[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Partial Molal Volumes of Potassium Chloride, Potassium and Sodium Iodides and of Iodine in Aqueous Solution at 25°

BY DUNCAN A. MACINNES AND MARGARET O. DAYHOFF

Using a magnetic float method, which is briefly described, the densities, at 25°, of aqueous solutions of potassium chloride, and of potassium and sodium iodides have been determined. Measurements have also been made of solutions containing potassium iodide and iodine, and sodium iodide and iodine. From these data the apparent and partial molal volumes of the salts, and the corresponding equivalent volumes of iodine, have been computed.

In order to interpret the results obtained with the e.m.f. centrifuge,[1] it is necessary to make use of values of the densities, ρ, of the solutions involved, and of the partial molal volumes, $\bar{V}$, of the substances taking part in the mechanism of the galvanic cell. The $\bar{V}$ values are obtained from density measurements at a series of concentrations. Although some density measurements of the required precision have already been made, many more data are needed. It has, therefore, been considered desirable to develop the magnetic float method, originally described by Lamb and Lee[2] and modified by Geffcken, Beckmann and Kruis,[3] to meet our requirements. The present communication is concerned with the data so far obtained and with the resulting apparent and partial molal volumes. The method used is outlined briefly, since it has been described in detail elsewhere.[4] In order to make comparison of the results obtained by this method with those found by the pycnometer, the densities of solutions of potassium chloride have been determined. A graphical comparison of such results is given in the article just mentioned. The measurements also include the densities of aqueous solutions of sodium and potassium iodides. In other series the densities were determined (a) of aqueous solutions in which the ratio of the percentage composition of KI to water was kept constant, but that of iodine varied, (b) the corresponding ratio of iodine to water was maintained at one value and that of potassium iodide changed, and (c) the ratio of the percentages of sodium iodide and water was held constant and that of iodine varied.

The Method

The procedure adopted involves the use of a float, A, of Fig. 1, in the shape of an inverted flask. In the stem of the float is placed a permanent magnet, M. The weight of the float is fixed by the use of lead shot so that it just fails to sink in the pure solvent. In making density determinations small platinum weights, w, are placed on top of the float until it slowly descends. A final adjustment is made by flowing a measured current through the solenoid, Y, until the float rises at a rate that is determined by observing the motion of the tip, T. If several values of the current are used it is found that the speed of rise is roughly a linear function of the current, and an extrapolation can be made to a value at which the float would neither rise nor fall. This process may be repeated with a solution, yielding data from which the density of the solution may be obtained. The solvent or the solution whose density is desired is contained in the vessel B-D-B, of about 350-cc. capacity, at the lower end of which is a depression D, into which the tip T of the float A may rest. The cover C-C fits into the main vessel with the aid of the ground joint G-G. Through the cover pass the tubes E and F, which hold the stirrer S, and the glass tube into which the platinum ring P is sealed. This ring prevents the float A from rising too high and holds it in place during stirring. The cover C-C also carries the hollow stopper K by the removal of which weights may be placed on the upper surface of the float A or additional solution may be added to that in the vessel B-D-B. The level of the thermostat water is shown at Z-Z. Thus the measuring vessel and cover are submerged. This has been found necessary for adequate temperature control. The solenoid, Y, consists of 50 turns of enamelled copper wire wound on slots in the six bakelite rods R which pass through the plastic rings U and V. With this arrangement the Joule heat generated in the solenoid passes quickly to the stirred water in the thermostat. The thermostat, which regulates to ± 0.001°, is provided with a double glass window through which the motion of the tip T of the float may be observed by means of a low power telescope, the eyepiece of which contains a scale in arbitrary units. The relative speeds of ascent of the float for different values of the current through the solenoid Y are found by timing the passage of the tip past chosen markings on that scale. A typical series of measurements of the relative speed, $1/t$, in which t is the time elapsed between the selected marks in the scale, at various values of the current i' through the solenoid, is plotted in Fig. 2. Such plots can be extrapolated graphically using a French curve to yield the limiting current i at which the float would neither rise nor fall. By adding different weights the factor f relating the weight w of the platinum to the limiting current i may be obtained. This is of the order of 0.2 mg. per milliampere with the floats being used. The shape of the curve shown in Fig. 2 remains constant with different values of the weight, w, for a given setting of the float with reference to the solenoid Y.

