

On the Effect of Continued Small Additions of Poisonous Substances on the Velocity of Gaseous Catalytic Reaction in Closed Vessels. By Dr F. HURN CONSTABLE, Fellow of St John's College.

[Received and read 2 May 1927.]

The Langmuir-Frenkel theory of surface action has been shown to involve a simple relation between the partial pressure of the catalyst poison, and the reduction in reaction velocity which results*. Very interesting observations have been made by Beebe† showing that the heat of adsorption of carbon monoxide on a reduced copper catalyst falls considerably and reaches a limiting value as the surface approaches saturation. Pease and Stewart‡ have shown that the presence of less than one per cent. of the total carbon monoxide that a given copper catalyst can adsorb will reduce the reaction velocity of the combination of hydrogen and ethylene at the surface of the copper by 88 per cent.

It is interesting to note that there are a number of explanations of the phenomenon noticed by Beebe, and that it would be expected to occur to some extent even with a homogeneous surface.

(a) As the surface becomes increasingly covered by the adsorbed molecules the work of desorption falls, because the external fields from the surface are weakened§.

(b) The portions of the surface with the most intense fields adsorb gas at pressures low enough for the remainder of the surface to be inactive as an adsorbent.

(c) Multimolecular films may be formed, the work of desorption being very much greater for the first unimolecular film, and falling to a limiting value as the number increases.

(d) Clusters of gas molecules may adhere to particular spots on the surface; thus though the surface may adsorb far less gas than would be required to form a complete unimolecular layer, it behaves as if unimolecular layers had been formed.

(e) The surface is covered with unimolecular layers interspersed with portions of the surface that are bare; thus the whole surface is incapable of holding gas in the adsorbed state.

* Constable, *Proc. Camb. Phil. Soc.*, vol. 23, pp. 172-182 (1926), "On the behaviour of the centres of activity of saturated surfaces during the initial stages of unimolecular reactions"; pp. 593-606 (1926), "Surface adsorption and the velocity of chemical action at gas solid interfaces."

† *J. Phys. Chem.*, vol. 30, pp. 1538-1544 (1926).

‡ *J. Amer. Chem. Soc.*, vol. 47, p. 1235 (1925).

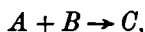
§ Becker, *Phys. Rev.*, vol. 28, pp. 341-361, has shown by direct experiment with caesium films on tungsten that the work necessary to remove an atom of caesium decreases as the fraction of the surface covered increases; but that the work done in removing a caesium ion increases under similar conditions.

The observations of Pease and Stewart show that the same small quantity of poison added to a closed vessel in which catalysis is occurring has a vastly greater effect initially than when the pressure of the poison has become considerable. The theory of centres of activity developed by Pease, Taylor, and Constable implies that there is a distribution of centres of all degrees of activity over the catalyst surface, and it is interesting to examine the data of Pease and Stewart to see whether any information can be obtained from their results as to the type of distribution present.

The direct result of the Langmuir-Frenkel theory is that saturated surfaces over which there is no variation of the activity of the individual centres should be much more sensitive to the first small quantities of poison than to the amounts which follow; and the purpose of this paper is to show the nature of this variation in the case of uni- and bi-molecular reactions. It can then be seen that the data on the poisoning of the hydrogenation of ethylene by increasing quantities of carbon monoxide show definitely that the mean life of the carbon monoxide molecule is very much greater on the centres which are most active in hydrogenation than on the rest of the surface, thus bringing forward additional evidence in favour of the enhanced fields on the most active spots on the surface.

The Initial Stages of the Poisoning of Unimolecular and Bimolecular Gas Reactions in Closed Vessels.

In these cases it is experimentally convenient to keep the pressure of the reactants constant, and measure the decrease in the initial catalytic activity as the absolute pressure of the poison increases. The initial rate of bimolecular reaction can conveniently be measured by the initial rate of fall of pressure in the closed vessel. Let the reaction be



and let a = the initial pressure of the reactant A ,
 b = the initial pressure of the reactant B ,
 x = the pressure of the poison.

