

Stability of Lyophobic Sols

ACCORDING to Verwey and Overbeek¹, the coagulation value of various electrolytes for aqueous sols is given by:

$$c = 8 \times 10^{-22} \frac{\gamma^4}{A^2 v^3} \text{ mol./litre,} \quad (1)$$

where $\gamma = \frac{e^z - 1}{e^z + 1}$, and $z = \frac{\varepsilon v \psi_0}{kT}$, $A = \pi^2 q^2 \lambda$.

The coagulating power of electrolytes is thus shown to depend on the electric potential on the surface of the colloidal particle (ψ_0), the valency of the coagulating ion (v), the absolute temperature (T), the number of atoms in 1 c.c. of the substance forming the colloidal particle (q), and the constant λ which appears in the equation $V = -\lambda/r^6$, giving the attractive potential due to the Van der Waals forces; ε is the electronic charge and k the Boltzmann constant. Although equation (1) is based on a rather crude physical model, namely, the interaction of plane electrical double layers, and although it has a limited range of applicability, being valid only if $d \cdot \kappa \gg 1$ ($1/\kappa$ is the thickness of the ionic atmosphere and d is the mutual distance of the interacting colloidal particles), that is, for weak interaction of colloidal particles only, it nevertheless leads to a quantitative formulation of the Schultze-Hardy rule.

Wo. Ostwald² formulated a theory of coagulation of lyophobic sols which does not consider the mutual interaction of individual colloidal particles, but concentrates on the physical state of the dispersing medium, namely, the electrolytic solution of the coagulating ions. According to this theory, based on a careful study of experimental results, the stability of a given sol is influenced only by the activity coefficient³ of the coagulating electrolyte. Independently of the type of electrolyte, the coagulation takes place at an approximately constant value of the activity coefficient of the coagulating ('dominant') ion. This theory, which seems to be just the opposite of the Verwey-Overbeek theory, may be formulated as follows:

$$f_c \approx \text{constant,} \quad (2)$$

where f_c is the activity coefficient of the 'dominant' ion at which the coagulation takes place.

It may be of interest to direct attention to the close connexion existing between Ostwald's rule $f_c \approx \text{constant}$, and the results of the simplified Verwey-Overbeek theory, which according to my knowledge has not been noticed in the literature. In fact, it may be shown that Ostwald's rule follows directly from the Verwey-Overbeek theory.

For symmetrical (1-1, 2-2, etc.) electrolytes the Debye-Hückel theory gives the activity coefficient of an ionic species in water at 25° C. as

$$-\log f_c = 0.509 \sqrt{c \cdot v^3}. \quad (3)$$

Substitution of equation (1) in equation (3) gives

$$-\log f_c = 1.44 \gamma^2 / A \cdot 10^{11}. \quad (4)$$

Since γ tends to unity even at moderate values of z , and A is a constant, equation (4) may be written as

$$-\log f_c \approx \text{constant,} \quad (5)$$

which is another form of the equation (2). Thus it is shown that, at least for symmetrical electrolytes, Ostwald's rule follows from Verwey-Overbeek's theory. The numerical value of the constant depends on the choice of the value for A . Unfortunately, Verwey-Overbeek's theory cannot give a value for A

without taking into account experimental results concerning the coagulation values of electrolytes.

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Zagreb. March 17.

¹ Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of the Stability of Lyophobic Colloids" (New York, Amsterdam, London, Brussels, 1948).

² Ostwald, Wo., *Koll. Z.*, **73**, 101 (1935); **75**, 39, 297 (1936); **76**, 159 (1936).

Inactivation of DDT by Soils

WE have read with interest the recent communication in *Nature* from H. Maes¹. His report of the work of I. Vincke, who has observed a rapid loss of insecticidal power of DDT on the walls of certain African houses in the Belgian Congo, provides further evidence for the sorption of DDT on lateritic soils described by us in 1951². It is also useful to find described a method for preventing this loss of efficiency; but we believe that the connexion between ability of soils to dehydrochlorinate DDT at elevated temperatures and loss of biological effectiveness is misinterpreted by Maes, and that the effect of spraying walls with phosphates is not due to inhibition of decomposition of DDT.

We have shown quite clearly that loss of effectiveness of surface deposits of DDT from wettable powders on certain soils is due to sorption of the DDT, and the presence of the undecomposed insecticide inside the soil structure can be demonstrated both colorimetrically and by recovery of crystalline DDT³. In addition, other insecticides, which are not susceptible to dehydrochlorination, disappear from the surface of soils in exactly the same way as DDT at rates which are approximately proportional to their vapour pressures. Possibly the sorbed DDT may be decomposed afterwards, particularly under dry conditions³; but the reaction is very slow at atmospheric temperatures compared with the sorption process and cannot account for the rapid loss of killing power against mosquitoes. However, as Downs *et al.*⁴ have shown, there is a correlation between ability to dehydrochlorinate DDT in the Fleck and Haller method and the rate of loss of effectiveness on a wide range of soils, and therefore "the reaction of catalytic decomposition at 130° C. affords a rapid method for foretelling the capacity of a soil for inactivating DDT".

We would suggest the following possible reasons for the beneficial effect of pre-spraying mud walls with phosphate solutions. The correlation found by Downs *et al.* between the iron oxide contents of soils and the life of DDT residues on these soils would suggest that it is the iron oxide which provides the active sorbing surface. The phosphate ions may react with this surface to reduce its activity. Also, reaction with the ferric ions in the soil will produce gelatinous complex iron phosphates which may actually block the fine capillaries of the mud and retard diffusion of the insecticide vapours.

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¹ Maes, H., *Nature*, **170**, 328 (1952).

² Hadaway, A. B., and Barlow, F., *Nature*, **167**, 854 (1951).

³ Hadaway, A. B., and Barlow, F., *Bull. Ent. Res.*, **43**, 281 (1952).

⁴ Downs, W. G., *et al.*, *Science*, **114**, 259 (1951).