Theoretical Approach to Physical Adsorption of Gases on Solid Surfaces

by

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고체 표면 위의 기체 흡착에 관한 이론적 연구

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ABSTRACT

The grand canonical ensemble partition function for the adsorbed phase of gases on solid surfaces is derived according to the transient state theory of significant liquid structure. The derived adsorption isotherms from the partition function for argon, nitrogen and benzene adsorbed on various adsorbents are in good agreement with the observed values. The surface pressure, the molar entropy, the molar internal energy and the molar heat of adsorption are calculated for benzene adsorbed on graphite. The molar entropy is minimum at near the pressure where a close packed monolayer is formed. The method of parameter determination is illustrated.

요 약

액체 구조의 천이상태 이론을 써서 고체 표면에 기체가 흡착된 계에 대한 상태합을 유도하였다. 이 상태합을 써서 아르곤, 질소, 벤젠 등이 여러 가지 흡착제에 흡착되었을 때의 흡착 등은 곡선을 계산하였으며, 이 계산 값들은 측정치와의 좋은 일치를 보여 준다. 그리고 벤젠이 흑연 표면에 흡착되었을 때의 표면압, 몰엔트로피, 몰에너지, 몰흡착열 들을 계산하였다. 몰엔트로피는 표면이 단분자층으로 완전히 덮였을 때 최소값을 갖는다. 아울러 흡착에 관여된 여러 가지 물리적인 성질들의 계산 방법을 설명하였다.

INTRODUCTION

There are two main approaches to physical adsorption of gases on solid surfaces. The one is by the monolayer assumption of the adsorbed film. There have been many theories developed under this assumption; for instance, works by Langmuir[1] with kinetic consideration, by Halsey et al[2] with an integration of the gas-solid interaction energy over a structureless semi-infinite solid, by Ross-Olivier[3] applying the de Boer-Hill[4] isotherm for a two dimensional mobile film interacting with a surface having a gaussian distribution of adsorption energies, by Honig et al[5] with the order-disorder formalism of Hijmans-de Boer[6], by Steele[7] with the grand canonical ensemble partition function, and by McAlpin-Pierotti[8] applying the theory of significant liquid structure of Eyring et al[9]. The other is by considering the multilayer adsorption. Brunauer-Emmett-Teller's work[10] with the kinetic consideration, Hill's theory[11] with the canonical ensemble partition function, and Kim-Oh's development[12] assuming that the molecules in the first adsorbed layer

are localized and that those in the above layers are non-localized belong to this category. The theoretical treatments of multilayer formation reviewed by Young and Crowell[13] indicate that the difficulties are similar to those encountered with problems of the liquid state.

Recently, Pak, Ahn and Chang[14] developed the transient state theory of significant liquid structure (hereafter referred as transient state theory of liquid). The theory has been applied to various liquids[15] and thermodynamic properties, surface tension and viscosity have been calculated with success. In this paper, the theory of liquid is applied to the multilayer adsorption, taking the grand canonical ensemble to formulate the partition function for the adsorbed phase.

II. THEORY

Theoretical Basis

The molecules adsorbed on the solid surface vibrate in the direction normal to the surface (referred as z-direction). The interaction energy falls off rapidly as the distance between adsorbate and adsorbent increases, and when the distance reaches to that of twice the molecular diameter of adsorbate the energy become very much smaller. Therefore, the vibrational frequency and the ground state energy of the freedom in z-direction for the first adsorbed layer differ from those for the layers above.

In lateral direction (referred as x-y plane) of the surface, they behave like a two dimensional solid or liquid or gas depending on the adsorbent-adsorbate interaction energy, temperature and the equilibrium pressure of the gaseous adsorbate. If the pressure is low and the temperature is high enough to overcome the potential energy barrier for lateral displacement, they become a gaseous film. On the other hand, if the pressure is high and the temperature is low enough for them unable to jump out of an equilibrium position, they become a solid film. In the intermediate pressure and temperature, they become a liquid film.

By analogy with the transient state theory of three dimensional liquid, the two dimensional liquid film can be assumed to have solid-like, transient, and gas-like

degrees of freedom. The molecule adsorbed at a stable equilibrium position has the solid-like degree of freedom. If vacant sites are available to an adsorbed molecule in addition to its equilibrium position, the moleclue possesses strain energy and has positional degeneracy equal to the neighboring vacant sites, which has the transient degree of freedom. When an adsorbed molecule aquires enough energy to jump out of the equilibrium position into neighboring vacant sites, it has gas-like degree of freedom.

Derivation of Partition Function

Let N_i be the number of molecules adsorbed at the i-th layer, and M be the number of adsorbed molecules in the first layer when the surface is completely covered with adsorbate. The surface area of the adsorbent, a is proportional to M, $a = \alpha M$, where α is the area occupied by an adsorbed molecule, which is assumed to be equal to the cross-sectional area of a solid molecule of adsorbate, i.e., $\alpha = \dfrac{1}{2^{1/6}} \left(\dfrac{V_s}{N_o} \right)^{2/3}$, V_s and N_o being the solid molar volume of the adsorbate and Avogadro's number, respectively. The total number of the adsorbed molecules, N, is equal to $\sum_{i=1}^{\infty} N_i$, and the number of adsorbed molecules substracted by the first layer molecules becomes $N_m = N - N_1 = \sum_{i=2}^{\infty} N_i$, where subscript m represents total layers excluding the first layer.

