[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Tracer-diffusion in Liquids. I. Diffusion of Tracer Amount of Sodium Ion in Aqueous Potassium Chloride Solutions

BY JUI HSIN WANG[1]

A method of measuring the diffusion of tracer amount of a radioactive ion in salt solution is developed. The diffusion coefficients of tracer amount of radioactive sodium ion in aqueous potassium chloride solutions of concentration between 0.00494 and 4.14 formular weight per liter are determined. It is shown that the "tracer-diffusion" coefficients of sodium ion in aqueous potassium chloride solutions as calculated by the Onsager theory agree with the measured values at various concentrations from infinite dilution up to about 0.05 formular weight per liter within experimental uncertainties. Above 0.1 formular weight per liter the "tracer-diffusion" coefficient of sodium ion first increases, reaching a maximum value near 1.3 formular weight per liter, and then starts again to decrease with increasing salt concentration. A qualitative explanation of the concentration dependence of the "tracer-diffusion" coefficient of sodium ion in concentrated aqueous potassium chloride solutions is attempted.

When tracer amount of a given ion diffuses in a salt solution of finite and uniform (except with respect to the diffusing tracer ion) concentration, the diffusion coefficient of the tracer ion may be regarded as constant along the diffusion path as long as the concentration of the tracer ion is everywhere negligible as compared to the total concentration of ions in the system. For example, when radioactive sodium ion of concentration below 10^{-4} molal diffuses in 1.0 molal aqueous potassium chloride or sodium chloride solution, the diffusion coefficient of the radioactive sodium ion, as well as all other except radioactive properties of the system, may be safely regarded as constant along the diffusion path. In the second case cited above, the term "self-diffusion" has often been used to designate this special case of "tracer-diffusion." Because of their special theoretical simplicity, these "tracer-diffusion" coefficients are particularly interesting in the insight they might provide on the molecular theory of liquid solutions. In the present work, the diffusion coefficients of tracer amount of radioactive sodium ion in aqueous potassium chloride solutions of concentrations between 0.00494 and 4.14 formular weight per liter at 25° are determined and discussed.

Method of Measurement

The capillary method previously described[2] is employed in the present work. According to this method, uniform capillaries, with lower ends sealed, were filled with aqueous potassium chloride solution of known concentration containing tracer amount of radioactive sodium ion and held vertically in a large circulating bath of aqueous potassium chloride solution of the same concentration but without radioactive sodium ion. The radioactive sodium ions were allowed to diffuse upward, and the concentration of tracer ion at the upper end of each capillary was kept at zero by convection current in the large bath. Under these conditions the integration of the one-dimensional Fick's equation for "tracer-diffusion"

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where c is the concentration of tracer ion at time t and diffusion coördinate x, and D is the "tracer-diffusion" coefficient which is independent of tracer concentration, leads to

$$\frac{c_{\mathrm{av}}}{c_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2 Dt/4l^2\right] \qquad (2)$$

In equation (2), c_{av} is the average concentration of tracer ion in the capillary at time t, c_0 is the initial concentration of the same ion, and l is the length of capillary. When the value of Dt/l^2 is greater than 0.2, which was always the case in the present work, the series on the right-hand side of equation (2) converges so rapidly that all terms following the first can be neglected with an error smaller than 0.2%. Thus equation (2) may be written as

$$\frac{Dt}{l^2} = \frac{4}{\pi^2}\ln\left(\frac{8}{\pi^2}\times\frac{c_0}{c_{\mathrm{av}}}\right) \qquad (3)$$

Equation (3) has always been used to calculate "tracer-diffusion" coefficients from the measured values of c_{av}/c_0 in the present work.

