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Kinetics of Chemisorption¹

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The Elovich equation $dq/dt = ae^{-\alpha q}$ where q is the amount chemisorbed at time t , and a and α are constants, is shown to be applicable to a large body of rate of chemisorption data. The significance of a and α is examined and shown to imply that the prime function of the gas, initially, is the production of surface sites which, over the course of the slow adsorption, decay at a bimolecular rate. The rate of slow chemisorption is governed solely by the availability of sites. Parallels to the proposed schemes are found in kinetics of luminescence and photoconductivity of solids.

1. Introductory

The activated adsorption of gases on solids which proceeds at a slow measurable rate is the simplest type of a heterogeneous surface reaction. Its kinetics over the course of the adsorption could therefore be expected to be relatively simple, and to be fundamental for the understanding of the kinetics of the heterogeneously catalyzed chemical reactions of which chemisorption obviously must be an essential element. Attempts to represent the sizable experimental data material by algebraic mass-action functions involving integral or fractional powers of the concentration or partial pressure of the adsorbable gas and a constant rate constant of a definite order have not on the whole been successful. More complex *ad hoc* rate laws involving corrective factors in terms of the surface coverage or even fractional powers of the time variable have been variously tried, but, apart from their lack of theoretical substantiation, their applicability is more often than not unconvincing and at best limited to one particular instance in each case. The fortuitous nature of such occasional fit is obvious.

In 1934, Zeldovich^{2a} and Zeldovich and Roginskii^{2b} found that the rate of adsorption of CO on finely divided MnO₂ between -78 and -39° decreases exponentially with the increase of the amount (or fraction) q of gas adsorbed,

$$dq/dt = ae^{-\alpha q} \quad (1)$$

with the exponent α remaining constant over the course of the process. That same equation was found by Elovich and Zhabrova³ to apply to up to 90–95% of the slow adsorptions of H₂ and of C₂H₄ on Ni reduced at low temperatures (250°), between -23 and +50°, and also to the rate of the hydrogenation reaction C₂H₄ + H₂ = C₂H₆ on the same catalyst. These authors also have indicated the procedure for testing equation (1) and for determining the parameters α and a from the experimental data. The integrated form of equation (1) can be written in the form

$$q = (2.3/\alpha) \log(t + t_0) - (2.3/\alpha) \log t_0 \quad (2)$$

$$\text{with } t_0 = 1/\alpha a \quad (3)$$

With a correctly chosen t_0 , the plot of q as a function

(1) Presented in part at the Symposium on Chemisorption of Gases on Solids conducted by the Division of Colloid Chemistry, Diamond Jubilee Meeting, New York, September 6, 1951.

(2) (a) Ya. Zeldovich, *Acta physicochim. (U.R.S.S.)*, 1, No. 3/4, 449 (1934); (b) S. Roginskii and Ya. Zeldovich, *ibid.*, 1, 554, 595 (1934).

(3) S. Yu. Elovich and G. M. Zhabrova, *Zhur. fiz. Khim.*, 13, 1761, 1775 (1939).

of $\log(t + t_0)$ should give a straight line with a slope = $2.3/\alpha$; equation (3) then gives a which obviously represents the initial rate of adsorption for $q = 0$. The test thus involves one single disposable parameter, t_0 , which is found by trial; with t_0 too small, the curve is convex, and with t_0 too large it is concave to the axis of $\log(t + t_0)$. This is illustrated in Fig. 1, drawn from the data of Burwell and Taylor⁴ for the adsorption of H₂ on Cr₂O₃ gel.

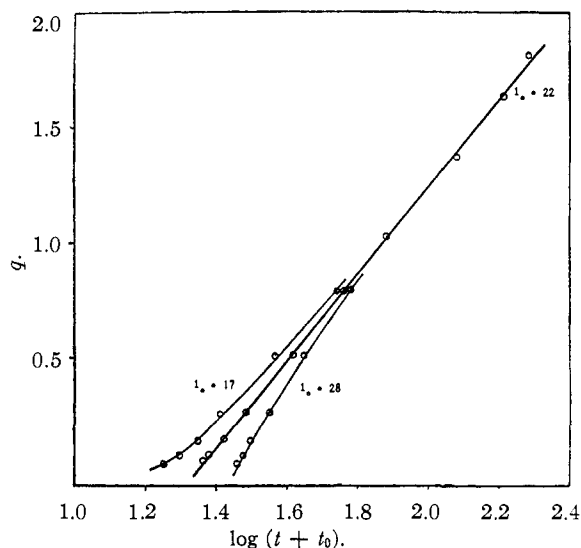


Fig. 1.— $q = \text{cc. (S.T.P.) H}_2$ on 1 g. of Cr₂O₃ gel; 0.5 atm.; 184°.

