

Table 2 shows that pure aragonite was the only type of calcium carbonate to precipitate from sea-water by CO₂ extraction. This finding has also been made by other workers². Furthermore, the rate of crystallization of aragonite in these experiments was so slow (even at the unnaturally high supersaturation value achieved by adding sodium carbonate to make the solution pH 9) that such crystallization can scarcely be used to explain the rapid formation of whittings seen in the sea off Doha.

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¹ Wells, A. J., and Illing, L. V., in *Developments in Sedimentology*, 1, 429, edit. by L. M. J. U. van Straaten (Amsterdam, 1964).

² Simkiss, K., *Nature*, 201, 492 (1964).

An Experimental Determination of the Photo-ionization Cross-section of Atomic Hydrogen

ALTHOUGH many theoretical calculations of the photo-ionization cross-section of atomic hydrogen have been performed (see review by Bates¹), no experimental determination of this quantity has previously been made. An experiment is being carried out here which has yielded a value for the photo-ionization cross-section of atomic hydrogen at 850.6 Å.

Atomic hydrogen is produced by flowing molecular hydrogen through a discharge tube in which an intense radio frequency discharge is run. This dissociates a large fraction of the hydrogen molecules. The mixture of atoms and molecules is then flowed quickly through an all-glass absorption cell which is attached to the exit slit of a one-metre normal-incidence vacuum monochromator. Radiation emerging from the exit slit passes down the absorption cell and is detected by a sensitized photomultiplier placed at the far end of the cell. The light source used to illuminate the entrance slit of the monochromator is similar to that described by Garton² and consists essentially of a short-duration high-current spark produced by discharging a capacitor bank. The light source is filled with low-pressure argon gas and the radiation produced by it consists mainly of emission lines of neutral and multiply ionized argon.

The intensity of the radiation emerging from the absorption cell is measured under three conditions: (i) intensity I_0 , with the absorption cell evacuated; (ii) I_1 , with the absorption cell filled with molecular hydrogen at pressure p_1 ; (iii) I_2 , with partially dissociated hydrogen in the absorption cell at total pressure p_2 . The degree of dissociation α is determined by the Wrede Harteck method³.

From (i) and (ii) the photo-absorption cross-section of molecular hydrogen, σ_M , can be determined from the equation:

$$I_1 = I_0 \exp \left(-N\sigma_M \frac{p_1}{760} \frac{273}{T} l \right) \quad (1)$$

where N is Loschmidt's number, 2.69×10^{19} particles/c.c., T is the absolute temperature of the gas (°K), and l is the length of the absorption cell (cm).

From a knowledge of α and p_2 , the partial pressures p_A , p_M of atomic and molecular hydrogen can be calculated. Thus, using (i) and (iii) and the result for σ_M derived from (1), the photo-ionization cross-section of atomic hydrogen, σ_A , can be found from the equation:

$$I_2 = I_0 \exp \left(- \left\{ N\sigma_A \frac{p_A}{760} \frac{273}{T} + N\sigma_M \frac{p_M}{760} \frac{273}{T} \right\} l \right) \quad (2)$$

p_1 , p_2 and α are measured at each end of the absorption cell and a correction for the concentration gradient along the length of the cell is applied.

Due to the difficulty in obtaining sufficient intensity at the photomultiplier to make reliable measurements, initial results have been confined to a wave-length, 850.6 Å, which corresponds to a strong emission line of the light source and a very small absorption cross-section of molecular hydrogen.

The mean value of the molecular cross-section (together with the probable error) at 850.6 Å is $(0.213 \pm 0.010) \times 10^{-18} \text{cm}^2$, which is not in agreement with Cook and Metzger's⁴ result of $\sim 3.2 \times 10^{-18} \text{cm}^2$ at this wave-length. This may be due to a difference in the effective resolution of the two systems; as there is no continuous absorption in this region the measured value of σ_M will depend critically on the resolution. Cook and Metzger used a continuum light source in conjunction with a monochromator with a pass band of 0.5 Å. Although our instrument has a similar bandpass, we used a line source and, as the width of the 850.6 Å IV line is probably of the order of or less than 0.1 Å, our resolution is much better than the bandpass of the instrument.

The mean value of the photo-ionization cross-section of atomic hydrogen at 850.6 Å is:

$$(5.15 \pm 0.18) \times 10^{-18} \text{cm}^2$$

This is in good agreement with the most recently available theoretical value which is given in graphical form by Bates¹. At 850.6 Å the theoretical value lies between 5.1 and $5.2 \times 10^{-18} \text{cm}^2$.

This work was initiated by Dr. R. B. Cairns and I thank him for his help during the early stages.

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¹ Bates, D. R., *Atomic and Molecular Processes* (Academic Press, New York, 1962).

² Garton, W. R. S., *Jn. Sci. Instr.* 36, 11 (1959).

³ Greaves, J. C., and Linnett, J. W., *Trans. Farad. Soc.*, 55, Pt. 8 (August 1959).

⁴ Cook, G. R., and Metzger, P. H., *J. Opt. Soc. Amer.*, 54, 968 (1964).

Structure of Catena-di- μ -Fluorodifluoro-diaquohafnium(IV) monohydrate (HfF₄·3H₂O)

ALTHOUGH the trihydrate of hafnium tetrafluoride and its dehydration products are stoichiometrically similar to the corresponding compounds of zirconium, it has been shown¹ that they are not isostructural. In general, compounds of the two elements do show identical structure (for example, the anhydrous fluorides²), and the fluoride hydrates must be particularly susceptible to differences in bond energy. The structure of ZrF₄·3H₂O has been reported previously³, and the hafnium analogue has now been investigated.

Crystals were prepared, as previously described¹, as an apparently homogeneous sample of colourless needles. Single crystal studies have, however, demonstrated the existence of two distinct species. One of these is monoclinic, $a = 25.48$, $b = 7.51$, $c = 23.02$ Å, $\beta = 150^\circ$, 16 molecules per unit cell. Reflexions are systematically absent for all hkl when $h + k$ is odd, and for hkl with k even, when $k/2 + 1$ is odd. Reflexions with k odd are weak and are markedly diffused along c^* , thus suggesting that the structure is at least partially disordered. Our investigation has not proceeded further than the location of the hafnium atom positions.

The other modification is also monoclinic, with $a = 6.70$, $b = 10.55$, $c = 7.71$ Å, $\beta = 94^\circ$, 4 molecules per unit cell, space group $P2_1/c$. The structure of these crystals had no such complications and has been solved by conventional methods. The current reliability factor, assuming isotropic thermal motion, is 0.14.

All light atoms were assumed to be fluorine for the purpose of structure factor calculation. The peak electron densities on a subsequent Fourier synthesis were 11.6, 10.7, 9.9, 9.4, 8.6, 6.7 and 6.5 electrons Å⁻³. The smallest