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A Note on the Relation between Entropy and Enthalpy of Solution

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The relation between entropy and enthalpy of solution for a series of non-polar solutes in a given non-polar solvent is discussed. It is considered that solution of a gaseous solute, without changing its concentration on going from gas phase to liquid solution phase, does not change its own entropy, all change of entropy being referred to the solvent. The entropy of the solvent changes because of surface effects around the solute molecules and a kind of long-range order introduced by the solute molecules. Two extreme cases are considered, (1) the case of an ideal solution, and (2) the case of a solute of hard attractionless spheres. The difference in entropy of solution between these extreme cases can be estimated. It can also be estimated by extrapolation from the experimental data on the entropy and enthalpy of solution, and these two estimates agree in order of magnitude. The fact that the relation between entropy and enthalpy of solution is linear is also shown to be a reasonable expectation, and effect of changing solvent as well as solute is considered. The groundwork is thus laid for a qualitative understanding of this relation between entropy and enthalpy of solution.

IT is well known that there is a relation between the entropies and enthalpies of solution of a series of non-polar gases or vapors in a given non-polar liquid solvent, provided the solute molecule is not larger than that of the solvent. This was apparently first remarked by Bell,[1] who noted that some relation between the energy and enthalpy of solution might be expected but gave no explanation of the form of the relation nor of the order of magnitude of the quantities involved; it was further discussed by Barclay and Butler.[2] A rather detailed theoretical discussion has been given by Frank and Evans.[3] In their treatment certain relations used in the discussion of pure liquids[4] were introduced into the theory of solutions only slightly, if at all, modified.[5] It is certainly of interest that this gives an equation which seems to fit pretty well the energy-enthalpy relation for solutions noted above; however, the physical significance and validity of this procedure are not entirely clear. This

being the case, it appears that some consideration of this problem from another point of view is still desirable.

In the present note we shall consider the properties of two extreme, hypothetical types of solution, namely (1) an ideal solution, and (2) a solution in which the solute molecules consist of hard spheres, which occupy space but do not exert attractive forces on the solvent molecules. Real solutions may usually be considered to stand somewhere between these extreme types, and it is possible to say something about the transition from one type to the other for any given solvent.

Notation.—Since we shall be interested in entropies of gas and liquid phases for solvent and solute and changes of entropy under various conditions, as well as a number of different volumes and free volumes, we require a system of notation with a variety of subscripts and suffixes, and capital and small letters. In the table which follows, a subscript i is used to denote component i. In the text i takes the value 1 for solvent and 2 for solute. To any of the symbols we may affix an asterisk, indicating that it refers to the case of an ideal solution, or we may add a subscript 0, indicating that it refers to the case in which the solute consists of hard-sphere molecules.

n_i = total number of moles of component i.

N_i = mole fraction of component i in liquid phase.

V = volume of liquid solution containing one mole of solute.

v_i° = molal volume of pure liquid component i.

v_i = molal volume of gaseous component i.

$V_{f,i}$ = molal free volume of component i in liquid solution.

$V_{f,i}^\circ$ = molal free volume of component i in pure liquid phase (see Eq. (5)).

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[1] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

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

[3] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).

[4] H. S. Frank, J. Chem. Phys. **13**, 493 (1945).

[5] For example, the use of Eq. II(10), together with the subsequent use of β_1 and β_2 as partial molal quantities on p. 508 of Frank and Evans; and the use of Eq. II(21) on p. 513.

S = total entropy of liquid solution.

S_i° = molal entropy of pure liquid component i.

$\bar{S}_i$ = partial molal entropy of component i in liquid solution.

$s_i(v_i)$ = molal entropy of gas at volume indicated.

$\Delta S_i(v_i) = \bar{S}_i - s_i(v_i)$ = entropy of solution of 1 mole of pure vapor component i at molal volume v_i in a large amount of solution of any given concentration (partial entropy of solution).

$\Delta S_i^\circ(v_i) = S_i^\circ - s_i(v_i)$ = molal entropy of condensation of pure component i from molal volume v_i in vapor phase.

ΔS_m = entropy of mixing.

ΔH_i = enthalpy of solution of 1 mole of pure vapor component i in a large amount of any given solution (partial enthalpy of solution).

ΔH_i° = enthalpy of condensation of pure component i.

