ADSORPTION ISOTHERMS OF GASES IN POROUS SOLIDS

A Thesis

Presented to

the Faculty of the Department of Physics

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Ъy

Sung Ho Suck

June 1968

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ABSTRACT

By the application of classical statistical mechanics, a new equation describing the adsorption isotherms for gases in percus solids is described as the phase equilibrium between a free gas phase, a compressed gas phase and an adsorbed gas phase in a closed system. Here the properties of adsorbed gas molecules above the first layer on the pore surface are approximated as those of a liquid, that is, the chemical potential and density of adsorbed gas molecules above the first layer are approximated as those of the liquid. This description of the adsorbed molecules is shown not only to describe adsorption data very well, but also to offer a means of explaining phenomena such as film transport and anomalous viscosities of gases in small pores or capillaries.

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I. INTRODUCTION

The concentration of gas molecules is found to be greater in the immediate vicinity of a surface than in the gas phase when a gas is allowed to come to equilibrium with a solid or liquid surface. The process by which this surface excess is formed is called adsorption. Adsorption of a gas on a solid is a spontaneous process. Adsorption processes may be classified as physical or chemical depending on the nature of the forces involved. Physical adsorption, also termed 'Van der Waals adsorption', is caused by molecular interaction forces, while chemical adsorption, usually abbreviated to 'chemisorption', involves transfer of electrons between the adsorbent and the adsorbate. The latter process involves essentially the formation of chemical compounds between the adsorbate and the outermost layer of adsorbent atoms.

Although introduced as early as 1914, the potential theory (1) of Polanyi is still regarded as fundamentally sound. According to this theory, the adsorbent exerts a strong attractive force upon the gas in its vicinity. This attraction gives rise to adsorption. The forces of attraction are so great that many adsorbed layers can form on the surface. Since the forces anchoring a molecule to the surface decay with distance, a multimolecular adsorbed film must be regarded as lying in an intermolecular potential gradient. The solid with its adsorbed film may be likened to the earth with its atmosphere surrounding it.

A fundamental advance in the theory of adsorption was made (2) (3) (4)when Langmuir (1912, 1915, 1926) introduced the idea that, owing to the regular arrangement of the atoms in the surface of a solid, the force acting on a gas molecule near the surface would depend on the distance of the gas molecule from the surface. He proposed that the effect of this could be taken into account by assuming that there is a definite number of sites per unit area of solid surface on which adsorption of gas atoms or molecules can take place, and that, when these sites are all occupied, the force acting on a molecule approaching the surface is so small that no further adsorpoccurs. The theory of Langmuir's isotherm is based on the tion fact that only a monolayer is formed from a parent gas on the surface of solid. According to this theory, there exists on the solid a number of sites X at which a single particle can be adsorbed in an energy state below that of a free particle at rest. It is further assumed that there is only one quantum state of adsorption at each site, and that there is no interaction between adsorbed molecules. Under the assumptions above, Langmuir's isotherm equation is obtained as,

$$\Theta = \frac{bP}{1+bP} \qquad (1)$$

where \ominus is the fraction of the sites filled by molecules, P is the pressure of the free gas, and b, a function of temperature.

To explain the phenomena of multilayer adsorption, there are (5) theories such as capillary condensation, polarization, and the BET

theory.⁽⁶⁾ According to the Langmuir isotherm, the monolayer fills up only for extremely high pressure in the parent gas. The BET theory due to Brunauer, Emmett, and Teller assumed:

1. the energy of adsorption on any site is independent of whether or not any neighboring site is occupied - in other words we neglect interaction between adsorbed particles.

2. each adsorbed particle itself becomes a site for possible further adsorption.

3. the energy of adsorption in any layer above the first is equal to W_L and independent of the layer depth. These assumptions lead to the BET isotherm equation

$$N = \frac{XYt}{kt(1-t+Yt)}$$
(2)

where x = the number of sites on the surface of an adsorbent,

N = the number of adsorbed molecules,
t =
$$e^{(M+W_L)/kT}$$
, and $\gamma = e^{W_1/kT}/e^{W_L/kT}$

where W_1 is the energy of adsorption of the first layer molecule and W_L , the energy of adsorption for molecules in higher layers. It is, also, noticed from the BET theory that the evaporation condensation properties of the molecules in the second and higher layers are similar to those of the liquid state.

It is well known that there are attractive forces between any two neutral atoms or molecules which are separated by a distance large compared to their own dimensions. These are known as Van der Waals forces and are of a long-range nature. These Van der Waals forces are electromagnetic in origin. As was first shown by London, they arise from second-order perturbation theory applied to the electrostatic interaction between two dipoles; the energy of the interaction being proportional to R^{-6} . If a pair of atoms or molecules come very close together, the overlapping of charges gives rise to repulsive forces. Thus the interaction potential is modified to yield the well known Lennard-Jones 6-12 potential

$$\Phi(R) = 4 \varepsilon \left[\left(\frac{c}{R} \right)^{12} - \left(\frac{c}{R} \right)^{6} \right]$$
(3)

(9) (10) The potential has been used recently by Halsey and Barker in treating the physical adsorption.

In developing the theory of physical adsorption, it has been generally assumed that all gas molecules disappearing from the free gas phase are adsorbed to the pore surfaces of the adsorbent, resulting in two phase equilibrium. When free gas molecules are allowed to come into the pores, some of the gas molecules will remain compressed in an intermediate space without losing their degrees of freedom, while other gas molecules will be adsorbed promptly on the surfaces of the pores.

The new model introduced in this paper is used to develop the physical adsorption isotherm equation under the assumptions that

1. There exist three phase equilibria; free gas, compressed gas and adsorbed gas phase.

2. The properties of adsorbed gas molecules above the first layer of gas molecules are similar to those of a liquid; i.e., the density of adsorbed gas molecules above the first layer is approximated by that of liquid.

