The Liquid State

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from this along the b axis. Chemical evidence indicates that the most probable structure for sucrose is α-glucopyranose-β-fructofuranose. Using the three criteria of cell dimensions, space group symmetry and cleavage planes this molecule is found to fit into the unit cell best with its long axis parallel to the short diagonal of the unit cell, i.e., the $\bar{1}\ 0\ 1$, and the flat sides of the rings parallel to the $0\ 1\ 0$. In such an arrangement the hydroxyl groups between the flat rings of adjacent molecules along the b axis approach to within 2.5–3A of each other. This at once suggests the existence of hydrogen bridges along the b axis between adjacent molecules, a view which is substantiated by the fact that cleavage planes parallel to the $0\ 1\ 0$ do not occur. On this basis it is possible to compute that there are in the unit cell probably about four free OH groups and twelve OH groups perturbed by hydrogen bridges, six each in the Δ and δ manners. It is believed that, owing to spatial restrictions within the crystal lattice, only these two types of perturbation occur. Since the hydrogen bridging is assumed to be associated only with OH groups, the numbers perturbed in Δ and δ fashions must be equal. This equality is consistent with the approximate equality in the intensities of absorption in the 1.51μ and 1.58μ bands.

The results of this study indicate that infra-red absorption spectroscopy involving polarized light may be a useful adjunct to x-ray analysis of organic crystal structures. For, the most intense absorption bands, at least in the *near* infra-red, are associated with hydrogen atoms, which are just the ones whose locations x-ray analysis is unable to determine. Of course, infra-red analysis cannot locate single atoms in crystals, but the dependence of intensity of absorption upon plane of polarization should be able to give the relative number of alignments in different directions of specific groups, such as OH groups.

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[1] Cross, Burnham and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).
[2] Errera and Mollet, Nature **138**, 882 (1936).
[3] Kinsey and Ellis, J. Chem. Phys. **5**, 399 (1937).
[4] Unpublished work of J. D. Bath and O. L. Sponsler, University of California at Los Angeles.

The Liquid State

In the description of the liquid state which they are developing, Eyring and Hirschfelder[1] more than once stress the fact that in their theory the *total* free volume in a liquid, as in a gas, is shared by all the molecules; in the entropy of melting of a simple substance the most important term is the contribution R, arising from the fact that the entire free volume is jointly used by all the molecules.

It will be suggested below that we can perhaps obtain a clearer idea of the difference between the liquid and solid states, if we recognize that almost the whole of the additional entropy of a simple liquid arises from the local relationship between a molecule and its neighbors. About
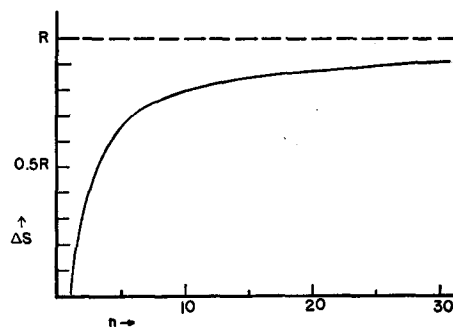

Fig. 1.

nine-tenths of the communal entropy R is due to a purely local sharing of free volume between a molecule and its immediate neighbors—a sharing of free volume which is intimately connected with those small fluctuations, which are impossible in a solid, but which in a liquid permit the viscous flow.

Consider first one mole of a gas contained in a fixed volume in which the partition function of a single molecule is f. Now suppose that by means of numerous partition walls the entire volume is divided into cells of equal size, each containing the same small number n of molecules (less than ten). The partition function for a molecule in any cell is now fn/N, and there are N/n cells. The entropy of the whole gas is

$$(N/n)(n \log (fn/N) - \log n!)k.$$

When there is one particle per cell ($n=1$), the gas, as Hirschfelder and Eyring[2] have pointed out, is comparable with a solid, its entropy being $Nk \log f/N$. If, starting with $n=1$, we remove a few of the dividing walls, until in each cell n becomes equal to, say, 5, the increase in entropy is given by

$$\Delta S = R\left(\log \frac{fn}{N} - \frac{1}{n}\log n!\right) - R\log \frac{f}{N} = R\left(\log n - \frac{1}{n}\log n!\right).$$

For $n=5$ this already has the value $0.655R$, and Fig. 1 shows how rapidly the value of ΔS rises with increasing n. If the gas is degenerate, $n!$ in the above expressions must be replaced by a number smaller than $n!$, which makes the entropy increase still more rapidly.

These ideas are applicable to a liquid, if in place of the volume we introduce the free volume of the molecules. Inside any one cell the molecules will share their free volume in common. It appears that when each cell contains only 27 molecules the entropy of the liquid already amounts to 90 percent of its value for a liquid with unconstrained molecules.

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[1] Eyring and Hirschfelder, J. Phys. Chem. **41**, 249 (1937). Kincaid and Eyring, J. Chem. Phys. **5**, 587 (1937).
[2] Hirschfelder, Stevenson and Eyring, J. Chem. Phys. **5**, 896 (1937).