Mass-Spectrograph Determination of the Relative Abundance of Heavy Hydrogen in a Sample

The method of diffusion through palladium has been employed by Harris, Jost and Pearse[1] to effect the separation of the hydrogen isotopes. The increase of concentration of the heavy hydrogen was determined spectroscopically, and it was reported that under the conditions of the experiment approximately a tenfold enrichment was obtained, with a resulting concentration of about one percent deuterium. The spectroscopic method has been subjected to criticism and it was proposed that a test of the enriched sample be made with the mass-spectrograph. The method of Bleakney[2] was not applicable as the mass-spectrograph employed here[3] is designed to operate at pressures of the order of 0.5 mm in the discharge tube with further aging in a drift space; and under these conditions 95 percent or more of all the ions obtained are triatomic. It seemed however that the triatomic ion of mass 4 ($H^1H^1H^{2+}$) observed by Bainbridge,[4] could be used to determine the concentration of heavy hydrogen where the relative percentage was small.

The triatomic ion in light hydrogen is formed by a reaction between the initial molecular ion and a neutral molecule as follows:

$$H^1H^{1+}+H^1H^1 \rightarrow H^1H^1H^{1+}+H^1.$$

In mixtures of heavy and light hydrogen the following reactions should occur:

$$H^1H^{2+}+H^1H^1 \rightarrow H^1H^1H^{2+}+H^1, \qquad (1)$$

$$H^1H^{1+}+H^1H^2 \begin{array}{l} \nearrow H^1H^1H^{2+}+H^1 \quad \text{(a)} \\ \searrow H^1H^1H^{1+}+H^2 \quad \text{(b).} \end{array} \qquad (2)$$

If f is the fraction of H^2 atoms relative to the total number of atoms, then $2f$ is the fraction of H^1H^2 molecules relative to the total, if f is small. Consequently, reaction number 1 above should yield an intensity of $H^1H^1H^{2+}$ ions of $2f$ relative to $H^1H^1H^{1+}$, and reaction number 2 should yield a relative intensity of f, making a total of $3f$. This reasoning involves the assumption that reactions 2(a) and 2(b) are equally probable, which may not be entirely justified; but any departure from this assumption should lie within the experimental error. It is also required that the ions should be aged sufficiently and f should be small enough so that there is no measurable number of H^2H^{2+} ions present.

A series of runs on a sample of the enriched hydrogen gave an average of about 1.5 percent of mass 4 ions relative to mass 3. This would indicate a relative concentration of hydrogen atoms of about 0.5 percent. A redetermination of the density of the original water used by Harris, Jost and Pearse was made by Dr. E. S. Gilfillan of the chemistry department and it was found that the concentration of heavy hydrogen was about 0.13 percent. The mass-spectrograph results thus indicate a fourfold enrichment by passage through palladium instead of 8 to 10 fold as previously reported.

The mass-spectrograph employing aged hydrogen ions, as was done in this experiment, furnishes a direct and simple method of determining the relative concentration of heavy hydrogen, providing the assumptions involved are justified. No ions of mass 5 or 6 could be observed owing to the small concentration of heavy hydrogen, but a complete study of the nature of aged ions in various mixtures of the hydrogen isotopes would yield interesting information concerning the atomic processes involved in the formation of the triatomic ions.

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May 8, 1934.

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[1] Harris, Jost and Pearse, Proc. Nat. Acad. Sci. **19**, 991 (1933).

[2] W. Bleakney, Phys. Rev. **44**, 256 (1933).

[3] O. Luhr, Phys. Rev. **44**, 459 (1933).

[4] K. T. Bainbridge, Phys. Rev. **42**, 1 (1932).

The Ultraviolet Absorption of Acetylene and Ethylene

For some time we have been investigating the far ultraviolet absorption of various simple hydrocarbons. We find, in the case of acetylene, a rich absorption spectrum which extends from 1520A to 1050A. The absorption is very strong and most of the bands appear with a pressure of only 0.001 mm of acetylene in the spectrograph, the light path being about 1.5 meters.

They can be conveniently divided into two classes. Class I contains bands possessing P, Q and R branches. They appear as narrow absorption doublets at low pressures. They have a sharp head and are shaded towards the red. The bands of Class II show a single head, and therefore contain only more diffuse P and R branches.

On account of the complexity of the spectrum some difficulty was experienced in analyzing it. Recently it has been enormously clarified by the use of the heavy hydrogen isotope. A comparison of the spectrum of light acetylene with that of heavy acetylene (C_2HD) immediately reveals the fundamental band of each electronic transition by its small isotopic shift which is due only to the change in zero point energy. In this way two Rydberg series were found, each containing more than ten terms. They have roughly the same limit and are given fairly well by the following formulas:

$$\text{I} \qquad \nu_0{}^n=92{,}000-R/(n-0.95)^2,$$

$$\text{II} \qquad \nu_0{}^n=92{,}000-R/(n-1.5)^2$$

$$n=3,\ 4,\ 5,\ \text{etc.}$$

The bands of class I fall into the first series and those of class II into the second. The first member of the second series coincides with the bands investigated by Kistiakowsky at 2300A but this may be accidental as those bands appear at much higher pressures.

