

On the Theory of the Freundlich Adsorption Isotherm

By J. Zeldowitch

It is shown that, at low values of q , the course of the isotherm obeying the $q = Cp^{\frac{1}{n}}$ law can only be explained in terms of a non-homogeneous surface. A quantitative elaboration of this standpoint leads to conclusions as to the dependence of the constants C and n upon temperature, in satisfactory agreement with experiment.

1. A large amount of available experimental data on the adsorption of gases on the surfaces of solid substances totally fails to agree with the predictions of the simple laws formulated by Langmuir. Moreover, already at very low coverings the linearity of the initial part of the isotherm represents not so much the actual results of experiments but rather the beliefs of theoreticians¹, this linearity of the adsorption isotherm being derived on the basis of general laws of statistical mechanics for adsorption on a homogeneous surface independently of this or other assumptions as to the inter-action between adsorbed particles, such as the dependence of the potential energy upon their mutual distances etc.²

Of the various empirical equations proposed for the adsorption isotherm, the greatest significance is undoubtedly possessed by the

so-called Freundlich isotherm, $q = Cp^{\frac{1}{n}}$. Its value for the description of experimental data is very well emphasized in the well known monograph by Mc Bain³. This formula was introduced in its time by analogy with the distribution of a substance between phases in which it exists in various states of association.

However, the experimental values of n very soon showed the impossibility of such a formulation; it was contradicted both by the

¹ Hückel, Adsorption u. Kapillarkondensation 1928, 52—61.

² We exclude only the possibility of dissociation in the absorbed layer.

³ Mc Bain, Adsorption of Gases and Vapors on Solids 1932, p. 5, 11, 14, 33.

fractional values of n uniformly changing with temperature and by such values as $n=10$ for the adsorption of iodine on starch ⁴.

The Freundlich isotherm is often obtained under conditions which physically exclude the dissociation of adsorbed molecules, as for example, for the adsorption of O_2 and Ar on SiO_2 at low temperatures ⁵. We may observe that since complete adsorption is limited by the size of the surface—at least under conditions standing far from condensation—there always begins at larger coverings a deviation of experimental data from the Freundlich isotherm possessing an unpleasant peculiarity, namely that $\lim q = \infty$, $p = \infty$.

It would not however be true to assert that the Freundlich isotherm is satisfied by experimental data only in so far as it practically coincides with the Langmuir isotherm C in a certain middle portion ⁶. In many cases an isotherm satisfying the Langmuir equation at high concentrations (correctly illustrating the saturation of the surface) definitely diverges from it at low concentrations following the non-linear Freundlich law, as seen, for example, in the data of Roginsky and the author ⁷ for the adsorption of CO_2 on MnO_2 ⁸.

2. We shall consider several proposed interpretations of the Freundlich isotherm. A number of attempts have been made to derive it from the conception of multiple adsorption, that is of an adsorbed molecule bound in n places to the surface occupying n elementary regions on the surface of the adsorbent. To such attempts belong in the first place the works of Chakravarti and Dhar ⁹, as well as an evidently independent though analogous calculation

⁴ Kuster, Liebig's Ann. d. Chem., **283**, 360 (1894).

⁵ Urry, J. Physic. Chem., **36**, 1836 (1932).

⁶ Langmuir, J. Amer. Chem. Soc., **40**, 1361 (1918).

⁷ Roginsky u. Zeldowitsch, Acta Physicochimica U. R. S. S. Vol. 1, No 3—4, p. 554 (1934).

⁸ The usual method of comparing the location of observed values on the curves and on the Langmuir isotherm using the $p-q$ graphs is not satisfactory in that the relatively large deviations of the observed and calculated values of q correspond to but small distances between the points and the curve for small values of q (near the origin). In this sense it would be more correct to make the comparison using the $\log p - \log q$ graphs. It can be easily shown that in these coordinates all Langmuir isotherms (with

arbitrary constants a and b , $q = \frac{ap}{p+b}$) can be obtained from one another by mere parallel translation.

