Summary

1. The velocity constant for the diacetone alcohol decomposition in the presence of dilute sodium hydroxide has been measured at 5° intervals from 0 to 50°.

2. The constancy of ratio of velocity constant to sodium hydroxide concentration has been confirmed over a limited concentration range at 25°.

3. The energy of activation, calculated from the Arrhenius equation for a series of temperature intervals, has been shown to be a function of temperature well outside the limits of error. E_{act} increases consistently from a value of 15,850 cal. at 5° to 17,250 at 32.5 and then decreases by about 400 cal. at 45°.

4. On the addition of 18.5% of methyl alcohol E_{act} increases by over 1700 cal. but the general character of the $E_{act}-T$ curve remains little changed to 30°.

5. The corresponding B values from the integrated Arrhenius equation, $\ln k = 2.3 B - (E_{act}/RT)$, both in water and the methyl alcohol solution parallel these E_{act} values and furnish experimental evidence for abandoning the unfortunate term "temperature independent constant" for this quantity.

6. The data show that the collision theory is inadequate and that the entropy of activation is an important quantity in considering solution reactions.

The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

Investigations of the entropy of substances at low temperatures have produced very important information regarding the structure of crystals, the work of Giauque and his collaborators being particularly noteworthy. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas;[1] subsequent to this discovery the phenomenon of rotation of molecules in crystals was found to be not uncommon. Also the entropy values of carbon monoxide[2] and nitrous oxide[3] show that in crystals of these substances the molecules are not uniquely oriented, but have instead a choice between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axes. It is pointed out in this note that the observed entropy of ice at low temperatures provides strong support for a particular structure of ice, and thus gives an answer to a question which has been extensively discussed during the past few years.

It has been generally recognized since the discovery of the hydrogen bond[4] that the unusual properties of water and ice (high melting and boiling points, low density, association, high dielectric constants, etc.) owe their existence to hydrogen bonds between water molecules. The arrangement of oxygen atoms (but not of hydrogen atoms) in crystals of ice is known from x-ray studies;[5] it is not a close-packed arrangement (as of sulfur atoms in the high-temperature form of hydrogen sulfide), but a very open one, like that of the silicon atoms in high-tridymite. Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms at the distance 2.76 Å., and it has been assumed that it is bonded to these atoms by hydrogen bonds, the number of hydrogen atoms being just that required to place one hydrogen atom between each pair of oxygen atoms. (Similarly in high-tridymite there is an oxygen atom between each pair of silicon atoms; we might say that each silicon atom is attached to four others by oxygen bonds.)

The question now arises as to whether a given hydrogen atom is midway between the two oxygen

(1) W. F. Giauque and H. L. Johnston, THIS JOURNAL, 50, 3221 (1928); L. Pauling, Phys. Rev., 36, 430 (1930).

(2) J. O. Clayton and W. F. Giauque, THIS JOURNAL, 54, 2610 (1932).

(3) R. W. Blue and W. F. Giauque, ibid., 57, 991 (1935); K. Clusius, Z. Elektrochem., 40, 99 (1934).

(4) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, 42, 1419 (1920).

(5) D. M. Dennison, Phys. Rev., 17, 20 (1921); W. H. Bragg, Proc. Phys. Soc. (London), 34, 98 (1922); W. H. Barnes, Proc. Roy. Soc. (London), A125, 670 (1929).

atoms it connects or closer to one than to the other. The answer to this is that it is closer to one than to the other. In the gas molecule the O–H distance is 0.95 Å., and the magnitudes of the changes in properties from steam to ice are not sufficiently great to permit us to assume that this distance is increased to 1.38 Å. In ice each hydrogen atom is about 0.95 Å. from one oxygen atom and 1.81 Å. from another.

We now ask whether each hydrogen atom (or rather hydrogen nucleus) has a choice of two positions along its oxygen–oxygen axis, independent of the positions of the other hydrogen nuclei. The answer is in the negative; for we know that the concentration of $(OH)^-$ and $(H_3O)^+$ ions in water is very small, and we expect the situation to be essentially unchanged in ice. Hence the hydrogen nuclei will assume positions such that each oxygen atom (with at most very few exceptions) will have two hydrogen atoms attached to it.