Then, the grand canonical ensemble partition function for the adsorbed molecules becomes

$$\Xi = \sum_{N_1=0}^{M} \sum_{N_m=0}^{\infty} Q(N_1, N_m, M, T) \lambda^{N_1+N_m} \qquad (1)$$

where λ is the absolute activity, $e^{\mu/kT}$, for the adsorbed molecule and $Q(N_1, N_m, M, T)$ is the canonical ensemble partition function for the given variables of N_1, N_m, M and T. Since the molecules at the first layer and at the remaining layers are in different energy states, $Q(N_1, N_m, M, T)$ is given by

$$Q(N_1, N_m, M, T) = Q_1(N_1, M, T) \cdot Q_m(N_m, N_1, T) \qquad (2)$$

According to the transient state theory of liquid, the canonical ensemble partition function for the first adsorbed layer, $Q_1(N_1, M, T)$, can be given as follows;

$$Q_1(N_1, M, T) = \frac{M!}{\{M-(N_{1s}+N_{1t})\}! N_{1s}! \ N_{1t}!}$$
$$\cdot q_{1z}^{N_1} q_{1s}^{N_{1s}} q_{1t}^{N_{1t}} \frac{1}{N_{1g}!} q_{1z}^{N_{1g}} \qquad (3)$$

where $q_{1s}=\dfrac{b_s\,e^{\frac{2}{3}E_{1s}/RT}}{(1-e^{-\theta_{1s}/T})^2}$ (3a)

$q_{1t}=\dfrac{b_t n(x_1-1)e^{\frac{2}{3}E_{1t}/RT}}{(1-e^{-\theta_{1t}/T})^2}$ (3b)

$q_{1g}=\dfrac{b_g(2\pi mkT)}{h^2}\alpha N_1(x_1-1)$ (3c)

and $q_{1z}=\dfrac{e^{E_{1z}/RT}}{1-e^{-\theta_{1z}/T}}$ (3d)

In equation(3) "b" represents the molecular rotational and the interatomic vibrational partition function. "θ" and "E" are the Einstein characteristic temperature and the ground state energy, respectively, and the subscripts s,t, g and z stand for the solid-like, the transient, the gas-like, and the z-direction, respectively. In the transient state theory of liquid molar vacant volume is represented by $(V-V_s)$ and the number of gas-like molecules is $N(V-V_s)/V$, where V is the molar volme of the liquid. Then, free volume per gas-like molecule is

$$\frac{V-V_s}{N_o\dfrac{V-V_s}{V}}=\frac{V}{N_o}=\frac{V_s x}{N_o}$$

where $x=V/V_s$. Likewise, if free area per molecule in the first layer is represented by αx_1,

$$N_1\frac{\alpha x_1-\alpha}{\alpha x_1}=N_1\left(1-\frac{1}{x_1}\right)$$

becomes number of gas-like molecules in the first layer, Then,

$$\alpha x_1\cdot N_1\left(1-\frac{1}{x_1}\right)=\alpha N_1(x_1-1)$$

represents total surface free area for the gas-like molecules in the first layer. Then,

$$N_{1s}+N_{1t}=N_1-N_1\left(1-\frac{1}{x_1}\right)=N_1\frac{1}{x_1}\quad(3e)$$

$n(x_1-1)$ is the positional degeneracy of the transient molecules in the first layer where n is the number of the nearest neighboring sites for molecules in the first layer which is equal to $6(V_s/V_{t.p.})$ $V_{t.p.}$ being the molar volume of the liquid at the triple point of the adsorbate.

The canonical ensemble partition function for the remaining layers, Q_m, becomes

$$Q_m(N_m,N_1,T)=\frac{(N_{ms}+N_{mt})!}{N_{ms}!N_{mt}!}q_{ms}^{N_{ms}}q_{mt}^{N_{mt}}q_{mg}^{N_{mg}}\frac{1}{N_{mg}!}q_{mz}^{N_m}\quad(4)$$

where $q_{ms}=\dfrac{b_s e^{\frac{2}{3}E_{1s}/RT}}{(1-e^{-\theta_{1s}/T})^2}$ (4a)

$q_{mt}=\dfrac{b_t n(x_m-1)e^{\frac{2}{3}E_{1t}/RT}}{(1-e^{-\theta_{1t}/T})^2}$ (4b)

$q_{mg}=\dfrac{b_g(2\pi mkT)}{h^2}\cdot\alpha N_1$ (4c)

and $q_{mz}=\dfrac{e^{E_{mz}/RT}}{1-e^{-\theta_{mz}/T}}$ (4d)

The surface free area αN_1 is the sum of the area for each layer excluding the first layer:

$$\alpha(N_1-N_2)+\alpha(N_2-N_3)+\alpha(N_3-N_4)+\cdots\cdots$$
$$=\alpha N_1\quad(4e)$$

The total number of the gas-like molecules excluding the ones in the first layer is assumed to be equal to $N_m\left(1-\dfrac{1}{x_m}\right)$; and then,

$$N_{ms}+N_{mt}=\frac{1}{x_m}N_m\quad(4f)$$

The positional degeneracy for the transient molecule becomes $n(x_m-1)$.

