Entropy of Organic Compounds from Calorimetric Data. Lack of Equilibrium in Crystalline Tetramethylmethane

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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 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.

Water Vapor Discharge and Hydrogen Peroxide Formation

The discharge (with or without electrodes) through water vapor may produce a mixture of the following molecules and atoms:
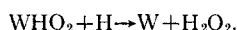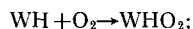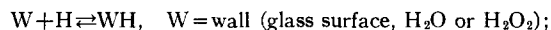
$$H, OH, H_2, O, O_2, H_2O \ (H_2O_2, HO_2, O_3).$$
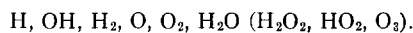
Some years ago Geib and Harteck[1] showed that between 30°K to 150°K and at pressures of 0.1–0.5 mm Hg hydrogen atoms and molecular oxygen react on the walls without activation energy with 100 percent efficiency to give pure hydrogen peroxide. If however the temperature is raised to 190°K, rather poor yields of H_2O_2 are obtained. Thus we were astonished, when Rodebush and Wahl suggested that the formation of hydrogen peroxide in the electrodeless water vapor discharge was due to a bimolecular association of OH radicals. Recently I carried out experiments on this and using an electrode discharge I got the following results:

Large quantities of H_2O_2 are collected in a trap cooled with liquid air both in the water vapor discharge and in the discharge through H_2, O_2 mixture. On the other hand, if the products are frozen out at −80°C both in the discharge tube itself and 10 cm from it, not a single drop of $N/10$ $KMnO_4$ solution is needed to oxidize the hydrogen peroxide.

These results now are an excellent agreement with those of Rodebush and Campbell,[2] who used an electrodeless discharge.

As the result of all experiments it must be stated: (1) It is quite unimportant whether or not electrodes are used; (2) Hydrogen peroxide is formed by the products of the water vapor discharge only at temperatures below −100°C; (3) Hydrogen peroxide is formed by a mixture of H atoms and molecular oxygen and a mixture of H atoms and O atoms at temperatures below −100°C; (4) H atoms are destroyed by adsorption and recombination at a glass surface cooled with liquid air, but not with solid carbon dioxide.[3]

This suggests the following mechanism[3] of hydrogen peroxide-formation

$$W + H \rightleftharpoons WH, \quad W = \text{wall (glass surface, } H_2O \text{ or } H_2O_2);$$

$$WH + O_2 \rightarrow WHO_2;$$

$$WHO_2 + H \rightarrow W + H_2O_2.$$

It seems rather difficult to show, that beside this process the recombination of OH radicals to H_2O_2 plays an important role (perhaps also as wall reaction) in the formation of H_2O_2, as Rodebush and Wahl[4] suggest. Experiment only shows that no such formation can be detected at temperatures above −100°C at low pressures.

In this connection one should discuss again both the reaction

$$H + H_2O_2 \rightarrow H_2O + OH[3]$$
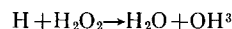
and the Bonhoeffer and Pearson mechanism[5]

$$2OH \rightarrow H_2O + O,$$
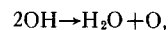
assigning to the latter some activation energy because of the work of Oldenberg.[6]

Rodebush and Wahl don't find O atoms[7] in their experiments. Possibly they react very fast, perhaps at every 10th collision, with OH to $O_2 + H$.

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  April 22, 1936.

[1] Geib and Harteck, Ber. d. D. Chem. Ges. **65**, 1551 (1932); Zeits. f. physik. Chemie **A170**, 1 (1934).
[2] Campbell and Rodebush, J. Chem. Phys. **4**, 293 (1936).
[3] Geib, Zeits. f. physik. Chemie **A169**, 161 (1934).
[4] Rodebush and Wahl, J. Chem. Phys. **1**, 696 (1933).
[5] Bonhoeffer and Pearson, Zeits. f. physik. Chemie **B14**, 5 (1931).
[6] Oldenberg, J. Chem. Phys. **3**, 266 (1935).
[7] See Oldenberg, reference 6, p. 273.

Entropy of Organic Compounds from Calorimetric Data. Lack of Equilibrium in Crystalline Tetramethylmethane

Recently Kassel[1] has calculated the entropy of *n*-butane from spectroscopic data and found a value 3.76 e.u. higher than that of Huffman, Parks and Barmore[2] which he suggests may be due to lack of equilibrium in the solid at low temperatures or to an error in the value extrapolated below 90°K. As the total extrapolated value is only 11.7 e.u., it is hardly possible that the error could be due to this cause unless a transition of rather large entropy change were involved.

We have recently measured the entropy difference between ordinary crystalline tetramethylmethane at the absolute zero and the gas at 25°C from calorimetric measurements carried down to 14°K, the extrapolated entropy being only 0.66 e.u. While the calculations are not entirely complete a comparison of a preliminary value of this calorimetric entropy difference with the entropy of the

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gas at 25°C shows the calorimetric value to be about 8 e.u. lower than the spectroscopic value. This indicates about 8 e.u. zero-point entropy in the ordinary crystal of tetra-methylmethane at the absolute zero, due to randomness caused by lack of equilibrium. There is an abnormal rise in the heat capacity of the solid prior to a transition at 140°K. In this region only is there evidence of hysteresis.

