

catalyst could be developed than those we have at present.

### Summary

In order to find the optimum alkali promoter concentration for iron synthetic ammonia catalysts, a series of doubly promoted catalysts was prepared by treating an aluminum oxide promoted catalyst with potassium hydroxide solutions of varying strengths. By adsorption meas-

urements the total surface areas and the surface concentrations of the promoters were determined for each catalyst, and the effects of temperature and gas composition on the kinetics of ammonia decomposition were investigated. The most active catalyst toward ammonia decomposition was obtained when about 30% of the catalyst surface was covered by the alkali promoter.

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## Adsorption of Nitrogen and the Mechanism of Ammonia Decomposition Over Iron Catalysts\*

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Since Taylor<sup>1</sup> advanced the concept of activated adsorption, a number of attempts have been made to show that adsorption and desorption processes constitute the rate determining step in certain catalytic reactions. One of the most interesting among these attempts is a recent theoretical treatment of the decomposition of ammonia that was proposed by Temkin and Pyzhev.<sup>2</sup> They adopted the conventional idea that the rate determining step was the desorption of nitrogen molecules from the surface but in their treatment of the problem they introduced a novel assumption. They discarded the generally held concept that the rate of desorption varies linearly with the fraction of the surface covered by adsorbed gas and assumed instead an exponential relationship, originally proposed by Langmuir<sup>3</sup>

$$w = k_d e^{h\theta} \quad (1)$$

where  $w$  is the rate of desorption,  $\theta$  is the fraction of the surface covered with adsorbed gas, and  $k_d$  and  $h$  are constants. A corresponding equation for the rate of adsorption was first obtained by Zeldowitsch.<sup>4</sup>

$$z = k_a p e^{-g\theta} \quad (2)$$

where  $z$  is the rate of adsorption,  $p$  is the pressure, and  $k_a$  and  $g$  are constants. Although these two equations were applied with success to a few cases of adsorption and desorption, it is obvious that

Eq. (1) breaks down for low values of  $\theta$  and Eq. (2) for high values of  $\theta$ . The rate of adsorption should be zero when  $\theta = 1$ , and the rate of desorption should be zero when  $\theta = 0$ . These conditions are not fulfilled by the two equations.

At equilibrium the rate of adsorption is equal to the rate of desorption. If one equates (1) and (2), one obtains the adsorption isotherm equation

$$\theta = (1/f) \ln a_0 p \quad (3)$$

where  $f$  and  $a_0$  are constants. This equation was first published by Frumkin and Slygin,<sup>5</sup> who credited Temkin with its derivation, but to our best knowledge the derivation has not been published to date. Equation (3) is not valid for either small or large adsorptions since it does not reduce to  $\theta = 0$  for  $p = 0$ , nor to  $\theta = 1$  for very large values of  $p$ . It is valid only in the middle range of adsorption, as will be shown later.

If the slow step in the decomposition of ammonia over iron catalysts is the rate of escape of nitrogen from the surface, then the rate of desorption as given by (1) can express the rate of ammonia decomposition. In this case  $\theta$  is the fraction of the surface covered by adsorbed nitrogen. The value of  $\theta$  is obtained from Eq. (3). Substituting (3) into (1), we get

$$-\frac{dP_{\text{NH}_3}}{dt} = w = k_d e^{(h/f) \ln a_0 p} \quad (4)$$

In the calculation of  $p$ , the equilibrium pressure of nitrogen, Temkin and Pyzhev adopted the assumption of Winter,<sup>6</sup> namely, that the amount of nitrogen on the surface is determined by the

\* A part of this paper is from the thesis of Robert G. Keenan, presented to the Faculty of the George Washington University in part satisfaction of the requirements for the degree of Master of Science. Not copyrighted.

(1) Taylor, *THIS JOURNAL*, **53**, 578 (1931).

(2) Temkin and Pyzhev, *Acta Physicochim.*, U. R. S. S., **12**, 327 (1940).

(3) Langmuir, *THIS JOURNAL*, **54**, 2798 (1932).

(4) Zeldowitsch, *Acta Physicochim.*, U. R. S. S., **1**, 449 (1934).

(5) Frumkin and Slygin, *ibid.*, **3**, 791 (1935).

(6) Winter, *Z. phys. Chem.*, **B13**, 401 (1931).

equilibrium with hydrogen and ammonia in the gas phase. Thus

$$p = P_{N_2} = K' P_{NH_3}^2 / P_{H_2}^3 \quad (5)$$

where  $K'$  is the equilibrium constant of the ammonia decomposition reaction. We may point out that this assumption is substantiated by the experimental results of Emmett and Brunauer,<sup>7</sup> who found that at high pressures the same amount of nitrogen is adsorbed from an equilibrium mixture of hydrogen, nitrogen and ammonia as from the equivalent partial pressure of pure nitrogen.