The simplicity of equation (1) and the ease of its verification prompted us to test it against the available experimental data of rates of adsorption. It developed that this equation is satisfactorily applicable to a very large body of data, covering an extended range of the whole course of the adsorption or reaction, and failing mostly only toward its end, where, incidentally, the experimental accuracy is often illusory. Deviations, other than those due to obvious uncertainties of the data, indicate intrinsic anomalies which partly can be correlated with anomalous effects established in other ways, partly raise new problems. The broad validity of equation (1) fully justifies its use as a normal standard against which to gauge significant and instructive anomalies of behavior. An attempt was further made to interpret the equation and its implications in the light of the concept of active centers and recent ideas on their dynamics, and to

(4) R. L. Burwell and H. S. Taylor, *THIS JOURNAL*, 58, 697 (1936).

point out correlations with allied manifestations of defect structures in the solid state.

2. Normal Isothermal Behavior

This is illustrated by Table I calculated from the data of Williamson and Taylor⁵ and by Fig. 2 representing the plot at 100°.⁶

°C.	Cc. (S.T.P.) t_0	α	10^{2a}	qt_0
100	7	8.5	1.64	0.14
132	4	7.0	3.60	.13

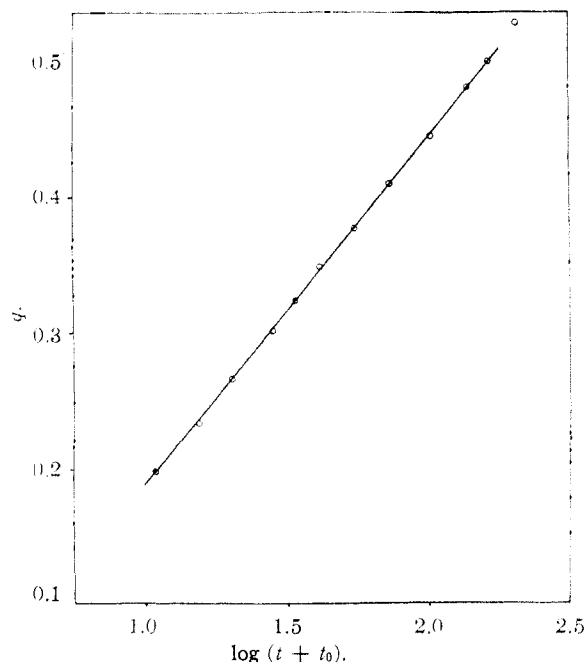


Fig. 2.— q = cc. (S.T.P.) H_2 on 1 g. of $2MnO \cdot Cr_2O_3$; 1 atm.; 100°.

The initial velocity a calculated from the correct t_0 by equation (3) is markedly less than the experimentally measured amount adsorbed over the first unit of time (from the first reading). This means that the slow adsorption, described by the kinetic law (1), is preceded by a very rapid massive initial adsorption. Its amount can be evaluated, as an approximation, from the Elovich plot by taking the value of q at the abscissa $\log t_0$, which amounts to an extrapolation to $t \rightarrow 0$; this extrapolated qt_0 is taken to represent the amount of the initial massive adsorption, *i.e.*, a rapid adsorption not governed by the exponential law. If one deducts this qt_0 from the observed "initial rate," the agreement with a calculated from t_0 becomes satisfactory. This initially massively adsorbed amount qt_0 is mostly nearly temperature-independent.

An occasionally occurring instance where this initial massive rapid adsorption goes over continuously into the subsequent slow adsorption and therefore cannot be separated therefrom by extrapolation to $t \rightarrow 0$, is illustrated by Table II, summarizing calculations on unpublished data of

(5) A. T. Williamson and H. S. Taylor, *THIS JOURNAL*, **53**, 2168 (1931).

