

NOTES

Needle-Shaped Crystals of Sodium Chloride Obtained by Percrystallization

BY HENRY TAUBER AND ISRAEL S. KLEINER

In 1917 the observation was made by Kober,¹ that if a collodion container, filled with a saturated ammonium sulfate or a saturated sodium chloride solution, and with the open end closed tightly with a cord, was suspended in the air and fanned in a warm room, crystals of these salts "crystallized on the outside and blew off like snow." He called this phenomenon "percrystallization." To our knowledge no use has been made since that time of this method of crystallization. While working on the purification of enzyme material, we thought that this method would afford a practical way of getting rid of the inorganic diffusible salts and at

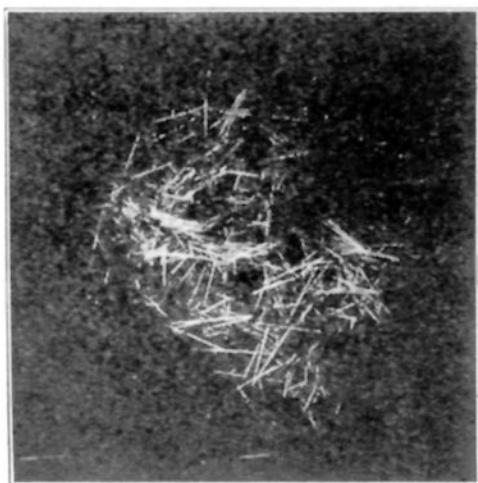


Fig. 1.—Crystals of sodium chloride obtained by percrystallization, natural size.

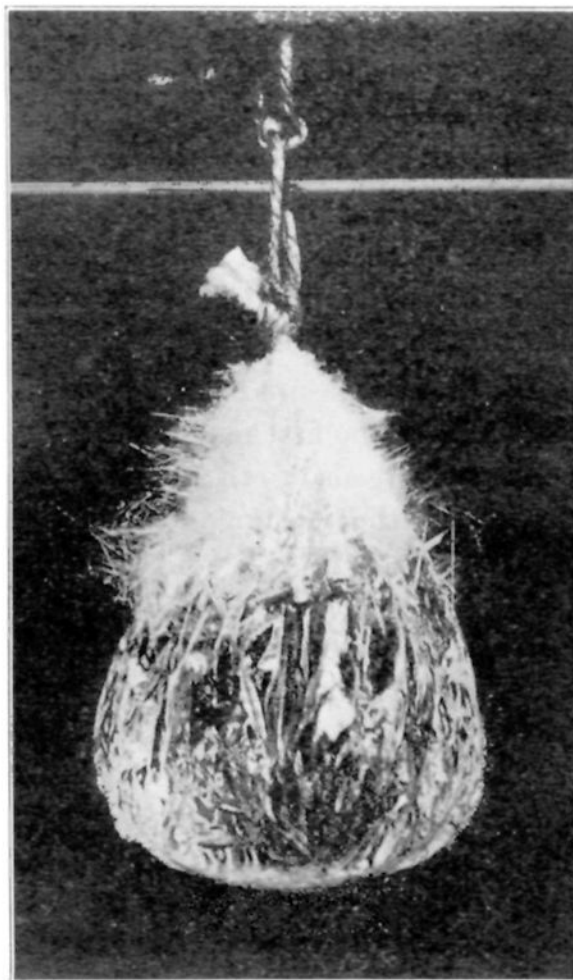


Fig. 2.—Collodion bag with sodium chloride needles forming by percrystallization.

the same time of concentrating the enzyme. We found that the sodium chloride, which was present in the enzyme-salt mixture, crystallized outside the collodion bag, but instead of the usual cubic habit, the sodium chloride crystallized in beautiful needles about 1 cm. long (see Fig. 1).

The procedure (without fanning), repeated with c. p. sodium chloride (Baker's), yielded the same needles. One hundred fifty cc. of a half-satu-

¹ Kober, *THIS JOURNAL*, 39, 944 (1917).

rated solution was placed in a 250-cc. collodion bag at 20°. Within one hour the needles (see Fig. 2) crystallized outside on the upper part of the bag, above the level of solution.

