mixtures of KCl and $AlCl_3$ in the molten state have been reported (*3*, *10*). Grothe used a vessel made of Supremax, calibrated by molten KCl–LiCl eutectic, the density of which was calculated from density equations for pure KCl and LiCl obtained from data by Klemm (*6*) and Jaeger and Rockstroh (*5*). He showed that the density of a molten mixture could be accurately calculated whenever $0.5 \leqq X_{KCl} \leqq 1.0$. His equation assumed an ideal mixture of KCl and $KAlCl_4$:

$$1/\rho = WF_{KCl}/[1.535 - 0.56 \times 10^{-3}(t - 768)]$$
$$+ WF_{KAlCl_4}/[1.33 - 0.6 \times 10^{-3}(t - 700)]$$

where WF = weight fraction and t = temperature in °C. However, he provided no data in the region $0 \leqq X_{KCl} \leqq 0.5$.

Gruen reported only two densities in the region $X_{KCl} \leqq 0.5$ at 300° C. The authors' investigations (*7*) required density determinations over a wider temperature and compositional range than had been reported previously.

EXPERIMENTAL

Anhydrous KCl and $AlCl_3$ were prepared as described elsewhere (*8*). Densities were determined by the use of quartz floats of differing densities (*2*). The floats, the densities of which had been determined by the standard pycnometric method, were sealed into an evacuated quartz cylindrical container (18-mm. I.D. diameter × 10 cm.) with the proper proportion of crystalline KCl and $AlCl_3$ to make 12 to 14 cc. of molten solution. The container was then placed into a spectrophotometric furnace (*9*) made from a single cylindrical piece of nickel with a 22-mm. bore down the center and six concentrically placed 300-watt Firerod heaters. Perpendicular to the heaters a small oblong opening had been drilled to allow light to pass through the sample. Temperature was accurately controlled by a precision temperature controller-magnetic amplifier–saturable reactor combination and was measured by a calibrated Pt-Pt-13% Rh thermocouple placed next to the sample and connected to a precision potentiometer. The entire sample and sample container were well within the furnace; temperature gradients were very small as evidenced by the manner in which floats sank as the density of the molten liquid at the surface decreased to that of the float upon increase of temperature and immediately returned to the surface when the same temperature was attained as temperature was lowered.

The experimental densities for various compositions and temperatures are provided in Table I. Corresponding density equations obtained by least-squares analysis of the authors' data coupled with limiting data of Boston (*2*) and of Huber, Potter, and St. Clair (*4*) are provided in Table II. Calculated densities from the equations are given in Table I along with differences. Data from other investigations are also given.

Polynomial equations for $A(X)$ and $B(X)$ have been obtained from values in Table II to facilitate interpolation and are given in Figures 1 and 2, respectively. $A(X)$ is a least-squares fit. Curiously enough, $B(X)$ could not be fitted accurately with polynomials of order less than six.

Table I. Experimental and Calculated Densities of Molten Mixtures of KCl and $AlCl_3$

X^n_{KCl}[a]	T °C.	ρ, Grams/Cc. Measured	ρ, Grams/Cc. Calcd.[b]	Difference	Ref.
0	188.5	1.293	1.294	−0.001	(*2*)
0	201.7	1.265	1.263	+0.002	(*2*)
0	211.2	1.238	1.241	−0.003	(*2*)
0	220.8	1.219	1.218	+0.001	(*2*)
0	190	1.33	1.291	+0.04	(*1*)[c]
0	245	1.19	1.163	+0.03	(*1*)[c]
0.2000	200	1.549	1.549	+0.000	
0.2000	231	1.521	1.519	+0.002	
0.2000	272	1.477	1.479	−0.002	
0.3333	224.1	1.598	1.581	+0.017	[c]
0.3333	323.5	1.515	1.502	+0.013	[c]
0.3333	434.3	1.429	1.415	+0.014	[c]
0.3333	526.0	1.359	1.342	+0.017	[c]
0.406	300	1.55	1.546	+0.00	(*10*)[c]
0.500	300	1.64	1.577	+0.06	(*10*)
0.5003	448.9	1.477	1.478	−0.001	
0.5003	512.0	1.435	1.436	−0.001	
0.5003	574.4	1.395	1.394	+0.001	
0.5003	628.4	1.359	1.359	+0.000	
0.5003	669.5	1.332	1.331	+0.001	
0.5003	772.8	1.262	1.263	−0.001	
0.518	635	1.373	1.371	+0.002	(*3*)
0.518	682	1.346	1.340	+0.006	(*3*)
0.649	640	1.414	1.411	+0.003	(*3*)
0.649	693	1.380	1.378	+0.002	(*3*)
0.6666	668.8	1.399	1.399	+0.000	
0.6666	671.2	1.397	1.397	+0.000	
0.6666	730.3	1.361	1.361	+0.000	
0.6666	778.3	1.332	1.332	+0.000	