If Eq. (5) is substituted into (4), one obtains

$$- \frac{dP_{NH_3}}{dt} = k \left( \frac{P_{NH_3}^2}{P_{H_2}^3} \right)^{h/f} \quad (6)$$

The kinetic equation found by Winter<sup>6</sup> for the decomposition of ammonia over an aluminum oxide supported iron catalyst was explained by Temkin and Pyzhev with the help of the empirical assumption that  $h/f = 0.5$ . Following their method, Love and Emmett<sup>8</sup> accounted for the kinetics of ammonia decomposition over doubly promoted iron catalyst 931 by assuming that the value of  $h/f$  was 0.3. The introduction of an empirical factor into the theoretical treatment makes the derived kinetic expressions semi-empirical.

In the present paper, we first derive equations for the rates of adsorption and desorption, and for the adsorption isotherm that are more general than Eqs. (1), (2) and (3), but include those equations as special cases. We then show that these equations enable us to calculate the adsorption isotherms of nitrogen on iron catalysts from rates of adsorption data. Finally, we show that the empirical factors introduced by Temkin and Pyzhev<sup>2</sup> and by Love and Emmett<sup>8</sup> can be calculated theoretically if the adsorption data are available. These are available for the doubly promoted iron synthetic ammonia catalyst 931, and the calculated kinetic equation is in very good agreement with the experimental results.

**A. The Adsorption Isotherm Equation.**—Langmuir<sup>9</sup> showed that at equilibrium the adsorption of molecules can be represented by the equation

$$a_1(1 - \theta)p = b_1\theta e^{-q/RT} \quad (7)$$

where  $q$  is the heat of adsorption, and  $a_1$  and  $b_1$  are constants. In the derivation it is assumed that  $q$  is also constant over the surface. Solving for  $\theta$  one obtains

$$\theta = \frac{(a_1/b_1)e^{q/RT}p}{1 + (a_1/b_1)e^{q/RT}p} \quad (8)$$

This is the Langmuir adsorption isotherm equation.

Let us subdivide the surface into surface elements  $ds$ , and let us make the entire surface area  $s = 1$ . We also assume that each of the surface elements is partly covered and partly bare, and that the fraction of each element covered,  $\theta_s$ , is given by Eq. (8). Summing over the entire surface we obtain  $\theta$ , the fraction of the entire surface covered with adsorbed molecules

$$\theta = \int_0^1 \theta_s ds = \int_0^1 \frac{\frac{a_1}{b_1} e^{q/RT} p}{1 + \frac{a_1}{b_1} e^{q/RT} p} ds \quad (9)$$

If  $q$  is assumed to be constant, integration of Eq. (9) gives Eq. (8). If  $q$  varies over the surface, *i. e.*, if  $q = q(s)$ , integration of Eq. (9) does not give the Langmuir equation. The form of the equation will depend on the form of the function  $q(s)$ . Let us assume that the heat of adsorption is a linear function of  $s$ , or

$$q = q_0 - \alpha s \quad (10)$$

where  $q_0$  is the heat of adsorption on the bare surface, and  $q_0 - \alpha$  is the heat of adsorption on the last part of the surface covered. An example of such linear variation is found in Roberts'<sup>10</sup> measurements of the heats of adsorption of hydrogen on tungsten. Substituting (10) into (9) we obtain

$$\theta = \int_0^1 \frac{a_0 e^{-\alpha s/RT} p}{1 + a_0 e^{-\alpha s/RT} p} ds \quad (11)$$

where the constant  $a_0$  is given by

$$a_0 = \frac{a_1}{b_1} e^{q_1/RT} \quad (12)$$

Integrating Eq. (11) and substituting the limits, we get

$$\theta = \frac{RT}{\alpha} \ln \frac{1 + a_0 p}{1 + a_0 e^{-\alpha/RT} p} \quad (13)$$

In the range of adsorption where  $a_0 p \gg 1 \gg a_0 e^{-\alpha/RT} p$ , we can neglect 1 in the numerator and  $a_0 e^{-\alpha/RT} p$  in the denominator, and get

$$\theta = \frac{RT}{\alpha} \ln a_0 p \quad (14)$$

This equation is identical with Temkin's Eq. (3) if we set

$$1/f = RT/\alpha \quad (15)$$

It should be noted, however, that while Temkin's equation is valid only in the middle range of adsorption, Eq. (13) is valid for the entire adsorption

(7) Emmett and Brunauer, *This Journal*, **56**, 35 (1934).

(8) Love and Emmett, *ibid.*, **63**, 3297 (1941).

(9) Langmuir, *ibid.*, **40**, 1361 (1918).

