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R. Parshad

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

On the Weak Associations in Water and in Aniline

R. PARSHAD
Physical Laboratory, Council of Scientific and Industrial Research, University Buildings, Delhi, India
January 22, 1946

PAULING'S concept of the hydrogen bond has explained a vast field of experimental data.[1] In this note we wish to show that his concept can be further used to explain the very interesting property of the comparative weakness of associations in water. For example, taking the energy of the hydrogen bond as the thermal energy required to rupture it, the energy of the hydrogen bond in water is 4.5–5 kcal./mole, compared to that of 6 kcal./mole for alcohols and 7–8 kcal./mole for carboxylic acids. It is probably not well realized that the "abnormal" properties of water are not only caused by its vast network of associations, but also because these associations are weak. It is not the mere presence of hydrogen bonds but their progressive breaking with increase of temperature, or pressure etc., which causes the open structure of water caused by extensive hydrogen bonding to crumble and bring in the abnormal properties. For that matter, carboxylic acids are hardly abnormal in the liquid states. Because of the nearly non-breaking of the strong dimers, the latter behave as single molecules until even vaporization. Indeed the vapor state rather than the liquid state of these acids may be called associated in the sense that water is in the liquid state.

While the extensive nature of the association in water may be explained as caused by favorable steric factors, (*viz.* all atoms in a state to be engaged in hydrogen bonds, the donating power of O in terms of H's to be equal to the accepting power, and the ability to be able to form hydrogen bonds on all sides (tetrahedral bonding), etc., the weak nature of these associations may be explained as follows.

According to Pauling, in the O−H valency link, there is resonance between the covalent state and the ionic state. A pair of electrons is at one time shared between O and H (covalent state) and in the next instant is all attracted on to O by its electronegativity, leaving the H a bare proton (ionic state). In the state of the ionic character of O−H, the proton H attracts and is attracted by an O of another O−H in virtue of the latter's total negative charge (when in the ionic state) and any unpaired electron pairs on it.

Here we consider two factors:

(1) As one O−H link of a water molecule is ionic, the O is negative, because of the pair of electrons that it has attracted on to itself. This negative charge on O will discourage the attraction of another pair of electrons from the other O−H link. In other words, the negative charge on O, formed because of the ionic character of O−H link, decreases the electronegativity of O and so the ionic character of the second O−H link. As both the O−H links are of course indistinguishable, this means that the ionic character of both the O−H's are reduced, and so the hydrogen bonds formed will be weak. The liquids like alcohols have one H to one O and so do not suffer this weakening of the ionic character.

(2) Consider the effect of an H, on O, not of its own valency link but that with which it is involved in a hydrogen bond.

O—**H** - - - - - - - - - **O**—H

In the above figure, the atoms concerned are in bold face. The **H** proton will attract electrons on **O**, and so the latter will increase its effective nuclear charge for its own H (on the right of the figure). The electronegativity of O is increased and so the ionic character of O−H, leading to increase of hydrogen bonding power.

The effects of (1) and (2) run in counter directions but evidently the effect of factor (1) is greater than that of (2), as in the former the mutual effect of O and H in the same valency link is considered. We may note here that derivation of factor (2) is contrary to that of Pauling.[2] According to him the O−H link concerned is strengthened (or its ionic character decreased). However, Pauling's derivation all the more supports the inference of weak associations in water.

The above considerations for water can also be used to explain why aniline containing an amino group forms no or very little hydrogen bonds, when it is also considered that N has lower electronegativity than O, and because of the extra phenyl group on N, lower number of unshared pair of electrons are left on N for attraction by a distant proton for forming a hydrogen bond. But the electron attracting property of the phenyl group itself will contribute some additional electronegative power to N, and because of this aniline may be more associated, if at all, than ammonia.

[1] L. C. Pauling, *Nature of the Chemical Bond* (Cornell University Press, New York, 1940).
[2] Reference 1, p. 326.

A Note on Communal Entropy. Remarks on a Paper by Henry S. Frank[1]

O. K. RICE
University of North Carolina, Chapel Hill, North Carolina
April 8, 1946

IN a recent series of interesting papers, Frank has discussed what he aptly calls the pictorial theory of the liquid state. These papers included, also, some consideration of the solid state, and the gas of hard elastic spheres.

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In the latter discussion, Frank[1] has come into conflict with some statements previously made by me.[2] On page 487 of reference 1, Frank discusses the communal entropy of a closely packed three-dimensional gas of hard elastic spheres. This I had estimated as $3R$ per mole on the basis of Eq. (2) of reference 2. Frank rejects my Eq. (2) and substitutes his Eq. (36), but grants that the latter is not itself satisfactory. My equation, applied first to a *simple* cubic array, rests on the assumption that motions in the three directions of space are independent of each other, provided the system is sufficiently closely packed. Thus if an atom A (hard elastic sphere) is displaced out of the line joining its two neighbors, B and C (Fig. 1), it is assumed that its motion along this line is unaffected. This is true if the displacement is small enough. But even if the atoms are densely packed, large fluctuations become appreciably probable if the number of atoms in the line is large. It is, therefore, necessary to place some *arbitrary* restriction on the total possible displacement of any atom, allowing it to be not greater than some finite multiple (which may, of course, be as large as we please, if the spheres are sufficiently densely packed) of the average distance between atoms. Some such condition is necessary in order to keep the system in the assumed simple cubic lattice; if left to itself, the system would presumably tend to go over to a lattice of the face-centered cubic, or some related type, which would have a greater entropy; but this is not the problem we are attempting to solve. Even though the simple cubic lattice is not a stable lattice unless some restrictions are placed on the motions of the atoms, it is still useful to consider it, because it may be used as a guide to the cases which have a greater resemblance to physical reality.