Drs. W. J. McCaughey of Ohio State University and J. B. Niederl of New York University examined these crystals and found that they belong to the regular cubic system.

The fact that the crystals mainly develop in one direction seemed to be worthy of note.

We are greatly indebted to Professors W. J. McCaughey and J. B. Niederl for examining the crystals.

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The Generalized Theory of Acid and Base Catalysis Applied to the Rate of Ionic Reactions

BY ROBERT LIVINGSTON

The rate of the catalytic decomposition of hydrogen peroxide in an acid bromine-bromide solution has been measured both in solutions of hydrobromic acid and in solutions containing sulfuric acid and potassium bromide.¹

The corrected rate constant, χ in the equation

$$v = \chi(\text{H}_2\text{O}_2)(\text{H}^+)(\text{Br}^-)\gamma_{\text{HBr}}^2$$

is about 10% higher for the solutions containing sulfuric acid. While it is not impossible that this difference is due to experimental error,³ it seems more probable that it is a real effect, probably due to the specific catalytic action of the acid molecule HSO_4^- .⁴ Although the generalized theory of acid (and base) catalysis has never been demonstrated for reactions between ions, there is no *a priori* reason why this type of reaction should not occur. On the assumption that HSO_4^- acts similarly to and simultaneously with H_3O^+ , the total rate equation would be

$$v = (\text{H}_2\text{O}_2)(\text{H}^+)(\text{Br}^-) \left[\chi_{\text{H}_2\text{O}}\gamma_{\text{HBr}}^2 + \chi_{\text{HSO}_4} \frac{(\text{HSO}_4^-)}{(\text{H}^+)} \frac{\gamma_{\text{HSO}_4^-} \gamma_{\text{Br}^-}}{\gamma_{\text{x}}} \right]$$

While this is qualitatively in agreement with the experimental facts, a quantitative test is impossible, owing to uncertainties in the computation

¹ (a) Bray and Livingston, *THIS JOURNAL*, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923).

² Livingston, *ibid.*, **48**, 53 (1926).

³ It might be due to "promoter action" or to negative catalysis, caused by a trace of some unknown impurity, or else to a systematic error in the determination of the activity coefficients.

⁴ Brönsted. *Chem. Rev.*, **5**, 231 (1928).

of (HSO_4^-) and the impossibility of determining $\gamma_{\text{HSO}_4^-} - \gamma_{\text{Br}^-} / \gamma_x$. In sufficiently dilute solutions these quantities might be computed from the Debye-Hückel limiting law; unfortunately, accurate rate measurements would be practically impossible in this region. The occurrence of generalized acid catalysis in this reaction might be tested by using solutions containing small concentrations of potassium bromide and a moderately weak, chemically inert acid in the presence of a high constant concentration of an inert salt, *e. g.*, sodium perchlorate.

Other ionic reactions might be expected to show a similar effect; for example, the oxidation of hydriodic acid by chloric acid,⁵ or the basic hydrolysis of the nitrourethan ion.⁶

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⁵ Bray, *J. Phys. Chem.*, **7**, 92 (1903).

⁶ Brönsted and Delbanco, *Z. anorg. allgem. Chem.*, **144**, 248 (1925).

The Entropy of Bromine from Spectroscopic Data

BY WELDON G. BROWN*

A recent fine structure analysis of the visible absorption bands of bromine by the writer¹ has provided data from which accurate values of the thermodynamic constants of bromine may be calculated. These calculations involve nothing essentially new, although certain consequences of a rather unique isotope situation become emphasized. In this note the entropy calculated from band spectrum data is to be compared with a less accurate value obtained from experimental measurements of the specific heat.

