considered previously[6] shows that near equilibrium during flow is maintained in this special case.

Summary

A criterion for near-equilibrium flow during isentropic expansion through a rocket nozzle has been derived. Schaefer's result[7] is shown to be valid for atomic recombinations in a system in which temperature and pressure changes produce concentration changes which are superimposed on the concentration changes associated with chemical reaction provided $-\Delta H/RT > 1$ and $\{[(-\Delta H/RT) - 1](\gamma - 1)\}^{-1} < 1$. These conditions are satisfied in the rocket motors usually encountered. Criteria for near-equilibrium flow under conditions which may be encountered in future work with rockets operating at exceedingly high temperatures are also discussed.

RECEIVED SEPTEMBER 21, 1948

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Extrapolation of Adsorption Isotherms to High Relative Pressures and the Determination of the Surface Pressure of Adsorbed Films on Solids

BY MELVIN A. COOK AND DOUGLAS H. PACK[1]

A recent publication[2] outlined the development of the equation for the unrestricted multimolecular

$$v/v_m = \sum_1^\infty i x^i d_i \Big/ \left(1 + \sum_1^\infty x^i d_i\right) \qquad (1)$$

adsorption of gases on solids. Here the d_i's are a series of interrelated constants different for each adsorbed layer and made up of α_i and β_i components such that $d_i = \alpha_i\beta_i$. The α_i's are factors determined by the energies of interaction of the adsorbate with the surface of the adsorbent, and the β_i's account for the interactions between the adsorbate molecules in the film. Equation (1) differs from the BET[3] equation only in the fact that the d_i's are all the same constant c in the BET theory; the theoretical basis for (1) differs from that of the BET equation only in the description of the adsorption forces.

In reference (2) only the important van der Waals attraction term for the adsorbate–adsorbent interactions, varying as r_i^{-3} (r_i = distance of the i^{th} layer from the surface of the solid), was taken into account, the repulsive and second and higher order attractive terms being neglected. In this approximation the α_i's were defined by the equation

$$\alpha_i = \exp. E_1(1 + 1/8 + 1/27 + \ldots + 1/i^3)/RT \qquad (2)$$

where E_1 is the (final) adsorbate–adsorbent interaction energy in the (nearly filled) first layer evaluated as an empirical constant. The β_i's were defined as

$$\beta_i = \exp. E_L(c_1 + c_2 + c_3 + \ldots c_i - i)/RT \equiv$$
$$\exp. E_L(c_1 - 1)(1 + {}^1/_2 + {}^1/_3 + \ldots + 1/i)/RT \qquad (3)$$

where E_L is the heat of condensation in the corresponding bulk liquid state of the adsorbate and the c_i's are constants related to the empirical constant c_1 as shown. Equation (3) was developed semi-empirically from the consideration that entropy variations in the various layers of the adsorbed film may be related to the average coördination number ratios between an *i-layer* film and the bulk liquid.

On the above basis equation (1) was found to reproduce quite accurately four experimental isotherms over the range from 0.05 to about 0.7–0.8 in relative pressure $x = p/p_0$, the experimental data in these cases being taken only in this range. More recently equation (1) has been examined by comparing it with some experimental isotherms in which the experimental data covered the entire range of relative pressures ($0 < x < 1.0$). Employing the definitions of d_i (equations (2) and (3)), equation (1) was found to reproduce the isotherm over the range from $x = 0.05$ to $x \cong 0.8$, but it predicted too much adsorption for $x > 0.9$ and too little adsorption for $x < 0.05$. It is considered that the discrepancies in the very low pressure region involve a fundamental weakness of the theory incurred by its failure to take account of (1) surface heterogeneities, and (2) the non-constancy of β_1 for various stages of filling of the first adsorbed layer. The discrepancies in the very high relative pressure region on the other hand apparently involve only the deliberate approximations in α_i and evidently may be largely eliminated by simply taking into account the repulsive term.

The present article introduces a simple modification of equation (2) including a theoretical repulsive term, and illustrates the utility of equation (1) in extrapolating isotherms to the relative pressure $x = 1.0$. Also, it seemed worth while to discuss in this article some of the convergence–divergence characteristics of equation (1) and to outline some methods designed to render the equation tractable in practical applications.

Repulsive Term in α_i.—According to approximate quantum mechanical treatments, the repulsive term in the van der Waals interaction should have the form $B_r e^{-r/\rho}$(B_r and ρ being

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[1] This work was supported by a grant from the University of Utah Research Fund.

[2] M. A. Cook, THIS JOURNAL, **70**, 2925 (1948).