In obtaining solution (2) for equation (1) it has been assumed that throughout the diffusion period, the concentration of tracer ion at upper end of each capillary was kept at zero by convection currents in the large bath. Preliminary experiments indicate that this boundary condition can be fulfilled by using a slowly rotating, mercury-seal stirrer with a large paddle which can produce sufficient convection in the bath without causing appreciable vibrations. It has also been found in these preliminary measurements that when there is insufficient or no stirring the actual length of the diffusion path is longer than the length of the capillary, and, if this occurrence is not taken into account, erroneous results will be obtained. When stirring is sufficient, however, it might be possible that a little solution in and near the top of the diffusion capillary be swept out by the convection current so that the actual diffusion path could be shorter than the measured geometric length of the capillary. In order to detect this possible error, uniform capillaries of equal cross-sectional area but of different length were filled with the same tracer solution and held vertically at equivalent positions in the same bath for diffusion measurements. Thus, suppose four uniform capillaries of length l_1, l_2, l_3 and l_4, respectively, and of equal cross-sectional area, are filled with the same solution, the tracer ions in each capillary are allowed to diffuse upward for different lengths of time t_1, t_2, t_3 and t_4, respectively. Since these four capillaries have equal cross-sectional area and are held at equivalent positions in the same convection bath, it is clear that the difference, Δl, between

---

(1) The present work is supported by a post-doctoral fellowship granted by du Pont de Nemours Co.

(2) J. H. Wang, THIS JOURNAL, **73**, 510, 4181 (1951).

length of diffusion path and geometric length of capillary must be the same for all four capillaries. Let A_1 be the measured total amount of radioactive tracer left in capillary No. 1 after diffusion. The average concentration of tracer ion along the entire diffusion path in capillary No. 1 is then given by $A_1/[(l_1 - \Delta l)a]$ where a is the cross-sectional area of capillary. Similarly, $A_2/[(l_2 - \Delta l)a]$ represents the corresponding concentration in capillary No. 2, etc. On applying equation (3) to capillaries No. 1 and No. 2 and eliminating c_0, we have

$$D\left(\frac{t_1}{l_1^2} - \frac{t_2}{l_2^2}\right) = \frac{4}{\pi^2}\ln\left[\frac{8}{\pi^2}\left(\frac{A_2(l_1 - \Delta l)}{A_1(l_2 - \Delta l)}\right)\right] \qquad (4)$$

Similarly, for capillaries No. 3 and No. 4 we have

$$D\left(\frac{t_3}{l_3^2} - \frac{t_4}{l_4^2}\right) = \frac{4}{\pi^2}\ln\left[\frac{8}{\pi^2}\left(\frac{A_4(l_3 - \Delta l)}{A_3(l_4 - \Delta l)}\right)\right] \qquad (5)$$

Equations (4) and (5) can be solved simultaneously for D and Δl.

In all preliminary measurements of this type carried out in the present work, the values of D obtained by solving equations (4) and (5) simultaneously have been found to be equal, within experimental uncertainty, to those calculated directly from equation (3) by neglecting Δl. An example is given in Table I.

TABLE I

DIFFUSION OF TRACER AMOUNT OF Na^+ IN 0.375 MOLAL KCl (aq.) AT 25°

(c_0 = 2835 counts per sec. per ml. of solution)

l, cm.	a, mm.^{2}	t, sec. $\times 10^{-5}$	A, counts/sec.	D, cm.^{2}/sec., calcd. from equation (3) by neglecting Δl
2.14	0.1870	1.209	3.94	1.30×10^{-5}
2.77	.1870	2.077	4.92	1.32×10^{-5}
4.10	.1870	4.340	2.56	1.32×10^{-5}
4.79	.1870	6.049	8.71	1.32×10^{-5}

D calculated from the above four set of values by solving equations (4) and (5) is 1.31×10^{-5} cm.^{2}/sec.

Values in Table I indicate that the Δl-correction is completely negligible under the operating conditions of the present work. However, such a preliminary measurement should in general always be made in diffusion measurements employing this capillary method before the Δl-correction can safely be neglected.

Experimental

Preparation of Tracer Solutions.—The Na^{22} (2.6 years half-life) used was produced through the bombardment of a magnesium target with deuterons, and processed according to a procedure described in an earlier article.[3]

Diffusion Apparatus.—The length of the uniform capillaries used vary from 1.97 to 4.79 cm., and cross-sectional area from 0.1870 to 0.2220 mm.^{2} The construction of these uniform capillaries and accessories has been described in a previous publication.[2]