3. The force of attraction between a gas molecule and a solid is chosen to be the London dispersion force.

4. The free gas follows Van der Waal's gas law, thus accounting only for the interaction of pairs of gas molecules.

Under the assumptions described above an adsorption isotherm equation is derived in this paper.

II. Three Phase Equilibrium

The gas molecules closer to the wall of a pore are in a stronger field of force than those farther away from the wall. In practice, it is found that a gradual though comparatively rapid increase in thickness of the adsorbed film sets in well before the pressure of the parent gas saturates, indicating a multilayer adsorption. The film becomes practically identical with a layer of the liquid phase as the pressure approaches saturation, with no apparent discontinuity in the process. However some of the gas molecules are not adsorbed but are in the potential field of the solid, and hence are in a compressed gas state, having different properties from the adsorbed gas molecules. The new adsorption mechanism introduced here involves the equilibrium of three phases, the free gas phase, the compressed gas phase, and the adsorbed gas phase.

This new model is compared with the models pictured by previous theories in Fig. 2-1 and Fig. 2-2.



"Macroporous" and "microporous" substances suggest that we may divide porous substances into at least two subgroups. Porous materials such as sponge or pumice can be classified as macroporous materials. In 1927 Scott Russel⁽¹¹⁾ distinguishing between macropores and micropores, fixed the borderline at a pore diameter of 5 \mathcal{M} (.0005 mm). Porous materials for which adsorption phenomena are important have pore diameters ranging in size down to less than 3 x 10⁻⁶ cm. It is difficult to assign a definite shape to the tortuous pores. If the mean dimensions of the irregularities of the pores are comparatively larger than the range of the forces between gas molecules and the adsorbent, the actual shape really does not matter very much. Thus in our model, the pores of the adsorbents are assumed to be cylindrical capillaries for mathematical convenience.

We shall neglect triple, quadruple, etc. collisions of gas molecules and assume that they only interact by collisions of pairs of molecules. Thus the real gas is a Van der Waal's gas. The interaction energy between a gas molecule and a solid is assumed to be purely due to London dispersion forces.

We consider the gas in a pore divided into separate regions as shown in Fig. 3, the kth region being a thin cylindrical shell of volume V_k at distance r_k from the axis and containing N_k molecules.



FIG.3 Cylindrical Pore

The motion of the N_k number of gas molecules in a region k with a volume V_k in a pore may be considered classically so that the Hamiltonian of the system can be written in the form

$$E_{\kappa} = \sum_{i=1}^{N_{\kappa}} \frac{P_{c}^{2}}{2m} + \bigcup_{c-c} + N_{\kappa}^{2}L_{c-s}$$
(4)

The first term is the total kinetic energy of the gas molecules in the k^{th} region of the pore. U_{c-c} , the second term is the total interaction energy among the compressed gas molecules, and finally

 \mathcal{U}_{C-S} is the interaction energy between a compressed gas molecule and the solid. This interaction energy is assumed to have the same value for all molecules in the same region. The second term may be adopted as the Lennard Jones 6-12 potential Eq. (3) in Chapter 1. The third term in Eq. (4) can be represented

$$U_{c-s}(r) = -c \int_{-\infty}^{\infty} \int_{r}^{2\pi} \left(\frac{c}{R_{c-s}^{2} + r^2 - 2rR\cos(\theta + \overline{z})^3} \right)^{2\pi}$$
(5)

where c is dispersion constant, and δ is the number of molecules per unit volume of the adsorbent. This is a superposition of pair interactions of solid molecules with a gas molecule, the potential being the Lennard Jones type, neglecting the repulsive part. The triple integral in Eq. (5) is integrated with respect to z first and then with respect to R. The result is

$$U_{C-S}(Y) = \frac{-c\delta\pi}{4Y} \begin{cases} \binom{2\pi}{6} (Y - R_0 C_{\Theta \Theta}) d\Theta}{2Ain^2 \Theta (Y^2 + R_0^2 - 2rR_0 (OS\Theta)^3)} \end{cases}$$
(6)
$$-\frac{1}{Y^2} \int_{0}^{2\pi} \frac{c\Theta S\Theta}{Sin^4 \Theta (Y^2 + R_0^2 - 2rR_0 C\Theta S\Theta)^3} \end{cases}$$

Let $X = r/R_0$, then the integrands in Eq. (5) are converted to dimensionless form as

$$\begin{aligned} \mathcal{U}_{c-s}(X) &= \frac{-C\delta\pi}{4R_{o}} \left\{ \int_{0}^{2\pi} \frac{-(X - \cos\theta)d\theta}{2\chi \sin^{2}\theta (1 + \chi^{2} - 2\chi \cos\theta)^{2}} \right. \end{aligned} \tag{7}$$

$$- \frac{1}{\gamma^{2}} \int_{0}^{2\pi} \frac{\cos\theta (1 - \chi \cos\theta)d\theta}{\chi^{3} \sin^{4}\theta (1 + \chi^{2} - 2\chi \cos\theta)^{2}} \end{aligned}$$

or

$$U_{c-s}(X) = -\frac{c\delta\pi}{4R_{o}^{3}} f(X)$$
(8)

The integral above has been evaluated and plotted by Yu⁽¹²⁾, using a numerical method. The dimensionless potential f(x) is plotted against X in Fig. 4. Note that near the wall we have cut off the computed curve and inserted a deep potential well, this is an approximate way of taking into account the repulsive part of the potential near the wall. This potential well is the order of a molecular diameter in thickness.