The relation of the density, ρ, of a solution to the measured quantities may be obtained as follows. If a weighted float is in equilibrium in a solution of density, ρ, the weight of the volume, V, of liquid displaced by the float and that, v, by the platinum weights, is equal to the weights, $W + w$, of the float and platinum less the lifting effect, fi, of the limiting current i. Thus, since $v = w/d$, in which d is the density of platinum

$$\rho\,(V + w/d) = W + w - fi \qquad (1)$$

and the density, ρ, is given by the expression

$$\rho = \frac{W + w(1 - \rho/d) - fi}{W + w_0(1 - \rho_0/d) - fi_0}\,\rho_0 \qquad (2)$$

in which w_0 and i_0 refer to measurements made with water. For the density of water at 25°, ρ_0, the value 0.99707_4 g./ml. was used in the computations which follow.[5] This equation may be used directly, a single approximation for the value of ρ used on the right-hand side of the equation being usually sufficient, or the equation may be solved for ρ. A study of the effects of the precision of the various terms on the precision of the density is given in the earlier publication.[4] However, with an 80-g. float the values of the limiting current, i, must be known to 0.4 ma. for a precision of one part in a million in the density. This accuracy in i is readily obtained. To achieve that precision in the density values it is necessary to eliminate other sources of error. Air bubbles must be prevented from sticking to the float and the platinum weights, and the isotopic constitution of the water used as solvent must be kept constant.

---

(1) B. R. Ray and D. A. MacInnes, *Rev. Sci. Inst.*, **20**, 52 (1949); D. A. MacInnes and B. R. Ray, THIS JOURNAL, **71**, 2987 (1949).

(2) A. B. Lamb and R. E. Lee, *ibid.*, **35**, 1666 (1913).

(3) W. Geffcken, C. Beckmann and A. Kruis, *Z. physik. Chem.*, [B] **20**, 398 (1933).

(4) D. A. MacInnes, M. O. Dayhoff and B. R. Ray, *Rev. Sci. Inst.*, **22**, 642 (1951).

(5) "Int. Crit. Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 25.

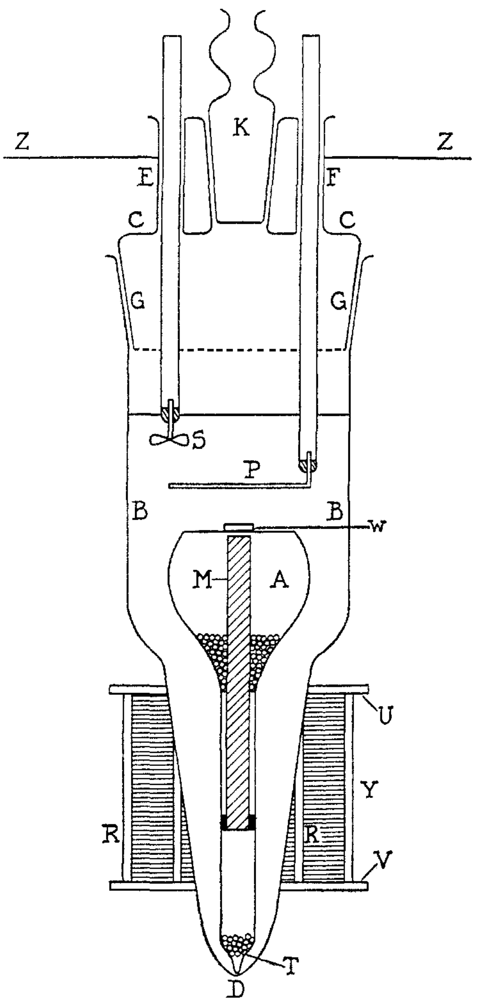

Fig. 1.