IDEAL SOLUTIONS

If two liquids form an ideal solution, the entropy of mixing is given by the classical expression

$$\Delta S_m^* = -n_1 R \ln N_1 - n_2 R \ln N_2, \qquad (1)$$

and the total entropy of the solution is given by

$$S^* = n_1 S_1^\circ + n_2 S_2^\circ - n_1 R \ln N_1 - n_2 R \ln N_2. \quad (2)$$

We then obtain for the partial molal entropy of the solute

$$\bar{S}_2^* = (\partial S^*/\partial n_2)_{T,p,n_1} = S_2^\circ - R \ln N_2. \qquad (3)$$

Let us now consider the entropy of solution of 1 mole of solute from the vapor phase into a very large quantity of solution of any given concentration, with $v_i = V$. This means that the solute enters the solution without change in its volume concentration. We have for this process

$$\Delta S_2^*(V) = \bar{S}_2^* - s_2(V)$$
$$= S_2^\circ - s_2(V) - R \ln N_2. \qquad (4)$$

We can write an equation defining $V_{f,2}^\circ$ as follows:

$$S_2^\circ - s_2(v_2) = R \ln(V_{f,2}^\circ/v_2). \qquad (5)$$

The free volume thus defined includes all effects of communal entropy.

An exactly ideal solution is one in which the solute and solvent are "exactly alike" although distinguishable; that is, their molecules have the same size and force fields.[6] In this case $V_1^\circ = V_2^\circ$

and $V_{f,1}^\circ = V_{f,2}^\circ$. Since V is the volume of solution containing 1 mole of solute, we have $V = V_2^\circ/N_2$. Setting $v_2 = V$, introducing the expression for V into Eq. (5), and substituting in Eq. (4), we obtain

$$\Delta S_2^*(V) = R \ln(V_{f,2}^\circ/V_2^\circ)$$
$$= R \ln(V_{f,1}^\circ/V_1^\circ). \qquad (6)$$

The ratio of molal free volume to molal volume simply represents the effect of neighboring molecules on the space available for the motion of any molecule in the field of those neighbors. Thus the effect of solution without change of concentration is simply the effect of neighboring molecules on the free space available.

NON-IDEAL SOLUTIONS

Equation (6) holds, of course, only for ideal solutions. We may, however, define a new quantity $V_{f,1}'$ by the general equation

$$\Delta S_2(V) = R \ln(V_{f,1}'/V_1^\circ). \qquad (7)$$

$V_{f,1}'$, then, may be said to give that volume left free by 1 mole of solvent for a particular solute. It seems possible, as Frank and Evans have noted, for $V_{f,1}'$ to become as large as, or even greater than, V_1°. At first sight this appears strange, for it seems then that the solute is free to move around in a greater volume than that which contains it, even though this volume itself is well filled with solvent molecules. Frank and Evans pointed out that this could only be explained as an effect of the solute on the solvent. An explanation of the nature of this effect, and an estimate of its order of magnitude, will be the principal aim of the present note.

We now consider the process of solution from a different point of view. We suppose that we have the solute in the volume which it is going to occupy, and pour the solvent in on it. Since this is a liquid system, dilute in the solute, the

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[6] There is, of course, no requirement from the thermodynamic definition of an ideal solution (giving the chemical potentials as functions of the mole fractions) that the molecules of solvent and solute be "exactly alike," and

there are many solutions, that are very close to ideal, for which this is certainly not the case. However, for a solution to be quantitatively ideal, it seems highly probable that this condition is necessary. It certainly seems to be necessary as far as the size of the molecules is concerned, though this is not very critical. [(See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939), pp. 353 ff.)] The effect of the force fields on the ideality of a solution as expressed by Eq. (1) is essentially the subject of the present note. We shall, hereafter, refer to the "exactly ideal" solution described here simply as an ideal solution.

TABLE I. Enthalpies and entropies of solution with acetone as solvent.

	Hard-sphere solute	Ideal solution
Partial enthalpy of solution	$\Delta H_{2,0} = -\Delta H_1^\circ = 7600$	$\Delta H_2^* = \Delta H_1^\circ = -7600$
Partial entropy of solution	$\Delta S_{2,0}(V) = 8$	$\Delta S_2^*(V) = -11.5$
Total entropy of solution	$\Delta S_{2,0}(V) + R = 10$	