The Gibbs distribution function depends not only on the energy but also on the number N of particles, in the body, and clearly the energy levels E_{nN} themselves also vary with N (this is indicated by adding subscript N). Then the thermodynamic potential Ω is derived as

$$\mathcal{L} = -kT \ln \left[\sum_{N} e^{\mathcal{L}N/kT} \sum_{n} e^{-E_{nN}/kT} \right]$$
(9)

Substituting Eq. (4) into Eq. (9) and setting $N = N_k$ we obtain



FIG. 4

Dimensionless Potential ENergr 11

$$-\Omega_{k} = -KT \ln \left[\sum_{N_{k}} e^{-\frac{M_{k}N_{k}}{2}} + \frac{1}{2} e^{-\frac{N_{k}}{2}} + \frac{1}{2} e^{-\frac{N_{k}}{$$

where Ω_{K} is the chemical potential of compressed gas in the pore and X_{c} is relative distance between compressed gas molecules. The quantity in the bracket above is the grand canonical partition function for the gas in the kth region.

We may consider a gas consisting of N_k identical molecules. Then in calculating the partition function one can integrate with respect to the coordinates of each molecule independently taking the integral over the whole gas volume occupied by the gas. The result, however, will have to be divided by the number of possible permutations of N_k molecules, i.e., by N_k . The thermodynamic potential \mathcal{L}_k is represented then as

$$\Omega_{k} = -kT \ln \left[\sum_{N_{k}}^{L} \frac{1}{N_{k}} e^{N_{k}(M_{c}-U_{c}-s)/kT} \left[e^{-\left(\sum_{c=1}^{N_{k}} \frac{P_{c}^{2}}{2m} + \bigcup_{c-c}\right)/kT} \right] (11)$$

For the time being, we consider triple, quadruple, etc. interactions of molecules including interactions of pairs of molecules. We obtain, following Landau and Lifschitz,

$$-\Omega_{k} = -PV_{k} = -KT \ln \left[\frac{1}{7} + \frac{3}{5}V_{k} + \frac{3^{2}V_{k}}{2!} \int_{e}^{-U_{12}/kT} dV_{2} + \frac{3^{3}V_{k}}{3!} \int_{e}^{-U_{123}/kT} dV_{2} dV_{3} + \cdots \right]$$
(12)

where

$$\xi = e^{(\mu_{c} - \nu_{c-S})/kT} \int e^{-p^{2}/_{2m}kT} d^{3}P$$

$$= \left(\frac{m_{k}T}{2\pi k^{2}}\right)^{3/2} \cdot e^{(\mu_{c} - \nu_{c-S})/kT}$$
(13)

 ${\tt U}_{12}$ is the interaction energy of two atoms and ${\tt U}_{123},$ the interaction of three atoms.

Lastly we divide Eq. (12) through by V_k and write the resulting series

$$P = kT \stackrel{\mathcal{B}}{\underset{n=1}{\overset{n}{\overset{n}}}} \frac{J_n}{n!} \stackrel{n}{\underset{\varsigma}{\overset{\gamma}{\overset{n}}}}$$
(14)

where

$$J_{1} = I , J_{2} = \int (e^{-U_{12}/kT} - I) dV_{2},$$

$$J_{3} = \iint (e^{-U_{123}/kT} - e^{-U_{12}/kT} - e^{-U_{23}} - e^{-U_{13}} + 2) dV_{2} dV_{3},$$
etc.
(15)

Differentiating Eq. (14) with respect to $\mathcal M$, we obtain the equilibrium number of molecules in the gas as

$$N_{\kappa} = V_{\kappa} \left(\frac{\partial P}{\partial M}\right)_{T, V_{\kappa}}$$
(16)

Bearing in mind that from the definition, $\frac{\partial 3}{\partial M_C} = \frac{3}{KT}$, we obtain

$$N_{k} = V_{K} \sum_{n=1}^{\infty} \frac{J_{n}}{(n-1)!} z^{n}$$
(17)

Now we retain the first two terms in Eq. (17), thus not taking into account the interaction of three, four, etc. molecules; we have the form

$$N_{k} = V_{k} (3 + J_{2} 3^{2}) = V_{k} (3 - 2B(T) 3^{2})$$
 (18)

where B is the second virial coefficient;

$$B(T) = \frac{1}{2} \int (1 - e^{-U_1 2/kT}) dV_k = -\frac{1}{2} J_2$$
 (19)

Recently, a number of studies of properties of gases in contact with high area solids at relatively high temperatures have been reported. At such high temperatures, physical pictures of monolayers as two dimensional liquid-like films no longer have much validity; rather, the adsorption should be viewed as an increase of gas density in the vicinity of the surface due to the attractive forces between solid and gas molecules. Our Equation (18) leads to the gas density as a function of position,

$$P(Y) = \left(\frac{mkT}{2\pi K^2}\right)^{3/2} e^{[\mathcal{U}_{a} - \mathcal{U}_{c-S}(Y)]/kT}$$

$$-2B(T) \left(\frac{mkT}{2\pi K^2}\right)^{3} e^{2[\mathcal{U}_{a} - \mathcal{U}_{c-S}(Y)]/kT}$$
(20)

However at sufficiently low densities we obtain

$$f(r) = e^{-u_{c-s}(r)} (\frac{m_{KI}}{2\pi r_{k}^{2}})^{2} e^{u_{c}/kT} = e^{-u_{c-s}(r)}$$
(21)

since B(t) rianglerightarrow 0. In fact our Eq. (21) is in agreement with the density as a function of position, as discussed by Steele, ⁽¹⁴⁾ obtained by introducing a simple Boltzman probability factor, showing that at sufficiently low temperatures, the maximum in $\int f$ is very sharp, and that at high temperatures this maximum is not only smaller, it is less sharp. This means that at low temperatures this phase is closer to the properties of the adsorbed phase than at high temperatures. In fact for a real gas at temperatures below the critical temperature the compressed gas very near the surface must be so dense as to suffer a phase transition to a liquid-like phase. We will return to this point in the next chapter.

