

Crystalline Structure and Physico-Chemical Properties in the Colloidal State.

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AS a result of the interesting investigations of P. P. Von Weimarn,¹ Graham's classification of matter into crystalloids and colloids has come into disfavour and it is now admitted on all hands that matter in a particular state of sub-division will in general exhibit colloidal properties. Thus the rôle of sizes in colloidal solutions cannot be over-emphasised as the colour and some of the most important surface properties such as adsorption are to a large extent function of the particle size. One is, however, apt to forget that in such particle sizes as constitute the colloidal state the surface reactivity is also considerably increased and there are rarely, if ever, colloidal particles which are chemically pure. Most hydrophilic colloids are hydrated in water, while the hydrophobic ones get a surface coating of oxides and sub-oxides or form complex solid solutions, while the organosols of metals obtained by arc-ing even by high frequency and low amperage currents at very low temperatures are seldom free from carbonised matter produced during arc-ing. The purity of the metal employed is thus in no way a criterion of the chemical purity of the resulting colloidal solution. Even a noble metal like platinum when in a colloidal state has been shown by Pennycuick² to be contaminated with PtO_2 and oxy-acids.

These films of impurities considerably mask the properties of the metals themselves and many of the reported changes of colour and other physical properties in colloidal solutions are due to the kinds of impurities occluded with the colloids or the influence of the solvent and oxygen on the fine-grained material. As a classical example of this may be cited the interesting work of Kohlschutter³ on the silver sols. These sols when prepared in Thuriangian and Jena glass vessels differ in colour; those in Thuriangian glass are yellowish brown to rose red and those in Jena glass reddish violet to dark blue. It was definitely shown that this difference in colour was neither due to the sizes nor to the

constituents of the walls of the vessels appreciably entering into the constitution of the micellæ, but was solely due to a different content of Ag_2O determined by the adsorption relationship on the walls. The accurate estimation of Ag and Ag_2O completely established this view.⁴ Besides colour, other physical properties such as density, magnetic susceptibility, electrical conductivity and solubility undergo profound changes in the colloidal state for similar reasons and when these impurities are removed chemically or physically the system shows a return to original properties. It is, however, quite conceivable that in the process of colloidalisation or crystallisation the system may undergo more profound changes, for example, a change in the crystal structure or an allotropic modification may take place owing to large pressures and temperatures developed during grinding or arcing or to some other causes such as action of light depending upon the specific properties of the material itself. When this happens, the physical or chemical removal of the film is incapable of completely restoring original properties of the system. This change is then really akin to an allotropic transformation and the new properties acquired are then not a function of the particle size but of the new crystal or molecular structure. This difference is of fundamental importance and has been ignored by many workers while accounting for changes observed in colloidalisation and crystallisation. The changes noticed are due not to particle sizes but to a definite change in crystal structure. One may recall here the famous controversy regarding the yellow and red oxides of lead. The earlier work of Ditte,⁵ Geuther⁶ and Ruer,⁷ etc., showed that the two forms were clearly distinguishable from each other. Glasstone,⁸ however, concluded that this difference in colour is due only to the different states of aggregation of the particles. But the later and

⁴ Freundlich, *Colloid and Capillary Chemistry*, 1926 Ed., pp. 374-375.

⁵ *Compt. Rend.*, 1882, **94**, 1310.

⁶ *Ann. der Chemie.*, 1883, **219**, 56.

⁷ *Zeit. anorg. Chem.*, 1906, **50**, 265.

⁸ *Jour. Chem. Soc.*, 1921, **119**, 1689 and 1914.

¹ *Grundzuge der Dispersoidchemie*, T. Steinkopf, Leipzig, 1911.

² *Jour. Amer. Chem. Soc.*, 1930, **52**, 4621.

³ *Zeit. f. Electrochemie*, 1908, **14**, 49.

more careful work by Applebey and Reid⁹ has definitely shown that Glasstone's conclusions are not justified and the two forms are structurally different, the crystalline and optical characteristics of the red oxide being tetragonal, uniaxial and negative and those of the yellow variety rhombic, biaxial and positive. Kohlschutter and Scherrer¹⁰ confirmed the difference in crystal structure by the X-ray method. Their specific diamagnetic susceptibilities are also different, the red variety having a value of $\chi = -0.211 \times 10^{-6}$ as against $\chi = -0.196 \times 10^{-6}$ for the yellow variety.¹¹

Another interesting case is that of the red and the yellow oxides of mercury where R. N. Mathur reports that the magnetic susceptibilities are identical ($-0.243 - 4 \times 10^{-6}$) in both cases which suggests the same crystal structure in both cases. This evidence is beautifully corroborated by Levi,¹² Fricke¹³ and Zschariasen¹⁴ who have attributed the colour to particle size as they find that the two oxides are crystallographically identical.

From these observations it is abundantly clear that there are certain physical properties such as colour which may be influenced both by crystal structure as well as particle size. There are other properties such as magnetic susceptibilities which are influenced only by change in the crystal structure or by occluded impurities and do not seem to be much influenced by particle size. The reported changes of magnetic susceptibilities by cold working by Honda and Shimizu¹⁵ in case of copper and tin can be satisfactorily accounted for on the view that in cold working the crystalline structure undergoes modification. This view has found general support by all workers in physics.

⁹ *Jour. Chem. Soc.*, 1922, **121**, 2129.

¹⁰ *Helv. Chim. Acta*, 1924, **7**, 337.

¹¹ Cf. R. N. Mathur, Thesis for the D.Sc. Degree, Punjab University.

¹² *Gazz. Chim. Ital.*, 1924, **54**, 709.

¹³ *Zeit. anorg. Allgem. Chem.*, 1927, **165**, 244.

¹⁴ *Zeit. physikal. Chemie*, 1927, **128**, 421.

¹⁵ *Nature*, 1930, **126**, 990; 1935, **135**, 108.

If the forces employed or generated in powdering or colloidalisation are capable of inducing a change in crystal structure, the colloid is likely to show variation in magnetic susceptibilities even after the adsorbed film has been removed, but if the powdering has only changed the particle size and not the crystal structure, the mere sizes will produce no difference in the value of χ when the entrained impurities have been washed away.

It looks to the writer that many old controversies regarding the behaviour of colloids can be reviewed in the light of the above observations. For example, Weigert¹⁶ advocates the view that the stream double refraction in colloidal solutions is dependent upon the size of particles and the distance between them and occurs only when both the particles and the distance between them are amicronic. Against this view is the evidence cited by Freundlich¹⁷ depending on the close relationship between this double refraction and the age of certain sols and the change in ultramicroscopic appearance and structure with age. These changes strongly support the view that the birefringence in such colloids is an intrinsic and not a mere rod double refraction. The X-ray method has also established that changes in crystalline structure on powdering may take place occasionally¹⁸ and the differences in physical and chemical properties obtained in some cases are a function not of the particle size but of crystal structure.

An examination of some of the physical properties of colloidal system such as the piezo-electrical behaviour in gels and the thermal and electrical conductivities of sols and gels will lead to important results particularly in systems where the colloidal state is accompanied by a change in crystal structure. As a matter of fact a complete review of properties of colloidal systems on this view may be well worth-while.

¹⁶ Cf. Weigert and Pohle, *Kolloid Zeit.*, 1921, **28**, 153.

¹⁷ Freundlich, *Colloid and Capillary Chemistry*, 1926 Ed., pp. 404 and 411.

¹⁸ Asahara, *Scientific Papers, Inst. Phys. and Chem. Research, Tokyo*, 1922, **1**, 23.