Potassium Chloride–Potassium Sulfate Molten Salt System

Densities, Surface Tensions, and Related Properties

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THE CONCEPT of surface tension is perhaps one of the most important in considering the properties and interactions of substances at high temperatures. In spite of the theoretical and practical value to the metallurgical, ceramic, and electrochemical industries, only a few literature reports deal with the measurement of surface tensions of binary molten salt systems. The majority of these investigations have been concerned with mixtures of alkali halides. Semenchenko and Shikhobalova (*8, 9*), however, studied the effect of the addition of alkali halides on the surface tensions of alkali sulfates over a very narrow range of composition.

The present investigation deals with measurement of the surface tensions and densities for the potassium chloride–potassium sulfate molten salt system over the entire composition range. The surface tensions have been determined by the single-tube, single-bubble modification of the maximum-bubble-pressure method. This method is the most suitable for obtaining precise data on molten salts and their mixtures and depends on the accuracy with which the maximum pressure difference between the inside and the outside of a very slowly growing bubble at the face of a capillary tip can be measured. Young and his students (*1, 10*) found that this pressure difference corresponds to that of a truly static bubble. Hence, values of surface tension may be calculated by the use of the Schroedinger equation (*7*):

$$\gamma_t = \frac{\bar{p}r}{2}\left[1 - \frac{2}{3}\left(\frac{r}{h}\right) - \frac{1}{6}\left(\frac{r}{h}\right)^2 \cdots\right] \tag{1}$$

γ_t = surface tension of melt at temperature t
$\bar{p}$ = maximum bubble pressure
r = radius of capillary tube at tip
h = $\bar{p}/(d - d')\,g$ = height manometer would read if filled with liquid whose surface tension is being measured
d = density of liquid at temperature t
d′ = density of gas above surface
g = acceleration due to gravity

Precise density data are important for the calculation of surface tension. The most suitable method for measuring density of molten salt mixtures has been hydrostatic weighing, employing a Westphal or an ordinary analytical balance. Jaeger (*2*) employed the method up to 1600° C. with good results, but claimed that condensation of salt vapors on the suspension wire limited the precision to two decimal places. Peake and Bothwell (*5*) eliminated this source of error simply yet effectively and were able to reproduce the depth of submergence of the bob. They obtained densities for the potassium chloride–barium chloride system with a maximum probable error of ±0.2% for the pure salts and ±0.3% for the mixtures. Few reports concerning densities for molten salt mixtures have involved sufficient precision to allow calculating reliable values of the partial molal volumes of the solution components. The desired precision for calculation of this property should be a maximum probable error of ±0.1% of the calculated value.

The densities for this system have been determined by a modification of the method of hydrostatic weighing which improves upon the precision. They have been calculated by

$$d_4^t = \frac{\Delta}{V_b} \tag{2}$$

where

$$\Delta = W_2 - W_1 + d_a\left(V_b - \frac{W_2 - W_1}{d_w}\right) + m_\gamma \tag{3}$$

d_4^t = density of melt at temperature t, relative to water at 4° C.
V_b = volume of platinum bob at temperature t
W_2 = apparent mass of bob in air
W_1 = apparent mass of bob in melt at temperature t
d_a = density of air
d_w = density of weights
m_γ = $\pi D\gamma/g$ = mass of liquid supported above normal surface of liquid because of surface tension
D = diameter of suspension wire
γ = surface tension of melt at temperature t
g = acceleration due to gravity

EXPERIMENTAL

Preparation and Analyses of Salt Mixtures. The potassium chloride used was Baker and Adamson reagent grade material dried for 16 hours at 600° C. to remove traces of water. The potassium sulfate (Baker and Adamson reagent grade) was dried for 24 hours at 900° C.

Mixtures of the salts were prepared by weighing the desired amount of each on a triple-beam balance and blending for not less than 5 minutes in a clean Waring blender. This produced a finely powered, homogeneous mixture which was ensured by stirring with a platinum stirrer when molten and when the temperature was near the upper limit of the desired range of measurements.

Following completion of the measurements, the melts were dissolved from the crucibles, aliquot portions of the samples were taken, and total chloride was determined by the Volhard method. The average deviation of 24 determinations was less than ±0.03%.

