TABLE VII

HEATS AND FREE ENERGIES OF FORMATION (KCAL./MOLE)

Substance	From the oxides $\Delta H_{298.15}$	From the oxides $\Delta F_{298.15}$	From the elements $\Delta H_{298.15}$	From the elements $\Delta F_{298.15}$
$CaO \cdot Al_2O_3(c)$	-3.69 ± 0.35	-5.36 ± 0.37	-554.8 ± 0.5	-526.8 ± 0.5
$12/7CaO \cdot Al_2O_3(c)$	$-2.71 \pm .38$	$-4.86 \pm .40$	-661.5 ± 0.8	-628.6 ± 0.8
$3CaO \cdot Al_2O_3(c)$	$-1.59 \pm .33$	$-4.09 \pm .40$	-850.0 ± 1.2	-807.9 ± 1.2

TABLE VIII

HEATS AND FREE ENERGIES OF REACTION (CAL./MOLE)

Reaction		$\Delta H_{298.15}$	$\Delta F_{298.15}$
$5/7CaO(c) + CaO \cdot Al_2O_3(c) = 12/7CaO \cdot Al_2O_3(c)$	(23)	$+980 \pm 260$	$+500 \pm 270$
$2CaO(c) + CaO \cdot Al_2O_3(c) = 3CaO \cdot Al_2O_3(c)$	(24)	$+2100 \pm 170$	$+1270 \pm 250$
$12/7CaO \cdot Al_2O_3(c) + 9/7CaO(c) = 3CaO \cdot Al_2O_3(c)$	(25)	$+1120 \pm 210$	$+760 \pm 260$

spect to decomposition into alumina plus tricalcium aluminate.

NOTE ADDED IN PROOF.—Recently E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, 60, 498 (1956), have reported new experimental work leading to $\Delta H_{298.15} = -151.79$ kcal./mole as the heat of formation of calcium oxide. As a consequence, the heats and free energies of formation of the calcium aluminates from the elements (reactions 7, 15, and 22 and values in the last two columns of Table VII) should be more negative by 1.14 kcal./mole of calcium. The heats and free energies of formation from the oxides remain unchanged.

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[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Freezing Point Method of Determining Free Energies in a 2-Component System Forming Compounds. Concentrated Aqueous Sulfuric Acid[1]

BY W. F. GIAUQUE, J. E. KUNZLER AND E. W. HORNUNG

RECEIVED JUNE 25, 1956

A method is described in which freezing point observations may be utilized to obtain the partial molal free energies at all concentrations in a two-component liquid in equilibrium with a series of pure compounds. The method is illustrated by the determination of the variation of the free energy of water in aqueous sulfuric acid from $A = 2$ to $A = -0.005$, where A repsents the water in $H_2SO_4 \cdot AH_2O$.

The use of the freezing point method for accurately determining the partial molal free energies in two-component solutions has been essentially restricted to aqueous solutions over the concentration range in which they may be brought into equilibrium with ice. There is a rather widely held feeling, perhaps based on numerous phase diagrams for somewhat similar components, usually metals, at high temperatures, that solid solutions are to be expected in most cases when various solid phases are formed. Many years of experience in calorimetric studies of a wide variety of substances, in this Laboratory, has led us to conclude that ice is not exceptional in its ability to crystallize from a solution in a highly pure state.

The problem of proving that a solid phase is pure is not one that can be solved easily even with the most careful of ordinary analytical procedures because we have at the same time found that it is, for example, extraordinarily difficult to crystallize compounds from water solutions without solution inclusions, "brine holes," within defects. However the heat effects accompanying eutectic melting, and changing solubility with temperature, make such liquid inclusions in crystals very obvious in the course of accurate heat capacity observations.

Theoretically, pure compounds are thermodynamically stable only at the absolute zero, where equilibrium solutions are ruled out in accordance with the third law of thermodynamics, but actually ordinary temperatures are close enough to the absolute zero so that highly pure substances can and usually do form. The existence of the law of simple multiple proportions and the large number of high quality atomic weight determinations based upon it supplies substantial evidence. This is not inconsistent with the fact that thermodynamic considerations make it certain that the equilibrium presence of foreign components in a solid will increase rapidly with increasing high temperatures.