[3] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

empirical constants). The form $B_r r^{-n}$ is, however, more frequently used and, because of its simplicity for the present purpose, it will be adopted here. Irrespective of the particular form adopted for the repulsive term, however, it is clear that it must show a much more rapid variation with distance than the r^{-6} (bulk matter) and r^{-3} (surface) attractive term. Consequently, this term will need to be included only in accounting for the binding energy in the first layer of the film. One may thus show that the inclusion of the repulsive term in α_i simply introduces a constant a as follows

$$\alpha_i = \exp. E_1(1 + a/8 + a/27 + \ldots + a/i^3)/RT \quad (4)$$

in which a is related to n in the term $B_r r^{-n}$ by the equation

$$3a/(a - 1) = n \quad (4a)$$

While n will probably not be the same constant for all adsorbate–adsorbent systems, Hill[4] has suggested applying Lennard–Jones' formula for the van der Waals interaction in the bulk state from which he obtained an adsorbate–adsorbent interaction of the form (using the present notations)

$$E_i = A/r_i^3 - B\ /r_i^9 \quad (5)$$

Here A and B_r are constants which may be related by taking the derivative of (5) with respect to r_i and equating (dE_i/dr_i) $r_i = r_1$ to zero. This gives

$$E_i = A/r_i^3 - Ar_1^6/3r_i^9 \quad (6a)$$

the more general case being

$$E_i = A/r_i^3 - \frac{3Ar_1{}^{n-3}}{nr_i{}^n} \quad (6b)$$

from which equations (4) and (4a) are derived. Using Hill's equation (6a) with $n = 9$, we obtain $a = 1.5$. Hill suggests applying (6a) to each separate adsorbate atom, taking account of the fact that the distance r_i will not be the same for each atom in the molecule. Here, however, we shall assume that (6a or 6b) may be applied with sufficient accuracy to the whole molecule assuming that r_i represents the distance from the effective center of the molecule to the active center on the solid surface, any greater refinement in E_i being unjustified at this stage in the present theory.

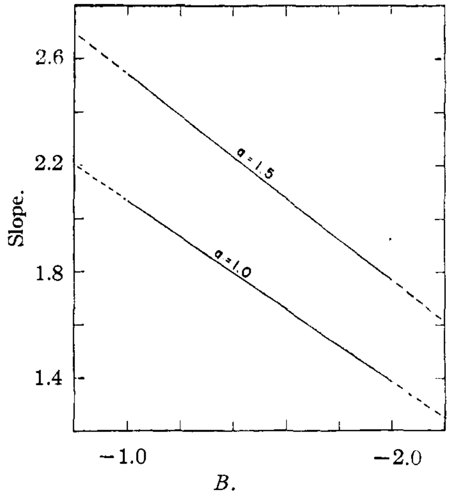

Fig. 1.—Slope ($v/v_m \div x$) of linear part of S-curve *vs.* B.

Manipulation of Equations at Large x.—The application of the equation (1) requires the evaluation of the two (major) infinite series $\sum_1^\infty ix^id_i$ and $\sum_1^\infty x^id_i$ which are further complicated by the two (minor) series in the d_i's. In view of the rapid convergence of the major series for small x, the solution of (1) offers no serious difficulties in the low relative pressure regions, and even up to relative pressures around $x = 0.8$. However, for $x > 0.8$ the series converge so slowly that their evaluation becomes very tedious. Fortunately, it is possible to shorten the labor considerably by replacing the summations beyond a certain number of terms by suitable integrals without incurring appreciable error.

The two empirical constants, E_1 and c_1 may be evaluated at small values of x (preferably for $x < 0.5$) by the methods outlined in reference (2) no problems of convergence being encountered in this region. In spite of this the evaluation of these constants would be quite tedious unless one were to make use of various labor saving devices such as tables of ix^i, x^i, etc. It is of interest to note in this connection that one seldom needs to carry through the process of iteration for c_1 and E_1 more than three times if the fact is taken into consideration that $t_2 (= v_2/v_m$ ref. 2) varies approximately linearly with c_1. Thus, after calculations have been made for two assumed values of c_1, one may nearly always pick out the true value by means of a linear c_1 *vs.* v_2/v_m plot, unless either, or both, of the first two assumed values of c_1 should happen to be selected too far from the true value. This can be easily avoided, and, as a matter of fact, the correct value of c_1 may sometimes be selected in the first trial by making use of Fig. 1 in which B, defined by the equation

$$B \equiv E_L(c_1 - 1)/RT \quad (7)$$

is plotted against the slope (in reduced $- v/v_m -$ units) of the essentially straight line portion of the sigmoid isotherms (usually extending from about 0.1 to perhaps 0.5 in x). Figure 1 was obtained by drawing the best straight lines through all of the points for $a = 1.0$ and $a = 1.5$, respectively, obtained in this and the previous study. It will be shown below that for $|B| > 2.0$ equation (1) is not properly divergent at $x = 1.0$. To avoid this difficulty when it occurs one might simply calculate c_1 directly from equation (7) for $B = -2.0$ (assuming that $|B|$ will never be appreciably greater than 2.0) leaving only a two empirical con-

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[4] T. L. Hill, *J. Chem. Phys.*, **16**, 181 (1948).

stant (v_m and E_1) equation to fit the curve. If it should turn out in some cases that $|B| >> 2$, B could be fixed at -2.0, and the a adjusted to be consistent with Figure 1 (by extrapolating or interpolating linearly between the two straight lines of Fig. 1) again leaving only the two constants (v_m and E_1) to be evaluated. That this procedure evidently leads to results generally in good agreement with observed isotherms even as x approaches closely to unity, and the further fact that values of B evidently hover around -2.0 for $a = 1.5$, are of possible interest in regard to the general validity of the theory.