There are two isotopes of bromine, 78.92 and 80.92, which, according to Aston's measurements,² are equally abundant. These give rise to three kinds of molecules, Br_2^{79} , $\text{Br}_2^{79,81}$ and Br_2^{81} , in the proportions 1:2:1, respectively. A slight difference in the molecular constants of the Br_2^{79} and Br_2^{81} molecules leads to slightly different entropies, but because of their equal abundance this becomes smoothed out when, in calculations of thermodynamic constants, one uses the data for the $\text{Br}_2^{79,81}$ molecule. There is an additional effect due to the lack of symmetry which results in the entropy of $\text{Br}_2^{79,81}$ being greater than the entropy of either of the symmetrical species by $R \ln 2$ per mole, or $1/2 R \ln 2$ per mole of the actual mixture since this species constitutes one-half of ordinary bromine.

The moment of inertia of bromine is sufficiently large and the centrifugal

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¹ Brown, *Phys. Rev.*, **39**, 777 (1932).

² Aston, *Proc. Roy. Soc. (London)*, **115**, 487 (1927); **132**, 489 (1931).

deformation sufficiently small to make applicable the approximation in summation of the rotational energy terms used by Gibson and Heitler, and by Giauque,³ in the case of iodine, namely

$$Q_{\text{rot.}} = \sum_i p_i e^{-\epsilon_i/kT} = \frac{4\pi^2 I k T}{h^2} = \frac{T}{2c_2 B}$$

where c_2 is the second radiation constant, and B is the fine structure constant obtainable directly from the spectral data. This expression applies to a symmetrical molecule. The entropy is then obtained by the well-known formula⁴

$$S^\circ = R \left[\ln Q + T \frac{d \ln Q}{dT} \right]$$

The band spectrum constants for the normal electronic state of $\text{Br}_2^{79,81}$ are as follows. The subscripts refer to the zero vibrational state.

$$\begin{array}{ll} B_0 = 0.08077 & \omega_0 = 322.2 \\ \alpha = 0.00027 & \omega_0 x_0 = 1.07 \end{array}$$

In the following table the molal entropies (ideal gas, pressure one atmosphere, at 298.1°K.), calculated as indicated above, are given for each of the three molecular species, together with the entropy of the 1:2:1 mixture exclusive of the entropy of mixing. It is to be noted that the entropy of the mixture, 59.32 E. U., is equal to the entropy of $\text{Br}_2^{79,81}$ minus $\frac{1}{2} R \ln 2$.

	$S_{\text{trans.}}$	+	$S_{\text{vib.}}$	+	$S_{\text{rot.}}$	=	$S_{298.1}^\circ$
$\text{Br}_2^{79,79}$	41.07		1.30		16.19		58.56
$\text{Br}_2^{79,81}$	41.11		1.31		17.59		60.01
$\text{Br}_2^{81,81}$	41.15		1.32		16.23		58.70
1:2:1 mixture	$\frac{1}{4}(58.56)$		$\frac{1}{2}(60.01)$		$\frac{1}{4}(58.70)$		59.32

Comparison with specific heat measurements can be made most conveniently at the melting point temperature, 265.8°K., at which the vapor pressure, according to Henglein,⁵ is 44.12 mm. From the band spectrum data we calculate $S_{265.8^\circ} (p = 44.1 \text{ mm.}) = 61.69$ E. U., assuming a perfect gas. The specific heat measurements of Suhrmann and v. Lude⁶ extend down to 20.5°K., but are few in number and somewhat erratic. From the smoothed points given by them we obtain, for the entropy of solid bromine at its melting point, 25.5 E. U., the uncertainty in which must be of the order 1.0 E. U. The entropy of vaporization at the melting point is 36.6 E. U. if we accept Henglein's value for the heat of vaporization, 9740 cal. The experimental value for the entropy of bromine gas at this temperature and pressure is then $25.5 + 36.6 = 62.1$ E. U., in good agreement with the value 61.69 calculated from spectroscopic data.

³ Giauque, *THIS JOURNAL*, **53**, 507 (1931).

⁴ Giauque, *ibid.*, **52**, 4808 (1930).

⁵ Henglein, *Z. Physik*, **11**, 1 (1922).