When the freezing point method of determining free energy is used, the presence of solution inclusions in "brine holes" is not important. Such inclusions will come to equilibrium internally and should have no effect on the equilibrium between the pure outer crystalline surface and the solution taken for analysis.

However, even when a series of compounds separate as essentially pure phases there is still a problem in the experimental determination of the continuous free energy relationship over the whole range of concentration. This type of calculation has not previously been discussed.

The Partial Molal Free Energies in Aqueous Sulfuric Acid from the Freezing Point–Composition Data.—The calculation of the change of partial

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(1) This work was supported in part by the National Science Foundation and by the Office of Naval Research, United States Navy. It may be reproduced or used in any way by the United States Government.

molal free energies from the freezing points in a two component system makes use of the usual equation[2]

$$\frac{d\Delta F/T}{dT} = -\frac{\Delta H}{T^2} \qquad (1)$$

ΔF and ΔH refer to the change of free energy and heat content accompanying dilution of a compound to a composition at which the solution is in equilibrium with the solid compound at the freezing point, where $\Delta F = 0$. In the usual calculations of this sort only one solid phase is utilized; however, in the case of aqueous sulfuric acid there are numerous solid phases in equilibrium with liquid. Each of the several hydrate compounds is in equilibrium over a certain portion of the composition range. In the present case, as shown by Gable, Betz and Maron,[3] overlapping is sometimes accessible due to the possibility of studying the freezing point curves below the stable eutectic temperatures when seeding with only one of the solid phases is employed.

Each of the several compounds may be adopted temporarily as a component within the range of composition in which its solid can be brought into equilibrium with the liquid. The variation of the partial molal free energy of water, $\bar{F}_{H_2O}$, may then be determined, over each of the ranges concerned, by the application of the Duhem Equation in terms of the variation of the appropriate temporary component.

It may be shown that the general equation

$$d\bar{F}_{H_2O} = \frac{1}{n - A}\, d\bar{F}_{H_2SO_4 \cdot nH_2O} \qquad (2)$$

applies to this procedure, where n may have values such as 0, 1, 2, 3, 4, etc., corresponding to anhydrous sulfuric acid and its several hydrates. A represents the number of moles of water associated with one of H_2SO_4 in any solution. A can be used as a negative quantity in the range "above 100%" sulfuric acid.

The quantity $1/(n - A)$ in eq. 2 becomes infinite and changes sign as the value of A equals and passes through n. This means that a calculation for the points where $A = n$ cannot be made. However when it is remembered that $(\bar{F} - \bar{F}^\circ)_{H_2O}$ has continuity through the composition region of each hydrate it will be seen that this problem can be solved in a straightforward manner. As would be expected it was found that very accurate freezing point–composition data were necessarily close to each side of a compound used for this purpose. The slopes of the curves for $A > n$ were found to join smoothly with the continuations for $A < n$ even for the most severe case of anhydrous acid. The matching curves at H_2SO_4 and at $H_2SO_4 \cdot H_2O$ are shown in Figs. 1 and 2. These were constructed from data to be given below.

The determination of absolute values of $(\bar{F} - \bar{F}^\circ)_{H_2O}$ required that the above procedure be extended from anhydrous acid to solutions sufficiently dilute so that the activity of water may be known by direct measurement of its partial pressure.