(6) In this and the following tables, the units are: time in minutes, q in cc. (STP)/g., a in cc. (STP)/g./min., α in cc.⁻¹.

Decrue⁷ on adsorption of H_2 on $ZnO \cdot Cr_2O_3$, extended over up to 8,000 minutes and apparently up to quite close to completion.

°C.	Cc. (S.T.P.) t_0	α	10^{2a}	qt_0
80	15.0	37		0.73
110	11.6	7.3		.78
132	10.8	6.5		.82

Over at least 90% of the total measured adsorption (over practically the whole range at 80°) the plots appear practically rectilinear in the coordinates q , $\log t$, which means that t_0 is too small to be distinguishable from zero. The initial massive adsorption goes over continuously into the subsequent slow adsorption, and the whole of the course of the adsorption appears kinetically monotonous, apparently starting with a very high a . As a result of this "degeneracy," the undoubtedly present initially massively adsorbed amount cannot be isolated with the aid of an extrapolation. As the next best approximation, we take the amount qt_0 adsorbed over the first minute. In cases where t_0 is too small to be assigned a value, a is evaluated from $qt_0 = (1/\alpha) \ln(1 + \alpha a)$, with α read from the slope as usual.

Further instances where the equation (1) was found uneventfully applicable are the chemisorption of H_2 on Pt (Maxted and Moon⁸), H_2 and D_2 on Ni (Iijima⁹), C_2H_4 on Ni (Iijima¹⁰), O_2 on CoO (Frazer and Heard¹¹), H_2 on Cu (Kwan¹²), CH_4 on Ni (Kubokawa¹³).

3. Isothermal Anomalies

The data of Sickman and Taylor¹⁴ on adsorption of H_2 on ZnO (recalculated for 1 g. from original data on 20 g. of ZnO) yielded Table III.

°C.	Cc. (S.T.P.) t_0	α	10^{2a}	qt_0
110	10	24	0.4	0.12
(132)	3	20	1.5	.10
184	1.5	11.4	5.0	.06
(218)	0.2	11.0	18	0)

The data at 132 and at 218° were taken from graphs. An unmistakable anomaly, absent on the 110° graph, appears on the plot at 184° (Fig. 3). Here, the slope, and consequently α , changes abruptly at a stage corresponding to adsorption of 0.53 cc./g. (at 220 minutes) out of a total of 0.70 cc./g. followed (at 1160 minutes). Over the remainder of the process, the deceleration is distinctly slower than over the first 75% of the total adsorption measured. Such discontinuous breaks are found in some not very frequent instances. If α is a characteristic of the nature of the sites involved in the absorption, this discontinuity indicates a

(7) Jean Decrue, unpublished data, Princeton, June, 1951.

(8) B. Maxted and C. H. Moon, *J. Chem. Soc.*, 1542 (1936).

(9) S. Iijima, *Rev. Phys. Chem. Japan*, **12**, 1 (1938).

(10) S. Iijima, *ibid.*, **14**, 68 (1940).

(11) J. C. W. Frazer and L. Heard, *J. Phys. Chem.*, **42**, 865 (1938).

(12) T. Kwan, *J. Res. Inst. Catalysis (Japan)*, **1**, 95 (1949).

(13) M. Kubokawa, *Rev. Phys. Chem., Japan*, **12**, 157 (1938).

(14) D. V. Sickman and H. S. Taylor, *THIS JOURNAL*, **54**, 602 (1932).

changeover from one kind of sites to another at a certain stage of the adsorption. It is reminiscent of a similar manifestation of surface heterogeneity, also limited to no more than two kinds of adsorption sites, demonstrated in recent years by Liang and Taylor¹⁵ through desorption and readsorption isobars with rising and again falling temperature. Significantly, these determinations did reveal surface heterogeneity in the adsorption of H₂ on ZnO, but not in the case of 2 MnO·Cr₂O₃. This is in agreement with the absence of a break on the Elovich plots for the latter adsorbent (data of Williamson and Taylor³) as contrasted with its presence on ZnO (data of Sickman and Taylor¹⁴). The Elovich plots thus appear to reveal isothermally the same phenomenon which the Liang and Taylor curves reveal under isobaric conditions.

