tion of a monolayer of hydrogen atoms, each of which would donate an electron to the nickel. It is to be noted that these observations give a powerful new method for studying the electronic consequences of chemisorption on metals. The interpretation offered for the effect described is parallel to that suggested by Suhrmann and Sachtler[14] for the change of work function produced by chemisorbed gases on metals.

The fall of catalytic activity near sintering temperatures of 450° is accompanied by other changes in properties of the catalyst; below this temperature the catalyst reoxidizes very vigorously when exposed to air, but is relatively stable above. Also, at this temperature there is a sharpening of the X-ray diffraction pattern and the thermomagnetic curves begin to become convex in shape. It is approximately the same temperature at which mobility of nickel atoms may be expected, as the Tammann temperature lies within this range. The drop in activity greatly exceeds the fall of specific surface during sintering. This suggests the existence of some intensive activity factor present in very small particles, over and above the effect of surface.

Acknowledgment.—It is a pleasure to acknowledge support of the Office of Naval Research in connection with this work. It is also the pleasant duty of Stephen Adler to acknowledge receipt of the Sinclair Research Fellowship.

EVANSTON, ILLINOIS

(14) R. Suhrmann and W. Sachtler, *Z. Naturforsch.*, **9**, [a] 14 (1954).

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. VIII. Density and Surface Tension of Molten Sodium Phosphates

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Density and surface tension data have been determined for the $Na_2O-P_2O_5$ melts with Na_2O/P_2O_5 mole ratios between 1.0 and 2.15, at temperatures from slightly above the liquidus to above 1000°, using special platinum equipment. The densities are given by the general relationship $d = 2.372 + 0.089\,(Na_2O/P_2O_5) - 0.000338t$, where d is the density in g./ml., t is the temperature, and Na_2O/P_2O_5 is the mole ratio in the molten phosphate. The surface tension values for ratios from 1.0 to 1.5 are given by the equation $\gamma = 150.6 + 67.7\,(Na_2O/P_2O_5) - 0.0379t$, where γ is the surface tension in dynes/cm. The surface tension and density data can be represented by the MacLeod equation, with the constant equal to 1.74 ± 0.07.

The density and surface tension of melts made by heating sodium trimetaphosphate at temperatures from above the liquidus to around 1200° have been measured by Jaeger.[1] The surface tension data were obtained using the method of maximum bubble pressure. In this study the measurements have been extended from the metaphosphate to beyond the pyrophosphate composition in the $Na_2O-P_2O_5$ system.

Experimental

Materials.—The $Na_2O-P_2O_5$ melts were prepared by melting varying proportions of dry sodium trimetaphosphate and dry tetrasodium pyrophosphate. The trimetaphosphate was prepared by heating a special grade of Monsanto insoluble sodium metaphosphate for several hours at 500°. The Na_2O/P_2O_5 mole ratio was 1.001 and the loss of weight on ignition with zinc oxide[2] was 0.08% in this sample of sodium trimetaphosphate which contained only spectrographically detectable amounts of impurities. The pyrophosphate was prepared by heating analytical reagent disodium phosphate, anhydrous, at 500°. Melts with Na_2O/P_2O_5 mole ratios greater than two were prepared by melting pyrophosphate with the desired proportion of crystalline trisodium orthophosphate and heating for an extended period to remove the water. The density measurements were found to be sensitive to traces of water; but the melts were all carefully dehydrated before the measurements were made.

The above preparations were carried out in platinum equipment and the compositions near the Na_2O/P_2O_5 ratio of unity were contaminated with enough dissolved platinum to cause a slight yellowing of the glasses quenched from the melts. Although previous work indicated that the platinum content of the discolored melts would be well below 1%, it is believed that platinum was present in all melts in considerably greater weights than any elements other than sodium, phosphorus and oxygen.

Methods and Procedure.—The samples were heated (in a platinum container) in a pot-type furnace equipped with a special lid to permit the desired manipulations from above. A small hole in the center of the lid permitted free movement of the supporting wire. The temperature of the liquid was measured to ±5° with a Pt:Pt–Rh thermocouple immersed a few centimeters in the liquid.