The previous paper (ref. 2) outlined the evaluation of c_1 and B. As a further remark in connection with the evaluation of the constants of equation (1), it is convenient in computing E_1, after selecting an appropriate value for c_1 or B, to make use of tables of α_1/α_2 for various values of α_2 and of the equation

$$\alpha_2 = 1\Bigg/\left\{\sum_2^\infty (i-1)x_m^i\beta_i\,(\alpha_i/\alpha_2)\right\} \tag{8}$$

where x_m is the relative pressure at which $v = v_m$, (v_m being evaluated[2] by the method of BET.).

For solving equation (1) all but the first $q-1$ terms may be evaluated by replacing $\sum_q^\infty ix^id_i$ and $\sum_q^\infty x^id_i$ by suitable integrals. The accuracy of this approximation will, of course, depend on the magnitude of q. With suitable tables of functions at hand it is convenient to select q, e. g., equal to 20, in which case the integral approximation will be well within tolerable limits of accuracy. For $q = 20$, α_i will have become substantially constant, hence

$$\sum_q^\infty ix^id_i \cong \alpha_q \int_q^\infty ix^i\,e^{B\sum_1^i 1/i}\,di \cong \alpha_q\,\beta_{q-1}\,q^{-B}\int_q^\infty x^i\,i^{(B+1)}\,di \tag{9}$$

x being a particular relative pressure and i the variable.

Making the substitution $i \ln x = -y$, (9) becomes

$$\sum_q^\infty ix^id_i \cong \alpha_q\,\beta_{q-1}\,q^{-B}\frac{1}{(-\ln x)^{(B+2)}}\int_{y=-q\ln x}^\infty e^{-y}y^{(B+1)}\,dy$$

For $B = -2$, this becomes

$$\sum_q^\infty ix^id_i \cong d_{q-1}\,q^2\int_{-q\ln x}^\infty \frac{e^{-y}}{y}\,dy \tag{9a}$$

which may be evaluated from tables by Jahnke and Emde,[5a] or W.P.A. tables.[5b] For values of B from -1 to -2 (the allowable range as shown below) (9) may be evaluated from tables of gamma functions $\Gamma(n)$ as follows:

$$\sum_1^\infty ix^id_i \cong d_{q-1}\,q^2(-q\ln x)^{-(B+2)}\left[\int_0^\infty e^{-y}\,y^{B+1}\,dy - \int_0^{-q\ln x} e^{-y}\,y^{B+1}\,dy\right] = d_{q-1}q^2(-q\ln x)^{(-B+2)}\left\{\Gamma(B+2) - \int_0^{-q\ln x}\left[1 - y + \frac{y^2}{2!} - \frac{y^3}{3!} + \frac{y^4}{4!} - \ldots\right]y^{B+1}\,dy\right\} =$$

$$d_{q-1}q^2(-q\ln x)^{-(B+2)}\Gamma(B+2) - d_{q-1}q^2\left\{\frac{1}{B+2} + \frac{q\ln x}{B+3} + \frac{(q\ln x)^2}{(B+4)\,2!} + \frac{(q\ln x)^3}{(B+5)\,3!} + \frac{(q\ln x)^4}{(B+6)\,4!} + \ldots\right\} \tag{9b}$$

Values of $\Gamma(B+2)$ may be obtained, for example, from Dwight[6] and the relation $\Gamma(n+1) = n\,\Gamma(n)$.

Similarly we obtain

$$\sum_q^\infty x^id_i \cong d_{q-1}\,q^{-B}\int_q^\infty x^ii^B di \tag{10}$$

which, for $B = -2.0$, becomes

$$\sum_q^\infty x^id_i \cong d_{q-1}\,q^2\left\{\frac{e^{q\ln x}}{q} + \ln x\int_{-q\ln x}^\infty \frac{e^{-y}}{y}\,dy\right\} \tag{10a}$$

and for $-1 > B > -2.0$

$$\sum_q^\infty x^id_i \cong d_{q-1}\,q(-q\ln x)^{-(B+1)}\left\{\Gamma(B+1) - \int_0^{-q\ln x}\left(1 - y + \frac{y^2}{2!} - \frac{y^3}{3!} + \frac{y^4}{4!} + \ldots\right)y^Bdy\right\} =$$

$$d_{q-1}q(-q\ln x)^{-(B+1)}\Gamma(B+1) - d_{q-1}q\left\{\frac{1}{B+1} + \frac{q\ln x}{B+2} + \frac{(q\ln x)^2}{(B+3)\,2!} + \frac{(q\ln x)^3}{(B+4)\,3!} + \ldots\right\} \tag{10b}$$