The "surface heterogeneity" manifested in these experiments involves two or a very few at most kinds of sites, and has nothing in common with the doctrine of "surface heterogeneity" put forward by Roginskii and his school, which assumes a spectral distribution of sites over activation energies according to a definite analytical distribution law. The present authors see no evidence for any such spectral distribution over activation energies of sites and take no cognizance of it.

A break identical with but somewhat less marked than that found on the 183° plot of Sickman and Taylor¹⁴ also appears in plotting the data of Strother and Taylor¹⁶ on the same gas and adsorbent, at the same temperature. Serious anomalies, involving either breaks in the opposite direction or even complete failure to yield a linear plot, appear in plotting high-temperature data, such as those of Strother and Taylor¹⁶ above 218°, or of Maxted and Moon⁸ at 306°. The suspicion that such deep anomalies may be connected with irreversible chemical reaction with the adsorbent is borne out by electron diffraction evidence of Ling Yang¹⁷ showing irreversible reduction H₂ + ZnO = H₂O + Zn above 300°.

4. Normal Temperature and Pressure Dependence

The temperature dependence of the rates of adsorption is determined by the variation with the temperature of the two parameters α and a . The typical normal behavior is illustrated by Table IV summarizing the results of our recalculation of the extensive data of Burwell and Taylor⁴ at different initial pressures p_0 .

A few facts, which also apply to the shorter tables given in the preceding, emerge clearly: (1) with rising temperature, α unmistakably decreases; (2) a increases with rising temperature, with an activation energy of the order of 10 kcal.; (3) allowing for the uncertainties of the extrapolation, the initial massive adsorption q_{t_0} increases with the temperature only slightly if at all; (4) at constant temperature, with decreasing initial pressure p_0 , there is a hint of a slight increase of α ; the initial a is approximately proportional to $p_0^{0.8}$

(15) S. C. Liang and H. S. Taylor, *THIS JOURNAL*, **69**, 1306 (1947).

(16) C. O. Strother and H. S. Taylor, *ibid.*, **66**, 586 (1934).

(17) Ling Yang, *J. Am. Electrochem. Soc.*, **97**, No. 4 (1950).

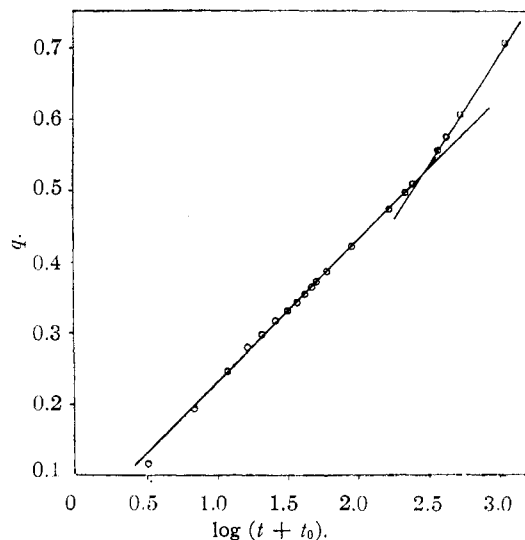


Fig. 3.— $q = \text{cc. (S.T.P.) H}_2 \text{ on 1 g. of ZnO; } 184^\circ$.

whereas q_{t_0} is almost strictly proportional to the initial p_0 .

TABLE IV

p_0 (atm.)	Cc. (S.T.P.) H ₂ adsorbed on 1 g. of Cr ₂ O ₃ ⁴ α °C.	α	$10^2 a$	$10^2 q_{t_0}$
1	154	2.7	1.7	9.3
1	184	1.05	3.3	13
1	218	0.9	12.5	16
0.5	110.5	15	0.20	6.7
.5	132	4.6	0.47	6.7
.5	154	3.2	0.80	7.4
.5	184	1.1	2.4	9.0
.5	218	0.20	6.7	(~20)
1	80	29	0.6	10 ^a
1	184	1.1	5.0	12.5
0.5	184	1.3	3.7	6.2
.25	184	1.4	2.0	3.6
.125	184	1.6	1.25	1.8

^a The data in the third group of Table IV refer to a different preparation.