At sufficiently low temperatures, monolayer adsorption may take place on the surface of a solid from a parent gas as in the adsorption of nitrogen molecules on charcoal. However, it may be possible to have particles on top of an adsorbed particle, thus resulting in multilayer adsorption as the pressure of the gas increases.

As we can see in Figure (4) those molecules very near the solid surface must be in a deep potential well. These molecules are assumed to loose all translational freedom and hence to exist as an adsorbed fixed monolayer.

We suppose that there exists on the solid a number X of sites at which a single particle can be adsorbed in an energy state below that of a free particle at rest. We further suppose that there is only one quantum state of adsorption at each site. Let there be N_a molecules adsorbed on the solid. The number of ways that molecules can be

assigned to sites is

$$\chi C_{Na} = \frac{\times !}{(\times - Na)! Na!}$$
(22)

Let the canonical partition function of a single molecule be q_a . The partition function Z_a for N_a molecules in a pore of X sites will be

$$\overline{Z}_{\alpha} = \frac{\times !}{(X - N_{\alpha})! N_{\alpha}!} g_{\alpha}^{N_{\alpha}}$$
(23)

Then the free energy of the adsorbed gas in the pore is obtained by using Stirlings approximation as

$$F = -kT[X \ln X - Na \ln Na - (X - Na) \ln (X - Na)$$

$$+ Na \ln Ga]$$
(24)

The chemical potential of this phase will be

$$\mathcal{M}_{a} = kT \ln \frac{Na}{(X-Na) \mathcal{F}_{a}}$$
(25)

Similarly we can formulate the partition function and free energy of a real gas to obtain,

$$F_{f} = F_{p} + \frac{N_{f}^{2} k T B(T)}{V_{f}}$$
(26)

where F_{p} is the free energy of a perfect gas, N_{p} is the total number of free gas molecules. Then we obtain for the chemical potential of the real gas,

$$\frac{\partial F_{f}}{\partial N_{f}} = M_{f} = M_{p} + 2\left(\frac{N_{f}}{V_{f}}\right) \times TB(T)$$
(27)

where \mathcal{M}_{p} is the chemical potential of a perfect gas;

$$M_{p} = -KT \ln \frac{V_{p}}{N_{p}} \left(\frac{mkT}{2\pi R^{2}} \right)^{\frac{3}{2}}$$
(28)

From the equation above we obtain

$$e^{MP/kT} = \frac{P}{kT} \left(\frac{2\pi K^2}{mkT}\right)^{3/2}$$
(29)

As mentioned earlier, the three phases, free gas (real gas outside of the pore) phase, compressed gas phase, and adsorbed gas phase must have the same chemical potential when the system is in equilibrium, or

$$\mathcal{M}_{f} = \mathcal{M}_{a} = \mathcal{M}_{c} \tag{30}$$

where \mathcal{M}_{a} is the chemical potential of adsorbed gas phase. From Eq. (25), (27) and (30), we obtain for the total number N_a of adsorbed molecules in the monolayer of one pore,

$$N_{a} = \frac{X \Lambda(T) e^{2 f_{f} B(T)}}{kT + \Lambda(T) e^{2 f_{f} B(T)} g_{a} P}$$
(31)

where

$$\Lambda(T) = \left(\frac{2\pi\hbar^2}{MkT}\right)^{3/2}$$
(32)

We now discuss the adsorption of a gas on the surface of a solid where the adsorbed molecules have an energy of adsorption below the energy of a molecule at rest in compressed gas phase. 'We may take the energy of the molecule at rest as the zero of energy; therefore the lowest energy of an adsorbed molecule is -W. Then the partition function for a single molecule of the monolayer is

$$\mathcal{F}_{a} = e^{w/k} T \tag{33}$$

Then Eq. (28) can be rewritten as

 $B \approx 0$

$$N_{a} = \frac{X \Lambda(T) e^{2\beta_{f}B} P e^{w/kT}}{kT + \Lambda(T) e^{2\beta_{f}B} P e^{w/kT}}$$
(34)

The equation above is the Langmuir adsorption isotherm derived statistically by Fowler⁽⁵⁾ but here with a correction factor from the Van der Waal's forces; for sufficiently low density of free gas molecules, we obtain the Langmuir isotherm⁽⁵⁾

$$N_{\alpha} \simeq \frac{X \Lambda(T) P e^{W/kT}}{kT + \Lambda(T) P e^{W/kT}}$$
(35)

since

This isotherm equation is not adequate to show how gas molecules disappear from the free gas phase, since molecules disappearing from the free gas exterior to the pores may exist in the pores in states other than the monolayer adsorption. In the next chapter we will show that the non-adsorbed molecules in a pore may exist in a condensed liquidlike thin film on the pore surface, and as a compressed gas phase in the remaining pore space.

III. Liquid-Like Adsorbed Film and Compressed Gas

The adsorbed layers beyond the first layer may have a structure similar to a liquid. The density of adsorbed gas beyond the first layer can be approximated by that of a liquid of the same substance. The first layer adsorption is different from the higher layer adsorption, since the adsorbate molecules in the first layer are in direct contact with the adsorbent and the effect of the adsorbent is quite strong in the first layer due to a very short range of action in the field of Van der Waals forces, i.e., the deep potential well as already described.

In gases, the molecular interaction is very weak, as this interaction increases, the properties of the gas deviate further and further from those of a perfect gas and eventually the gas becomes a condensed body, that is, a liquid. In the latter the molecular interaction is strong and the properties of this interaction (and hence the properties of the liquid) depend to a large extent on the precise nature of the liquid. One can, however, find an interpolation formula, qualitatively describing the transition from gas to liquid.

