in part to polymerization, and the rate of polymerization is seen to be proportional to the square root of the radiation intensity. The coloration produced in polystyrene by β-irradiation in air is approximately proportional to the radiation dosage. The maxima of absorption occur at approximately 340 mμ. Very little color change is observed in the case of irradiation in vacuum.

We have assumed that the amount of energy required to cleave a bond in a molecule is independent of the molecular size. If this assumption is true, the number of bonds cleaved per unit time per unit weight of the polymers should be the same for a given radiation intensity regardless of the molecular size or distribution. On the other hand, the fraction of the molecules polymerized under such conditions should be inversely proportional to the number of molecules per unit weight of the molecules. This is indeed borne out in the radiation-induced polymerization of fractionated styrene polymers as shown in Table VI.

TABLE VI

COMPARISON OF FRACTION OF MOLECULES POLYMERIZED WITH INITIAL MOLECULAR WEIGHT

Initial mol. wt. (M)	$[\eta]_0$	$[\eta]_f$	f	Time, hr. (t)	f/t	$f/tM \times 10^{18}$
7.97×10^4	0.41	0.43	0.09	113	8×10^{-4}	1
2.445×10^5	0.82	0.92	0.22	117.5	19×10^{-4}	0.76
6.97×10^6	1.575	2.04	0.54	121.17	44×10^{-4}	0.64

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

Densities, Molal Volumes and Electrical Conductivities of the Molten System Molybdenum Trioxide–Sodium Molybdate[1]

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A report is contained herein of densities, molal volumes and electrical conductivities of molten mixtures of molybdenum trioxide and sodium molybdate. Values for these properties at 825° for the mixtures have been obtained by extrapolation and interpolation of the data plotted. New data for the single components are compared with those of other investigators. Activation energies were found to be 5.39 kcal. mole^{-1} for the oxide and 4.88 kcal. mole^{-1} for the salt.

Introduction

In recent years, increasingly larger numbers of investigators have reported data for various transport processes for molten materials. This increased interest in studying fundamental properties of such systems has been motivated largely, in many instances, by the desire to find out if there exist correlations among properties of molten systems just as have been found with reasonably good success, at lower temperatures, for electrolytes and their solutions in various media.

When one recognizes the fact that a molten salt, for example, is essentially a highly concentrated and strong electrolyte, it is understandable why one would hope that, in the future, it will be possible to extend existing theories, for concentrated aqueous solutions of strong electrolytes, to molten salts. Moreover, the finding of a molten solvent, of high dielectric constant and extremely low conductivity, for salts would permit perhaps more meaningful comparisons between dilute molten mixtures involving that solvent and aqueous solutions.

The work of this paper includes measurements of the densities and electrical conductivities of molten mixtures of molybdenum trioxide and sodium molybdate. No literature reports have been found, up to the present time, for the mixtures with which this paper is concerned. However, a few reports appear in the literature on the single components. van Arkel and others[2] include molybdenum trioxide in their study of the electrical conductivity of molten oxides. However, their work for this substance may be open to some question because of certain inconsistencies, *viz.*, (1) their data indicate a higher specific conductivity for molybdenum trioxide (4.65 ohm^{-1} cm.$^{-1}$ at 950°) than that reported by Edwards and co-workers[3] for an ionic salt like sodium chloride (4.05 ohm^{-1} cm.$^{-1}$ at 950°) and (2) their melting point value of 847° for the oxide is considerably different from the 795 ± 4° reported by others[4,5] for molybdenum trioxide. The data of the present paper are considerably different from those of van Arkel[2] for molybdenum trioxide. No density data for this oxide are found in the literature.

For sodium molybdate, electrical conductivity data[6] (range 843–1408°) and density data[7] (range 699–1212°) have been reported by Jaeger and his associates. Both sets of measurements appear to have been carried out with considerable care. In fact, their data above 1200° are surprisingly consistent in view of the fact that Spitsyn and Kuleshov[8] report that the heating of sodium molybdate for 6 hours at 1200° results in a loss of weight and

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[1] Research sponsored by office of Ordnance Research (Philadelphia Ordnance District), Contract No. DA-36-034-ORD-853 Project No. TB4-901 (340).