(10) Roberts, *Proc. Roy. Soc. (London)*, **A152**, 445 (1935).

isotherm. For  $p = 0$ , it reduces to  $\theta = 0$ , and for very large values of  $p$  we can neglect 1 both in the numerator and denominator, obtaining  $\theta = 1$ .

**B. The Rate of Adsorption and Desorption.**—The rate of desorption in general may be expressed by the equation

$$w = b\theta e^{-E_d/RT} \quad (16)$$

where  $E_d$  is the energy of activation of the desorption process. This expression was first proposed by Taylor.<sup>1</sup> Although for the sake of convenience  $E_d$  was usually treated as a constant, it is a well-known experimental fact that it varies considerably over the surface.

We shall now remove the restriction regarding the constancy of  $E_d$  over the surface and derive an equation for the rate of desorption from a heterogeneous surface. We subdivide again the surface into surface elements  $ds$ , and make the entire surface again  $s = 1$ . The correct procedure now would be to start with a partial coverage of each surface element  $ds$ , equal to  $\theta_s$  in Eq. (9), then solve a desorption equation separately for each surface element, and finally integrate over all of the surface elements. However, this would lead to an integral that cannot be evaluated in a closed form. We adopt therefore an approximation method that leads to a simple expression, and is likely to be valid in many cases.

Let us assume first that the desorption has proceeded for some time. If the variation of  $E_d$  over the surface is not too small, then the parts of the surface having lower  $E_d$  values will lose the adsorbed gas much faster than the parts where  $E_d$  is higher. Since it is also true that the surface elements having high  $E_d$  values have high heats of adsorption as well,<sup>11</sup> the regions least affected by desorption will be those that come closest to being completely covered at equilibrium. It will therefore be permissible in many cases to assume that during the process of adsorption the surface may be subdivided into two parts: an almost completely covered part, and an almost completely bare part. One may then replace Eq. (16) by an integral in which  $E_d$  is assumed to be variable, and the integration is to be carried out over that part of the surface which is assumed to be almost completely covered. Thus the integra-

(11) Practically all experimental evidence points in the direction that the parts of the surface having the largest heats of adsorption have the smallest energies of activation of adsorption. Since the energy of activation of desorption is the sum of the heat of adsorption and the energy of activation of adsorption, it follows that the parts of the surface having the largest energies of activation of desorption have also the largest heats of adsorption.

tion is to be extended from  $s = 0$  to the highest value of  $s$  that still corresponds to the covered region. This highest value is equal to  $\theta$ , the fraction of the surface covered at the instant of consideration.

$$w = \int_0^\theta b e^{-E_d/RT} ds \quad (17)$$

If  $E_d$  is constant over the surface, the integration of Eq. (17) gives Eq. (16). If, however,  $E_d = E_d(s)$ , the integration gives a different expression.

Let us assume that  $E_d$  decreases linearly with  $s$ , or

$$E_d = E_d^0 - \beta s \quad (18)$$

Substituting (18) into (17) we get

$$w = b e^{-E_d^0/RT} \int_0^\theta e^{\beta s/RT} ds \quad (19)$$

Integrating and substituting the limits we obtain

$$w = b e^{-E_d^0/RT} (RT/\beta) (e^{\beta\theta/RT} - 1) \quad (20)$$

For  $\theta = 0$ ,  $w$  reduces to zero, and for  $\theta = 1$ ,  $w$  reaches its maximum value. For sufficiently large values of  $\theta$ , the  $-1$  in the brackets can be neglected, and Eq. (20) reduces to Langmuir's exponential desorption Eq. (1) with

$$k_d = b e^{-E_d^0/RT} (RT/\beta) \quad (21)$$

and

$$h = \beta/RT \quad (22)$$

It should be remembered that Eq. (20) is a good enough approximation only if the variation of  $E_d$  over the surface is not too small; in other words, if  $\beta$  is sufficiently large.

The derivation of the rate of adsorption equation is completely analogous to the derivation of the rate of desorption equation. The original equation proposed by Taylor is

$$z = ap(1 - \theta)e^{-E_a/RT} \quad (23)$$

In place of this we adopt the equation

$$z = \int_\theta^1 a p e^{-E_a/RT} ds \quad (24)$$

We assume a linear increase with  $s$  in the energy of activation of the adsorption

$$E_a = E_a^0 + \gamma s \quad (25)$$

Substituting and integrating between the limits  $\theta$  and 1 we obtain the equation

$$z = a p e^{-E_a^0/RT} (RT/\gamma) (e^{-\gamma\theta/RT} - e^{-\gamma/RT}) \quad (26)$$

