

Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes

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DIGITAL OBJECT IDENTIFIER
<http://dx.doi.org/10.1063/PT.3.1619>
The article by Thorne Lay and Hiroo Kanamori is an interesting and informative contribution to the understanding of the seismic energy release of the 1994 Northridge earthquake. It is a pity that the authors did not provide a more detailed discussion of the seismic energy release of the 1994 Northridge earthquake. The authors state that the seismic energy release of the 1994 Northridge earthquake was approximately five times as much energy as the 1994 Northridge earthquake. This is a very interesting result, but it is not clear how the authors arrived at this conclusion. The authors state that the seismic energy release of the 1994 Northridge earthquake was approximately five times as much energy as the 1994 Northridge earthquake. This is a very interesting result, but it is not clear how the authors arrived at this conclusion. The authors state that the seismic energy release of the 1994 Northridge earthquake was approximately five times as much energy as the 1994 Northridge earthquake. This is a very interesting result, but it is not clear how the authors arrived at this conclusion.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

ΔH and ΔS , so that instead of falling far away from the Barclay-Butler line they fall somewhere near it, but in the "wrong" places—i.e., in a range of ΔH and ΔS values higher than their molecular weights and molecular volumes would normally correspond to.

Another point which needs to be mentioned here is that these substances constitute the cases in which the free volume picture is least clear-cut. The occurrence of hydrogen bonds in these liquids introduces a specific non-classical element into the motions (both translational and rotational) of the molecules in the liquid state. On the other hand, by using a sort of principle of correspondence, we can see that, however bad the focus, the free volume camera we have used

to make pictures of the simpler liquids must also give some sort of picture for these. And until some better basis is devised for comparing the associated liquids with the non-associated it seems probable that the free volume concept will continue to be useful for this purpose.

SOLUTIONS

The interpretation of liquids which has been given above receives further, and not inconsiderable, support from data on solutions. It also permits interesting conclusions to be drawn from solution data. The necessary extension of the theory, together with an analysis of experimental results, will be found in the following paper, No. III of this series.

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Free Volume and Entropy in Condensed Systems

III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes

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The ideas of the first and second papers in this series, which make it possible to interpret entropy data in terms of a physical picture, are applied to binary solutions, and equations are derived relating energy and volume changes when a solution is formed to the entropy change for the process. These equations are tested against data obtained by various authors on mixtures of normal liquids, and on solutions of non-polar gases in normal solvents. Good general agreement is found, and it is concluded that in such solutions the physical picture of molecules moving in a "normal" manner in each others' force fields is adequate. As would be expected, permanent gases, when dissolved in normal liquids, loosen the forces on neighboring solvent molecules producing a solvent reaction which increases the partial molal entropy of the solute. Entropies of vaporization from aqueous solutions diverge strikingly from the normal behavior established for non-aqueous solutions. The nature of the deviations found for non-polar solutes in water, together with the large effect of temperature upon them, leads to the idea that the water forms frozen patches or microscopic icebergs around such solute molecules, the extent of the iceberg increasing with

the size of the solute molecule. Such icebergs are apparently formed also about the non-polar parts of the molecules of polar substances such as alcohols and amines dissolved in water, in agreement with Butler's observation that the increasing insolubility of large non-polar molecules is an entropy effect. The entropies of hydration of ions are discussed from the same point of view, and the conclusion is reached that ions, to an extent which depends on their sizes and charges, may cause a breaking down of water structure as well as a freezing or saturation of the water nearest them. Various phenomena recorded in the literature are interpreted in these terms. The influence of temperature on certain salting-out coefficients is interpreted in terms of entropy changes. It appears that the salting-out phenomenon is at least partly a structural effect. It is suggested that structural influences modify the distribution of ions in an electrolyte solution, and reasons are given for postulating the existence of a super-lattice structure in solutions of LaCl_3 and of EuCl_3 . An example is given of a possible additional influence of structural factors upon reacting tendencies in aqueous solutions.

INTRODUCTION

IN the first of two preceding papers¹ (hereinafter to be referred to as I and II) the concept

¹ H. S. Frank, *J. Chem. Phys.* **13**, 478, 493 (1945).

of free volume was re-examined, and relations were worked out between free volume changes and changes in entropy in isothermal processes. In the second paper these free volume relation-

ships were used to derive an equation connecting ΔS with ΔH for the process of vaporization of a liquid. This equation was compared with the empirical rule of Barclay and Butler,² and it was found that the comparison provided an instructive interpretation of the physical details of the condensation, or vaporization, process.

Free volume treatments of liquids have been extended to binary mixtures before,³ but never, to our knowledge, from the empirical point of view of the present series of papers. In this third paper the method of the first two is generalized to binary systems, and it is shown that the simplest sort of generalization suffices to bring the empirical rules of Bell⁴ and of Barclay and Butler² for solutions of "normal" substances within the framework set up for the interpretation of pure liquids. In addition, it is found that the "anomalous" entropy of formation found by Scatchard, Lacher, and their coworkers⁵ for mixtures of various pairs of liquids bears a relationship to the heat of mixing which is predictable by this theory.

The establishment of a plausible physical interpretation of partial molal entropies in solutions of normal substances furnishes the necessary background for the discussion of the very abnormal case of aqueous solutions. It is found that the peculiar nature of water plays a very important role in determining the solubility behavior in it both of non-polar and of ionic substances, and the numerical values of entropy of hydration both for non-polar and for ionic solutes are used to draw pictorial conclusions regarding their effect on the water structure. In the latter case, the conclusions reached are supported by data from many other fields, and suggest interesting possibilities for electrolyte theory.

² I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.* **34**, 1445 (1938).

³ E.g., E. A. Guggenheim, *Proc. Roy. Soc. (London)* **A148**, 304 (1935); J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.* **5**, 896 (1937).

⁴ R. P. Bell, *Trans. Faraday Soc.* **33**, 496 (1937).

⁵ (a) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.* **43**, 119 (1939). (b) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.* **61**, 3206 (1939). (c) G. Scatchard, S. E. Wood, and J. M. Mochel, *ibid.*, **62**, 712 (1940). (d) G. Scatchard and C. L. Raymond, *ibid.* **60**, 1278 (1938). (e) J. R. Lacher and R. E. Hunt, *ibid.* **63**, 1752 (1941). (f) J. R. Lacher, W. B. Buck, and W. H. Parry, *ibid.* **63**, 2422 (1941).

DERIVATION OF EQUATIONS

In order to study solutions by the methods we have been developing, it is convenient, as before, to start with a gaseous mixture and use the rigorous isothermal equation

$$\Delta S = S_g - S_l = R \ln [V_g / \gamma V_f] \quad \text{I (50)}$$

to get across to the liquid. V_g is the volume of the gas, and V_f is the free volume in the liquid; γ is a "free angle ratio." We may recall that V_f is always defined in terms of the geometrical mean of the momentary v 's (box volumes) of all the molecules. Nothing is changed, then, in essence, in going to systems in which molecules of more than one type are present. Since even d' in II (5) is an average, (5), (6), and (3) of II can be used as before to derive

$$V_f = \frac{fb^3g^3}{h^3n^3} V_l \left[\frac{RT}{\Delta E_v} \right]^3; \quad \gamma V_f = \beta V_l \left[\frac{RT}{\Delta E_v} \right]^3 \quad \text{II (10)}$$

as before, where V_l is the volume of the liquid, ΔE_v its molal energy of vaporization, and f , b , g , h , and n are numbers. It will be seen from their definitions in II that in addition to ΔE_v , f , b , g , h , n , and γ all have meanings in a binary solution, as averages, which are just as good as those they have in pure liquids. β is defined as $(\gamma fb^3g^3)/(h^3n^3)$ and for normal liquids has values at 25°C between 2 and 10, roughly. For a mixture it will be expected to vary smoothly as the composition is changed. We shall use the substitution

$$\beta = \beta_1^{N_1} \times \beta_2^{N_2}, \quad (1)$$

where N_1 and N_2 are the respective mole fractions. The significance of this is discussed below.

Now for a binary gas mixture we may write⁶

$$S = n_1 R \left[\ln \frac{Q'_1 V}{n_1 N} + T \frac{d \ln Q'_1}{dT} + 1 \right] + n_2 R \left[\ln \frac{Q'_2 V}{n_2 N} + T \frac{d \ln Q'_2}{dT} + 1 \right], \quad (2)$$

where n_1 and n_2 are numbers of moles, Q' is the partition function (for one molecule) without the volume factor, N is Avogadro's number, and the other symbols have obvious meanings. This can

⁶ Cf., for example, J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (New York, 1940), Chapter 6.

be written

$$S = n_1 B_1(T) + n_1 R \ln \frac{V}{n_1} + n_2 B_2(T) + n_2 R \ln \frac{V}{n_2}$$

$$= n_1 B_1(T) + n_2 B_2(T) + (n_1 + n_2) R \ln \frac{V}{n_1 + n_2}$$

$$- n_1 R \ln N_1 - n_2 R \ln N_2, \quad (3)$$

or,

$$S = N_1 B_1(T) + N_2 B_2(T) + R \ln v_g$$

$$- N_1 R \ln N_1 - N_2 R \ln N_2,$$

S , V , etc. being molal quantities, and N_1 , N_2 mole fractions, following the notation of Lewis and Randall.⁷ Then, by I (50), for the complete condensation of a mixture of n_1 moles of A and n_2 moles of B ,

$$\Delta S = S_l - S_g = (n_1 + n_2) R \ln \frac{\gamma V_f}{V_g}$$

$$= (n_1 + n_2) R \ln \frac{\gamma V_f}{V_g}, \quad (4)$$

whence

$$S_l = (n_1 + n_2) S_l = (n_1 + n_2) [N_1 B_1(T) + N_2 B_2(T)$$

$$+ R \ln (\gamma V_f) - R \sum N_i \ln N_i].$$

Inserting II (10)

$$S_l = (n_1 + n_2) S_l = (n_1 + n_2) [N_1 B_1(T)$$

$$+ N_2 B_2(T) + R \ln v_l + R \ln \beta$$

$$+ 3R \ln RT - 3R \ln \Delta E_v - R \sum N_i \ln N_i]. \quad (5)$$

Here ΔE_v , the molal energy of vaporization of the liquid mixture, is the internal energy liberated in the condensation process considered, and equals

$$\Delta E_v = E_g - N_1 \bar{E}_1 - N_2 \bar{E}_2. \quad (6)$$

We also recall that $V_l = N_1 \bar{V}_1 + N_2 \bar{V}_2$.

We may now differentiate for \bar{S}_1 in the liquid mixture, obtaining

$$\bar{S}_1 = \frac{\partial S_l}{\partial n_1} = S_l + (n_1 + n_2) \frac{\partial S_l}{\partial n_1} - S_l + N_2 \frac{\partial S_l}{\partial N_1}$$

$$= S_l + N_2 \left[B_1(T) - B_2(T) + R \frac{\bar{V}_1 - \bar{V}_2}{V_l} + R \ln \beta_1 \right.$$

$$\left. - R \ln \beta_2 + 3R \frac{\bar{E}_1 - \bar{E}_2}{\Delta E_v} + R \ln \frac{N_2}{N_1} \right], \quad (7)$$

⁷ G. N. Lewis and M. Randall, *Thermodynamics* (New York, 1923).

$$= B_1(T) + 3R \ln RT + R \ln \beta_1 + R \ln V_l$$

$$- 3R \ln \Delta E + R \frac{\bar{V}_1 - V_l}{V_l}$$

$$+ 3R \frac{\bar{E}_1 - E_l}{\Delta E} - R \ln N_1. \quad (8)$$

(Henceforth ΔE will be written instead of ΔE_v .) In obtaining (7) and (8) we have used (1) and treated $\ln \beta_1$ and $\ln \beta_2$ as partial molal quantities (see below). For the pure substance A ,

$$S_1^\circ = B_1(T) + R \ln \beta_1^\circ + R \ln V_1^\circ$$

$$+ 3R \ln RT - 3R \ln \Delta E_1^\circ,$$

so that

$$\bar{S}_1 - S_1^\circ = -R \ln N_1 + R \ln \frac{\beta_1}{\beta_1^\circ} + R \ln \frac{V_l}{V_1^\circ}$$

$$- 3R \ln \frac{\Delta E}{\Delta E_1^\circ} + R \frac{\bar{V}_1 - V_l}{V_l} + 3R \frac{\bar{E}_1 - E_l}{\Delta E}. \quad (9)$$

Using (9) and the corresponding equation for $\bar{S}_2 - S_2^\circ$, we may obtain an expression for the entropy of formation of a binary liquid solution

$$\Delta S = S_l - N_1 S_1^\circ - N_2 S_2^\circ = -N_1 R \ln N_1$$

$$- N_2 R \ln N_2 + N_1 R \ln \frac{\beta_1}{\beta_1^\circ} + N_2 R \ln \frac{\beta_2}{\beta_2^\circ}$$

$$+ R \ln \frac{V_l}{V_1^{\circ N_1} V_2^{\circ N_2}} - 3R \ln \frac{\Delta E}{\Delta E_1^{\circ N_1} \Delta E_2^{\circ N_2}},$$

the other terms cancelling, or

$$\Delta S + R \sum N_i \ln N_i$$

$$= R \ln \frac{\beta}{\beta} + R \ln \frac{V_l}{\bar{V}} - 3R \ln \frac{\Delta E}{\Delta E}, \quad (10)$$

$$\bar{\beta} = \beta_1^{\circ N_1} \beta_2^{\circ N_2}; \quad \bar{V} = V_1^{\circ N_1} V_2^{\circ N_2};$$

$$\bar{\Delta E} = \Delta E_1^{\circ N_1} \Delta E_2^{\circ N_2}. \quad (11)$$

Equation (10), which might have been inferred from (5) by inspection, states that the entropy of formation of a binary liquid mixture deviates from the ideal entropy of mixing by an amount determined by the deviation of β , V_l , and ΔE taken for the solution, from the logarithmic means of these quantities for the pure components.

TABLE I.