Enthalpies in cal. mole^{-1}, entropies in cal. mole^{-1} deg.$^{-1}$

solute molecules may occupy any preassigned positions, regardless of whether the solvent is present or not. We may thus say that the partition function of the solute is unaltered by the presence of the solvent, and we may, somewhat artifically perhaps, refer all entropy effects to the solvent.[7] In considering the entropy of the solvent, we may assume that all solute molecules are held in fixed positions, since in the partition function for the solute all possible positions are included. From this point of view Eq. (7) gives the effect of the solute on the entropy of the solvent; however, a slight correction is required. For it is evident that the process we have just considered gives the total entropy of solution of 1 mole of solute rather than the partial entropy of solution. The total entropy change will be $S - s_2(V) - n_1 S_1^\circ$ instead of $\Delta S_2(V) = \bar{S}_2 - s_2(V)$. Since $S = n_1 \bar{S}_1 + n_2 \bar{S}_2 = n_1 \bar{S}_1 + \bar{S}_2$ (since $n_2 = 1$), we see that the entropy change for the process considered is equal to $\Delta S_2(V) + n_1 \bar{S}_1 - n_1 S_1^\circ$. For a dilute solution this may be shown[8] to be equal to $\Delta S_2(V) + R$.

For a solution that is ideal as well as dilute, the total entropy of solution $\Delta S_2^*(V) + R$ of one mole of solute molecules will be negative; this follows from Eq. (6) because $V_{f,1}^\circ$ is always very considerably smaller than V_1°. But in an ideal solution the solvent molecules in the immediate neighborhood of a solute molecule are in the same environment as any other solvent molecules, since the force fields are the same. The lowering of entropy of the solvent implied by Eq. (6) cannot, therefore, be referred to any change in the range of motion of the individual solvent molecules in the neighborhood of solute molecules. It must, on the contrary, be attributed to the introduction of a certain degree of long-range order, produced by having the solute molecules held in fixed position. This restriction in position is transmitted through the neighboring molecules to the solvent, even though the range of motion of these molecules about their equilibrium positions is not altered. It is rather the equilibrium positions themselves which are affected.

To understand better the situation in non-ideal solutions, let us consider the case in which the solute is assumed to be composed of hard-sphere molecules, which exert no force on the solvent molecules. (This means that the enthalpy of solution, $\Delta H_{2,0}$ is actually positive because of the energy necessary to produce the hole in the solvent into which the solute molecule is going to go. Roughly, assuming that the hole is the same size as a solvent molecule, we may say that $\Delta H_{2,0}$ is equal to $-\Delta H_1^\circ$.)[9] If the solute is like a hard sphere, we may expect that a fixed arrangement of solute molecules will be much less effective, if effective at all, in inducing long range order in the liquid. Furthermore, since the energy will not be lowered by proximity of solvent to solute molecules, the solvent molecules around a solute molecule will be reasonably free to arrange themselves in such a way as to allow a maximum of freedom of motion. There will thus be a gain in entropy, similar to the gain in entropy when the free surface of a liquid is increased. This gain in entropy is to be equated to $\Delta S_{2,0}(V) + R$.

APPLICATION TO THE EXPERIMENTAL DATA

Let us now apply these ideas to dilute solutions in a typical solvent, acetone. We use the data collected by Frank and by Frank and Evans,[10]

[7] Somewhat similar considerations have been carried out by R. H. Fowler and E. A. Guggenheim, pp. 372 ff of reference 6, but they did not attempt to consider the solvent effects fully in setting up the chemical potentials. See also Barclay and Butler, reference 2, p. 1454.

[8] We have $\bar{s}_1 = s_1^\circ - R \ln N_1$, since Raoult's law holds for a dilute solution. $N_1 = n_1/(n_1 + 1)$ with $n_2 = 1$. With $n_1 \gg 1$ this becomes $N_1 \sim 1 - n_1^{-1}$, and $\ln N_1 \sim -n_1^{-1}$, whence the relation follows immediately.

[9] For a calculation of the energy necessary to form a hole in a liquid, see R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), second edition, p. 844.