Giauque and associates have found a similar state of affairs for carbon monoxide[3a] and nitrous oxide[3b] and predicted the occurrence of the phenomenon in the case of organic compounds. Pauling has discussed the situation for some simple molecules.[4]

In view of the large discrepancy in the case of tetra-methylmethane one must view entropies of organic compounds calculated from calorimetric data assuming a perfect crystal (i.e., zero entropy at the absolute zero) with considerable doubt even though they be based on heat capacities taken down to liquid hydrogen temperatures or lower.

At present the only source of a reliable value or the entropy of neopentane is a calculation based on spectroscopic data and a knowledge of the moments of inertia. Such a calculation yields a value of 79.85 e.u. at 25° and 1 atmos. neglecting nuclear spin. This value is the translational and rotational entropy 73.98 e.u.[1] plus the entropy of vibration (5.87 e.u.) calculated from the Raman frequencies determined by Rank and Bordner,[5] using the following multiplicities: 335, (2); 414, (3); 733, (1); 925, (3).

The complete calorimetric data will be submitted for publication in the near future.

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[1] Kassel, J. Chem. Phys. **4**, 277 (1936).
[2] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[3a] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).
[3b] Blue and Giauque, ibid. **57**, 991 (1935).
[4] Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).
[5] Rank and Bordner, J. Chem. Phys. **3**, 248 (1935).

The Raman Effect and the Dissociation of KHSO$_4$

It has been found by Rao[1] and others that a study of the Raman effect offers a means of determining the degree of dissociation of concentrated solutions, where other methods are not applicable, and thus supplies valuable information with respect to the physical and chemical properties of such solutions. Woodward,[2] Nisi,[3] and Bell and Jeppesen[4] have observed the Raman effect in KHSO$_4$ at one concentration but made no observations on the change in the degree of dissociation with the concentration.

They found that $\overset{-}{HSO_4}$ ions occur in a concentrated aqueous solution of KHSO$_4$ and that these ions partially dissociate into $\overset{+}{H}$ and $\overset{--}{SO_4}$. This is precisely what might be expected from chemical considerations which indicate that KHSO$_4$ would dissociate in two stages:

$$KHSO_4 \rightarrow \overset{+}{K} + \overset{-}{HSO_4}; \quad \overset{-}{HSO_4} \rightarrow \overset{+}{H} + \overset{--}{SO_4}.$$
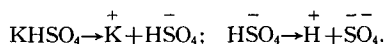
Since other studies of the Raman effect in concentrated solutions indicate that normal salts are completely dissociated at all concentrations, and that in strong acids the degree of dissociation increases with dilution, it is of interest to consider what happens in the Raman spectrum of an acid salt like KHSO$_4$ when the concentration of the solution is changed.

By means of a high speed spectrograph of low dispersion the Raman effect was photographed in four aqueous solutions of KHSO$_4$ of the following concentrations: 13, 21, 28, 34 percent. The solutions were enclosed in the usual type of Wood tube and illuminated by mercury arc lamps. The Raman spectra were excited by the 4358A and 4047A lines. The frequencies of the observed Raman lines expressed in wave numbers (cm^{-1}) for concentrations of 13 percent and 34 percent have been recorded in Table I.

TABLE I.

CONCENTRATION	$\overset{-}{HSO_4}$	$\overset{-}{HSO_4}$	$\overset{--}{SO_4}$	——	——
13%	1058	917	978	611	438
34%	1040	906	975	599	436

The ions to which these observed Raman lines have been attributed are indicated by the headings of the columns in the table. There is a change in frequency of the Raman lines with the dilution of the solution. A similar effect has been observed by Woodward and Horner[5] and also by Bell and Jeppesen[4] in the case of aqueous solutions of H$_2$SO$_4$. The reality of such a change in frequency due to a change in concentration has been questioned by Mitra[6] but his observations on aqueous solutions of magnesium sulphate and lithium sulphate were concerned only with the Raman line 981 cm^{-1} which has been attributed to $\overset{--}{SO_4}$. For this line the change in frequency due to the change in the concentration of the solution is small compared to the changes observed for the other lines.

From a comparison of the intensities of the Raman lines as indicated by the microphotometer curves, the relative degrees of dissociation of the solutions with respect to the
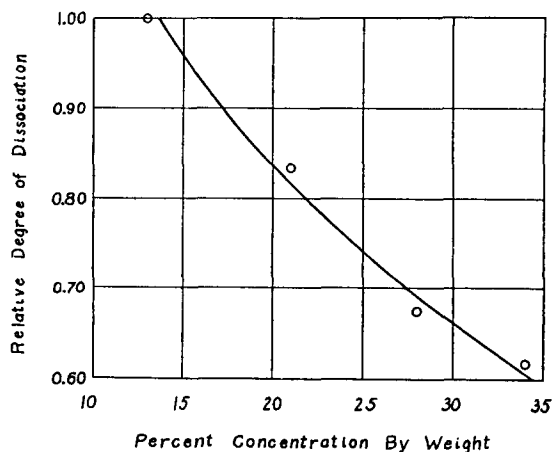

FIG. 1