The apparatus as described above has been used in three different ways. (a) Solutions of the desired compositions are made up outside the apparatus and their densities determined individually. (b) A weighed amount of water is placed in the measuring vessel, and the equilibrium conditions, as to weight of Pt and current, determined; an additional Pt weight is then put on the float and a concentrated solution of the substance under study is added to the water by means of a weight buret until, after stirring, the float can be raised by a small current through the solenoid. (c) Water is placed in the measuring vessel as in (b), strong solution is added from the weight buret, Pt weights are added until the float just sinks, and the final adjustment is made electromagnetically. With procedures (b) and (c) a series of density measurements of solutions of increasing concentration may be made with one sample of solvent.

Materials and Purification

Water.—The water used in these determinations was obtained from our still for producing conductivity water. A large enough supply was obtained so that for any series of measurements all of the water used had the same isotopic constitution.

Potassium Chloride.—A good commercial grade of this salt was recrystallized and fused. Before making up solutions the material was further dried at about 100°.

Potassium and Sodium Iodides.—The best available material was recrystallized twice and the resulting crystals were centrifuged to remove adhering solution. The crystals were next dried in vacuum in an Abderhalden apparatus at 100°. In making up the solutions the crystals were placed in a platinum boat, inserted in a Richards bottling apparatus[6] and heated, without fusion, to 450°, in a current of dry nitrogen. The boat and contents were then pushed, while still in the apparatus, into a bottle, and a stopper inserted. Weighing was then carried out without danger of absorption of water from the atmosphere.

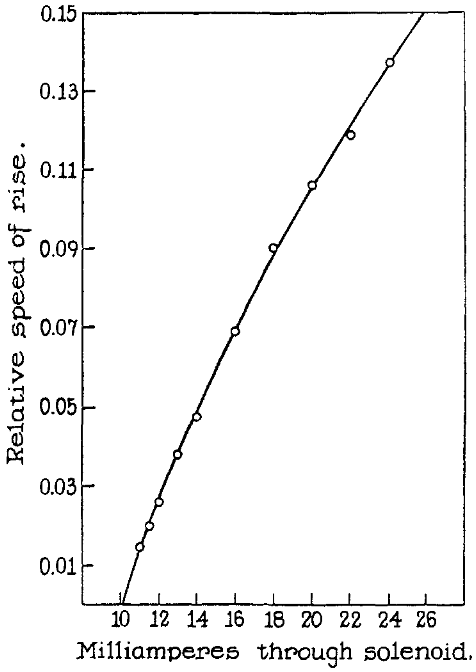

Fig. 2.

Iodine.—The commercial grade was resublimed twice, once from a mixture with potassium iodide. The iodine solutions were made up by weight. The amount of iodine lost during the density measurements was found to be less than 0.05%, and would have inappreciable effect on the results. In this determination the differential electrometric titration method of MacInnes and Dole[7] was used, and calibrated against solid iodine.

Results and Discussion

The apparent molal volume, ϕ_a, of a component, a, in a solution of volume, V, is given by the formula

$$\phi_a = \frac{V - V_0}{n_a} \qquad (3)$$

in which V_0 is the volume of the solvent before the component, a, is added and n_a is the number of moles of that component dissolved. In Table I the compositions and densities of solutions of potassium chloride and of solutions of potassium and sodium iodides are given. In column 4 of that table the corresponding apparent molal volumes are listed. For potassium chloride solutions these ϕ values agree very closely with those obtained by a dilatometer method by Kruis[8] and with those found from data given by the magnetic float procedure by Geffcken and Price.[9] They can be expressed within the small experimental error by the empirical equation

$$\phi_{KCl} = 26.50 + 3.26\sqrt{m} - 1.12m \qquad (4)$$

in which m is the molality (moles per 1000 g. of H_2O).

The table also contains apparent molal volumes, for smaller ranges of concentration, for KI and NaI solutions.

---

(6) T. W. Richards and H. G. Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

(7) D. A. MacInnes and M. Dole, THIS JOURNAL, **51**, 1119 (1929).

(8) A. Kruis, *Z. physik. Chem.*, **B34**, 1 (1936).

(9) W. Geffcken and D. Price, *ibid.*, **B26**, 81 (1934).