Determination of Density. APPARATUS. The apparatus was substantially the same as that described by Peake and Bothwell (*5*) but with three significant modifications: A special-purpose Gram-atic balance was employed in place of their ordinary analytical balance, the anticondensation tube was modified, and the elevating mechanism was modified. Figure 1 shows the apparatus as used here.

The special purpose Gram-atic balance was positioned 90° to the left of the balance as described, and was rigidly supported on an angle iron frame resting on a piece of boiler plate bolted firmly to a 6-inch slab of concrete resting of top of a pipe frame. This arrangement allowed lateral adjustment to position the balance, and hence the suspension wire and bob, over the furnace, and minimized external vibrations to the balance. A plywood housing with Plexiglas doors and windows was constructed around the balance to minimize effects of draft and temperature change. Heat radiated from the furnace was absorbed by a water-cooled radiation shield positioned directly below the balance support. The radiation shield also held the anticondensation tube in position by a modified alignment arrangement.

The silica anticondensation tube previously employed allowed the majority of dry air to emerge from the top. This caused fluctuations in the apparent mass of the bob in air and in the melt when the more precise balance was

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used. To prevent this, a modified anticondensation tube was prepared with the inlet side-arm tube entering at a point 2 inches from the bottom of the tube. No drag on the wire, fluctuation in the apparent mass of the bob, or condensation of salt vapors was detected with this arrangement.

The third modification was made in the mechanism for elevating and lowering the furnace. A sprocket gear was attached to the shaft of the elevating mechanism reduction gear, and a bicycle link chain passed over this gear and a similar one attached to a shaft set between two self-aligning bearings 15 inches to the left and on the same vertical level. Attached to this was the drive gear for the elevating mechanism. This arrangement permitted convenient access to the elevating mechanism and the balance controls from a position facing the balance.

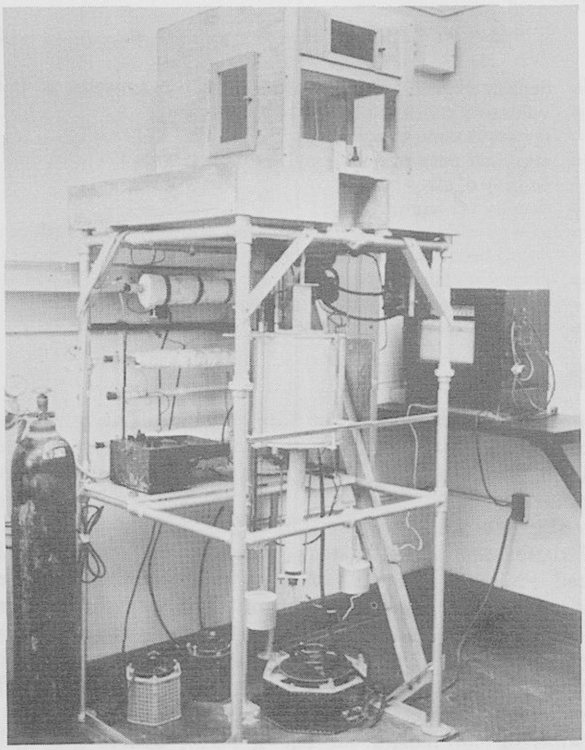

Figure 1. Density apparatus

PROCEDURE. The procedure was substantially that followed by Peake and Bothwell, including the method of reproducing the depth of submergence of the bob and a known length of suspension wire.

Location of the surface of the melt was extremely accurate. When the furnace and its contents and the bob were in thermal equilibrium, the balance beam was released and allowed to come to rest. The furnace was elevated very slowly until a very noticeable deflection of the balance scale indicated that the bob had reached the surface.

Temperature measurements were made by a Chromel-Alumel thermocouple introduced through the crucible support inside the furnace tube and held flush against the thin tip of a silica protecting tube which was in contact with the bottom of the crucible containing the melt. The thermocouple was carefully calibrated against a platinum–platinum plus 10% rhodium thermocouple whose hot junction was suspended in the melt. No measurements were made until the recorder to which the thermocouple was attached indicated thermal equilibrium over a 5- to 10-minute period. The extreme sensitivity of the balance provided an additional check on the constancy of the temperature, as small changes in temperature would change the apparent mass of the bob in the melt. Data were taken only when at least three readings gave exactly reproducible results.

