Rate Equation for the Chemisorption of Nitrogen on Ammonia Synthesis Catalysts

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The present author put forward a power rate law[1] expressed by

$$-\frac{\mathrm{d}p}{\mathrm{d}t}=kp\theta^{-\alpha} \tag{1}$$

to describe adequately the rate of the chemisorption of nitrogen on a promoted iron catalyst. Zwietering and Roukens[2] also investigated the same system and applied their data to the Elovich type equation of the form

$$-\frac{\mathrm{d}p}{\mathrm{d}t}=kpe^{-g\theta} \tag{2}$$

Recently Scholten and Zwietering[3] expressed their view that the experimental data due to Kwan are well subscribed in the Eq. (2) rather than (1). Whether or not experiments conform to these equations can be demonstrated viz., power rate law should give a linear relation in the logarithmic plot of $-1/p\cdot\mathrm{d}p/\mathrm{d}t$ against θ while the Elovich equation a linear semi-log plot. The purpose of the present note is to show a semi-log plot on the data already published by this author and discuss the consequences.

Rate data at 300 and 400C given in Table II of the previous paper[4] are far below equilibrium and permit ignoring the desorption of nitrogen. They are reproduced in Fig. 1 in a semi-log scale. Apparently experimental plots are curved convexly against θ-axis. Such curvilinear plots in a semilog scale were reproducible with respect to any $p-t$ run measured in a constant volume on the re-reduced catalyst, hence throwing doubt on the validity of the Elovich equation.

Experimental data obtained repeatedly on a re-reduced catalyst were found however to shift more or less in relation each other with each run, probably due to different surface states. Thus, if one plot several runs in a semi-log scale, than an approximate linear relation may appear within the experimental accuracy. A straight line of this kind has been demonstrated by Scholten and Zwietering[3].

If, on the other hand, one plot the experimental data for any single run in a logarithmic scale, a good linear relation holds with a break near $\theta=0.08$. Such a plot has been preferred by this author and presented together with those of other runs in the previous paper[4]. Unfortunately the measurements were only within a small range of coverage. Further works are needed to confirm the linearity of the latter kind at a higher coverage.

Assuming that the linear portion extends far beyond $\theta=0.08$, activation energies for

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1) T. Kwan, *J. Res. Inst. Catalysis*, **3**, 16 (1953); This Bulletin, **27**, 70 (1954).

2) P. Zwietering and J. J. Roukens, *Trans. Faraday Soc.*, **49**, 543 (1954).

3) J. J. F. Sholten and P. Zwietering, ibid., **53**, 1363 (1957).

4) T. Kwan, *J. Res. Inst. Catalysis*, **3**, 109 (1955).

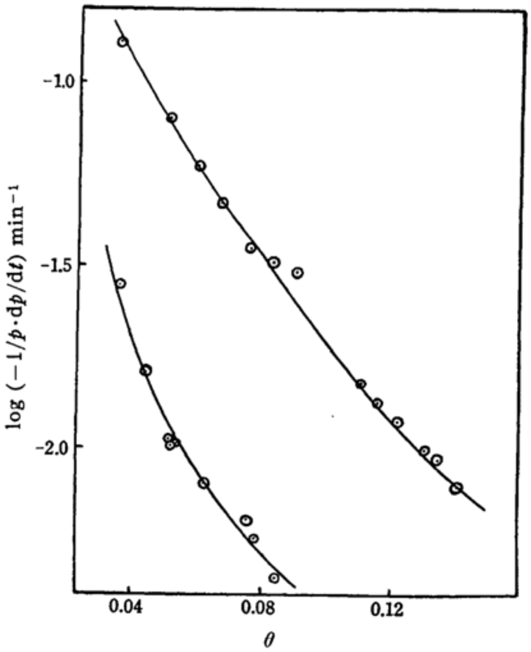

Fig. 1. Chemisorption rate of nitrogen as a function of coverage θ constructed from a single $p-t$ run obtained by Kwan[4]. T: 300° and 400°C.

the chemisorption of nitrogen were given by[4]

$$E=11\log\theta+23\ \text{kcal./mole}$$

Apart from the numerical value, this functional form for E seems compatible with the result of Zwietering and Roukens that the experimental E is not linear but concave against θ-axis at higher coverage of their measurements. Such a curved portion, when plotted against $\log\theta$, gives a linear portion in accordance with the above function—a family of power rate law.

Such an argument has been a frequent problem in adsorption—for instance the shape of adsorption isotherm and the corresponding heat curve. The author expressed his view elsewhere[5] that the Langmuir type isotherm is useful at lower coverage only, whereas the Freundlich equation provides an excellent validity at higher coverage. As a consequence, the isothermal heat curve appears to be somewhat reverse-s-shaped or linear against $\log\theta$ at higher coverage, e.g., hydrogen on a reduced nickel powder[6]. Schuit et al. observed adsorpiton isotherms for hydrogen on nickel-on-silica and derived a linear heat decrease with θ. On closer inspection, the heat-coverage relation is, according to them[7], slightly sigmoidal in character. It is the opinion of this author that different viewpoints expressed by Zwietering et al. and the author mentioned above may lie in a situation such was revealed in the adsorption of hydrogen on a nickel sample.

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[5] T. Kwan, *Advances in Catalysis*, **6**, 67 (1954).

[6] S. Ohkoshi and T. Kwan, *J. Res. Inst. Catalysis*, **4**, 199 (1957).

[7] G. C. A. Schuit et al., "Chemisorption" edited by Garner, 39 (1957) Butterworths Scientific Pub. London.