The Adsorption of Hydrogen on Tungsten Powders

George Halsey and Hugh S. Taylor

Additional information on J. Chem. Phys.

sorbents might not always have the unique values assigned.

POSSIBILITY OF A CHOICE BETWEEN THE TWO ISOTHERMS

It is conceivable that a mathematical analysis of the two isotherms would suggest a basis for preferring one to the other. No such choice can be made as a result of the present analysis. The fact that the two equations are both equally in agreement with many of the experimental isotherms determined during the past ten years promises to make such a choice particularly difficult. If it is a fundamental property of adsorbed films under these experimental conditions to obey the two-dimensional equation of state of condensed films, then it might be considered fortuitous that the equation derived by Brunauer, Emmett, and Teller, with appropriate constants, expresses the adsorption isotherm over a considerable pressure range. On the other hand, if the kinetic theory of these authors, from which their equation was derived, is an exact expression of the performance of vapors and adsorbents at moderate relative pressures, for a great many systems the surface pressure and area will correspond to the two-dimensional equation of state expressed by Eq. (2), and therefore will be in agreement with the Jura and Harkins isotherm.

The nature of the relationship between the two isotherms has been most recently summarized by Jura and Harkins,[14] who concluded that "it is apparent that there is no conflict." It was predicted that new developments in theoretical and experimental studies of phase transitions would improve the agreement. In investigations of this sort, consideration should be given to the mathematical relationship between the equations that has been demonstrated by Emmett[13] and in the present paper.

[14] G. Jura and W. D. Harkins, J. Am. Chem. Soc. 68, 1941 (1946).

The Adsorption of Hydrogen on Tungsten Powders

GEORGE HALSEY AND HUGH S. TAYLOR
Frick Chemical Laboratory, Princeton, New Jersey
(Received May 12, 1947)

An analysis of the extensive experimental data of Frankenburg on the adsorption of hydrogen by metallic tungsten powder between -194 and $750°C$ has been made, using the Fowler-Guggenheim treatment of adsorption phenomena as the mode of approach. It has not been found possible to interpret the data in terms of interaction between the adsorbed species on a *uniform* adsorbent surface. It is shown that the experimental data can be interpreted on the basis of a non-uniform surface without interaction, the heterogeneity of the surface being specified in terms of an exponential distribution of sites given by the distribution function $N = ce^{-\chi/\chi_m}$, where χ represents the energy difference between the lowest energy state of the gas and the lowest energy of the adsorption complex. Such a distribution function yields the experimentally observed relation $d \ln p/d \ln\theta = \text{constant}$ at constant temperature. Such a heterogeneity is especially significant in the case of tungsten metal which hitherto has been treated as an essentially uniform surface. The quantity χ_m has been found to vary with the temperature. The significance of this variation has been briefly explored.

A COMPREHENSIVE study of the adsorption of hydrogen on tungsten powders has been recorded by W. G. Frankenburg,[1] and he has presented a series of isotherms between $-194°$ and $750°$. Special attention was given to

[1] J. Am. Chem. Soc. 66, 1827 (1944); 66, 1838 (1944).

the cleanliness of the metal surface, and the hydrogen was adsorbed rapidly at the temperatures employed. These data form an excellent example of an adsorption equilibrium in a localized mono-layer. Frankenburg's analysis of his data led to an empirical relation, the logarithm

of the adsorbed hydrogen varying linearly with the logarithm of the gas pressure. The plot of these isothermal lines, when extrapolated, appears to intersect at a point corresponding to approximately 3150-mm hydrogen pressure.

In the present communication these data are analyzed from the standpoint of statistical mechanics, proceeding from the treatment of such adsorption phenomena by Fowler and Guggenheim.[2] Their treatment of localized mono-layers presents initially a thermodynamic derivation of the Langmuir adsorption isotherm. They emphasize the semiquantitative nature of the equation, becoming in some cases "useless owing to the ignoring of the interaction between adsorbed molecules." Their treatment is therefore modified to include interaction between the molecules which has for its effect an apparently increasing resistance to adsorption as the surface sites are filled, if the interactions are of a repulsive nature.