Density.—The densities were determined by application of Archimedes' principle using a procedure similar to that described by Jaeger.[3] A platinum bob of known volume, suspended by means of a fine wire from the beam of an analytical balance, was weighed in air and then submerged in the liquid. Corrections were made for the surface tension of the liquid by adding to the buoyancy the product of the surface tension and the circumference of the wire (diameter = 0.0508 cm.) supporting the bob. The densities were then calculated by dividing the volume of the bob into the sum of the difference in weights in air and in the liquid and the surface tension correction.

The bob used in this work was fabricated by attaching a thin platinum wire to a short section of 0.20-inch diameter platinum rod. The bob weighed about 15.5 grams in air. The volume of the bob was obtained from the weights in air and in water of known temperature and density. The volumes of the bob at the higher temperatures were calculated from the measured volume at room temperature and the known coefficient of volume expansion for platinum.

Surface Tension.—The surface tension measurements were made with a du Nouy interfacial tensiometer. The regular platinum–iridium ring supplied with the instrument was modified for high temperature usage by welding on the top of its supporting bars an eight inch extension of platinum wire. The platinum extension was jointed to the connecting shaft of the instrument with a loose fitting hook and eye.

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(1) F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

(2) Procedure used in analytical laboratories of Monsanto Chemical Company. Details will be included in Scott's "Standard Methods," 6th Edition.

(3) F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 278–282.

The instrument was then calibrated by adding class S weights to the ring, and measuring the twist of the torsion wire required to balance the weight. The calibration curve used throughout the work was obtained by constructing a linear plot of the pull in grams on the ring *versus* the tensiometer reading. The procedure followed in taking the measurements was standard as given in the literature[4] accompanying the instrument except that the torsion arm was kept in the zero position during a measurement by raising the upper portion of the instrument with the column adjusting screw. Thus, it was not necessary to raise and lower the sample itself, as is generally the practice.

Correction factors were applied to the data as outlined by Harkins and Jordan.[5]

Results

Density.—The densities of the Na_2O–P_2O_5 melts with mole ratios lying between 1.0 and 2.0 are given in Table I. Linear plots of density *versus* temperature were constructed, and straight lines of the general form

$$d = mt + c \qquad (1)$$

were fitted to the data, where d is the density in g./ml., t is the temperature, m is the temperature coefficient in g./ml./°C., and c is a constant. The values thus obtained for m and c for each composition measured are also included in Table I. Over the range in composition studied within experimental error, the temperature coefficient is the same, and the average value is -0.000338 g./ml./°C. The constant c was found to vary linearly with the Na_2O/P_2O_5 mole ratio in the melt and, therefore, the density can be expressed by one general relation in terms of the Na_2O/P_2O_5 mole ratio in the liquid and the temperature. This relation is

$$d = 2.372 + 0.089(Na_2O/P_2O_5) - 0.000338t \qquad (2)$$

where d is the density in g./ml., Na_2O/P_2O_5 is the mole ratio and t is the temperature in degrees centigrade of the Na_2O/P_2O_5 melt. The results obtained are given by equation 2 with a deviation of ±0.2%. The absolute accuracy of the data is probably not as good because of the magnitude of, and uncertainty in the surface tension correction.

TABLE I

DENSITY OF MOLTEN SODIUM PHOSPHATES

Na_2O/P_2O_5 mole ratio in melt	Temp., °C.	Wt. in air minus wt. in liquid (g.)	Surface tension correction (g.)	Vol. of bob[a] (ml.)	Density of melt (g./ml.)	Data fitted to relation $d = mt + c$: $-m$ (g./ml./°C.)	c (g./ml.)
1.0	679	1.5691	0.031	0.7158	2.236		
	770	1.5476	.031	.7175	2.200		
	862	1.5300	.030	.7189	2.171		
	950	1.5144	.030	.7210	2.142	0.000339	2.464
1.1	713	1.5705	.032	.7181	2.232		
	771	1.5676	.033	.7194	2.224		
	848	1.5451	.032	.7209	2.187		
	958	1.5226	.031	.7230	2.148	.000342	2.476
1.3	708	1.5841	.034	.7187	2.253		
	769	1.5711	.034	.7194	2.232		
	864	1.5510	.034	.7209	2.198		
	872	1.5534	.034	.7213	2.200		
	944	1.5384	.033	.7227	2.174		
	958	1.5347	.033	.7230	2.168	.000338	2.491
1.5	788	1.5813	.036	.7198	2.248		
	844	1.5656	.306	.7208	2.221		
	900	1.5532	.036	.7218	2.202		
	963	1.5415	.035	.7235	2.178	.000339	2.508
1.67	883	1.5677	.038	.7216	2.225		
	940	1.5581	.037	.7223	2.209		
	944	1.5487	.037	.7237	2.191		
	1036	1.5415	.037	.7244	2.179	.000338	2.527
2.0	1043	1.5453	.041	.7224	2.196		
	1066	1.5387	.040	.7231	2.184	.000333	2.542