⁶ Suhrmann and v. Lude, *ibid.*, **29**, 71 (1924).

However, the entropy, as calculated above, cannot be used for chemical purposes without reference to the entropy of mixing of isotopes. This entropy of mixing is $\frac{3}{2} R \ln 2$ per mole, while for the free atoms (or for HBr, for example) it is $R \ln 2$ per mole. If, by convention, the entropy of mixing of the atoms is to be excluded, the value for the entropy which we have calculated must be reduced by $\frac{1}{2} R \ln 2$. For bromine gas in its standard state this results in the value $S_{298.1}^{\circ} = 58.63$ E. U. The value is thus the same as if the additional entropy of $\text{Br}_2^{79,81}$ resulting from its additional states had been considered as a part of the entropy of mixing of isotopes. This places Br_2 on the same basis as HBr, the entropy of which has been calculated from band spectrum data by Giauque.⁷

The equilibrium constants for the dissociation of bromine at high temperatures, calculated by means of the Gibson and Heitler⁸ equation and the band spectrum constants, are in poor agreement with the experimental values of Bodenstein.⁹ The discrepancy, for which no explanation is offered, amounts to 0.15 in $\log K$ and is constant with temperature. The writer plans a further check on the entropy of bromine through the use of the experimental data for the dissociation of iodine bromide. An analysis of the iodine bromide absorption bands, which will provide the necessary spectroscopic data, is now in progress. *

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⁷ Giauque, *THIS JOURNAL*, **50**, 2193 (1928).

⁸ Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

⁹ Bodenstein, *Z. Elektrochem.*, **22**, 327 (1916).

The Recombination of Hydrogen Atoms

BY GEORGE E. KIMBALL

In a recent paper Steiner¹ has made some very interesting calculations on the rate of recombination of hydrogen atoms by triple collisions with hydrogen atoms and molecules as third bodies. He assumes that the recombination takes place in two steps: (1) the formation of an atom pair, or quasi-molecule, and (2) the stabilization of the energy-rich atom pair by collision with a third body during its lifetime τ . Throughout this work Steiner has overlooked the fact that there is another, equally probable, mechanism for the recombination. This mechanism may also be divided into two steps, but these are now: (1') collision of a hydrogen atom with a hydrogen molecule, and (2') collision of this quasi-molecule with a new hydrogen atom to form two hydrogen molecules.

Steiner finds theoretically that the diameter of a hydrogen atom in (1)

¹ Steiner, *Z. Physik. Chem.*, **B15**, 249 (1932).

is $2.5\text{--}3.5 \times 10^{-8}$ cm., and that the lifetime τ of the atom pair is $2.5\text{--}4.5 \times 10^{-14}$ sec. By comparison of the theory with experiment he then finds that the effective diameter of H_2 as a stabilizing third body must be $6.7\text{--}12.5 \times 10^{-8}$ cm. By considering the mechanism (1'), (2') we find that the required diameter of the molecule H_2 is a much more reasonable value.

The rate of process (1') is given by

$$Z_{AM} = 2 \sqrt{2\pi} N_L^2 \sigma_1^2 \left(\frac{3RT}{2M} \right)^{1/2} [C_H][C_{H_2}] \quad (1)$$

and the stationary concentration of the quasi-molecules H_3 is given by

$$[C_{H_3}] = \frac{Z_{AM} \bar{\tau}}{N_L} = 2 \sqrt{2\pi} N_L \sigma_1^2 \left(\frac{3RT}{2M} \right)^{1/2} [C_H][C_{H_2}] \bar{\tau} \quad (2)$$