Pair	Energies, volumes, and excess entropies of mixing for equimolal solutions.*					
	C ₆ H ₆ -C ₆ H ₁₂	CCl ₄ -C ₆ H ₁₂	C ₆ H ₆ -CCl ₄	C ₂ H ₄ Br ₂ -C ₆ H ₅ Cl	C ₂ H ₄ Br ₂ -C ₆ H ₇ NO ₂	C ₆ H ₅ Cl-C ₆ H ₇ NO ₂
100 V^M/V°	0.65	0.16	0.003	0.31	0.10	-0.08
ΔE mixing cal./mole	175.8	34.2	30.2	94	122	29
$T\Delta S^E$ calc. cal./mole	77.3	14.7	12.4	37.2	48.3	11.2
$T\Delta S^E$ exp. cal./mole	101.4	17.5	10.7	46	30	-36
	Properties of the pure components.					
	C ₆ H ₆	C ₆ H ₁₂	CCl ₄	C ₂ H ₄ Br ₂	C ₆ H ₅ Cl	C ₆ H ₇ NO ₂
V° cc	89.3	108.6	97.1	87.0	102.7	89.3
ΔE° cal./mole	7460	6600	7170	9450	9510	9780

* Data of Scatchard, Lacher and coworkers, see reference 5. $T = 30^\circ\text{C}$. Calculated values obtained by using Eq. (12).

Except for β , (10) contains only experimental quantities. There seems to be no rigorous way of treating β , but it also seems reasonable to expect the approximate rule $\log \beta = 1.57 - 0.000115\Delta H$, obtained in II for normal liquids, to apply rather well to mixtures of normal substances. That is, if we insert II (21) into (10) we should expect a rule of rather good generality and utility. We can hope that individual deviations from it will be small except in mixtures involving solutions which we have other reasons for considering abnormal.

This assumption (remembering that $\Delta H = \Delta E + RT$, sensibly) gives us

$$\Delta S + R \sum N_i \ln N_i = 0.000526R(N_1 \Delta E_1^\circ + N_2 \Delta E_2^\circ - \Delta E) + R \ln \frac{V_l}{\bar{V}} - 3R \ln \frac{\Delta E}{\bar{\Delta E}} \quad (12)$$

COMPARISON WITH EXPERIMENT

The left-hand side of (12) is easily recognized as the non-ideal entropy of formation of the solution ΔS^E , that is, the relative entropy of the solution in excess of the classical entropy of mixing, which is $-R \sum N_i \ln N_i$. The accurate work of Scatchard, Wood, and Mochel,^{5(a)-(c)} and of Lacher and his co-workers,^{5(e), (f)} has established the existence of such excess entropy in binary mixtures of normal liquids. Since V_l , \bar{V} , ΔE , and $\bar{\Delta E}$ for the various pairs considered can also be obtained from the published data, an experimental test of (12) is possible, and the result of such a test upon equimolal mixtures for six pairs of liquids is given in Table I.

It will be observed that, with the exception

of the pairs containing 1-nitropropane, the values of $T\Delta S^E$ calculated from (12) agree with the experimental ones as to order from larger to smaller, and are remarkably close to them in absolute magnitude. Even for the pair benzene-cyclohexane, where the difference is greatest, it amounts to less than 25 percent of the experimental value and corresponds to only 0.07 e.u.

For the pairs containing nitropropane, (12) gives values of ΔS^E which are too high, and a possible reason is suggested by the fact, pointed out by Lacher, that for the nitropropane-chlorobenzene mixture, both ΔS^E and ΔV of mixing are negative. While we do not go as far as Lacher does in attributing to ΔV the determining influence upon ΔS^E , the negative ΔV in this case calls for comment due to the fact that for the same mixture ΔE (or ΔH) of mixing is positive. In a pure liquid, if a positive ΔE accompanied a negative ΔV at constant temperature, this would mean a net repulsive force between the molecules. Here, we know that for pure chlorobenzene and pure nitropropane the internal pressure is strongly attractive,⁸ and it does not seem reasonable to imagine a radical change in force fields when they are mixed. Negative ΔV , however, means that, on the average, the molecular centers of gravity are closer together in the mixture than in the pure liquids. Positive ΔE means that the molecular contacts are not more "intimate" in the sense of compound formation or specific attraction, but rather the reverse. The natural assumption is that the molecules in the mixture somehow tend to pack

⁸ J. H. Hildebrand, *Solubility* (New York, 1936), second edition.

together more neatly so as to make more economical use of space. But the magnitude of ΔV depends both on geometrical and on dynamical factors—it will in general be different at room temperature from what it would be at 0°K. If the room temperature contraction were less than the virtual one at 0°K, we would have, as here observed, negative ΔV with positive ΔE . This can be stated differently by saying that the positive ΔE means that the actual contraction which takes place is “too small,” so that the mixture is somewhat “expanded” as compared with the pure liquids. The sort of packing which produced this result, however, would reduce the average γ , the ratio which measures the freedom of molecular rotation in the liquid, to a value for the mixture which might be markedly lower than the (geometrical) mean for the pure liquids. This would presumably lower the ratio $\beta/\bar{\beta}$ below the value provided for in (12), and would account for an experimental value of ΔS^E more negative than the calculated one.

As a matter of fact, what we have previously learned about β prepares us for such specific effects, which may be presumed to be present to a greater or less extent, and with positive or negative sign, in other cases also. Attributing such deviations in β to the factor γ relates this discussion to Scatchard's original suggestion^{5(a)} as to the possible cause of the large positive ΔS^E in the benzene-cyclohexane mixture. This can be seen if we put into words the physical interpretation of (12), which asserts the positive ΔH (or ΔE) of mixing (*a*) shows that the free volume cells in the mixture are larger than the (geometrical) mean size in the pure liquids and (*b*) corresponds to a decrease in the interference the molecules suffer in their rotational motion. Scatchard's suggestion was equivalent to saying that the second factor is the dominant one, plus the special assumption—now seen to be unnecessary, and subsequently disproved by him through his studies in the benzene-carbon tetrachloride and cyclohexane-carbon tetrachloride pairs—that the whole effect is caused by “too great” a restriction of rotation in pure benzene and/or pure cyclohexane. Our suggested explanation of the discrepancy between the measured ΔS^E of the benzene-cyclohexane pair and the value

calculated from (12) is that for some reason β for the pair is higher than II (21) would predict.

In view of the conditional nature of the dependence of β on ΔH discovered in II, we consider that the results of Table I furnish substantial support to the physical picture of liquids and liquid solutions which underlies (12).

Table II shows corresponding comparisons for three mixtures of ethyl alcohol and chloroform, the data being those of Scatchard and Raymond.^{5(d)} For 12 mole percent alcohol, the value of ΔS^E calculated from (12) agrees well with the experimental one, suggesting that when it is dilute enough, alcohol in chloroform behaves about as normally as ethylene bromide in chlorobenzene—both of these pairs are made up of molecules with rather large dipole moments. By the time the mole fraction of alcohol reaches 0.28, however, the specific abnormality of this substance (tendency to form hydrogen bonds) seriously disturbs the agreement, and in 80 mole percent alcohol (12) fails grossly, as was to have been expected. Owing to the hydrogen bonding tendency of the alcohol, it is less easy here than before to interpret the relationship of the sign of ΔV to that of ΔE . It may be remarked that these systems also fail to obey Lacher's rule, set up for those of Table I, that ΔS^E is approximately representable as a linear function of ΔV .

RELATIONSHIP TO IDEAL AND REGULAR SOLUTIONS

If (12) is correct, or even if (10) is correct and the relation of β to $\bar{\beta}$ is not subject to a very strict, and implausible, condition, it follows that an ideal binary solution⁹ can exist only when the

TABLE II.

Energies, volumes, and excess entropies of mixing for alcohol-chloroform mixtures*			
$N_2(C_2H_5OH)$	0.12	0.28	0.80
$100 V^M/V^\circ$	0.03	0.00	-0.39
ΔE mixing cal./mole	168.6	156.9	-192.3
$T\Delta S^E$ calc. cal./mole	64.0	48.0	-89.8
$T\Delta S^E$ exp. cal./mole	72.8	-1.8	-267
	CHCl ₃	C ₂ H ₅ OH	
V° cc	82.85	58.65	
ΔE° cal./mole	6680	9490	

* Data of Scatchard and Raymond, reference 5(d).

⁹ E.g., J. H. Hildebrand, reference 8, Chapter 2.

molal volumes and molal internal energies of the components are equal. Only then can V_i , which, for an ideal solution must equal $N_1V_1^\circ + N_2V_2^\circ$, equal \bar{V} , and ΔE equal $\Delta \bar{E}$; and if these conditions are not met, ΔS must differ from the ideal entropy of mixing. Another conclusion from (12) is that the non-ideal *regular* solution¹⁰ (one with non-ideal volume and heat change on mixing but with ideal ΔS) cannot exist at all (except for fortuitous cancellations which do not affect the principle). This does not lessen the usefulness of ideal and regular solutions as concepts which provide categories for the classification of real systems. It appears, however, that for estimating activities when values are at hand for ΔH of mixing, entropies based on (12) should be used instead of the assumption of a "regular" ΔS .

The idea that solutions for which ΔE of mixing is not zero should have non-ideal ΔS of formation is, of course, not new. Kirkwood,¹¹ for example, has shown how a difference in force fields around the two types of molecules produces departure from randomness of configuration, which affects both ΔE and ΔS of mixing. Kirkwood, however, along with others¹² who have calculated such effects, simplified the calculation by considering the distribution of molecules in cells which did not change in size on going from pure liquids to mixtures. It is precisely this change in cell size which we have discussed, together with changes in interference with internal motion. Scatchard^{5(a)-(c)} used Kirkwood's equation to compute the entropy anomaly to be expected from the "sorting" effect for some of the systems discussed above and found it, for those cases, to be opposite in sign to the observed effect, and much smaller in magnitude. This indicates that the free volume effect as calculated from (12) is, in solutions of this type, of much the greater importance, as Kirkwood himself concluded on the basis of older data.

It is of interest to note that in principle our Eq. (10) takes implicit account of the "sorting" or non-random distribution effect just discussed. This is because β contains the factor f , which was defined in I and II by the relationship

$V_f = Nvf$, where V_f is the molal free volume of the liquid and v the average size of the free volume cell of an individual molecule. f contains contributions for fluctuations, including encroachment of one molecule on the free volume of another. These are determined by the numbers and kinds of microscopic configurations compatible with the total energy of the system, and since the sorting effect consists in a new condition imposed on such compatibility, it will, in principle, show up in f .

In practice, however, we have not been able to predict values of f even in the simplest real systems, and in pure liquids the best we could do was to use entropy data for an empirical determination of β , in which f appears along with other equally troublesome factors. The rough empirical rule II (21) relating β to ΔH , which we inserted into (10) to obtain (12) therefore takes no account of the sorting effect. As we have seen above, this is of no practical consequence, since the effect is smaller than the uncertainties in the far larger effects which (12) does represent.

DILUTE SOLUTIONS

Changing subscripts in (8) and combining with (3) written for pure substance B in the gas phase gives

$$\begin{aligned} \Delta S_2 = S_{2g} - \bar{S}_2 = R \ln V_{2g} - R \ln \beta_2 \\ - R \ln V_l - 3R \ln \frac{RT}{\Delta E} + R \frac{V_l - \bar{V}_2}{V_l} \\ + 3R \frac{E_l - \bar{E}_2}{\Delta E} + R \ln N_2, \quad (13) \end{aligned}$$

as the molal entropy of vaporization of substance B from a solution. If the solution is assumed to be of vanishingly small concentration in B , V_l and ΔE will be the values for pure A . Again, V_{2g} and V_{1g} are the same if the same standard state is used throughout for the gas phase. Substituting V_{1g} for V_{2g} in (13) and using II (14)

$$\begin{aligned} \Delta S_2 = \Delta S_1^\circ - R \ln \frac{\beta_2}{\beta_1^\circ} \\ + R \frac{V_1^\circ - \bar{V}_2}{V_1^\circ} - 3R \frac{\Delta E_1^\circ - \Delta E_2}{\Delta E_1^\circ}, \quad (14) \end{aligned}$$

¹⁰ J. H. Hildebrand, reference 8, p. 65.

¹¹ J. G. Kirkwood, J. Phys. Chem. **43**, 97 (1939).

¹² E.g., G. S. Rushbrooke, Proc. Roy. Soc., London **A166**, 296 (1938).

where ΔS_2 is the change of entropy and ΔE_2 the increase in internal energy when one mole of substance B is vaporized from infinitely dilute solution in liquid A , the standard state of the vapor being a partial pressure of 1 atmosphere, and that of the solute a hypothetical mole fraction of unity. Use has again been made of the convention that $E \equiv 0$ for a gas, so that $\Delta E_1 = -\bar{E}_1$, and $\Delta E_2 = -\bar{E}_2$.

(14) shows that the entropy change considered should differ from the entropy of vaporization of the pure solvent by an amount determined by the relative values of β_2 and β_1° , \bar{V}_2 and V_1° , and ΔE_2 and ΔE_1° . Before it can be tested against experimental data, it is necessary to make a substitution for $\ln \beta_2$. Here again, as in interpreting (11), we can give no rigorous treatment, but shall use II (21) to represent the dependence of $\ln \beta_2$ on ΔE_2 . Here it is necessary to point out that $\ln \beta_2$, as we have defined it, is a *partial molal* quantity. For according to (1)

$$(n_1 + n_2) \ln \beta = n_1 \ln \beta_1 + n_2 \ln \beta_2, \quad (15)$$

and in obtaining (7) we have assumed that

$$N_1 d \ln \beta_1 + N_2 d \ln \beta_2 = 0; \quad (16)$$

(16) can be justified both on the grounds that any other assumption would be equally arbitrary, and also by analogy with the exact equation

$$N_1 dS_1 + N_2 dS_2 = 0,$$

since $\ln \beta_1$ appears in (8) as an additive term in \bar{S}_1 . Having made this assumption, $\ln \beta_2$ is the rate of change of the extensive quantity $(n_1 + n_2) \ln \beta$ with the number of moles of substance B added to the solution, and in (14) $\ln \beta_2$ is the molal rate of change of $(n_1 + n_2) \ln \beta$ as an infinitesimal amount of solute is added to the pure solvent. Correspondingly, $\Delta E_2 = -\bar{E}_2$, where \bar{E}_2 is the molal rate of change of the internal energy as an infinitesimal amount of solute is added to the solvent.

