Structure and Formation of Colloidal Particles.

THE joint discussion between the Sections of Physics and Chemistry held on Sept. 2 at the meeting of the British Association at Leeds, on the subject of the structure of colloidal particles, directed attention to the remarkable progress which has been made in recent years in the elucidation of the texture of disperse systems.

Both Sir William Bragg, who presided, and also Dr. Freundlich laid emphasis on the importance of the method of examination by means of X-rays as well as on the limitations of the method. If the particles of a colloid are crystalline but not orientated in any specific direction, such as in gold and silver sols dispersed in water, a characteristic line photograph is obtained, whilst in addition, if the particles are orientated round an axis, as is the case in certain fibres, a spot pattern photograph is obtained. In many cases it is found that the broad diffuse rings indicating an amorphous character are replaced by the line photograph of the crystalline material as the suspension grows older, and we thus obtain a convenient method for determining the velocity of crystallisation of these substances.

When X-ray photographs are taken of liquids, it is found that in certain liquids, for example, cyclohexane, the rings are much more distinct and sharply bounded than in others; similarly, in the photographs taken of iron, prepared for the synthesis of ammonia by the catalytic method, both broad and thin rings can be obtained dependent on the method of preparation and the period of sintering. It is clear that we are dealing with materials which have a tendency to orientate themselves to form crystal nuclei.

It is somewhat unfortunate that the measurement of the breadth and intensity of the lines alone does not allow us to distinguish between two effects, whether the change in line breadth and intensity is associated with a change in the size of the micro crystals or a growth in the number of orientated particles. At the present time a method of distinguishing between these two factors is a matter of some importance.

Whilst the X-ray method alone gives no definite clue to the shape of the particle, it does at least give some indication of the processes by which crystals grow more readily in certain directions than in others; thus, the lamellar or flake-like character of large crystals of the fatty acids is readily anticipated from the crystal form determined by this method. Since, however, the shape of the particles is defined by magnitudes although submicroscopic yet greater than molecular in size, we may obtain information on this point by optical methods. A distinction between spherical and non-spherical particles can readily be made by observance of the scintillations in the ultra microscope or the double refraction of light in sols streaming through a channel, and even by the light absorption of colloidal solutions; thus, many sols, such as arsenious trisulphide and non-stretched gelatine, are found to be spherical.

The optical behaviour of streaming sols in a Tyndall beam gives some indication of the shape of the particles when these are not spherical; thus, it is possible to distinguish between attenuated string- or rod-like particles in contrast to those plate-like or lamellar in form. The optical evidence for the rod-like structure of the colloidal particles of sols such as benzopurpurin or vanadium pentoxide is again supported by the shape of the macro crystals of these materials grown in the ordinary way. It is, indeed,

stated in the literature that benzopurpurin crystals can be grown so long and slender that they will pass through the pores in a filter paper in their end-on position, and that the crystals themselves are in continuous flexion under the influence of the Brownian agitation.

It is somewhat remarkable that the crystals of silver sols, which from their crystal growth one might reasonably anticipate to be either octahedral or possibly cubic in form, actually appear to deviate from the regular structure towards a lamellar form.

Such optical methods provide weapons with which the problem of the mechanism of formation of colloidal particles can be attacked. Von Weimarn's well-known criterion of the magnitude of the dispersion coefficient permits the prediction of the form of an insoluble product formed by interaction of two soluble salts. In cases where the dispersion coefficient is high, colloidal solutions or even gels may be obtained; the individual particle size is partly determined by the dispersion coefficient and the growth rate may be termed, with Haber, the grouping velocity. The clusters or aggregates of molecules thus formed at haphazard must, in order to become a crystalline assemblage, become orientated in their space lattices. This action may proceed at various rates; the velocity of orientation may be, and frequently is, very different from the grouping velocity.

It is thus possible to prepare numerous colloids, both in the crystalline as well as the amorphous state, by suitable adjustment of these two velocities. By rapid condensation of silver vapour admixed with naphthalene at liquid air temperature, for example, the preparation of colloidal amorphous silver can be effected, whilst under the ordinary conditions for preparing both colloidal silver or gold, the particles are completely crystalline, an indication that the velocity of orientation is extremely high.

These changes from the amorphous to the crystalline in solid substances can thus take place at different rates and are at least to a certain extent under control; that mechanical effects, such as stretching or pressure, effect orientation of the cell units in substances as varied as rubber, gelatine, and waxes, is definitely revealed by X-ray examination. An equally complex but interesting field for study is the structure of aerosols or smokes. As was pointed out by Prof. Whytlaw-Gray, the study of smokes is rendered more difficult by the fact that smokes are unstable and continue to undergo processes of aggregation and precipitation. Nevertheless, from photomicrographs it is possible to recognise definite crystal structure in many of such aggregates: in others the smoke particles appear as small spheres. It is at present a matter of interesting speculation whether the conceptions of von Weimarn and Haber on the conditions of formation of particles in solutions are not applicable in this field also.

It is frequently argued that problems such as the shape or form of colloid particles may be a matter of deep scientific interest, but that the industrial chemist is satisfied provided that his suspension or smoke fulfils certain standard arbitrary tests, for example, grain size. A brief consideration of the relatively great covering powers of plate-like particles in paints and glazes, or the factors governing the adhesion of fungicides, to mention but two cases, shows that the discussion held at Leeds was full of import to numerous industries.

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