Electrical Conductance and Density in Molten Tungsten(VI)Oxide–Alkali (Li, Na, K) Tungstate Systems

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Precise measurements of electrical conductance and density are reported for molten tungsten (VI) oxide–alkali (Li, Na, K) tungstate systems. The method of least squares has been applied to the raw data in order to obtain second order and first order equations which represent the temperature dependence of specific conductance and density, respectively, in the three systems. Data for these systems extend to nearly 60 mole % WO_3 because phase diagrams for these systems do not indicate higher solubility for the tungsten (VI) oxide in the tungstate melts.

THE PRECISE MEASUREMENT of physical properties of molten materials is especially important because such data are useful in the efforts of chemists to find correlations between properties and the structures of the substances in these fused systems. Density data for two of the single alkali tungstate salts, namely, K_2WO_4 and Na_2WO_4, have been reported by Jaeger (*3*). Conductance data for pure Na_2WO_4 were obtained by others (*4*). Density data and conductance data for tungsten (VI) oxide, lithium tungstate, and for mixtures of the oxide with these alkali tungstates do not appear to have been reported in the literature.

EXPERIMENTAL

General experimental details were essentially the same as those described elsewhere (*6*) by the senior investigator and his associates. The techniques employed in the density measurements were largely those suggested by Janz and Lorenz (*5*). In these measurements, the platinum bob, with a weight of 27 grams (weighed to the nearest 0.1 mg.), was suspended from one arm of a Christian Becker chainomatic balance by means of a platinum-rhodium alloy wire of 0.01 inch diameter (B. & S. gauge 30). For this size wire, surface tension corrections were negligible. For the resistance measurements, the assembly consisted of a Leeds and Northrup Co. precision Jones Bridge (Catalog No. 4666), a Hewlett-Packard Co. oscillator (20 c.p.s. to 20 kc., Model 201-C), and a General Radio Co. tuned amplifier and null detector (Type 1232-A). All leads were shielded. Each dip-type conductance cell of clear fused quartz and of the basic design described by others (*7*), was calibrated by standard procedures before and after each use. Cell constants of these cells ranged from 231 to 267 $cm.^{-1}$ Cumulative attack of the quartz by tungstate melts made it necessary to discard a cell after two of three "runs". All resistance measurements were made at a frequency of 2000 cycles. This frequency was used alone because resistances were frequency independent for the range, 500 c.p.s. to 20 kc.

A Marshall tubular testing furance with platinum-rhodium allow wire windings was used for the heating and melting of all samples. Furnace temperatures were controlled to 0.5° C. All samples were heated and melted in a platinum-rhodium alloy crucible while an atmosphere of pure argon gas was maintained in the furnace chamber.

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A Leeds and Northrup Co. Type K-3 potentiometer (Catalog No. 7553-5) and an NBS-calibrated Pt–Pt 10% Rh thermocouple were used to measure temperatures of the melts. The anhydrous chemicals of reagent-quality were obtained from the S.W. Shattuck Co. of Denver, Colo. Melting-points, as determined by the method of thermal analysis for these substances, were in agreement with literature values. X-ray diffraction powder patterns for three of the chemicals (WO_3, Li_2WO_4, and Na_2WO_4) agreed with the powder data found for these compounds in the A.S.T.M. Data File. Chemical analysis of K_2WO_4 based on total tungsten indicated a purity of 99.6%.

RESULTS AND DISCUSSION

The method of least squares has been applied to the raw data in order to obtain equations which represent the temperature dependence of specific conductance and of density in the three tungstate systems. Second order equations (specific conductance as a function of temperature) and first-order equations (density as a function of temperature) are presented in Tables I and II, respectively. Both tables contain standard deviations and temperature ranges over which the equations are valid. Density data obtained in this research for the molten tungstates of sodium and potassium agree with those reported by Jaeger (*3*).

In other research in which conductance and density data were obtained for certain molten molybdate systems (*6*), resemblance was observed between the conductance-composition plots and the phase diagram of the corresponding systems. Delimarskii and Markov (*1*) discuss at length, instances where several investigators have observed this same type of resemblance for molten binary systems.

The conductance-composition plots are of two kinds, namely, plots in which the conductance values for the several melt compositions are for an arbitrarily-chosen temperature and plots in which each conductance is for a temperature that is a fixed number of degrees above the melting-point for the composition involved. When the two kinds of plots are constructed for the tungstate systems of this report, there is observed only slight resemblance between the conductance-composition plots and the phase diagrams for the corresponding systems.