TABLE I

DENSITIES AND APPARENT AND PARTIAL MOLAL VOLUMES OF KCl, NaI AND KI AT 25°

Weight, %	Mole per 1000 g. H_2O	Density, 25°	Apparent mol. vol., ϕ	Partial mol. vol., $\bar{V}$
		KCl		
0.064129	0.008607	0.997486	26.67	26.93
.064129	.008607	.997485	26.72	26.93
.097536	.013096	.997695	27.10	27.03
.097536	.013096	.997698	26.87	27.03
.113859	.015290	.997802	26.86	27.08
.113859	.015290	.997802	26.89	27.08
1.16605	.156666	1.004460	27.62	28.09
1.16605	.156666	1.004461	27.61	28.09
1.16605	.156666	1.004463	27.60	28.09
2.51475	.34601	1.012999	28.03	28.60
2.51475	.34601	1.012999	28.03	28.60
4.28146	.59997	1.024303	28.35	28.96
4.28146	.59997	1.024303	28.35	28.96
		NaI		
0.6560	0.04404	1.002093	35.55	35.62
1.0293	.06937	1.004972	35.55	35.69
1.3088	.08846	1.007132	35.62	35.73
1.8316	.12445	1.011209	35.61	35.80
2.2144	.15104	1.014197	35.72	35.85
2.8784	.19769	1.019442	35.75	35.92
2.9548	.20309	1.020056	35.71	35.93
		KI		
1.5801	0.096706	1.008627	45.81	45.95
1.5801	.096706	1.008625	45.83	45.95
3.0888	.19198	1.019882	45.95	46.12
3.0682	.19066	1.019729	45.94	46.12
3.0876	.19190	1.019878	45.92_4	46.12
3.0876	.19190	1.019878	45.92_6	46.12

TABLE II

DENSITIES AND APPARENT AND PARTIAL EQUIVALENT VOLUMES OF IODINE IN SOLUTION WITH POTASSIUM IODIDE AND SODIUM IODIDE AT 25°

Weight % salt	Weight % iodine	Density	Apparent eq. vol.	Partial eq. vol.	Method
		KI			
3.0888	0	1.019882	...	...	a
3.0764	0.4028	1.023017	29.77	30.02	a
3.0545	1.1105	1.028550	30.01	30.11	a
3.0332	1.8018	1.034004	30.12	30.20	a
3.0682	0	1.019729	...	...	a
3.0469	0.6956	1.025145	29.93	30.06	a
3.0348	1.0915	1.028240	30.07	30.10	a
3.0103	1.8891	1.034547	30.09	30.21	a
3.0876	0	1.019878_3	...	...	a
3.0863	0.04104	1.020195_1	30.28	29.98	c
3.0845	.09909	1.020644_0	30.23	29.98	c
3.0820	.17913	1.021266_2	30.03	29.99	c
3.0876	0	1.019878_0	...	...	a
3.0846	.09564	1.020616_7	30.27	29.98	c
3.0823	.16954	1.021193_0	29.94	29.99	c
3.0803	.23628	1.021709_9	30.01	30.00	c
3.0785	.29531	1.022168_2	30.02	30.00	c
		NaI			
2.9548	0	1.020056	...	...	a
2.9433	.3777	1.022986	29.97	29.96	a
2.9291	.8292	1.026512	29.90	29.96	a
2.9169	1.2581	1.029884	29.99	29.96	a
2.9042	1.6994	1.033382	29.95	29.96	a

An important part of this research was that of obtaining accurate values of the equivalent volumes of iodine in solutions of potassium iodide and of sodium iodide. (In this case it is convenient for computations to use as n_a in Eq. 3 the number of equivalents of uncharged iodine, I^0.) The earliest data from which these constants may be derived were obtained by Tolman[10] and some preliminary measurements are recorded by MacInnes and Ray.[1] The data obtained in this research are given in Table II together with the computed equivalent volumes. The figures obtained using method (a), indicated in the last column of the table, were found using solutions which were made up independently. Those indicated by (c) involved the use of a weight buret as outlined above.

