A NOTE ON "THE DECOMPOSITION OF METHANE ON THE SURFACE OF PLATINUM".

By Masao Kubokawa.

In the preceding papers[1][2], it was reported that the velocity of the decomposition of methane by platinum was represented by an equation containing a new constant named 'retardation exponent' and that the equation proved to be also applicable to other reactions in which the reaction products were strongly adsorbed by catalysts. The retardation exponent was explained qualitatively from the viewpoint of the heterogeneity of a catalytic surface, the equation being derived in approximate ways.

From a study of the energy distribution of the active centres of a catalyst[3], some quantitative explanation could be given to the retardation exponent, which will be mentioned below[4].

When more than one of the reaction products are adsorbed strongly on a catalyst in a reaction where a single reactant decomposes, the following velocity equation has been derived from Langmuir's isotherm assuming that the surface is homogeneous[5] :

$$\frac{dx}{dt} = k \cdot \frac{(a-x)}{x} \qquad (1)$$

where k is the velocity constant, a the initial amount of the reactant, x the decomposed amount at time t.

When simple equations, such as (1), are applicable to reactions on actually heterogeneous surfaces, it may be assumed that reactions proceed in the same form of the velocity equation on every active centre though the centres are of different characters[6]. This assumption has been justified when the form of

---

1) *Rev. Phys. Chem. Japan*, 11, 82 (1937).

2) *ibid.*, 11, 96 (1937).

3) *ibid.*, 11, 202 (1937).

4) It has been concluded in the preceding paper that irreversible adsorption of the reaction products takes place on highly active centres. This phenomenon, however, was treated in this paper as diminishing the active centres in the course of the reaction, the adsorption equilibrium being always established on the other hand.

5) e.g. Hinshelwood, "*Kinetics of Chemical Change in Gaseous Systems*", p. 320, Oxford (1933).

6) The same form of the velocity equation can be easily deduced from Langmuir's isotherm in the case where either a reactant or products adsorb extremely strongly or weakly even though there would be much variation in their adsorption coefficients corresponding to the variation in the kinds of centres.

the velocity equation does not vary with successive additions of catalytic poison[3].

Now assuming that the centres from 1 to m always participate in a reaction, we have

$$k = \sum_1^m k_i \, .$$

If the number of the centres participating in the reaction is decreased successively by continued small additions of a poison which adsorbs on a catalyst and yet is indifferent to the reaction, k will become a function of y, the adsorbed amount of a poison, and the following relation is obtained when y is small from equation (8) of the preceding paper[3]:

$$k = \frac{c}{y^{\gamma-1}} \, , \tag{2}$$

where c and γ are constant, and the relation between γ and h, the distribution constant, is as follows:

$$\gamma = \frac{h}{RT} \, .$$

When the product itself is a poison and the number of kinds of the centres participating in the reaction decreases successively, y may be written as

$$y = c'x \, , \tag{3}$$

because the adsorbed amount of the product is considered to be proportional to the amount present in the system, c'·being a constant of proportion.

Substituting (2) and (3) in (1), we have

$$\frac{dx}{d\pi} = \varkappa \cdot \frac{(a-x)}{x^\gamma} \, , \tag{4}$$

where $\varkappa$ is a new constant, and γ becomes equal to the retardation exponent n.

Taking θ as the temperature of preparation of a catalyst, we have the relation $h = R\theta$ according to Schwab. Accordingly so long as the temperature of the reaction is lower than the temperature of preparation of the catalyst, we have

$$\gamma > 1.$$

From this consideration, it can be explained that the retardation exponent is larger than 1 and that it varies according to the nature of a catalyst[7].

---

7) It has been observed that the retardation exponent n is varied by the change of pressure of the reactant. This fact cannot be explained by any variation in γ, so that it may be done by variation in the form of velocity equation. Such a case as the variation of n by the change of temperature of the reaction disagrees with the change of γ may be explained in the same way.

The author wishes to express his thanks to Prof. S. Horiba for his guidance.

The Laboratory of Physical Chemistry,
Kyoto Imperial University.