Equation (1) for $B = -2$ thus becomes

$$v/v_m = \frac{\left(\sum_1^{q-1} ix^id_i\right) + d_{q-1}q^2\int_{-q\ln x}^\infty \frac{e^{-y}}{y}\,dy}{1 + \left(\sum_1^{q-1} x^id_i\right) + d_{q-1}q^2\left\{\frac{e^{q\ln x}}{q} + \ln x\int_{-q\ln x}^\infty \frac{e^{-y}}{y}\,dy\right.} \tag{1b}$$

and for $-1 > B > -2$, (1) may be written

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(5) (a) Jahnke and Emde, "Tables of Functions," Dover Publications, New York, N. Y., 4th ed., 1945, pp. 1, 6–9. (b) Federal Works Agency, W. P. A., New York City, "Tables of Sine, Cosine and Exponential Integrals" (1940).

(6) H. B. Dwight, "Tables of Integrals and other Mathematical Data," The Macmillan Co., New York, N. Y., 1947.

$$v/v_{\mathrm{m}} = \frac{\left(\sum_{1}^{q-1} i x^i d_{\mathrm{i}}\right) + d_{q-1}q^2(-q \ln x)^{-(B+2)}\Gamma(B+2) - d_{q-1}q^2\left\{\frac{1}{B+2} + \frac{(q \ln x)}{B+3} + \frac{(q \ln x)^2}{(B+4)\,2!} + \frac{(q \ln x)^3}{(B+5)\,3!} + \ldots\right\}}{1 + \left(\sum_{1}^{q-1} x^i \mathrm{d}_{\mathrm{i}}\right) + \mathrm{d}_{q-1}q(-q\, ln\, x)^{-(B+1)}\Gamma(B+1) - \mathrm{d}_{q-1}q\left\{\frac{1}{B+1} + \frac{q \ln x}{B+2} + \frac{(q \ln x)^2}{(B+3)\,2!} + \frac{(q \ln x)^3}{(B+4)\,3!} + \ldots\right\}} \tag{1c}$$

Limits on B.—For $x = 1.0$ we have

$$v/v_{\mathrm{m}} = \frac{\left(\sum_{1}^{q-1} i d_{\mathrm{i}}\right) + d_{q-1}q^{-B}\int_q^{\infty} i^{B+1}\,\mathrm{d}i}{1 + \left(\sum_{1}^{q-1} d_{\mathrm{i}}\right) + d_{q-1}q^{-B}\int_q^{\infty} i^{B}\,\mathrm{d}i} = \infty \tag{11}$$

From (7) we see that $B < 0$, since $c_1 < 1.0$. Moreover, from (11) $B \geqslant -2$ in order that $v/v_{\mathrm{m}} \longrightarrow \infty$ as $x \longrightarrow 1.0$. Also, (11) becomes indeterminate for $B \geqslant -1$. In fact, it will be shown that values of $B \geqslant -1$ are unacceptable because they lead to infinite values of the surface pressure π of the adsorbed film. We thus conclude that B will be restricted by the physical conditions of the problem to the region $-1.0 > B \geqslant -2.0$. In view of uncertainties in the theory of a and the fact that errors in E_1 will in general be largely compensated in c_1 (and B) one has little reason, however, to be disturbed if B should sometimes turn out to be a little less than -2.0 (for we are still assured of the fact that v will be infinite for $x >$ 1.0). One could, of course, avoid this technical difficulty by adjusting a to make $B = -2.0$ and this should perhaps be done if the discrepancy should turn out to be quite large, (*e.g.*, $-B = 2.5$).

High Relative Pressure Extrapolations.—Jura and Harkins[7] have published several type II isotherms admirably suited for a careful evaluation of equations (1), (4) and (4a) in that their data extend over the entire region $0 < x < 1.0$. Figure 2 presents their experimental data for nitrogen (at 77.3°K.) on anatase, together with theoretical curves for a values of 1.0, 1.3 and 1.5. It is quite significant that, while the agreement between the observed and calculated curves is independent of a for $x < 0.8$, excellent agreement is obtained only for $a = 1.5$ as $x \rightarrow 1.0$ in agreement with Hill's form (6a) of E_{i}. Calculations were also made for water, *n*-butane and *n*-heptane on anatase only for $a = 1.5$, and, except for *n*-heptane, the agreement is excellent over the entire range $0.05 < x < 1.0$ as shown in Fig. 3. In *n*-heptane a large discrepancy between the experimental and calculated data are encountered for $x > 0.9$. There seems to be no way of resolving this difficulty except that perhaps the saturation pressure used in