⁹ Chakravarti u. Dhar, Kolloid-Z. **43**, 377 (1907).

carried out by Zeise¹⁰ for the particular case of adsorption of a diatomic molecule on two elementary regions. But in both of the works mentioned there was a very crude error; it was assumed that the probability of the adsorption of a molecule occurring, let us say, on two elementary regions is directly proportional to $(1 - \theta)^2$ (where θ is the portion of the surface covered by adsorbed gas). But it is absolutely clear that such an expression can be obtained only through the tacit assumption that the probability is equal for the distribution of the two atoms of an adsorbed molecule on any two arbitrary elementary regions located at any arbitrary distance from one another. In other words, this signifies dissociation on the surface. Likewise, the assumption as to the probability of the desorption of a molecule being proportional to θ^2 has the same meaning; the latter probability indeed signifies the equal probability of the desorption as a molecule of any two arbitrary atoms located on the surface, i. e. it again leads to the admission of dissociation. We mentioned above the general character of the linearity characterizing the initial region of the adsorption isotherm on a uniform surface. The isotherms derived by Chakravarti and Dhar, $q = C \frac{p^{\frac{1}{n}}}{b + p^{\frac{1}{n}}}$, and by Zeise, $q = \sqrt{\frac{ap}{p + b}}$,

are interesting in that, together with the non-linearity of the isotherm at the beginning ($q \propto p^{\frac{1}{n}}$, $q \propto \sqrt{p}$), they account for the trend of the isotherm towards saturation at $p \rightarrow \infty$. Their excellent applicability corroborates the general behaviour of the usual course of adsorption described in paragraph 1.

A number of derivations of the Freundlich isotherm are based on the well known formula of Gibbs

$$q = \frac{1}{RT} \frac{d\sigma}{d \log p} = \frac{p}{RT} \frac{d\sigma}{dp},$$

by means of which the Freundlich isotherm is obtained with the help of one or other non-legitimate assumptions as to the dependence of σ upon q : $\pi \Omega = nRT!!$ where $\pi = \sigma_0 - \sigma$ is the surface pressure, Ω is the surface occupied by one gram molecule of adsorbed substance,

¹⁰ Heino Zeise, Z. physik. Chem., **136**, 385 (1928).

i. e. the reciprocal of q (Rideal¹¹) or $\sigma = \sigma_0 \left(1 - \frac{q}{q(\infty)}\right)$ according to Chakravarti and Dhar (loc. cit.); or finally the taken ad hoc $\frac{\sigma_0 - \sigma}{\sigma} = Cp^{\frac{1}{n}}$ according to Freundlich¹².

Now it is evident that at sufficient dilution, any adsorbed substance behaves, whatever its two-dimensional mobility may be, as a two-dimensional ideal gas, i. e. in conformity with the equation of state $\pi\Omega = RT$. Superimposed upon the Gibbs equation, this furnishes one of the proofs—if only they be needed—of the linearity of the initial part of the isotherm on a uniform surface¹³.

3. For a number of elementary regions with given properties—heat of adsorption, vibrational volume, arbitrarily distributed on the surface—the adsorption isotherm of Langmuir, $q = \frac{ap}{p+b}$, is obtained strictly (the ordinary assumptions are that not more than one molecule can be adsorbed on each elementary space, all other mutual interactions being neglected).

In this formula b depends upon the properties of the space elements considered, whilst a is proportional to their number. The isotherm is linear at $p \ll b$; for p being of the same order as b , the rise of q begins to lag strongly behind the rise of p . Hence the non-linearity of the experimental isotherm of adsorption (the convexity,

$\frac{d^2q}{dp^2} < 0$) in some regions of pressure must be considered as a proof of the presence on the surface of points with values of b in the Langmuir formula which are (for the given gas) smaller, or at least comparable with those pressures obtained. (This is true only in the case in which strong repulsive long-acting forces between atoms, as for example for Cs on W are physically eliminated).

A rational explanation of the Freundlich adsorption isotherm will be obtained if we find a distribution of points of the surface, according to adsorptive capacity, so that the superposition of the

¹¹ Rideal, Surface Chemistry, 1931, p. 184; Henry, Phil. Mag. 44, 689 (1922).

¹² Freundlich, Kapillarchemie, 2-te Aufl. 1 Band, S. 82, 1930.

¹³ Hückel, Adsorption u. Kapillarkondensation, S. 172.