The electrical conductance of the single alkali (Li, Na, K) tungstates may be attributed to the presence of the simple ions in the melts. A reasonably complete theory of con-

Table I. Specific Conductance Equations for WO_3, K_2WO_4, Na_2WO_4, Li_2WO_4, and Mixtures

Compn., Mole %	Specific Conductance $k = a + bt + ct^2$ (Mho. Cm.$^{-1}$) a	$b \times 10^2$	$c \times 10^6$	Std. Dev., Mho. Cm.$^{-1}$	Temp. Range, °C.
100 WO_3					
100 K_2WO_4	−8.2953	1.7633	−8.0295	0.0022	946°–1024°
100 Na_2WO_4	−1.4108	0.3451	−0.2058	0.0095	706°– 871°
100 Li_2WO_4	−7.5067	1.8733	−8.8034	0.0174	762°– 903°
		K_2WO_4–WO_3 System			
Mole % WO_3					
10.45	−38.80	7.9646	−39.636	0.0406	885°–1029°
19.89	−7.5436	1.6402	−7.5248	0.0190	842°–1016°
30.00	−5.4936	1.2501	−5.8822	0.0130	773°– 955°
40.58	−2.3562	0.5650	−2.3923	0.0057	674°– 819°
49.82	−2.3111	0.5492	−2.4324	0.0023	754°– 770°
57.87	−2.8809	0.6150	−2.5011	0.0020	759°– 912°
70.12	−2.8156	0.5601	−2.0875	0.0012	891°–1010°
		Na_2WO_4–WO_3 System			
10.33	−2.7481	0.6718	−2.4958	0.0064	701°– 869°
20.54	−6.0743	1.5506	−7.1943	0.0160	653°– 803°
30.59	−3.1368	0.7399	−2.4220	0.0223	689°– 850°
40.40	−7.2754	1.7201	−8.5600	0.0068	741°– 881°
50.01	−4.5634	1.0326	−4.4555	0.0042	767°– 905°
55.02	−7.0013	1.5476	−7.0320	0.0040	750°– 888°
60.00	−4.4509	0.9625	−4.0364	0.0016	780°– 923°
		Li_2WO_4–WO_3 System			
11.14	−5.7237	1.4048	−5.7978	0.0240	734°– 907°
20.49	−5.2597	1.2773	−4.8237	0.0102	716°– 897°
30.08	−0.6063	0.1086	1.9898	0.0086	735°– 890°
40.02	−7.4648	1.7642	−7.6694	0.0113	757°– 938°
50.01	−2.1491	0.4558	−0.3923	0.0088	769°– 924°
55.05	−6.0152	1.3336	−5.5948	0.0048	805°– 952°

Table II. Density Equations for WO_3, K_2WO_4, Na_2WO_4, Li_2WO_4, and Mixtures

Compn., Mole %	rho ρ Density $\rho = a - bt$ (G./Cc.) a	$b \times 10^3$	Std. Dev., G./Cc.	Temp. Range, °C.
100 WO_3				
100 K_2WO_4	3.8447	0.7273	0.0068	944°–1053°
100 Na_2WO_4	4.5199	0.9067	0.0026	714°– 880°
100 Li_2WO_4	4.9055	0.8053	0.0032	764°– 901°
	K_2WO_4–WO_3 System			
Mole % WO_3				
10.45	4.0771	0.8452	0.0014	904°–1029°
19.89	4.2444	0.9074	0.0061	860°– 987°
30.00	4.5322	1.0157	0.0023	803°– 910°
40.58	4.9553	1.3341	0.0056	682°– 851°
49.82	5.3326	1.5620	0.0036	655°– 783°
57.87	5.4865	1.5196	0.0061	772°– 943°
70.12	5.8898	1.5538	0.0024	897°– 999°
	Na_2WO_4–WO_3 System			
10.33	3.9344	−0.0510	0.0638	685°– 880°
20.54	4.9976	1.1167	0.0047	654°– 815°
30.59	5.2325	1.2262	0.0033	688°– 880°
40.40	4.4159	−0.0312	0.0574	737°– 882°
50.01	5.8825	1.5570	0.0075	758°– 899°
55.02	5.7113	1.2289	0.0042	775°– 898°
60.00	5.9636	1.4244	0.0038	782°– 926°
	Li_2WO_4–WO_3 System			
11.14	5.0160	0.8511	0.0021	733°– 959°
20.49	5.2819	0.9913	0.0029	714°– 923°
30.08	5.5275	1.1124	0.0031	736°– 930°
40.02	5.7696	1.1903	0.0049	755°– 978°
50.01	6.0776	1.3411	0.0043	764°– 968°
55.05	5.9718	1.1628	0.0065	809°– 939°

ductance for mixtures of the alkali tungstates with tungste(VI)oxide must await the availability of other data for these systems. In the present report, one will observe that the conductance and density measurements extend only up to about 60 or 70 mole % WO_3. Phase diagrams for these systems (2) do not indicate higher solubility for the tungsten(VI)oxide in the tungstate melts.

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