For  $\theta = 1$ ,  $z$  reduces to zero, and for  $\theta = 0$ ,  $z$  reaches its maximum value. For sufficiently small values of  $\theta$  the term  $-e^{-\gamma/RT}$  can be neglected

and Eq. (26) reduces to the exponential Eq. (2) of Zeldowitsch with

$$k_a = ae^{-E_a^0/RT}(RT/\gamma) \quad (27)$$

and

$$k_d = \gamma/RT \quad (28)$$

Thus the isotherm Eq. (13), the rate of adsorption Eq. (26) and the rate of desorption Eq. (20) under certain conditions reduce to Eqs. (3), (2) and (1), respectively. Within the limitations imposed upon them by the assumptions used in their derivations, Eqs. (13), (20) and (26) are valid in the entire range of adsorption, whereas Eqs. (1), (2) and (3) only in the ranges previously discussed. In the derivations the underlying assumptions were that the surface of the adsorbent is not homogeneous, and that the heat of adsorption and the energies of activation of desorption and adsorption exhibit the linear dependence expressed in Eqs. (10), (18) and (25), respectively.

Even if the surface of an adsorbent is entirely homogeneous, one can still obtain for the rates of adsorption and desorption exponential variation with the fraction of the surface covered, if one assumes forces of attraction or repulsion between the adsorbed molecules or atoms.<sup>12</sup> The instantaneous rate of desorption is again given by Eq. (16). If we assume that the forces are repulsive, the energy of activation of desorption from the covered surface will be smaller than that from the bare surface. The decrease in the energy of activation will be proportional to the number of molecules on the surface, or to  $\theta$ . If it is assumed that the variation with  $\theta$  is linear, we may write

$$E_d = E_d^0 - \beta\theta \quad (29)$$

Substituting (29) into (16) we obtain for the rate of desorption

$$w = b\theta e^{-(E_d^0 - \beta\theta)/RT} \quad (30)$$

or rearranging

$$w = be^{-E_d^0/RT}\theta e^{\beta\theta/RT} \quad (31)$$

By similar argument one obtains for the rate of adsorption

$$z = a\theta e^{-E_a^0/RT}(1 - \theta)e^{-\gamma\theta/RT} \quad (32)$$

As  $\theta$  approaches 1, Eq. (31) reduces to Eq. (1), and as  $\theta$  approaches 0, Eq. (32) reduces to Eq. (2).

When equilibrium is reached the rate of adsorption is equal to the rate of desorption. One

can therefore calculate the isotherm equation from Eqs. (20) and (26), or from Eqs. (31) and (32). Using the former pair one obtains

$$a\theta e^{-E_a^0/RT}(RT/\gamma)(e^{-\gamma\theta/RT} - e^{-\gamma/RT}) = b e^{-E_d^0/RT}(RT/\beta)(e^{\beta\theta/RT} - 1) \quad (33)$$

If  $\beta$  and  $\gamma$  are reasonably large and  $\theta$  is not too close to either 0 or 1, we can neglect the terms  $-e^{-\gamma/RT}$  and  $-1$ . Rearranging we get

$$(a/b)e^{(E_d^0 - E_a^0)/RT}(\beta/\gamma)\theta = e^{(\beta + \gamma)\theta/RT} \quad (34)$$

Furthermore, since

$$E_d^0 - E_a^0 = q_0 \quad (35)$$

and

$$\beta + \gamma = \alpha \quad (36)$$

we can substitute these into Eq. (34), and obtain

$$(a/b)e^{q_0/RT}(\beta/\gamma)\theta = e^{\alpha\theta/RT} \quad (37)$$

Taking logarithms one gets Temkin's equation

$$\ln a_0\theta = \alpha\theta/RT \quad (38)$$

The meaning of  $a_0$  is now somewhat different from that given in (12)

$$a_0 = (a/b)e^{q_0/RT}(\beta/\gamma) \quad (39)$$

The additional factor of  $\beta/\gamma$  has the order of magnitude of unity. The difference between (39) and (12) is of course due to the different approximations involved in their derivations. The approximation involved in the derivation of (39) is not as good as that involved in the derivation of (12). The reason for this is that the derivation of (39) includes the rather drastic assumptions used in the derivations of Eqs. (20) and (26).

One can derive the isotherm equation for the case of repulsion between the adsorbed molecules by equating the rates of adsorption and desorption expressed in Eqs. (32) and (31)

$$a\theta e^{-E_a^0/RT}(1 - \theta)e^{-\gamma\theta/RT} = b e^{-E_d^0/RT}\theta e^{\beta\theta/RT} \quad (40)$$

Rearranging and substituting according to Eqs. (35) and (36) we obtain

$$(a/b)e^{q_0/RT}\theta = [\theta/(1 - \theta)]e^{\alpha\theta/RT} \quad (41)$$

Equation (41) cannot be solved explicitly for  $\theta$  but it can be solved for  $p$

$$p = [\theta/a_0(1 - \theta)]e^{\alpha\theta/RT} \quad (42)$$

where  $a_0$  has the same meaning as in Eq. (12).