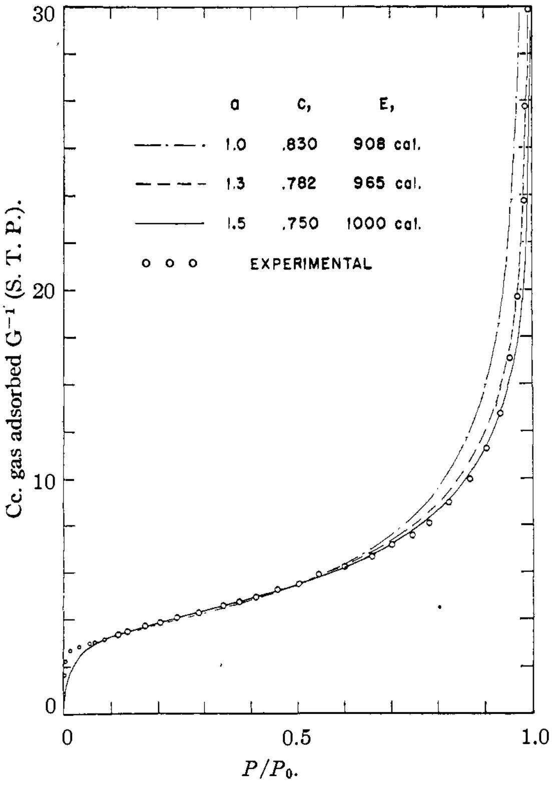

Fig. 2.—Influence of the repulsive term on the calculated adsorption isotherm of nitrogen on anatase—comparison with experimental.

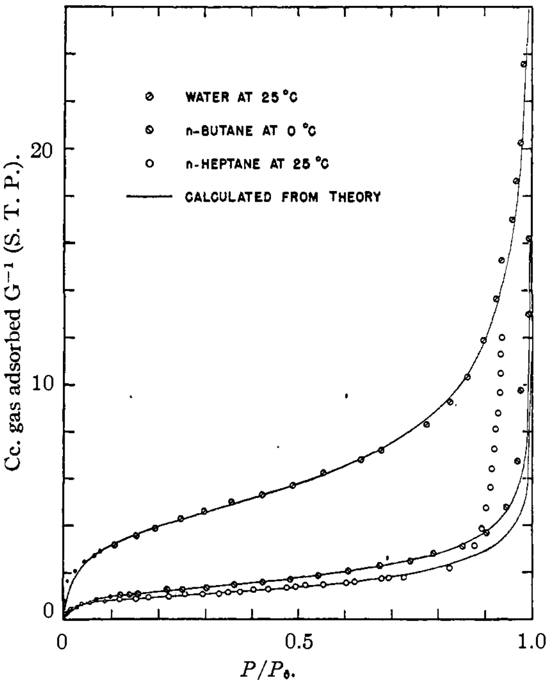

Fig. 3.—Comparison of theoretical and experimental adsorption isotherms.

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[7] G. Jura and W. D. Harkins, THIS JOURNAL, 66, 1356 (1944).

TABLE I

CONSTANTS OF EQUATION (1) FROM SEVERAL ADSORPTION ISOTHERMS

Adsorbate	Adsorbent	T, °K.	v_m, cc./g.	a	c_1	$-B$	E_1, cal./mole	Constants from data of
Nitrogen	Anatase	77.3	3.23	1.0	0.830	1.473	908	Jura and Harkins
Nitrogen	Anatase	77.3	3.23	1.3	.782	1.888	965	Jura and Harkins
Nitrogen	Anatase	77.3	3.23	1.5	.750	2.166	1000	Jura and Harkins
Water	Anatase	298.1	3.50	1.5	.884	2.056	3420	Jura and Harkins
n-Butane	Anatase	273.1	1.07	1.5	.796	2.00	3030	Jura and Harkins
n-Heptane	Anatase	298.1	.776	1.5	.863	2.00	3800	Jura and Harkins
Methyl acetate	Vitrous silica	298.1	1.12	1.0	.952	.675	2410	Palmer and Clark[8]
Methyl acetate		298.1	1.12	1.5	.912	1.250	2730	
Nitrogen	Fe-Al$_2$O$_3$ catalyst	77.3	135	1.0	.862	1.200	898	Emmett and Brunauer[9]
Nitrogen		77.3	135	1.5	.775	1.950	998	
Argon	Fe-Al$_2$O$_3$ catalyst	90.1	126	1.0	.884	0.970	852	Emmett and Brunauer[9]
Argon		90.1	126	1.5	.823	1.49	918	