Then, the grand canonical ensemble partition function is expressed as follows:

$$\Xi=\sum_{N_1=0}^{M}\frac{M!}{\left(M-\frac{1}{x_1}N_1\right)!\left(\frac{1}{x_1}N_1\right)!}\left\{\sum\frac{\left(\frac{1}{x_1}N_1\right)!}{N_{1s}!N_{1t}!}q_{1s}^{N_{1s}}q_{1t}^{N_{1t}}q_{1g}^{\left(1-\frac{1}{x_1}\right)N_1}\right.$$
$$\left.\cdot\frac{1}{\left[\left(1-\frac{1}{x_1}\right)N_1\right]!}q_{1z}^{N_1}\right\}\lambda^{N_1}$$
$$\cdot\sum_{N_m=0}^{\infty}\left\{\sum\frac{\left(\frac{1}{x_m}N_m\right)!}{N_{ms}!N_{mt}!}q_{ms}^{N_{ms}}q_{mt}^{N_{mt}}q_{mg}^{N_{mg}}\frac{1}{\left[\left(1-\frac{1}{x_m}\right)N_m\right]!}q_{mz}^{N_m}\right\}$$
$$\cdot\lambda^{N_m}\quad(5)$$

The sums over $\left(\frac{1}{x_1}N_1\right)$ and $\left(\frac{1}{x_m}N_m\right)$ mean the summations of all the terms satisfying the conditions $N_{1s}+N_{1t}=\dfrac{1}{x_1}N_1$ and $N_{ms}+N_{mt}=\dfrac{1}{x_m}N_m$, respectively. By summing the terms in brackets the equation (5) can be simplified as

$$\Xi=\sum_{N_1=0}^{M}\frac{M!(q_1\lambda)^{N_1}}{\left(M-\frac{1}{x_1}N_1\right)!\left(\frac{1}{x_1}N_1\right)!}\sum_{N_m=0}^{\infty}\left\{q_m\lambda N_1^{\left(1-\frac{1}{x_m}\right)}\right\}^{N_m}$$
$$\cdot\frac{1}{\left[\left(1-\frac{1}{x_m}\right)N_m\right]!}\quad(6)$$

where $q_1=(q_{1s}+q_{1t})^{\frac{1}{x_1}}\left(q_{1g}\frac{e}{N_{1g}}\right)^{\left(1-\frac{1}{x_1}\right)}q_{1z}$ (6a)

and $q_m=(q_{ms}+q_{mt})^{\frac{1}{x_m}}\left(q_{mg}\frac{1}{N_1}\right)^{\left(1-\frac{1}{x_m}\right)}q_{mz}$ (6b)

The running index N_m in equation (6) is trasformed to $\left(1-\dfrac{1}{x_m}\right)N_m$, and then the second summation is done as follows;

$$\Xi=\sum_{N_1=0}^{M}\frac{M!(q_1\lambda)^{N_1}}{\left(M-\frac{1}{x_1}N_1\right)!\left(\frac{1}{x_1}N_1\right)!}\cdot\frac{x_m}{x_m-1}$$

$$\cdot\sum_{(1-\frac{1}{x_m})N_m=0}^{\infty}(q_m\lambda)^{\frac{x_m}{x_m-1}N_1)^{(1-\frac{1}{x_m})N_m}}\frac{1}{\left[\left(1-\frac{1}{x_m}\right)N_m\right]!}$$

$$=\frac{x_m}{x_m-1}\sum_{N_1=0}^{M}\frac{M!(q_1\lambda)^{N_1}}{\left(M-\frac{1}{x_1}N_1\right)!\left(\frac{1}{x_1}N_1\right)!}e^{(q_m\lambda)^{\frac{x_m}{x_m-1}}N_1}$$

$$(7)$$

The summation of equation (7) is performed after transforming the running index N_1 to $\dfrac{1}{x_1}N_1$ to give

$$\Xi=\frac{x_1 x_m}{x_m-1}\sum_{\frac{1}{x_1}N_1=0}^{M}\frac{M!}{\left(M-\frac{1}{x_1}N_1\right)!\left(\frac{1}{x_1}N_1\right)!}$$

$$\left\{\left(q_1\,\lambda\,e^{(q_m\lambda)^{\frac{x_m}{x_m-1}}}\right)^{x_1}\right\}^{\frac{1}{x_1}N_1}$$

$$=\frac{x_1 x_m}{x_m-1}\left\{1+\left(q_1\lambda e^{(q_m\lambda)^{\frac{x_m}{x_m-1}}}\right)^{x_1}\right\}^{M}$$

$$(8)$$

Taking logarithm of equation (8) gives

$$\ln\,\Xi=\ln\frac{x_1 x_m}{x_m-1}+M\ln\left\{1+\left(q_1\lambda e^{(q_m\lambda)^{\frac{x_m}{x_m-1}}}\right)^{x_1}\right\}$$

$$(9)$$

The first term of the righthand side of equation (9) is negligibly small compared with the second term, accordingly

$$\ln\,\Xi=M\ln\left\{1+\left(q_1\lambda e^{(q_m\lambda)^{\frac{x_m}{x_m-1}}}\right)^{x_1}\right\}$$

$$(10)$$

Determination of Parameters

The value of λ can be determined using the equilibrium condition between the adsorbed phase and the gaseous adsorbate at a given temperature and pressure

$$\lambda=e^{\mu/kT}=e^{\mu*/kT}\xi=\lambda*\xi \qquad(11)$$

where $\xi\left(=\dfrac{P}{P_o}\right)$ is the relative pressure; P_o being the saturation vapor pressure; and $\mu*$ and $\lambda*$ are the chemical potential and the absolute activity of the gas at $\xi=1$, respectively.