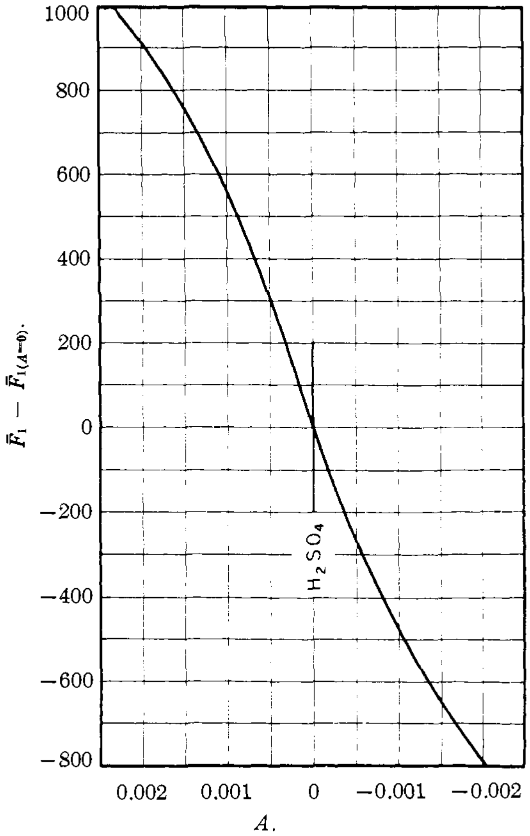

Fig. 1.—Alignment of free energy curves on each side of absolute sulfuric acid; A = moles H_2O per mole H_2SO_4; $\bar{F}_1$ in calories per degree per mole H_2O.

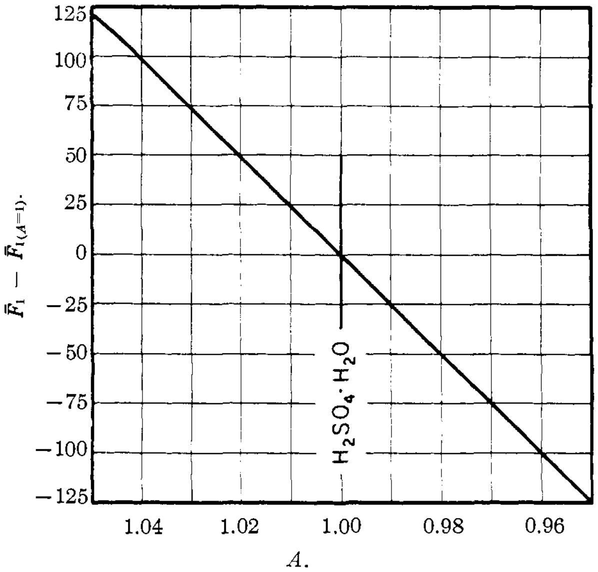

Fig. 2.—Alignment of free energy curves on each side of sulfuric acid monohydrate; A = moles H_2O per mole H_2SO_4; $\bar{F}_1$ in calories per degree per mole H_2O.

We attempted to use the melting curve data of Gable, Betz and Maron[3] from the anhydrous acid to the tetrahydrate; however this excellent piece

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[2] G. N. Lewis and M. Randall, "Thermodynamics and The Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 278.

[3] C. M. Gable, H. F. Betz and S. H. Maron, THIS JOURNAL, **72**, 1445 (1950).

of work was not done with the idea of providing data for free energy calculations and the accuracy was insufficient. Kunzler and Giauque[4] made freezing point measurements over the range $A = -0.005$ to $A = 2$, and Hornung and Giauque[5] measured the partial pressure of water at $A = 2$, 3 and 4 to determine the absolute activity of this component and connect with related data at the lower concentrations.

The data obtained by utilization of several compounds can be connected at the eutectics. $\bar{F}_{H_2O}$ can thus be evaluated in terms of the final reference state in place of the temporary points of reference.

The total free energy of dilution of sulfuric acid, as represented by the equation

$$H_2SO_4 + AH_2O = H_2SO_4 \cdot AH_2O \qquad (3)$$

can then be calculated by means of the equation

$$\Delta F = \int_0^A (\bar{F} - \bar{F}^0)_{H_2O} dA \qquad (4)$$

The Purity of the Solid Phases.—The solid phases of interest in connection with the present determination of free energy from freezing point data are anhydrous sulfuric acid and the monohydrate. Unfortunately, at the time the calorimetric measurements[6] were made on these solid phases, about 1940, we had not expected to use the data to show that the phases crystallized as pure compounds. However, Kunzler and Giauque[4] made supplementary measurements which made it possible to prove that maximum melting sulfuric acid corresponded to pure H_2SO_4 within a few thousandths of one per cent. The data, which apply to the $H_2S_2O_7$ side of H_2SO_4, show that all $H_2S_2O_7$ present in the liquid near the melting point of H_2SO_4 is still in solution at the H_2SO_4–$H_2S_2O_7$ eutectic. It was also shown that maximum melting $H_2SO_4 \cdot H_2O$ was of that composition to within 0.01% and probably to within 0.005%.