As a first approximation in solving the interactive case, Fowler and Guggenheim consider the case in which the molecules have a completely random distribution among the sites. This treatment is modified to include the effect of the interactive forces on the equilibrium distribution. This interaction on a uniform surface is rejected by the present authors, in what follows, as an explanation of the isotherms on tungsten powders. We shall consider, therefore, the simple random case, because for the interactive case the refinement lessens the effect of the interaction in the sparsely covered regions of the isotherms. As will presently appear, the interaction is too small even in the more favorable simple case.

INTERACTION ON A UNIFORM ABSORBENT SURFACE

Fowler and Guggenheim derive the equation,

$$p = p_0 \frac{\theta}{1-\theta} e^{2\theta w/kT}, \qquad (1)$$

where p is the gas pressure, p_0 is a function of the condition of the materials employed, independent of θ, the extent of surface covered. The

[2] R. H. Fowler, and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Teddington, England, 1939), Chapter X, p. 421.

term w is a measure of the interaction. The differential heat of adsorption (which Frankenburg derives from his data) can be obtained by inserting Eq. (1) in the Clapeyron-Clausius equation (2), which we express in terms of the heat of adsorption, q, per molecule.

$$-q = k\frac{d \ln p}{d 1/T} = k\frac{d \ln p_0}{d 1/T} + 2\theta w. \qquad (2)$$

The heat of adsorption q is, in this case, a linear function of θ. Such a result is not in agreement with the data of Frankenburg who finds a linear relation between $\log\theta$ and q over most of the plot.

If Fowler and Guggenheim's treatment is formulated to include the effect of higher interactions than between pairs of adsorbed species, instead of writing for the energy of interaction, ϵ,

$$\epsilon = N_s(\theta^2 w),$$

where N_s is the total number of sites, one may write

$$\epsilon = N_s(\theta^2 w + \theta^3 v + \cdots),$$

where the higher terms allow for groups of three, etc. That is, the energy of a cluster is not the sum of the energies of all the pairs in the cluster. For the partial potential, μ, Fowler and Guggenheim write

$$\frac{\mu}{kT} = \frac{1}{kT}\left(\frac{\partial F}{\partial N_A}\right) = \ln\frac{\theta}{1-\theta} - \ln a_0 + \frac{1}{N_s kT}\left(\frac{\partial \epsilon}{\partial \theta}\right). \qquad (3)$$

Here, N_A is the number of occupied sites and a_0 contains the partition function of the materials. Inserting the more general energy of interaction, the absolute activity, λ, is

$$\lambda = e^{\mu/kT} = \frac{\theta e^{(2\theta w + 3\theta^2 v + \cdots)/kT}}{(1-\theta)a_0}. \qquad (4)$$

The absolute activity of the gas phase is

$$\lambda_g = \frac{p}{kT}\frac{h^3}{(2\pi mkT)^{\frac{3}{2}}j_A}, \qquad (5)$$

where j_A is the partition function for vibration and rotation in the gas. Thus,

$$p = p_0 \frac{\theta}{1-\theta} e^{(2\theta w + 3\theta^2 v + \cdots)/kT}, \qquad (6)$$

where p_0 is of the form

$$p_0 = \frac{(2\pi m)^{3/2}(kT)^{5/2}j_G(T)}{h^3 j_s(T)} e^{-\chi_0/kT}, \qquad (7)$$

where χ_0 is the energy difference between the lowest energy states of the gas and the adsorption complex. A discussion of its variability will follow. From the expression for p, Eq. (6),

$$-q = k\frac{d \ln p}{d(1/T)} = k\frac{d \ln p_0}{d(1/T)} + 2\theta w + 3\theta^2 v + \cdots, \quad (8)$$

and the slope of $-q$ versus θ is given by

$$\frac{-dq}{d\theta} = 2w + 6\theta v + \cdots \qquad (9)$$

which shows that, when the coverage is low, $-dq/d\theta = 2w$. Frankenburg's curve for q versus θ has its maximum slope when θ is small and it has no inflexion. It follows, therefore, that w must have a positive value, and the coefficients of the higher terms, $v, \cdots$ must be negative. Up to a rather large value of θ (0.2–0.3) the slope of the curve $-dq/d\theta$ is very large. If higher interactions were suppressed this would be equivalent to having q versus θ given by the projected tangent to this early slope. With Frankenburg's data the slope is so large that the heat of adsorption would become negative long before θ reached unity. Actually the tangent would reach zero heat with θ in the neighborhood of 0.1 to 0.2.

