

## Statistically Modeled Adsorption Isotherms for the Multilayer Gas Molecules Adsorbed on Non-porous Solid Adsorbents of Two and Three Groups Sites

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**Abstract**—The adsorption isotherms with each saturation vapor pressure factor ( $c_{s1}$ ,  $c_{s2}$  or  $c_{s3}$ ) for two groups of sites in two cases of the multilayer and for three groups of sites in one case of the multilayer are derived statistically in heterogeneous non-porous solid adsorbents without interactions among the adsorbed molecules. When some sites of BET isotherm are substituted by less energetic sites, the two-group isotherm obtained by the substitution shows less adsorption over the whole range of relative pressure than the BET isotherm prior to the substitution, at any combined values of  $f_1$  with  $M_1$  of the two-group isotherm with the same saturation vapor pressure factor. A method to get the monolayer sites ( $v_m$ ) from the ratios of the experimental isotherm to the theoretical isotherm at the whole relative vapor pressure minimizing the standard error is suggested. Our two- or three-group isotherms calculated through many experimental adsorption isotherm data selected appropriately provide larger values of  $v_m$  than those obtained from BET isotherms. Differential heat vs.  $v/v_m$  and Bose-Condensation heat are mentioned.

Key words: Statistical Thermodynamics, Two-group Site Adsorption Isotherm, BET Isotherm

### INTRODUCTION

In studying a catalytic reaction one should, in general, know the porosity and the surface area of the catalyst. They are basic materials for studying the reaction characters. In order to study these porosity and surface area of the adsorbents we conducted experiments on gas adsorption. The equations to describe the adsorptions theoretically well are the Langmuir adsorption isotherm for the monolayer adsorption and BET adsorption isotherm for the multilayer adsorption. In addition, there are a number of theoretical equations, but they are a little different from the present study. And we get used to studying the separation and the refinement of the mixed gas and the purification of gas, air, water, waste water and etc. through the adsorption. However the theoretical adsorption study for the porosity is recorded in the next literature.

In 1918 Langmuir derived the monolayer adsorption isotherm kinetically for gas molecules adsorbed on the homogeneous surface of adsorbents without attractions among the adsorbed molecules [Langmuir, 1918]. After that Tompkins developed statistically the adsorption isotherm for localized monolayer on the energetically heterogeneous surface of the solid with no lateral interaction [Tompkins, 1950]. Then the amount of gas adsorbed is calculated independently according to each group. And the total amount of the gas adsorbed on all groups of sites is obtained by adding the amount of the gas adsorbed on each group. We should not calculate that independently according to each group (it is much more than that obtained by the relationships among groups). The statistical surface monolayer adsorption isotherms on two and three groups of sites in the heterogeneous adsorbent are derived in the literature [Kim, 2000]. Hill [Hill, 1946] derived BET isotherm [Brunauer et al., 1938] statistically on one group of homogeneous adsorption sites for the multilayer adsorption since it was deriv-

ed kinetically by Brunauer, Emmett and Teller. It is found to be in good agreement with some experimental data for relative pressures less than about 0.5 [Pickett, 1945; Gregg et al., 1969]. But the theoretical BET isotherm deals with only one type of the identical adsorption sites. Even if the solid surfaces with which we have dealt until now are composed entirely of the identical atoms and uniform, they may have more than one different group of adsorption sites. Therefore, the exact fitness of the BET isotherm to the experimental adsorption data seems to be considerably limited. Hence if the adsorption isotherm does not belong to BET isotherm, the number of groups of adsorption sites can be assumed to be 2, 3 or at most several. Since the adsorbents are composed of the electronic bonding around a nucleus, we can consider the nucleus to be a mountain and the electrons to be a valley. When gas molecules are adsorbed on the adsorbent, the part localized by electrons of the adsorbate is attracted toward the nucleus site of the adsorbent which has the positive (+) charge. In physical adsorption, electron exchanges between the gas molecules and the adsorbent do not occur. The attraction and the repulsion of both nuclei and both electrons of the gas molecules and the adsorbent are harmonized electrostatically. The adsorption heat comes into being because of the collision of the electrons of the gas molecules and the adsorbent, the rotation, vibration and translation of the adsorbed gas molecules. The sites are composed of one, two, or three nuclei of the adsorbent. The two- or three-nucleus site may be stronger than the one nucleus site. The adsorption of gas molecules which have large branches may need the many nucleus site of an adsorbent such as a zeolite. On the other hand, in low vapor pressure the gas molecules are adsorbed on the stronger two- or three-nucleus sites first. This is the reason why the BET isotherm equation is fitted to the experimental data only in the beginning relative vapor pressure.

Here the multilayer adsorption isotherms are derived on two- and three-different groups of adsorption sites since the extension

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over more groups of sites brings many mathematical difficulties and expressions. Detailed surveys for the isotherms on heterogeneous surfaces are given in the literature [Jaroniec et al., 1988; Rudzinski et al., 1992].

Each group has a different adsorption interaction environment. The environmental differences between groups may be the potential strength which is a result of the contribution of all charges present in the structure, the potential frameworks and the potential volume size for kinematic, vibrational, rotational and electronic movement of adsorbed molecules. The movements of the adsorbed molecules are generally assumed to be independent in statistical calculation, that is, the molecules adsorbed on each group of the adsorbent are independent of those on another group of sites and even the other molecules on the same group of sites.