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[8] V. I. Spitsyn and I. M. Kuleshov, *J. Gen. Chem.*, (*U.S.S.R.*), **21**, 445 (1951) (English translation); *C. A.*, **46**, 1907b (1952); *ibid.*, **45**, 5553i (1951).

enrichment of the solid residue in MoO_3. The data of the present research agree reasonably well with the findings of Jaeger[6,7] for the salt.

Experimental

Materials Used.—Baker Analyzed Reagent and Fisher Certified Reagent grades of both molybdenum trioxide and sodium molybdate dihydrate were employed in the work. The two chemicals were dried and dehydrated, respectively, by heating to constant weight in an oven overnight at 180°, and then used without further treatment. Thermal analysis studies carried out earlier on the two chemicals revealed that the drying and dehydration techniques were adequate to give pure substances with sharp melting points. The average weight per mixture was 550 grams.

Analysis of the cooled melts of molybdenum trioxide and sodium molybdate was not successful because of the inability to devise an accurate analytical procedure. Exploratory separation techniques such as either crystallization of MoO_3 at 0° and/or precipitation of molybdate as calcium molybdate were without value. X-Ray analysis, although not available conveniently in this work, might have yielded satisfactory results. It is believed by the present authors that there were no significant composition changes, due to volatility of MoO_3, for mixtures containing more than 75 mole % MoO_3. According to weight-loss-on-heating data obtained in this laboratory, a 30-g. sample of pure MoO_3 decreased in weight by 3 g., when heated at 850° for 3 hours in a porcelain crucible. Now, if one considers this weight-loss figure and assumes that the vapor pressure of MoO_3 in a mixture, *e.g.*, Mixture No. 9, was unaffected by the presence of a second component (not appreciably volatile at the same temperature); then, in such a highly unlikely case, the percentage of MoO_3 in the mixture would be decreased by less than 2 mole %.

Density Measurements.—A Westphal balance, thoroughly shielded from any heat above the furnace, was used for the density measurements. The sinker was a tungsten slug encased in Vycor or opaque quartz and it was suspended from the balance by means of B & S gage No. 24 platinum wire to minimize surface tension effects. Platinum wire of smaller diameter broke frequently and therefore could not be used except at the risk of introducing a larger error. In the measurements, the sinker was balanced in the hot air above the 250-ml. porcelain crucible containing the melt and then a reading was made for balance of the sinker in pure sodium chloride. The sinker was then freed from adhering salt by washing, dried next, and finally balanced in the melt of unknown density. In each measurement, every effort was made to maintain the same depth of immersion of sinker and wire in the melt. Then, the unknown density was calculated by the formula

$$D_x = \frac{D_{NaCl} \times \text{Reading in the melt}}{\text{Reading in molten NaCl}}$$

The density of NaCl was calculated from the equation ($D_{NaCl} = 1.969 - 0.524 \times 10^{-3}t$, for the range 830–1100°) of Edwards[3] and others. Calculation of the unknown density was made also by using a more refined expression

$$D_x \text{ (at } T) = \frac{R_{melt} \times D_{NaCl}}{R_{NaCl}\,(1 + \beta_s \Delta t)}$$

where R = reading at balance-point; β_s = coefficient of thermal expansion of Vycor or quartz; and Δt = temperature change from the temperature at which the density of NaCl was measured. However, this expression reduces to the simpler one when cognizance is taken of the fact that the $\beta\Delta t$ term is small enough to be negligible. Moreover, the temperature coefficient of density for sodium chloride is fairly small.

Since the present work was completed, Peake and Bothwell[9] have reported a simple and reliable means, devised by them, for elimination of the error caused by condensation of volatile material upon the wire supporting the sinker in determining densities of melts. In the work of the present paper, condensation of volatile matter on the platinum wire presented difficulty principally in mixtures containing more than 75 mole % MoO_3. The solid condensate, in such cases, was scraped carefully from the wire before taking a final reading.

Electrical Conductivity.—A dip-type cell, designed by the senior author and constructed of either Vycor or of opaque quartz, was employed in the work. A full description of the cell appears elsewhere[10] in the literature. An improvement for the quartz cell was made by using a quartz rod, 4 mm. in diameter, to connect the upper part of each vertical arm of the cell to the handle for greater strength.

