

conditions have been rather neglected by physicists, particularly in recent years.

In my experiments, a form of apparatus has been devised in which a metallic bellows, closed by a needle valve, contains the gas-free liquid under test, and the possibility of inward leakage of atmospheric air is avoided by completely surrounding the bellows and valve by the same liquid. The needle valve being closed, tension is gradually applied to the liquid by slowly filling a suspended can by means of a small jet of water. The water flow is turned off the moment a sudden downward movement of the can indicates that the liquid has broken. The can is then weighed complete with the contained water, and the tension which existed in the liquid immediately prior to breaking is calculated from the known effective cross-section of the bellows.

The liquids so far examined by this method are alcohol, ether and lubricating oil. It would be premature to quote results in detail at the present stage. However, it appears that the maximum tension which the above liquids will withstand for long periods under the conditions described is simply related to their surface tensions and vapour pressures. The maximum tension increases as the temperature is lowered, and this increase can be largely explained by the changes in surface tension and vapour pressure.

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### Crystal Structure of Phosphorus Pentabromide

It has been shown<sup>1</sup> that phosphorus pentachloride has an ionic type of crystal structure which is tetragonal and contains  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$  groups. Phosphorus pentabromide is entirely different in crystalline form. It is orthorhombic, and X-ray investigations give for the unit cell  $a = 5.6$ ,  $b = 16.9$ ,  $c = 8.3$  Å, with four molecules per unit cell. The space group is  $Pbcm$  and the four phosphorus atoms are therefore necessarily equivalent crystallographically and chemically. The possibility of a structure containing two different complexes similar to those in phosphorus pentachloride does not arise in this case. It is impossible to fit in four molecules of  $\text{PBr}_5$  of the trigonal bipyramidal form, and the appearance of the diffraction patterns is entirely unlike that of a molecular compound. Patterson and Fourier methods were used to elucidate the structure. It was found that the structure contains tetrahedral  $[\text{PBr}_4]^+$  groups located so that a plane of symmetry passes through each, and the fifth bromine is present as a bromide ion removed from the phosphorus at a distance about twice that of the four covalently linked atoms. It is natural to expect the stability of the octahedral complex to diminish with increasing radius of the halogen atoms so that the change-over from the constitution  $[\text{PCl}_4]^+ [\text{PCl}_6]^-$  to  $[\text{PBr}_4]^+ \text{Br}^-$  is not surprising.

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<sup>1</sup> Powell, Clark and Wells, NATURE, 145, 149 (1940).

### Formation of Aggregates and Structures in Dilute Solutions of Hydrogen Bentonites

A YIELD value is noticeable in hydrogen bentonites at a concentration lower than that at which thixotropy first appears. This seems to happen generally with bentonites. Some natural calcium bentonites show coacervation<sup>1</sup>. Coacervation of fine sub-fractions of a natural bentonite has been reported<sup>2</sup> at concentrations above the thixotropic range. Hydrogen bentonites, however, show coacervation over a wide range and even below the thixotropic range of concentrations. Near about the concentration at which yield value becomes noticeable a sharp change in several properties has been observed. The cataphoretic velocity rapidly increases and tends to a maximum. The conductivity,  $\Lambda$ , per gram of colloid can be calculated from the relation  $\Lambda = 1000 (\lambda_c - \lambda_u)/C$ , where  $\lambda_c$  is the specific conductivity at a concentration of  $C$  grams per litre and  $\lambda_u$  that of its ultra-filtrate; it passes through a minimum if plotted against  $C$  or  $\sqrt{C}$ .

Aggregation during coagulation is often associated with an increase in the cataphoretic velocity<sup>3</sup>. Also the mobility of 'monomeric ions' of 'colloidal electrolytes' has been found to increase when they associate to form 'micelle ions' and pass through a maximum, whereas the equivalent conductivity of the electrolyte as a whole passes through a minimum<sup>4</sup>. The hydrogen ion activity of hydrogen bentonite changes almost proportionally with concentration. The total acidity calculated from the inflexion point<sup>5</sup> in the sodium hydroxide titration curve does not generally vary with concentration, though a variation has been observed for one subfraction of a hydrogen bentonite<sup>6</sup>.

The conductivities per gram of colloid calculated from the relation  $\Lambda' = a_H (l_H + l_{\text{coll}})/C$ , where  $l_H$  and  $l_{\text{coll}}$  are the mobilities of hydrogen and 'colloid' ion respectively, are appreciably greater than  $\Lambda$ . The free charge per particle calculated from  $a_H$ , assuming the activity coefficient to be unity, is of the order of 500 or 1,000 electron units. Onsager's conductivity equation<sup>7</sup> for a similar electrolyte in true solution is inadequate to explain the form of the  $\Lambda$ ,  $\sqrt{C}$  curve.

The special features of these titration curves<sup>8</sup> and the discrepancy between observed and calculated conductivities per gram colloid are, however, met with in hydrogen clays and other similar colloidal systems<sup>9</sup> but are not of immediate interest. The sols have strong absorption. Interpretation of the measurements of extinction coefficient is difficult. The latter decreases with the concentration and passes through a minimum. Somewhat similar changes have been observed with colloidal dyes<sup>9</sup> and ascribed to aggregate formation. The 'true viscosity' increases with  $C$  at a rate much greater than that corresponding to a linear relationship.

Neither Einstein's equation nor Smoluchowski's modification of it can account for the high viscosity or its variation with concentration. Also the high viscosity cannot be fully accounted for by the anisometry of the particles. Hauser and LeBeau<sup>10</sup> observed that the apparent specific gravity,  $\rho_A$ , of subfractions of a natural bentonite increases with concentration and approaches a limiting value. However,  $\rho_A$  observed by them in the most dilute solutions is definitely less than the true specific