Diffusion Manipulation.—In each diffusion measurement three or four capillaries were filled, by means of fine pipets, with potassium chloride solution of known concentration containing tracer amount of radioactive sodium ion. These capillaries were then held vertically in a rapidly circulating bath of 1-liter capacity containing potassium chloride solution of same chemical concentration as that in the capillaries but without the tracer amount of radioactive sodium ion. The capillaries were held vertically in such a manner that about $^9/_{10}$ of the length of each capillary was immersed in the circulating bath of inactive potassium chloride solution, with about $^1/_{10}$ of the length near the top of each capillary protruding out of the surface of the bath of inactive potassium chloride solution. After 20 minutes or so when thermal equilibrium had been attained between solutions inside and outside of each capillary, these capillaries were lowered into the interior of the inactive potassium chloride solution, and, at this moment, the radioactive sodium ion in each capillary started their upward diffusion. The 1-liter baths, which contain potassium chloride solutions and the capillaries, were themselves completely immersed in the water of a big constant temperature bath. The temperature of the big bath was kept at 25.00 ± 0.01°. The temperature fluctuation in the 1-liter baths should, therefore, be somewhat smaller than 0.01°, and that in the capillaries should be still smaller.

The diffusion time was so adjusted that after diffusion only about $^1/_5$ of the original tracer was still left in each capillary. After each diffusion period, the capillaries were taken out of each bath, and the solution was drawn out of each capillary separately by means of fine pipets. Each capillary was washed ten times or more with a large excess of distilled water. The sample solution, together with all the washings of each capillary was evaporated to dryness on a copper disk, and had its total radioactivity measured. The concentration of radioactive sodium ion in each capillary before diffusion was also determined by weighing out 5- to 10-mg. samples of the original solution by means of a semi-micro balance that has an accuracy of 0.005 mg. These samples of original potassium chloride solutions containing radioactive sodium ion were also evaporated to dryness on copper disks and had their radioactivity measured together with the samples taken after diffusion.

Measurement of Radioactivity.—The radioactivity of all samples was measured with a thin mica window G-M Counter together with an Autoscaler. The diffusion coefficients were calculated from the measured ratios of c_{av}/c_0 by means of equation (3). In the case of diffusion in concentrated potassium chloride solutions where the samples contained enough inert solid to cause considerable decrease in counting efficiency due to self-absorption, calculated amount of inert potassium chloride solution was added to each sample solution before evaporation so that all samples of each batch contain about the same amount of inert solid. Since the calculated diffusion coefficient depends only on the ratio c_{av}/c_0, the possible error due to self-absorption was thus eliminated.

Results

The measured values of the diffusion coefficients of tracer amount of sodium ion in aqueous potassium chloride solution of various concentrations at 25.00° are listed in Table II.

TABLE II

DIFFUSION COEFFICIENTS OF TRACER AMOUNT OF Na^+ IN KCl(AQ.) AT 25°

Concn. of KCl soln., formular weight per liter	$D \times 10^5$, cm.^{2}/sec.	Concn. of KCl soln., formular weight per liter	$D \times 10^5$, cm.^{2}/sec.
0.00494	1.313 ± 0.036	0.375	1.33 ± 0.022
.0125	1.32 ± .035	.564	1.36 ± .033
.0375	1.30 ± .020	.800	1.40 ± .020
.0550	1.29 ± .023	1.000	1.42 ± .021
.09375	1.28 ± .031	1.500	1.43 ± .029
.1035	1.30 ± .037	2.000	1.40 ± .027
.150	1.32 ± .035	3.000	1.34 ± .022
.250	1.31 ± .013	4.14	1.26 ± .03

Each value listed in Table II is the average result of at least four measurements. The standard deviations listed in Table II vary from 1.0% for 0.250 molal to 2.7% for 0.00494 molal potassium chloride solution. In general, the probable error (0.674 times the standard deviation) is larger for

---

[3] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

very dilute than for concentrated solutions. This unavoidable inaccuracy is chiefly due to the statistical fluctuations in radioactive counting. Thus because of the limited specific activity of the radioactive sodium used, the counting rates are so low for potassium chloride solutions below 0.01 molal that even to get ±2% accuracy in counting data already requires inconveniently long counting periods.