The second approximation for Eq. (8) in Chapter II gives

$$P = KT \xi \left(1 + \frac{J_2}{2} \xi \right)$$
(36)

and

$$N_{k} = V_{k} \Im (1 + J_{2} \Im)$$
 (37)

Eliminating Ξ from the two equations above we obtain, to the same accuracy

$$P = \frac{N_{k}kT}{V_{k}} - \frac{N_{k}^{2}kT}{2V_{k}^{2}}\overline{J}_{2}$$
(38)

where

J2

$$= -2B(T) = -2(b - \frac{a}{kT})$$
(39)

The J_2 is the same in each region of a pore since the closed system is in equilibrium.

Rearranging Eq. (38), one obtains the required interpolation equation of state for a real gas, that is, Van der Waal's equation,

$$\left[P + \alpha \left(\frac{N_{k}}{V_{k}}\right)^{2}\right] \left(V_{k} - N_{k}b\right) = N K T$$
(40)

The isotherms given by this equation are shown in Figure 5 below.



Then Eq. (40) can be converted into the following expression,

$$(P + a P^{2})(P - b) = KT$$
(41)

where $\int = \frac{N_k}{V_k}$, the number density.

From Eq. 40, we obtain the critical values of temperature, pressure,

and volume as

$$\bar{I}_{c} = \frac{8}{27} \frac{a}{bK}$$
, $\bar{P}_{c} = \frac{1}{27} \frac{a}{b^{2}}$, and $\bar{V}_{c} = 3 N_{k} \dot{b}$ (42)

At a temperature $T < T_c$ Eq. (41) yields $\left(\frac{\partial P}{\partial P}\right)_T \leq 0$ over certain ranges of density which is physically impossible. This number density varies over the region of the inhomogeneous two-phase equilibrium state. Thus we take the critical number density $\int_C = \frac{1}{3b}$ as the approximate number density at which the phase transition occurs for $T < T_c$ as well. Then we obtain

$$P_{c} \approx P(Y_{o}) = \left(\frac{m \, kT}{2\pi \, K^{2}}\right)^{3/2} e^{\left[\mathcal{M}_{a} - \mathcal{U}_{c-s}(Y_{o})\right]/kT} - 2B(T) \left(\frac{m \, kT}{2\pi \, K^{2}}\right)^{3} e^{2\left[\mathcal{M}_{a} - \mathcal{U}_{c-s}(Y_{o})\right]/kT}$$
(43)

at the distance $\mathbf{Y}_{\mathbf{x}}$ where the gas-liquid transition occurs, or

$$\int_{C} \simeq f(r_{0}) = \int_{f} e^{-U_{C-S}(r_{0})/kT} - 2B \int_{f}^{2} e^{-2U_{C-S}(r_{0})/kT}$$
where
$$\int_{f} = \frac{N_{f}}{V_{f}} = \left(\frac{mkT}{2\pi\pi^{2}}\right)^{3/2} e^{-Mf/kT}$$
(44)

is the density of free gas.

Realizing $\mathcal{M}_{a} = \mathcal{M}_{f}$ at equilibrium, Eq. (43) can be further converted into the form,

$$f(r_{0}) = \frac{P}{kT} e^{[\lambda f_{f}BkT - u_{c-S}(r_{0})]/kT} + J_{2}(\frac{P}{kT})^{2} 2[f_{f}BkT - u_{c-S}(r_{0})]/kT}$$
(45)

 $-U_{C-S}(Y_0)/kT$, we obtain,

$$e^{-u_{c-s}(r_{0})/kT} = \frac{kT}{4BP} (1 \pm \sqrt{1-8BS(r_{0})})e^{-2F_{H}B}$$
 (46)

From the equation above, the interaction energy $U_{C-S}(\gamma_0)$ between a solid and a molecule in the adsorbed gas layer at the distance Υ_0 at which the liquid-gas interface exists, is

$$U_{C-S}(Y_0) = 2BKT f_{f} - KT ln \frac{KT}{4BP} (1 \pm \sqrt{1 - 8BP(Y_0)})$$
(47)

Plotting a curve of $U_{C-S}(Y)$ versus $(R_0 - Y)^3 = Z_0^{-3}$, the thickness of a thin liquid-like gas film, we obtain a straight line, if $D \ll R_0$, determining a constant of proportionality \ll . Thus we find the following approximate relation,

$$U_{c-s}(r_o) \approx - \alpha Z_o^{-3} \tag{48}$$

where the negative sign is introduced because the potential energy of a molecule in a pore is due to attractive forces. The α in equation above is obtained as

$$d = \mathcal{A}_{6} c \delta \pi^{2} \tag{49}$$

by using the numerical values of $U_{\zeta-S}(\gamma)$ obtained by Yu, shown in Figure 4. In Eq. (49), C is the dispersion constant and δ is the number of molecules per unit volume of the adsorbent.

Substituting Eq. (48) into (47) and rearranging the result, we obtain the thickness Z_{n} of the adsorbed gas film beyond the first layer of adsorbed gas,

$$Z = \begin{bmatrix} \alpha \\ kT \ln \frac{kT \lambda(n)}{4BP} e^{-2f_{+}B} \end{bmatrix}$$
(50)

where

$$\lambda(Y_{0}) = 1 \pm \sqrt{1 - 8BP(Y_{0})}$$
(51)

The average number density of the liquid-like adsorbed gas film in a pore is

$$P_{L} = \frac{N_{L}}{V} = \frac{N_{L}}{\pi Z(2R-Z)L}$$
 (52)

where L is the length of a cylindrical pore. Then the total number of molecules in the liquid-like adsorbed gas film is

$$N_{L} = \int_{L} \pi Z_{0}(2R - Z_{0}) L$$
(53)

Substituting Eq. (50) into (53), we obtain

$$N_{L} = \int_{L} \Pi L \left\{ 2R \left(\frac{\Delta}{kT \ln \frac{kT \lambda (r_{0})}{4BP} e^{-2P_{f}B}} \right)^{3} - \left(\frac{\Delta}{kT \ln \frac{kT \lambda (r_{0})}{4BP} e^{-2P_{f}B}} \right)^{2/3} \right\}$$
(54)

From Eq. (54) it is noticed that as pressure increases the number of molecules of a liquid-like adsorbed gas increases, and that for the thin liquid-like adsorbed gas film the number of gas molecules adsorbed is linearly proportional to the surface area of a pore, as the second term in Eq. (54) is negligibly small for the thin layer adsorption.