There are a number of premelting heat capacity measurements in the work of Rubin and Giauque[6] which give some information about the monohydrate. A careful re-examination of the original data has shown that the resistance thermometer was subject to small strains at and above the eutectic melting temperature as well as at the two points which are so labeled in Series 1 of Table III in their publication.[6] Since detailed thermocouple observations had been taken simultaneously during all measurements, as a usual precaution, the heat capacity values mentioned above have now been recalculated in terms of the thermocouple data. These measurements also involve unusual problems with respect to the longer time required for equilibrium and consequently a greater heat leak. Fortunately the temperature observations had been taken for about 30 minutes after each heat input. The last nine values of Series 1 and the two values of Series 3, Table III of Rubin and Giauque[6] should be 23.79, 24.47, 26.08, 25.67 (same), 26.29, 26.93, 27.71, 28.49 (same), 29.80, 28.98, and 31.97 cal. deg^{-1} mole^{-1}, respectively. The amount of heat absorbed in premelting may be estimated from the excess heat capacity, evaluated by extrapolating the heat capacity curve for the unmelted solid through the temperature range below the melting point. The monohydrate is off composition on the water side as was determined by heat absorption at the $H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 2H_2O$ eutectic temperature.

With the freezing point–composition data tabulated below, and since values of the partial molal heat contents, partial molal heat capacities, and the temperature coefficient of the latter, are available,[7] it is a straightforward matter to calculate the amount of excess water per mole of monohydrate which is present in the liquid phase during each premelting measurement. A similar calculation can be made at the eutectic temperature. In these calculations the solid phase is assumed to be pure and the results are examined to see if they are consistent with this assumption. If, for example, a solid solution with excess water crystallized instead of a pure phase one would expect the absolute amount of excess water remaining in the liquid to become depleted during crystallization along the freezing point curve and be at a minimum at the eutectic.

The data are summarized in Table I. Perhaps it should be emphasized that ideal solutions are not assumed in this calculation since all partial molal properties are available.

TABLE I

PREMELTING DATA ON $H_2SO_4 \cdot H_2O$

T_{av}	ΔT	Cal. melting mole mono	Excess H_2O mole mono
	Series 1		
257.96	6.79	2.3	0.0014
264.74	6.95	3.6	0.0014
271.55	6.90	8.8	0.0016
	Series 3		
268.24	8.02	5.7	0.0014
275.70	7.14	22.6	0.0016
	Measurement including eutectic melting		
231.74	6.50	6.6	0.0015

There is no evidence to indicate that the crystallization of a solid solution was removing water from the remaining liquid, within the limit of accuracy. However, the test is not nearly as severe as one might wish. The premelting results do not extend closely enough to the melting point because, as mentioned above, these 1940 results were not intended for this purpose.

The best test of the absence of solid solutions in a case of this kind would be to use the technique described by Hildenbrand and Giauque[8] for the case of ammonium oxide. The analogous experiment here would be to start with a small amount of H_2SO_4–$H_2SO_4 \cdot H_2O$ eutectic and to measure the eutectic heat of fusion as a function of water addition, with intermittent melting, stirring and refreezing, until the $H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 2H_2O$ eutectic appeared. The abrupt diappearance of one eutectic and the simultaneous appearance of the other would indicate no solid solution. This procedure can be made highly accurate.

It may be noted that only the $H_2S_2O_7$ side of the H_2SO_4, and the $H_2SO_4 \cdot 2H_2O$ side of the $H_2SO_4 \cdot H_2O$ melting curves are supported by premelting heat data. However, as stated above, the anhydrous acid and its monohydrate are pure at their maximum melting temperatures. Even if solid solutions existed to the extent of one or two tenths of a per cent. it would not change our results within the limit of accuracy. We believe however that any subsequent investigation of this problem will find that all solid phases in the H_2SO_4–H_2O system crystallize in a highly pure state. Results showing this to be the case with $H_2SO_4 \cdot 4H_2O$ have been given by Hornung and Giauque[9] and Hornung, Brackett and Giauque[10] who showed that eutectic melting, premelting, and titration all agreed to 0.006% on the sulfuric acid side of the pure compound.