Since Eq. (14) in Hill's paper [Hill, 1946] was not explained well on the pure liquid (saturated vapor), we dealt with it by plugging the saturation vapor pressure factor into the isotherm equation. He also derived the localized unimolecular isotherm on the heterogeneous surface in a different way [Hill, 1949]. Timmermann [Timmermann, 1989] has derived three sorption stages isotherm (tss), improved by adding the third sorption stage to the two stages of BET isotherm and using the grand partition function. But the tss isotherm equation is the mathematically expanded isotherm equation including the BET isotherm equation. In the present derivation the procedure formulated by Hill for BET isotherm over one group of sites is similarly extended over two and three groups of sites.

The total thermodynamically possible state number of a system is the sum of the equally probable microstates calculated by each macrostate. A macrostate partition function of all molecules adsorbed on two or three groups of sites of the adsorbent is approximated to be the product of the total partition functions of all the molecules adsorbed on each group. Here the total partition function becomes the product of the partition function by Fermi-Dirac statistics for all the molecules adsorbed on the surface and the partition function by Bose-Einstein statistics for all the molecules adsorbed on from the second to the infinitive layer or a limited layer of each group of sites. A macrostate partition function represents the sum of equally probable microstates that correspond to the macrostate of the system at the constant temperature.

No lateral interactions occur among the adsorbed molecules, and the adsorption energies at all sites are not altered during the adsorption process. Finally, many comparisons are made between the present two- or three-group isotherms with the experimental data. And the monolayer sites and the surface areas are calculated.

The parts consist of section 1, 2 and 3. Sections 1 and 2 deal with the multilayer adsorption isotherms for two groups of sites and section 3 for three groups of adsorption sites.

## STATISTICAL MODELING

### 1. Adsorption Isotherm for Two Groups of Adsorption Sites with Infinite Number of Layers

We suppose that  $N_i$  indistinguishable molecules are independently distributed among  $B_i$  identical sites of the adsorbent surface by Fermi-Dirac statistics [Sears et al., 1975], according to which there can be no more than one molecule in each permitt-

ed adsorption site. Here the subscript  $i$  represents the group of the identical adsorption sites. Hence its configurational partition function, which denotes the number of ways placing the adsorbed molecules  $N_i$  over the sites  $B_i$ , is obtained by taking a combination of  $B_i$  identical sites taking  $N_i$  molecules at a time as follows:

$$\frac{B_i!}{(B_i - N_i)!N_i!}$$

Let us say that  $q_i$  is the molecular partition function of a molecule adsorbed on one site among the identical sites of group  $i$  and it refers to the total number of the microscopic molecular states of the adsorbed molecule. Hence the complete partition  $q_{N_i}$  for  $N_i$  molecules adsorbed on  $B_i$  sites of group  $i$  in the adsorbent is obtained by the product of  $N_i$  square of the partition function  $q_i$  with the above configurational partition function [McQuarrie, 1975; Adamson, 1990] as follows:

$$q_{N_i} = \frac{B_i! q_i^{N_i}}{(B_i - N_i)!N_i!} \quad (1)$$

Since the site is fixed, each molecular partition function  $q_i$  in each adsorption site is considered to be distinguishable. This requires only  $N_i$  square in  $q_i$  without dividing Eq. (1) by  $N_i!$  again.

It is supposed that the solid adsorbent has two groups, 1 and 2, of the adsorption sites where the electronic energies of the adsorbed molecules relative to the ground state energy of zero at infinite separations from the solid adsorbents are  $D_1$  and  $D_2$ , respectively. Then the molecular partition functions of the molecules adsorbed on sites of groups 1 and 2 are  $j_1 \exp(D_1/kT)$  and  $j_2 \exp(D_2/kT)$ . Here  $j_1$  and  $j_2$  are the localized partition functions of all internal degrees of freedom of the molecules adsorbed on groups 1 and 2. The localized partition functions can be classified into translational, vibrational and rotational partition functions.  $k$  and  $T$  are Boltzman constant and the absolute temperature of the system. The above simplified localized partition function will favorably allow the statistical calculations because our model calculations need the ratio between groups. This represents the same notion as Van Dun and Mortier [Van Dun et al., 1988a, b] who derived the cation distribution equations for three groups of sites of zeolites.

Suppose that  $N$  is the total number of the gas molecules adsorbed on two groups of sites over all layers of the solid adsorbent,  $N_{11}$  the number of the gas molecules adsorbed on group 1 of sites in the first layer and  $N_{12}$  the number of the gas molecules adsorbed on group 2 of sites in the first layer. Let us put the adsorption proportional constant between groups  $M_1$  as a ratio of  $N_{12}$  to  $N_{11}$ . Therefore  $N_{12}$  becomes  $M_1 N_{11}$ . Let us suppose that there are  $B_1$  and  $B_2$  sites of groups 1 and 2 per unit surface of the solid adsorbent. The spatial arrangement of the sites between groups is considered to be immaterial. Then if  $N_{11}$  and  $M_1 N_{11}$  ( $=N_{12}$ ) molecules are Fermi-Dirac statistically distributed on  $B_1$  and  $B_2$  sites in the adsorbent surface, the complete partition function  $Q_s$  ( $N_{11}$ ,  $M_1$ ,  $B_1$ ,  $B_2$ ,  $T$ ) of the adsorbed molecules on the both groups of the first layer is determined by multiplying the complete partition function of each group at the constant temperature as follows:

$$Q_s(N_{11}, M_1, B_1, B_2, T) = \prod_{i=1}^2 q_{N_i} \\ = \frac{B_1!}{(B_1 - N_{11})!N_{11}!} \{j_1 \exp(D_1/kT)\}^{N_{11}}$$

$$\frac{B_2!}{(B_2 - M_1 N_{11})! (M_1 N_{11})!} \{j_2 \exp(D_2/kT)\}^{M_1 N_{11}} \quad (2)$$