An isotherm, formally the same as (42), was derived by R. H. Fowler<sup>13</sup> on the basis of statistical mechanics, and by Laidler, Glasstone and Eyring<sup>14</sup> on the basis of the theory of absolute reaction rates. It should be noted that when  $\theta = 0.5$ , the

(13) Fowler, *Proc. Camb. Phil. Soc.*, **32**, 144 (1936).

(14) Laidler, Glasstone and Eyring, *J. Phys. Chem.*, **8**, 659 (1940).

(12) This was realized by Temkin and Pyzhev also

fraction  $\theta/(1 - \theta) = 1$ , and Eq. (42) reduces to Temkin's Eq. (3).

If the forces between the adsorbed particles are attractive instead of repulsive, one obtains an equation of the same form as (42), except  $\alpha$  in the exponent is replaced by  $-\alpha$ .

We may summarize now the foregoing discussion. We have derived equations for the adsorption isotherm, the rate of adsorption and the rate of desorption for the cases (1) when the surface is heterogeneous, and the heat of adsorption and the energies of activation of adsorption and desorption exhibit linear variations between their maximum and minimum values, and (2) when there are forces of attraction or repulsion between the adsorbed particles, and the heat of adsorption and the energies of activation of adsorption and desorption vary linearly with the fraction of the surface covered. The two isotherm Eqs. (13) and (42) reduce to Temkin's Eq. (3) in the middle adsorption range, the two rate of desorption Eqs. (20) and (31) reduce to Langmuir's exponential Eq. (1) when  $\theta$  approaches 1, and the two rate of adsorption Eqs. (26) and (32) reduce to Eq. (2) of Zeldowitsch when  $\theta$  approaches 0.

**C. Calculation of the Adsorption Isotherm from the Rate of Adsorption.**—It is now a generally recognized fact that the surfaces of catalysts are strongly heterogeneous. We see no *a priori* reason why the heat of adsorption for any gas over a certain surface should show an exactly linear decrease from a maximum to a minimum value, but often physical regularities or even irregular variations can be approximated fairly closely by a straight line function. If the deviation from linearity is not too great we would expect that Eq. (13) should give a good fit for the adsorption isotherm. If the variation of the energy of activation of adsorption is also approximately linear, then Eqs. (20) and (26) should also be obeyed. This appears to be the situation for the activated adsorption of nitrogen by the doubly promoted iron synthetic ammonia catalyst 931. The rate of adsorption as well as the equilibrium adsorption of nitrogen on this catalyst were investigated by Emmett and Brunauer.<sup>7</sup> We shall show now that if the rate of adsorption is known at a certain temperature, the adsorption isotherm at the same temperature can be calculated with the help of the equations discussed in the previous section.

The net rate of adsorption of a gas on a surface

is actually the difference between the rate of adsorption and the rate of desorption. If  $\theta$  is not too close to either 0 or 1 we may write<sup>15</sup> on the basis of Eqs. (26) and (20)

$$\frac{d\theta}{dt} = ap e^{-E_a^0/RT} (RT/\gamma) e^{-\gamma\theta/RT} - be^{-E_d^0/RT} (RT/\beta) e^{\beta\theta/RT} \quad (43)$$

The fraction of the surface covered is

$$\theta = v/v_m \quad (44)$$

where  $v$  is the volume of gas adsorbed at time  $t$  and pressure  $p$ , and  $v_m$  is the volume of gas necessary to cover the entire surface with a unimolecular adsorbed layer. Substituting into Eq. (43) we obtain

$$dv/dt = k_a p v_m e^{-\gamma v/v_m RT} - k_d v_m e^{\beta v/v_m RT} \quad (45)$$

where  $k_a$  and  $k_d$  are constants, as a comparison with (43) shows. Actually Eq. (45) has four constants that can be evaluated from the experimental rate curve:  $k_a v_m$ ,  $k_d v_m$ ,  $\gamma/v_m$  and  $\beta/v_m$ . At the beginning of the adsorption, *i. e.*, for small values of  $t$ , the rate of desorption may be neglected as a first approximation. Plotting the logarithm of the rate against the volume adsorbed one should then obtain a straight line, the intercept and slope of which give the two adsorption constants,  $k_a v_m$  and  $\gamma/v_m$ . Substituting these constants into the values of the rates of adsorption in the vicinity of equilibrium, *i. e.*, where the rate of desorption is large, one can obtain the two other constants. The four constants can be then improved by successive approximations until the best fit of the experimental curve is obtained.

As an example the constants were calculated from the rate of adsorption curve of nitrogen on doubly promoted iron catalyst 931 (1.3%  $Al_2O_3$ , 1.6%  $K_2O$ ) at 397° (ref. 7, Fig. 2, Run 10). Table I gives the values of the constants and the rates calculated by means of Eq. (45). One can get an equally good fit for the entire measurable adsorption range for the 405° rate curve also. On the other hand it is impossible to evaluate the constants from the two rate curves obtained in the neighborhood of 450°, because the initial adsorption was too rapid.