Langmuir isotherm on each „kind“ of points leads to $q = Cp^{\frac{1}{n}}$. Mathematically the problem is formulated as a linear integral equation of the first kind

$$q(p) = \int_0^{\infty} \frac{pa(b)db}{p+b} \quad (1)$$

where $q(p)$ is the equation of the observed adsorption isotherm and $a(b)$, is the function to be determined. The condition of the convergence of the integral $\int_0^{\infty} a(b)db$ corresponds to a finite limit of adsorption at $p \rightarrow \infty$.

In the original Langmuir's (l.c.⁶) explanation of adsorption on a non-uniform surface, we meet with two kinds of formulae; for adsorption on crystal surfaces, Langmuir writes $q = \sum \frac{a_i p}{p+b_i}$; for adsorption on amorphous surfaces, where there is the possibility of a continuous change of b , he writes $q = \int \frac{ap}{p+b} ds$. The integral is taken for the whole geometric surface. The points with equal values of b are not considered as a separate group, nor is the function $a(b)$ introduced.

Let us now pass to the solution of integral equation (1). Mathematics gives no general method for the solution of equations of this type. Such a condition more than justifies the application of our method consisting in guessing rather than finding the solution and based on the special properties of the „nucleus“ of the equation, the function $p/p+b$.

We schematise the Langmuir isotherm with given b and $q = \frac{ap}{p+b}$ replacing it by two straight lines

$$q = \frac{a}{b}p, \quad 0 < p < b; \quad q = a, \quad b < p \quad (2)$$

which qualitatively represent the initial and saturation portions of the isotherm.

After such a substitution, the solution is obtained very simply

$$q(p) = \int_0^p a(b) db + \int_p^\infty \frac{a(b)p}{b} db \quad (3)$$

Differentiating the equation with respect to p , we easily obtain

$$q'(p) = \int_p^\infty \frac{a(b)}{b} db$$

and

$$q''(p) = -\frac{a(p)}{p}; \quad a(p) = -pq''(p) \quad (4)$$

whereby equation (1) is approximately solved. It is easy to see that this solution correctly represents the fundamental properties of the true $a(p)$: the requirement $a(p) > 0$ gives the evident condition for a superimposition of the Langmuir isotherms, $q''(p) < 0$.

In the same way it is easy to see that automatically we have:

$$\int_0^\infty a(b) db = q(\infty), \quad (5)$$

$a(b)$ determined by (4).

The approximate character of our method is evident from the simplest example $q(p) = \frac{a_0 p}{p + b_0}$; the true $a(b)$ equals $a_0 \delta(b - b_0)$ where δ is the Dirac function; our method gives a somewhat loose distribution in the neighbourhood of $b = b_0$.

4. Let us return to the Freundlich isotherm. We easily find the corresponding expression

$$a(b) = Ab^{\frac{1}{n}-1}. \quad (6)$$

In order to make $\int_0^\infty a(b) db$ convergent, it is sufficient to break off $a(b)$ at some b_0 . The infinity value of $a(b)$ at $b = 0$ is not harmful, since $\int_0^{b_0} b^{\frac{1}{n}-1} db$ converges.

After substituting the expression found for $a(b)$ back into the exact formula (1), we have

$$q(p) = Ap \int_0^{b_0} \frac{b^{\frac{1}{n}-1} db}{p+b}. \quad (7)$$

In general the above integral cannot be taken in a finite form for an arbitrary value of n .

Let us separately consider its asymptotic behaviour at $p \ll b_0$ and $p \gg b_0$. At small pressures we have

$$q(p) = Ap^{\frac{1}{n}} \int_0^{b_0/p} \frac{x^{\frac{1}{n}-1} dx}{1+x}; \quad x = \frac{b}{p} \quad (8)$$

giving the limit

$$\lim_{p \rightarrow 0} q(p) = \frac{A\pi}{\sin \frac{\pi}{n}} p^{\frac{1}{n}} \quad (9)$$

because as known $\int_0^\infty \frac{x^{k-1} dx}{1+x} = \frac{\pi}{\sin k\pi}$, $0 < k < 1$. Expressing A in terms of the saturation, which we have determined by formula (5), we obtain

$$\lim_{p \rightarrow 0} q(p) = \frac{q(\infty) \pi b_0^{-\frac{1}{n}}}{n \sin \frac{\pi}{n}} p^{\frac{1}{n}}. \quad (10)$$

Formulae (9) and (10) show that the distribution (6) as found by the author actually leads to the Freundlich isotherm at low pressures.