If we use the Bose-Einstein statistical distribution [Sears et al., 1975] for the second to infinite layer, it is meaningless to discern two groups of sites for them because the number of the gas molecules which can occupy any one site, whether it belongs to a large energetic group or small one, is unlimited. By using Bose-Einstein statistics for the molecules  $N - N_{11} - M_1 N_{11}$  from the second to infinite layers adsorbed on the top of  $N_1 + M_1 N_{11}$  sites in the first layer, the complete partition function for the molecules becomes

$$Q_m(N_{11}, M_1, N, T) = \frac{(N-1)!}{(N_{11} + M_1 N_{11} - 1)! (N - N_{11} - M_1 N_{11})!} \{j_m \exp(D_m/kT)\}^{(N - N_{11} - M_1 N_{11})} \quad (3)$$

In Eq. (3)  $j_m \exp(D_m/kT)$  is the molecular partition function of a molecule adsorbed on any one site from the second to infinite layer. Then  $j_m$  and  $D_m$  are its localized partition function of all internal degrees of freedom and its electronic energy of the adsorbed molecule relative to the ground state energy of zero at the infinite separation from the second to infinite layer. From now on the latter is called the Bose-Einstein energy. Since the molecules adsorbed on the first layer and the molecules adsorbed from the second to infinite layer are distributed independently among the given sites, a macrostate partition function [Sears et al., 1975] for the total molecules adsorbed on both groups with the given total energy  $U$  of the system is obtained by multiplying Eqs. (2) and (3):

$$Q_{\Omega}(N_{11}, M_1, N, B_1, B_2, T) = \sum_{N_{11}} \left[ \frac{B_1!}{(B_1 - N_{11})! N_{11}!} \{j_1 \exp(D_1/kT)\}^{N_{11}} \times \frac{B_2!}{(B_2 - M_1 N_{11})! (M_1 N_{11})!} \{j_2 \exp(D_2/kT)\}^{M_1 N_{11}} \times \frac{N!}{(N_{11} + M_1 N_{11})! (N - N_{11} - M_1 N_{11})!} \{j_m \exp(D_m/kT)\}^{(N - N_{11} - M_1 N_{11})} \right] \quad (4)$$

where unit needed in Eq. (3) is neglected as compared to  $N$  and  $N_{11} + M_1 N_{11}$ . In Eq. (4)  $t_1$  of  $Q_{\Omega}$  designates the macrostate of the system. Then the total energy  $U$  of the system of all molecules adsorbed on the sites of the adsorbent becomes [Sears et al., 1975]

$$U = D_1 N_{11} + D_2 M_1 N_{11} + D_m \{N - (1 + M_1) N_{11}\} \doteq N u_1 \quad (5)$$

In Eq. (5)  $u_1$  is the average adsorption energy of an adsorbed molecule with respect to all groups and layers. From Eq. (4) the total macrostate partition function obtained by the sum  $\Omega_1$  of all states concerning all macrostates becomes

$$\Omega_1 = \sum_{\Omega_1} Q_{\Omega_1}(N_{11}, M_1, N, B_1, B_2, T) \quad (6)$$

It is considered that the largest macrostate term in Eq. (6) dominates the total macrostate partition function  $\Sigma Q_{\Omega_1}(N_{11}, M_1, N, B_1, B_2, T)$ . So the values which give the largest term are found for  $(\partial \ln Q_s Q_m / \partial N_{11}) = 0$  as follows:

$$\left( \frac{B_1 - N_{11}}{N_{11}} \right) \left( \frac{B_2 - M_1 N_{11}}{M_1 N_{11}} \right)^{M_1} \left\{ \frac{N - (1 + M_1) N_{11}}{(1 + M_1) N_{11}} \right\}^{1 + M_1} = \beta_1 \quad (7)$$

where

March, 2000

$$\beta_1 = \left( \frac{j_m}{j_1} \right) \left( \frac{j_m}{j_2} \right)^{M_1} \exp \left\{ \frac{D_m - D_1 + M_1 (D_m - D_2)}{kT} \right\} = \left( \frac{q_m}{q_1} \right) \left( \frac{q_m}{q_2} \right)^{M_1} \quad (7')$$