As Table I shows, the rate of adsorption decreases very rapidly. In the measurable range the rate decreases 50-fold. Equation (45) reproduces

(15) This assumption, of course, brings us back to Temkin's Eqs. (1), (2) and (3). Equations (43), (45) and (46) are merely more explicit forms of Eqs. (1), (2) and (3), with the meaning of the six constants,  $k_a$ ,  $k_d$ ,  $h$ ,  $p$ ,  $f$  and  $\alpha$  clarified by the derivations given in the present paper.

TABLE I  
ADSORPTION OF NITROGEN ON CATALYST 931 AT 397° AND  
752 MM.

$k_a v_m = 0.0200$ ;  $k_d v_m = 0.000957$ ;  $\gamma/v_m = 2100$  calories;  
 $\beta/v_m = 800$  calories.

$v$ , cc. at S. T. P.	$dv/dt$ (obs.), cc. at S. T. P. per min.	$dv/dt$ (calcd.), cc. at S. T. P. per min.
1.90	0.74	0.75
2.05	.61	.59
2.20	.49	.46
2.35	.37	.37
2.50	.29	.29
2.65	.24	.23
2.80	.20	.18
2.95	.16	.14
3.10	.12	.11
3.25	.083	.084
3.40	.062	.063
3.55	.049	.048
3.85	.027	.025
4.00	.016	.016

this decrease quite accurately, as the third column of the table shows. The more interesting fact is, however, that using the same constants that were evaluated from the rate curve, one can calculate the adsorption isotherm with surprising accuracy. Moreover, using the same constants one can deduce the correct kinetic equation for the rate of decomposition of ammonia on the same catalyst and at the same temperature, as will be seen later.

At equilibrium  $dv/dt = 0$ , it follows therefore from Eq. (45) that the two terms on the right side of the equation are equal. Rearranging terms we obtain the isotherm equation

$$\ln p = \ln \frac{k_d}{k_a} + \frac{\beta + \gamma}{v_m RT} v \quad (46)$$

A plot of  $\ln p$  against  $v$  should thus be a straight line. The intercept of the line can be calculated from two of the constants of Table I and the slope from the other two constants. Emmett and Brunauer<sup>7</sup> determined the adsorption isotherm of nitrogen on the same catalyst at 396° (Fig. 4 of their paper). Table II gives the observed and the calculated isotherm points. The very satisfactory agreement between theory and experiment gives considerable support to the belief that

TABLE II  
ADSORPTION ISOTHERM OF NITROGEN ON CATALYST 931  
AT 396°

$p$ , mm.	$v$ (obs.), cc. at S. T. P.	$v$ (calcd.), cc. at S. T. P.
25	2.83	2.88
53	3.22	3.22
150	3.69	3.70
397	4.14	4.15
768	4.55	4.45

the assumptions on the basis of which Eqs. (45) and (46) were derived are adequately fulfilled for the adsorption of nitrogen over the doubly promoted iron catalyst 931.

Emmett and Brunauer found that the isosteric heat of adsorption for nitrogen on catalyst 931 was 35,000 calories per mole between 2.6 and 3.6 cc. of gas adsorbed, and the value of  $q$  was constant within the experimental error. According to the above calculations, since  $(\beta + \gamma)/v_m = \alpha/v_m = 2900$  calories, the heat of adsorption should have decreased in the above range by 2900 calories. However, the experimental error in the determination of  $q$  was much too great to make this a serious objection to the correctness of the above considerations. The values of  $q$  were so strongly scattered that if we assume that  $q$  was equal to 35,000 cal. at an adsorption of 3.1 cc., the 1450 calories more at 2.6 cc., and the 1450 calories less at 3.6 cc. could easily have been missed.

We have made similar calculations for the adsorption of nitrogen on the singly promoted catalyst 921 (1.3%  $Al_2O_3$ ), also investigated by Emmett and Brunauer.<sup>7</sup> There was a rate of adsorption run available at 406° (Fig. 3, Run 1 in their paper), and an adsorption isotherm at 404° (Fig. 4). The isotherm calculated from the rate run showed almost as good agreement with the experimental isotherm as that shown in Table II for the doubly promoted catalyst.

In spite of the success of Eq. (45) in fitting Emmett and Brunauer's data for the rate of adsorption of nitrogen on iron catalysts, it must be pointed out that the use of the equation is limited by three assumptions used in its derivation.

(1) The variation in the energy of activation of adsorption and desorption can be expressed by the linear Eqs. (25) and (18), respectively.