For $p > b_0$ we expand $\frac{p}{p+b} = 1 - \frac{b}{p} + \dots$ and integrate each term separately.

The result is:

$$q(p) = q(\infty) \left(1 - \frac{1}{n+1} \frac{b_0}{p} + \dots \right). \quad (11)$$

At high pressures this coincides with the separate individual Langmuir isotherms to within the terms of higher orders in $\frac{b_0}{p}$.

All these results agree with the above-mentioned experimental data of the author.

5. The quantities b , by which we characterized the adsorptive properties of the point of the surface, can be written in the form $Ge^{-\frac{Q}{RT}}$, where G but slightly changes with temperature in comparison with the exponent. Assuming that the value of G is the same for all points on the surface, we find the function of the distribution of points on the surface according to the differential heats of adsorption of the gas $A(Q)$. We have:

$$A(Q) dQ = a(b) db = D' e^{-\frac{Q}{nRT}} dQ, \quad Q > Q_0 \quad (12)$$

where D' is independent of Q whilst Q_0 is determined from $b_0 = Ge^{-\frac{Q_0}{RT}}$. Denoting nRT by θ , and normalizing for $q(\infty)$ by a formula analogous to (5) we easily obtain

$$A(Q) = q(\infty) \theta e^{+\frac{Q_0}{\theta}} e^{-\frac{Q}{\theta}} = Fe^{\frac{Q_0-Q}{\theta}}, \quad Q > Q_0. \quad (13)$$

Distribution (13) has a very remarkable appearance. In its form it coincides with the Boltzmann expression with the modulus of distribution θ . Attempts at finding a direct physical explanation of this result are thwarted by the apparent dependence of θ not only upon the state of the surface, but also upon the nature of the gas, the adsorption of which is given by the Freundlich law. But in spite of this, formula (13) gives a character of verisimilitude to the observed constancy of the function $A(Q)$ leading to the Freundlich isotherm. It seems plausible that on the training or sintering of the surface, the liberation or the destruction of points with various Q will proceed in such a way as to satisfy the exponential relation involving only a change in the constants F , Q_0 , and in particular in θ .

An increase in n and eventually in θ for the adsorption of CO_2 on charcoal upon the raising of the training temperature of the latter was also found by Magnus and Cahn¹⁴. The same effect was also observed by the author for CO_2 on MnO_2 (l. c.⁷). In both cases the isotherm followed the Freundlich law down to very low pressure.

¹⁴ Magnus u. Cahn, Z. anorg. allg. Chem., 155, 205 (1926).

6. $A(Q)$ in formula (13) does not contain in direct form either the temperature of the adsorption experiment or the obtained values of n .

Let us now proceed in the backward direction to find from given $A(Q)$ the dependence of the constants n and C of the Freundlich isotherm on the temperature for which the isotherm was drawn (considering that the surface and hence also $A(Q)$ are constant).

Remembering the way in which we introduced θ we easily find

$$n = \frac{\theta}{RT}; \quad \frac{1}{n} = \frac{RT}{\theta}. \quad (14)$$

The exponent $1/n$ of the Freundlich isotherm is linearly dependent upon temperature.

At sufficiently high temperatures, when the values of $1/n$ determined according to (14) are greater than unity, the theory gives a simple linear course of the isotherm at the beginning; the isotherm in the form $q = Ap^{\frac{1}{n}}$, $\frac{1}{n} > 1$ could not have been obtained by superimposition of the Langmuir isotherm. In fact, in this case $a(b)$, as before, has the form (6) with $1/n$ greater than 1, but the asymptotic form given by formulae (8) and (9) is no longer true, since

$$\int_0^{\infty} \frac{x^{k-1} dx}{1+x}, \quad k > 1$$

is divergent. In place of this we represent $q(p) = Ap \int_0^{b_0} \frac{b^{\frac{1}{n}-1} db}{p+b}$

and make use of the existence at $1/n - 1 > 0$ of $\lim_{p \rightarrow 0} \int_0^{b_0} \frac{b^{\frac{1}{n}-1} db}{p+b} =$

$$= \int_0^{b_0} b^{\frac{1}{n}-2} db = \frac{1}{\frac{1}{n}-1} b_0^{\frac{1}{n}-1}. \text{ Expressing } A \text{ in terms of } q(\infty)$$

we obtain in place of formula (10)

$$\lim_{p \rightarrow 0} q(p) = \frac{q(\infty) b_0^{-1}}{\frac{1}{n}-1} p \simeq q(\infty) \frac{p}{b_0}. \quad (15)$$