Discussion

For the diffusion of tracer amount of one kind of ions in a solution of electrolyte of otherwise nearly constant composition, the activity coefficient of the diffusing tracer ion is sensibly constant along the diffusion path, and Onsager[4] has shown that the diffusion potential and electrophoretic effect are both negligibly small, and that in dilute solutions the decrease in diffusion coefficient with increasing salt concentration can be completely attributed to the relaxation effect of the ion-atmospheres. He showed that the diffusion coefficient D_j of tracer amount of ions of the jth kind in a salt solution is given by the following limiting law for dilute solutions

$$D_j = \omega_j \left[kT - \frac{\kappa e_j^2}{3\mathfrak{D}} \left(1 - \sqrt{d(\omega_j)} \right) \right] \tag{6}$$

with

$$\omega_j = \frac{RT\lambda_j^0}{|Z|F^2} \tag{7}$$

$$d(\omega_j) = \frac{\bar{\lambda}}{\bar{\Gamma}} \sum_i \frac{t_i}{(\omega_i + \omega_j)} \tag{8}$$

$$\bar{\lambda} = \sum_i n_i e_i^2 \omega_i \tag{9}$$

$$t_i = n_i e_i^2 \, \omega_i / \bar{\lambda} \tag{10}$$

$$\kappa^2 = \frac{4\pi}{\mathfrak{D}kT} \bar{\Gamma} \tag{11}$$

$$\bar{\Gamma} = \sum_i n_i e_j^2 \tag{12}$$

where e_i is the absolute electric charge and Z_i the charge in electronic units of ion i, κ_i is the inverse mean radius of ion-atmospheres, n_i the concentration in number of ions per cc., λ_i^0 the limiting ionic conductance of ion i, $\mathfrak{D}$ the dielectric constant of solvent, k the Boltzmann's constant, R the gas constant, F the Faraday constant and T the absolute temperature.

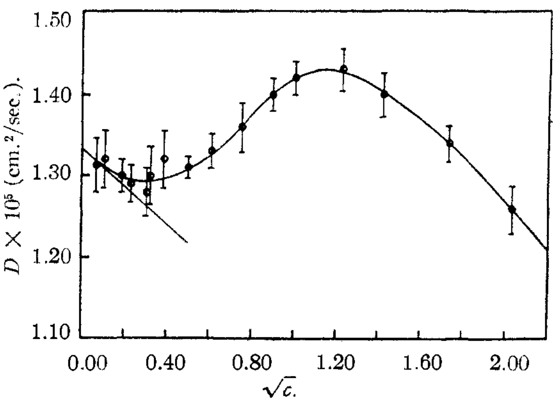

Fig. 1.—Diffusion coefficient of tracer amount of Na$^+$ in aqueous potassium chloride solutions at 25°.

If we express λ_j^0 in (coulomb/sec.) × (cm.²/volt), F in coulombs, R in joules per °C. per mole, and replacing n_i by c_i which denotes concentration in moles per liter, equation (6) can be written as

$$D_j = \frac{RT\lambda_j^0}{|Z_j|F} - \frac{\lambda^0|Z_j|F}{3N\mathfrak{D}} \times 2.694 \times 10^{16} \sqrt{\frac{4\pi}{\mathfrak{D}RT}} \left[1 - \sqrt{d(\omega_j)} \right] \sqrt{\sum_i c_i \; Z_i^2} \tag{13}$$

For the diffusion of tracer amount of ions of species No. 1 in salt solution containing ions of species No. 2 and No. 3, we have

$$c_1 \cong 0,$$
$$c_2|Z_2| = c_3|Z_3|$$

and since equation (8) may be written as

$$d(\omega_j) = \frac{1}{\sum c_i Z_i^2} \sum_i \frac{c_i|Z_i|\lambda_i^0}{\dfrac{\lambda_i^0}{|Z_i|} + \dfrac{\lambda_j^0}{|Z_j|}}$$

we have

$$d(\omega_1) = \frac{|Z_1|}{|Z_2| + |Z_3|} \left[\frac{|Z_2|\lambda_2^0}{|Z_2|\lambda_1^0 + |Z_1|\lambda_2^0} + \frac{|Z_3|\lambda_3^0}{|Z_3|\lambda_1^0 + |Z_1|\lambda_3^0} \right] \tag{14}$$