From the general form [Sears et al., 1975] of the combined thermodynamic 1st and 2nd law of two states for the adsorbed molecules on adsorbents as a nonisolated open PVT system we have

$$T \Delta S = \Delta U + P \Delta V - \mu \Delta N \quad (8)$$

where  $\Delta S$  is the entropy difference,  $\Delta U$  the total energy difference,  $\Delta V$  the total volume (no. of sites) difference,  $\Delta N$  the difference in number of the adsorbed gas molecules, between two states, and where  $P$  is the total pressure of the adsorbate and  $\mu$  the chemical potential of the adsorbate. For the constant numbers of adsorption sites  $B_1$  and  $B_2$  used instead of constant volume  $V$ , Eq. (8) becomes

$$T \Delta S = \Delta U - \mu \Delta N \quad (9)$$

If we take the partial derivative of Eq. (9) with respect to  $\Delta N \rightarrow 0$ , Eq. (9) can be written as

$$T \left( \frac{\partial S}{\partial N} \right)_{B,T} = \left( \frac{\partial U}{\partial N} \right)_{B,T} - \mu_N \quad (10)$$

By inserting Eq. (4) into  $(\partial S / \partial N)_{B,T} = k(\partial \ln Q_{\Omega} / \partial N) = k(\partial \ln Q_s Q_m / \partial N)$  and Eq. (5) into  $(\partial U / \partial N)_{B,T}$  we get for the chemical potential  $\mu_N$  of the adsorbed gas molecule

$$\frac{\mu_N}{kT} = \frac{u_1}{kT} - \ln \frac{N}{N - N_{11} (1 + M_1)} - \ln \left\{ j_m \exp \left( \frac{D_m}{kT} \right) \right\} \quad (11)$$

Generally the chemical potential of a molecule in the gas phase [Knuth, 1966] is known as

$$\frac{\mu_G}{kT} = \frac{\mu^0}{kT} + \ln \frac{p}{p_0} \quad (12)$$

where  $\mu^0$  is the standard chemical potential which is only a function of temperature and  $p_0$  the saturated vapor pressure of the adsorbate. Since the adsorption is measured at the equilibrium state between  $\mu_N$  and  $\mu_G$ , equating Eq. (11) to Eq. (12) gives

$$\ln \frac{N}{N - N_{11} (1 + M_1)} + \ln \frac{p}{p_0} = - \frac{\mu^0}{kT} + \frac{u_1}{kT} - \ln \left\{ j_m \exp \left( \frac{D_m}{kT} \right) \right\} \quad (13)$$

For the saturated gas ( $p = p_0$ ), Eq. (13) becomes

$$c_{s1} = \frac{N_s - (1 + M_1) N_{11s}}{N_s} = j_m \exp \{ (\mu^0 - u_1 + D_m) / kT \} \quad (14)$$

In Eq. (14)  $N_s$  is the total number of the adsorbed molecules and  $N_{11s}$  the number of the molecules adsorbed on the sites of the first layer and group 1 at the saturated vapor pressure. Let  $c_{s1}$  be called as the saturation vapor pressure factor, which may include effects of the slippery and the combination of the attraction and the repulsion of the adsorbed molecules at the saturation vapor pressure. It becomes the ratio of the molecules adsorbed on both groups of the sites from the second to infinite layer to the total molecules adsorbed on both groups of the sites over all layers. By combining Eq. (13) with Eq. (14) we obtain

$$c_{s1} = \frac{N - (1 + M_1) N_{11}}{N} \quad (15)$$

where

$$x = \frac{p}{p_0} \quad (15')$$

So  $c_{s1}$  should be always less than unity as Eq. (15) also shows and  $f$  called in the procedure deriving the tss isotherm equation [Timmermann, 1989] indicates. By combining Eqs. (7) with (15) we get the adsorption isotherm equation  $\theta$  on two groups of adsorption sites only in the first layer and one group from the second to infinite layer as follows:

$$\left\{ \frac{1+M_1-\theta(1-c_{s1}x)}{1+f_1} \right\} \left\{ \frac{f_1(1+M_1)-M_1\theta(1-c_{s1}x)}{1+f_1} \right\}^{M_1} \left( \frac{c_{s1}x}{1-c_{s1}x} \right)^{1+M_1} = \beta_1 \quad (16)$$

where

$$\theta = \frac{N}{B_1+B_2} \quad (16')$$

$$f_1 = \frac{B_2}{B_1} \quad (16'')$$

In Eq. (16)  $\theta$  is a nonlinear function of  $x$  with four unknown constants  $f_1$ ,  $M_1$ ,  $c_{s1}$  and  $\beta_1$ . It can be obtained numerically.

When  $f_1=1$ ,  $M_1=1$ ,  $\beta_1=\beta^2$  and  $c_{s1}=c_s$  for one group of sites, Eq. (16) reduces to the BET equation including the saturation vapor pressure factor  $c_s$ . This was first derived by Anderson [Anderson, 1946] differently from the present method and later called as the GAB isotherm [Timmermann, 1989]. The meanings of  $c_s$  and  $f$  in the GAB isotherm are almost the same. Coincidentally, when we derived the two-group adsorption isotherm by using Fermi-Dirac statistics for the first layer and Bose-Einstein statistics for the second to infinitive layer by differentiating two groups, we got the same result as Eq. (16).

## 2. Adsorption Isotherm for Two Groups of Adsorption Sites over the First to $n$ Limited Number of Layers

In section 1 we derived the adsorption isotherm for two groups of sites with an infinite number of adsorption layers, but in this section we derive the adsorption isotherm by discerning two groups of sites over from the first to  $n$  limited layer.