Because interactions at low coverage are almost exclusively isolated-pair interactions and because, when all the sites are covered, there are two pair-interactions per atom, it follows that the lowest value of θ at which the tangent to the initial portion of the curve could cross $q=0$ would be, with the help of all the higher order interactions, when $\theta = \frac{1}{4}$. Frankenburg's data could conform to this condition did they involve low energy repulsions. On the contrary, in order to account for the extremely steep initial slope of the $q - \theta$ curve a value of w/kT of ~ 100 or more would be required. The early interactions would involve a term e^{100} in the exact treatment, a condition which renders a poor argument for interaction actually impossible. An alternative statement of this conclusion is that pair-interaction is more than sufficient to prohibit adsorp-

tion, which is clearly impossible since vigorous adsorption occurs on the surface at small θ.

This argument is deemed sufficient to show that we cannot interpret the Frankenburg data on the basis of a theory of interaction on a uniform surface. It can further be pointed out that the isotherms yielded by such a theory are clearly not straight lines on a plot of $\log p$ versus $\log \theta$. Nor do they tend to meet in a point as Frankenburg found. Rather, in common with all isotherms with a saturation value, they tend to become asymptotic to a line of constant coverage.

Thus, no interaction theory on a uniform surface can explain a differential heat of adsorption with increased coverage which has an initial slope $dq/d\theta$ greater than $0.25q_{initial}$. Accordingly, the case of a heterogeneous surface must necessarily be examined.[3] While, in this case, interactions between neighboring molecules undoubtedly exist, it is simpler, at the outset, to begin by considering heterogeneity alone without interactions. It emerges that this ideal case, omitting interaction, is adequate to provide a reasonable basis for the analysis of Frankenburg's isotherms.

THE NON-UNIFORM ADSORBENT SURFACE

Consider a surface with variable energy differences between the lowest energy state of the gas and the lowest energy state of the adsorption complex. For any particular value of χ the Langmuir isotherm is applied:

$$\frac{\theta_\chi}{1 - \theta_\chi} = \frac{p}{p_0} = \frac{p}{ae^{-\chi/kT}}. \qquad (10)$$

By setting $p_0 = ae^{-\chi/kT}$, the effect of variable χ has been separated from the remainder of the partition-function ratio. The total coverage is given by

$$\theta = \int N_\chi \theta_\chi d\chi, \qquad (11)$$

where N_χ is the distribution function of sites, usually normalized to $\int N_\chi d\chi = 1$. Solving the

[3] There are many such efforts previously made. See Fowler, *Statistical Mechanics* (Cambridge University Press, Teddington, England, 1936), second edition, p. 833. Also, Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1943), p. 74.

Langmuir expression for θ_χ,

$$\theta_\chi = \cfrac{1}{\cfrac{a}{p}e^{-\chi/kT}+1} \qquad (12)$$

the expression for θ becomes

$$\theta = \int \cfrac{N_\chi d\chi}{\cfrac{a}{p}e^{-\chi/kT}+1}. \qquad (13)$$

Case 1: N is Constant

To evaluate the integral it is necessary to assume a form for N_χ. One form that permits integration with indefinite limits obtains when N_χ is constant. Then if $\int N_\chi d\chi = 1$, $N = 1/\Delta\chi$ where $\Delta\chi$ is the range of integration, $\chi_{upper} - \chi_0$. Inserting this value in the expression (13) for θ yields

$$\theta = \frac{1}{\Delta\chi}\int \cfrac{d\chi}{\cfrac{a}{p}e^{-\chi/kT}+1}$$

$$= 1 + \frac{kT}{\Delta\chi}\ln\cfrac{1+\cfrac{a}{p}e^{-(\chi_0+\Delta\chi)/kT}}{1+\cfrac{a}{p}e^{-\chi_0/kT}}. \qquad (14)$$