Equations (13) and (14) have been used by Gosting and Harned[5] to calculate the self-diffusion coefficients of Na$^+$ and I$^-$ in aqueous sodium iodide solutions, and of Ag$^+$ in aqueous silver nitrate solutions. Their calculated values showed fair agreement with the values determined experimentally by Wang and Kennedy[3] and by Whitway, MacLennan and Coffin.[6]

For the diffusion of tracer amount of Na$^+$ in aqueous potassium chloride solutions, if we take the limiting equivalent conductances $\lambda_{K^+}^0 = 73.52$, $\lambda_{Cl^-}^0 = 76.36$, $\lambda_{Na^+}^0 = 50.11$ at 25°[7], equations (13) and (14) can be combined to give

$$D \times 10^5 = 1.334 - 0.236\sqrt{c} \tag{15}$$

The diffusion coefficients listed in Table II as determined in the present work are plotted *vs.* the square root of volume-molal concentration in Fig. 1. The straight line in the dilute concentration represents equation (15) as given by the Onsager theory.

It is seen that below 0.05 molal concentration the measured values agree with the values calculated by means of equation (15) within experimental uncertainty. Above 0.1 molal, however, the diffusion coefficient of tracer amount of Na$^+$ starts to increase with increasing concentration of potassium chloride solution, reaching a maximum value near 1.3 molal, and then starts to decrease again with increasing potassium chloride concentration.

The Onsager–Fuoss theory[8] of transport processes in electrolytic solutions was based on the Debye–Hückel treatment of ion-atmospheres in

---

(4) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(5) L. J. Gosting and H. S. Harned, THIS JOURNAL, **73**, 159 (1951).

(6) Whitway, MacLennan and Coffin, *J. Chem. Phys.*, **18**, 229 (1950).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

(8) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

dilute solutions, and was, therefore, never meant to be applied to solutions of concentrations higher than, say, 0.01 molal for uni-univalent electrolytes. Attempts to extend the Onsager–Fuoss phenomenological theory of irreversible processes to concentrated solutions would encounter at least as much difficulty as the extension of Debye–Hückel theory of equilibrium properties to concentrated solutions, and are, therefore, unlikely to be very successful. In concentrated solutions, two additional factors which have been left out of consideration in the Onsager–Fuoss phenomenological theory become important, *viz.*, the specific interaction between ions and that between ions and solvent molecules. Evidently these two factors are not mutually independent, because the specific interaction between the ions is influenced by the nature of the specific interaction between ions and solvent molecules and *vice versa*. It is quite clear, therefore, that no attempted theory which neglects either of these two factors can be successful in explaining diffusion in concentrated solution of electrolytes.

The general problem of diffusion in concentrated solution of electrolytes is so complicated that even a qualitative picture of all the relevant factors has not yet been obtained. For the diffusion of tracer amount of an ion in salt solution, however, the composition (except with respect to tracer) of liquid along the diffusion path is constant, and the theoretical problem becomes much simpler. A possible picture which may qualitatively explain the dependence of the "tracer-diffusion" coefficient of Na^+ on the salt concentration of aqueous KCl solution is the following.

In the concentration range from infinite dilution up to the maximum concentration at which the Onsager–Fuoss theory still holds, all ions are as fully hydrated as they are at infinite dilution, and the "distortion" (if any) that exists in the structure of "solvent" water immediately surrounding each hydrated ion is practically the same as that at infinite dilution. Since the average distances between ions in solutions within this concentration range is so large, the hydration as well as the interaction between the hydrated ion and the immediately surrounding "solvent" water molecules remain essentially the same at all concentrations within this range. The only effect of increasing salt concentration in this range, then, is to increase the interionic attraction due to long range electrostatic forces. Consequently, the concentration dependence of "tracer-diffusion" coefficient can be satisfactorily explained by computing the relaxation effect of the Debye–Hückel ion-atmospheres as has been shown by Onsager and Fuoss.