Let us consider a sufficiently closely packed simple cubic array of N hard elastic spherical atoms packed in a cube of length l. Letting $K=(2\pi mkT/h^2)^{3N/2}$, the total partition function of this system will be given, assuming classical statistics, by[3]

$$Q^N=K\int\int\cdots\int dx_1dx_2\cdots dx_Ndy_1dy_2\cdots dy_Ndz_1dz_2\cdots dz_N. \quad (1)$$

In evaluating the integral we allow the x's, y's, and z's to take all possible values, keeping, however, each numbered atom in its particular place in the array. This latter condition makes it unnecessary to divide by $N!$, since we do not allow exchange of atoms. Since motions in the three

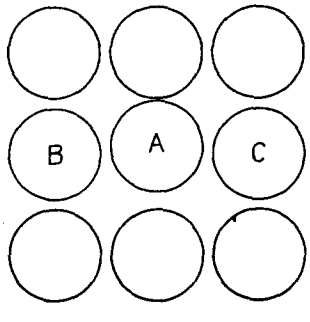

FIG. 1.

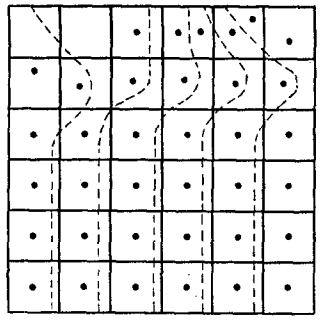

FIG. 2.

directions of space are independent, we may separate the x, y, and z parts of the integration, and since these parts are exactly alike, we may write

$$Q^N=K\left(\int\int\cdots\int dx_1dx_2\cdots dx_N\right)^3. \quad (2)$$

The integral consists of integrations along $N^{\frac{1}{3}}$ exactly similar rows of $N^{\frac{1}{3}}$ atoms each. Hence

$$Q^N=K\left(\int\int\cdots\int dx_1dx_2\cdots dx_{N^{\frac{1}{3}}}\right)^{3N^{\frac{2}{3}}} \quad (3)$$

Except for the restrictions on large displacements this integral is just that evaluated by Tonks.[4] It is clear from pages 4 and 5 of reference 2 that reasonable restrictions can be placed on the fluctuations without appreciably altering the value of this integral. We, therefore, insert Tonks' value with the appropriate changes ($N^{\frac{1}{3}}$ for N), obtaining

$$Q^N=K[(l-N^{\frac{1}{3}}\sigma)^{N^{\frac{1}{3}}}/N^{\frac{1}{3}}!]^{3N^{\frac{2}{3}}} \quad (4)$$

where σ is the diameter of the spheres. If $N^{\frac{1}{3}}$ is large enough $1/N^{\frac{1}{3}}!=e^{N^{\frac{1}{3}}}(N^{\frac{1}{3}})^{-N^{\frac{1}{3}}}$, excluding a factor whose logarithm will be negligible. Letting $v=l^3/N$ be the volume per atom, and setting $\theta=\sigma^3/v$, the expression becomes

$$Q^N=Ke^{3N}v^N(1-\theta^{\frac{1}{3}})^{3N}, \quad (5)$$

entirely equivalent to Eq. (2) of reference 2. As noted in reference 2, this is greater by the factor e^{3N} than the partition function which would be obtained if each sphere were confined to its own cell, the cells being all equal in size and completely filling the space. The molal communal entropy is, therefore, $3R$. How to take care of the case where the spheres are packed in a cubic close-packed (cubic face-centered) type of arrangement, rather than simple cubic, is probably sufficiently indicated in reference 2. This involves a certain estimate, rather than a rigorous straight-forward deduction, but it is undoubtedly a good estimate and, in any event, in itself, it in no way affects the communal entropy. The change to the cubic face-centered type may, on account of the blocking of fluctuations, have a slight effect on the communal entropy, somewhat similar to the effect due to restricting the size of the fluctuations in the simple cubic array.