To compute the differential heat, $-q$, by means of the Clapeyron-Clausius equation (2), the expression for θ must be solved for p. Two approximations, corresponding to the low and high pressure approximations in the simple Langmuir theory can be made. For low pressure the poorest sites are totally vacant, in which case $(a/p)e^{-\chi_0/kT} \gg 1$. The isotherm then becomes

$$1-\theta = \frac{kT}{\Delta\chi}\ln\cfrac{\cfrac{a}{p}e^{-\chi_0/kT}}{1+\cfrac{a}{p}e^{-(\chi_0+\Delta\chi)/kT}}$$

$$= -\frac{kT}{\Delta\chi}\ln\left(\frac{p}{a}e^{\chi_0/kT}+e^{-\Delta\chi/kT}\right). \qquad (15)$$

Hence,

$$-q = \frac{kd\ln p}{d1/T} = \text{const.}$$

$$-\cfrac{(1-\theta)\Delta\chi e^{-(1-\theta)\Delta\chi/kT} - \Delta\chi e^{-\Delta\chi/kT}}{e^{-(1-\theta)\Delta\chi/kT} - e^{-\Delta\chi/kT}}. \qquad (16)$$

At high pressure, $(a/p)e^{-(\chi_0+\Delta\chi)/kT}$ becomes small and the best sites are covered. Then,

$$1-\theta = \frac{kT}{\Delta\chi}\ln\left(1+\frac{a}{p}e^{-\chi_0/kT}\right) \qquad (17)$$

and

$$p = \cfrac{ae^{-\chi_0/kT}}{e^{(1-\theta)\Delta\chi/kT}-1} \qquad (18)$$

and

$$-q = \frac{kd\ln p}{d1/T} = \text{const.} - \cfrac{(1-\theta)\Delta\chi e^{(1-\theta)\Delta\chi/kT}}{e^{(1-\theta)\Delta\chi/kT}-1}. \qquad (19)$$

These equations, complex as they are, do not account for Frankenburg's data, unless a number of segments are arbitrarily patched together. It is usual to measure q and assume that this function represents the distribution pattern of the surface. These equations indicate that this procedure is not sound. There is always a complex relationship even in the simple case when N_χ is constant. An exception may be noted in the simplification possible when the two approximations which have been used apply simultaneously. In this case, adsorption has no beginning or end in either direction and the normalization becomes meaningless. It is replaceable by a factor m adjusted to make θ emerge in the proper units.

$$1-\theta = mkT\ln\frac{a}{p}e^{-\chi_0/kT}. \qquad (20)$$

Replacing $a\,e^{-\chi_0/kT}$ by p_0,

$$1-\theta = mkT\ln\frac{p}{p_0}. \qquad (21)$$

From this logarithmic isotherm (21), it follows that

$$\ln p = \frac{1-\theta}{mkT}+\ln p_0$$

and

$$-q = \frac{kd \ln p}{d^1/T} = \frac{1-\theta}{m} + \frac{kd \ln p_0}{d(1/T)}.$$

This is a linear relationship between θ and q. In this case, therefore, the distribution and the heat have the same functional form. Whenever the heat function is not linear, as in Frankenburg's results, analysis of the problem with finite limits is difficult. Applicability of the two approximations already employed, permits a more complex function to be used, which, at the same time makes the analysis possible.

Case 2: Exponential Distribution for N

With a distribution of the form

$$N_\chi = ce^{-\chi/\chi_m} \qquad (22)$$

over the whole range of χ, positive and negative,

$$\theta = c \int_{-\infty}^{+\infty} \frac{e^{-\chi/\chi_m}}{\dfrac{a}{p} e^{-\chi/kT} + 1} d\chi. \qquad (23)$$

Inserting Z for $(a/p)e^{-\chi/kT}$ the expression can be written

$$\theta = \left(\frac{a}{p}\right)^{-kT/\chi_m} ckT \int_0^\infty \frac{Z^{(kT/\chi_m - 1)}}{1+Z} dZ. \qquad (24)$$

This integral has the value[4] $\pi \, \mathrm{cosec} \, \pi kT/\chi_m$. This expression has the approximate value χ_m/kT for large values of this quantity. This expression will not be carried in further equations because other terms involving T are indistinguishable.