It was also considered desirable to determine the effect of the addition of iodine on the value of the apparent molal volume of potassium iodide. To this end solutions were made up containing varying amounts of the salt, but with a substantially constant ratio of free iodine to water. The results of the density measurements are given in Table III. In computing the apparent molal volumes in the fourth column the volume V_0 of the "solvent" in Eq. 3 was obtained from the relation $V_0 = V_w + n_I\phi_I$ in which V_w is the volume of the pure water, n_I is the number of equivalents of iodine, and ϕ_I is a mean value, 30.09, of the apparent equivalent volume of iodine, from Table II. Such a solvent is, of course, unrealizable in this case, without the presence of the solute, potassium iodide.

TABLE III

DENSITIES AND APPARENT AND PARTIAL MOLAL VOLUMES OF POTASSIUM IODIDE IN SOLUTION WITH IODINE AT 25°

Weight % KI	Weight % I^0	Density	Apparent mol. volume	Partial mol. volume
2.0961	1.4839	1.024246	45.81	46.06
2.3346	1.4802	1.026037	45.81	46.10
3.1047	1.4686	1.031843	45.95	46.24
3.1320	1.4682	1.032063	45.89	46.24
3.7839	1.4582	1.037040	45.93	46.34
4.8089	1.4427	1.044938	46.06	46.48
5.5905	1.4309	1.051032	46.15	46.58

In the interpretation of the results from the e.m.f. centrifuge, for which the data given in this paper were mainly obtained, it is the partial molal or equivalent volumes, $\bar{V}$, rather than the apparent volumes, ϕ, which are utilized. The partial molal volume $\bar{V}_a$ of a component a is defined by $\bar{V}_a = (\partial V/\partial n_a)_{T,P,n_b,n_c}$ the subscripts n_b,n_c indicating that the other components are to be kept constant. Eq. 3 may be given the form

$$\phi_a = (V - V_0)/m_a \qquad (5)$$

in which V_0 is the volume of 1,000 g. of water and m_a is the molality. By differentiating and rearranging Eq. 5 we obtain

$$\bar{V}_a = \partial V/\partial m_a = \phi_a + m_a(\partial\phi_a/\partial m_a) \qquad (6)$$

With this expression and Eq. 4, we have for the partial molal volume of potassium chloride

---

[10] R. C. Tolman, *Proc. Am. Acad. Arts Sci.*, **46**, 109 (1910).

$$\bar{V}_{KCl} = 26.50 + 4.89\sqrt{m} - 2.24m$$

with which the values for these constants in the last column of Table I were computed.

For sodium and potassium iodides in water, a good approximation to the experimental results is given by

$$\phi_{NaI} = 35.37 + 0.80\sqrt{m}$$
$$\phi_{KI} = 45.55 + 0.87\sqrt{m}$$

Using Eq. 6 we obtain

$$\bar{V}_{NaI} = 35.37 + 1.20\sqrt{m}$$
$$\bar{V}_{KI} = 45.44 + 1.30\sqrt{m}$$

Similarly, for potassium iodide in 1.46% iodine as solvent

$$\phi_{KI} = 45.26 + 1.48\sqrt{m}$$

and

$$\bar{V}_{KI} = 45.26 + 2.22\sqrt{m}$$

where m is the number of equivalents of potassium iodide in 1,000 g. of iodine and water.

By comparing the values of $\bar{V}_{KI}$, shown in Tables I and III, it will be seen that the presence of dissolved iodine has a very small effect on that constant.

In Table II it will be observed that the values of the apparent equivalent volumes, ϕ_I, at different concentrations of iodine are nearly constant. For iodine in approximately 0.2 N potassium iodide solution

$$\phi_I = 29.98 + 0.73m$$

and from Eq. 6

$$\bar{V}_I = 29.98 + 1.46m$$

where m is the number of equivalents of iodine in 1000 g. of potassium iodide and water. Similarly, for iodine in sodium iodide solution

$$\phi_I = \bar{V}_I = 29.96$$

Acknowledgment.—The authors are indebted to Elaine Lackman and Grace Peters for help in making the measurements.