[a] The nominal mole fraction will be altered slightly by the correction for Al_2Cl_6 which escapes to the vapor phase. The correction is given by

$$X^a_{KCl} = \frac{0.082\, X^n_{KCl}\, GT}{0.082GT - 3.576PVX^n_{KCl}}$$

where G = mass of KCl in the sample (grams); T = absolute temperature (° K.); P = pressure in atmospheres; V = volume of container minus volume of liquid X^n_{KCl} = nominal mole fraction of KCl; X^a_{KCl} = actual mole fraction of KCl. In these systems, V was about 10 cc. The samples with the largest errors $X^n_{KCl} = 0.200$ at 272° C. or $X^n_{KCl} = 0.3333$ at 526° C., would be corrected to $X^a_{KCl} = 0.2020$ and $X^a_{KCl} = 0.3355$ providing a pressure of 135 atm. were to develop. The authors tested three quartz containers by sealing water into them and recording the temperature and calculating the pressures at which they ruptured: 77, 135, and 130 atm. The authors conclude that the liquid compositions were not significantly changed even at the highest pressures possible. [b] Calculated by $\rho = A(X) - B(X) \times 10^{-3}\, t$ °C. from the equation for $A(X)$ in Figure 1 and the sixth order polynomial for $B(X)$ in Figure 2. [c] Bias, probably caused by Al_2O_3 suspended in melt.

Table II. Equations for the Density of Molten Mixtures of KCl–AlCl$_3$

ρ in grams/cc. = $A(X) - B(X) \times 10^{-3} t$ ° C.

X_{KCl}	$A(X)$	$B(X)$	S_d[a]	S_{d_1}[b]	S_{d_2}[c]	N[d]	Comments
0	1.7337	2.3345	0.0024	0.0105	0.051	4	Data from (2)
0.2000	1.7478	0.9894	0.0020	0.0054	0.023	3	
0.3333	1.7731	0.7901	0.0025	0.0022	0.0056	4	$A(X)$ believed to be biased (Figure 1 and Table I). $A(X)$ = 1.758 preferred.
0.5003	1.7762	0.6645	0.0076	0.0007	0.0012	6	
0.6666	1.9067	1.6100	0.0002	0.0010	0.0014	4	
1.0000	1.956	0.565					Data from (4)

[a] S_d = Standard deviation of a single measurement within the range of experimental measurement. [b] S_{d_1} = Standard deviation of $A(X)$. [c] S_{d_2} = Standard deviation of $B(X)$. [d] N = Number of data used in least-squares fit.

However, since the sixth order polynomial is well behaved in the region $0 \leqq X_{KCl} \leqq 1$, it can be used with confidence. An exponential form for $B(X)$ was also attempted but required as many constants for the required accuracy as the polynomial. If the nature of B at $X = 0$ is not included in the fit, then a simpler equation results. This is also shown on Figure 2 but only gives values with accuracies of ±0.020 for $B(X)$.

DISCUSSION

Table I and Figures 1 and 2 show that data are consistent with those of Boston (2) and Grothe (3). Some bias appears to be in Biltz's (1) data since they do not agree with Boston's (2). From the authors' experience with one sample (X_{KCl} = 0.3333) where some Al$_2$O$_3$ or hydrated alumina had formed, the results of Biltz and Vogt were suspected to be high for the same reason. The best test of consistency is a comparison of densities measured by Grothe (3) with densities calculated from these equations obtained from consideration of only the authors' data coupled with limiting data by Boston (2) and Huber, Potter, and St. Clair (4). Agreement is remarkably good with a standard deviation of only ±0.004 gram per cc.

Using the equations in Figures 1 and 2, it is possible to calculate the molar volumes of molten mixtures of KCl and AlCl$_3$. These results are given in Figure 3. A marked negative deviation occurs within the limits $0 \leqq X_{KCl} \leqq 0.3$ at 200° C., $0 \leqq X_{KCl} \leqq 0.4$ at 400° C., or $0 \leqq X_{KCl} \leqq 0.5$ at 600° C. This has been attributed to complex ion formation and will be discussed in more detail in another paper (7).