In the expression for θ, there are no constants involving p under the integral. Now, if the exponential retarding adsorption in the region of negative $\chi(e^{+\chi/kT})$ increases more rapidly than the available sites (e^{χ/χ_m}), the infinite integral will converge and become independent of the variable. The condition for convergence is $\chi_m/kT > 1$. Hence,

$$\theta = ckT \left(\frac{p}{a}\right)^{kT/\chi_m} f(kT/\chi_m), \qquad (25)$$

where $f(kT/\chi_m)$ is written for the infinite integral.

[4] D. Bierens de Haan, *Nouvelles Tables d'Integrales Definies* (Amsterdam, 1867), Table 16, No. 1.

From this expression it follows that

$$\ln \theta = \frac{kT}{\chi_m} \ln p + \text{const.} \qquad (26)$$

and

$$\frac{d \ln p}{d \ln \theta} = \frac{\chi_m}{kT}, \qquad (27)$$

which is the functional relation between p and θ found by Frankenburg. Similarly, as found by Frankenburg for the main portion of his data,

$$-q = \frac{kd \ln p}{d^1/T} = \text{const.} + \chi_m \log \theta. \qquad (28)$$

For some value of θ, q is zero. If the value for the constant in the equation for q is independent of temperature, then the value of θ that makes q equal to zero is the same for all temperatures. Extrapolation of Frankenburg's data supports this constancy with respect to temperature. If we select, as a normalization condition, this value as $\theta = 1$, the constant becomes zero and

$$-q = \chi_m \log \theta, \qquad (29)$$

and

$$\ln p = \frac{\chi_m}{kT} \ln \theta + \ln p_0. \qquad (30)$$

When $p = p_0$ all of the isotherms intersect. Frankenburg finds this value by extrapolation to be 3150 mm. At the point of intersection, for powder 9799, θ has the value $S = 1000 \times 10^{-8}$ mole H_2 per g tungsten powder. At this point all of the sites with positive energies would not be filled (unless $T = 0°K$) but enough of the sites of negative energy are filled to make the net heat effect zero. Frankenburg did not reach this point experimentally.

Below a certain coverage, $\theta = 0.015$, Frankenburg found that the differential heat of adsorption was constant. This indicates a breakdown, in the sparsely covered region, of the hypothesis in the present treatment that the best site is always covered and that, therefore, $-q$ should increase indefinitely. This low pressure region doubtless has an effective χ and can be treated on the basis of a simple Langmuir isotherm.

Granting the validity of the treatment here proposed, it should be pointed out that the slope ($\ln p$ versus $\ln \theta$), 2.0–2.06, indicates that the

adsorption is atomic rather than molecular. This is the accepted view. The total effect of this modification is that Eqs. (29) and (30) become, respectively,

$$(p/p_0)^{\frac{1}{2}} = \theta^{\chi_m/kT} \qquad (31)$$

and

$$-q = 2\chi_m \ln\theta. \qquad (32)$$

The constant χ_m, which is the energy at which the sites are a fraction $1/e$ of those when $\chi = 0$, is a function of temperature which is approximately linear. It is somewhat difficult to reconcile this continuous change in χ_m over the temperature range with the calculations of Frankenburg in which he found q to be constant below 529°C. He himself indicates the reason for the discrepancy when he details the calculation of q, in which the slopes are adjusted on the basis of his modification of the Langmuir treatment.