[a] For Na_2O/P_2O_5 equal to 1.0 and 2.0, volume of bob was 0.7034 ml. at 18.7°. In all other determinations the volume of the bob was 0.7054 ml. at 22.5°.

Surface Tension.—The surface tension values for the Na_2O–P_2O_5 melts over the range in Na_2O/P_2O_5 mole ratio from 1.0 to 2.2 are given in Table II. These data were also fitted to straight lines of the general formula

$$\gamma = st + b \qquad (3)$$

where γ is the surface tension in dynes/cm., t is the temperature, s is the temperature coefficient in dynes/cm./°C., and b is a constant. Within an average deviation of less than 1%, the temperature coefficient is the same, *i.e.*, -0.0379 dyne/cm./°C., for the liquids with Na_2O/P_2O_5 mole ratios be-

TABLE II

SURFACE TENSION DATA FOR MOLTEN SODIUM PHOSPHATES

Na_2O/P_2O_5 mole ratio in melt	Temp., °C.	Grams pull on ring[c]	Harkins and Jordan correction factor	Surface tension, dynes/cm.	Data fitted to equation $\gamma = st + b$: $-s$(dynes/cm/°C.)	b(dynes/cm.)
1.0	732	2.42	0.951	188.1		
($\bar{n}$ = 163)[a]	808	2.40	.952	186.1		
	896	2.34	.951	182.0		
	977	2.30	.950	179.0	0.0407	218.5
1.0	713	2.45	.952	191.0		
($\bar{n}$ = 172)	761	2.43	.952	189.2		
	859	2.39	.952	186.0		
	967	2.32	.951	180.7	0.0400	219.6
1.08	776	2.48	.953	192.9		
($\bar{n}$ = 24)	858	2.43	.953	189.4		
	966	2.38	.952	185.3	0.0393	223.3
1.29	660	2.69	.957	210.2		
($\bar{n}$ = 6.8)	708	2.67	.957	208.9		
	807	2.63	.958	206.0		
	899	2.58	.957	202.0		
	984	2.55	.957	199.1	0.0375	235.9
1.50	816	2.82	.964	221.6		
($\bar{n}$ = 3.7)	816	2.83	.964	223.0[b]		
	864	2.81	.964	221.0		
	910	2.78	.964	218.8		
	968	2.76	.964	217.5	0.0333	249.6
1.75	932	3.01	.970	238.0		
($\bar{n}$ = 2.6)	972	2.98	.970	235.3		
	1010	2.95	.969	233.7		
2.0	1012	3.14	.973	250.0		
	1028	3.13	.973	249.5		
	1034	3.10	.972	246.0		
	1056	3.07	.972	244.0		
2.17	994	3.26	.976	260.1		
	1008	3.25	.976	259.0		
	1032	3.23	.976	258.0		
	1046	3.20	.975	255.4		

[a] $\bar{n}$ = average chain length in quenched glass as determined by end-group titration. [b] Value determined at end of run. [c] $R/r = 52.8$; r = radius of wire; $R = 0.951$ = mean radius of ring. Tensiometer reading = 83.5 × pull on ring in grams.

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[4] Central Scientific Company Bulletin 101, "Cenco-du Nouy Tensiometers," Chicago, Illinois.