Substituting Eq. (13) into Eq. (18) in Chapter 2 and integrating over all the space of the compressed gas phase, we obtain the following form,

$$N_{e} = \left(\frac{m_{kT}}{2\pi\pi^{2}}\right)^{3} e^{M_{c}/kT} \int_{0}^{R_{o}-Z'-D} \int_{0}^{2\pi} \int_{\frac{1}{2}}^{\frac{1}{2}} e^{-U_{c-S}/kT} rdyd\theta dZ$$

-2 B(T) $\left(\frac{m_{kT}}{2\pi\pi^{2}}\right)^{3} e^{2M_{c}/kT} \int_{0}^{R_{o}-Z'-D} \int_{0}^{2\pi} \int_{-\frac{1}{2}}^{\frac{1}{2}-ZU_{c-S}/kT} rdyd\theta dZ$ (55)

where R_0 is the radius of a pore, Z' is the thickness of an adsorbed gas film, and D is a distance from the wall to the position where dimensionless potential f(x) is cut off.

Thus employing Eq. (27), (29) and (30) in Chapter 2 we obtain from Eq. (55) the total number N_c of molecules in the compressed gas phase

$$N_{e} = \frac{P}{kT} e^{2\beta_{f}B} \left[I \left(R_{o} - Z'_{, D, T} \right) - 2B_{kT}^{P} \right) e^{2\beta_{f}B} I \left(R_{o} - Z'_{, D, T} \right) \right] (56)$$

where \int_{Γ} is the number density of free gas,

$$P_f = \frac{N_f}{V_f} , \qquad (57)$$

and

$$I(R_{0}-Z', P, T) = \int_{0}^{R_{0}-Z'-P} \int_{0}^{2\pi} \int_{-\frac{L}{2}}^{\frac{L}{2}} -\mathcal{U}_{c-s}(r)/kT$$
(58)

and

$$I(R_{0}-Z', D, \frac{T}{2}) = \int_{0}^{R_{0}-Z'-D} \int_{0}^{2\pi} \int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{u_{c-s}(r)/k(\frac{T}{2})}{r dr d \sigma d Z}$$
 (59)

Thus with Eqs. (54) and (56) we have, in this chapter, completed the expressions for the number of gas molecules both in the liquid-like gas film and the compressed gas phase.

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IV. A Complete Adsorption Isotherm

We consider a closed system with a given volume and a given number of gas molecules. A porous material with bulk volume V with porosity φ is dropped into this system. Then the pore surface becomes promptly covered with a unimolecular adsorbed layer at a certain temperature and a considerable increase in pressure will bring forth the formation of the higher layers of adsorption, each absorbed molecules being a site for another layer adsorbed molecule. If the pore space still permits, gas molecules would be compressed in an intermediate space due to the attractive forces of the adsorbents. If the number of gas molecules in the first layer, the liquid-like adsorbed film, and the compressed gas region are respectively N₁, N_L, and N_c, the total number of gas molecules in a pore is

$$N = N_1 + N_L + N_r \tag{60}$$

If there are M pores in a porous body of a bulk volume V, then the total number of gas molecules in all the pores of the porous body is

$$N_{t} = M \left(N_{1} + N_{L} + N_{c} \right) \tag{61}$$

Noticing that N_a , the number of adsorbed gas molecules derived as monolayer adsorption in Chapter 2 is identified as N_1 , the complete adsorption isotherm will be described as

$$N_{t} = \frac{SA(T) e^{2} P_{t}^{B} e^{w/kT} P}{kT + A(T) e^{2} P_{t}^{B} e^{w/kT} P} + M P_{L} TL \left\{ 2R \left(\frac{\alpha}{kT \ln \frac{kTA(P_{0})}{4B} e^{2} P_{t}^{B}} \right)^{\frac{1}{3}} - \left(\frac{\alpha}{kT \ln \frac{kTA(P_{0})}{4B} e^{2} P_{t}^{B}} \right)^{\frac{1}{3}} - \left(\frac{\alpha}{kT \ln \frac{kTA(P_{0})}{4B} e^{2} P_{t}^{B}} \right)^{\frac{1}{3}} \right\} + \frac{M I e^{2} P_{t}^{B} B}{kT} P - \frac{2M I B \left(e^{2} P_{t}^{B} B \right)^{2}}{(kT)^{2}} P^{2}$$
(62)

Where S=MX.

In Eq. (62), the B(T), the second virial coefficient was introduced by taking into account the interactions of pairs of molecules. If there is no interaction among the gas molecules, the adsorption isotherm equation (62) should lead to the adsorption isotherm equation obtained by Yu⁽¹²⁾ since she derived the adsorption isotherm under the assumption that the gas in pores is an ideal gas, thus neglecting Van der Waal's interaction between gas molecules. Clearly Eq. (62) leads to Yu's adsorption isotherm as expected if the interaction among gas molecules is very weak, that is,

$$N_{t} \simeq \frac{MI(R_{o}, p, T)}{KT} P_{t} \frac{\Lambda S e^{W/kT} P}{KT + \Lambda e^{W/kT} P}$$
(63)

The important point here is that without the Van der Waal's interaction between gas molecules the compressed liquid film cannot occur. (12) The integration $I(R_0, DT)$ in Eq. (62) as obtained by Yu can be expressed by curve fitting techniques as

$$I = \Pi R_{o}^{2} L G \left(\frac{P}{R_{o}}, n \right), \text{ where } n = \frac{C d \Pi^{2}}{4 R_{o}^{3} k T}$$
 (64)

The values of G are tabulated in the appendix of her thesis.