Results. Table I shows the experimentally determined densities for various melt compositions. These data have been plotted, and from the resulting linear curves, values of density at 1100° C. have been calculated (Table II).

Results of this investigation may be expressed by the equation $d_4^t = 1.502 - 0.00058\ (t - 800°)$ grams per ml. for the density of pure potassium chloride. This agrees very well in both magnitude and temperature coefficient with the results given by Mashovetz and Lundina (*4*) and Peake and Bothwell (*5*).

Only one other value has been reported for the density of molten potassium sulfate. Jaeger (*2*) obtained the equation $d_4^t = 1.872 - 0.000545\ (t - 1100°)$ grams per ml. $d_4^t = 1.858 - 0.00055\ (t - 1100°)$ grams per ml. expresses the results of this work. Agreement is excellent in temperature coefficient but only fair in magnitude.

Table I. Densities of KCl-K_2SO_4 Mixtures[a] in Grams per Milliliter

T, ° C.	d_4^t	T, ° C.	d_4^t	T, ° C.	d_4^t	T, ° C.	d_4^t	T, ° C.	d_4^t
0% K_2SO_4		15.3% K_2SO_4		22.3% K_2SO_4		32.4% K_2SO_4		43.1% K_2SO_4	
983	1.398	922	1.536	910	1.605	897	1.682	904	1.741
961	1.411	914	1.540	899	1.611	884	1.691	895	1.745
949	1.418	880	1.560	885	1.620	880	1.692	883	1.752
916	1.433	872	1.565	871	1.628	868	1.699	864	1.765
893	1.448	864	1.569	860	1.636	856	1.708	857	1.769
873	1.459	854	1.576	848	1.643	845	1.716	846	1.775
859	1.468	843	1.584	842	1.647	835	1.721	837	1.780
852	1.472	830	1.591	834	1.653	820	1.729		
841	1.478	818	1.598	819	1.660	811	1.736		
816	1.488	802	1.607	811	1.666	799	1.742		
794	1.501			796	1.676				
791	1.504								
45.0% K_2SO_4		55.2% K_2SO_4		69.4% K_2SO_4		80.2% K_2SO_4		100% K_2SO_4	
919	1.741	950	1.767	1059	1.780	1095	1.795	1138	1.838
915	1.745	941	1.772	1049	1.785	1093	1.795	1128	1.842
904	1.751	930	1.779	1026	1.788	1081	1.803	1117	1.848
897	1.755	917	1.785	1016	1.794	1070	1.807	1109	1.853
880	1.766	899	1.798	1010	1.799	1058	1.812	1099	1.858
867	1.771	886	1.805	999	1.805	1050	1.817	1097	1.856
850	1.782			988	1.811	1041	1.821	1088	1.861
844	1.784			978	1.818	1031	1.826	1087	1.861
				966	1.824	1016	1.831	1075	1.866
						1005	1.839		

[a] All compositions in mole per cent.

Table II. Densities, Their Temperature Coefficients, and Molal Volumes for Molten KCL-K_2SO_4 Mixtures

$$d_4^t = d_4^{1100} - k(t - 1100°)$$

Mole % K_2SO_4	d_4^{1100}, G./Ml.	$-k \times 10^3$, G./Ml./° C.	Molal Vol., 1100°, Ml./Mole
0.0	1.328	0.58	55.97
15.3	1.427	0.61	62.70
22.3	1.487	0.62	64.88
32.4	1.557	0.62	68.43
43.1	1.622	0.60	72.28
45.0	1.632	0.60	72.98
55.2	1.679	0.59	77.02
69.3	1.764	0.60	82.20
80.2	1.790	0.54	86.17
100.0	1.858	0.55	93.64

Table III. Surface Tensions of KCL-K_2SO_4 Mixtures[a]