All the observed facts go to show that one of the valence electrons between the two carbons is excited and that the two series are due to the different coupling of its orbital momentum with the internuclear axis. Thus the upper levels of class I can be provisionally designated as $P\Pi$ levels and those of Class II as $P\Sigma$ levels.

As many as ten vibrational transitions accompany some of the fundamental electronic transitions. Their analysis is greatly simplified by the magnitudes of the isotopic shifts. It appears that the CC bond is weakened considerably in the upper states whereas the CH bond remains practically unaltered. This is in agreement with the fact that no CH vibration is excited by absorption from the normal state and also that the shift in zero point energy is only about 20 cm^{-1}. All the bands of appreciable intensity are included in our classification.

The band system at 1520A shows strong predissociation. The next system at 1340A is slighly diffuse whereas all the bands at shorter wave-lengths appear to be sharp. If it is assumed that the predissociation is due to interaction with the normal state, then the heat of dissociation of C_2H_2 into CH+CH must be slightly less than 8.1 electron-volts or the energy of the triple CC bond is slightly less than 187 Cal./Mol.

The situation is similar in ethylene. The bands are somewhat more diffuse and only one Rydberg series is observed. Predissociation occurs at 1750A giving the heat of dissociation corresponding to $C_2H_4 \rightarrow CH_2 + CH_2 \equiv 7.05$ electron-volts or the strength of the $C=C$ bond $\leqq 162$ Cal./Mol.

The bond strengths are in good agreement with the best chemical data. It is thus clear that the work is going to be of considerable value in the recently developed chemistry of free radicals.

The early part of the work was done in collaboration with Dr. G. B. Collins.

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The Orientation of the CO_3 Groups in Ammonium Bicarbonate Crystal

Ammonium bicarbonate, $(NH_4)HCO_3$ crystallizes in the orthorhombic system and its structure has recently been analyzed by x-ray methods by Mooney.[1] He finds that the CO_3 groups in the crystal are all oriented with their planes parallel to *a*(100), and that the dimensions of the CO_3 groups are practically the same as in the normal carbonates.

Measurements on the magnetic anisotropy of the crystal confirm these conclusions. Denoting by x_a, x_b and x_c the principal gram molecular diamagnetic susceptibilities of the crystal along its *a*, *b* and *c* axes, respectively, it is found that

$$x_b - x_a = 5.0; \qquad x_c - x_a = 4.5$$

in 10^{-6} c.g.s. e.m.u., x_b and x_c are thus nearly equal and greater than x_a by about 4.7×10^{-6}, which is practically the same as the value of the magnetic anisotropy of the CO_3 group in calcite, aragonite, strontianite and witherite, obtained by Krishnan, Guha and Banerjee.[2] This shows that the CO_3 planes in ammonium bicarbonate crystal are oriented parallel to one another in the *a*(100) plane, and that the magnetic anisotropies of these CO_3 groups, and hence presumably their structure also, are the same as in the normal carbonates quoted above.

In strong contrast to the magnetic behavior of ammonium bicarbonate is that of potassium bicarbonate. The latter crystal (which is monoclinic) exhibits a much feebler anisotropy, which shows that the planes of the different CO_3 groups in the unit cell of this crystal must be considerably inclined to one another.

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April 17, 1934.

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[1] Mooney, Phys. Rev. **39**, 861 (1932).

[2] Krishnan, Guha and Banerjee, Phil. Trans. **A231**, 235 (1933).

Two New Phenomena at Very High Pressure

It has long been surmised that there should be another modification of bismuth, denser than the liquid phase, stable only under high pressure, in analogy to the high pressure modifications of ice. Attempts to produce this new phase by the application of pressures up to 20,000 kg/cm^2 have, however, been unsuccessful. I have recently found that this modification is produced reversibly from the ordinary solid phase at room temperature at about 25,000 kg/cm^2. The transition is accompanied by a volume decrease of about 9 percent. By extrapolation, the liquid should be about 5 percent more dense than the ordinary solid at the reversible melting point under 25,000 kg/cm^2, so that we may expect the new solid to be formed from the liquid with a contraction of the order of 4 percent. The next obvious step is to raise the temperature in order to find the location of the triple point between the two solids and the liquid, but this must wait for modifications in the present apparatus.

Hitherto the irreversible transition from white to black phosphorus has not been produced at temperatures below 200°C, where the pressure necessary is about 12,000 kg/cm^2. I have just made black phosphorus from white at room temperature by the application of about 35,000 kg/cm^2. In appearance to the eye the mass is indistinguishable from regular black phosphorus, but there was no trace of any red phosphorus on the exterior surfaces;