experimentally. Like Posner et al.5, we have observed on the infra-red spectra obtained with natural hydroxyapatite a band  $|(3,560 \text{ cm}.^{-1})$  corresponding to the vibration of free OH groups. The same band appears when larger crystals of hydrated tricalcium phosphate, obtained by treating in the hydrothermal bomb, are studied: in this way, the amount of adsorbed water is much smaller than in the untreated compound, and the band corresponding to free OH groups clearly appears.

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# Calcium Exchange of Bone Salts considered as a Measure of the Crystal Surface

COMPARING the in vitro calcium-45 uptake by bone salts (ashed by a method slightly modified from that of Gabriel) from alcoholic and aqueous calcium-45 labelled calcium chloride solutions, we have been able to demonstrate the occurrence of remodelling phenomena (chemical reaction between the solid and the ions dispersed in the liquid phase, recrystallization sensu stricto) and of an isoionic exchange, which reaches an equilibrium when 8 per cent of the calcium ions of the solid are involved. All remodelling processes being discarded, we believe that this figure corresponds to a pure exchange value. In our conditions, the intracrystalline ion exchange by thermal vibration is too slow to interfere with the surface exchange process<sup>1</sup>.

In a recent paper<sup>2</sup> Engström, correlating X-ray diffraction data and electron microscopy investigations, states that the needle-like crystal of bone salt has an average diameter of about 50 Å. This figure is also given by Molnar<sup>3</sup>.

If the needle-like crystal is considered as a cylinder of the same length, the base surfaces not being taken into account, one may calculate, as a percentage, the ratio-plane volume of the surface/volume of the crystal—in the following way:

$$rac{\pi h(2Rd-d^2)}{\pi R^2 h}$$
 × 100 (per cent)

where h is the length of the crystal; R is the radius of the crystal base, d is the third dimension of the surface plane volume. After simplifying, it becomes :

$$\frac{2Rd - d^2}{R^2} \times 100 \text{ (per cent)}$$

which in the particular case of bone crystals gives :

$$\frac{4,900}{625} = 7.85 \text{ per cent}$$

when d is equal to the unit (1 Å.).

It is interesting to point out that the length of the crystal is of no importance for this calculation. This calculated figure corresponds closely to the experimental exchange value in such a way that the latter may be considered a real measure of the crystal surface. This assumption implies that the composition of the surface is not different from the composition of the bulk of the crystal. If the ratio is expressed in m.<sup>\*</sup>/gm. we obtain a value 250 m.<sup>\*</sup>/gm., which also fits the published figures4.

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## Lifetime of the Pyrene Dimer

THE appearance of a new fluorescence emission band in concentrated solutions of pyrene was attributed by Förster and Kasper<sup>1</sup> to an excited dimer formed by combination of an excited singlet molecule with an unexcited molecule. Stevens and Hutton<sup>2</sup> have recently reported the lifetime of the dimer emission to be  $1.8 \times 10^{-3}$  sec. During tests of a new photoelectric spectrophosphorimeter an attempt was made to record this long-lived emission. The instrument was a modification of a spectrofluorimeter previously described<sup>3</sup>, but in which two 800 c./s. choppers were used, one being situated in the beam of the exciting light and one in the beam of the fluorescence light. The choppers were driven by synchronous motors, and by rotation of one of the motors the choppers could be put into or out of phase so that the fluorescence monochromator could be made to record either the sum of the fluorescence and phosphorescence spectra or the phosphorescence spectrum alone. By adjustment of the photomulti-plier voltage and by variation of the amplifier gain, the overall sensitivity could be increased by a factor of 104.

The operation of the instrument was checked by measurement of the visible phosphorescence from a 0.005 per cent solution of eosin in anhydrous glycerol which was reported by Mlle. Boudin<sup>4</sup> to have a life-time of about  $10^{-9}$  soc. We found the ratio of the intensities of fluorescence and phosphorescence to be, within a factor of two, the same as the value reported by Mlle. Boudin.

The efficiency of the choppers was tested by measurements on aerated solutions of fluorescein and anthracene, and it was found that the recorded