The Freezing Point Data.—The smoothed values of the freezing points of H_2SO_4 from $A = -0.005$ to the monohydrate–anhydrous acid eutectic, where $A = 0.3673$, are given in Table II.

In a preliminary calculation values of $\bar{F}_1$ in the region of negative values of A can only be tabulated relatively to each other since the quantity $1/A$ in the Duhem Equation becomes infinite when $A = 0$. Similarly those in the positive region of A have only relative meaning. These preliminary relative free energies are not given since they have exactly the same relative values on each side of $A = 0$ as those entered in Table II as $\bar{F}_1 - \bar{F}_1(A = 0)$ after the final graphical treatment.

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[4] J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 5271 (1952).

[5] E. W. Hornung and W. F. Giauque, *ibid.*, **77**, 2744 (1955).

[6] T. R. Rubin and W. F. Giauque, *ibid.*, **74**, 800 (1952).

[7] W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, to be published.

[8] D. L. Hildenbrand and W. F. Giauque, THIS JOURNAL, **75**, 2811 (1953).

[9] E. W. Hornung and W. F. Giauque, *ibid.*, **77**, 2983 (1955).

[10] E. W. Hornung, T. E. Brackett and W. F. Giauque, *ibid.*, **78**, in press (1956).

TABLE II

THE FREEZING POINTS AND RELATIVE PARTIAL MOLAL FREE ENERGIES OF H_2SO_4 AND H_2O IN AQUEOUS ACID NEAR ANHYDROUS H_2SO_4

A = Moles H_2O/mole H_2SO_4, θ = f.p. lowering, 0°C. = 273.15°K., f.p. pure H_2SO_4 = 283.521°K., $H_2SO_4 - H_2SO_4 \cdot H_2O$ eutectic = 238.29°K., $\bar{F}_2 = \bar{F}_{H_2SO_4}$, $\bar{F}_1 = \bar{F}_{H_2O}$ cal. deg.$^{-1}$ mole^{-1}

A	θ	$\bar{F}_2 - \bar{F}_2^\circ$	$\bar{F}_1 - \bar{F}_{1\,(A=0)}$	A	θ	$\bar{F}_2 - \bar{F}_2^\circ$	$\bar{F}_1 - \bar{F}_{1\,(A=0}$
−0.005	0.272	−2.56	−1360	0.002	0.096	− 0.765	915
− .003	.136	−1.28	−1035	.003	.191	− 1.422	1180
− .002	.0729	− .687	− 795	.005	.403	− 3.07	1591
− .001	.0228	− .215	− 475	.010	.982	− 8.18	2294
− .0008	.0150	− .145	− 398	.015	1.560	− 14.33	2719
− .0006	.0088	− .087	− 314	.05	5.37	− 49.49	3960
− .0004	.0041	− .042	− 223	.10	10.89	−102.4	4696
− .0002	.0011	− .012	− 122	.15	16.65	−157.8	5141
0	0	0	0	.20	22.62	−215.7	5473
.0002	.0011	− .014	144	.25	28.93	−276.9	5746
.0004	.0046	− .049	262	.30	35.61	−341.6	5983
.0006	.0103	− .102	368	.35	42.63	−409.8	6194
.0008	.0179	− .169	465		H_2SO_4–$H_2SO_4 \cdot H_2O$ eutectic		
.001	.0265	− .251	554	.3673	45.23	−435.7	6261

TABLE III

THE FREEZING POINTS AND RELATIVE PARTIAL MOLAL FREE ENERGIES OF $H_2SO_4 \cdot H_2O$ AND H_2O IN AQUEOUS ACID NEAR SULFURIC ACID MONOHYDRATE

A = moles H_2O/mole H_2SO_4, θ = f.p. lowering, f.p. $H_2SO_4 \cdot H_2O$ = 281.639, 0°C. = 273.15°K., $\bar{F}_{mono} = \bar{F}_{H_2SO_4 \cdot H_2O}$, $\bar{F}_1 = \bar{F}_{H_2O}$ cal. deg.$^{-1}$ mole^{-1}