Let us now make the following assumptions (to be supported later by a discussion of the entropy) regarding the structure of ice.

(1) In ice each oxygen atom has two hydrogen atoms attached to it at distances of about 0.95 Å., forming a water molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming hydrogen bonds.

(3) The orientations of adjacent water molecules are such that only one hydrogen atom lies approximately along each oxygen–oxygen axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to appreciably stabilize any one of the many configurations satisfying the preceding conditions with reference to the others.

Thus we assume that an ice crystal can exist in any one of a large number of configurations,[6] each corresponding to certain orientations of the water molecules. The crystal can change from one configuration to another by rotation of some of the molecules or by the motion of some of the hydrogen nuclei, each moving a distance of about 0.86 Å. from a potential minimum 0.95 Å. from

(6) One of the large number of configurations is represented by the structure of ice suggested by J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933); these authors also suggested that at temperatures just below the melting point (but not at lower temperatures) the molecular arrangement might be partially or largely irregular.

one oxygen atom to another one 0.95 Å. from an adjacent oxygen atom. It is probable that both processes occur. As an example of a change from one to another configuration, we may consider one of the puckered rings of six oxygen atoms occurring in ice
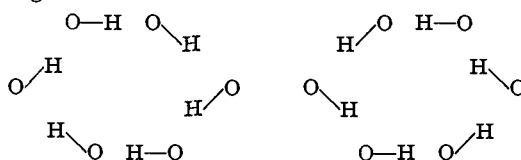
Change from one of the two cyclic arrangements of hydrogen nuclei to the other is permitted by our postulates. The fact that at temperatures above about 200Å. the dielectric constant of ice is of the order of magnitude of that of water shows that the molecules can orient themselves with considerable freedom, the crystal changing under the influence of the electric field from unpolarized to polarized configurations satisfying the above conditions. On cooling the crystal to low temperatures it freezes into some one of the possible configurations; but it does not go over (in a reasonable period of time) to a perfect crystal with no randomness of molecular orientation. It will have at very low temperatures the entropy $k \ln W$, in which W is the number of configurations accessible to the crystal.

Let us now calculate W, using two different methods.

There are N molecules in a mole of ice. A given molecule can orient itself in six ways satisfying condition 2. However, the chance that the adjacent molecules will permit a given orientation is $^1/_4$; inasmuch as each adjacent molecule has two hydrogen-occupied and two unoccupied tetrahedral directions, making the chance that a given direction is available for each hydrogen of the original molecule $^1/_2$, and the chance that both can be located in accordance with the given orientation $^1/_4$. The total number of configurations for N molecules is thus $W = (^6/_4)^N = (^3/_2)^N$.

The same result is given by the following equivalent argument. Ignoring condition 1, there are 2^{2N} configurations with hydrogen bonds between adjacent oxygen atoms, each hydrogen nucleus having the choice of two positions, one near one oxygen atom and the other near the other. Some of these are ruled out by condition 1. Let us now consider a given oxygen atom and the four surrounding hydrogen atoms. There are sixteen arrangements of the four hydrogen nuclei. Of

these ten are ruled out by condition 1—one gives $(H_4O)^{++}$, four give $(H_3O)^+$, four $(OH)^-$ and one O^{--}. This condition for each oxygen atom thus permits only $^6/_{16} = ^3/_8$ of the configurations, the total number of permitted configurations being accordingly $W = 2^{2N}(^3/_8)^N = (^3/_2)^N$.

The contribution of this lack of regularity to the entropy of ice is thus $R \ln ^3/_2 = 0.805$ E. U. The observed entropy discrepancy of ice at low temperatures is 0.87 E. U., obtained by subtracting the entropy difference of ice at very low temperatures and water vapor at standard conditions, for which the value 44.23 E. U. has been calculated from thermal data by Giauque and Ashley,[7] from the spectroscopic value 45.101 E. U. for the entropy of water vapor given by Gordon.[8] The agreement in the experimental and theoretical entropy values provides strong support of the postulated structure of ice.[9]

The structure of ice is seen to be of a type intermediate between that of carbon monoxide and nitrous oxide, in which each molecule can assume either one of two orientations essentially independently of the orientations of the other molecules in the crystal, and that of a perfect molecular crystal, in which the position and orientation of each molecule are uniquely determined by the other molecules. In ice the orientation of a given molecule is dependent on the orientations of its four immediate neighbors, but not directly on the orientations of the more distant molecules.