$N$  is the number of the total molecules adsorbed on two groups of sites in all adsorption layers of the solid adsorbent.  $N_{11}$  and  $N_{12}$  are also the numbers of the molecules adsorbed on the sites of groups 1 and 2 in the first layer,  $N_{21}$  and  $N_{22}$  the numbers of the molecules adsorbed on the sites of groups 1 and 2 in the second layer,  $\dots$ , and  $N_{n1}$  and  $N_{n2}$  the numbers of the molecules adsorbed on the sites of groups 1 and 2 in the  $n$ th layer. And let us assume the adsorption proportional constant  $M_1$  between groups differently as done in section 2-1 as follows:

$$M_1 = \frac{N_{12}}{N_{11}} = \frac{N_{22}}{N_{21}} = \dots = \frac{N_{n2}}{N_{n1}} \quad (17)$$

If the indistinguishable molecules  $N_{11}$  and  $N_{12}$ ,  $N_{21}$  and  $N_{22}$ ,  $\dots$ ,  $N_{n1}$  and  $N_{n2}$ , are independently adsorbed on sites  $B_1$  and  $B_2$ ,  $N_{11}$  and  $N_{12}$ ,  $\dots$ ,  $N_{n1}$  and  $N_{n2}$ , the complete partition function by Fermi-Dirac statistics for the molecules adsorbed in the first layer becomes the same as done in section 2-1, and the complete partition functions for the molecules adsorbed from the second to  $n$ th layer become for group 1 of sites

$$Q_{m1}(N_{11}, N_{21}, \dots, N_{n1}, N, M_1, n, T)$$

$$= \frac{(N_{11})! \{j_{m1} \exp(D_{m1}/kT)\}^{N_{11}-N_{11}}}{(N_{11}-N_{21})! (N_{21}-N_{31})! \dots (N_{n-11}-N_{n1})! N_{n1}!} \quad (18)$$

and for group 2 of sites

$$Q_{m2}(N_{11}, N_{21}, \dots, N_{n1}, N, M_1, n, T) = \frac{(M_1 N_{11})! \{j_{m2} \exp(D_{m2}/kT)\}^{M_1 N_{11}-M_1 N_{11}}}{\{M_1 (N_{11}-N_{21})\}! \{M_1 (N_{21}-N_{31})\}! \dots \{M_1 (N_{n-11}-N_{n1})\}! (M_1 N_{n1})!} \quad (19)$$

And as done in the section 1, the total energy  $U$  of the interacting system for all the molecules adsorbed on all the sites of the adsorbent becomes

$$U = D_1 N_{11} + D_2 M_1 N_{11} + D_{m1} \left( \frac{N}{1+M_1} - N_{11} \right) + D_{m2} \left( \frac{M_1 N}{1+M_1} - M_1 N_{11} \right) = N u_2 \quad (20)$$

In Eq. (20)  $u_2$  is the average adsorption energy of an adsorbed molecule with respect to all groups and layers. Therefore, a macrostate partition function for all adsorbed molecules at the constant total energy  $U$  is obtained by summation of the independent product of Eqs. (2), (18) and (19) as follows:

$$Q_{12}(N_{11}, N_{21}, \dots, N_{n1}, N, M_1, B_1, B_2, n, T) = \sum_{N_{11}} \dots \sum_{N_{n-11}} Q_s Q_{m1} Q_{m2} \quad (21)$$

where the limits of the summation in Eq. (21) are unknown and also are not needed here. From Eq. (21) the total macrostate partition function is obtained by the sum of the possible states with respect to all the macrostates  $\Omega_2$  as follows:

$$\Omega_2 = \sum_{N_{11}} Q_{12}(N_{11}, N_{21}, \dots, N_{n-11}, N, M_1, B_1, B_2, T) \quad (22)$$

In Eq. (22) the largest macrostate term is approximated to dominate. So the values of  $N_{11}$ ,  $N_{21}$ ,  $\dots$ , and  $N_{n-11}$  which give this term are found from

$$\sum_l \frac{\partial \ln Q_s Q_{m1} Q_{m2}}{\partial N_{11}} = 0 \quad l=1, 2, \dots, n-1 \quad (23)$$

using the following Eq. (24) for  $N_{n1}$

$$N_{n1} = \frac{N}{1+M_1} - N_{11} - N_{21} - \dots - N_{n-11} \quad (24)$$

To satisfy Eq. (23) each expanded term of Eq. (23) should be zero. Hence by combining Eqs. (2), (18) and (19) through Eq. (23) with Eq. (24) we obtain for  $(\partial \ln Q_s Q_{m1} Q_{m2} / \partial N_{11}) = 0$

$$\left\{ \frac{(B_1 - N_{11})(B_2 - M_1 N_{11})^{M_1}}{M_1! \beta_2} \right\}^{\frac{1}{1+M_1}} \left( \frac{N_{n1}}{N_{n-11} - N_{n1}} \right) = N_{11} - N_{21} \quad (25)$$

where

$$\beta_2 = \left( \prod_{j=1}^{M_1} j \right) \exp \{ \{ D_{m1} - D_1 + M_1 (D_{m2} - D_2) \} / kT \} \quad (25')$$

and for  $(\partial \ln Q_s Q_{m1} Q_{m2} / \partial N_{21}) = 0$ ,  $\dots$ ,  $(\partial \ln Q_s Q_{m1} Q_{m2} / \partial N_{n-21}) = 0$  and  $(\partial \ln Q_s Q_{m1} Q_{m2} / \partial N_{n-11}) = 0$

$$\begin{aligned} (N_{11} - N_{21}) \left( \frac{N_{n1}}{N_{n-11} - N_{n1}} \right) &= N_{21} - N_{31} \\ &\vdots \\ (N_{n-11} - N_{n-21}) \left( \frac{N_{n1}}{N_{n-11} - N_{n1}} \right) &= N_{n-21} - N_{n-11} \end{aligned}$$

$$(N_{n-21} - N_{n-11}) \left( \frac{N_{n1}}{N_{n-11} - N_{n1}} \right) = N_{n-11} - N_{n1} \quad (26)$$