A	θ	$\bar{F}_{mono} - \bar{F}^0_{mono}$	$\bar{F}_1 - \bar{F}_{1(A=1)}$	A	θ	$\bar{F}_{ono} - \bar{F}^\circ_{mono}$	$\bar{F}_1 - \bar{F}_{1(A=1)}$
				1.05	.278	− 3.08	121
.3673	43.35	−638.8	−1875	1.08	.485	− 7.64	192
.40	37.72	−558.2	−1752	1.10	.750	− 11.75	238
.45	30.66	−456.8	−1576	1.15	1.650	− 25.75	351
.50	24.54	−368.0	−1409	1.20	2.88	− 44.74	461
.55	19.30	−291.7	−1250	1.25	4.43	− 68.49	567
.60	14.86	−226.3	−1095	1.30	6.27	− 96.48	669
.65	11.09	−169.8	− 946	1.35	8.39	−128.3	767
.70	7.96	−122.3	− 800	1.40	10.76	−163.5	860
.75	5.43	− 84.0	− 657	1.45	13.37	−201.7	950
.80	3.42	− 53.25	− 519	1.50	16.19	−242.3	1036
.85	1.89	− 29.61	− 384	1.55	19.22	−285.1	1118
.90	.824	− 12.97	− 252	1.60	22.46	−330.3	1196
.92	.523	− 8.17	− 201	1.65	25.90	−377.4	1271
.94	.289	− 4.53	− 150	1.70	29.52	−425.9	1343
.95	.201	− 3.29	− 125	1.75	33.31	−475.7	1412
.96	.130	− 2.00	− 100	1.80	37.28	−526.7	1478
.97	.072	− 1.12	− 75	1.85	41.41	−578.5	1541
.98	.0324	− .50	− 50	1.90	45.69	−630.8	1602
.99	.0081	− .122	− 24		$H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 2H_2O$ eutectic		
1.00	0	0	0	1.9303	48.36	−662.7	1638
1.01	.0079	− .121	24	1.95	50.13	−683.4	1660
1.02	.0310	− .49	49	2.00	54.70	−735.7	1716
1.03	.0692	− 1.09	74		$H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 3H_2O$ eutectic		
1.04	.124	− 1.94	98	2.0702	61.34	−808.5	1791

It is evident that the relative values of $\bar{F}_1$ must be continuous through the value $A = 0$ and they can be separately plotted and joined graphically as shown in Fig. 1. It is important that the slopes should be found to join smoothly within small limits if such a procedure is to be accepted. It is also evident from Fig. 1 that observations into the very dilute solutions are essential. For example had the observations ceased at $A = -0.001$ and $A = +0.001$ the extrapolation and matching of the curves near pure H_2SO_4 would have involved appreciable error. The graph in Fig. 1 shows that the slopes on each side of $A = 0$ are sufficiently consistent at $A = \pm 0.0002$ so that data closer to pure sulfuric acid could have essentially no effect on the result.

The smoothed freezing point data over the range in which sulfuric acid monohydrate is the solid phase are given in Table III. Here the relatively large dissociation of the monohydrate in solution results in a much less rapid change in $\bar{F}_1$ in passing through the point where $A = 1$, compared to the region near $A = 0$. Thus it is rather a simple matter to line up the $\bar{F}_1$ curves on the two sides of the monohydrate. These curves are shown in Fig. 2. Values for the eutectics at $H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 2H_2O$ and $H_2SO_4 \cdot H_2O$–$H_2SO_4 \cdot 3H_2O$ are included in Table III although only the anhydrous-monohydrate eutectic was utilized in the final free energy calculations to be given later.[7]

In order to place all of the partial molal free energy values of water in terms of pure water as a standard reference state the above results must be connected to other data near $A = 2$. This will be done in a final paper[7] which will summarize the partial molal free energies, heat contents and heat capacities, along with the low temperature thermodynamic data on the several solid hydrates.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LEEDS]

Models Relating Molecular Reactivity and Diffusion in Liquids

BY RICHARD M. NOYES

RECEIVED MARCH 23, 1956

Models are developed by which the tendency of an isolated pair of molecules to react with each other is related to the frequency and magnitude of relative diffusive displacements. Although most experimental tests will show little discrimination, the individual parameters of diffusive motion can be estimated from the effect of scavenger concentration on quantum yield of photochemical dissociation. Data currently available suggest that diffusion in liquids involves almost continuous motion and small individual displacements, and does not involve "jumps" of the order of a molecular diameter that are opposed by significant potential barriers.