computing the experimental data may have been in error. This is indicated from the fact that the experimental curve seems to be approaching about $x = 0.94$ asymptotically rather than $x = 1.0$ as one would expect. In fact, assuming this to be the case there is no difficulty in fitting the experimental curve with equation (1) with $a = 1.5$. It is interesting that no indication of this strange occurrence is to be found in any part of the curve below a relative pressure of 0.9. Table I lists values of the various constants of equation (1) for the cases illustrated in Figs. 2 and 3 together with others studied in reference (2) which are here recalculated for $a = 1.5$, previous calculations being carried out only for $a = 1.0$. While, as shown in Table I, $B < -2.0$ in nitrogen and water on anatase for $a = 1.5$, this discrepancy is not considered significant. The divergence difficulty at $x = 1.0$ would be cleared up by taking $B = -2.0$ and $a = 1.38$, but the agreement in the range $0.85 - 0.95$ in x would not be as good as when the values $B = -2.166$ and $a = 1.5$ are used. It is of interest that the use of $a = 1.5$ tends to change the values of E_1 and c_1 in the right direction to agree with experimental differential net heats and expected theoretical coördination ratios, respectively, although several extraneous factors must still be operating to give values of c_1 which from theory seem peculiarly high.

Surface Pressure of the Adsorbed Film.—Bangham's[10,11] equation for the surface pressure π of an adsorbed film of gas on a solid obtained by the integration of Gibbs' adsorption equation in terms of data from the adsorption isotherm may be written

$$\pi = \gamma_s - \gamma_{sf} = \frac{RT}{V\Sigma}\int_0^x \frac{v\,dx}{x} \qquad (12)$$

where γ_s is the surface tension of the solid, γ_{sf} that of the film covered solid, V is the molar volume of the gas, Σ the specific area of the solid, v the volume of gas adsorbed per gram of adsorbent, and x the relative pressure p/p_0 of the gas. Evaluating the integral (12) between zero and the saturation pressure p_0, we obtain in cases of perfect wettability

$$\pi_{0-1} = \gamma_s - \gamma_{Ls} - \gamma_L \qquad (13)$$

where γ_{Ls} is the interfacial tension between the solid and the film, and γ_L is the surface tension of the adsorbate in the liquid state, the subscripts on π indicating the limits of integration. Equation (13) is useful, as shown by Jura and Harkins,[12] in determining the work of adhesion W_A, the spreading coefficient $S_{L/s}$, and the free energy of emersion f_E. It may also be used to establish a lower limit to the surface tension of the solid which, when a sufficiently polar adsorbate is used, may, in some cases, approach quite closely the true surface tension γ_s. By correlating this with theoretical data, from which one may establish an upper limit to γ_s, one may be able to bracket γ_s in some cases within quite close limits. Equations (12) and (13) are of further considerable interest in that they may be used to provide a critical test of the validity of the various theoretical adsorption equations. In this connection Jura and Harkins[12] have carried out graphical integrations of (12) for several of their own experimental isotherms. Their method is complicated by two troublesome extrapolations, one in the region where x approaches zero and the other in the region where x approaches unity. They minimized the difficulties inherent in these extrapolations, however, by obtaining experimental adsorption data covering as completely as possible the entire adsorption isotherm. Their work thus provides valuable data for an evaluation of our theoretical adsorption equation.

Integration of Surface Pressure Equation.—The validity of the theoretical adsorption equation (1) with

$$d_i = \alpha_i\beta_i = \exp\left\{E_1\left(1 + \frac{1.5}{8} + \ldots + \frac{1.5}{i^3}\right) + E_L(c_1 - 1)\left(1 + {}^1/_2 + \ldots + \frac{1}{i}\right)\right\}\Big/RT \qquad (14)$$

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(8) W. G. Palmer and R. E. D. Clark, *Proc. Roy. Soc.* (*London*), **A149**, 360 (1935).

(9) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1552 (1937).

(10) D. H. Bangham, *J. Faraday Soc.*, **33**, 805 (1937).

(11) Alexander, "Colloid Chemistry," Vol. VI, Chapter 1, Reinhold Publishing Corp., New York, N. Y., 1946.

(12) G. Jura and W. D. Harkins, THIS JOURNAL, **66**, 1356 (1944)

may be evaluated by means of equation (12) and the results of Jura and Harkins. Substituting (1) and (14) in (12) and integrating we obtain

$$\pi_{x_1-x_2} = \frac{RTv_{\mathrm{m}}}{V\Sigma}\int_{x_1}^{x_2}\frac{\sum\limits_{1}^{\infty}(ix^{i-1}d_{\mathrm{i}})\mathrm{d}x}{1+\sum\limits_{1}^{\infty}x^{i}d_{\mathrm{i}}} \equiv$$

$$\frac{2.303RTv_{\mathrm{m}}}{V\Sigma}\left|\log\left(1+\sum_{1}^{\infty}x^{i}d_{\mathrm{i}}\right)\right|_{x_1}^{x_2} \qquad (15)$$