Another example is the treatment of the data of Emmett and Brunauer¹⁸ on chemisorption of N₂ on Fe.

TABLE V

°C.	Cc. (S.T.P.) N ₂ on 1 g. of Fe ¹⁸ α	$10^2 a$	$10^2 q_1$
224	31	~1	2.4
271	30	16	5.45
328	32	47	8.5
330	30	68	10

The corresponding values of t_0 are, respectively, 4, 0.2, 0, 0. At 224°, a was determined both from $t_0 = 4$ and from q_1 , both determinations giving closely agreeing figures; at 271, 328 and 330°, a was determined from q_1 . The initially massively adsorbed amount is excluded from a at 224°, but included in it at the higher temperatures; hence the jump of a between 224 and 330°. The reproducibility of the original data is open to question in view of the surprisingly large jump of the adsorption in the two-degree interval between 328 and 330°, but the remarkable constancy of α is striking.

(18) P. H. Emmett and S. Brunauer, *THIS JOURNAL*, **56**, 35 (1934).

This magnitude can at most be temperature-independent, as in this instance, or else decrease with rising temperature, which is by far the more common behavior. The opposite behavior was never observed. Data of the same authors at 405 and at 450° cannot be fitted into any Elovich plot. Evidently, at these higher temperatures, the solid-gas interaction must be deeper than mere chemisorption. Parenthetically, the rate curve at 450 intersects the 405° curve.

5. Temperature Dependence Anomalies

Treatment of the data of Ogden and Taylor¹⁹ yields Table VI.

TABLE VI

°C.	Cc. (S.T.P.) α	H ₂ adsorbed on 1 g. of ZnO·MoO ₃ ¹⁹ 10 ^{2a}	10 ^{2q} t ₀
110	7.8	0.053	0.2
132	4.1	.16	.5
154	1.5	.60	.3
218	12	.15	.3
254	12	.50	.6

There is a distinct anomaly between 154 and 218°, with α recovering from its fall and jumping to a value nearly 10 times as great, and a decreasing with rising temperature. The reality of that anomaly is confirmed by data of Sastri and Ramanathan,²⁰ the treatment of which is shown in Table VII.

TABLE VII

°C.	Cc. (S.T.P.) α	H ₂ adsorbed on 1 g. of ZnO·MoO ₃ ²⁰ 10 ^{2a}	10 ^{2q} t ₀
184	16	0.54	7.6
250	6.0	2.5	10.7
300	9.2	0.47	25
350	9.5	0.31	44

Quantitative agreement cannot, of course, be expected, but the presence, between 250 and 300°, of an anomaly of the same type as that seen in Table VI is striking. These anomalies are obviously indicative of a change in the nature of the sites responsible for the chemisorption. The concept of an activation energy, even for the initial rates, clearly loses its meaning in these temperature ranges where a new kind of active sites comes into operation.

6. Significance of the Equation

The validity of equation (1) over an extended range of the slow chemisorption process, during which time the pressure of the adsorbable gas has varied considerably, indicates that of the two "reactants," gas and solid sites, it is the mass action of the latter only that determines the rate at each moment. The mass action of the gas determines the initial rate a . It is as if beyond that stage, in the following slow process, the sites were always in relatively much shorter supply as against a comparatively abundant supply of gaseous reactant, except, of course, in the final stages where depletion of the gas must make itself felt (and the $e^{-\alpha q}$ law fail). A proof of the relative unimpor-

tance of a variation of the amount of available gas at a stage where the decline of sites has already been under way, can be seen in experiments of Ogden¹⁹ in which the gas was being replenished at intervals; no changes of the rate are detectable in the Elovich plots at such points.

The implication of all these facts is that the rate of slow chemisorption is governed by the availability of sites and, further, that chemisorption eliminates sites over and beyond actual occupancy.