Although diffusive motion of molecules involves many random displacements for small distances at high frequency, most quantities calculable from experimental measurement require only the macroscopic diffusion coefficient and do not depend on the microscopic parameters. Therefore, they do not distinguish between a model of diffusion in liquids in which displacements of the order of a molecular diameter are opposed by a potential barrier, and another model in which more frequent but shorter displacements are opposed by a very much lower barrier.[1] Moreover, temperature coefficients measured at constant pressure do not yield direct information on barrier heights because of the accompanying thermal expansion of the liquid.

One approach to the study of liquids is to use highly reactive molecules to probe small regions of solution for short times. If a molecule is produced in a medium containing a random distribution of molecules capable of reacting with it, conventional kinetic treatments assume that the probability of reaction in the next interval of time remains constant for unreacted molecules independent of the time since their formation. We have shown previously[2] that the reactivity actually falls asymptotically and nears its limiting value after about 10^{-9} second in ordinary liquids. The deviation from conventional kinetics can be described in terms of the relative reactivity of a pair of isolated molecules in an infinite volume of solvent.

Our previous publications[2,3] have developed kinetic equations in terms of parameters involving relative reactivity of a pair of molecules. In the present paper, we relate these parameters more directly to those of molecular diffusive motion and examine the applicability to accessible measurements.

Parameters Involving Relative Reactivity

The parameters of importance for describing relative reactivity of two isolated molecules are

α = probability two molecules will react during an encounter

β = probability two molecules separating from a nonreactive encounter will ultimately encounter each other at least once more

β_0 = probability two molecules whose centers were initially separated by a distance r_0 will ultimately encounter each other at least once more

β' = probability two molecules separating from a nonreactive encounter will ultimately react with each other

β_0' = probability two molecules whose centers were initially separated by a distance r_0 will ultimately react with each other

$h(t)\,dt$ = probability two molecules separating from a nonreactive encounter at time zero will react with each other between t and $t + dt$

Some of these parameters can be inter-related by the equations

$$\beta' = \int_0^\infty h(t)\,dt \tag{1}$$

$$\begin{aligned}\beta_0' &= \alpha\beta_0 + \alpha(1-\alpha)\beta_0\beta + \alpha(1-\alpha)^2\beta_0\beta^2 + \alpha(1-\alpha)^3\beta_0\beta^3 + \ldots \\ &= \alpha\beta_0/(1 - \beta + \alpha\beta)\end{aligned} \tag{2}$$

$$\beta' = \alpha\beta/(1 - \beta + \alpha\beta) \tag{3}$$

At long times, the function $h(t)$ varies inversely as $t^{3/2}$ for random relative diffusion in three dimensions; but it must be smaller at short times so that the integral over all time is finite. We have previously[3] used the discontinuous function

$$\begin{aligned} h(t) &= 0 & 0 < t < 4a^2/\beta'^2 \\ &= a/t^{3/2} & 4a^2/\beta'^2 < t < \infty \end{aligned} \tag{4}$$

where a is a constant having dimensions sec.$^{1/2}$ The theory of random flights[4] predicts that the probability of finding a particle near its initial position at time t later is given by $(c/t^{3/2})e^{-c'/t}$ where c and c' are constants. If $h(t)$ fits this form,

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(1) R. M. Noyes, *J. Chem. Phys.*, **23**, 1982 (1955).

(2) R. M. Noyes, *ibid.*, **22**, 1349 (1954).

(3) R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

(4) S. Chandrasekhar, *Revs. Modern Phys.*, **15**, 1 (1943).