Measurement of the electrical conductivities was made by making use of the classical Wheatstone bridge principle. The chief components in the bridge circuit, in addition to the cell, were the following Leeds and Northrup instruments: Audio Frequency Oscillator (500, 1000 and 2000 cycles); Tuned Audio Frequency Amplifier; Type K-2 Potentiometer; and Telephone Receivers. Bright platinum disk electrodes, welded to platinum leads, dipped into the vertical arms of the cell. Conductivities of the melts were found to be independent of the depth of immersion of the platinum disk electrodes. Nevertheless, final readings were usually made with discs in lowest position. Cell constants were determined by using specific conductivities for molten sodium chloride (ref. 3, Table II) or saturated NaCl[11] at room temperatures or saturated KCl at room temperatures. The values for saturated KCl were calculated indirectly by referral to NaCl. Those data appear in Table III. Strangely, precise measurements for saturated KCl solutions appear not to have been reported in the literature. Cell constant values were reasonably constant, regardless of the reference temperature, because thermal expansion of Vycor and quartz is extremely small over a wide temperature range.

Alternating current of 1000 cycles sec.$^{-1}$ from the oscillator was used satisfactorily in all measurements. No significant variation in resistance was observed when measurements were made at 500 and 2000 cycles sec.$^{-1}$. Apparently, polarization effects, if present, were negligible.

Temperature.—Three electric crucible furnaces (Hoskins Electric Co. Types FD-104 and F. A.-100.36 and Hevi Duty Electric Co. Type HDT-812), cylindrical in shape and in two chamber dimensions, 5 × 5 in. (the first furnace) and 8 × 18 in. (the last two), and controlled by an indicating millivoltmeter pyrometer (up to 1000°), were available for melting all mixtures contained in 250-ml. porcelain crucibles. Temperature readings (millivolt readings of the Leeds and Northrup Students' Potentiometer converted to Centigrade degrees) in the melts were made by means of the usual platinum–platinum–10% rhodium combination. Calibration of this thermocouple was carried out at the melting points of tin, lead, zinc and antimony. Although a thin-walled quartz or mullite protection tube was used to encase the platinum thermocouple dipping into the molten metals and mixtures to a depth of 2 inches, sufficient time was allowed for attainment of thermal equilibrium of the thermocouple before making the temperature measurements.

Experimental Results and Discussion of the Data

Densities and molal volumes of MoO_3—Na_2MoO_4 melts appear in Table I. A plot of density (825°) as a function of composition is shown in Fig. 1. Except for mixture No. 4 (28 mole % MoO_3), all other mixtures for which measurements were made over a range of temperatures show, as expected, a decrease in density with increasing temperature. At 825°, the density (D) increases as a linear function of composition (X, mole % MoO_3) up to about 50 mole % MoO_3. The equation expressing the relationship is $D = 4.1 \times 10^{-3}X + 2.68$. There is no correlation between any one of these facts and the temperature–composition diagrams mapped out by Hoerman[5] and Groschuff[5] independently for this system.

Electrical conductivities of molten mixtures of MoO_3 and Na_2MoO_4 are found in Table II. The

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TABLE I

DENSITIES AND MOLAL VOLUMES OF MoO_3–Na_2MoO_4 MELTS[a]

No.	MoO_3, mole %	Temp., °C.	Density, g./ml.	Molal vol. (825°), cc./mole
1	0.0	825	2.68	76.9
2	10.0	828	2.73	73.2
3	20.0	..	..	..
4	28.0	828	2.79	67.5
		794	2.79	
		751	2.79	
		698	2.79	
5	34.0	790	2.84	..
		740	2.88	
		690	2.94	
		(825°)	(2.82)	65.5
6	50.0	816	2.90	60.3
7	60.0	757	3.01	
		687	3.09	
		661	3.13	
		(825°)	(2.96)	57.0
8	70.0	809	3.05	
		776	3.09	
		652	3.24	
		(825°)	(3.03)	53.7
9	78.0	746	3.14	
		704	3.18	
		675	3.21	
		665	3.22	
		648	3.24	
		(825°)	(3.06)	51.5
10	88.0	844	3.06	
		797	3.10	
		730	3.16	
		(825°)	(3.08)	49.2
11	90.2	881	3.01	
		834	3.07	
		776	3.10	
		(825°)	(3.08)	48.7
12	100.0	909	2.98	
		832	3.08	
		(825°)	(3.09)	46.6

[a] Values in parentheses were read directly from a large graph of Fig. 1.