Proceeding as before, then,

$$\begin{aligned} \Delta S_2 = \Delta S_1^\circ - 0.000526R[\Delta E_1^\circ - \Delta E_2] \\ + R \frac{V_1^\circ - \bar{V}_2}{V_1^\circ} - 3R \frac{\Delta E_1^\circ - \Delta E_2}{\Delta E_1^\circ}, \quad (17) \end{aligned}$$

or, numerically,

$$\begin{aligned} \Delta S_2 = \Delta S_1^\circ - 0.001045[\Delta E_1^\circ - \Delta E_2] \\ + 1.986 \frac{V_1^\circ - \bar{V}_2}{V_1^\circ} - 5.96 \frac{\Delta E_1^\circ - \Delta E_2}{\Delta E_1^\circ}. \quad (18) \end{aligned}$$

Since the term in \bar{V}_2 is small compared to the others, (18) predicts that ΔS_2 should be, for any one solvent, very close to a linear function of ΔE_2 (and therefore of ΔH_2). It also predicts, however, that both constants in the linear equation should be specific for the solvent employed.

EXPERIMENTAL TEST FOR DILUTE SOLUTIONS

Bell,⁴ using the gas-solubility data of Horiuti,¹³ has made calculations, and found regularities, which were used by Barclay and Butler² in support of their empirical rule that the linear Eq. II (16) which connects ΔS and ΔH of vaporization of pure liquids also represents ΔS_2 and ΔH_2 for these dilute solutions. We have repeated Bell's calculations for the temperatures 25°C and 40°C (Bell chose 20°C and our 25°C results agree closely with his when reduced to his standard states) and have also calculated "predicted" values of ΔS_2 , using (18) and Horiuti's values for \bar{V}_2 in the same systems. Table III shows a comparison of ΔS_2 values as calculated (a) "experimentally," from the temperature dependence of the gas solubilities, (b) "theoretically" from (18), and (c) by the Barclay-Butler rule, using II (17). Data obtained by Barclay and Butler on various solutes in acetone, and in ethyl alcohol, are also included, the absence of \bar{V}_2 data in these cases, however, making it impossible to use (18) here. Figure 1 shows the same results, the experimental values (at 25°C) of ΔS_2 being represented by crosses, those calculated from (18) by circles, and II (17) by the solid lines. Squares represent values for other temperatures.

Here again, considering the extent to which specific effects are expected to appear, we consider that the data, excepting those on SO_2 , give full support, both to the physical picture behind (18) and to the Barclay-Butler rule,

¹³ J. Horiuti, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **17**, 125 (1931).

TABLE III. Heats (in calories per mole) and entropies (in e.u.) of vaporization of gases from certain non-polar solvents.

Solvent	Solute		ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B-B)	Solvent	Solute		ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B-B)
CCl ₄ ^a	H ₂	25°	-1260	11.7	11.2	11.2	C ₆ H ₆	O ₂	25°	-380	12.8	12.7	12.3
		40°	-1380	11.3	10.4	10.5			40°	-370	12.9	11.9	11.7
CCl ₄	N ₂	25°	-590	12.6	11.8	12.0	C ₆ H ₆	CH ₄	25°	360	13.5	13.5	13.2
		40°	-680	12.3	11.0	11.3			40°	270	12.7	12.7	12.5
CCl ₄	CO	25°	-340	12.9	12.1	12.3	C ₆ H ₆	C ₂ H ₆	25°	2250	15.9	15.8	15.5
		40°	-390	12.7	11.4	11.7			40°	2220	15.8	15.0	14.9
CCl ₄	O ₂	25°	-10	13.4	12.7	12.7	C ₆ H ₆	C ₂ H ₄	25°	2180	16.1	15.9	15.5
		40°	0	13.4	12.1	12.2			40°	2090	15.7	14.9	14.8
CCl ₄	CH ₄	25°	700	14.0	13.5	13.6	C ₆ H ₆	C ₂ H ₂	25°	3170	18.7	17.4	16.7
		40°	640	13.8	12.9	13.0			40°	3030	18.2	16.5	15.9
CCl ₄	C ₂ H ₆	25°	2710	16.8	16.1	16.1	C ₆ H ₆	SO ₂	25°	6720	25.3	22.2	21.1
		40°	2760	16.9	15.5	15.6			40°	6260	23.7	20.9	19.9
CCl ₄	C ₂ H ₄	25°	2340	16.2	15.7	15.7	C ₆ H ₆	N ₂ O	20°	2170	15.9		
		40°	2540	16.9	15.3	15.2							
CCl ₄	C ₂ H ₂	25°	2330	16.7	15.8	15.6	C ₆ H ₆ ^b	He	20°	-2710	9.6		
		40°	2490	17.2	15.4	15.3							
CCl ₄	SO ₂	25°	5700	24.3	20.4	19.8	C ₆ H ₆ ^b	A	20°	-860	11.3		
		40°	4960	21.9	18.8	18.3							
CCl ₄	N ₂ O	20°	2450	16.5			C ₆ H ₆ ^c	H ₂ O	25°	4100	18.4		17.8
C ₆ H ₅ Cl	H ₂	25°	-1240	12.2	13.6	11.2	(CH ₃) ₂ CO	H ₂	25°	-1240	11.9	11.8	11.2
		40°	-1290	12.1	13.1	10.6			40°	-1290	11.8	11.1	10.6
C ₆ H ₅ Cl	N ₂	25°	-630	13.3	14.0	12.0	(CH ₃) ₂ CO	N ₂	25°	-640	12.8	12.1	12.0
		40°	-680	13.1	13.4	11.3			40°	-720	12.5	11.4	11.3
C ₆ H ₅ Cl	CO	25°	-290	13.7	14.4	12.5	(CH ₃) ₂ CO	CO	25°	-360	13.0	12.6	12.3
		40°	-350	13.5	13.9	11.8			40°	-430	12.8	11.9	11.7
C ₆ H ₅ Cl	O ₂	25°	-110	13.8	14.7	12.6	(CH ₃) ₂ CO	O ₂	25°	-330	13.0	12.8	12.4
		40°	-160	13.7	14.2	12.0			40°	-430	12.6	12.1	11.7
C ₆ H ₅ Cl	CH ₄	25°	610	14.4	15.4	13.5	(CH ₃) ₂ CO	CH ₄	25°	380	13.8	13.5	13.2
		40°	560	14.2	14.9	13.0			40°	270	13.4	12.8	12.5
C ₆ H ₅ Cl	C ₂ H ₆	25°	2470	16.7	17.4	15.8	(CH ₃) ₂ CO	C ₂ H ₆	25°	2090	16.2	15.7	15.3
		40°	2360	16.3	16.7	15.1			40°	2000	15.9	16.0	14.7
C ₆ H ₅ Cl	C ₂ H ₄	25°	2370	16.7	17.3	15.7	(CH ₃) ₂ CO	C ₂ H ₄	25°	2180	16.1	15.9	15.5
		40°	2130	16.0	16.5	14.8			40°	2090	16.0	16.3	14.8
C ₆ H ₅ Cl	C ₂ H ₂	25°	2810	17.8	18.0	16.2	(CH ₃) ₂ CO	C ₂ H ₂	25°	4100	19.2	19.0	17.8
		40°	2670	17.3	17.3	15.5			40°	4200	19.4	19.7	17.4
C ₆ H ₅ Cl	SO ₂	25°	7370	27.8	23.3	21.9	(CH ₃) ₂ CO	SO ₂	25°	3150	11.4	17.8	16.7
		40°	6170	23.9	21.5	19.8			40°	3300	11.9	18.6	16.3
C ₆ H ₅ Cl	N ₂ O	20°	2460	16.9			(CH ₃) ₂ CO	N ₂ O	20°	2870	17.7		
C ₆ H ₆	H ₂	25°	-1460	11.5	11.5	11.0	(CH ₃) ₂ CO ^b	He	20°	-3240	7.2		
		40°	-1620	11.0	10.5	10.1							
C ₆ H ₆	N ₂	25°	-960	12.1	11.8	11.6	(CH ₃) ₂ CO ^b	Ne	20°	-1960	10.8		
		40°	-1070	11.8	10.8	10.9							
C ₆ H ₆	CO	25°	-560	12.7	12.3	12.1	(CH ₃) ₂ CO ^b	A	20°	-740	11.4		
		40°	-680	12.3	11.4	11.3							
		25°	-560	12.7	12.3	12.1	(CH ₃) ₂ CO ^d	CS ₂	30°	5840	20.6		
		40°	-680	12.3	11.4	11.3							
		25°	-560	12.7	12.3	12.1	(CH ₃) ₂ CO ^d	C ₆ H ₆	30°	7740	22.3		
		40°	-680	12.3	11.4	11.3							

TABLE III.—Continued.

Solvent	Solute	ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B-B)
(CH ₃) ₂ CO ^d	CHCl ₃ 30°	8690	24.5		
(CH ₃) ₂ CO ^d	C ₆ H ₆ Cl 30°	9660	24.9		
CH ₃ CO ₂ CH ₃	H ₂ 25°	-1230	12.0	12.7	11.2
	40°	-1250	11.9	11.7	10.6
CH ₃ CO ₂ CH ₃	N ₂ 25°	-680	12.5	13.0	11.9
	40°	-740	12.3	11.9	11.3
CH ₃ CO ₂ CH ₃	CO 25°	-340	12.9	13.5	12.3
	40°	-430	12.6	12.4	11.7
CH ₃ CO ₂ CH ₃	O ₂ 25°	-340	12.8	13.6	12.3
	40°	-390	12.7	12.6	11.7
CH ₃ CO ₂ CH ₃	CH ₄ 25°	330	13.5	14.9	13.2
	40°	270	13.3	13.4	12.5
CH ₃ CO ₂ CH ₃	C ₂ H ₆ 25°	2060	16.0	16.5	15.3
	40°	2230	16.5	15.6	15.0
CH ₃ CO ₂ CH ₃	C ₂ H ₄ 25°	2170	16.1	16.8	15.4
	40°	2050	15.8	15.6	14.7
CH ₃ CO ₂ CH ₃	C ₂ H ₂ 25°	4450	20.2	20.2	18.3
	40°	4830	21.5	19.8	18.2

Solvent	Solute	ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B-B)
CH ₃ CO ₂ CH ₃	SO ₂ 25°	4140	14.9	19.8	17.9
	40°	4200	15.1	19.0	17.4
CH ₃ CO ₂ CH ₃	N ₂ O 20°	2890	17.5		
C ₂ H ₅ OH ^d	CS ₂ 30°	6710	24.1		
C ₂ H ₅ OH ^d	C ₆ H ₆ 30°	8310	26.7		
C ₂ H ₅ OH ^d	CHCl ₃ 30°	8910	27.9		
C ₂ H ₅ OH ^d	C ₆ H ₅ Cl 30°	9980	28.5		
C ₂ H ₅ OH ^d	SO ₂ 30°	6610	24.2		
C ₂ H ₅ OH ^d	NH ₃ 30°	6810	24.6		
C ₂ H ₅ OH ^d	CCl ₄ 30°	7940	25.8		
(C ₂ H ₅) ₂ O	H ₂ 25°	-1440	9.9	9.8	11.0
(C ₂ H ₅) ₂ O	N ₂ 25°	-380	12.0	11.1	12.3
(C ₂ H ₅) ₂ O	CO 25°	-100	12.4	11.6	12.6
(C ₂ H ₅) ₂ O	O ₂ 25°	-10	12.4	11.9	12.7
(C ₂ H ₅) ₂ O	CH ₄ 25°	800	13.4	13.1	13.8

* Unless otherwise indicated, properties listed are calculated from the data of J. Horiuti, Sci. Pap. Inst. Phys. Chem. Research, Tokyo 17, 125 (1931).

Horiuti presents measurements on solubilities of gases and coefficients of dilatation by absorption which permit calculation of ΔH , ΔS_2 (experimental), and ΔS_2 from Eq. (18).

$$\Delta H = RT - RT^2 \frac{\partial \ln(\gamma v_i)}{\partial T}$$

$$\Delta S(\text{exp.}) = -R \ln \gamma - RT^2 \frac{\partial \ln(\gamma v_i)}{\partial T} + R \ln RT + R - R \ln v_i$$

which is seen to include the empirical result that the specificities implied in (18) are not great in dilute solutions of normal substances.

The experimental values of ΔS_2 for SO₂ stand out in striking contrast to the general agreement we have found for "normal" solutes in "normal" solvents. That SO₂ should be more abnormal than the other substances considered is perhaps not surprising in view of the combination it presents of high dipole moment and comparatively small molecular size. It is nevertheless gratifying to find evidence that the abnormality is not random, but is systematic, and a definite property of SO₂. This is provided by Fig. 2, which plots ΔS_2 vs. ΔH_2 for SO₂ in the various solvents used by Horiuti. The fact that the values both for 25° and for 40° give a good straight line (excepting an unexplained anomaly

where γ is the Ostwald Solubility Coefficient and v_i is the molal volume of the solvent.

^b Bell, Trans. Faraday Soc. 33, 496 (1937).

Bell obtained these values from the work of Lannung (J. Am. Chem. Soc. 52, 68 (1930)), on the solubilities of the rare gases. Bell's standard state for the gas is the same as ours, but for the solution he employs the state at which concentration of the solution is equal to concentration in the gaseous state. Conversion to our units requires the addition of the term $R \ln RT - R \ln v_i$, or $20.08 - 4.575 \log v_i$, where v_i is the molal volume of the solvent.

^c International Critical Tables, III, 389.

^d Barclay and Butler, Trans. Faraday Soc. 34, 1448 (1938).

Standard states of these authors are $N_2 = 1$ for the solution and $p = 1$ mm Hg for the gas. From their values we subtract $R \ln 760 = 13.2$ e.u.

in the CCl₄ case) means that a relationship still exists between ΔS_2 and ΔH_2 . The difference between these lines and the "expected" Barclay-Butler line measures the extent to which the SO₂ differs from normal substances in this respect.

The SO₂ result is of interest in connection with a conjecture put forward by Bell,⁴ who noted that his selection from Horiuti's data gave points which lay in accurate straight lines when plotted for different solutes in the same solvent, and much poorer ones for the same solute in different solvents. This was in contrast with the early result of Evans and Polanyi,¹⁴ who found good regularity for the second type of plotting. Bell's suggestion is that the relative sizes of solvent and solute molecules determine the type of

¹⁴ M. G. Evans and M. Polanyi, Trans. Faraday Soc. 32, 1333 (1936).