In Table I are given Frankenburg's average slopes and the variation of χ_m with temperature. The values of χ_m were calculated by use of the formula, based on atomic adsorption,

$$\chi_m = \frac{kT}{2} \frac{d \ln p}{d \ln\theta}. \qquad (33)$$

Since χ_m was considered constant with respect to $1/T$ throughout the preceding derivations, the equations will be re-examined in respect to $-q$. The derivation of the isotherm is not impaired; hence, from Eq. (26) it follows that

$$-q = \frac{kd \ln p}{d(1/T)} = \text{const.} + \ln\theta \left(\chi_m - T \frac{\partial \chi_m}{\partial T} \right). \qquad (34)$$

The slope of the differential-heat curve plotting $-q$ *versus* $\ln\theta$,

$$\chi_m{}^0 = \frac{d(-q)}{d \ln\theta} = \chi_m - T \frac{\partial \chi_m}{\partial T}, \qquad (35)$$

is still independent of θ but now is a function of T. The constancy of q with respect to temperature is so often encountered or implied that it is of interest to deduce the most general law that will yield it. If $\chi_m{}^0$ is a constant, the differential

TABLE I. Variation of $d \ln p/d \ln\theta$ and χ_m with temperature.

Temperature °K	$\dfrac{d \ln p}{d \ln\theta}$	χ_m kcal.
99	(67.4)	6.65
200	(24.1)	4.83
273	16.63	4.54
373	10.81	4.01
473	7.58	3.58
573	5.60	3.21
673	4.17	2.84
773	3.06	2.37
873	2.31	2.02
973	1.85	1.80

equation

$$-T \frac{\partial \chi_m}{\partial T} + \chi_m = \chi_m{}^0 \qquad (36)$$

has the solution

$$\chi_m = \chi_m{}^0 + cT \quad \text{or} \quad -q = \chi_m{}^0 \ln\theta, \qquad (37)$$

where c is the constant of integration. If $c = 0$, $\chi_m = \chi_m{}^0$, which is the special case of constant χ_m treated earlier. The data of Frankenburg are not specially suited to this case but are fairly satisfactory over the middle range. The expression

$$\chi_m = 16.6 - 0.005(T - 273°)$$

where the data are given in kcal. per mole and the corresponding expression for the heat of adsorption, Q, per mole,

$$-Q = 2.3 \times 16.6 \log\theta,$$

conform more closely but not entirely satisfactorily to the Frankenburg data. The form that appears to fit the data best is

$$\chi_m = \chi_m{}^0 + c \ln T, \qquad (38)$$

whence

$$-q = \chi_m{}^0 - c(\ln T + 1) \ln. \qquad (39)$$

Numerically, in kcal. per mole and °K, the expression becomes

$$\chi_m = 4.45 - 5.0 \log\frac{T}{300}.$$

Hence, the numerical expression for Frankenburg's data over the main portion of his iso-

therms, would be

$$\frac{p_{\text{mm}}}{1350} = \left(\frac{m_{\text{H}_2}}{1.00 \times 10^{-5}}\right)^{\frac{[9.90 - 10 \log(T/300)]}{RT}}$$

In this expression, m_{H_2} is moles H_2 per gram of tungsten, powder No. 9799, which was used in the high temperature runs. For powder No. 9798 the term 1.00×10^{-5} must be replaced by 0.360×10^{-5} because of the smaller surface per gram of this powder.

The variation of χ_m with temperature indicates that it is not alone χ which varies from site to site on the surface of the tungsten. A term in χ proportional to T is to be associated with a varying entropy of adsorption over the surface. The exact meaning of an entropy term may not be immediately apparent. If the term in the adsorption equation that varies over the surface is not $e^{-\chi/kT}$ but an expression of the form

$$e^{a\chi}e^{-\chi/kT} = e^{-\chi(1-aT)/kT}, \qquad (40)$$

then the expression for $\ln\theta$ becomes

$$\ln\theta = \frac{kT}{m(1-cT)} \ln p. \qquad (41)$$

If χ is independent of the temperature, as just assumed, a variation in χ_m such as was found necessary in the preceding must result. Taking the values found for the constants into account, it means that when the energy of adsorption changes by 16.6 kcal., the change in the entropy of adsorption is 5 entropy units or 0.3 entropy unit per kcal. change in energy of adsorption.

ACKNOWLEDGMENT