The most probable values of x_1 and x_m can be determined by solving the following equations simultaneousy.

$$\left(\frac{\partial\ln\Xi}{\partial x_1}\right)_{x_m,\,\lambda,\,T,\,M}=0$$
$$\left(\frac{\partial\ln\Xi}{\partial x_m}\right)_{x_1,\,\lambda,\,T,\,M}=0$$
$$(12)$$

Perfoming the differentiations of equation (12) gives

$$\left(1-\frac{1}{e^{y_1}}\right)\left(\frac{1+\omega_1}{x_1-1}\right)+\ln x_1-\frac{1}{x_1}=-D-1-\ln q_{1z}$$
$$-\ln\lambda*-\ln\xi$$
$$y_m-\left(1-\frac{1}{e^{y_m}}\right)(1+\omega_m)=-\ln q_{ms}-\ln q_{ms}-\ln q_{mz}$$
$$-\ln\lambda*-\ln\xi$$
$$(13)$$

where $D=\ln\left\{\dfrac{b_g(2\pi mkT)e\alpha}{h^2}\right\}$ (13a)

$y_i=\ln\{1+n'(x_i-1e^{-\omega i}\},\ (i=1\text{ and } m)$ (13b)

$n'=n\left(\dfrac{1-e^{-\theta/iT}}{1-e^{-\theta i/T}}\right)^2\dfrac{b_t}{b_s}$ (13c)

and $\omega_i=\dfrac{2}{3}\cdot\dfrac{E_s-E_{it}}{RT}$ (13d)

Equation (13d) is equal to

$$\omega_i=\frac{2}{3}\frac{aE_s}{n(x_i-1)RT}$$

As it is assumed in the transient state theory of liquid "a" being a proportionality constant. The parametric values "a", "E_s", "θ_s" and "θ_t" can be found in the previous paper of Chang et al[14]. Taking $E_{mz}=(1/3)$ $\cdot E_s$, and $\theta_{mz}=\theta_s$, θ_{1z} can be calculated from the following equation.

$$\frac{\theta_{1z}}{\theta_{mz}}=\sqrt{\frac{E_{1z}}{E_{mz}}} \qquad(14)$$

where E_{1z} is obtained by a semiempirical method (Section IV of this paper), and then of x_1 and x_m at the various of ξ are determined from equation (13) The values of q_1 and q_m are found from the following equations:

$$\ln q_1\lambda=\frac{1}{x_1}(\triangle+y_1-\ln x_1-x_1)-\left(1-\frac{1}{e^{y_1}}\right)\left(\frac{1+\omega_1}{x_1-1}\right)-f$$

$$(15)$$

$$\ln q_m\lambda=\left(1-\frac{1}{e^{y_m}}\right)(1+\omega_m)-\left(1-\frac{1}{x_m}\right)(\triangle+y_m) \qquad(16)$$

where $\triangle=\ln q_{ms}-D+1$ and $f=(q_m\lambda)^{\zeta}$; ζ being equal to $x_m/(x_m-1)$.

If $x_1=1$, equation (15) becomes

$$\ln q_1=\ln q_{1s}+\ln q_{1z} \qquad(17)$$

and if $x_m=1$, equation (16) becomes

$$\ln q_m=\ln q_{ms}+\ln q_{mz} \qquad(18)$$

Thus, all the parameters in equation (10) are determined at a given temperature and pressure.

Statistical Thermodynamic Relations

The thermodynamic equation of state for the adsorbed film is

$$dE = TdS - \Phi dM + \mu dN \qquad (19)$$

where $\dfrac{\Phi}{\alpha} \equiv \phi$ is the surface pressure and S is the entropy for the N number of adsorbed molecules.