If the momentary rate of adsorption dq/dt is proportional to the momentary surface concentration n of active sites, plain molecule-per-site inactivation would call for $-dn/dq = \text{const.}$, and $n = n_0 - q$, *i.e.*, simple first-order kinetics of chemisorption, inconsistent with the observed $e^{-\alpha q}$ law. That law calls for

$$n = n_0 e^{-\alpha q} \quad (4)$$

where n_0 is the site density at $q \approx 0$; the corresponding differential equation is

$$-dn/dq = \alpha n \quad (5)$$

it expresses the fact that the decrease of n with increasing q is proportional to n . The rate of site incapacitation

$$-dn/dt = \alpha n (dq/dt) \quad (6)$$

which, on account of (4) can also be written²¹

$$-dn/dt = (\alpha a/n_0)n^2 \quad (7)$$

or, if the initial rate $a = k_0 n_0$

$$-dn/dt = k_0 \alpha n^2 \quad (8)$$

The alternative expressions (6) and (8) call to mind two possible pictures of the mechanism of site incapacitation through chemisorption. Equation (6) corresponds to multiple repeated site-molecule collisions, resulting in annihilation of a number of sites prior to definitive adsorption of the molecule, with α expressing the probability of successful annihilation. The form of equation (6) is that characteristic of one rate induced by another rate. Equation (8) reflects a bimolecular site-site interaction at the stage of slow adsorption. As the two expressions are formally interchangeable, they must correspond to basically one and the same process. To our minds, form (8) appears more instructive, on account of the correlations outlined in the following.

Circumstantial support for bimolecular site decay can be adduced from a field apparently distant but actually very closely akin to heterogeneous catalysis, that of luminescence of solid luminophors. Antonov-Romanovskii²² and Levshin²³ have established experimentally bimolecular (second-order) recombination kinetics for the decay of the active luminescence centers in ZnS-Cu and CaS-Sm phosphors. Bimolecular decay rate laws (second-order in center concentration) were also found to govern the rate of decay of the photoconductivity of at least certain typical impurity semiconductors (Gur-

(21) The significance of α can be seen from the formulation

$$\alpha = -(d \ln n/dt)/(dq/dt)$$

where α is a quotient of the relative rate of site disappearance and the rate of chemisorption.

(22) V. V. Antonov-Romanovskii, *Doklady A.N. SSSR*, **2**, 93 (1936).

(23) V. L. Levshin, *Acta Phys. Polon.*, **5**, 301 (1936); V. L. Levshin and E. R. Rikman, *Doklady A.N. S.S.S.R.*, **20**, 445 (1938).

(19) G. Ogden and H. S. Taylor, *Trans. Faraday Soc.*, **30**, 1178 (1934); G. Ogden, Thesis, Princeton, 1934.

(20) M. V. C. Sastri and K. V. Ramanathan, *J. Phys. Chem.*, **56**, 220 (1952).

evich, Tolstoi and Feofilov²⁴) and electron beam-induced electric conductivity (Arkhangelskaya and Bonch-Bruevich²⁵) all under conditions of sufficiently strong excitation, *i.e.*, sufficiently high initial concentration of active centers. All these instances are clearly analogs of our equation (8). A further analogy with the rate of decay of catalytically active centers is provided by the often observed "broken" decay of luminescence centers, *i.e.*, the existence of two (but never more than three) rectilinear portions of different slopes, reminiscent of our Fig. 3.

The analogy goes farther. In a search for the meaning of the *initial* rate of chemisorption, a , one is reminded of Volkenshtein's²⁶ novel theory of activated excitation of surface sites in the very process of adsorption. Assuming the rate of production of active centers, under the action of a chemisorbable gas under the pressure p to be $k(N - n)p$, where n is the momentary, and N the maximum possible site concentration, (hence $N - n$ the distance from the maximum, *i.e.*, the driving force) and the rate of the accompanying spontaneous decay, $k'n$, the condition of stationarity is

$$k(N - n)p = k'n \quad (9)$$

and hence the steady-state site concentration

$$n_0 = \frac{kNp}{kp + k'} \quad (10)$$

an expression which is numerically tantamount to some fractional-order $p^{1/m}$ ($m > 1$). The "initial" rate is proportional to n_0 , hence of the same fractional order $1/m$. Such empirical fractional-order initial rates of heterogeneous reactions are widespread, and, where there are sufficient data, seem to be the rule in chemisorption (see above, comments after Table IV).