T, ° C.	γ, Dynes/Cm.	T, ° C.	γ, Dynes/Cm.	T, ° C.	γ, Dynes/Cm.
0% K_2SO_4		15.2% K_2SO_4		21.3% K_2SO_4	
927	87.3	908	92.8	925	97.5
917	88.1	903	92.9	916	98.9
907	88.3	888	94.0	899	99.2
906	88.5	882	94.4	884	100.5
895	88.8	868	95.3	864	101.8
883	89.6	857	96.3	846	103.6
872	91.1	846	97.0	843	102.9
871	90.8	830	98.6	830	104.9
859	91.6	815	99.1	820	105.9
851	92.5				
847	92.6				
835	93.5				
35.4% K_2SO_4		44.7% K_2SO_4		60.2% K_2SO_4	
908	106.2	909	110.9	981	117.8
895	107.5	900	111.4	968	119.5
883	108.6	893	111.9	959	120.2
874	109.0	883	112.5	948	120.9
873	109.0	876	113.0	947	121.0
849	110.4	870	113.4	935	122.4
836	111.5	861	114.0	920	122.8
823	112.2	852	114.8	911	123.8
818	112.6	840	115.7	910	123.0
		819	117.4		
69.9% K_2SO_4		79.2% K_2SO_4		100% K_2SO_4	
1000	120.1	1051	123.9	1121	138.6
994	120.5	1042	124.2	1121	138.6
986	120.9	1035	124.4	1120	138.5
971	121.8	1026	125.4	1117	138.9
962	122.2	1018	125.5	1116	138.9
953	122.7	1009	126.7	1115	138.9
949	122.8	999	126.9	1112	139.2
940	124.3	998	126.9	1109	139.4
				1108	139.5
				1108	139.4
				1107	139.5
				1100	140.0
				1100	140.1
				1099	140.5

[a] All compositions in mole per cent.

Table IV. Surface Tensions, Their Temperature Coefficients, and Molal Free Surface Energies for Molten KCL-K_2SO_4 Mixtures

$$\gamma_t = \gamma^{1100} - k(t - 1100°)$$

Mole % K_2SO_4	γ^{1100} Dynes/Cm.	$-k$, Dyne/Cm./° C.	μ^{1100} Ergs
0.0	74.7	0.071	1099
15.2	78.1	0.075	1231
21.3	84.2	0.076	1356
35.4	91.8	0.074	1558
44.7	97.0	0.070	1706
60.2	110.6	0.068	2039
69.9	114.2	0.059	2169
79.2	120.6	0.064	2353
100.0	140.2	0.072	2896

The maximum probable error involved in these density measurements is on the order of ±0.1% of the calculated value for the pure salts and less than ±0.15% for the solutions. The precision is more than adequate to permit calculation of surface tensions and molal free surface energies for this system.

It is felt that the precision obtained in these density measurements made with a Gram-atic balance is also sufficient to permit calculation of the partial molal volumes of the components of solutions of molten salts. This system, however, precludes this calculation, because molal volume isotherms indicate no deviation from ideality.

DETERMINATION OF SURFACE TENSION

Apparatus and Procedure. The apparatus and procedure were substantially those used by Peake and Bothwell (*6*).

Results. Table III contains the experimentally determined values of surface tensions for the potassium chloride–potassium sulfate molten salt system. These data have been plotted and from the linear curves resulting, surface tensions at 1100° C. for each composition have been determined. These values, with the temperature coefficients of surface tension and molal free surface energies for each composition, are presented in Table IV. Molal free surface energies have been calculated, since isotherms of this property may show all types and magnitudes of interactions between various species existing in the melt more clearly than do surface tension isotherms.

Results of this investigation indicate that the surface tension of pure potassium chloride may be expressed by the

$$\gamma_t = 96.0 - 0.071\ (t - 800°) \text{ dynes per cm.}$$

in excellent agreement with the results given by Jaeger (*2*) and Peake and Bothwell (*6*). The surface tension of pure potassium sulfate may be expressed by the equation

$$\gamma_t = 140.2 - 0.072\ (t - 1100°) \text{ dynes per cm.}$$

Jaeger (*3*) reported:

$$\gamma_t = 142.8 - 0.066\ (t - 1100°) \text{ dynes per cm.}$$

This represents only fair agreement in both magnitude and temperature coefficient.

The precision of these results as determined by the maximum probable error is estimated as ±0.6% or less of the calculated values for both pure salts and solutions.

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