Integrating equation (19) gives

$$E = TS - \Phi M + \mu N \qquad (20)$$

Equation (20) is rearranged as

$$\Phi M = TS + \mu N - E \qquad (20')$$

Diffrentiating equation (20) and introducing equation (19) into the resulting equation, the equation of state with the independent variables of T, μ and M is obtained as follows:

$$d(\Phi M) = SdT + Nd\mu + \Phi dM \qquad (21)$$

According to the statistical thermodynamics and by using equation (10) the following relation is obtained:

$$\Phi M = \phi \alpha M = kTM \ln\{1 + (q\lambda e^f)^{x_1}\} \qquad (22)$$

The adsorption isotherm is given by

$$\sigma \equiv \frac{N}{M} = \frac{\lambda}{M}\left(\frac{\partial \ln \mathcal{Z}}{\partial \lambda}\right)_{T,M} = \frac{x_1 q(1+\zeta f)}{1+q} \qquad (23)$$

where $q = (q_1 \lambda e^f)^{x_1}$

From equations (21) and (22) the surface pressure is obtained as

$$\phi = \frac{kT}{\alpha} \ln(1+q) \qquad (24)$$

The entropy is found by differentiating equation (21) with respect to T at constant μ and M, after introducing equation (22) into equation (21).

$$S = \left(\frac{\partial(\Phi M)}{\partial T}\right)_{\mu, M} = kM\ln(1+q) + kTM \cdot \frac{q}{1+q}$$
$$\cdot \left(\frac{\partial \ln q}{\partial T}\right)_\mu \qquad (25)$$

The molar entropy for the adsorbed molecules, S, is given by

$$S_o = S \cdot \frac{N_o}{N} = \frac{S}{M} \cdot \frac{M}{N} \cdot N_o = \frac{S}{M} \cdot \frac{N_o}{\sigma} \qquad (26)$$

Introduction of equations (23) and (25) into equation (26) gives

$$S_o = -R(U + \ln\lambda) \qquad (27)$$

where

$$U = -\frac{1}{1+\zeta f}\left\{\frac{1+q}{x_1 q} \ln(1+q) + \frac{T\partial \ln q_1}{\partial T} + \zeta f T\frac{\partial \ln q_m}{\partial T}\right\} \qquad (27a)$$

The molar heat of adsorption is expressed as

$$\triangle H_o = (S_g - S_o)T = RT\left(U + \frac{5}{2} + T\frac{\partial \ln b_g}{\partial T}\right) \qquad (28)$$

where S_g is the molar entropy for the gaseous adsorbate.

From equations (20), (23), (24) and (27) the molar internal energy for the adsorbed molecules is found as

$$E_o = \frac{E}{\sigma} \cdot \frac{N_o}{M} = -RT(U + \ln\lambda) - RT\ln(1+q) + RT\ln\lambda$$
$$= -RT\{U + \ln(1+q)\} \qquad (29)$$

III. RESULTS

Adsorption Isotherm

The calculated adsorption isotherms by using equation (23) and the observed values at 77.5°K and 90.1°K for argon and nitrogen adsorbed on graphite P-33(1000°C), are compared in figures 1 and 2, respectively.
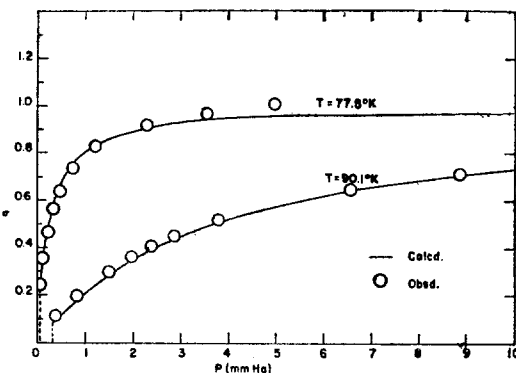

Fig. 1. Comparison of the calculated adsorption isotherms with the observed values[17] for argon adsorbed on P-33(1000°C).
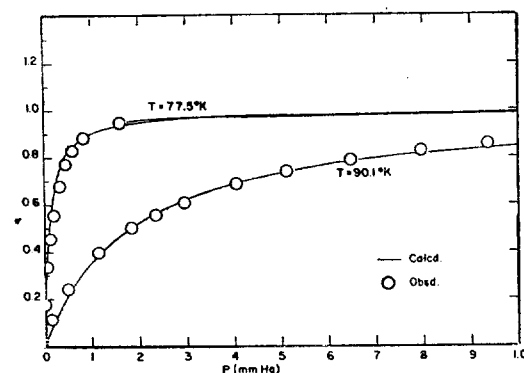

Fig. 2. Comparison of the calculated adsorption isotherms with the observed values[17] for nitrogen adsorbed on P-33(1000°C).

The calculated adsorption isotherms and the observed values at 90. 1°K (P$_0$=1. 30 atm.) for argon adsorbed on iron synthetic ammonia catalyst (Cat. 931) and on silica gel are compared in figure 3.
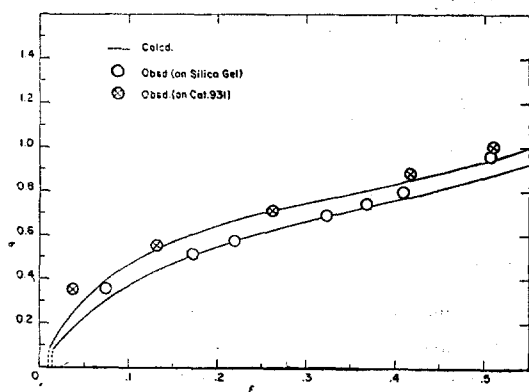
The calculated adsorption isotherms for argon and nitrogen adsorbed on graphite at near the respective crtical temperatures are shown in figure 5.

Fig. 3. Comparison of the calculated adsorption isotherms at 90. 1°K with the observed values for argon adsorbed on Cat. 931 (upper solid line) and on silica gel (lower solid line)[19].