While this seems to settle the problem from a formal mathematical point of view, it may be possible to bring out the difference between a closely packed aggregate of

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spheres and a dilute gas, for which the communal entropy per mole is only R, more graphically. If the spheres are very densely packed, under the restrictions noted above a sphere cannot get out of its row and column. (For convenience we restrict ourselves to two dimensions.) On the other hand, consider the situation which may arise in the case of point atoms, as illustrated by Fig. 2. This figure shows a square divided into cells by solid lines, one cell for each atom. If we assume that the atoms may pass the cell boundaries, we can get a situation such as shown in Fig. 2. This may be considered as produced in the main by fluctuations in the top row only. It can also be produced by another set of fluctuations as is indicated by the broken lines. Since the two sets produce indistinguishable configurations, they give rise to only one state of the system. In the case of closely packed spheres, however, the two sets of fluctuations, if they were of the same order of magnitude relative to the free space (therefore taking the molecules out of their individual cells), would, nevertheless, give only small displacements relative to the diameter of the spheres. The two sets of small displacements would give rise in this case to distinguishable configurations. It is, therefore, seen that the closely packed spheres can have a greater communal entropy than the dilute gas, because in the latter case row and column fluctuations interfere and overlap, giving rise to indistinguishable configurations.

Frank has quite properly called attention to the arbitrary nature of communal entropy. It depends upon the size of the "natural" cell which one chooses in the first place, when one assumes that each atom is assigned to its own cell. However, it is agreed that, insofar as possible, the cells should be assigned so that they are of equal size, and completely fill the space available. Then the assignment is easy in the case of a densely packed gas of hard elastic spheres. When the atoms exert forces on each other, it becomes a little more difficult. I made an estimate of communal entropy in this case because I wished later to combine the partition function for a gas of hard elastic spheres with that of a Debye solid in setting up the partition function for a liquid, assuming each part carried its own communal entropy factor. It seemed reasonable to do this if the excitation of communal entropy was comparable in the two cases. Otherwise some special means of averaging might have been necessary. Though the Debye solid was found to have a communal entropy only 77 percent as excited as the dense gas of hard spheres, this did not seem sufficiently different to render any special computation necessary.

In order to make a fair comparison of the communal entropy in the two cases, it seemed necessary to define the "natural" cell for a Debye solid in a manner as nearly analogous as possible with the definition for the hard elastic spheres. If, in the hard-sphere case, all atoms are fixed in position except one, this one has a free volume 2^3 times as large as if it were confined to its own cell. It was, therefore, assumed that if all the atoms of a Debye solid were held fixed except one, this one also would move in an effective volume equal to 2^3 times its natural cell. It is known that this atom would vibrate with the root-mean-square value of the frequencies of the normal modes. Therefore, it seemed reasonable to say that a solid in which all atoms moved with this same mean frequency (Einstein model) was one in which the molal entropy was $3R \ln 2$ times as great as it would be if each atom were confined to its "natural" cell, and the communal entropy of the Debye solid was calculated by comparison with the Einstein model, on this basis. In any event, it seems more "natural" to me to define the "natural" cell by means of an average frequency. Frank prefers the Debye maximum frequency, which seems "artificial" to me. However, nothing can be proved about this. I merely wish to emphasize that I had a real reason for choosing the natural cell as I did in view of the purpose I had in mind.

Errata to reference 2. On page 3 of reference 2 (last sentence beginning in the first column) where it reads, "If this result is multiplied by the momentum integral and divided by h," replace h by h^N. This gives what we have called Q^N (though in this case it is for a one-dimensional array) and Q (correctly given by Eq. (1) of reference 2) is the partition function referred to a single atom.

At the end of page 6 and beginning of page 7, it was inadvertently stated "that the partition function per molecule of a Debye solid is $e^{\frac{1}{2}}kT/h\nu_m$." This is the partition function *per degree of freedom* and was used as such.

[1] H. S. Frank, J. Chem. Phys. **13**, 478 (1945).
[2] O. K. Rice, J. Chem. Phys. **12**, 1 (1944). For some errata see *ibid.* **12**, 521 (1944) and the end of this article.
[3] Q^N is called Q by Frank; to be consistent with my own Eq. (2) I retain Q for the partition function referred to a single atom.
[4] L. Tonks, Phys. Rev. **50**, 955 (1936).

Postscript to the Foregoing Note by O. K. Rice

HENRY S. FRANK
Lingnan University, Canton, China
April 8, 1946

I GREATLY appreciate the opportunity to see Professor Rice's "Note on Communal Entropy" in advance of publication, and to place on record as promptly as possible my agreement with the derivation he has given of the limiting partition function for a simple cubic array of hard attractionless spheres compressed toward the limit of complete mutual contact, and with the conclusion which it establishes, that $3R$ is the correct theoretical fluctuation entropy for this case, appropriate to the choice of $l^3(1-\theta^{\frac{1}{2}})^3/N$ as the elementary cell. Rice's derivation also makes it possible to see where my "superficially straightforward" generalization of the one-dimensional case to three dimensions fails in this application. The latter corresponds, for the present model and for distinguishable particles, to letting each atom permute only with other atoms in the same linear arrays with it in the x, y, and z directions. A correct method of counting, permitting all $N!$ permutations, reproduces both Rice's mathematics and his result.

When the system becomes more expanded, the motions become too complicated for simple analytical discussion. There are doubtless several ways of "breaking down" the process by which the fluctuation entropy decreases as θ decreases, and the picture given here by Rice is very instructive in throwing light on one of them.

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