By introducing Eqs. (20) and (21) into  $\mu_n/kT = (u_2/kT) - (\partial \ln Q_2 / \partial N)$  at the equilibrium data point and combining its result into Eq. (11) for the chemical potential of the adsorbate gas we have

$$c_{s2}x = c_{s2} \frac{p}{p_0} = \frac{N_{n1}}{N_{n-11} - N_{n1}} \quad (27)$$

where

$$x = \frac{p}{p_0} \quad (15')$$

$$c_{s2} = \frac{N_{n1s}}{N_{n-11s} - N_{n1s}} = \{j_{m1}j_{m2}\}^{\frac{1}{1+M_1}} \exp \left\{ \left( \mu^0 - u_2 + \frac{D_{m1} + M_1 D_{m2}}{1 + M_1} \right) / kT \right\} \quad (27')$$

In Eq. (27)'  $N_{n-11s} - N_{n1s}$  and  $N_{n1s}$  are the number of empty sites of groups 1 in the (n-1)th layer and the number of the occupied sites of group 1 in the nth layer at the saturation vapor pressure. The saturation vapor pressure factor  $c_{s2}$  represents the ratio of the occupied sites of nth layer to the empty sites of (n-1)th layer.  $c_{s2}$  should be also less than unit to terminate the adsorption and to maintain the geometric balance of the adsorption at nth layer. After introducing Eq. (27) into Eqs. (25) and (26) and by multiplying each side of Eqs. (25) and (26) we get the amount of the adsorbed molecules on the nth layer of group 1

$$N_{n1} = \left\{ \frac{(B_1 - N_{11})(B_2 - M_1 N_{11})^{M_1}}{M_1! \beta_2} \right\}^{\frac{1}{1+M_1}} (c_{s2}x)^n \quad (28)$$

And after adding each side of Eqs. (25) and (26), with manipulating of the result we get the amount of the adsorbed molecules on the first layer of group 1

$$N_{11} = \left\{ \frac{(B_1 - N_{11})(B_2 - M_1 N_{11})^{M_1}}{M_1! \beta_2} \right\}^{\frac{1}{1+M_1}} \left\{ \frac{c_{s2}x - (c_{s2}x)^{n+1}}{1 - c_{s2}x} \right\} \quad (29)$$

By Eqs. (24), (25), (26), (27) and (28) we get the n limited multilayer adsorption isotherm equation for two groups of adsorption sites as follows:

$$\begin{aligned} & \frac{N}{B_1 + B_2} \\ &= \frac{(1 + M_1) \{ (N_{11} - N_{21}) + 2(N_{21} - N_{31}) + \dots + (n-1)(N_{n-11} - N_{n1}) + nN_{n1} \}}{B_1 + B_2} \\ &= B \left\{ \frac{(B_1 - N_{11})(B_2 - M_1 N_{11})^{M_1}}{M_1! \beta_2} \right\}^{\frac{1}{1+M_1}} \\ & \quad \times \left( \frac{c_{s2}x}{1 - c_{s2}x} \right) \left\{ \frac{1 - (c_{s2}x)^n}{1 - c_{s2}x} + \frac{(n-1)(c_{s2}x)^n}{1 - c_{s2}x} - n(c_{s2}x)^n \right\} \end{aligned} \quad (30)$$

where

$$B = \frac{1 + M_1}{B_1 + B_2} \quad (30')$$

By using the numerical methods for the relationship of Eqs. (30) and (30)' we can also obtain the adsorption isotherm.

When  $B_1 = B_2$ ,  $M_1 = 1$ ,  $\beta_2 = \beta^2$  and  $c_{s2} = c$ , for one group of sites, Eq. (29) reduces to BET isotherm equation with a limited number of n layers including the saturation pressure factor  $c_s$ . Unfortunately,

satisfactory experimental data for comparison are not found yet. But we may compare the isotherm with the experimental data in the same way as Brunauer et al. [1938] did in their paper. The comparison near the saturation vapor pressure also does not do fine.