Some regions of Figure 3 represent a hypothetical liquid state. Figure 4 summarizes the regions of reality by superimposing the phase diagram of KCl–AlCl$_3$. The upper temperature limit of investigation is also included.

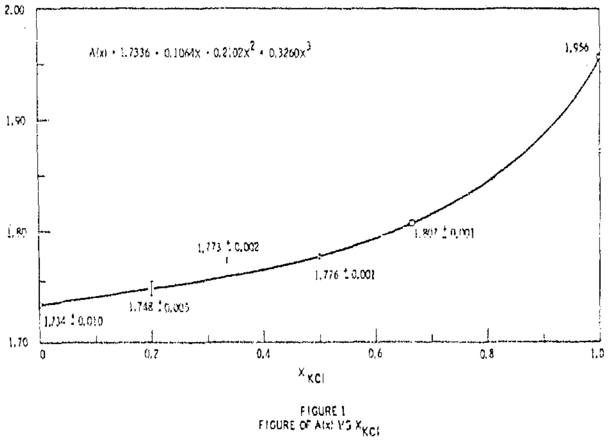

Figure 1. Variation of the parameter A(X) vs. the mole fraction of KCl in the melt

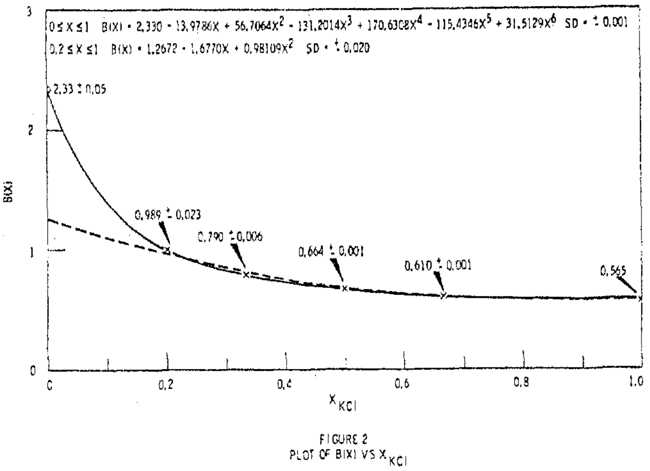

Figure 2. Variation of the parameter B(X) vs. the mole fraction of KCl in the melt

