

SmallAngle XRay Scattering from Metal Deposits Made by Evaporation

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barriers are caused by the interaction of the two opposing intermolecular forces of attraction and repulsion acting individually. For high viscosity not only high attracting forces are needed but also high repulsive forces. By the interaction of these two opposite forces the molecules tend to get fixed up in space so to speak; this fact means high viscosity. The departure from complete correspondence between cohesion and viscosity arises because cohesion is a measure of difference of attractive and repulsive energies while viscosity depends individually upon both. Our concept at once explains the following pertinent facts.

(1) *Increase of viscosity with pressure.* With decrease of volume under pressure, both the attractive and repulsive forces increase, leading to an increase of viscosity. Moreover, as these forces are inverse functions of distance, their rate of increase will increase with the decrease of the intermolecular distance. Further, since the repulsive forces are of much shorter range they will, after a stage, increase much faster than the attractive forces. This leads to a rate of increase of viscosity which increases fast with pressure. On the other hand, the rate of fall of compressibility with pressure will be rapid in the beginning and slower afterwards as it is related to the difference of attractive and repulsive energies, which increases in the beginning but decreases at still higher pressures.

(2) *Viscosity and association.* It has been shown² that molecules of associated liquids do not only have great attractive forces but also have significant repulsive forces. This may be physically explained as being caused by the hydrogen bonds, in which the distance between two oxygen atoms of interacting molecules (O—H—O) decreases so much as to produce repulsive forces as well. This tendency is further increased due to the semipermanent nature of the hydrogen bond links, so that, due to the hindered relation of the molecules concerned, the intermolecular forces become more of a first order than second order.

(3) *Behavior of water.* Remembering that compressibility decreases with breaking of associations,³ and that the associations break under pressure and with increase of temperature, the odd behavior of water in its change of viscosity and compressibility with pressure and temperature will be explained.

(4) *Decrease of viscosity with temperature.* This is the easiest thing to explain and also follows from the current theories. With the increase of temperature at constant volume, both the attractive and repulsive energies will increase because of the smoothing out of intermolecular distribution functions. Even if that is not so or if the effect is negligible, the increase of kT will increase the probability of jump of the potential barriers, leading to decreased viscosity.

At constant pressure, the intermolecular distances increase, leading to a more rapid decrease of both kinds of forces and so leading to a faster decrease of viscosity.

Further details of the theory and its quantitative aspects will be taken up in a later paper.

¹ For example, Andrade's Theory, Phil. Mag. 17, 494, 698 (1934); Eyring's Theory, Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

² Parshad, Doctorate Thesis, Punjab University, India, 1946.

³ Parshad, Ind. J. Phys. 19, 47 (1945).

Small-Angle X-Ray Scattering from Metal Deposits Made by Evaporation

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THE formation of dull or black films during the evaporation of a metal has been the subject of considerable conjecture. Numerous diffraction studies of "evaporated" metal films have been reported,^{1,2,3} but the small-angle scattering properties of these deposits have been overlooked. We have examined aluminum and copper deposits produced at 10^{-2} and 10^{-4} mm by means of Debye-Scherrer and small-angle diagrams, and have found that the black deposits exhibited marked small-angle scattering of x-rays (Fig. 1) and bright deposits did not; however, the Debye-Scherrer diagrams were substantially alike regardless of the wide variations in the reflectivity of the metal surface toward white light.

Aluminum was evaporated from a tungsten wire and deposited on glass surfaces at various distances from the source. In the case of copper, a tantalum heater was used permitting the evaporation of relatively large quantities of metal.⁴ To minimize the possibility of compound forma-

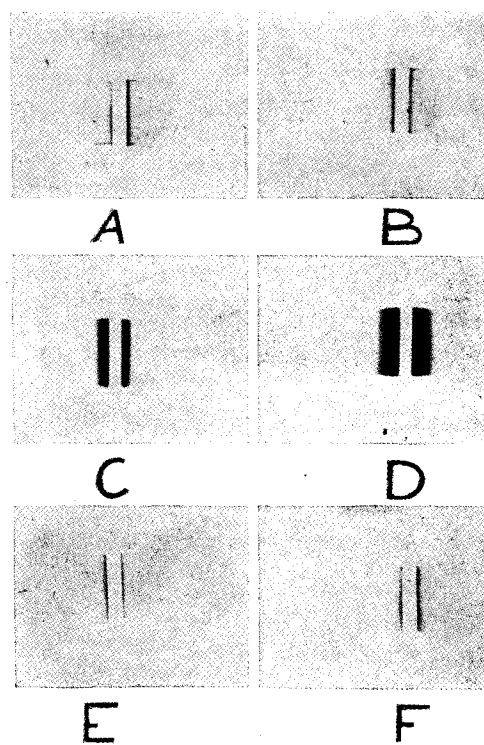


FIG. 1. Small-angle x-ray scattering of bright and dark metallic deposits. A. Bright aluminum foil made at 10^{-4} mm. B. Bright copper foil made at 10^{-4} mm. C. Aluminum black made at 10^{-2} mm. D. Copper black made at 10^{-2} mm. E. Bright aluminum foil made at 10^{-2} mm (when condensation is close to source). F. Bright copper foil made at 10^{-2} mm (when condensation is close to source).

tion for the metal deposits formed at 10^{-2} mm, the pressure in the evaporation chamber was regulated by allowing helium to leak into the system. The deposits were scrapped from the glass base and examined with filtered copper radiation. The distance between sample and photographic plate was 50 cm for the small-angle work and the method used to evaluate particle size was the same as described by Jellinek and Fankuchen.⁵ The identical specimens were then used in the Debye-Scherrer camera for the purpose of observing line-broadening effects.

