

An Equation for the Kinetics of Activated Adsorption

FOR an understanding of the nature of so-called activated adsorption, the kinetic characteristics of these types of processes are of the greatest importance. From the first conception of Taylor one might expect to find kinetic equations, based on the molecular kinetic theory of Langmuir, taking into account the low condensation coefficient increasing with the temperature. But, as I have shown in a lecture on activated adsorption given in Moscow (1932) at the IX Physical-Chemical Conference¹, of all cases of activated adsorption known at this time, not one obeys these equations. The well-known diffusion kinetics equations also cannot be applied to these systems.

Somewhat later, in our laboratory, J. Zeldowitch showed that for the chemisorption of carbon monoxide on manganese dioxide, the velocity of the process can be well expressed by the following simple equation:

$$\frac{dq}{dt} = V_0 e^{-\alpha q}; \quad V_0 = b e^{-E/RT} \quad (1)$$

where q is the quantity of gas adsorbed during the time t , α and b are constants, characteristic for the given system². On account of the high value of α , the velocity of adsorption diminishes several tenfold before saturation is half reached.

At first we did not assign fundamental significance to this empirical equation, but an analysis of the literature has shown that the kinetics of most of the known cases of activated adsorption, differing widely in their chemical nature and temperature range, follow an analogous law. Thus, for example, this equation written in a more convenient form:

$$q = \frac{1}{\alpha} \ln(t + t_0) + C \quad (2)$$

where $t_0 = \frac{1}{\alpha V_0}$ and $C = \frac{1}{\alpha} \ln \alpha V_0$

is satisfied by the data of Emmet and Brunauer³ on the sorption of nitrogen in iron, those of Benton and Drake⁴ for oxygen on silver, those of Taylor and Sickman⁵ for hydrogen on zinc oxide, etc.

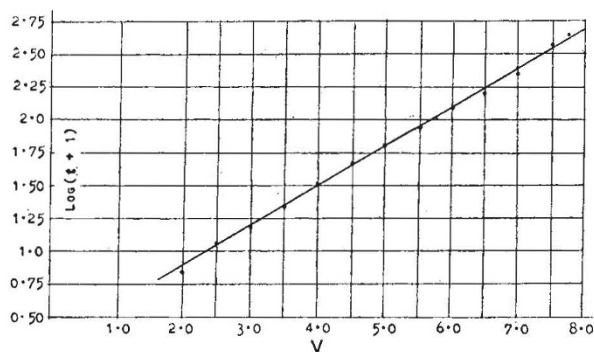


FIG. 1.

It is easy to show that the adsorption of ethylene on nickel in a recent paper of Steacie and Stovel⁶ is very well expressed by this equation. The agreement is shown on Fig. 1 which shows the activated sorption as a function of time, for the 142° curve in Fig. 1 of Steacie and Stovel's paper. Thus we may suppose that an equation of type (2) is a general

equation for the kinetics of activated sorption. It is easy to show that equations (1) and (2) cannot be derived from the usual ideas as to the character of activated adsorption, and that they lead to a very peculiar picture of the course of such processes, which at the same time gives an explanation for the appearance of large steric factors (another characteristic of activated adsorption).

We shall return to these equations in a fuller paper to appear soon.

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¹ S. Roginsky, *J. Phys. Chem. (Russ.)*, **5**, 175; 1934.

² S. Roginsky and J. Zeldowitch, *Acta physico-chemica*, **1**, 1934 (in print).

³ Emmet and Brunauer, *J. Amer. Chem. Soc.*, **56**, 35; 1934.

⁴ Benton and Drake, *ibid.*, **56**, 255; 1934.

⁵ Taylor and Sickman, *ibid.*, **54**, 602; 1932.

⁶ Steacie and Stovel, *J. Chem. Phys.*, **2**, 581; 1934.

Absorption of Light in Gases

CONTINUING an earlier experiment¹, we have measured the absorption of light by caesium vapour in the presence of helium. We find that the addition of helium greatly reduces the absorption by caesium, about 3 cm. of helium being sufficient to reduce it to half the value obtained for caesium in vacuum. Frank² and Mrozowski³ have shown that the continuous molecular absorption of mercury, zinc and cadmium vapours is proportional to $P\gamma$, where P is the vapour pressure and γ is a constant (for one wave-length). For different wave-lengths, γ lies between 1 and 2. Thus the absorption increases less rapidly than the molecular concentration. Their results may perhaps be explained if there is a reduction of absorption, due to collisions between atoms and molecules in the vapour, similar to the effect we have found in caesium and helium.

Other work⁴ has shown that the absorption of light by reacting gas mixtures is not equal to that calculated by summing the absorption of the constituents, the absorption being apparently increased.

Thus it is not possible to assume that in general the absorption of a gas is simply proportional to the concentration of the atom or molecule producing the absorption. It would appear probable that many calculations (particularly in photo-chemistry and stellar physics) may need revision in the light of the above results.

In all experiments where a large pressure effect has been found, the absorption has been due to transitions involving one unquantised state. It is known⁵ that the magnitude of the line absorption of atoms (where two quantised states are involved) is not greatly affected by the addition of foreign gases. Further experiments on continuous absorption and molecular band absorption are in progress.

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¹ *Proc. Roy. Soc., A*, **143**, 472; 1934.

² *Phys. Z. Sowjet Union*, **4**, 637; 1933.

³ *Z. Phys.*, **91**, 600; 1934.

⁴ *NATURE*, **134**, 848, Dec. 1, 1934.

⁵ Fuchtbauer, Joos and Dinkelacker, *Ann. Phys.*, **71**, 204; 1923.