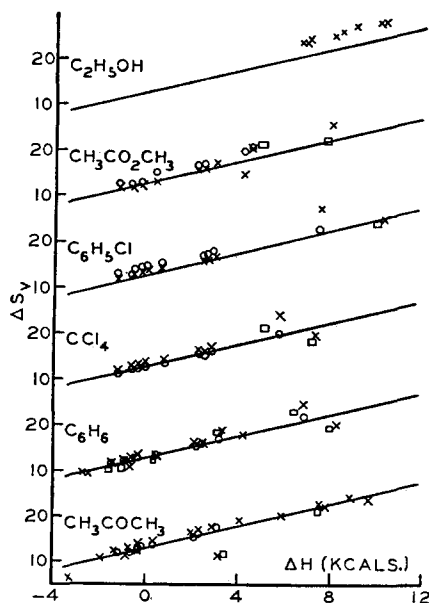


FIG. 1. ΔS_2 vs. ΔH^2 for gases in non-polar solvents. The solid line is the revised Barclay-Butler line. Points are from data of Table III.

regularity, so that a good straight line should be obtained for a series of solutes all of which have small molecules, in a solvent made up of larger molecules, or for a single solute of large molecular size in a series of smaller-molecule solvents. The success of Barclay and Butler (the same thing can be seen in Fig. 1) in fitting all of Bell's points to a single straight line shows that with a mole fraction standard state there is not much to choose between the methods of plotting for those solutions. The result found with SO_2 , however, raises a similar question. Here the important thing seems to be a specific peculiarity in the force field of the SO_2 . Since we are dealing with solutions very dilute in SO_2 , it is an individual SO_2 molecule, rather than SO_2 in bulk, to which the peculiarity must be ascribed.

In their plots for solutions in acetone and alcohol, Barclay and Butler remarked that ΔS and ΔH for pure acetone give a point which falls in the line representing solutes in acetone, and pure alcohol falls on the line for alcoholic solutions. (18) gives a reason why this should be true, and Fig. 1 shows that it is true for the other solvents as well. For normal solutes in normal solvents, however, the result is rather trivial, since all of the points fall near the

Barclay-Butler line. The alcohol solutions are discussed separately below.

APPARENT FREE VOLUME AND SOLVENT REACTION

The numerical values of ΔS_2 for the permanent gases in normal solvents are of great interest. If the equation

$$\Delta S = R \ln (V_g / \gamma V_f) \quad I \quad (50)$$

is applied naively to obtain a value for V_f from the value of ΔS_2 ($=11.73$ e.u.) for H_2 in CCl_4 ,

$$\log (\gamma V_f) = 4.389 - (11.73/4.575) = 1.824;$$

$\gamma V_f = 67$ cc approximately. Since $\gamma \leq 1$, this means that on this basis the *apparent* free volume of H_2 is at least 67 cc in a liquid of total volume 96.4 cc (the molal volume of CCl_4). For CH_4 in CCl_4 the corresponding figures are

$$\log (\gamma V_f) = 4.389 - (14.00/4.575) = 1.34;$$

$\gamma V_f = 22$ cc, about. If these values of V_f were for real free volumes, they would mean, for example, that most of the volume of liquid CCl_4 is accessible to H_2 molecules. For H_2 and Ne in benzene, Bell's calculations from Lannung's¹⁵ data give ΔS_2 values which are even worse, as they correspond, on this basis, to a free volume greater than the entire volume of the liquid solvent, i.e., to a net gain in entropy when a given volume of gas dissolves in the same volume of solvent.

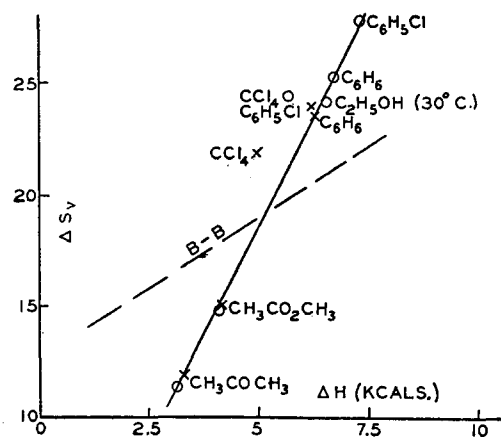


FIG. 2. ΔS_2 vs. ΔH_2 for SO_2 in non-polar solvents. The Barclay-Butler curve is indicated by the broken line. 25° values are indicated by circles, 40° values by crosses.

¹⁵ A. Lannung, J. Am. Chem. Soc. 52, 68 (1930).

This apparent paradox is easily resolved by making a more realistic application of the general principles of I, and writing

$$\Delta S = R \ln \frac{V_g^{n_B} (\gamma V_f)_A^{n_A}}{(\gamma V_f)_B^{n_B} (\gamma V_f)_A^{n_A}} \quad (19)$$

for the process of removing n_B moles of solute from the dilute solution considered and obtaining as a final state n_A moles of pure liquid solvent and n_B moles of solute as perfect gas. ΔS can be interpreted rigorously in terms of free volumes only when these are the logarithmic means of the free volumes of all of the molecules involved in the process. When we so interpret it, we are able to understand the otherwise very peculiar apparent free volumes obtained above. What happens physically is that when a gas molecule enters the liquid it enters a state of great confinement. This by itself would produce a loss in entropy, perhaps somewhat less than the loss when a molecule of the solvent condenses from vapor to liquid, but hardly more than 3 or 4 e.u. less. The solvent molecules which the gas molecule now has as its neighbors, however, find themselves under less restraint than before. This is reflected, for example, in the fact that \bar{V}_2 of H_2 in CCl_4 at 25° is 41 cc. That is, when a molecule of H_2 enters it, the liquid increases in volume almost half as much as when a CCl_4 molecule enters it. Since an H_2 molecule does not "occupy" anything like this volume, a considerable part of \bar{V}_2 is a local expansion of the solvent. The forces acting on the neighboring CCl_4 molecules are weaker than before, and this permits them to vibrate in an effectively larger space, and therefore also to rotate somewhat more freely. This results in a gain in entropy, and for H_2 and CH_4 in CCl_4 this solvent reaction almost (and for He and Ne in benzene it more than) compensates for the effect of confinement of the solute molecule. Due to the occurrence of partial molal quantities in it, (18) includes this solvent reaction.

Since the idea of solvent reaction is an important one, we may attempt a rough estimate of the magnitude of the effect in the solutions of normal solutes in normal solvents which we have been considering. The entropy of vaporization of pure CCl_4 is 22.3 e.u. This means that

if H_2 in CCl_4 had the same free volume as CCl_4 itself has, and if there were no solvent reaction, ΔS_2 for H_2 in CCl_4 would be 22.3 e.u. Now H_2 , being a much smaller molecule, will be expected to be able to "fill crevices" much better than CCl_4 can, which will increase the size of its free volume box. One would guess that a factor of 2 would be too small to represent this effect, but that a factor of 10 would be ample. To be on the safe side, we allow 5 e.u. corresponding to a free volume cell for H_2 somewhat more than 10 times the size of the cell for CCl_4 . Since the vibrations in a condensed system are coupled, a separate consideration of the motion of the H_2 without taking account of that of its CCl_4 neighbors is very arbitrary, and, strictly, or thermodynamically, no separation of these motions is possible. It is still instructive, however, to compare the "hypothetical" ΔS_2 of 17.3 e.u., obtained by subtracting the 5 units just discussed from ΔS_1° , with the experimental one of 11.7 e.u. Such a comparison suggests that something like 5.5 e.u. of entropy in the solution must be ascribed to the extra freedom of CCl_4 molecules which we have been discussing.

ALCOHOLIC SOLUTIONS

In II it was found that when water, alcohols, and amines are plotted in the Barclay-Butler diagram for pure liquids, they give points which fall above the standard line, but within 2 e.u. or so of it, and it was remarked that this deviation is rather smaller than might have been expected. A similar comparison for solutions can be seen in Fig. 1. Here, as before, the difference amounts to some 2 e.u., ΔS of vaporization from alcohol being larger.

As remarked above, the fact that ΔS for a pure solvent lies on the line which represents ΔS_2 for solutes dissolved in it agrees with (18), in which ΔS_2 "starts out," as it were, from ΔS_1° as a point of reference. As a matter of fact, (18) suggests that the abnormality of alcohol as a solvent is to be looked for not in the distance between the alcohol line and the normal line, but in the difference in slopes of the lines. Figure 1 shows that this difference is not great—indeed it is not greater than the differences between the slopes of the corresponding lines drawn for non-polar solvents. We are led to the somewhat surprising

TABLE IV. Heats and entropies of vaporization of gases from aqueous solution.

Solute	Temp.	ΔH	ΔS°	Solute	Temp.	ΔH	ΔS°
H ₂	25 ^a	1280	26.0	Xe ^c	25°	4490	33.6
	40 ^{ob}	426	23.7		50°	2680	28.0
	80 ^{ob}	-170	21.8		80°	720	22.1
N ₂	25 ^a	2140	29.8	Rn ^c	25°	5050	34.3
	40 ^{ob}	1990	29.3		50°	3100	28.2
	80°	180	23.9		80°	720	21.1
CO	25 ^a	3910	29.8	Methyl alcohol ^a	25°	11240	35.0
	40 ^{ob}	1970	28.5	Ethyl alcohol ^a	25°	12880	40.8
	80 ^{ob}	10	22.6	<i>n</i> -Propyl alcohol ^a	25°	14420	46.5
O ₂	25 ^a	2990	31.3	<i>iso</i> -Propyl alcohol ^a	25°	13450	43.5
	40 ^{ob}	2070	30.1	<i>n</i> -Butyl alcohol ^a	25°	15940	52.0
NO	25 ^a	2680	29.4	<i>iso</i> -Butyl alcohol ^a	25°	15240	50.4
	40 ^{ob}	2270	28.1	<i>sec</i> -Butyl alcohol ^a	25°	15060	49.4
CO ₂	25 ^a	4730	30.6	<i>tert</i> -Propyl alcohol ^a	25°	14440	47.6
	40 ^{ob}	3870	28.2	<i>n</i> -amyl alcohol ^a	25°	17500	58.0
COS ^a	25°	5800	35.1	<i>tert</i> -amyl alcohol ^a	25°	15690	52.1
N ₂ O ^a	25°	4840	31.6	ethyl amine ^a	25°	12910	42.2
CH ₄ ^a	25°	3180	31.8	ethyl acetate ^a	25°	11710	43.1
C ₂ H ₆	25°	4430	35.4	Di-ethyl ether ^a	25°	12760	50.5
C ₂ H ₄ ^a	25°	3790	31.3	acetone ^a	25°	10090	35.1
C ₂ H ₂ ^a	25°	3360	25.6	glycerol ^a	25°	24730	66.8
He ^c	25°	840	26.5	chloroform ^a	25°	9800	43.8
	50°	710	26.1	NH ₃ ^d	25°	5040	20.4
	80°	550	25.5				
Ne ^c	25°	1880	28.8				
	50°	1280	26.6				
	80°	580	24.7				
Ar ^c	25°	2730	30.2				
	50°	1840	27.2				
	80°	710	23.5				
Kr ^c	25°	3550	32.3				
	50°	2350	27.8				
	80°	740	23.2				

^a Butler, Trans. Faraday Soc. 33, 235 (1937). Butler employs as standard states $N_2=1$ for the solution and $p=1$ mm Hg for the gas. Translation to our standard states of $N_2=1$ and $p=1$ atmosphere requires subtraction of the term $R \ln 760=13.2$ e.u. from Butler's values.

^b Landolt-Bornstein, fifth edition, Vol. I, p. 762, list α the Bunsen absorption coefficient, the volume of gas when reduced to 0° and 760 mm, absorbed by one volume of water when the partial pressure of the gas amounts to 760 mm. We convert α to γ the Ostwald solubility coefficient and employ this coefficient in the following equations to obtain ΔH and ΔS :

$$\Delta H = RT - RT^2 \frac{\partial \ln (\gamma V_l)}{\partial T},$$

$$\Delta S = -R \ln \gamma - RT^2 \frac{\partial \ln (\gamma V_l)}{\partial T} + R \ln RT + R - R \ln V_l.$$

^c D. D. Eley, Trans. Faraday Soc. 35, 1283 (1939). Eley's standard states are 1 atmosphere pressure for the gas and a concentration of one mole per liter for the solution. Therefore to Eley's values we add $R \ln 18/1000=8.0$ e.u.

^d Landolt-Bornstein, fifth edition, supplement 1, p. 764.

conclusion that the interaction between ethyl alcohol and the solutes dissolved in it produces, at infinite dilution, an entropy effect which is not very different, in its relation to the heat of solution, from what is found with a normal solvent. It is true that when argon, for example, dissolves in alcohol, the Ostwald solubility coefficient is very different from that, say, in benzene. And

when the temperature variations in these solubility coefficients are used to get ΔS values, the two solutions will give quite different results. We have seen, however, that reduction to a mole fraction basis (the Ostwald coefficients give a volume basis in the first instance) is necessary before the figures will be comparable. We have also seen that as between, say, benzene and

carbon tetrachloride as solvents, the difference in ΔS_1° must also be taken into account. What we are now saying is that when the corresponding difference is taken into account between the solution in alcohol and that in benzene, and the ΔS_2 values are plotted against ΔH_2 , the agreement in behavior as solvents between benzene and alcohol is as good as that between benzene and carbon tetrachloride. This is a rather remarkable result, and means that, in this sense, and for these solutes, the Barclay-Butler rule has succeeded in throwing onto ΔH of formation the entire burden of the abnormality of the alcoholic solutions.