[10] H. S. Frank, ref. 4; see especially p. 499; H. S. Frank and M. W. Evans, ref. 3; see pp. 514–515.

and present the relevant material in Table I. The enthalpy values are obtained as indicated from the enthalpy of condensation of acetone. To get $\Delta S_2^*(V)$ we take the entropy of vaporization and the density, and using Eq. (5) (applied, however, to the solvent instead of the solute) calculate that at 25°C the value of $V_{f,1}^\circ/V_1^\circ$ is 0.0030. We then use Eq. (6). The table of Frank and Evans shows how $\Delta S_2(V)$ and ΔH_2 vary from solute to solute. (Actually they list the energy and enthalpy for evaporation from solution to form a gas at 1 atmosphere at 25°C, so their values differ by a sign and a constant additive amount from ours.) By extrapolation we find that the value of $\Delta S_{2,0}(V)$ given in the table is that which corresponds to

$$\Delta H_2 = \Delta H_{2,0} \cong +7600.$$

Had there been no surface effect $\Delta S_{2,0}(V) + R$ would have been zero, assuming that there is no long-range order under these conditions. It is, therefore, natural to compare the $8 + R = 10$ cal. mole^{-1} deg.$^{-1}$ with the surface entropy to be expected. The surface entropy of a liquid is closely related to the Eötvös constant, $-d(V_1^\circ {}^{\frac{2}{3}}\gamma)/dT$, where γ is the surface tension. If we divide this by $N^{\frac{2}{3}}$, where N is Avogadro's number, the expression may be interpreted as the surface entropy per molecule. (This follows because γ is the surface free energy per unit surface, and $(V_1^\circ/N)^{\frac{2}{3}}$ is very close to the surface occupied by a molecule at the surface.) The Eötvös constant for acetone is, from data in the Landolt-Börnstein Tables, 1.8 erg mole$^{-\frac{2}{3}}$ deg.$^{-1}$, which makes $-N^{-\frac{2}{3}}d(V_1^\circ {}^{\frac{2}{3}}\gamma)/dT$ equal to 2.5×10^{-16} erg deg.$^{-1}$. Comparing this to the Boltzmann constant $k = 1.37 \times 10^{-16}$ erg deg.$^{-1}$, we see that the surface entropy is a little less than $2R$ or 4 cal. deg.$^{-1}$ per mole of molecules at the surface.

The surface area about a solute molecule is of the order of four times the area occupied by a molecule at the surface. One would not expect the entropy connected with unit area to be the same as for a flat surface, and the 10 cal. mole^{-1} for the surface entropy in the solution of a hard sphere gas is certainly of the correct order of magnitude.

We may look at this from a slightly different point of view. There will probably be about 10 nearest neighbors about a solute molecule. Each

neighbor, therefore, has about 1.0 cal. deg.$^{-1}$ mole^{-1} of surface entropy, about one-fourth as much as a free surface molecule. In a recent paper,[11] we estimated the surface entropy per molecule of a liquid by a rough statistical calculation and found a value about half as great as that given by the Eötvös constant. In our calculation we neglected the decrease in density at the surface layer, which undoubtedly results in an increase in the surface entropy. On the other hand, this decrease in density is probably not appreciable in the neighborhood of a solute molecule. Further, a molecule at the surface of a small spherical hole inside a liquid is not nearly as free as a molecule at a flat surface. Therefore, the value of 1.0 cal. deg.$^{-1}$ mole^{-1} for the solvent molecules about the hard-sphere solute molecule seems entirely reasonable.

We may now be in a position to understand the linear relation between $\Delta S_2(V)$ and ΔH_2, simply as the start of a series expansion. It has, as we have noted, been pointed out by Barclay and Butler that there should be some sort of relation between $\Delta S_2(V)$ and ΔH_2 for a given solvent, and this is also obvious from the discussion given above. We expand about the values for a hard-sphere solute, writing

$$\Delta S_2(V) = \Delta S_{2,0}(V) + a_1(\Delta H_2 - \Delta H_{2,0}) + a_2(\Delta H_2 - \Delta H_{2,0})^2 + \cdots. \quad (8)$$

The question then reduces to a decision as to whether the first term in this expansion is the dominant one. $\Delta S_2(V)$ can be divided into two parts, as discussed above, the surface entropy and the entropy (negative in sign, of course) associated with long-range order, and each one of these can be expanded in a series like Eq. (8).

Let us consider the surface entropy first. As we have noted, this part is contributed by all the nearest neighbors of a solute molecule, and in the range from ideal solution to solution of hard spheres it goes from 0 to 1.0 cal. per mole per deg. for each nearest neighbor, in the case of acetone. This corresponds to a change in the effective free volume of each nearest neighbor molecule by a factor 1.65. Over this great a range the free volume change might be expected to deviate somewhat from being a linear function of the force exerted by the solute molecule on

[11] O. K. Rice, J. Chem. Phys. 15, 314 (1947).