For practical applications, we will convert the quantity N_t appearing in Eq. (62) into the volume V at STP occupied by all the gas molecules in the closed system by the ideal gas law

$$P_{S} V = N_{t} K T_{\beta}$$
 (65)

where P_s is standard pressure and T_s standard temperature.

It is easily understood to obtain the relation

$$\frac{N_t}{S} = \frac{V}{V_m}$$
(66)

where $V_{\rm m}$ is the total volume of gas at STP necessary to saturate all the adsorbed monolayer. And S, the total number of sites for gas molecules in all the pores of a porous body.

With the help of Eq. (64) and (65) Eq. (62) will be converted into the following expression

$$V = \frac{V_{m} \Lambda(T) e^{W/kT} e^{2f_{4}B}}{KT + \Lambda(T)P e^{W/kT} e^{2f_{4}B}} + M(f_{4})P(T) + \frac{\sqrt{KT} \Lambda(T)P e^{W/kT} e^{2f_{4}B}}{KT + \frac{\sqrt{KT} \Lambda(T)P + \frac{\sqrt{KT} \Lambda(T)P}{4BP} e^{2f_{4}B}} + \frac{V_{m} V_{p} G (e^{2f_{4}B})}{S K T} + \frac{V_{m} V_{p} G (e^{2f_{4}B})}{S K T} + \frac{2V_{m} V_{p} B G (e^{2f_{4}B})}{S (kT)^{2}} + \frac{2V_{m$$

where $V_p = M(\pi R_o^2 L)$, the total pore volume of a porous body, and γ_s is the number density at STP.

V. Comparison of the Theory to Experiment

As we have already noticed, the Langmuir adsorption isotherm equation does not fit most of the experimental results. The BET theory based on Langmuir's theory explains adsorption isotherms for higher pressure regions comparatively better than many other theories known so far. However in both the Langmuir and BET theory the phase equilibrium between free gas and adsorbed gas phase was treated in a non-realistic fashion. Thus the two theories lead to the question of why other gas molecules do not exist in the pore space if volume is still available. Again this suspicion suggests the existence of another gas phase which we have been calling the compressed gas phase.

For the practical comparison of our theoretical results to experiment, we need to further examine the isotherm Eq. (67) of previous Chapter 4. Realizing that $e^{2\beta_{f}B} \approx 1$ for the free gas, it may be easily seen that this equation is approximated as, since $D = \left(\frac{\alpha}{kT \ln \frac{kT \wedge e^{2\beta_{f}B}}{4BP}}\right)^{3}$ $<< R_{o}$, and $\frac{2BP}{kT} << 1$, $V \simeq -\frac{V_{m} \Lambda(T)e^{W/kT}P}{kT + \Lambda(T)e^{W/kT}P} + \frac{V_{m} V_{P}G}{S \times T}P$ (68) $+ \left(\frac{\beta_{V_{R}}}{KS}\right) \sum \left(\frac{\alpha}{KT \ln \frac{kT \wedge e^{2\beta_{f}B}}{4BP}}\right)^{3}$

where $\Sigma = M 2 \pi R L$ the total surface area of a porous body. With the third term absent, we have Yu's adsorption isotherm equation

$$V = \frac{V_m \Lambda(t) e^{W/kT} P}{KT + \Lambda(t) e^{W/kT} P} + \frac{V_m V_p G}{s K_T} P$$
(69)

To obtain volume adsorbed per gram of adsorbent, we substitute V_p by $\oint M/d$, with \oint , the porosity, M, the total mass of the adsorbents and d, the density of the adsorbent. We further need to replace \sum , the total surface area by \mathcal{O}^- , the specific surface area. Then Eq. (68) can be rewritten as

$$V = \frac{V_{m} \Lambda(T) e^{W/kT} P}{kT + \Lambda(T) e^{W/kT} P} + \frac{\Phi M/d G}{S_{s} kT} P$$

$$+ \left(\frac{\beta V_{k}}{\beta_{s}}\right) \sigma \left(\frac{d}{kT \ln \frac{kT \Lambda}{4BP}}\right)^{\frac{1}{3}}$$
(70)

The second term in the equation above is not only dependent on the specific surface area but also on the structure of the solid. This equation can be further converted into the form,

$$V = \frac{V_{m} \cdot \delta(T) \times}{1 + \delta(T) \times} + \frac{\phi M/d \cdot G \cdot \delta(T)}{P_{s} \times T} P_{s} \times (71)$$
$$+ \left(\frac{P_{r}}{P_{s}}\right) - \left(\frac{\lambda}{KT} \ln \frac{\kappa T \lambda}{4BP_{s} \times}\right)^{\frac{1}{3}}$$

where $x = \frac{P}{P_0}$, P_0 being the saturation vapor pressure of the adsorbate at the temperature of the experiment, and γ (T) is defined

$$\Upsilon(T) = \frac{P_o \Lambda(T) e^{W/kT}}{KT}$$
(72)





The third term in Eq. (71) may be expressed explicitly in terms of critical point values of T, V and P, the dispersion constant, and number density as

$$\begin{pmatrix} P_{L} \\ F_{S} \end{pmatrix} \sigma \left(\frac{0.46 C \sigma \pi^{2}}{k T lm \frac{T P_{c}}{T_{c} p} \left(I I \sqrt{1 - \frac{27}{3} (I - \frac{27}{8T} C)} \right) \right)^{1/3}$$
(73)

The experimental results obtained by Joyner, Weinberger, and (15) Montgomery for gas adsorption on three different types of carbon which ' they called carbon 1, carbon 2, and carbon 5 are shown in Fig. 6 where nitrogen was used as the adsorbate. The validity of the isotherm equation above is tested with these data. In Fig. 6, the adsorption isotherms (68) are plotted by adopting the same values that Joyner et (15) al used. For

carbon 4, $V_m = 428.6 \text{ cc}$, $= 20.4 \text{ m}^2/\text{gr}$ carbon 2, $V_m = 318.3 \text{ cc}$, $= 36.6 \text{ m}^2/\text{gr}$ carbon 5, $V_m = 179.1 \text{ cc}$, $= 22.4 \text{ m}^2/\text{gr}$, and $\sqrt[3]{(T)} = 79.6$.