AQUEOUS SOLUTIONS OF NON-ELECTROLYTES

Really striking deviations from the "standard" behavior we have been describing and interpreting are found in the data for aqueous solutions listed in Table IV and plotted in Fig. 3. These are, again, values for molal ΔS and ΔH of vaporization of various non-ionic solutes from infinitely dilute water solutions at 25°C calculated to the standard states of 1 atmosphere for the gases or vapors, and a hypothetical mole fraction of unity in solution. It appears that there is one rather good straight line which represents non-polar solutes, and another which represents the alcohols and amines, while several solutes of intermediate polarity fall between these two lines. Three important features stand out in connection with the line for non-polar solutes. First, all of the ΔS_2 values are "too high" by amounts in excess of 10 e.u.; second, the slope of the line is about half again as great as that of the "standard" one (0.0019 *vs.* 0.00124); third, the line comes nowhere near to the point for ΔS_1° of pure water. A fourth distinctive feature of these solutions, to which we shall return shortly, is the way they respond to temperature changes. It is clear that some new influence is at work here, and comparison with the results for SO_2 and for alcoholic solutions makes it clear that this is related in some unique way to the properties of water. That it is related to the properties of water in bulk and does not operate on isolated water molecules is clear from the discussion below, but also follows

from the normal behavior of water as a solute in benzene, Table III and Fig. 1.

The values of ΔS_2 and ΔH_2 for the solutions of the rare gases in water have been calculated before, by Lange and Watzel¹⁶ and by Eley¹⁷ as well as by Butler,¹⁸ though only in the last of these papers does any attention seem to have been called to the remarkable nature of the results. In all three cases, the calculations were made from the values given by Valentiner¹⁹ for the solubilities of the gases in water. Since Valentiner's work consisted in smoothing the rather discrepant earlier data, it seems at first somewhat unsafe to draw from it such important conclusions as we shall be led to. On the other hand, independent measurements on methane, ethane, oxygen, etc., give similar results, so that we shall accept Valentiner's figures, and the calculations Eley has based on them.

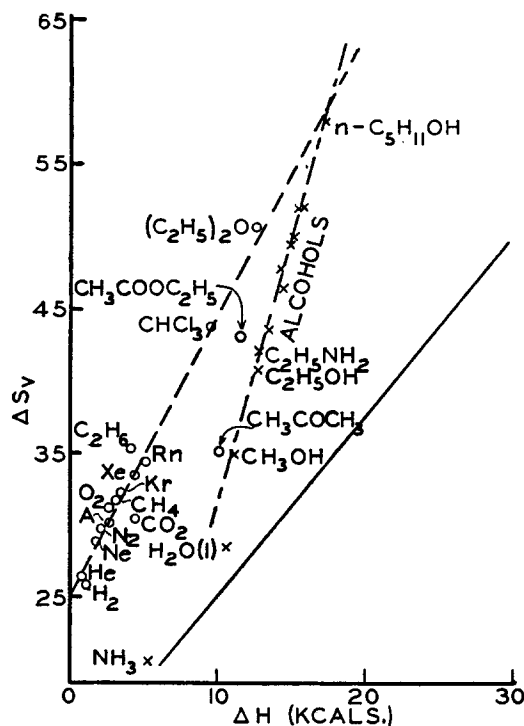


FIG. 3. ΔS_2 for non-ionic solutes in water at 25°C. Data are from Table IV.

¹⁶ E. Lange and R. Watzel, *Zeits. f. physik. Chemie* **A182**, 1 (1938).

¹⁷ D. D. Eley, *Trans. Faraday Soc.* **35**, 1281 (1939).

¹⁸ J. A. V. Butler, *Trans. Faraday Soc.* **33**, 229 (1937); J. A. V. Butler and W. S. Reid, *J. Chem. Soc. London*, 1171 (1936).

¹⁹ S. Valentiner, *Zeits. f. Physik* **42**, 253 (1927).

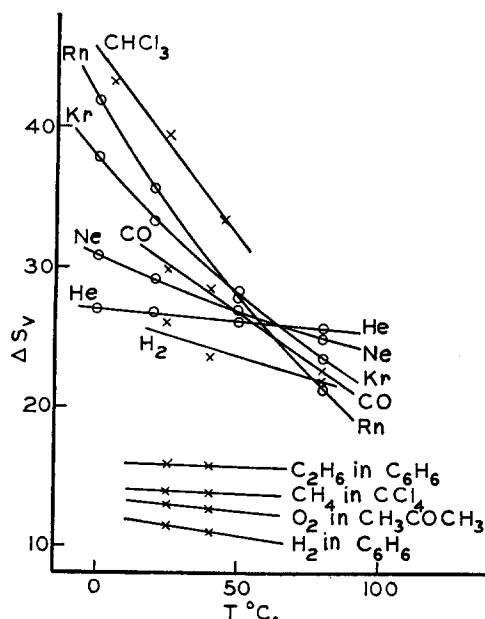


FIG. 4. ΔS_2 vs. temperature for gases in water. A number of gases in non-polar solvents have been included for comparison. Values for the rare gases were taken from Eley's paper (reference 17), the correcting factor of $R \ln (18/1000)$ being added to his values.

Figure 4 shows ΔS_2 values plotted for a series of temperatures, with values for solutions in non-polar solvents included for comparison. The effect of temperature changes on the aqueous solutions is no less striking than the comparison of the 25° values with "normal" behavior. Taken together, they seem to lead, without much ambiguity, to the following physical picture. When a rare gas atom or a non-polar molecule dissolves in water at room temperature it modifies the water structure in the direction of greater "crystallinity"—the water, so to speak, builds a microscopic iceberg around it.* The extent of this iceberg is the greater the larger the foreign atom. This "freezing" of water produced by the rare gas atom causes heat and entropy to be lost, beyond what would "otherwise" have been expected. The heat adds on to the otherwise smaller heat of solution of the gas, producing the rather considerable positive ΔH

* Throughout the rest of this paper we shall use the word iceberg, without quotation marks or apology, to represent a microscopic region, either of pure water or surrounding a solute molecule or ion, in which water molecules are tied together in some sort of quasi-solid structure. It is not implied that the structure is exactly ice-like, nor is it necessarily the same in every case where the word iceberg is used.

of vaporization. The loss in entropy is what causes ΔS of vaporization to be so remarkably large. As the temperature is raised, these icebergs melt, giving rise to the enormous partial molal heat capacity of these gases in water, which may exceed 60 cal./deg./mole. The magnitude of this effect naturally depends on the size of the iceberg originally present, so it is greatest in Rn, and at the higher temperatures the order of ΔS_2 for the rare gases has actually reversed itself, ΔS of vaporization of Rn being smaller than that of He. This presumably means that here the expansion of the system by intrusion of a radon atom loosens the water considerably more than with helium, and the resulting gain in entropy of the system shows up in the lower value of ΔS_2 . This corresponds to the "ordinary" solvent reaction which we found in non-polar solvents. Such a tendency should also exist in cold water, where, however, it is overshadowed by the iceberg effect. At still higher temperatures ΔH_2 becomes negative; the solubility of most gases in water shows a minimum when plotted against temperature. This means that at these temperatures the structure of water has been broken down so far as to remove most of its peculiarity as a solvent, and agrees with the x-ray²⁰ and Raman effect²¹ findings on the effect of temperature on the structure of water.

The assumption that the rare gases and hydrocarbon gases form icebergs when they dissolve in cold water receives some support from the existence of crystalline hydrates of these substances. There is, of course, no general correlation between solute species and solid phases (cf. Na_2SO_4 solution above and below the temperature of transition between Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$), but in the case, for example, of the rare gases,²² or of hydrocarbons,²³ the existence of solid hydrates indicates at any rate that the geometric and energetic relations between the non-polar solute and the water molecules involve no innate antagonism to complex formation.

²⁰ J. Morgan and B. E. Warren, *J. Chem. Phys.* **6**, 666 (1938).

²¹ P. C. Cross, J. Burnham, and P. A. Leighton, *J. Am. Chem. Soc.* **59**, 1134 (1937).

²² R. de Forcrand, *Comptes rendus* **135**, 950 (1902), **176**, 355 (1923).

²³ E.g., E. G. Hammerschmidt, *Ind. Eng. Chem.* **26**, 851 (1934).

The assumption of iceberg formation gives a pictorial interpretation for the observation of Butler¹⁸ that the insolubility of non-polar substances in water is an entropy, rather than an energy phenomenon. Large non-polar molecules have stronger van der Waals force fields around them than do small ones, and are more strongly held in any condensed phase, including aqueous solutions. The larger they are, however, the larger the icebergs which they produce in water, and therefore the greater the loss in entropy involved in dissolving them. Butler's series of values for ΔH_2 and ΔS_2 for the alcohols in water is very instructive in this connection. These give a line (mentioned above) which does not come far from passing through ΔS_1° for water. CH_3OH has about the same ΔS_2 value as C_2H_6 . This is presumably only partly due to iceberg formation in the case of CH_3OH , however, part of the effect being also attributable to the hydrogen bonds which it itself forms. But this hydrogen bonding produces a much larger ΔH_2 than is found for C_2H_6 , shifting the CH_3OH point to the right in the plot (Fig. 3). The relative importance of hydrogen bonding (of the solutes) and iceberg formation shifts in favor of the latter as the hydrocarbon chain of the alcohol increases, and the points for the higher alcohols fall progressively closer and closer to the non-polar solute line, finally coming very near to it for amyl alcohol.

It may be permissible at this point to speculate as to the "cause" of iceberg formation when a non-polar solute molecule dissolves in water. While we have not succeeded in formulating any very satisfactory detailed picture, a rather suggestive idea is that this is an example of a sort of microscopic operation of the Le Chatelier principle. Any solute molecule occupies a space that is large compared with what would be required if it were not there, and therefore even helium causes the water to expand somewhat. Cold water is unique in that there exists in it a mobile equilibrium between different structures,²⁴ in which there are probably several structures represented by moderately large populations. One of these structures is more open than any other and it seems reasonable to imagine that at the edge of a patch of this material there is a greater pro-

portion of "available" space than elsewhere. We might therefore expect a foreign molecule to find its way to such an edge location, and to stabilize it to such effect as to increase the population of the iceberg material. Such icebergs might or might not fuse together about the solute molecule.

IONIC SOLUTIONS

Another remarkable phenomenon appears when the heats and entropies of hydration of rare gas ions are listed, as in Table V, and com-

TABLE V. Ionic solutes in aqueous solution.

Ion	ΔH^a	ΔS_v^b	$\Delta S^{st,c}$	$\Delta \text{Bingham}^d$
F^-	122.6	40.9	+3.5	-13.6
Cl^-	88.7	26.6	-10.2	+0.28
Br^-	81.4	22.7	-13.9	+3.09
I^-	72.1	18.5	-17.9	7.58
NO_3^-		26.8 (16.8)	-19.4	3.06
Ac^-				-21.4
SO_4^{--}		56.4 (50)		-20.4
H^+		38.6		-6.41
Li^+	121.2	39.6	+1.1	-14.0
Na^+	94.6	33.9	-4.0	-9.60
K^+	75.8	25.3	-12.0	+0.28
Rb^+	69.2	23.1	-14.1	1.86
Cs^+	62.0	21.3	-15.7	2.59
NH_4^+		30.5 (25.5)	-11.7	+0.44
Mg^{++}		84.2		-36.5
Cu^{++}		82.0		-34.7
Zn^{++}		81.3		-35.6
Ca^{++}		65.5		-31.3
Sr^{++}		63.7		-28.4
Ba^{++}		55.6		-25.3
Al^{+++}		133.5 (± 10)		-70.5
Fe^{++}		120.5 (± 5)		-52.2
CH_3NH_3^+				-6.3
$(\text{CH}_3)_2\text{NH}_2^+$				-10.4
$(\text{CH}_3)_3\text{NH}^+$				-34.4
$(\text{CH}_3)_4\text{N}^+$				-14.0
$(\text{C}_2\text{H}_5)_3\text{NH}_3^+$				-15.2
$(\text{C}_2\text{H}_5)_2\text{NH}_2^+$				-25.7
$(\text{C}_2\text{H}_5)_3\text{NH}^+$				-33.1
$(\text{C}_2\text{H}_5)_4\text{N}^+$				-34.3
$(\text{C}_3\text{H}_7)_4\text{N}^+$				-74.3
$\text{C}_6\text{H}_5\text{NH}_3^+$				-25.6

^a Molal ΔH of vaporization of ions from aqueous solution at 25°C. Values (in kg cal./mole) taken from W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. 7, 108 (1939).

^b Molal ΔS of vaporization of ions at 25°C from a hypothetical mole fraction of unity in aqueous solution to a hypothetical gas state at 1 atmosphere pressure. Values (in e.u.) for the monatomic ions were obtained by using the Sackur equation for the gas, and the aqueous entropy data of Latimer, Pitzer, and Smith (see reference 25). The absolute partial molal entropy of Cl^- in hypothetical molal solution is taken as 18.1 e.u. (see reference 26). For NO_3^- , NH_4^+ , SO_4^{--} , vibrational and rotational entropies in the gas state were computed using interatomic distances and vibration frequencies as follows: NO_3^- , $\text{N}-\text{O}=1.21\text{Å}$, 720 cm^{-1} (2), 830 cm^{-1} , 1050 cm^{-1} , 1350 cm^{-1} (2) NH_4^+ , $\text{N}-\text{H}=1.0\text{Å}$, 1403 (3), 1712 (2), 3043, 3123 (3); SO_4^{--} , $\text{S}-\text{O}=1.5\text{Å}$, 620 (3), 450 (2), 980, 1100 (3). For comparison with monatomic ions, restriction of rotation in the dissolved state was estimated at about 10 e.u. for NO_3^- , 5 e.u. for NH_4^+ , and 6 e.u. for SO_4^{--} . The values obtained by subtracting out these quantities are shown in parenthesis.

^c Hypothetical extra entropy of vaporization (e.u. per mole) due to the effect of the ions in the structure of the solution. Computed by use of Eq. (20).

^d Molal fluidity elevations of the ions, taken from Bingham (see reference 29).

²⁴ J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

pared, as in Fig. 5, with the corresponding quantities for non-polar substances. Here ΔS_2 has been computed from the Sackur equation and the S_2 values of Latimer, Pitzer, and Smith,²⁵ and converted to our standard states, using the Eastman-Young²⁶ convention that the absolute partial molal entropy of Cl^- is 18.1 e.u. We expect, of course, that the presence of the ionic charge will have a large effect on the energy of the system, and are not surprised to find ΔH values 7 to 10 times as great as those characteristic of non-ionic solutes. The fact that the ΔS_2 values, however, are in exactly the same range (18 to 40 e.u.) as those for the non-polar solutes is less easily predictable. The sort of situation we are confronted with is strikingly illustrated by comparing the loss in entropy on dissolving a K^+ ion and a Cl^- ion, both of which have the electronic structure of argon, with the loss on dissolving two argon atoms in water. The values are $25.3 + 26.6 = 51.9$ e.u. and $30.2 + 30.2 = 60.4$ e.u., respectively. The effect of the charges is actually to *lessen* the entropy loss. The phenomenon is the more interesting when we remember that Latimer and his co-workers²⁷ have succeeded in accounting rather well for the entropy loss on dissolving the ions by identifying it with the entropy of polarization of the water by the ionic charges, treating water as a continuous dielectric, as in classical electrolyte theory.