TABLE II

ELECTRICAL CONDUCTIVITIES OF MoO_3–Na_2MoO_4 MELTS

No.	MoO_3, mole %	Density used, g./ml.	Temp., °C.	Cell constant, cm.$^{-1}$	Specific conductivity (k), ohm^{-1} cm.$^{-1}$	Equiv. conductivity (Λ), ohm^{-1} cm.^{2}/eq.
1	0.0		964°	91.1	1.940	74.55
			885	91.1	1.699	65.29
			856	91.1	1.605	61.68
		2.68	(825°)	91.1	(1.505)	(57.84)
			804	91.1	1.432	55.03
			751	91.1	1.260	48.42
2	10.0		953°	91.1	1.782	...
			905	91.1	1.622	...
			851	91.1	1.486	45.31
		2.73	(825°)	91.1	(1.410)	(42.99)
			800	91.1	1.348	41.11
			752	91.1	1.192	...
3	20.0		827°	166	1.508	...
			(825°)	166	(1.500)	...
			760	166	1.290	
			751	166	1.266	...
4	28.0		828	166	1.560	33.79
		2.79	(825°)	166	(1.540)	(33.36)
			751	166	1.258	27.25
			698	166	1.050	22.74
			649	166	0.875	18.95
5	34.0	2.82	(825°)	244	(1.485)	(29.02)
			806	244	1.425	27.85
			751	244	1.250	24.33
			714	244	1.111	21.71
			692	244	1.045	20.42
			656	244	0.944	18.45
6	50.0	2.90	(825°)	211	(1.280)	(19.34)
			793	211	1.185	...
			762	211	1.088	...
			760	211	1.085	...
			709	211	0.954	...
			700	211	0.898	...
			676	211	0.825	...
			654	211	0.768	...
7	60.0		827°	211	1.263	...
		2.96	(825°)	211	1.250	16.20
			774	211	1.024	
			686	211	0.830	
			674	211	0.787	
			659	211	0.762	
			640	211	0.703	
8	70.0	3.03	825°	211	1.185	13.27
			805	211	1.128	
			758	211	0.995	
			730	211	0.916	
			712	211	0.837	
			694	211	0.793	
			662	211	0.690	
			641	211	0.630	
9	78.0	3.06	(825°)	211	1.170	11.78
			802	211	1.086	
			796	211	1.071	
			792	211	1.054	
			790	211	1.039	
			756	211	0.930	
			693	211	0.730	
			640	211	0.543	
10	88.0	3.08	(825°)	211	0.785	6.99
			817	211	0.767	
			815	211	0.767	
			809	211	0.765	
			805	211	0.773	
			714	211	0.649	
			708	211	0.637	
11	90.2		890°	211	1.140	...
		3.08	(825°)	211	(0.975)	(8.46)
			819	211	0.955	
			812	211	0.921	
			785	211	0.875	
12	100.0		914°	260	1.092	8.48
			833	260	0.915	7.11
		3.09	(825°)	260	(0.900)	(6.99)
			797	260	0.844	6.56
			835	260	0.920	7.14

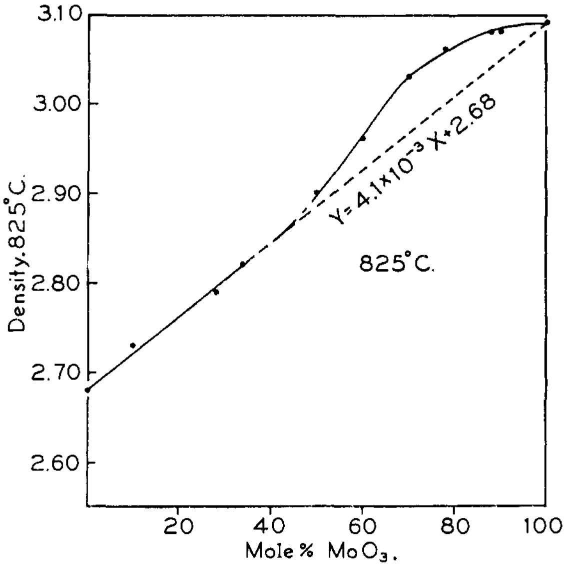

Fig. 1.—Density isotherm (825°) for MoO_3–Na_2MoO_4 mixtures.

specific conductivity increases in every case as a linear function of the temperature. An inspection of the conductivity–composition isotherm (825°) of Fig. 2, reveals a slight similarity between this diagram and the temperature–composition[4] diagram for the same system.