When the concentration of solution increases beyond the above range, the mean distance and hence the number of "solvent" water molecules situated between the nearest oppositely charged ions continue to decrease. Thus it becomes increasingly difficult for the decreasing number of "solvent" water molecules to orient themselves to maintain the most stable semi-crystalline structure that exists in the "solvent" water in the immediate vicinity of the hydrated ions at infinite dilution. Consequently, a greater degree of "distortion" would be present in the structure of immediately surrounding "solvent" water for solutions of concentration above the Debye–Hückel range. This greater "distortion" would decrease the activation energy of the hydrated ion for diffusion, and cause the "tracer-diffusion" coefficient to increase with increasing salt concentration.

From a macroscopic point of view, the above described "distortion" effect corresponds to a decrease in dielectric constant of the solvent medium. Hückel[9] explained the increase in activity coefficients of ions by this saturation effect which tends to decrease the dielectric constant of solvent medium and hence increase the self-energy of the ions. While Hückel's correction for this saturation effect may be incomplete, his qualitative explanation is certainly plausible. In the case of "tracer-diffusion" we may likewise assume that the decrease of dielectric constant of the solvent increases the self-energy of the tracer-ion in its normal state. Since the self-energy of a tracer-ion in its activated state is equal to the work consumed in charging an ion of certain finite effective radius imbedded in a solvent of dielectric constant corresponding to a larger degree of random arrangement of water molecules,[10] it should be comparatively less affected by this saturation effect. The over-all influence of this saturation effect on diffusion would be to decrease the activation energy and hence causes the diffusion coefficient to increase with increasing salt concentration.

However, since the dielectric constant of solvent cannot decrease to a value below zero, the increasing self-energy of the ions should not exceed a limiting value corresponding to the self-energy of the hydrated ions imbedded in a medium with dielectric constant somewhat above zero as the concentration of salt solution increases. On the other hand, the relaxation effect, due to mutual attraction between oppositely charged ions, tends to increase continually with increasing salt concentration up to very high concentrations. Furthermore, because of the decrease of the dielectric constant of the solvent the relaxation effect in a real solution should increase with salt concentration faster than that in a hypothetical solution of ions dissolved in a medium of constant dielectric constant. Thus at still higher salt concentrations, the relaxation effect should eventually dominate the effect of increase of self-energy, and cause the "tracer-diffusion" coefficient again to decrease with increasing salt concentration. Figure 1 indicates that the "tracer-diffusion" coefficient of Na^+ in aqueous potassium chloride solution starts again to decrease with increasing salt concentration at about 1.3 molal, showing that the effect of increasing self-energy of ion due to increased distortion in solvent and the relaxation effect are just about to compensate each other at this concentration which

---

[9] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

[10] In the activation process for the diffusion of a radioactive sodium ion, at least part of the hydrogen bonds between the hydrate water molecules and the immediately surrounding "solvent" water molecules must be broken or distorted, thus producing a larger degree of randomness in the orientation of the immediately surrounding "solvent" water molecules. Here the term "hydrated water molecules" refers to the average number of water molecules that are carried along by the sodium ion as the latter diffuses.

corresponds to a mean distance of about 8.5 Å. between neighboring ions. This value of mean distance is not unreasonable if we recall that the crystallographic ionic radii of Na^+, K^+ and Cl^- are 0.95 1.33 and 1.81 A., respectively, and that the average length of water molecules in pure water is about 3 Å.

When the concentration of salt solution is so high that the ions can no longer get enough water molecules from the system to become fully hydrated, one may expect the oppositely charged ions to share their water of hydration or even to form pairs by direct contact of bare ions. Under such circumstances, one may expect the activation energy for "tracer-diffusion" to be so high that the diffusion coefficients may be very much smaller than the corresponding values at infinite dilution. However, since in these highly concentrated solutions the ions are no longer fully hydrated, they would diffuse with a smaller mass, and hence faster inherent velocity. It is not possible to decide which of these two effects dominates by making "tracer-diffusion" measurements in potassium chloride solution in this concentration range because of it low solubility. Preliminary measurement shows that the "tracer-diffusion" coefficient of Na^+ in 12 molal lithium chloride solution is about one-fifth as large as that in infinitely dilute solution, indicating that the effect of increase of activation energy discussed above is the dominating one. However, more experimental work is desirable before definite conclusions can be drawn for "tracer-diffusion" in concentrated electrolytic solutions. Measurements of the diffusion of various tracer-ions in different salt solutions at various concentrations and temperatures are in progress in this Laboratory. The results will be reported in subsequent articles of this series.