Now while a significant amount, perhaps 10–15 e.u., of the 30.2 e.u. that make up ΔS_2 of argon is iceberg entropy, and therefore roughly comparable to the dielectric lining up of the water molecules by the ionic charge, another important part is caused by the restriction of the argon atom into a free volume box of some sort. Qualitatively, some contribution from this cause must also be present for the ions. When this is added to the dielectric loss, the net expected ΔS_2 for the ions is a good bit larger than the observed value. This is still true when the ion is pictured as freezing the first layer of water molecules into a state of some sort of dielectric saturation (see below). The conclusion is that in an ionic solution there is “too much” entropy, just as in the rare

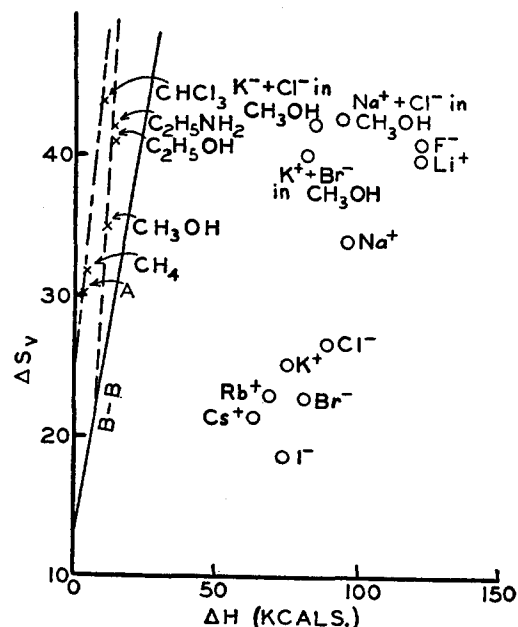


FIG. 5. ΔS_2 vs. ΔH_2 for alkali and halide ions in aqueous solution. The Barclay-Butler line, as well as the lines for the rare gases in water and alcohols in water, taken from Fig. 3, have been included. Data are from Table V.

gas solution there was “too little.” The probable explanation is that around the ions, beyond the first “saturated” region of water molecules, there is a region or belt in which the water structure is broken down, or melted, or depolymerized, as compared with ordinary water.

Pictorially, this effect of an ion is easy to understand. In the normal 4-coordinated water structure we may think of 5 water molecules in a tetrahedron, one O at the center, with four others in some sort of tetrahedral positions around it. Two of these peripheral oxygens are using “their own” hydrogens to bind them to the central oxygen, while two are held by hydrogens which “belong” to the central water molecule. This means that the kind of tetrahedron which will fit satisfactorily into an extended patch of ice-like water has at two of its corners water molecules which have one type of orientation, while the orientation at the other two corners must be different. Assume now that it is desired to fit a positive ion, Na^+ , say, into the structure. The most favorable way to do this will be to give it a coordination shell of four water molecules, and to let these assume positions around it in which the O's are at the corners of a tetrahedron.

²⁵ W. M. Latimer, K. S. Pitzer, and W. V. Smith, J. Am. Chem. Soc. **60**, 1829 (1938).

²⁶ M. B. Young, Thesis, University of California, 1935.

²⁷ W. M. Latimer, Chem. Rev. **18**, 349 (1936).

But now, even if the resulting tetrahedron is of the right size, it can still not fit well into an iceberg. For there can be little doubt that the strong field of the ionic charge orients all four of the waters the same way (in this case with hydrogens out), instead of two one way and two another as required for a perfect fit. Things will therefore not come out even. When we include the influence of ionic size it is clear that it will be necessary to go out some distance from a positive ion before the water has "recovered itself" sufficiently to have its characteristic structure and entropy. An exactly corresponding discussion can be given for a negative ion and a similar one for the case where more than one layer of water is "frozen" to the ion.

Any attempt to estimate the numerical magnitude of this melting effect must be based on rather arbitrary assumptions for which in the first instance no strict justification can be given. As in the discussion of the solvent reaction when H_2 dissolves in CCl_4 , what is involved is an attempt to separate, for our own conceptual convenience, effects which are essentially parts of a single inseparable phenomenon. However, we have a physical picture which furnishes certain categories which must be valid in principle, and it is an instructive exercise in a sort of bookkeeping to attempt to assign appropriate entropy contributions to them. We shall, moreover, find *a posteriori* support for our results.

To begin with, when a gas ion dissolves, it enters a free-volume box, and in our standard states 20–25 e.u. is a sort of "par" value for the corresponding loss of entropy per mole. Since the forces between the ion and its water neighbors are large, we could increase this figure somewhat, but shall, instead, attribute the extra entropy loss to the water, and accept a value of 20 e.u. for the free-volume effect. In considering the solvent reaction, it has been usual to consider it in two parts. We shall need four, but shall begin with the two customary ones. The first is the effect on the first layer of water molecules, and we shall treat this very simply by assuming, as usual, that it contains 4 water molecules (for the univalent ions we are considering) and that each of these, as compared with "ordinary" water, has lost half as much entropy as it would have on freezing to ice. Since ΔS of fusion (calculated as

virtual at 25°C) of water is about 6 e.u. per mole, this gives, roughly, 12 e.u. lost by the water in the first layer around the ion. Again as usual, we treat the rest of the water as a polarized dielectric medium. For this, we take Latimer's²⁷ equation $\Delta S = 22z^2/r$ for the entropy loss (z = ionic charge), using now for r the radius of the ion plus the oxygen-oxygen distance in ice, or $\Delta S_D = 22z^2/(r_i + 2.8)$. We do not know how much error is involved in this approximation, but the effect is in any case of secondary magnitude.

The third solvent reaction effect is the specific influence of the ion on the structure of the water beyond the first layer. We shall call it $\Delta S''$ and it will be positive when the net qualitative effect on the structure of the water has been to intensify it, as is the case with rare gas atoms, and negative when there is a net breaking effect—when icebergs have been melted.

Finally, the considerations of the first paper of this series make it clear that a fluctuation term must be added to the entropy of the solution as a whole. This arises because no individual patch of the solution, whether it contain an ion or not, has a structure which is just like that of the average of the solution as a whole, and the possibility of changes in position and extent of the "firmer" and "looser" patches produces extra entropy. Correspondingly, the water around one individual ion will always have a structure which is slightly more or slightly less pronounced than the average for all the ions of that type, and the amount of this variation is related to the "temperature-dependence" entropy discussed in I. Formally, the fluctuation entropy we are now speaking of is represented by a term in $T(d \ln Q)/(dT)$ where Q is the complete partition function of the solution. We have no way of evaluating this, and even if we had it would still be necessary to differentiate it to get the partial molal contribution for the ion under discussion.

We shall therefore have to treat this fluctuation term as we treated similar ones in I and II, and call it a part of $\Delta S''$. This is physically reasonable also, since it is the existence of structure in the solution which gives rise to this particular fluctuation effect, and this fluctuation term is a part of the total "structural entropy" of the solution.

Adding up these guesses, we get, for a singly charged ion,

$$\Delta S_2 = 20 + 12 + \frac{22}{r_i + 2.8} + \Delta S^{st}, \quad (20)$$

whence

$$\Delta S^{st} = \Delta S_2 - 32 - \frac{22}{r_i + 2.8}. \quad (20')$$

Table V gives values of ΔS^{st} computed from (20'), and it will be noted that it makes all of the alkali and halide ions except Li^+ and F^- appear to have a net structure-breaking effect over and above the other things they do when they dissolve in water, and that for the larger ions the effect is considerable.

In practice, (20') makes ΔS^{st} a catch-all which should reflect not only the structural features which it purports to represent, but also any changes from ion to ion in the first-layer freezing and the free-volume contributions. The probable magnitude of such changes is discussed further below. Numerically, however, we may note here that it seems likely that any criticism of the numbers used should result in raising the 12 e.u. and 20 e.u. to larger values. This would make ΔS^{st} still more negative, and would strengthen our contention that a structure-breaking effect occurs. When more is known about the structure of these solutions it will doubtless be clearer how each of the effects discussed contributes to the relationship, discovered by Latimer and his coworkers, between ΔS_2 and the crystallographic radii of the ions.

Mention must be made of the interesting paper of Eley and Evans,²⁸ in which they attempt to calculate ΔS_2 for monatomic ions. We shall not

discuss it in detail, since they did not consider either the structure or the fluctuation terms we have introduced, and their assumptions regarding the free-volume contribution are in conflict with ours. As they themselves state, however, their model is greatly over-simplified, and the importance of their paper lies in pointing out some of the factors which a complete theory must take into account.

STRUCTURE AND PROPERTIES OF AQUEOUS ELECTROLYTES

If our knowledge of electrolytic solutions were restricted to the information which we have so far adduced, the most that could be said for the values of ΔS^{st} listed in Table V would be that they fall well enough into the general physical picture of entropy changes which we have been developing, and that they are not in conflict with any facts which have come to our attention. They gain very greatly, however, in their claim for serious consideration, when regarded in the light of evidence from (a) viscosity and (b) heat capacity data.

Bernal and Fowler²⁴ have called attention, as have earlier workers in more general terms, to the connection between the effect of dissolved ions on the structure of water and their influence on the viscosity, or fluidity, of the solution. Bingham²⁹ has tabulated the "ionic elevations" (Δ) of fluidity which may be ascribed to the individual ions if K^+ and Cl^- are assumed equivalent (on the basis of their closely equal ionic conductances). Bingham's study is concerned with concentrations high enough (0.1M–1.0M) for the Jones and Dole³⁰ term in the square root of concentration to have been completely swamped by the specific linear term. The general agreement with experiment, however, of his fluidity values for various concentrations as calculated from these Δ 's makes it appear that they have some meaning for dilute solutions also. Values of Δ quoted from Bingham's paper are listed in Table V. Their parallelism with ΔS^{st} is clear, and will be discussed more fully below. The ions which increase the fluidity of water, presumably by "depolymerization," are ones to which, quali-

TABLE VI. Partial molal heat capacities at infinite dilution.

Solute	$\bar{C}_{P_2}^\circ$ (cal./deg./mole)	Solute	$\bar{C}_{P_2}^\circ$
HCl	-32.5	NaCl	-23.8
HBr	-33.0	NaBr	-24.3
HI	-33.7	NaI	-25.0
LiCl	-16.2	KCl	-29.0
LiBr	-16.7	KBr	-29.5
LiI	-17.4	KI	-30.2

Values calculated by F. D. Rossini, Bur. Stand. J. Research, 7, 47 (1931).

²⁸ D. D. Eley and M. G. Evans, Trans. Faraday Soc. 34, 1093 (1938).

²⁹ E. C. Bingham, J. Phys. Chem. 45, 885 (1941).

³⁰ G. Jones and M. Dole, J. Am. Chem. Soc. 51, 2950 (1929).

tatively, we have ascribed large net structure-breaking effects.

Again, the rather large negative partial molal heat capacities of the ions are well known³¹ and attempts³¹ have been made to explain them on the basis of the electrostatic picture of the water as a dielectric medium, subject to polarization and electrostriction by the fields of the ions. Qualitatively such a representation, or a more refined one which pictures the effect of the field on water molecules instead of upon a continuous medium, shows that the existence of the strong fields should decrease the heat capacity of the system. On the other hand, it must predict, as an effect of ionic size, and therefore of ionic field, that \bar{C}_{P2}° of LiCl, for example, should be more negative than that of NaCl, which should, in turn be more negative than that of KCl. Likewise, for the different halides, \bar{C}_{P2}° should become more negative in the order NaI—NaBr—NaCl. Exactly the reverse is the case, as shown in Table VI, the values being Rossini's³² virtual ones for infinite dilution. Our picture of the structure of the solution, on the other hand, in analogy with the explanation found for the large positive \bar{C}_{P2} values of the rare gases, suggests that, since an appreciable part of the heat taken up when cold water is warmed goes to melt icebergs, an ionic solution in which some of the icebergs had already been melted should take up less heat when warmed. This should contribute a negative term to \bar{C}_{P2} which should be biggest in the cases where the ions had the greatest structure-breaking effect. Comparison of Tables V and VI shows that this is what is observed.

The idea that ions have a depolymerizing effect on water is not new, of course, though we know of no other treatment in which it has been used for the purpose to which we are applying it. It is a part, or a consequence, of Tamman's³³ internal pressure analogy, and can be applied to explain the values of partial molal volumes, expansibilities, compressibilities, etc. In these cases, however, the basis for distinguishing struc-

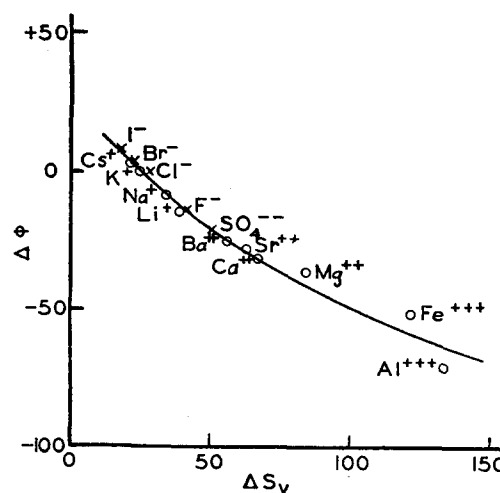


FIG. 6. ΔS_2 in e.u. vs. molal fluidity elevation in rhes. Data are from Table V.

ture-breaking from polarization or electrostriction effects is not clear cut, and this is also true in the interpretation of the effect of salts on the temperature of maximum density. In contrast to this, we feel that the conclusions from viscosity and heat capacity are straight-forward, and signify that there is real physical meaning, both in the concept symbolized by ΔS^* , and in the rather large negative values obtained for this quantity in the cases of the larger univalent ions.