It should be pointed out that a finite residual entropy calculated for a substance from experimental data obtained at temperatures extending down to a certain temperature, with extrapolation below that point, may arise either from failure of the experimenter to obtain thermodynamic equilibrium in his calorimetric measurements or from error in the extrapolation. Measurements made under ideal conditions and extended to sufficiently low temperatures would presumably lead to zero entropy for any system.

Other Crystals with Residual Entropy

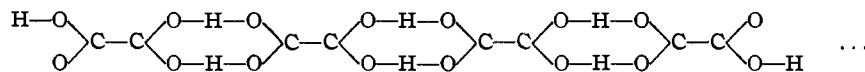Our knowledge of the structure of crystals permits the prediction to be made that many other crystals will be found to have residual entropy at very low temperatures as a result of some randomness of atomic arrangement. It is probable, however, that experimental verification of the residual entropy would be difficult for most of the cases mentioned below.

Diaspore, $AlHO_2$, contains groups OHO with hydrogen bonds.[10] As in water, we expect the hydrogen nucleus to be closer to one oxygen atom than to the other. Inasmuch as there is no restriction on the choice of the two positions, each oxygen atom forming only one hydrogen bond, this would lead to a residual entropy of $R \ln 2$ per mole of $AlHO_2$. The same residual entropy is expected per HO_2 group for other crystals containing this group (staurolite).

Hydrogen bonds may not always lead to residual entropy. For example, the crystal lepidocrocite,[11] FeOOH, contains infinite strings of oxygen atoms joined by hydrogen bonds, $^OH_OH^OH_OH^OH$. If we assume that the choice of two positions by a hydrogen nucleus is restricted by the requirement that each oxygen have one and only one attached hydrogen, then there are two accessible configurations per string. This lack of definiteness does not lead to an appreciable residual entropy for a large crystal.

In the double molecules of formic acid, with the structure[12] $HC\langle\begin{smallmatrix}O-H-O\\O-H-O\end{smallmatrix}\rangle CH$ and in other monocarboxylic acids forming double molecules, we expect that the interaction within a carboxyl group is strong enough to permit only the two configurations in which one hydrogen nucleus is attached to each carboxyl group to be stable at low temperatures. This would lead to a residual entropy of $^1/_2 R \ln 2$ per RCOOH.

By a similar argument we calculate for β-oxalic acid (anhydrous), which contain finite strings[13] of molecules

$$H-O\rangle C-C\langle\begin{smallmatrix}O-H-O\\O-H-O\end{smallmatrix}\rangle C-C\langle\begin{smallmatrix}O-H-O\\O-H-O\end{smallmatrix}\rangle C-C\langle\begin{smallmatrix}O-H-O\\O-H-O\end{smallmatrix}\rangle C-C\langle\begin{smallmatrix}O\\O-H\end{smallmatrix} \cdots$$

the residual entropy $R \ln 2$ per mole of $(COOH)_2$, whereas α-oxalic acid, containing layers with the dealized structure[13] in which there are infinite sequences of carboxyl groups attached by hydrogen bonds, would have no appreciable residual

(7) W. F. Giauque and M. F. Ashley, *Phys. Rev.*, **43**, 81 (1933).

(8) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(9) The existence of this residual entropy of ice at very low temperatures was discovered by Giauque and Ashley (ref. 7), who preliminarily ascribed it to the persistance of rotation of ortho-water molecules (comprising $^3/_4$ of the total) about their electric-moment axes, giving an entropy of $^3/_4 R \ln 2 = 1.03$ E. U.

(10) F. J. Ewing, *J. Chem. Phys.*, **3**, 203 (1935).

(11) F. J. Ewing, *ibid.*, **3**, 420 (1935).