The regular rise of $1/n$ with temperature to unity and a sudden stop at this value is very clearly observed in the excellent work of Urry (l.c.⁵). We borrow from him the curve $1/n - T$ for O_2 on SiO_2 (fig. 1).

The explanation of the regularity as given by Urry is that the Freundlich isotherms (below 195°) are caused by capillary condensation, and the linear ones (above 195°) are due to ordinary molecular adsorption. Not to speak of the fact that the Freundlich isotherms can often be observed under the conditions when capillary condensation is absolutely excluded, Urry's own data led him to assume that for oxygen in capillaries $T_{crit.} = 195^\circ$ instead of the usual value 155° and to apply the theory of capillary condensation to capillaries with radii down to 10^{-8} . All this makes his explanation but little convincing.

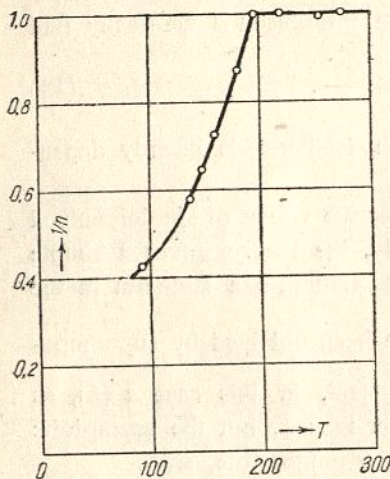


Fig. 1

Let us finally consider the temperature dependence of the coef-

ficients of $p^{1/n}$ or of p in the formulae (10) and (15).

Discarding (for details of this see below) the factors $n \sin 1/n$ and $1/n - 1$, of the order of unity, we find:

$$C = q(\infty) b_0^{-1/n} = q(\infty) \left(G e^{-\frac{Q_0}{RT}} \right)^{1/n}$$

$$\log C = \log q(\infty) + \frac{Q_0}{nRT} - \frac{1}{n} \log G = \log q(\infty) + \frac{Q_0}{\theta} - \frac{RT}{\theta} \log G$$

$$\log C = K_1 - \frac{RT}{\theta} \log G. \quad (16)$$

The $\log C$ changes linearly with T (and not with $1/T$ as one might expect) up to $T = \theta/R$ (at which $1/n = 1$). This relationship is

well corroborated by Urry's data (fig. 2) but also by the data of Miss Ida Homfray¹⁵ (fig. 3) for the adsorption of CO on charcoal at temperatures of 200—300°K, where it is already difficult to speak about condensation. From the slope of the curve it is possible

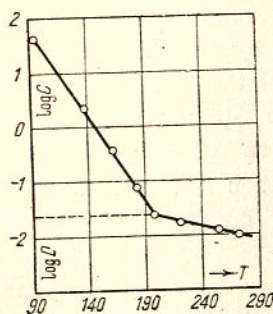


Fig. 2

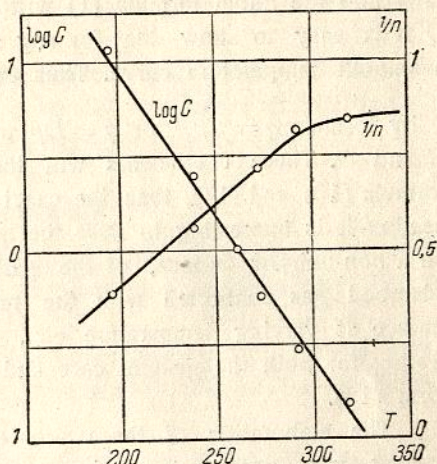


Fig. 3

to calculate G , and further the probability of desorption of individual molecules.