The symbols used in these equations are those used by Steiner, except that σ_1 is the collision diameter for a hydrogen atom colliding with a hydrogen molecule, and $\bar{\tau}$ is now the mean life of the quasi-molecule H_3 . The number of three-body collisions of this type is then given by

$$\begin{aligned} Z_3 &= 2 \sqrt{2\pi} N_L^2 \sigma_2^2 \left(\frac{4RT}{3M} \right)^{1/2} [C_H][C_{H_3}] \\ &= 8\pi \sqrt{2} N_L^3 \frac{RT}{M} \sigma_1^2 \sigma_2^2 \tau [C_H]^2 [C_{H_2}] \end{aligned} \quad (3)$$

or, on introducing the statistical weight factor $1/4$

$$Z_3^* = 2\pi \sqrt{2} N_L^3 \frac{RT}{M} \sigma_2^2 \sigma_1^2 \bar{\tau} [C_H]^2 [C_{H_2}] \quad (4)$$

where σ_2 is the effective diameter for the collisions of H with H_3 .

We may safely assume that σ_1 is about the same as Steiner's σ_{AA} , that is, $2.5\text{--}3.5 \times 10^{-8}$ cm. The value of $\bar{\tau}$ is, however, different. In order to estimate the value of $\bar{\tau}$ we must know the potential energy curve for three hydrogen atoms. Such a curve has been calculated by Eyring and Slater (to appear in THIS JOURNAL). The theoretical curve found by these authors agrees well with the empirical curves given by Lennard-Jones.² The curve consists of the coulombic energy, less one-half the interchange energy, plus the van der Waals energy for two hydrogen atoms. There is no minimum in this curve such as that in the curve for two hydrogen atoms, and any definition of the collision distance is somewhat arbitrary. A hydrogen atom with the mean thermal energy of 600 cal. will be at a distance of 2.35×10^{-8} cm. from the hydrogen molecule when it is brought to rest. If we assume that the molecule and atom are in contact when the potential energy between them is one-tenth of its maximum value of 600 cal. a simple calculation shows that the time of contact is 6.58×10^{-14} sec.

We may now use the values we have found for σ_1 and $\bar{\tau}$ to calculate σ_2 from the experimentally found rate of reaction. If we assume that all

² Cf. Fowler, "Statistical Mechanics," Cambridge, 1929, Chap. X.

of the recombination with H_2 as the third body takes place by this mechanism we find that σ_2 lies between 3.6 and 5.5×10^{-8} cm. Since the recombination probably takes place by both this mechanism and Steiner's the true value of the diameter σ_2 is somewhat smaller.

On the other hand, if we assume σ_2 to be equal to Steiner's σ_{AM} , which is not unreasonable, we find that our mechanism will go at a rate three to six times the rate of Steiner's mechanism.

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A STUDY OF MOLECULAR ORGANIC COMPOUNDS. IV.¹ THE MOLECULAR ORGANIC COMPOUNDS OF PHENOL, THEIR PARACHORS AND REFRACTIVITIES²

BY C. A. BUEHLER, J. H. WOOD, D. C. HULL AND E. C. ERWIN

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The molecular organic compounds of phenol, as a group, represent one of the simplest types. These compounds, although possessing fairly sharp melting points, decompose so readily into the original components that attempts to gain any information as to their structure by chemical methods have been unsuccessful. In the present investigation two physical methods have been applied to the study of the structure of some of these molecular compounds.

In Table I are listed the compounds which have been isolated and studied. Most of these have only previously been shown to exist by their freezing point curves. Worthy of note are the great number of them, the usual molecular ratios of 1:1 and 2:1 and the fact that the second components all contain amino groups.

The parachors as determined, both for some of the components and their molecular compounds, by the formula of Sugden³ are given in Tables II and III. Among the components it is to be noted that the observed parachors are lower than the calculated values and with increasing temperature a steady rise occurs much in the same way as with the alcohols and fatty acids.⁴ The same relation exists among the molecular compounds although the temperature coefficients and the differences between

¹ Contribution III, THIS JOURNAL, 53, 4094 (1931).

² Parts of this paper are taken from the Masters' Theses presented by David C. Hull and E. C. Erwin at the University of Tennessee.

³ Sugden, "The Parachor and Valency," George Routledge and Sons, Ltd., London, 1930, p. 30.

⁴ Sugden, Ref. 3, p. 167.