A New Adsorption Rate Equation

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(Received September, 29, 1953)

The adsorption of nitrogen on an iron synthetic ammonia catalyst has been investigated at 300–500°C and a new adsorption rate equation

$$-\frac{dp}{dt}=k_a p\theta^{-\alpha}-k_d\theta^{\beta} \qquad (1)$$

was found to be applicable to the experiment. Here, p the pressure of nitrogen, θ the fraction of surface covered by adsorbed nitrogen and α and k_a etc. are constants characteristic of certain intervals of surface coverage. An examination of various adsorption data so far reported indicates that this equation is of general applicability.

Eq. (1) can be expressed alternatively as,

$$\left.\begin{aligned} &-\frac{dp}{dt}=k_a p\theta^{-\alpha}\left(1-\frac{p_e}{p}\right) \\ \text{or}\quad &\log\left(-\frac{1dp}{pdt}\Big/1-\frac{p_e}{p}\right)=-\alpha\log\theta+\log k_a \end{aligned}\right\} \qquad (2)$$

where p_e is the pressure of nitrogen which would be in equilibrium with θ at time t and obtainable from the data of adsorption isotherms.

If we evaluate the value of $-dp/dt$ graphically from the adsorption rate curve and plot the values of $\log\left(-\frac{1dp}{pdt}\Big/1-\frac{p_e}{p}\right)$ as ordinate and $\log\theta$ as abscissa, the result is three straight lines. The inclination of the straight line is zero at a region of lower surface coverage, becoming then discontinuously steep with increasing adsorption. Such inclinations or values of α determined at 400°C are presented in the Table below.

$Fe-N_2$ $T=400°C$

θ	<0.025	0.025< <0.08	0.08<
α	0	1.4	3.0

Adsorption isotherms were found to obey Freundlich's equation, $\log\theta=\frac{1}{n}\log P+\log K$, but the n in the equation changes discontinuously at that coverage corresponding to that of α. From the formulae of the *forward* rate and the equilibrium we can now get $k_d\theta^\beta$ for that of the reverse rate with the relation of

$$K=\left(\frac{k_a}{k_d}\right)^{\frac{1}{\alpha+\beta}},\quad n=\alpha+\beta \qquad (3)$$

If we assume that $n=1$ (Henry's law) and $\alpha=0$ in the region of low coverage and consequently $\beta=n-\alpha=1$, eq. (1) leads to its particular form

$$-\frac{dp}{dt}=k_ap-k_d\theta \qquad (4)$$

This is a Langmuir type of adsorption rate equation and was used by Barrer[1] and Kubokawa[2] respectively for $C-H_2$ and $Ni-CH_4$ with success. The adsorption rate of hydrogen on copper is proportional to hydrogen pressure in the region far removed from equilibrium[3]. This is fulfilled by eq. (4). There are also numerous other examples which follow satisfactorily eq. (2). The values of α thus determined are summarized in the accompanying Table.

System	Temp. °C	α	Ref.
$Ni-H_2$	−78	5,2	(4)
$C-H_2$	482	1,2	(5)
$ZnO-H_2$	184	3,4	(6)
$Cr_2O_3-H_2$	154	0,8	(7)
$CuCr_2O_4-O_2$	200	2,4	(8)

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