The rest of the needed values of physical quantities are: $T_c = 128^{\circ}K$, $P_c = 33.54$ atms, $T = 78.15^{\circ}K$, $c = 125.6 \times 10^{-60}$ erg-cm⁶, $S = \frac{3.12 \times 10^{23}}{cc}$ and $f_{\perp} = 1.64 \times 10^{22}/cc$ at $78.15^{\circ}K$.

With these values we have used equation (71) to plot the curves shown as the dotted lines in Figure 6. Also plotted separately are the isotherms (12)deduced by Yu, which consist of the first two terms of this equation, and the isotherms of Langmuir, which is just the first term of this equation.

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It is to be noted that the first term, the Langmuir isotherm, is not an adequate description of the data except over a very limited range of pressures.

On the other hand the Yu isotherm, the first two terms, is a good description of the data up to relative pressures of about 0.6. Thus the third term of Eq. (68) is only of significance for relative pressures above about 0.6. The fit of the complete equation to the data is seen to be excellent all the way up to pressures of 0.9 for all three isotherms.

The way in which the successive terms of the equation approximate to the data suggests the following simple test to evaluate the correctness of this isotherm equation in the higher pressure ranges, even without complete numerical values for all the parameters in the equation.

The difference between the experimental curves and Yu's adsorption isotherm is just the third term in Eq. (71), that is,

$$\Delta = \left(\frac{f_{L}}{f_{S}}\right) \sigma \left(\frac{\alpha}{kT \ln \frac{\kappa_{T} \lambda(Y_{0})}{4B \rho_{0} \chi}}\right)^{1/3}$$
(74)

Further, we obtain by rearrangement

or

$$\frac{1}{\Delta^{3}} = \left(\frac{kT}{\Delta}\right) \left(\frac{R}{P_{L}}\right)^{3} \left(\frac{1}{\sigma}\right)^{3} \left(\ln\frac{P_{0}}{P} + \ln\frac{kT\lambda}{4BP_{0}}\right)$$
(75)

$$\frac{1}{\Delta^{3}} = \left(\frac{kT}{\alpha}\right) \left(\frac{R}{R}\right)^{3} \left(\frac{1}{\sigma}\right)^{3} \left(\ln\frac{P_{a}}{P} + \ln\frac{kT\Delta}{4BR}\right)$$
(76)









× 1/100003 13 C4 H10 at 0° (Adsorption On Iron) 28 24 20 16 ,2 8 H In Pa ./ •2 •3 FIG. 12 1 against In Pa



where P_a is the atmospheric pressure. Thus experimental data should yield a linear plot of $\frac{1}{\Delta^3}$ against $\ln \frac{P_0}{P}$ or $\ln \frac{P_0}{P}$ according to our theory. The values of Δ are chosen to be the difference between the experimental curves of adsorption isotherms and linear curves, at sufficiently high pressures, judged from the Yu adsorption isotherm equation. Figure 7 shows this difference plotted in this fashion for the carbon 5 isotherm of Figure 6. Indeed it is linear within the accuracy of the data.

Thus encouraged we have taken the data of Brunear et al ⁽¹⁶⁾ ⁽¹⁾ for adsorption isotherms on silica gel and on an iron catalyst respectively, and as shown in Figures(8) and (11) have made an estimate of where the straight line portions of the Yu isotherm should occur for each isotherm. Then the difference between these estimated straight lines and the data curves have been read off and plotted as $1/a^3$ versus $\ln (P_{P})$ and $\ln (P_{A}/p)$ in Figures 9, 10, 12 and 13. Indeed we find in every case that the resulting plot is linear as dictated by the theory.

Discussion and Conclusions

Applying the methods of classical statistical mechanics we have derived a new equation describing the adsorption isotherms for gases in porous solids. The gas is treated as a Van der Waals gas and the London dispersion forces between solid and gas are incorporated. The new adsorption isotherm equation gives the number of gas molecules disappearing from the free gas phase into the pores of the solid as the sum of three parts:

(1) those adsorbed on the solid surface to form a fixed monolayer,

(2) those existing in the free pore space to form a compressed gas phase, and

(3) those condensed on the fixed monolayer to form a liquidlike gas film.

This last part exists only for temperatures below the critical temperature.

This isotherm equation has been shown to describe well the experimental data of adsorption found in the literature. Furthermore the relative importance of the three terms over different ranges of values of the equilibrium pressure is entirely consistent with their physical basis. Other existing adsorption theories yield isotherm equations which fit data almost equally well, the BET theory in particular.

The main features which recommend the new equation over those given by other theories are as follows:

a) The theory explains different portions of the isotherms as being dominated by different mechanisms. b) The prediction of a liquid film of definite thickness on the pore wall at a given temperature offers a means of explaining film transport and anomalous viscosities of gases in micropores or capillaries.

c) The important role of the phase transition at the critical temperature of the gas in distinguishing the mechanisms of adsorption at temperatures above and below the critical temperature is exhibited.

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