atic, that is, the greater the halogen (Cl, Br) content of a compound the greater these deviations become.[3] My results, $\chi = -0.58 \times 10^{-6}$ for acetone and $\chi = -0.485 \times 10^{-6}$ for chloroform, are within the limit of error of previous measurements recorded by other authors.

HANS BUCHNER.

Institute of Physics,
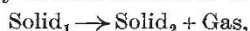University of Munich,
July 26.

[1] *Proc. Roy. Soc.*, **131**, 1931, p. 209, and NATURE, **128**, 1931, p. 152.
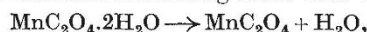[2] NATURE, **127**, 1931, p. 975.
[3] Pascal, *Ann. de Chim. et Phys.*, **19**, p. 67 ; 1910.

Function of Water Vapour in the Dissociation of a Salt Hydrate.

IN measuring the influence of the gaseous product upon the velocity of dissociations of the type

$$Solid_1 \longrightarrow Solid_2 + Gas,$$

we have found an interesting effect with the reaction :

$$MnC_2O_4.2H_2O \longrightarrow MnC_2O_4 + H_2O,$$

which goes on slowly in a vacuum at $76°$, at which temperature the dissociation pressure is approximately 135 mm.

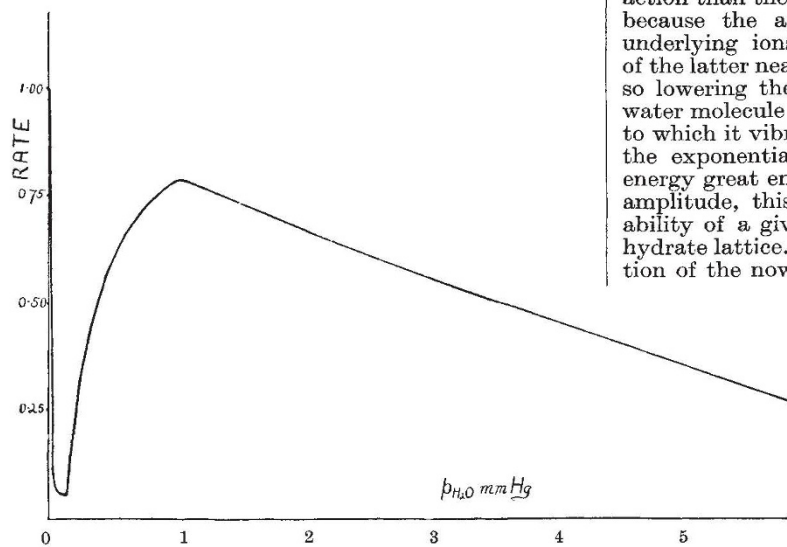The reaction rate under otherwise constant conditions is sensitive to quite small concentrations of
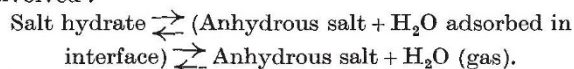

FIG. 1.

water vapour. Plotted against a linear scale of water vapour pressures, the quotient

$$\frac{\text{Rate in vacuum}}{\text{Rate at } pH_2O}$$

(shown in the diagram as 'rate') at first falls sharply ; this appears to be the normal behaviour of salt hydrates. But with increasing water vapour pressures the rate passes through a minimum at about 10^{-1} mm. (that is $<10^{-3}$ of the dissociation pressure) and then rises, to pass through a maximum of the same order as the rate in vacuum ; thereafter it falls again along a more gentle curve eventually to zero at the dissociation pressure. So far as we know at present, this minimum and maximum is a unique case.

In rough outline the following picture might provide a qualitative explanation of the effect : the reaction is experimentally of the usual 'interface' type, that is, dependent upon the presence of the anhydrous phase. It possesses a large temperature coefficient,

so that the rate-governing process is subject to a considerable activation, presumably in vibrational degrees of freedom. In our view, two stages are involved :

Salt hydrate $\rightleftharpoons$ (Anhydrous salt + H_2O adsorbed in

interface) $\rightleftharpoons$ Anhydrous salt + H_2O (gas).

Water molecules in the hydrate lattice adjoining the anhydrous phase require a smaller vibrational energy to enable them to break out of the lattice because of the attraction exerted by the ions on the opposite side of the reaction zone ; hence the reluctance of the reaction to take place in the absence of the second solid phase.

Water vapour in the gas phase establishes an adsorption equilibrium in the interface zone between the two solids rapidly in comparison with the slow chemical reaction. The net rate of decomposition is now decreased (*a*) because it is the difference between two opposing rates, (*b*) because a fraction of the interface is blocked for decomposition by the adsorbed molecules already present.

As the two-dimensional density of adsorbed molecules increases (with the arbitrarily maintained partial pressure) a stage will be reached in which the gaps in the adsorption layer are more or less surrounded by other adsorbed molecules. We suppose that these gaps may be much more effective in promoting the reaction than the corresponding area not so surrounded, because the adsorbed molecules polarised by the underlying ions virtually carry the attractive field of the latter nearer to the hydrate side of the interface, so lowering the force constant between the hydrate water molecule and the rest of its lattice, with respect to which it vibrates in the reaction zone. Because of the exponential factor governing the chance of an energy great enough to give the molecule an assigned amplitude, this may increase enormously the probability of a given molecule breaking loose from the hydrate lattice. At the same time, the mutual attraction of the now rather numerous adsorbed molecules polarised by oppositely charged ions will decrease the probability of a given molecule contributing to the reverse reaction by passing from the adsorbed layer back to the lattice. The combined effect is to cause the net rate to rise again, and clearly it must pass through a maximum and fall again more slowly as the gaps available for the forward reaction become filled up and the number of molecules in a position to contribute to the reverse reaction is still further increased. Ultimately the two opposing rates become equal at the dissociation pressure.

The initial rapid fall with very small fractions of the dissociation pressure explains the well-known difficulty of approaching the equilibrium in many salt hydrate systems experimentally.

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Magnetism of Colloidal Gold.

IN three previous notes in NATURE[1] it has been pointed out that the diamagnetism of graphite, antimony, and bismuth decreases with particle size. This was most striking in graphite and less in antimony and bismuth. In a later communication on the same subject[2] I adopted two methods of