This integration is performed by making use of the identity

$$\sum_{1}^{\infty} ix^{i}d_{\mathrm{i}} \equiv x\frac{\mathrm{d}}{\mathrm{d}x}\left(1+\sum_{1}^{\infty}x^{i}d_{\mathrm{i}}\right) \qquad (16)$$

(Whenever it is necessary to evaluate $\sum\limits_{1}^{\infty} x^{i}d_{\mathrm{i}}$ where x is less than unity but still large enough that the series converges very slowly, one may make use of the integral approximations of equation (10)). Equation (15) integrated over the entire isotherm becomes

$$\pi_{0-1.0} = 2.303\,\frac{RTv_{\mathrm{m}}}{V\Sigma}\log\left(1+\sum_{1}^{\infty}d_{\mathrm{i}}\right) \qquad (17)$$

The term $\sum\limits_{1}^{\infty} d_{\mathrm{i}}$ may be evaluated as accurately as desired by means of the approximation

$$\sum_{1}^{\infty} d_{\mathrm{i}} \cong \sum_{1}^{q-1} d_{\mathrm{i}} + \alpha_{\mathrm{q}}\int_{q}^{\infty}\beta_i\,di \cong \alpha_{\mathrm{q}}\,\beta_{\mathrm{q}-1}q^{-B}\int_{q}^{\infty} i^{B}\,d_{\mathrm{i}} =$$

$$d_{q-1}q^{-B}\left|\frac{i^{(B+1)}}{B+1}\right|_{q}^{\infty} \qquad (18)$$

where $B = E_{\mathrm{L}}\,(c_1 - 1)/RT$ and the integer q is chosen large enough that α_{q} is, within close limits, the limiting value of the series α_i. Hence, (17) becomes

$$\pi_{0-1} = \frac{2.303RTv_{\mathrm{m}}}{V\Sigma}\log\left\{1+\sum_{1}^{q-1}d_{\mathrm{i}} + d_{q-1}q^{-B}\left|\frac{i^{(B+1)}}{B+1}\right|_{q}^{\infty}\right\} \qquad (19)$$

It is evident that B must be less than minus one in order that π_{0-1} will remain finite. This and the fact that $v \rightarrow \infty$ as $x \rightarrow 1.0$, show that the acceptable limits on B are $-1 > B \geqslant -2$. For $B < -1.0$, (19) gives

$$\pi_{0-1} = 2.303\frac{RTv_{\mathrm{m}}}{V\Sigma}\log\left(1+\left(\sum_{1}^{q-1}d_{\mathrm{i}}\right)\frac{-d_{q-1}\,q}{B+1}\right) \qquad (19a)$$

In the BET equation (ref. 3)

$$v/v_{\mathrm{m}} = c\sum_{1}^{\infty}ix^{i}\Big/\left(1+c\sum_{1}^{\infty}x^{i}\right) \qquad (20)$$

B is zero. The BET equation is, therefore, unsatisfactory from the viewpoint of the Gibbs adsorption equation. This situation was pointed out by Cassel.[13] The same argument of course, applies to the various modifications of the BET equation (*e.g.*, Anderson's[14] and Pickett's[15] equations in which attempts are made to apply the BET equation at high relative pressures). In the low relative pressure region ($x < 0.35$) one can, of course, justify the BET equation and various modifications of it[16,17] from the viewpoint of the Gibbs theorem. Moreover, in this region the present theory is consistent with the BET equation because of the very rapid convergence of the series of equation (14) at low x.

Results

Since (14) is not in agreement in most cases with experimental isotherms for $x < 0.05$, the integration of (12) by application of (1) and (14) can logically be carried out only over the range $0.05 < x < 1.0$. Thus, it is still necessary to employ a graphical integration such as that of Jura and Harkins[12,18,19] to evaluate $\pi_{0-0.05}$. Our evaluations of $\pi_{0-1.0}$, therefore make use of the equations

$$\pi_{0-1.0} = \pi_{0-.05} + \frac{2.303RTv_{\mathrm{m}}}{V\Sigma}\log\left\{\frac{1+\left(\sum\limits_{1}^{q-1}d_{\mathrm{i}}\right) - d_{q-1}q/(B+1)}{\left(1+\sum\limits_{1}^{\infty}(0.05)^{i}\,d_{\mathrm{i}}\right)}\right\} \qquad (21)$$

in which $\pi_{0-.05}$ is taken from the work of Jura and Harkins. Table II gives values of $\pi_{0.05-1.0}$ calculated from (15) for $x_1 = 0.05$ and $x_2 = 1.0$. Values of $\pi_{0-.05}$ shown in Table II were taken from Jura and Harkins[12] (Fig. 8). The values $\pi_{0-1.0}$ obtained from (21) are compared with $\pi_{0-1.0}$ data obtained by Jura and Harkins using the graphical method.