[5] W. D. Harkins and H. F. Jordan, THIS JOURNAL, **52**, 1751 (1930).

tween 1.0 and 1.5. The values of s and b for these compositions are included in Table II. Although there is some indication that the temperature coefficient increases to larger negative values for the ratios near 2.0, valid conclusions cannot be drawn here because of the narrow temperature range covered for these materials. The values of b increase linearly with the Na_2O/P_2O_5 mole ratio in the melt. From this linear relationship and the average temperature coefficient, the surface tension of an Na_2O/P_2O_5 melt can be expressed by the general relation

$$\gamma = 150.6 - 0.0379t + 67.7(Na_2O/P_2O_5) \qquad (4)$$

where γ is the surface tension in dynes/cm., t is the temperature in degrees centigrade, and Na_2O/P_2O_5 is the mole ratio in the liquid. The average deviation of the experimental data from the equation is ±0.8%.

Discussion of Results

The results given here on the density of the sodium metaphosphate melt ($Na_2O/P_2O_5 = 1$) are in excellent agreement with those reported by Jaeger[1] at temperatures from 750 to 850. However, Jaeger reports a somewhat higher temperature coefficient, so that his values are lower than ours at the higher temperatures.

The surface tension of sodium metaphosphate at 1000° reported by Jaeger[1] is 4–5% higher than the value obtained in this work using the ring method. More recent studies[6] of the method of maximum bubble pressure have pointed out the necessity of applying certain correction factors which Jaeger did not use; however, enough information concerning Jaeger's work is not available to enable a recomputation of his data and comparison of it with that obtained here by the ring method.

An apparent molecular weight for the molten sodium phosphates can be estimated from the surface tension and density data using the relation

$$M = -\frac{k^{3/2}}{\left[\frac{\partial\gamma}{\partial T}v^{2/3} + \frac{2\gamma\partial v}{3v^{1/3}\partial T}\right]^{3/2}} \qquad (5)$$

derived by differentiating the Eötvös equation with respect to temperature.[7] In eq. 5, M is the molecular weight, k is the Eötvös constant, γ is the surface tension, $\partial\gamma/\partial T$ is the temperature coefficient of surface tension, v is the specific volume, and $\partial v/\partial T$ is the temperature coefficient of the specific volume. These melts would be expected to be more like the associated liquid water, than like normal liquids, and for water the value of k is 1. Using this value of k and the experimental data reported here, the degrees of polymerization calculated from eq. 5 for the sodium phosphate melts at temperatures near the liquidus range from *ca.* 9 at an Na_2O/P_2O_5 mole ratio of 1.0 to *ca.* 12 at a ratio of 1.5. This means that the effective molecular weights in the molten state, as estimated in this way, appear to be relatively low compared to the high degree of polymerization, *i.e.*, 250 or more, found in solutions of the quenched glasses with Na_2O/P_2O_5 mole ratios near unity.

The surface tension and density data for all of these Na_2O/P_2O_5 melts can be represented by the Macleod equation

$$\frac{\gamma^{1/4}}{d - d'} = C \qquad (6)$$

in which d', the density of the vapor is neglected. The constant C is equal to 1.74 ± 0.07. This constant appears to be independent of temperature, but shows a trend toward higher values with increasing Na_2O/P_2O_5 mole ratio in the phosphate, within the limits indicated above.

By dividing Sugden's parachor[8] by the Macleod constant, C, the molecular weight can be quite well estimated for organic compounds. Although values for the parachor equivalents are not known for phosphorus and sodium and the number of bonds from the phosphorus atom is not well understood, these values can be approximated. Such approximations lead to degrees of polymerization around unity for these sodium phosphate melts.

The low values of the degree of polymerization (*ca.* 9 from the Eötvös equation and 1 from the Macleod equation) appear to be in accord with the concept previously developed[9] in this series of papers that a random reorganization process is continuously underway in sodium phosphate melts. The low degree of polymerization probably represents a time-averaged size of the units involved in the reorganization with extra weighting of the smaller units. However, it should be noted that extension of the Eötvös, Macleod, and Sugden expressions to ionized melts represents a considerable extrapolation and hence the resulting conclusions can, at best, be only a weak confirmation of the random reorganization theory.[9]

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(6) S. Sugden, *J. Chem. Soc.*, **121**, 858 (1922).

(7) This treatment of the equation was suggested by Professor Tormod Forland, Department of Ceramics, The Pennsylvania State University, private communication.

(8) S. Sugden, *J. Chem. Soc.*, **125**, 32 (1924).

(9) John R. Van Wazer, This Journal, **72**, 644 (1950).