A suggestion for a more definite picture of the effect of an ion on the structure of the solution is furnished by Fig. 6, where ΔS of vaporization of the ions is plotted against Bingham's Δ values. The fact that from Li^+ on through Ba^{++} , SO_4^{--} , Mg^{++} , etc., to Al^{+++} the greater and greater ΔS values continue to be accompanied by roughly proportional decrements in fluidity is very striking. (Incidentally, the fact that the positive and negative ions and the ions of different valence give points which fall so nearly on the same curve means either that the Eastman-Latimer^{26,27} assumption of -4.6 e.u. for the absolute entropy of H^+ , and Bingham's assumption that K^+ and Cl^- have equal effects on fluidity, are both correct, or else that they are in error by compensating amounts.) In going down this series of ions we cannot believe that the large and progressive decrease in fluidity is owing primarily to an effect in the immediate neighborhood of the ion—an effect which is becoming more and more intense. We must rather

³¹ See, for example, H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (New York, 1943), Chapter 8, Section 4, for data and bibliography.

³² F. D. Rossini, *Bur. Stand. J. Research* 7, 47 (1931).

³³ G. Tamman, *Über die Beziehung Zwischen den inneren Kräften und Eigenschaften der Lösungen* (Leipzig, 1907).

assume that whatever influence is being exerted by the ion is affecting a larger and larger region around it, so that a solution of Al^{+++} owes both its low entropy and its high viscosity to the existence, around each Al^{+++} ion, of a large patch of "frozen" water. According to this picture, as one goes back up the curve, through Mg^{++} and Li^+ to Cl^- , Cs^+ , and I^- , the size of the frozen patch becomes smaller and smaller, until its influence is overcome by the thawed belt outside of it, and the net structural entropy and the net effect on fluidity are both positive.³⁴

Now the entropy loss by the ion and its immediate water neighbors is probably greater in Al^{+++} than in I^- , but perhaps not tremendously greater, for there are two kinds of saturation which limit the amount of entropy which can be lost in such a region. One is a Debye³⁵ saturation due to the form of the Langevin³⁶ function which relates dipole orientation to field strength. The other is a quantum effect as a result of which the effective or virtual free volume box in which a particle vibrates cannot become smaller than a value determined by the uncertainty principle³⁷—this is what prevents the entropy contribution $R \ln v$ from becoming negative, as it would if classical laws held in low temperature or high force regions. These two saturation effects bring about a state of affairs in which, since the field near the "surface" of an I^- ion is already very strong—of the order of 10^7 volts per centimeter—even multiplying it by 50, which is about what happens (presumably) in going to Al^{+++} , cannot decrease the entropy of the immediate neighborhood by any enormous amount. The 20 e.u. difference between ΔS_2 for I^- and Li^+ , and the nearly 100 e.u. difference between Li^+ and Al^{+++} are therefore to be ascribed largely to spreading out of the frozen region around the ion, along, presumably, with some diminution—perhaps even the disappearance—of the positive entropy contribution from a thawed belt. These changes are properly represented in ΔS^{st} , and the existence of the saturation phenomenon makes (20') not entirely naive in attempting, as a first approximation, to use the

same free-volume and first-layer contributions for all univalent ions, even though 32 e.u. may not necessarily be the right value for the sum of these roughly constant terms.

Two additional types of data lend direct confirmation to the picture we have outlined. One is found in the study by Frank and Robinson³⁸ of entropies of dilution. This study led them to conclude, as we have done, that each ion has a specific influence on the structure of the solution, and it is noteworthy that the ions to which they ascribed a large structure-breaking effect are just those for which we have found large negative values for ΔS^{st} . For Li^+ they found, as we have done, a net structure-promoting tendency. NH_4^+ in NH_4Cl , however, they found to be structure-promoting, while we, both in respect of ΔS_2 and of Δ , find it to be almost indistinguishable from K^+ , which presumably has a net structure-breaking effect. We offer as a tentative explanation of this discrepancy the suggestion that, due to the split charge and hydrogen-bonding faculty of NH_4^+ , the type of structural influence it exerts on the water is unusual, producing no regions either of marked freezing or of marked thawing. As the solution becomes more concentrated, it would be necessary to assume that this unusual type of structure around the NH_4^+ was able to some extent to overcome the thawing tendency around the Cl^- ions so as to produce less net structure-breaking in the solution than is found, at the same concentration, with KCl .

Second, a series of investigations which lend very striking support to the iceberg picture are reported by Freed³⁹ and his co-workers on the line spectra of solutions of europium ion, Eu^{+++} . They found evidence of lattice vibrations coupled with the main electronic transitions, and concluded that the Eu^{+++} ion must be surrounded by a quasi-solid patch of material capable of supporting these vibrations. Freed's comment is: "Although it is too early to be definite as to how far from the europium ions the oscillating units need be assumed to extend in a good approximation, it seems that they extend farther than most of us are prepared to accept at present."

While no ΔS_2 value for Eu^{+++} is available,

³⁴ Cf. the discussion of Prins (J. Chem. Phys. 3, 72 (1935)) of "hygroscopic" vs. "non-hygroscopic" ions.

³⁵ P. Debye, *Polare Molekeln* (Leipzig, 1929).

³⁶ P. Langevin, Ann. Chim. Phys. 8, 70 (1905).

³⁷ Cf. J. E. Mayer and M. G. Mayer, reference 6, p. 217.

³⁸ H. S. Frank and A. L. Robinson, J. Chem. Phys. 8, 933 (1940). See also literature there cited.

³⁹ S. Freed, Rev. Mod. Phys. 14, 105 (1942).

comparison of \bar{S}_2 values for Al^{+++} and Fe^{+++} suggest an estimate of about 100 e.u. for this quantity. This would correspond to a very considerable frozen patch around the Eu^{+++} ion. While many detailed points remain to be considered it seems reasonable to suggest identifying our iceberg with Freed's oscillating unit.

Finally, there are two other fields in which indirect, but suggestive, support can be found for the picture. We mention, first, the work of Latimer and Slansky⁴⁰ on the entropy of solvation of several alkali halides in absolute methanol. Their data (average ΔS_2 for M^+ and X^- against average ΔH_2), which are plotted in Fig. 5, show that on the average about 15 e.u. more entropy are lost on dissolving an ion in methanol than on dissolving it into the same volume of water. We account for $R \ln (32/18) \times (1/0.761) = 1.6$ e.u. of this in the greater mole fraction of solute in the methanol solution. For the balance, we agree with Latimer and Slansky that the methanol can be expected to lose more entropy in the electric field of an ion, but an estimate based on a virtual ΔS of fusion at 25°C, and on a comparison of the temperature dependence of dielectric constant with that of water, indicates that this difference may amount to 10 e.u. or less. As Latimer and Slansky point out, our ignorance of effective ionic radii in methanol solutions makes such a discussion rather speculative, but we suggest that there may well remain a difference which can be accounted for by the fact that no appreciable gain in entropy is to be expected in methanol on the score of structure-breaking, whereas we have estimated that in aqueous solutions this effect has increased \bar{S}_2 and decreased ΔS of hydration for the larger alkali and halide ions by amounts of from 5 to 10 e.u.

The other speculation is suggested by the negative signs and comparative values of the fluidity elevations listed by Bingham for the alkyl ammonium ions. (Table V) It would be difficult to calculate ΔS_2 values for these ions, and the identification of negative Δ values with iceberg formation is less straightforward here than in the case of a small rare gas ion. The ionic fluidity should, in fact, be affected by size and shape effects on the viscous drag of the ion itself,

and comparison of Δ values for mono-, di-, tri- and tetramethyl ammonium ions, and for their ethyl homologues, indicates the existence of specific shape, or hydrogen-bonding, or symmetry effects. The series tetramethyl, tetraethyl, tetrapropyl ammonium ions, however, shows a decrease in Δ which seems too large to be accounted for by effects related to the Stokes Law drag on the "simple" ion. Also, though these data are assembled from several sources, some quite old, the effects are so large as almost certainly to be real. It appears, therefore, that an ion which introduces large non-polar groups into water causes iceberg formation, much as the non-polar groups themselves would do in the absence of the ionic charge.

At first glance this seems inconsistent with the direct variation we have postulated of size of iceberg with ionic potential $\varphi = |z|e/r_i$ from I^- to Al^{+++} . As just suggested, however, the mechanism of iceberg formation with R_4N^+ is comparable to that for C_2H_6 , rather than to the quite different thing which Al^{+++} does to water. We therefore accept the conclusion that large icebergs, of different "origin" but with similar entropy and fluidity effects, are formed around ions at both ends of the scale of ionic potential. It is understood, of course, that very small ionic fields can be obtained for this purpose, only by "padding" univalent ions with non-polar groups.

A fact which increases the attractiveness of the idea of icebergs about tetraalkyl ammonium ions is that it fits in with the observation of Fowler, Loebenstein, Pall, and Kraus,⁴¹ that certain tetra *n*-butyl ammonium and tetraisoamyl ammonium salts form "high hydrates"—i.e., crystals containing 18 to 60 molecules of water of crystallization, and melting at from 5° to 40°C. They observed no such hydrates with salts of smaller cations, and it is noteworthy that the largest number of water molecules was found with tetrabutyl ammonium acetate, the acetate ion having the most negative Δ value of the anions they mention, and presumably again owing this large negativity to the presence of a methyl group.

We have had occasion before to recall that there is no general structural connection between

⁴⁰ W. M. Latimer and C. M. Slansky, J. Am. Chem. Soc. 62, 2019 (1940).

⁴¹ D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus, J. Am. Chem. Soc. 62, 1140 (1940).

solute species and the solid phases with which they are in equilibrium. In the case, however, of $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Ac}^-\cdot 60\text{H}_2\text{O}$, we find it difficult to see how this crystal would form except through the aggregation of heavily hydrated particles already in existence. It would be most interesting to know the entropy of fusion of this crystal, which melts to a solution of something less than 1M concentration. We hazard the conjecture that it is small. If it were necessary to freeze even 50 of the water molecules *in the process of solidification*, ΔS of fusion should be of the order of 300 e.u., and ΔH of the order of 65–70 cal./g. If, however, the freezing of the water is largely complete in the liquid phase, these values should be much lower.*

Our iceberg hypothesis for the tetraalkyl ammonium and acetate ions has a reasonable relationship, also, to the well-known surface activity of higher alkyl ammonium ions and of long-chain fatty acid anions. When the non-polar part of an ion becomes big enough, the ion is forced out of the solution. As pointed out above, this is an entropy effect. It produces a measurable lowering of surface tension even in tetramethyl ammonium halides and in sodium butyrate. The properties we have just been discussing may therefore be regarded as marking the rudiments or preliminaries of detergency. This implies that a complete study of surface phenomena should take explicit account of the effect of solutes on the structure of water.

RELATIONSHIP TO ELECTROLYTE THEORY

If the picture we have been developing of the structure of aqueous solutions of ions is correct,

* The question arises whether the purely "non-polar" icebergs formed around rare gas atoms and other non-polar molecules influence the fluidity of solutions in the same way as "ionic" icebergs do. A preliminary experiment, performed at the suggestion of Professor Lewis, suggests that they do not. A saturated solution of chloroform (at 25°C) was found to have a viscosity within 0.2 percent of that of water. Since this solution is about 0.07M in CHCl_3 , and since ΔS_2 for CHCl_3 is about the same as for Li^+ or F^- , we might have expected a change of about 1 percent in viscosity. That it does not occur can be interpreted only by introducing an *ad hoc* assumption, albeit a not unreasonable one. This is that the icebergs formed when a non-polar solute dissolves in water may not form firm continuous masses in which solute molecules are embedded. It would then require the presence of ionic fields or of hydrogen bonds (cf. viscosity of alcohol-water mixtures) to cause the icebergs to assume the "fused," or massive form about the solute particles which produces the increase in viscosity.

TABLE VII. Standard entropy change in e.u. per mole for the transfer of N_2O (or O_2) to pure water from alkali halide solutions of about 0.5M and 1.0M (and 2.0M) concentration.

	Cl	Br	I
Li	-0.24 -0.40		0.5M salt 1.0M salt
Na	O_2 +0.34 +0.08 +0.11		
K	-0.12 -0.15	-0.27 -0.33	-0.36 -0.73
Rb	-0.05 -0.21		
Cs	+0.04		

Values calculated by use of Eq. (23) and data quoted by Randall and Failey (see reference 42), from Geffeken (see reference 43).

it should have interesting consequences for conventional electrolyte theory, and we conclude this paper with a brief mention of a few possibilities.

Salting-Out Effect

The first is that a more extended study than has yet been made of the effect of temperature on salting-out effects may show that salting-out is to a considerable degree—perhaps even predominantly—a structural phenomenon. Some indication of this already exists, and can be simply obtained from the recalculation by Randall and Failey⁴² of older salting-out data. They calculated $K = m/P$ for gases in pure water and in salt solution, where P is the partial pressure of the gas in atmospheres, and m is the number of moles of gas per 1000 grams of water in the equilibrium solution. This enables them to write $\gamma = K(\text{water})/K(\text{salt solution})$ for the activity coefficient of the gas in the salt solution. We note, however, that since the K 's are very closely constant down to infinite dilution of the gas, γ is also the true or thermodynamic equilibrium constant for the reaction

$$\text{Gas (in salt solution)} = \text{Gas (in pure water)}, \quad (21)$$

so that

$$\Delta F^\circ = -RT \ln \gamma \quad (22)$$

⁴² M. Randall and C. F. Failey, Chem. Rev. **4**, 271 (1927).

gives the free energy of transfer of a mole of gas from a hypothetical solution in which there is one mole of gas per 1000 g of water in the salt solution under discussion, to the hypothetical molal solution of gas in pure water. ΔS° for this transfer, then, is given by

$$\Delta S^\circ = - \left(\frac{\partial \Delta F^\circ}{\partial T} \right)_{P, m_3} \\ = R \ln \gamma + RT \left(\frac{\partial \ln \gamma}{\partial T} \right)_{P, m_3} \quad (23)$$

In their Table 4, Randall and Failey give, for a number of alkali halide solutions, γ values for N_2O at 15°C and 25°C, which can be used in (23) since the molality of the salt is the same for both temperatures. The data are those of Geffcken,⁴³ and from the regularities which emerge from our calculations we conclude provisionally that the precision is high enough to make our results significant. These results are shown in Table VII, along with three values for O_2 in NaCl solutions. In every case, a correction has been made for the fact that, in a dilute solution of gas in salt water, the mole fraction of the gas is less than it would be in pure water in the ratio 1: $(1 + (2m_3/55.51))$. This should produce a decrease in entropy when the reaction (21) takes place. The size of this term in the N_2O cases considered is either 0.036 or 0.072 e.u.