TABLE II

SURFACE PRESSURE OF VARIOUS FILMS ON ANATASE (DYNES/CM.)(Σ = 13.8 SQ. M./G.)

Adsorbate	$\pi_{0-.05}$[a] Graphical	$\pi_{0-1.0}$[a] Graphical	$\pi_{0-1.0}$ Equation (11)
Nitrogen (77.5°K.)	23.2	55.5	53.2
Water (298.1°K.)	63.6	187.0	183.8
n-Butane (273.1°K.)	8.0	42.3	41.6
n-Heptane (298.1°K.)	10.7		39.7
		37.1	38.9
		($\pi_{0-0.9}$)	($\pi_{0-0.9}$)

[a] Taken from Fig. 8 of ref. 7.

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The results in Table I show that the theoretical adsorption isotherm (1) not only has the correct form required by the Gibbs adsorption theorem but also that it yields quite accurate data on surface tension lowering for relative pressures above about 0.05. It should perhaps be noted, however, that this is true in all cases studied only when the repulsive term in the adsorbate–adsorbent interaction is taken into account, two examples being found (Table I, in which equation (1), with $a = 1.0$ instead of 1.5, leads to an improper ($B > -1$) solution of the Gibbs equation.

The method developed in this paper for calculating $\pi_{0.5-1.0}$ is not necessarily restricted to type II (and III) isotherms; it may be applied equally well to isotherms (types IV and V) in which capillary condensation occurs, since the surface pressure π will not be affected by the pore structure of the solid. It is necessary only that the isotherm have a large enough free or unrestricted adsorption region for $x > 0.05$, *e.g.*, $0.05 < x < 0.2$ or $0.05 < x < 0.5$, etc.), to allow one to evaluate the constants E_1, c_1, and v_m.

One will observe that the surface pressure of the film which forms at $x = 0.05$, *i.e.*, $\pi_{0-0.05}$, is generally a large part of the surface pressure of the film at saturation pressures, *i.e.*, $\pi_{0-1.0}$. For example, Table II shows that $\pi_{0-0.05}/\pi_{0-1.0}$ is 0.43 for nitrogen on anatase. Moreover, one cannot be sure of the accuracy of $\pi_{0-0.05}$ determined graphically in view of the uncertainties in the graphical method of extrapolation to $x = 0$ and necessary experimental errors in the adsorption data in the low x region. These considerations thus emphasize the need for further theoretical developments for handling problems in the $0 < x < 0.05$ region.

Summary

The theory of adsorption developed in an earlier publication including, however, the repulsive term previously neglected is shown to agree with several type II isotherms over the entire range of relative pressures from 0.05 to 1.0. Methods are outlined for handling the complex infinite series of the theoretical equation, and the convergence and divergence properties of the equation are discussed.

The Bangham equation derived from the Gibbs adsorption equation for the surface pressure π of an adsorbed film is integrated by means of the theoretical adsorption isotherm. The calculated surface pressures are shown to be in excellent agreement with data determined by Jura and Harkins from graphical integration of the Bangham equation employing the experimental adsorption isotherms. The theory offers a method for evaluation of surface pressure from all types of physical adsorption isotherms including those exhibiting capillary condensation.

RECEIVED AUGUST 13, 1948

[CONTRIBUTION NO. 13 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thermodynamic Properties of Thiophene[1]

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The thermodynamic properties of sulfur compounds are of interest for several reasons. From a practical point of view, the increasing interest in the sulfur compounds occurring in or derivable from petroleum makes it important to have an extensive knowledge of the properties of these substances. Such information would be useful in the refining of petroleum and in the preparation of sulfur derivatives of hydrocarbons. Also, the thermodynamic properties of the simpler sulfur compounds are of interest because of the information such data would yield with respect to their molecular structures. Finally, as in the case of hydrocarbons, a study of representative members of a homologous series of sulfur compounds would yield relationships permitting the estimation of properties of compounds which had not been studied.

The study of some sulfur compounds of interest to the petroleum industry has recently been added to the Bureau of Mines program of thermodynamic research. Thiophene, because of its importance and intrinsic interest, was chosen as the first compound to be studied in this field. Listed below, in their order of presentation in this paper, are the several types of investigation carried out: Section (1), low-temperature heat capacity; Section (2), vapor pressure; Section (3), heat of vaporization, vapor heat capacity, gas imperfection, and entropy of the ideal gas; Section (4), heat of combustion and heat of formation; Section (5), thermodynamic functions from spectroscopic and molecular structure data. From these investigations, relatively complete thermodynamic information about thiophene in the low pressure region has been obtained.

The Material.—Two samples of thiophene differing somewhat in their histories were used

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(1) Portions of this paper were presented at the Atlantic City Meeting of the American Chemical Society, April, 1947.

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