

among which is interspersed a liquid phase. In consequence of adsorbed ions, the boundary surfaces of the two phases would have a greater conductivity than either phase, and where continuous, would form highly conducting bridges between the electrodes.

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<sup>1</sup> A. Gemant, *Z. Phys.*, **75**, 613; 1932.

### Calcium Sulphate Hemihydrate

MUCH attention has been given to calcium sulphate hemihydrate since it was recognised as the active principle of plaster of Paris, but its characteristics as a crystal species have hitherto remained somewhat vague.

Several workers have reported on the preparation of the pure substance in the wet way by various methods, but always in the form of excessively small crystals. It has now been found possible to grow crystals of 'hemihydrate' of a thickness of 0.5–1 mm. and length of 3–4 mm. from solutions of calcium sulphate in hydrochloric, sulphuric, or nitric acids under the proper conditions as to dilution of the solvent and temperature. These crystals belong to the trigonal system and consist of the hexagonal prism 10 $\bar{1}$ 0 capped by an obtuse rhombohedron 01 $\bar{1}$ 2 and terminated by small developments of the base 0001. The axes have lengths  $a = 6.76$  Å. and  $c = 6.24$  Å., so that three molecules are comprised in the unit cell, the density of the crystal being not far below that of anhydrite. Details will be published in a forthcoming paper.

In its air-dry condition the crystal usually contains no more than 4.0–4.5 per cent of water, corresponding rather to 3 CaSO<sub>4</sub>·H<sub>2</sub>O than to 2 CaSO<sub>4</sub>·H<sub>2</sub>O. The moisture content of 'hemihydrate' has, however, been shown by Linck and Jung and others, working upon less well-defined materials, to be held in the same way as that of zeolites. This is now confirmed with the trigonal crystals, which may be made to give up water to within a tenth per cent or less of complete dehydration without losing form or transparency; on exposure to moist air they then gradually regain the original degree of hydration. On 'dead-burning' they are converted into pseudomorphs consisting of ordinary anhydrite.

Brought into contact with water, the crystals yield solutions supersaturated with respect to CaSO<sub>4</sub>·2H<sub>2</sub>O, though the effect is not so striking as with plaster of Paris; in a short time bunches of dihydrate needles are seen growing out of favoured spots on the hexagonal prisms.

It seems, then, that anhydrite is dimorphous; we have the orthorhombic, comparatively inert modification, and a trigonal one stable only up to 200° or thereabouts, which can take up water zeolitically. The behaviour of this latter in contact with water is what causes plaster to set. There may well be no essential difference between the 'soluble anhydrite' and the 'hemihydrate' accepted in the literature of calcium sulphate.

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### The Value of $e/m$

EDDINGTON<sup>1</sup> originally proposed the relation  $hc/2\pi e^2 = 136$ , and later<sup>2</sup> revised this to 137. Still later he proposed<sup>3</sup> a second relation, namely, the ratio of  $M$ , the mass of the proton, to  $m$ , the mass of the electron, is 1847.6<sup>4</sup>. This second relation, combined with the value of the Faraday and Aston's mass of O<sup>16</sup> leads<sup>4</sup> to  $e/m = (1.77031 \pm 0.00014) \times 10^7$  E.M. units. If, finally, one assumes the correctness of Bohr's formula for the Rydberg constant, there results<sup>4</sup>,  $h = (6.5490 \pm 0.0011) \times 10^{-27}$  erg. sec.,  $e = (4.775855 \pm 0.000048) \times 10^{-10}$  E.S. units.

Bond<sup>5</sup> has very recently noted that the best experimental value of  $e/m$ , which he takes to be 1.759, is approximately 136/137 of Eddington's calculated value. This new relationship is, however, closer than Bond states, since  $136/137 (1.77031) = 1.7574$ , and the best experimental value is now actually 1.757. Thus Dunnington<sup>6</sup>, from a new magnetic deflection method for free electrons, obtains  $1.757 \pm 0.0015$ . Gibbs and Williams<sup>7</sup>, from the interval of corresponding H $\alpha$  and H $\beta$  spectral lines obtain  $1.757 \pm 0.01$ . Kinsler and Houston<sup>8</sup>, from the Zeeman effect of Cd and Zn lines, get  $1.7570 \pm 0.0010$ .

The method used by Kretschmar<sup>9</sup> yields not  $e/m$  but  $e/m \cdot (e^{1/3}/h)^{10}$ . The observed value of this relation combined with Bohr's formula for the Rydberg constant, leads to  $e/m = 1.7564$ , if the oil-drop value of  $e$  ( $= 4.768$ ) is assumed correct, and to  $\sim 1.760$ , if the value of  $e$  ( $\sim 4.803$ ) deduced from grating values of X-ray wave-lengths is assumed correct. These last two results are based on a recalculation of Kretschmar's observations by me, using improved auxiliary data. Hence Kretschmar's work leads to a value of  $e/m$  entirely consistent with other recent work if one assumes the correctness of the oil-drop value of  $e$ , 4.768, but not if the grating value, 4.803, is used.

If the reader will pardon an additional intrusion into the popular domain of numerology<sup>11</sup>, it may be noted that  $4.803/4.768 = 137/136$ , to one part in 10<sup>5</sup>.

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<sup>1</sup> A. S. Eddington, *Proc. Roy. Soc., A*, **122**, 358; 1929.

<sup>2</sup> A. S. Eddington, *Proc. Roy. Soc., A*, **126**, 696; 1930.

<sup>3</sup> A. S. Eddington, *Proc. Roy. Soc., A*, **134**, 524; 1931.

<sup>4</sup> See R. T. Birge, *Phys. Rev.*, **40**, 319; 1932.

<sup>5</sup> W. N. Bond, *NATURE*, **133**, 327, March 3, 1934.

<sup>6</sup> F. G. Dunnington, *Phys. Rev.*, **43**, 404; 1933.

<sup>7</sup> R. C. Gibbs and R. C. Williams, *Phys. Rev.*, **44**, 1029; 1933.

<sup>8</sup> L. E. Kinsler and W. V. Houston, *Phys. Rev.*, **45**, 104; 1934.

<sup>9</sup> G. G. Kretschmar, *Phys. Rev.*, **43**, 417; 1933. See also H. R. Robinson, J. P. Andrews and E. J. Irons, *Proc. Roy. Soc., A*, **143**, 48; 1933.

<sup>10</sup> K. Shiba, *Sci. Papers, Inst. Phys. and Chem. Res.*, Tokyo, **21**, 123; 1933.

<sup>11</sup> See E. T. Bell "Numerology", reviewed in *NATURE*, **133**, 80, Jan. 20, 1934.

### Reaction Mechanism of Oxidation-Reduction Processes

CERTAIN considerations introduced by Franck and Haber<sup>1</sup>, Haber and Willstätter<sup>2</sup> and Haber and Weiss<sup>3</sup> can be developed to give a simple mechanism for oxidation-reduction processes in solution, which reproduces in all cases investigated the experimental observations, both qualitatively and quantitatively. The relation sometimes observed<sup>4</sup> between reaction velocity and electrochemical potential can also be obtained, so that for the first time a comprehensive theoretical treatment becomes possible.