(2) The change in the energy of activation of adsorption and desorption over the surface is steep ( $\beta$  and  $\gamma$  are large).

(3) The rate is measured in the middle range of adsorption ( $\theta$  is not too close to either 0 or 1).

Particularly assumption (2) limits the use of Eq. (45). Attempts to fit some of the rate of adsorption data of Taylor and Sickman<sup>16</sup> obtained for the adsorption of hydrogen on zinc oxide, and of Frazer and Heard,<sup>17</sup> obtained for the adsorption of oxygen on chromite catalysts, were not successful. It seems that the rate of adsorption did not

(16) Taylor and Sickman, *THIS JOURNAL*, **64**, 602 (1932).

(17) Frazer and Heard, *J. Phys. Chem.*, **42**, 855 (1938).

decrease as sharply over the surface as is demanded by Eq. (45). We intend later to derive equations that are valid for a more gradual decrease in the rate of adsorption.

**D. Calculation of the Kinetics of the Decomposition of Ammonia.**—The constants evaluated from the rate of adsorption curve at 397° and given in Table I enable us not merely to calculate the adsorption isotherm at that temperature, but also to calculate the kinetic equation for the decomposition of ammonia over catalyst 931. The slow step in the decomposition is assumed to be the desorption of nitrogen molecules from the surface which is given by

$$w = k_d e^{\beta\theta} / RT \quad (47)$$

We assume that the surface of the iron catalyst is heterogeneous and that the heat of adsorption decreases linearly from a maximum to a minimum value over the surface, as expressed by Eq. (10). Furthermore, because of the very strong variation of  $q$  over the surface, ( $\alpha/v_m = 2900$  calories), we can use the Temkin Eq. (3) instead of Eq. (13) over almost the entire adsorption range. Thus  $\theta$  is given by Eq. (14)

$$\theta = (RT/\alpha) \ln a_0 P_{N_2} \quad (48)$$

where  $P_{N_2}$  is the partial pressure of nitrogen in equilibrium with  $\theta$ . Finally we assume with Temkin that  $P_{N_2}$  can be obtained from Eq. (5). Substituting we get

$$w = k_d e^{(\beta/\alpha) \ln a_0 K' (P_{NH_3}^2/P_{H_2}^3)} \quad (49)$$

or

$$w = k (P_{NH_3}^2/P_{H_2}^3)^{\beta/\alpha} \quad (50)$$

where  $k$  is given by

$$k = k_d (a_0 K')^{\beta/\alpha} \quad (51)$$

Equation (50) is identical with the equation derived by Temkin and Pyzhev for the kinetics of the ammonia decomposition except that they have used an empirical factor for the exponent instead of the theoretically correct expression  $\beta/\alpha$ .

Since adsorption data are available for doubly promoted iron catalyst 931, one can calculate at once the kinetic equation for the rate of ammonia decomposition over this catalyst. From the constants of Table I it follows that  $\beta/\alpha = \beta/(\beta + \gamma) = 800/2900 = 0.276$ . Substituting this value into Eq. (50) we obtain

$$w = k \frac{P_{NH_3}^{0.56}}{P_{H_2}^{0.83}} \quad (52)$$

The kinetic expression found by Love and Emmett was

$$-\frac{dP_{NH_3}}{dt} = k \frac{P_{NH_3}^{0.60}}{P_{H_2}^{0.85}} \quad (53)$$

The agreement between the theoretical and the experimentally found mechanism is well within the experimental error.

In the previous section it was mentioned that the adsorption isotherm can be calculated from the rate curve for singly promoted catalyst 921 also. Although the kinetics of ammonia decomposition over this catalyst was never investigated, there is good reason to believe that it would be similar to the kinetics exhibited by two other singly promoted catalysts, 954 and 191, investigated by Love and Emmett<sup>8</sup> and Love and Brunauer.<sup>18</sup> The rate of ammonia decomposition over these catalysts shows a very complex dependence on the partial pressures of hydrogen and ammonia, and on the temperature. It seems that at lower temperatures the reaction proceeds by a different mechanism, in which the slow step is not the desorption of the nitrogen from the surface. However, at higher temperatures the mechanism of the decomposition is probably the same as on the doubly promoted catalyst, so there the considerations advanced above ought to apply.