### 3. Adsorption Isotherm for Three Groups of Adsorption Sites in the First Layer and One Group of Sites in from the Second to Infinite Layer

In this section we also extend the treatment of section 1 to the case of three groups of sites in the first layer of the adsorbent and one group of sites from the second to infinitive layer. N is also the number of the total molecules adsorbed over all layers in solid adsorbent surface.  $B_1$ ,  $B_2$  and  $B_3$  are the numbers of the sites of groups 1, 2 and 3 per unit surface of the solid adsorbent.  $N_{11}$ ,  $N_{12}$  and  $N_{13}$  are also the number of the molecules adsorbed on the sites of groups 1, 2 and 3 in the first layer. And let us assume the adsorption proportional constants among groups as

$$M_1 = \frac{N_{12}}{N_{11}} \text{ and } M_2 = \frac{N_{13}}{N_{11}} \quad (31)$$

If then  $N_{11}$ ,  $M_1 N_{11}$  and  $M_2 N_{11}$  indistinguishable molecules are Fermi-Dirac statistically distributed among  $B_1$ ,  $B_2$  and  $B_3$  sites in the adsorbent surface, the complete partition function  $Q_{s2}$  ( $N_{11}$ ,  $M_1$ ,  $M_2$ ,  $B_1$ ,  $B_2$ , T) of the adsorbed molecules on the first layer becomes

$$\begin{aligned} Q_{s3}(N_{11}, M_1, M_2, B_1, B_2, B_3, T) &= \prod_{i=1}^3 q_{N_i} \\ &= \frac{B_1!}{(B_1 - N_{11})! N_{11}!} \left\{ j_1 \exp \left( \frac{D_1}{kT} \right) \right\}^{N_{11}} \frac{B_2!}{(B_2 - M_2 N_{11})! (M_2 N_{11})!} \\ & \quad \left\{ j_2 \exp \left( \frac{D_2}{kT} \right) \right\}^{M_1 N_{11}} \frac{B_3!}{(B_3 - M_2 N_{11})! (M_2 N_{11})!} \left\{ j_3 \exp \left( \frac{D_3}{kT} \right) \right\}^{M_2 N_{11}} \end{aligned} \quad (32)$$

By Bose-Einstein distribution for the multilayer adsorption from the second to infinite layer the complete partition function  $Q_{m3}$  ( $N_{11}$ ,  $M_1$ ,  $M_2$ , N, T) for  $N - N_{11} - M_1 N_{11} - M_2 N_{11}$  molecules adsorbed on the top of  $N_{11} + M_1 N_{11} + M_2 N_{11}$  sites of the first layer becomes

$$\begin{aligned} Q_{m3}(N_{11}, M_1, M_2, N, T) &= \frac{(N-1)!}{\{ (1 + M_1 + M_2) N_{11} - 1 \}! \{ N - (1 + M_1 + M_2) N_{11} \}!} \\ & \quad \left\{ j_{m3} \exp \left( \frac{D_{m3}}{kT} \right) \right\}^{\{ N - (1 + M_1 + M_2) N_{11} \}} \end{aligned} \quad (33)$$

A macrostate partition function  $Q_{t3}$  ( $N_{11}$ , N,  $M_1$ ,  $M_2$ ,  $B_1$ ,  $B_2$ , T) for the total adsorbed molecules over all layers at the constant internal energy U is expressed by multiplying Eqs. (32) and (33) independently and summing over all possible values of  $N_{11}$  which are not known as follows:

$$Q_{t3}(N_{11}, N, M_1, M_2, B_1, B_2, B_3, T) = \sum_{N_{11}} Q_{s3} Q_{m3} \quad (34)$$

The total adsorption energy of the system can be expressed as

$$\begin{aligned} U &= D_1 N_{11} + D_2 M_1 N_{11} + D_3 M_2 N_{11} + D_{m3} \{ N - (1 + M_1 + M_2) N_{11} \} \\ &\approx N u_3 \end{aligned} \quad (35)$$

In Eq. (35)  $u_3$  is also the average adsorption energy of an adsorbed molecule with respect to all groups and layers. From Eq. (34) the total macrostate partition function is obtained as the sum of the

possible states with respect to all the macrostates  $\Omega_3$  as follows:

$$\Omega_3 = \sum_{i3} Q_{i3}(N_{11}, N_{21}, \dots, N_{n-11}, N, M_1, B_1, B_2, T) \quad (36)$$

By following the same procedure of section 1 we get the adsorption isotherm equation  $\theta$  on three groups of the sites in the first layer and one group of the sites in the second to infinite layer as follows:

$$\left\{ \frac{(1+M_1+M_2)}{1+f_1+f_2} - (1-c_{s3}x)\theta \right\} \times \left\{ \frac{f_1(1+M_1+M_2)}{1+f_1+f_2} - (1-c_{s3}x)M_1\theta \right\}^{M_1} \\ \times \left\{ \frac{f_2(1+M_1+M_2)}{1+f_1+f_2} - (1-c_{s3}x)M_2\theta \right\}^{M_2} \times \left\{ \frac{c_{s3}x}{1-c_{s3}x} \right\}^{1+M_1+M_2} = \beta_3 \quad (37)$$

where

$$\theta = \frac{N}{B_1 + B_2 + B_3} \quad (37)'$$

$$f_1 = \frac{B_2}{B_1} \text{ and } f_2 = \frac{B_3}{B_1} \quad (37)''$$

$$\beta_3 = \left( \frac{j_{m3}}{j_1} \right) \left( \frac{j_{m3}}{j_2} \right)^{M_1} \left( \frac{j_{m3}}{j_3} \right)^{M_2} \\ \exp \left\{ \frac{(D_{m3}-D_1)+M_1(D_{m3}-D_2)+M_2(D_{m3}-D_3)}{kT} \right\} \quad (37)'''$$

In Eq. (37) the saturation vapor pressure factor becomes

$$c_{s3} = \frac{N_s - (1+M_1+M_2)N_{11s}}{N_s} = j_{m3} \exp \left( \frac{\mu^0 - u_3 + D_{m3}}{kT} \right) \quad (38)$$

In Eq. (38)  $c_{s3}$  is the same form of Eq. (14) in section 1. In Eq. (37)  $\theta$  is also a non-linear function of  $x$  with the six unknown variables  $f_1$ ,  $f_2$ ,  $M_1$ ,  $M_2$ ,  $c_{s3}$  and  $\beta_3$  and can be obtained numerically.