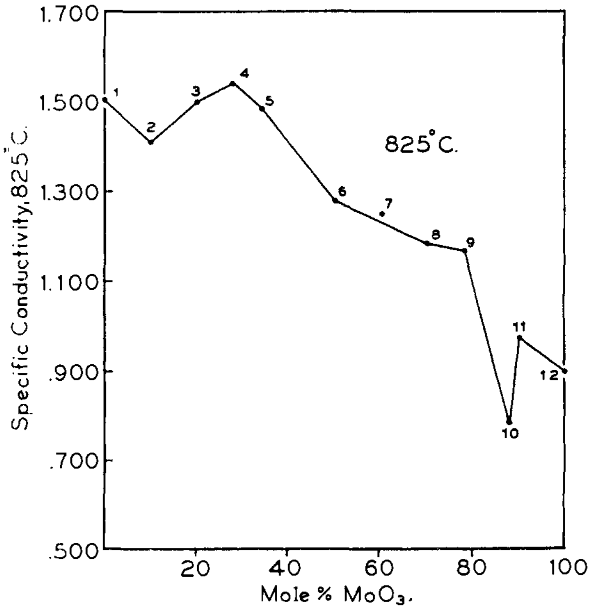

Fig. 2.—Specific conductivity isotherm (825°) for MoO_3–Na_2MoO_4 mixtures.

The eutectic compositions of the latter diagram correspond to Mixtures 4 and 9 of this work. In Fig. 2, conductivities for these two mixtures appear as a maximum and a pseudomaximum, in that order. No satisfactory explanation can be offered for the slight similarity and for the fact that conductivities observed for most of the mixtures are higher than (instead of lower than) those one might predict on the basis of an additivity rule for mixtures.

Table III

Specific Conductivities (Satd. Aqueous KCl)

Temp., °C.	Cell constant, cm.$^{-1}$	Specific conductivity, ohm^{-1} cm.$^{-1}$
23	257	0.341
25	185	.362
30	185	.407

Plots (not given) of log Λ *vs.* $1/T$ for the data of Tables IVA and IVB show good straight lines. For MoO_3, $\log \Lambda = -1170(1/T) + 1.91$; for Na_2MoO_4, $\log \Lambda = -1060(1/T) + 2.72$. Activation energies for conductance of molybdenum trioxide and sodium molybdate were obtained from the slopes of the lines (U = 2.303 × 1.986 × slope of log Λ *vs.* $1/T$) and found to be 5.39 and 4.88 kcal. mole^{-1}, respectively.

Table IVA

Equivalent Conductivities of Molten MoO_3

No.	Temp., °C. (t)	Temp., °K. (T)	Specific conductivity (k), ohm^{-1} cm.$^{-1}$	Equiv. conductivity (Λ), ohm^{-1} cm.^{2}/eq.	log Λ	$1/T \times 10^4$
12a	914°	1187°	1.092	8.48	0.928	8.40
b	833	1106	0.915	7.11	0.852	9.01
c	(825°)	(1098)	(0.900)	(6.99)	(0.845)	9.09
d	797	1070	0.844	6.56	0.817	9.35
e	835	1108	0.920	7.14	0.854	9.01

Table IVB

Equivalent Conductivities of Molten Na_2MoO_4

No.	Temp., °C. (t)	Temp., °K. (T)	Specific conductivity (k), ohm^{-1} cm.$^{-1}$	Equiv. conductivity (Λ), ohm^{-1} cm.^{2}/eq.	log Λ	$1/T \times 10^4$
1a	964°	1237°	1.940	74.55	1.873	8.07
b	885	1158	1.699	65.29	1.815	8.62
c	856	1129	1.605	61.68	1.790	8.85
d	(825)	1098	(1.505)	(57.84)	1.762	9.09
e	804	1077	1.432	55.03	1.741	9.26
f	751	1024	1.260	48.42	1.685	9.80

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