(12) L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(13) S. B. Hendricks, *Z. Krist.*, **91**, 48 (1935).
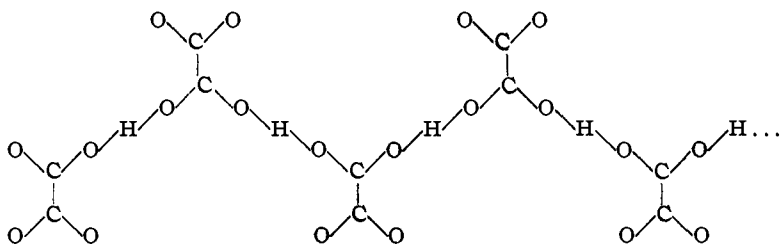
entropy. The experimental verification of this prediction by heat capacity measurements and the study of the equilibrium between the two forms might be practicable.

At present it is not possible to predict with confidence whether the hydrogen nucleus between two fluorine atoms connected by a hydrogen bond has the choice of two positions (as for oxygen atoms) or not. The FHF distance of 2.35 Å. is somewhat greater than twice the H–F distance in HF, 0.91 Å., although the difference (29%) is not so great as for OHO and H–O (45%). The question would be answered by a determination of the residual entropy of potassium hydrogen fluoride, KHF_2, or of some other crystal containing the HF_2 group; the residual entropy would be $R \ln 2$ if the potential function for the hydrogen nucleus has two minima rather than one. The same residual entropy would also be shown by KH_2F_3, KH_3F_4, etc. If crystalline hydrofluoric acid contains cyclic molecules $(HF)_6$, with the structure

$$H^{FHF}H$$
$$F \qquad \qquad F,$$
$$H_{FHF}H$$
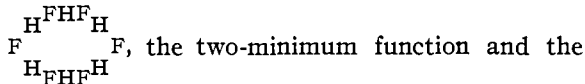
the two-minimum function and the restriction that one hydrogen is attached to each fluorine would lead to a residual entropy of $^1/_6 R \ln 2$ per mole of HF.

Hydrogen bonds between unlike atoms, as in NH_4F, would not lead to residual entropy.

Residual entropy may also result from the multiplicity of stable positions for atoms other than hydrogen. In γ-Al_2O_3 and γ-Fe_2O_3 the oxygen ions are arranged in a close-packed framework, which provides nine positions for every eight cations. The x-ray data[14] indicate that the cations are distributed essentially at random among these positions, leading to a residual entropy of $^3/_2 R \ln {}^{27}/_{16} = 1.558$ E. U. per mole of R_2O_3. In pyrrhotite,[15] $Fe_{1-\delta}S$, the sulfur atoms have a hexagonal arrangement, the iron atoms being distribu-

ted apparently at random among the positions provided, of which they occupy the fraction $1 - \delta$. In the cubic tungsten bronzes,[16] Na_xWO_3, the sodium ions occupy the fraction x of the available positions. These crystals would presumably show residual entropy of mixing of the ions W^{5+} and W^{6+} as well as the entropy of random distribution of the sodium ions. A somewhat similar case is provided by the hexagonal form of silver iodide,[17] in which at room temperature each silver atom has the choice of four or five positions a few tenths of an Ångström apart. At liquid air temperatures, however, most of the atoms settle into one position, so that no residual entropy would be shown.

Many crystals show an uncertainty in structure similar to that of CO and NNO or of solid solutions. For potassium cyanate the x-ray data[18] indicate that each cyanate ion has the choice of two orientations, NCO and OCN, which would lead to the residual entropy $R \ln 2$. In spinel, $MgAl_2O_4$, and other crystals with the spinel structure, the bivalent and trivalent cations are distributed with considerable randomness among the available positions,[19] leading to a residual entropy corresponding to a crystalline solution. In muscovite,[20] $KAl_2(AlSi_3)O_{10}(OH)_2$, one aluminum and three silicon atoms per formula are distributed, presumably with considerable randomness, among the available tetrahedral positions. The same phenomenon, leading to residual entropy, without doubt occurs in many aluminosilicates.

Crystals of cadmium bromide[21] and nickel bromide[22] prepared in certain ways show a type of randomness which does not lead to any appreciable residual entropy, provided that the crystals are not extremely small. This randomness of structure ("Wechselstruktur," alternating layer structure) consists in a choice between two positions for each layer of a layer structure, leading to an entropy of $k \ln 2$ for each layer, which remains

(14) G. Hägg and G. Söderhohn, Z. physik. Chem., **B29**, 88 (1935); G. Hägg, ibid., **B29**, 95 (1935); E. J. W. Verwey, Z. Krist., **91**, 65 (1935); E. Kordes, ibid., **91**, 193 (1935).