Then, following the method of calculation given by the author*, the fraction of any time interval during which the centres of activity that activate A are occupied by A is

$$\frac{\mu_A \tau_A a}{\mu_A \tau_A a + \mu_B \tau_B b + \mu_C \tau_C x + \xi'}$$

* *Nature*, vol. 117, p. 230 (1926). The symbols are defined here.

where ξ is the fraction of any time interval that the centres holding A are left free,

$$\mu = \left(\frac{1}{2\pi MRT} \right)^{\frac{1}{2}},$$

and τ_L is the mean life of the molecule L on the centre. Similarly, the fraction of any period of time that the second series of centres are occupied by B is

$$\frac{\mu_B \tau_B' b}{\mu_A \tau_A' a + \mu_B \tau_B' b + \mu_C \tau_C' x + \xi'},$$

for the surface fields of force holding and activating the molecules B need not be the same as those holding A .

Bimolecular reaction is impossible while the reactants are separated*; thus the velocity is proportional to the probability that the reactants should be present side by side simultaneously on the centres of activity capable of activating both. The rate of reaction, conveniently measured by the initial rate of fall of pressure, is given by

$$\frac{da}{dt} = \frac{\mu_A \tau_A \mu_B \tau_B' ab}{(\mu_A \tau_A a + \mu_B \tau_B b + \mu_C \tau_C x + \xi) (\mu_A \tau_A' a + \mu_B \tau_B' b + \mu_C \tau_C' x + \xi')}.$$

The fractional reaction velocity is given by the ratio of the initial velocity, when the pressure of poison is x , to the initial rate of reaction in the absence of poison.

Therefore

$$v = \frac{1}{\left(1 + \left\{ \frac{\mu_C \tau_C}{\mu_A \tau_A a + \mu_B \tau_B b + \xi} \right\} x \right)} \frac{1}{\left(1 + \left\{ \frac{\mu_C \tau_C'}{\mu_A \tau_A' a + \mu_B \tau_B' b + \xi'} \right\} x \right)} \dots (1)$$

$$\text{or} \quad v = \frac{1}{(1 + \lambda_1 x)} \frac{1}{(1 + \lambda_2 x)}.$$

In some bimolecular reactions the poison may only have an appreciable mean life on one type of centre; thus the expression obtained for the reduction of the rate of the initial stages of the combination is the same as would be obtained for a unimolecular reaction, *i.e.*,

$$v = \frac{1}{\left(1 + \left\{ \frac{\mu_C \tau_C}{\mu_A \tau_A a + \mu_B \tau_B b + \xi} \right\} x \right)} \dots \dots \dots (2).$$

* Larmor, *Proc. Lit. Phil. Soc. Manchester*, vol. 52 (No. 10), p. 28 (1908), has pointed out the possibilities arising from this principle in connection with gas reactions.

The Efficiency of Continued Small Additions of Poison in Reducing the Reaction Velocity in the Initial Stages of Catalysis in Closed Vessels.

The percentage reduction in the initial rate of reaction due to the addition of poison at pressure x is given by $100\delta v/v$; and a measure of the effectiveness of the next increment δx in the pressure of the poison is the value of $\delta v/v \delta x$.

For bimolecular reaction

$$\frac{1}{v} = 1 + \alpha x + \beta x^2 \dots \dots \dots (3),$$

where $\alpha = \frac{\mu_C \tau_C}{\sum \mu_A \tau_A a + \xi} + \frac{\mu_C \tau_C'}{\sum \mu_A \tau_A' a + \xi'} \equiv \lambda_1 + \lambda_2,$

and $\beta = \frac{\mu_C \tau_C \mu_C \tau_C'}{(\sum \mu_A \tau_A a + \xi)(\sum \mu_A \tau_A' a + \xi')} \equiv \lambda_1 \lambda_2;$

therefore $\frac{1}{v} \frac{\partial v}{\partial x} = -\alpha \left\{ \frac{1 + \frac{2\beta}{\alpha} x}{1 + x(\alpha + \beta x)} \right\} \dots \dots \dots (4).$