One striking result is that for N_2O , ΔS° is negative in every case except that of CsCl. The theory of Debye and McAulay⁴⁴ is easily shown to predict

$$\Delta S^\circ = -RT \ln \gamma \left[\frac{\partial \ln D_0}{\partial T} - \frac{\partial \ln \beta^*}{\partial T} + \frac{\partial \ln b_i}{\partial T} + \frac{\partial \ln V}{\partial T} \right], \quad (24)$$

β^* is defined by $D = D_0[1 - \beta^*n]$ and expresses the proportionate decrease in the dielectric constant produced by one molecule of gas per cc of solution. b_i is the average salting-out radius of the ions, and V the volume of a given mass of solution. If the simplest assumptions about β^*

and b_i are made, the term in $\partial \ln D_0/\partial T$ will dominate ΔS° , which will therefore be positive. This means that the results of Table VII for N_2O can be reconciled with the Debye-McAulay theory only by making rather definite *ad hoc* assumptions about the temperature dependence of β^* and of b_i . Physically, also, the customary picture of the salting-out effect is that the non-polar gas molecules are squeezed out of the neighborhood of the ions by the preferential attraction of the latter for the polar water molecules. The existence of these regions of impaired accessibility should, other things being equal, lower the partial molal entropy of the dissolved gas by reducing the effective value of the mixing term— $R \ln N_g$. This, again, should result in a positive ΔS° for (21).

We know of no explanation for the values and trends shown in Table VII which can be made complete without some arbitrary assumptions. The negative sign of most of the ΔS° values for N_2O , however, seems to be in reasonable accord with the picture we have arrived at of iceberg formation when N_2O dissolves in pure water, and of a disturbance by ions of the structure of the solution. If the latter makes it more difficult for the N_2O to form its icebergs, then the partial molal entropy of N_2O should be less negative in salt solution than in pure water, and ΔS° for (21) should be negative, as it is. The fact that LiCl has a greater effect of this sort than KCl, and that the effect of CsCl is opposite in sign could then be accounted for by the fact that Li^+ is a competitive iceberg former, whereas Cs^+ has loosened the water so as to make iceberg formation easier for the N_2O .

The last idea would predict that ΔS° should become more positive from KCl to KI, in opposition to the observed trend. Professor Olson⁴⁵ has suggested a possible explanation of this, along the lines of his discussion⁴⁶ of certain kinetic salt effects. This takes into account the direction in which different solutes tend to orient water molecules, and would introduce here the idea that if an increase in size of positive ions, which orient water with hydrogens out, causes an increase in ΔS° for N_2O , then an increase in size

⁴⁵ A. R. Olson, private communication.

⁴³ W. Geffcken, Zeits. f. physik. Chemie 49, 257 (1904).

⁴⁴ P. Debye and J. McAulay, Physik. Zeits. 26, 23 (1925).

⁴⁶ A. R. Olson and L. K. J. Tong, J. Am. Chem. Soc. 66, 1555 (1944).

of negative ions, which orient water with the hydrogens in, might well have the opposite effect.

Such a picture could also accommodate the fact that in NaCl, ΔS° for O_2 appears to be positive. For although N_2O and O_2 both build icebergs in pure water, there is no reason why they should be icebergs with the same orientation of the water molecules, so that the presence of NaCl might promote their formation in one case and hinder it in the other.

What has just been said, plus the question whether the peculiar dependence of ΔS° for O_2 on the concentration of NaCl is real, suggests that further experimental work in this field should prove illuminating.

Superlattice Formation

The large influence of a highly charged cation on the fluidity of its solution argues a certain mechanical strength, or rigidity, in the iceberg it forms around itself. This suggests that the other ions in the solution, if they do not themselves have too powerful a structure-breaking influence, may find some interference from this cause with their "normal" motions. For example, it may well be that in a solution of $LaCl_3$ the large iceberg which we assume to exist around the La^{+++} ion makes it more difficult for a Cl^- to come near it than would "otherwise" be the case. This would modify the Debye-Hückel ion cloud in such a direction that both positive and negative ions would be less influenced by ions of opposite sign than the Debye-Hückel theory predicts. This would account in a qualitative way for the observed positive deviation of the activity coefficient of $LaCl_3$ from the limiting law, a deviation which has always been most puzzling.⁴⁷

This line of thought may be carried farther. If the La^{+++} and Cl^- are held apart by the icebergs around the La^{+++} , then the spacing of the ions will be more "regular" than Debye-Hückel theory predicts. If such an effect is sufficiently pronounced, we may obtain a "superlattice," and the logarithm of the activity coefficient can be expected to vary with the cube root of the concentration, as in the old Ghosh⁴⁸ theory. Figure 7 shows a representation of the very ac-

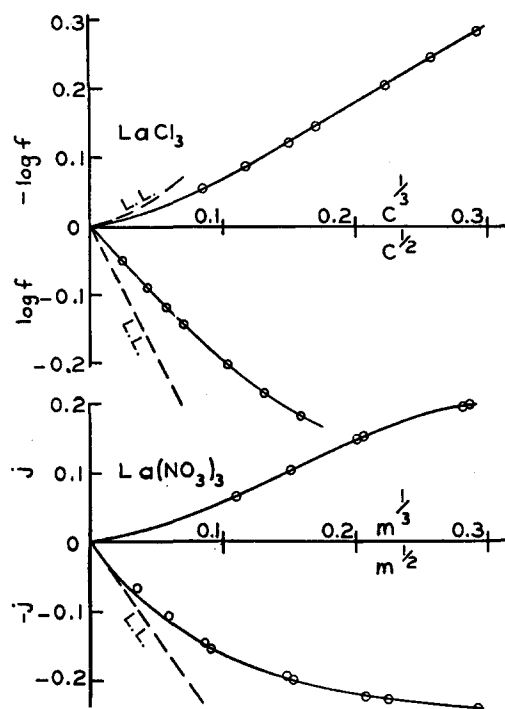


Fig. 7. $\log f$ for $LaCl_3$ vs. $c^{1/3}$ and $c^{1/2}$. Data of T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. 61, 200 (1932). j for $La(NO_3)_3$ vs. $m^{1/3}$ and $m^{1/2}$. j values were calculated from the freezing points recorded by Hall and Harkins, J. Am. Chem. Soc. 38, 2658 (1916).

curate data of Shedlovsky and MacInnes, in which $\log f$ is plotted against the square root and against the cube root of the concentration. The linearity of the latter plot is striking, and while it does not prove the existence of a superlattice, it does seem to make it credible. We assume, of course, that at exceedingly high dilutions the square root law holds as usual, for here the fact that the ions would only very rarely come close to each other in any case makes meaningless the prohibition of close encounters.

Figure 7 also shows corresponding plots (in this case of j^7) for $La(NO_3)_3$,⁴⁹ and here it is clear that no marked peculiarity of the sort just mentioned exists. Comparison of the values of ΔS° for Cl^- and NO_3^- suggests the reason. If the large structure-breaking tendency of NO_3^- bears a relation to the "strength" of the La^{+++} iceberg which enables it, so to speak, to "clear a path" for itself, then it will be able to approach the

⁴⁷ T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. 61, 200 (1939).

⁴⁸ J. C. Ghosh, J. Chem. Soc. 113, 449 (1918).

⁴⁹ R. E. Hall and W. D. Harkins, J. Am. Chem. Soc. 38, 2658 (1916).

La^{+++} ion more or less as envisaged in the Debye-Hückel theory.⁵⁰ Even here, however, we suspect that there is some interference with the penetration of the last one or two layers of water molecules, as otherwise there should be negative deviations from the limiting law.⁵¹

Here again we can obtain corroborative indications from the work of Freed.³⁸ He has shown that in the case of Eu^{+++} there are characteristic differences between the effects of concentration changes on the absorption spectra of aqueous solutions of EuCl_3 and $\text{Eu}(\text{NO}_3)_3$. These differences can be interpreted as meaning that NO_3^- ions can approach the Eu^{+++} much more freely than Cl^- ions can. Since europium and lanthanum salts must be very closely similar in the thermodynamics of their solutions, Freed's results must be taken as bearing upon the differences found between LaCl_3 and $\text{La}(\text{NO}_3)_3$. While, as before, many questions of detail remain to be discussed, there seems here to be some support for the superlattice picture in the chloride solutions.

There are one or two other cases, notably those of LiCl ⁵² and of KF ,⁵³ in which the activity coefficient curves in dilute solutions seem to have the "wrong" shape, and in which there are present ions to which we have attributed an iceberg building tendency. Both of the salts mentioned give $\log \gamma - (c)^{\frac{1}{2}}$ curves which, if reliable, have rather extended linear portions, and it is possible that super-lattice formation occurs to some extent in their solutions. We are inclined to suspect that in all electrolytes structural effects exert a more or less pronounced influence on the ionic distribution, and that this should be listed among the factors which cooperate to produce the "normal" deviations of real electrolytes from the Debye-Hückel limiting law.⁵⁴

⁵⁰ There is some indication that against the icebergs formed around Th^{++++} , even NO_3^- may be unable to move freely. See Prins, reference 34.

⁵¹ H. S. Frank, J. Am. Chem. Soc. **63**, 1789 (1941).

⁵² G. Scatchard and S. S. Prentiss, J. Am. Chem. Soc. **55**, 4355 (1933).

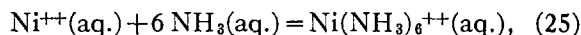
⁵³ G. Karagunis, A. Hawkinson, and G. Damköhler, Zeits. f. physik. Chemie **A151**, 433 (1930).

⁵⁴ There may be here also a possibility of explaining the peculiar trends found by J. Lange (Zeits. f. physik. Chemie **A168**, 147 (1934)) among the freezing points of solutions of tetraalkyl ammonium halides.

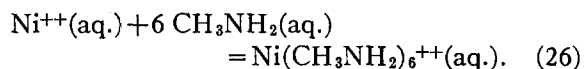
INFLUENCE OF STRUCTURE ON EQUILIBRIA IN SOLUTION

One way in which structural influences could affect equilibria is implicit in the last paragraph, since the "concentration constant" for a chemical equilibrium is altered by changes in activity coefficients, and any influence affecting the latter will be observed in the former as well. Another type of effect which structural peculiarities may be able to have on reaction tendencies in aqueous solutions is illustrated by some provisional results obtained by Professor Calvin,⁵⁵ to whom we are indebted for permission to discuss them in advance of publication.

Bjerrum⁵⁶ has investigated the equilibrium



and Calvin has studied this and the analogous reaction



He finds for (25) $\log K = 9.13$ at 23°C , and $\log K = 8.81$ at 30°C ; for (26) $\log K = 8.64$ at 15°C , and $\log K = 9.12$ at 35°C . These figures correspond, for (25), to $\Delta H = -19 \text{ kg.cal.}$;

$\Delta S = -22 \text{ e.u.}$ and, for (26) to $\Delta H = +9.7 \text{ kg.cal.}$; $\Delta S = +73 \text{ e.u.}$ This last result is so remarkable as, at first sight, to be nearly incredible, for it asserts that the methyl amine complex, though about as stable as the ammonia complex, is formed endothermically. That it is endothermal agrees, according to Calvin, with an estimate of space requirements which indicates that there is not quite enough room for the methyl groups if bond lengths and van der Waals' radii are normal. What drives the reaction forward, if the data are reliable, is the positive ΔS , which is 95 e.u. greater than that found for (25).

Allowing for some uncertainty in the numbers, it therefore appears that there are some 75–100 e.u. of entropy to account for as a difference between (25) and (26). A part of this is undoubtedly to be ascribed to the difference between the

⁵⁵ M. Calvin, private communication.

⁵⁶ J. Bjerrum, *Metal Ammine Formation in Aqueous Solutions* (Copenhagen, 1941); Chem. Abstr. **35**, C 527 (1941).

\bar{S}_2 values for $\text{Ni}(\text{NH}_4)_6^{++}$ and $\text{Ni}(\text{CH}_3\text{NH}_2)_6^{++}$. Comparison²⁵ of Mg^{++} ($\bar{S}_2 = -31.6$) and Ba^{++} ($\bar{S}_2 = +2.3$) indicates that change in size of a divalent ion is accompanied by large entropy effects, and Kraus⁵⁷ remarks that many ions which increase the viscosity of solutions give ammonia complexes which have the opposite effect. $\text{Ni}(\text{NH}_3)_6^{++}$, however, is already rather large, so that the extra size resulting from the methyl groups should fall far short of being able to account for 75 e.u. difference in \bar{S}_2 , even after allowance is made for the likelihood that the large size of the amine complex may well cooperate with its double change to produce more structure-breaking.

As a possible explanation for the rest of the difference in ΔS° between (25) and (26) we call attention to the fact that from Fig. 3 we can estimate that ΔS of vaporization of CH_3NH_2 may be as much as 10 e.u. greater than that of NH_3 . That is, the methyl group imposes an iceberg-

forming tendency on the CH_3NH_2 which lowers its partial molal entropy very considerably. In the neighborhood of nickel-ammonia complex ions, however, we have assumed a structure-breaking tendency, and if this were so strong that the methyl amine, when complexed, was unable to form its iceberg, then, as compared with the ammonia complex, the methyl amine complex might form with a ΔS more positive by $6 \times 10 = 60$ e.u. This explanation is conjectural, the more so as the solutions in which the reactions are carried out are not dilute, being about 2M in NH_4NO_3 or 3M in $\text{CH}_3\text{NH}_3\text{NO}_3$, respectively. The suggestion nevertheless presents itself that further experimental work on reactions of this type might reveal the existence of structural factors which would have to be taken into account in interpreting chemical mechanisms. In particular, one is tempted to speculate on the possible influence of factors of this kind in biological equilibria, where aqueous solutions are involved of substances which carry non-polar groups.

⁵⁷ C. A. Kraus, *The Properties of Electrically Conducting Systems* (New York, 1922), p. 178.