(15) G. Hägg and I. Sucksdorff, Z. physik. Chem., **B22**, 444 (1933).

(16) G. Hägg, ibid., **B29**, 192 (1935).

(17) L. Helmholz, J. Chem. Phys., **3**, 740 (1935).

(18) S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925).

(19) T. F. W. Barth and E. Posnjak, J. Washington Acad. Sci., **21**, 255 (1931); F. Machatschki, Z. Krist., **80**, 416 (1931).

(20) L. Pauling, Proc. Nat. Acad. Sci., **16**, 123 (1930); W. W. Jackson and J. West, Z. Krist., **76**, 211 (1930).

(21) J. M. Bijvoet and W. Nieuwenkamp, ibid., **86**, 466 (1933).

(22) J. A. A. Ketelaar, ibid., **88**, 26 (1934).

inappreciable, inasmuch as the number of layers in a crystal (other than an extremely small crystal) is very small compared with the number of atoms.

In this connection it might be mentioned that there exists the possibility that ice may crystallize with such an alternating layer structure. The oxygen-atom arrangement assigned to ice corresponds to superimposing double oxygen layers in the sequence ABAB—(A at 00, B at $^1/_3$ $^2/_3$, C at $^2/_3$ $^1/_3$ of a hexagonal net). The sequence ABC-ABCABC— would also lead to an arrangement (diamond) such that each oxygen atom is surrounded by four others arranged tetrahedrally, which is indeed, so far as I can see, just as satisfactory as the reported arrangement. There is no good evidence that such a cubic modification of ice has been observed. However, the arbitrariness of orientation which we have found to exist for the water molecules in ice suggests that there may also be an arbitrariness in the sequence of double oxygen layers, with configurations such as ABABABCBCB— occurring. Such an alternating layer structure would have hexagonal symmetry, might develop faces at angles corresponding to the axial ratio $c/a = 1.63$, and would not be distinguishable so far as residual entropy is concerned from a crystal with fixed oxygen atom

arrangement. The x-ray data show that the sequence of layers is not completely random, the structure being essentially ABABAB—; it is possible, however, that a change in the sequence, corresponding to twinning on the basal plane, occurs occasionally.

I am indebted to Professor W. F. Giauque for discussing the question of the structure and entropy of ice, as well as related questions, with me.

Summary

It is suggested that ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbors, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each O–O axis. There are $(^3/_2)^N$ such configurations for N molecules, leading to a residual entropy of $R \ln \,^3/_2 = 0.805$ E. U., in good agreement with the experimental value 0.87 E. U.

The structure and entropy of other crystals showing randomness of atom arrangement are discussed.

The Radial Distribution Method of Interpretation of Electron Diffraction Photographs of Gas Molecules

BY LINUS PAULING AND L. O. BROCKWAY

Introduction

The only method of interpretation of electron diffraction photographs of gas molecules which has been used to any great extent is the so-called *visual method*, involving the correlation of apparent maxima and minima on the photographs with maxima and minima on simplified theoretical curves calculated for various models of the molecule under consideration. This method of interpretation, originally developed by Wierl,[1] has been thoroughly tested by Pauling and Brockway[2] who have shown it to yield values of interatomic distances accurate to within about 1% (estimated probable error). The main disadvantage of the method is that it does not involve a straightfor-

ward process of determining the structure of a molecule from the analysis of experimental results, but consists instead in the testing (and rejection or acceptance) of any structures which may be formulated, a tedious calculation being required for each structure.

We have developed a new method of interpretation of the photographs which does not suffer from this disadvantage. This *radial distribution method*, which is closely related to the method of interpretation of x-ray diffraction data developed by Zernike and Prins[3] for the study of the structure of liquids and applied by Warren and Gingrich[4] to crystals, consists in the calculation (from

(1) R. Wierl, *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1932).

(2) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(3) F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927); see also P. Debye and H. Menke, *Ergeb. Tech. Röntgenkunde*, Akad. Verlagsges., Leipzig, Vol. II, 1931.

(4) B. E. Warren and N. S. Gingrich, *Phys. Rev.*, **46**, 368 (1934).