Acknowledgment.—The author is indebted to Professor H. S. Harned whose constant encouragement and support made the present work possible, and to Professor J. G. Kirkwood who read and commented on the manuscript. He should thank Professor H. C. Thomas for kindly providing facilities for handling radioactivity. He is also indebted to Professor J. W. Kennedy and Mr. A. M. Friedman who first brought to his attention the problem of Δl-correction.

NEW HAVEN, CONNECTICUT
RECEIVED SEPTEMBER 19, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Heats of Reaction of Some Oxides of Americium and Praseodymium with Nitric Acid and an Estimate of the Potentials of the Am(III)–Am(IV) and Pr(III)–Pr(IV) Couples[1]

BY L. EYRING,[2] H. R. LOHR AND B. B. CUNNINGHAM

The heats of reaction at 25° of $Pr_2O_{3(c, C\ form)}$ with 6.02 *M* and 1.00 *M* nitric acid, of $PrO_{2(c)}$ with 6.02 *M* nitric acid and 6.02 *M* nitric acid–0.1 *M* fluoboric acid, and of AmO_2 with 6.02 *M* nitric acid–0.1 *M* fluoboric acid have been measured. From these measurements and other thermodynamic data heats of formation of $Pr^{+3}{}_{(aq)}$, $Pr(NO_3)_{3(aq)}$, $Pr(NO_3)_{3(aq,\ in\ HNO_3.54H_2O)}$, $Pr(NO_3)_{3(aq,\ in\ HNO_3 \cdot 7.5H_2O)}$, $Pr(NO_3)_{3(aq,\ in\ HNO_3 \cdot 0.017HBF_4 \cdot 7.5H_2O)}$, $PrO_{2(c)}$, $Am^{+4}{}_{(aq)}$ and $AmO_{2(c)}$ are calculated. From these data and estimated entropy values the potentials of the couples: $Am^{+3}{}_{(aq)} + H^+{}_{(aq)} = Am^{+4}{}_{(aq)} + {}^1/_2H_{2(g)}$, and $Pr^{+3}{}_{(aq)} + H^+{}_{(aq)} = Pr^{+4}{}_{(aq)} + {}^1/_2H_{2(g)}$ are estimated to be −2.4 volts and −2.9 volts, respectively, with an uncertainty of about ±0.2 volt in each case.

It has been shown previously[3] that the potential of the Am(III)–Am(IV) couple in acid solution is more negative than −2.0 volts. The work described in this paper was undertaken to evaluate the magnitude of the potential more precisely. The chemistry of americium is of special interest in that it is the first of the transuranium elements in which the stability of the tripositive state is comparable to that observed for some of the lanthanide elements.

In the course of development of this work it was necessary to use a substitute material as a "stand-in" in perfecting the techniques which were intended ultimately to be applied to americium, which is available in very limited quantities. Praseodymium was chosen for this purpose because of a convenient similarity in the chemical properties of its dioxide to that of americium. The work reported here thus permits an approximate evaluation of the potential of the (III)–(IV) couple of praseodymium as well as that of americium.

Since it was known that the potential of the americium couple was so negative as to make the tetrapositive state unstable in acidic aqueous solution, it did not appear feasible to measure the potential in the conventional manner by incorporating the couple in a reversible chemical cell.

We chose, therefore, to evaluate the free energy of this reaction by the less accurate method of evaluating its heat and estimating the entropy change.

Unless otherwise noted, our ΔH and ΔS values refer to a temperature of 298° K. Results are expressed in kcal./mole for the reaction as written.

Accepted values for entropies, heats of formation, etc., are those given in "Selected Values of Chemical Thermodynamic Properties" (hereafter abbreviated SVCTP), issued by the National Bureau of Standards.

Our results are not corrected to unit activities, since the activity coefficients of the +3 and +4

---

(1) Presented at the 118th Meeting of the American Chemical Society at Chicago, Illinois, September, 1950.

(2) Now at the Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City, Iowa. Part of the data reported here was included in a dissertation submitted by L. Eyring to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.2 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).