The Debye-Scherrer patterns of all samples showed no particular orientation effects and aside from general darkening of the background of the photograms for the black deposits, line broadening, due to small particle size was not apparent (see Fig. 2). The average particle size for aluminum and copper black as calculated from the small-angle scattering was 110Å and 90Å, respectively; the bright deposits formed close to the heater during the same evaporation experiment (pressure 10^{-2} mm) gave negligible scattering at small angles, indicating that the crystals were about 10^{-5} cm.

Jellinek and Fankuchen⁵ showed that for fairly homogeneous specimens of γ -alumina, crystallite sizes calculated from small-angle scattering and line-breadth measurements of Debye-Scherrer patterns were in good agreement. If gross inhomogeneities exist in a specimen as in the case of the aluminum and copper black, small-angle scattering will indicate the presence of the fine particles or crystallites only, whereas the Debye-Scherrer diagrams will reveal the existence of the coarser crystallites.

The formation of black deposits by evaporation can be considered a general method of preparing colloidal metal particles, the colloidal condition apparently being caused by the arrival of clusters of atoms at the surface. Reorganization and crystal growth of the film depends upon the surface mobility of the condensed atoms. Since the activation energy for migration over the surface of a solid is greater for an atom in a cluster than for a single atom, on the surface of the sub-phase, we have an explanation for the invariable occurrence of black deposits when the mean

free path inside the vacuum chamber was much smaller than the distance between the source and the condensing surface. The formation of bright deposits and relatively coarse crystallites close to the source when the pressure was 10^{-2} mm were probably not only due to the comparability of the mean free path and the distance from the source to the condensing surface, but also to the somewhat higher temperature that prevailed near the source.

¹ Andrade, *Trans. Faraday Soc.* **31**, 1157 (1935).

² Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1943), p. 440.

³ Milligan and Focke, *J. Phys. Chem.* **45**, 107 (1941).

⁴ W. C. Caldwell, *J. App. Phys.* **12**, 779 (1941).

⁵ Jellinek and Fankuchen, *Ind. Eng. Chem.* **37**, 158 (1945); also see Jellinek, Solomon, and Fankuchen, *ibid.*, **18**, 172 (1946).

A New Concept about the Mechanism of Passivity of Iron in Nitric Acid

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December 19, 1947

MANY theories¹ have been advanced from time to time to explain the passivity of iron in concentrated nitric acid. In the following we offer a new concept.

In 1944 electrochemical evidence was obtained² showing the existence of a hydrogen or hydride film on aluminum, spaced between the well-known oxide film and the metal itself. In our view, the tenacity and strength of the oxide film is due to this hydrogen film.

We were led to believe that the passivity of iron in concentrated nitric acid might also be due to this intermediate hydrogen film, with the difference that, whereas in the case of aluminum the film could be produced in the atmosphere, on iron it would come from the acid itself, possibly as a result of an initial metal-acid interaction. This hydrogen film adsorbed on iron would, in our view, attract an oxygen or oxygen-rich film (helped in this process by the attraction of iron itself for oxygen), and the latter oxygen-rich film would stop further oxidation.

Experimentally, when a piece of iron is inserted in nitric acid, a potential due to this hydrogen film should be expected before the known noble potential due to the oxygen-rich film is recorded. A platinum electrode was dipped in concentrated nitric acid and some time later an iron electrode was at once inserted in the acid. The potentials produced right from the making of the cell were amplified by a d.c. amplifier and measured on a cathode-ray oscillograph. In acid of concentration 68.8 percent by weight at 32.6°C, the potential of the cell rose to 1.25 volts almost instantaneously, and then in 0.05 second fell to a steady potential of about 0.2 volt. During its decrease, the potential passed through a "plateau" where its rate of fall was the lowest. As concentration of acid decreased, the initial rise of potential occurred in two steps: first an almost instantaneous rise as before and then a continued slower rise through about 0.1 volt. The rate of fall of potential after it had reached the maximum also decreased. For example, in acid 45.6 percent by weight, at 32.6°C, the time taken to reach the steady low potential was one second.

We have reasons to believe that the initial potential is

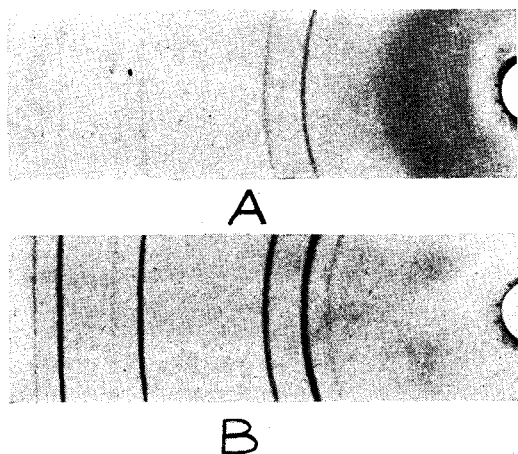


FIG. 2. A, Aluminum black made at 10^{-2} mm.
B, Aluminum bright foil made at 10^{-4} mm.