The apparent energy of activation of the decomposition of ammonia over doubly promoted catalyst 931 can also be calculated by a method similar to that outlined by Temkin and Pyzhev.<sup>2</sup> It is obtained from the temperature coefficient of the rate constant  $k$  by the equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (54)$$

Substituting for  $k$  from (51) one gets

$$\frac{E}{RT^2} = \frac{d \ln k_d}{dT} + \frac{\beta}{\alpha} \left( \frac{d \ln a_0}{dT} + \frac{d \ln K'}{dT} \right) \quad (55)$$

The expressions for  $k_d$ ,  $a_0$  and  $K'$  were given in Eqs. (21), (12) and (5). If it is assumed that in these equations the temperature dependence of all other terms is small compared with the temperature dependence of the exponential terms, one gets

$$\frac{E}{RT^2} = \frac{E_d^0}{RT^2} - \frac{(\beta/\alpha)q_0}{RT^2} + \frac{(\beta/\alpha)Q}{RT^2} \quad (56)$$

where  $Q$  is the heat of the ammonia decomposition for two moles of ammonia, *i. e.*, 25,000 calories.

The values of  $E_d^0$  and  $q_0$  can be obtained by ex-

(18) Love and Brunauer, *THIS JOURNAL*, **64**, 745 (1942).

trapolation from the adsorption data of Emmett and Brunauer. The value of  $q$  is 35,000 calories at 3.1 cc. of nitrogen adsorbed, and since  $\alpha/v_m = 2900$  calories,  $q_0 = 35,000 + (3.1)(2900) = 44,000$  calories. Using the experimental values of  $E_a$ , and  $\gamma/v_m = 2100$  calories, one obtains by extrapolation for  $E_a^0 = 10,800$  calories per mole. Thus  $E_d^0 = 54,800$  calories. Substituting into (56) one gets

$$E = 54,800 - (0.276)(44,000) + (0.276)(25,000) = 49,500 \text{ cal./mole}$$

If instead of Eq. (48) we use the more correct Eq. (13) to express  $\theta$ , we obtain for the apparent energy of activation of the ammonia decomposition the equation

$$E = E_d^0 - \frac{\beta}{\alpha} q_0 + \frac{\beta}{\alpha} Q - \frac{\beta}{\alpha} \left( \frac{a_0 p e^{-\alpha/RT}}{1 + a_0 p e^{-\alpha/RT}} \right) (\alpha - q_0 + Q) \quad (57)$$

In the derivation of this equation we have neglected 1 in the numerator in comparison with  $a_0 p$  in Eq. (13). The first three terms on the right side of Eq. (57) are the same as in Eq. (56). The other terms in the present case amount at most only to about 500 calories. Thus the calculated value of the apparent energy of activation of the decomposition of ammonia over doubly promoted iron catalyst 931 is approximately 49,000 calories per mole. This is to be compared with the experimentally determined value of 45,600  $\pm$  2000 calories per mole, obtained by Love and Emmett.<sup>8</sup> The agreement may be considered fair, since in the calculation of  $E$  the temperature dependence of all but the exponential terms was neglected.

In conclusion we wish to express our great indebtedness to Professor Edward Teller of George Washington University for the help and criticism he gave us in the preparation of this paper.

### Summary

1. Equations were derived for the rate of adsorption, the rate of desorption and the adsorption isotherm for the cases (a) when the surface is heterogeneous, and the heat of adsorption and the energies of activation of adsorption and desorption exhibit linear variations between their maximum and minimum values, and (b) when there are forces of attraction or repulsion between the adsorbed particles, and the heat of adsorption and the energies of activation of adsorption and desorption vary linearly with the fraction of the surface covered. It was shown that these equations in the appropriate adsorption regions reduce to the equations published by Temkin and Pyzhev.

2. With the help of these equations adsorption isotherms of nitrogen on iron catalysts were calculated from rates of adsorption data. The calculated isotherms show very good agreement with the experimental isotherms.

3. Using the constants evaluated from rates of adsorption data, a kinetic equation was derived for the rate of ammonia decomposition on doubly promoted iron catalyst 931 that agrees well with the experimentally found equation. An approximately correct value for the apparent energy of activation of the decomposition was also obtained from the adsorption data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

## Molal Volumes of Solutes. VI. Potassium Chlorate and Hydrochloric Acid

BY O. REDLICH AND J. BIGELEISEN<sup>1</sup>

In the fourth paper of this series<sup>2</sup> the available precise data of molal volumes of electrolytes at low concentrations have been reviewed. It was concluded that this material definitely confirms the limiting law previously derived from the theory of Debye and Hückel. However, as the experimental basis is small, new data are desirable, especially in view of some objections which

have been raised against the validity of the limiting law. Moreover, accurate data properly extrapolated will be useful in several questions: first, in a systematic classification of the individual deviations from the limiting laws occurring in the thermodynamic properties at moderate concentrations; second, in efficient tests of Born's equation as carried out for acetic acid in the fifth paper<sup>3</sup> of this series. Finally, according to Fajans,<sup>4</sup> we

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(2) O. Redlich, *J. Phys. Chem.*, **44**, 619 (1940).

(3) O. Redlich and J. Bigeleisen, *Chem. Rev.* (1942).

(4) K. Fajans, *J. Chem. Phys.*, **9**, 283 (1941).