The adsorption isotherm at 293. 15°K (P$_0$=0. 0992 atm.) for benzene adsorbed on the basal plane of graphite (graphitized carbon black) is calculated covering the range of the relative pressure from 0. 0 to 1. 0 and is compared it with the observed value in figure 4.
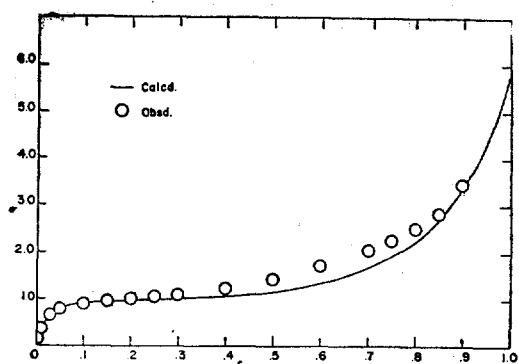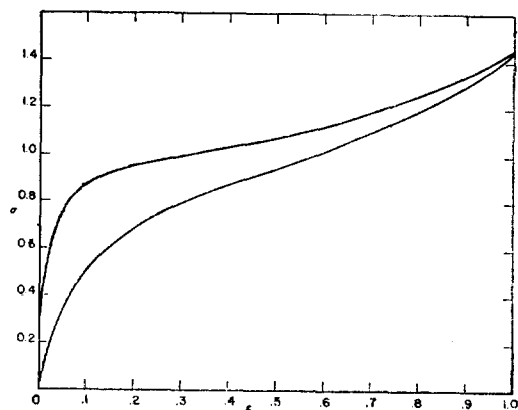

Fig. 5. The calculated adsoption isotherms for argon at 150°K (P$_0$=50 atm.) (lower solid line) and nitrogen at 120°K (P$_0$=22atm.) (upper solid line) on P-33 (1000°C).

Thermodynamic Properties

The calculated surface pressure, molar entropy and molar internal energy for benzene adsorbed on graphitized carbon black at 293. 15 °K are shown in figures 6, 7 and 8, respectively.

Fig. 4. Comparison of the calculated adsorption isotherm at 293. 15 °K with the observed value for benzene adsorbed on graphite[20].
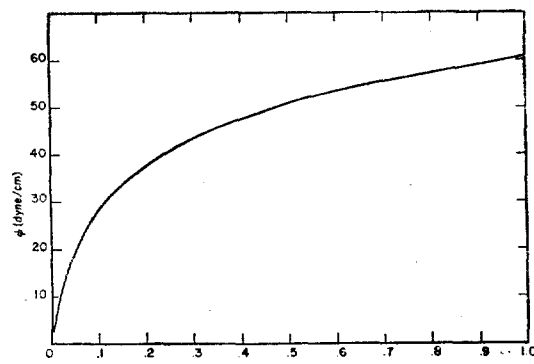

Fig. 6. The calculated surface pressure for benzene adsorbed on graphite at 293. 15 °K.
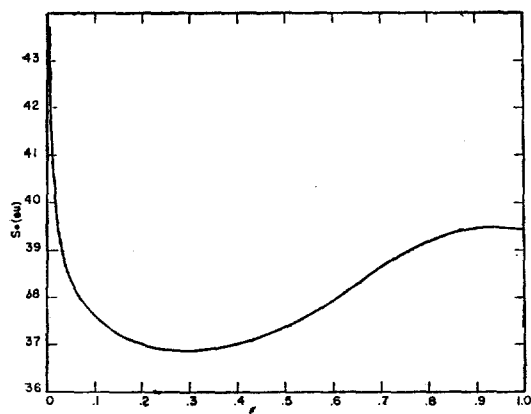
Fig. 7. The calculated molar entropy for benzene adsorbed on graphite at 293. 15°K.
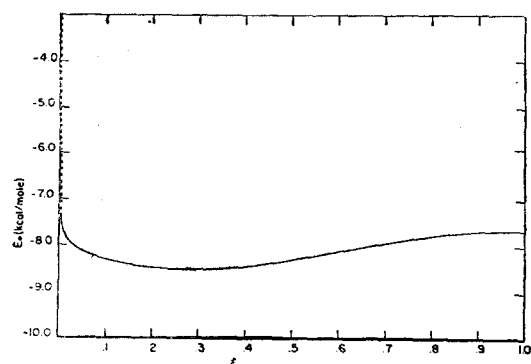

Fig. 8. The calculated molar internal energy for benzene adsorbed on graphite at 293. 15 °K

The calculated molar heat of adsorption for benzene adsorbed on graphitized carbon black at 293. 15 °K is compared with the observed differential heat of adsorption in figure 9.
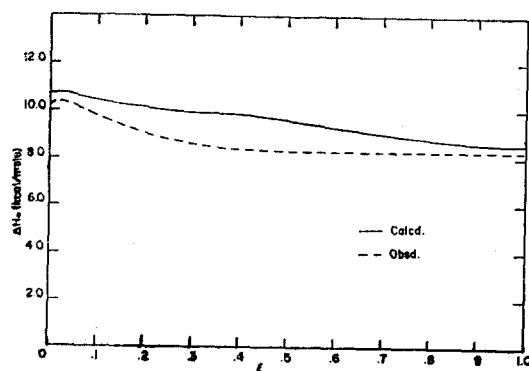
Fig. 9. Comparison of the calculated molar heat of adsorption for benzene adsorbed on graphite at 293. 15°K with the observed differential heat of adsorption[20].