NEW YORK 21, N. Y. RECEIVED SEPTEMBER 12, 1951

[CONTRIBUTION FROM THE VITRO CORPORATION OF AMERICA, FORMERLY THE KELLEX CORPORATION, JERSEY CITY, N. J.]

The Constitution of the Uranates of Sodium[1]

BY C. A. WAMSER, J. BELLE, E. BERNSOHN AND B. WILLIAMSON

Chemical and X-ray diffraction analyses, and the interpretation of pH and conductance data, indicate that two sodium uranates, $Na_2U_7O_{22}$ and $Na_6U_7O_{24}$ (or mixtures thereof) are obtained when uranium is precipitated from uranyl nitrate solution by sodium hydroxide. When sodium hydroxide is added to the point of incipient precipitation (requiring 1 or more moles of NaOH per mole of U), basic uranyl ions of the type $UO_3UO_2^{++}$ and $(UO_3)_2UO_2^{++}$ are formed. The further addition of sodium hydroxide (to NaOH/U = 2.29) effects the quantitative precipitation of uranium as $Na_2U_7O_{22}$. This primary uranate reacts with further sodium hydroxide (to NaOH/U = 2.86) to produce $Na_6U_7O_{24}$, which is the species stable in the presence of excess alkali.

Until the work of Flatt and Hess[2] it had been generally accepted that the addition of alkali hydroxide to solutions of uranyl salts resulted in the precipitation of uranyl hydroxide which then reacted with alkali to form the diuranate $Na_2U_2O_7$. Other investigators[3-5] postulated the uranates $2Na_2O\cdot5UO_3$, $2Na_2O\cdot7UO_3$ and $Na_2O\cdot8UO_3$, respectively, on the basis of chemical analysis or pH data.

Flatt and Hess[2] established, on the basis of a phase rule study, that only two uranates, most closely represented by $K_2O\cdot7UO_3$ and $2K_2O\cdot5UO_3$ (or mixtures thereof), are formed when uranyl nitrate is treated with potassium hydroxide.

Because of the amorphous character of the uranates obtained by precipitation, most of the evidence for their composition has been obtained indirectly.

Most of the previous investigations have not recognized the pronounced effect of aging of the precipitate. Unless equilibrium conditions are closely approached, erroneous conclusions may be deduced from analyses of the precipitates or from measurements on the supernatant liquors.

By preparing the precipitates under carefully controlled conditions approaching equilibrium, and by thorough washing according to a definite experimentally established pattern, it was found possible to obtain analytical and X-ray diffraction data capable of consistent interpretation in terms of definite compounds of sodium and uranium.

Experimental

In the present investigation a series of mixtures was prepared each of which contained a measured volume of an aqueous solution of uranyl nitrate of definite concentration treated with measured volumes of standard carbonate-free sodium hydroxide (added dropwise with continual stirring). Each mixture was diluted to the same final volume with water and allowed to stand in a sealed container at room temperature for five days with occasional agitation. All precipitations were carried out at 25 ± 5°. Under these conditions (which approximate equilibrium conditions) the character of the precipitates obtained facilitated separation and effective washing by centrifugation.

The mother liquors were analyzed for free alkali and uranium content and their pH and conductance determined.

The precipitates were washed by repeated dispersion in water and separation by centrifugation. The method of washing uniformly employed was established by the observed behavior of those precipitates which had been formed at the higher pH values. It was observed that the concentration of free alkali in the water washings decreased to a constant (low) value on repeated application of water and that this alkalinity was maintained on exhaustive washing. On this basis, the precipitates were washed only to the point at which the alkalinity of the filtrate first reached its minimum value. It was demonstrated that this alkali actually resulted from the hydrolysis of the sodium uranate and not by desorption

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 11, 1951.

[2] R. Flatt and W. Hess, *Helv. Chim. Acta*, **21**, 1506 (1938).

[3] J. Metzger and M. Heidelberger, THIS JOURNAL, **31**, 1040 (1909).

[4] H. Guiter, *Bull. soc. chim.*, 403 (1946).

[5] H. Guiter, *ibid.*, 275 (1947).