For unimolecular reaction

$$\frac{1}{v} = 1 + \alpha x,$$

where $\alpha = \frac{\mu_C \tau_C}{(\mu_A \tau_A a + \mu_B \tau_B b + \xi)};$

thus $\frac{1}{v} \frac{\partial v}{\partial x} = -\alpha \left\{ \frac{1}{1 + \alpha x} \right\} \dots \dots \dots (5).$

Since α is the sum of λ_1 and λ_2 , while β is the product $\lambda_1 \lambda_2$, the maximum value of $\frac{1}{v} \frac{\partial v}{\partial x}$ is $-\alpha$ and this value falls considerably as x increases* since the multiplying factor becomes continuously

* Note that $\frac{1 + \frac{2\beta}{\alpha} x}{1 + x(\alpha + \beta x)} = \frac{1 + \frac{2\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} x}{1 + x \left(\lambda_1 + \lambda_2 + \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} x \right)},$

and is always less than unity provided that

$$(\lambda_1 + \lambda_2) + \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} x > \frac{2\lambda_1 \lambda_2}{\lambda_1 + \lambda_2},$$

i.e.

$$(\lambda_1 + \lambda_2)^2 + \lambda_1 \lambda_2 x > 2\lambda_1 \lambda_2,$$

$$\lambda_1^2 + \lambda_2^2 + \lambda_1 \lambda_2 x > 0,$$

which is always satisfied by a molecule which has a positive mean life on the centres of activity. The variation in ξ with x has been neglected, but such variation would only intensify the effect already predicted. The variation is absent with saturated centres, and it seems probable that the 'centres of activity' in many cases are always covered by adsorbed molecules.

smaller; thus equation (4) shows that for bimolecular reaction the efficiency of a catalyst poison, on a catalyst composed of a uniform distribution of centres of activity, falls off as the pressure of the poison increases. Such evidence alone is thus valueless to show the presence of a distribution of centres of activity. The relation for unimolecular reaction shows the fall in the efficiency still more plainly, and it is probable that quite a number of bimolecular reactions follow this simple law.

Thus, in the simple unimolecular formula (2), unless it be shown definitely that λ is variable with x , it cannot be deduced from evidence of this type that there is a distribution of centres of catalytic activity over the surface.

Pease and Stewart have made deductions of this nature from observations of the pressure of carbon monoxide and the corresponding reduction in the rate of hydrogenation of ethylene by copper in a closed vessel. Their results show that λ is variable in formula (2).

TABLE I. *Showing the variation of λ with x .*

Volume of carbon monoxide in catalyst bulb, i.e. kx where k is constant	Fractional activity of catalyst	$\frac{1/v - 1}{x} = 1/k\lambda$
0.05	0.108	165
0.08	0.092	123
0.33	0.084	33
0.69	0.077	17
1.97	0.050	9.6
9.14	0.013	8.5

The interpretation to be placed on the variation in λ is that the mean life of the carbon monoxide molecule relative to the reactants is many times greater on the most active centres than it is on the least active. If $1/v$ be plotted against x , these data give a straight line which cuts the x axis at a value of $x = 0.88$. The behaviour of the surface therefore approximates to that of a homogeneous distribution of centres once the most active portions of the surface are covered. The results below are calculated assuming the initial activity to be 0.12. They show an agreement with the values to be expected for homogeneous distribution which is good considering the experimental errors in the measurement of the pressure of the poison.

TABLE II. *Showing the approximate constancy of λ when the most active centres are poisoned.*

Fractional reaction velocity	Calculated fractional reaction velocity from $1/v = 1 + 0.88x$	x
1.00	1.00	0.00
0.90	0.96	0.05
0.77	0.93	0.08
0.70	0.79	0.33
0.64	0.62	0.69
0.42	0.36	1.97
0.11	0.11	9.14

The ratio of the greatest value of $k\lambda$ in Table I (165) to the value in Table II (0.88) shows that the carbon monoxide molecule occupies the most active centres very much longer than the reacting gases; while on the less active centres the mean life of the carbon monoxide molecules is comparable with that of the reactive gases. The observations of Pease and Stewart thus show clearly that a great difference exists between the surface fields of force on the centres of activity involved in the two cases.