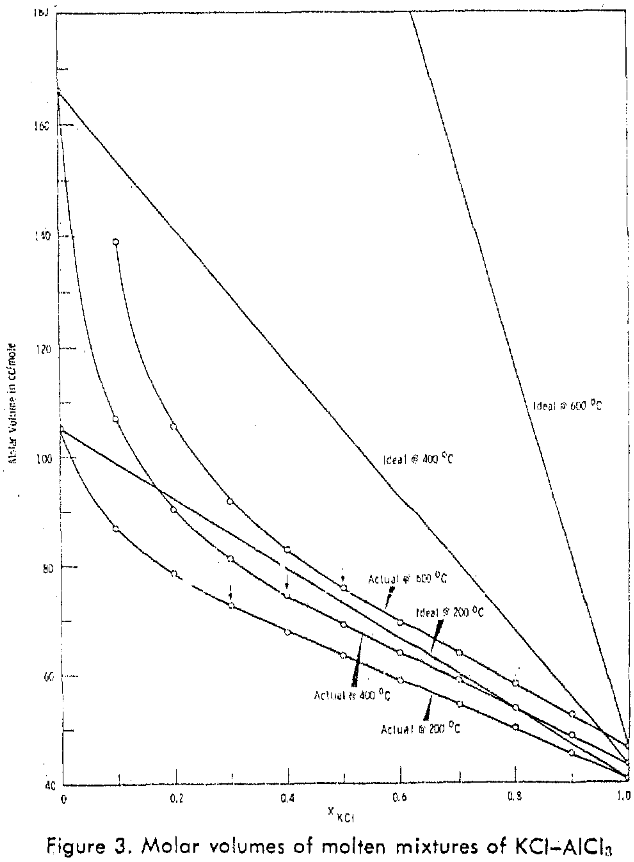

Figure 3. Molar volumes of molten mixtures of KCl–AlCl$_3$

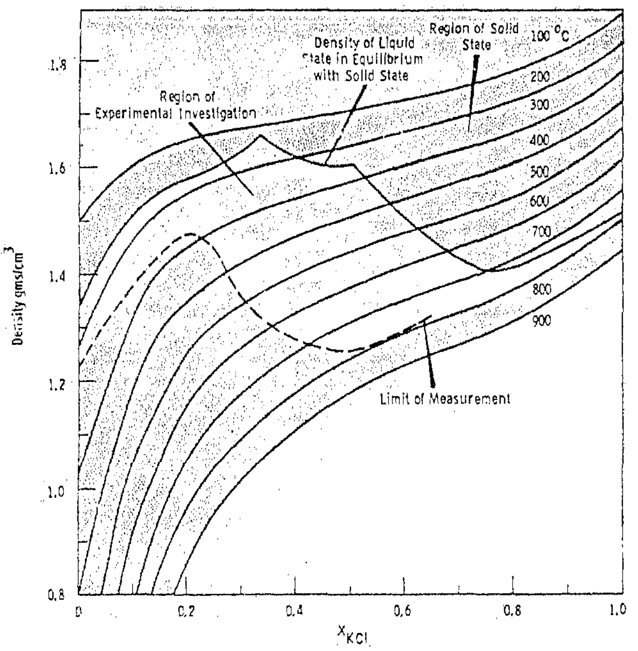

Figure 4. Density of molten mixture of KCl and $AlCl_3$
Phase diagram has been superimposed to show regions of reality

NOMENCLATURE

ρ = density in g./cc.
WF = weight fraction
t = degrees Centigrade
X = mole fraction
G = mass of KCl in sample
T = absolute temperature, ° K.
P = pressure in atm.
V = volume of container minus volume of liquid in cc.
S_d = standard deviation of a single measurement, g./cc.
S_{da} = standard deviation of $A(X)$, g./cc.
S_{db} = standard deviation of $B(X)$, g./cc. deg.
N = number of data used in least-squares fit

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CORRECTION

In the article "Transport Properties of the Normal Paraffins at Attenuation" by T. R. Galloway and B. H. Sage [J. CHEM. ENG. DATA 12, 59 (1967)] a number of errors appeared in Table V. The errors in the original table resulted from the improper use of conversion factors in arriving at the Chapman-Cowling diffusion coefficients expressed in square feet per second. The corrected Table V follows.

Table V. Chapman-Cowling Diffusion Coefficient for Binary Systems at Atmospheric Pressure[a]

System	Temp., ° F.	Chapman-Cowling Diffusion Coefficient, Sq. Ft./Sec.	Ref.
Methane-air	32	210.97×10^{-6}	Jost (*26*)
Ethane-nitrogen	77	159.31	Boyd (*5*)
n-Butane-nitrogen	77	103.33	Boyd (*5*)
n-Hexane-air	70	86.44	Schlinger (*50*)
	100	90.72	Schlinger (*50*)
	100	92.80	Reamer (*44*)
	130	100.40	Schlinger (*50*)
n-Hexane-nitrogen	59	81.48	Cummings (*18*)
n-Hexane-oxygen	59	81.05	Cummings (*18*)
n-Heptane-air	70	76.46	Schlinger (*50*)
	100	83.36	Schlinger (*50*)
	150	93.64	Reamer (*44*)
	160	98.70	Schlinger (*50*)
	160	98.18	Reamer (*44*)
	170	100.95	Reamer (*44*)
	190	106.07	Schlinger (*50*)
n-Octane-air	195	100.27	Reamer (*44*)
n-Octane-nitrogen	86	76.42	Cummings (*18*)
n-Octane-oxygen	86	75.88	Cummings (*18*)
n-Decane-nitrogen	194	90.52	Cummings (*18*)
n-Dodecane-nitrogen	259	87.51	Cummings (*18*)
Av. dev.[b]		0.014	
Std. dev.[c]		0.017	

[a] Atmospheric pressure is taken to be 14.696 p.s.i.a.
[b] Average deviation defined by:

$$s = \left\{\sum_{1}^{N} \left[(D_{Chjr} - D_{(Chjp)}) / D_{Chjr}\right]\right\} / N$$

[c] Standard error of estimate defined by:

$$\sigma = \left\{\sum_{1}^{N} \left[(D_{Chjr} - D_{Chjp}) / D_{Chjr}\right]^2 / (N - 1)\right\}^{1/2}$$