Physical Properties of adsorbates

The calculated physical properties for argon, nitrogen and benzene, which are used in the calculation of the adsorption isotherms and the thermodynamic properties, are listed in the following tables 1 and 2.

TABLE 1. Physical properties of adsorbates which are independent of adsorbent.

	Argon	Nitrogen	Benzene
a E, cal/mole	1771	1507	10424
a θ_s °K	47. 65	54. 18	54. 88
a θ_t °K	47. 33	50. 05	48. 63
a a	0. 006152	0. 02066	0. 07537
a n	5. 345	5. 505	5. 280
b α Å²	13. 07	14. 54	27. 69

a, reference 14; b, calculated from the solid molar volume by using the relation given in section II.

TABLE 2. Physical properties of adsorbates which depend on adsorbent.

	$a\,\dfrac{E_{1z}}{\text{cal/mole}}$	$a\,\theta_{1z}$ °K	$b\,V_{\sigma=1.0}$ cc/g
A on P-33(1000°C)	1710	81. 0	c 2. 78
N₂ on P-33(1000°C)	1977	107. 5	c 1. 90
A on Cat. 931	1062	61. 49	d 1. 20
A on silica gel	990	59. 37	e 239
C₆H₆ on graphite	5905	71. 55	f 0. 123/m²

a, calculated according to the method illustrated in section IV; b, the volume of the adsorbed gas at S. T. P. which corresponds to a close packed monolayer formation; c, reference 17; d, reference 18; e, reference 19; f, reference 20, the value per m² of the adsorbent surface.

In table 3 the calculated values of x_1 and x_m at various vulues of ξ for benzene adsorbed on graphite are listed.

Table 3. The calculated values of x_1 and x_m for benzene adsorbed on graphite at 293.15 °K.

ξ	x_1	x_m
0.00390	37.91 1.15050	63.06
0.005	1.11493	49.38
0.01	1.089133	25.35
0.03	1.067416	9.1990
0.05	1.059576	5.96276
0.1	1.049577	3.53000
0.2	1.038860	2.30275
0.3	1.030192	1.88504
0.4	1.000000	1.67024
0.5	1.000000	1.53665
0.6	1.000000	1.44349
0.7	1.000000	1.37301
0.8	1.000000	1.31595
0.9	1.000000	1.26638
1.0	1.000000	1.21853

IV. DISCUSSIONS

There are liquid-gas phase transitions at P=0.317 mmHg in the isotherm of 90.1 °K and at P=0.0616 mmHg in the isotherm of 77.5°K for argon adsorbed on P-33 (1000 °C) as shown in figure 1. The calculated isotherms are in good agreement with those of the observed values.

As shown in figure 2 for the nitrogen adsorption isotherms on P-33 (1000°C), the calculated isotherms are in good agreement with the observed values. The liquid-gas phase transitions occur at P=0.00861 mmHg in the isotherm of 77.5°K and at P=0.0541 mmHg in the isotherm of 90.1°K.

As shown in figure 3 for the argon adsorption

isotherms on Cat. 931 and on silica gel, the calculated isotherms are in good agreement with those of the observed values. The liquid-gas phase transitions occur at ξ=0.0146 in the lower curve and at ξ=0.010 in the upper curve of figure 3. The solid-liquid phase transitions occur at about ξ=0.92 in the lower curve and at about ξ=0.87 in the upper curve which are not shown in the figure.

The calculated benzene adsorption isotherm on graphite which is shown in figure 4 is in good agreement with that of the observed value. The liquid-gas phase transition of the isotherm occurs at ξ=0.00390 and the solid-liquid phase transition occurs at about ξ=0.36. The solid-liquid phase transition of the isotherm occurs continuously in contrast with the liquid-gas phase transition.

As shown in table 3, at ξ=0.00390 two values of x_1, 37.91 and 1.15050 are obtained. The large value 37.91 is for the gaseous film and the small one 1.15050 is for the liquid film. When x_1=1.0, the solid film is formed. The value of x_m does not approach to 1.0 at 293.15 °K. This shows that the solid film of the second and the above layers cannot be formed at the temperature.

The type II adsorption isotherm approaches to the type I, if E_{1z} is large and temperature increases to the critical point as shown in figure 5 for argon and nitrogen.

As shown in figure 7, the molar entropy for the adsorbed benzene on graphite is minimum at about ξ=0.3 which is the relative pressure for formation of a close packed monolayer. As shown in figure 8, the molar internal energy curve for benzene adsorption on graphite versus ξ a minimum value is observed in the vicinity of the relative pressure where the entropy becomes minimum.

The calculated molar heat of adsorption of benzene on graphite is very comparable with the observed differential heat of adsorption as shown in figure 10.