For the latter we obtain $w = \alpha e^{-\frac{Q}{RT}}$ where α has the very plausible value of $5 \cdot 10^{11} - 10^{12}$ 1/sec. The temperature dependence of D ($q = Dp$, $T > \theta/R$) is trivial

$$\log D = R_2 + \frac{Q_0}{RT}. \quad (17)$$

Some difficulties arise for n approaching unity; here $1/n \sin \frac{\pi}{n}$.

(formula 10) and $\frac{1}{1/n - 1}$ (formula 15) tend towards infinity. This is

¹⁵ Ida Homfray, Z. physik. Chem., **74**, 120 (1911). Data taken from Freundlich, l. c., p. 160.

connected with the fact that on approaching the limits $n = 1$, each of the integrals (8) as well as the corresponding integrals for formula (15) shows an ever diminishing convergence. Hence the difference between the asymptotic course of the isotherm $p \rightarrow 0$ and its actual course with p and q differing from zero, is found to increase. Substituting the distribution (13) into the initial formula (1) written with the integration variable Q it is easy to show that for any arbitrary $p \neq 0$ $q(p, T)$ exhibits a smooth temperature curve. Thus expressing the adsorption at finite

p by formula $q = Cp^{\frac{1}{n}}$ or $q = Dp$ we never have infinite values of C and D . These coefficients will then obey rather the approximate formula (16) and (17), than the exact formula for $p \rightarrow 0$. In this connection it is interesting to raise the question of the heat of adsorption on a non-uniform surface, of the part of the specific heat of the adsorbed gas connected with the redistribution of the gas on the surface at varying temperature etc., the question being equally interesting for both the general case and also for the distribution of the form (13).

The elaboration of these problems, however, would be, at the present stage, nothing more than a mathematical exercise. We must only point to the fact that for (13) the specific heat has a maximum at T approaching $\frac{\theta}{R}$, which is the sharper the smaller the value of $\frac{q}{q(\infty)}$, and that the differential heat of absorption at $T=0$ obeys the equation

$$(Q)_q = Q_0 + \theta \lg \frac{q(\infty)}{q}. \quad (18)$$

Closing up on this, I wish to emphasize that the main object of the present work has been not a quantitative theory of adsorption on non-uniform surfaces, but an attempt for a correct qualitative interpretation of some experimental data. In the theory of adsorption „It is almost laughable to see how the same data are adduced as verification. Each hypothesis scores a numerical triumph for the same data“. (Mc Bain, 1. c., p. 439). Thus, for example, as shown in the author's chapter on adsorption in Semenov-Joffé's

textbook „Molecular Physics“¹⁶, the fulfillment of the predictions of the Polanyi theory by no means proves the liquid state of adsorbed matter, but only shows that the vibrational volume is the same as in the liquid. (This statement is exact at the middle point, $q = \frac{1}{2}q(\infty)$, of the Langmuir isotherm, and very nearly so at all measurable coverings).

It is scarcely worth while to produce more examples taking for evidence, in place of a few, a whole continuum of the values of constants as could be done in the integral formula (1).

Summary

1. A critical examination has been made of the various proposed explanations for the deviation of the adsorption isotherm from linearity at small coverings.

2. An integral equation for adsorption on non-uniform surfaces has been derived and an approximate method for its solution given.

3. A distribution of surface points according to the heat of adsorption corresponding to the Freundlich isotherm $q = Cp^{\frac{1}{n}}$ has been found.

4. Proceeding from the simplest assumptions the following relations have been found for the temperature variation of the constants n and C :

$$\frac{1}{n} = \frac{T}{T_k}, \quad \log C = AT + B$$

for the range $T < T_k$ and

$$\frac{1}{n} = 1, \quad \log C = \frac{D}{T} + E$$

for $T > T_k$, where A, B, D, E and T_k are constants.

This work has been carried out independently and simultaneously with the work of Temkin dealing with the adsorption on a non-uniform surface (performed at the Karpov Institute).

¹⁶ N. N. Semenov and A. F. Joffé, „Molecular Physics“, in print in the Ukraina State Technical Press.

My thanks are due to M. Temkin for the possibility of a discussion before the publication of our papers.

The difference in methods, objects and partly results, seems to be great enough to warrant the separate publication of our articles.

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