It is understood that the establishment of the steady state must be very rapid, and be definitely completed at some near-initial stage. At the stage where sites are produced and multiply, their elimination by adsorptive occupation must be lagging far behind their fast multiplication. This is definitely a thing of the past at the time t_0 which marks the beginning of pure second-order *decay* of the sites explosively produced in the near-initial short incubation period. The main part of production of sites appears to have been largely completed at the very earliest stage, when the spontaneous decay is not yet significant: hence the practically first-order dependence of q_{t_0} on the gas pressure.

The assumption of a spontaneous first-order decay of newly produced sites during the formative stage, $k'n$, can also be supported by analogies with physical solid-defect phenomena. Whereas under sufficiently strong excitation, the decay of luminescence, photoconductivity, and cathodoconductivity, were generally found to be bimolecular with

respect to center concentration, the rate of decay on weak or short excitation, *i.e.*, at low center concentrations, tends to be unimolecular, as was shown by Antonov-Romanovskii,²⁷ Arkhangelskaya and Bonch-Bruevich,²⁵ and particularly convincingly by Krylova²⁸ who observed a changeover from second to first-order decay kinetics on the same phosphor, (ZnS·Zn, or ZnS·Cu, Co), depending on the amount of excitation energy supplied.

In chemisorption, this analogy-supported picture amounts to a quasi-explosive production of active sites upon contact with the adsorbable gas, offset by a first-order spontaneous decay, resulting in an "initial" steady-state site concentration, and marked at that stage by a more or less considerable "massively" adsorbed amount. From that point on, production of new sites having ceased definitely, slow adsorption sets in, with bimolecular disappearance of sites and correspondingly exponential decline of the rate of adsorption. The limit between the two stages can happen to be blurred to the point of continuous transition from one to the other; this case corresponds to the "degeneracy" where q_{t_0} cannot be exactly separated from the subsequent slow adsorption.

Bimolecular annihilation of sites is an analog of the pairing-up of conduction electrons into "doublets," theoretically shown by Volkenshtein and Bonch-Bruevich²⁹ to occur in ionic crystals at sufficiently high excess electron concentrations. The extension of that concept to bimolecular pairing-off of lattice defects, *i.e.*, catalytically active centers is obvious.

The conclusion that sites do not pre-exist on a surface, but are produced on contact between the solid and the gas, has also been reached, from other considerations, by Milliken, Mills and Oblad.³⁰

An interaction between sites in the course of the adsorption process can provide an alternative interpretation of the frequently observed fall of the differential heat of adsorption H with increasing q , usually accounted for on the assumption of a definite "distribution of sites over activation energies," or by a direct interaction between adsorbed molecules, not very probable at the sparse coverages involved in chemisorption. If H is composed of two terms, $H' + H''$, of which H' is the heat of the chemisorption proper, and constant, and H'' the heat evolved in the interaction between sites, the latter term ought to be proportional to n , hence $H'' = H_0'' e^{-aq}$, *i.e.*, decreasing with increasing q .

We wish to acknowledge our indebtedness to Dean Hugh S. Taylor for his lively interest from the beginning of this study, and his frequent pointers to sources and facts of activated adsorption.

NEW YORK, N. Y.

(27) V. V. Antonov-Romanovskii, *J. Phys. U.S.S.R.*, **6**, 120 (1942); **6**, 120 (1942), **7**, 153 (1943).

(28) E. S. Krylova, *Zhur. Ekspl. Teoret. Fiz.*, **20**, 905 (1950).

(29) F. F. Volkenshtein and V. L. Bonch-Bruevich, *ibid.*, **20**, 624 (1950).

(30) T. H. Milliken, Jr., G. A. Mills and A. G. Oblad, *Faraday Soc. Discussion*, 279 (1950).

(24) D. B. Gurevich, N. A. Tolstoi and P. P. Feofilov, *Zhur. Ekspl. Teoret. Fiz.*, **20**, 769 (1950).

(25) V. A. Arkhangelskaya and A. M. Bonch-Bruevich, *Doklady AN S.S.S.R.*, **77**, 229 (1951).

(26) F. F. Volkenshtein, *Zhur. fiz. Khim.*, **23**, 917 (1949).