The adsorption isotherms, at 90.1°K, for argon and nitrogen on adsorbents which have the various values of $r \equiv E_{1z}/E_{mz}$ are shown in figures 10 and 11, respectively.
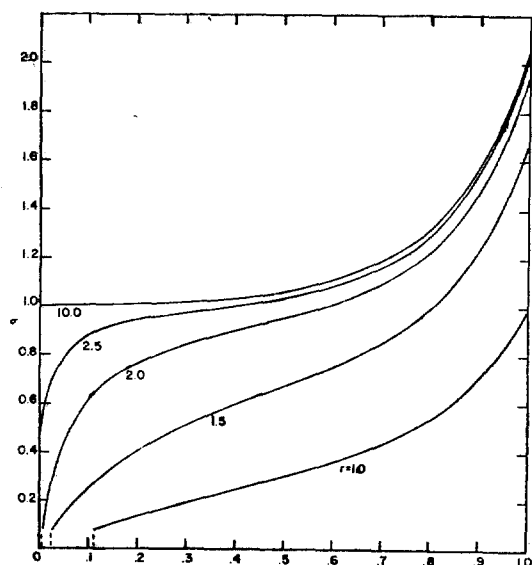
From the plot of σ versus ξ for various values of r as shown in figures 10 and 11, the values of ξ at $\sigma=1.0$, $\xi_{\sigma=1.0}$, are obtained. Then $(E_{1z}-E_{mz})/(RT)$ is plotted against $-\ln\xi_{\sigma=1.0}$ for argon and nitrogen at temperatures 77.5°K and 90.1°K. It is found that all the 4 curves coincide each other showing linearity. The slope of the curve is about 2.5 as shown in figure12.
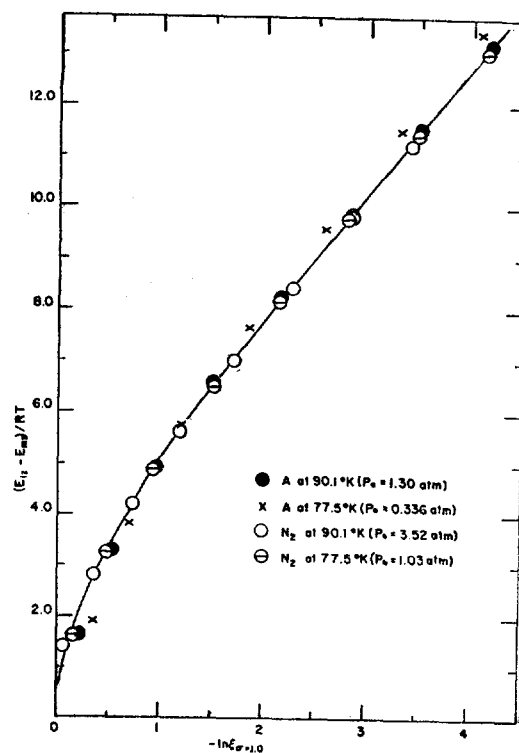

Fig. 10. The adsorption isotherms of argon, at 90.1 °K, on adsorbents having various values of r.

● A at 90.1°K (P₀ = 1.30 atm)
X A at 77.5°K (P₀ = 0.336 atm)
○ N₂ at 90.1°K (P₀ = 3.52 atm)
⊖ N₂ at 77.5°K (P₀ = 1.03 atm)

Fig. 12. The plot of $(E_{1z}-E_{mz})/(RT)$ against $-\ln\xi_{\sigma=1.0}$ to give a linear curve.

This fact means that $-\ln\xi_{\sigma=1.0}$ is proportional to $(E_{1z}-E_{mz})/(RT)$ with the proportionality constant, $\tau=1/2.5$, which is independent of temperature and the kind of adsorbates if they are non-polar molecules. According to kinetic consideration, it can be assumed that

$$P_{\sigma=1.0}=Ce^{-\frac{\tau E_{1z}}{RT}} \qquad (30)$$

and

$$P_0=Ce^{-\frac{\tau E_{mz}}{RT}} \qquad (31)$$

Fig. 11. The adsorption isotherms of nitrogen, at 90.1°K, on adsorbents having various values of r.

where C is a constant. Taking logarithms of equations
(3)) and (31), and substracting the resuling equation
of (30) from that of (31), it gives

$$-\ln\frac{P_{\sigma=1.0}}{P_0}=-\ln\xi_{\sigma=1.0}=\tau\cdot\frac{E_{1z}-E_{mz}}{RT} \qquad (32)$$

This indicates that the above fact illustrated in figure
12 is theoretically sound.

In figures (11) and (12), the type III adsorption
isotherms can be found if $r=1$.

For powdered adsorbent samples, it is found that
at high relative pressure, $\xi>0.5$, capillary condensa-
tion and pendular ring condensation take place and at
very low pressure surface heterogeneity effect is pro-
nounced. For this work surface homogeneity is assu-
med and, therefore, at very low pressure where surface
heterogeneity is pronounced, the calculated values do
not agree with observed data very well. On the other
hand, at very high relative pressure, where $\xi>0.5$,
due to effects of capillary condensation and pendular
ring condensation, agreement of calculated and expe-
rimental values can not be expected.

In developing this theory, neither localization nor
non-localization of the adsorbed molecules is assumed,
and it is found that this theory explains very well in
both cases.

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