its neighbors and hence[12] on ΔH_2, and the logarithm of the free volume, which determines $\Delta S_2(V)$, would also be expected to deviate to some extent from being a linear function of the free volume itself. However, these deviations would not be expected to be exceedingly great even with a 65 percent change in free volume, and the experimental data do not actually cover more than about two-thirds of the range between the ideal solution and the hard-sphere solute. And the change in surface entropy contributes only a small part of the variation of $\Delta S_2(V)$ between these extreme types of solution. The greater part of this variation is to be referred to the introduction of long-range order. But this is an effect which is actually shared among many molecules of solvent, so that the change in free volume for any one molecule will be so small that one need have no surprise if the experimental range does not extend beyond that in which the first term of the series expansion of Eq. (8) suffices. This, of course, is not a rigorous explanation of the linearity between ΔH_2 and $\Delta S_2(V)$, but does make it seem plausible. Frank and Evans obtained a linear relation, but this was done by carrying an empirical linear relation between the ΔH's and ΔS's of pure liquids into the equation for the solutions.

The slope of the $\Delta S_2(V)$ vs. ΔH_2 line, which may be expressed as

$$a_1 = [\Delta S_2{}^*(V) - \Delta S_{2,0}(V)]/(\Delta H_2{}^* - \Delta H_{2,0}), \quad (9)$$

is almost the same for a considerable number of solvents. This may be understood in terms of the variation of $\Delta S_2{}^*(V)$ with $\Delta H_2{}^*$ for a series of different solvents. This, of course, is the same as the variation of $\Delta S_2{}^\circ(V)$ with $\Delta H_2{}^\circ$.

Let us write $\delta\Delta S_2{}^*(V)$ and $\delta\Delta H_2{}^*$ for the differences between the respective indicated quantities for two solvents. Then since $\Delta H_{2,0} = -\Delta H_2{}^*$ we will have

$$\delta(\Delta H_2{}^* - \Delta H_{2,0}) = 2\delta\Delta H_2{}^*.$$

This means that if a_1 is to be the same for the two different solvents, we should, from Eq. (9), have

$$\delta[\Delta S_2{}^*(V) - \Delta S_{2,0}(V)] = 2a_1\delta\Delta H_2{}^*.$$

$\delta\Delta S_{2,0}(V)$ may be expected to be close to zero, because $\Delta S_{2,0}(V)$ is contributed entirely by the surface entropy, and the Eötvös constant has roughly the same value for most common solvents. We might thus expect to find $\delta\Delta S_2{}^*(V) \cong 2a_1\delta\Delta H_2{}^*$. Actually, empirically, it is found that $\delta\Delta S_2{}^*(V) \cong a_1\delta\Delta H_2{}^*$, since the slope of the $\Delta S_1{}^\circ(V)$ vs. $\Delta H_1{}^\circ$ line for different solvents is approximately the same as that of the $\Delta S_2(V)$ vs. ΔH_2 line for solutions with a common solvent. But for the usual solvents $\delta\Delta S_1{}^\circ(V)$ is such a small fraction of $\Delta S_2{}^*(V) - \Delta S_{2,0}(V)$ that the empirical relation between $\Delta S_1{}^\circ(V)$ and $\Delta H_1{}^\circ$ does not require that the $\Delta S_2(V)$ vs. ΔH_2 lines for the different solvents be appreciably different. It thus appears that the similar values of a_1 for the different solvents may merely reflect the similarity of the solvents used.

On the other hand, the fact that the $\Delta S_1{}^\circ(V)$ vs. $\Delta H_1{}^\circ$ line has about the same slope as most of the $\Delta S_2(V)$ vs. ΔH_2 lines for the various solvents is a remarkable fact, noted by Barclay and Butler,[2] but still not fully explained. In going from one solvent to another, for which $\Delta H_1{}^\circ$ is greater, there is no change in surface entropy, since this is zero with either pure solvent or ideal solution; the decrease in entropy arising from long-range order, however, is caused by two factors, (1) the increased force exerted by the particular atom which is condensed into the solution, and (2) the increased force which all neighbor atoms exert on each other. On the other hand, in going from one solute to another which has a greater ΔH_2 in the same solvent there is a decrease in entropy on account of the surface effect, but there is no decrease in entropy on account of factor (2) of the preceding sentence. The surface effect in the case of changing solutes must, therefore, approximately balance factor (2) in the case of changing from one pure solvent to another.

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[12] This depends upon the existence of a fairly simple relation between the force exerted by neighbor molecules and the mutual energy, which means that the potential energy curves must in all cases be of similar shape.