Eqs. (16), (30) and (37) become the type III isotherms (BDDT classification [Brunauer et al., 1940]) if  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  are respectively larger than one.

## RESULTS AND DISCUSSION

When the BET isotherm which has  $j_m/j_s=1$  and  $D_1-D_m=400$

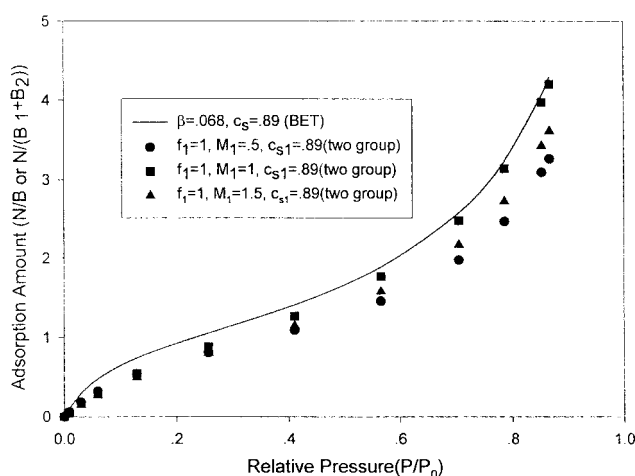


Fig. 1. BET isotherm of  $j_m/j_s=1$  and  $D_1-D_m=400$  cal/mol and two group sites isotherms [Eq. (16)] of  $(j_m/j_1)(j_m/j_2)^{M_1}=1$ ,  $D_1-D_m=400$  cal/mol and  $D_2-D_m=200$  cal/mol at 75 K.

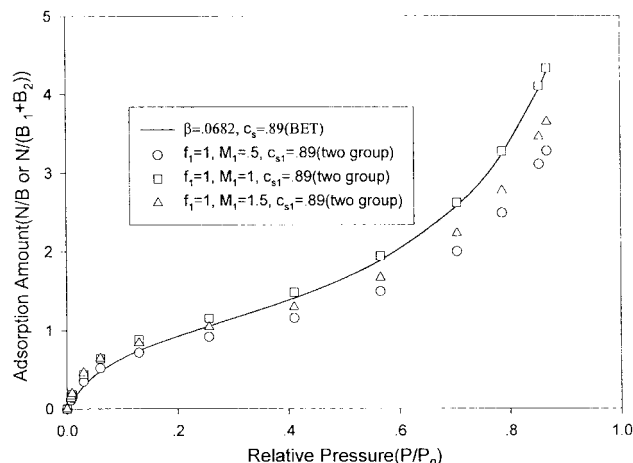


Fig. 2. BET isotherm of  $j_m/j_s=1$  and  $D_1-D_m=400$  cal/mol and two group sites isotherms [Eq. (16)] of  $(j_m/j_1)(j_m/j_2)^{M_1}=1$ ,  $D_1-D_m=400$  cal/mol and  $D_2-D_m=600$  cal/mol at 75 K.

cal/mol is changed into the two-group isotherm which has  $(j_m/j_1)(j_m/j_2)^{M_1}=1$ ,  $D_1-D_m=400$  cal/mol and  $D_2-D_m=200$  cal/mol, holding the saturation vapor pressure factor ( $c_s$  or  $c_{s1}$ ) as 0.89, the isotherms are shown in Fig. 1. If then the half sites (for  $f_1=1$ ) of the adsorbent surface of two-group isotherm Eq. (16) have the same adsorption energy difference as BET isotherm and its other half sites have the smaller adsorption energy difference than BET isotherm, the changes of  $M_1$  values of the two-group isotherm cannot bring more adsorption than the BET isotherm. In Fig. 2 when the above BET isotherm is changed into the two-group isotherm which has  $D_2-D_m=600$  cal/mol instead of only  $D_2-D_m=200$  cal/mol, it represents that the two-group isotherm shows more adsorption than the BET isotherm over the beginning range of the relative vapor pressure. This is the Fermi-Dirac statistical region. But if some of the BET surface sites are substituted by the more energetic sites, the formed two-group isotherm does not show more adsorption than the BET isotherm before the substitution over the some range of the relative vapor pressure except for the same values of  $f_1$  and  $M_1$ . Therefore, the increase of the adsorption group of sites is not favorable to the increase of the adsorption at the same physical conditions. Whether the adsorption isotherm belongs to one group or two groups,  $j_m$  seems to be smaller than  $j_1$  or  $j_2$  [Kim, 2000] in type II isotherm. Then the equilibrium between the adsorption and the desorption of the molecules are accomplished and the adsorbed molecules can affect the pressure of the system with the geometric valance. This fact indicates that the increase of the adsorption group of sites results in the decrease of the adsorption at the same physical condition according to Eq. (16).

In Figs. 3-10 the theoretical isotherms obtained from Eq. (16) by our best fit minimizing the standard error are plotted with experimental data which were obtained from the adsorption isotherms of (1) nitrogen and argon on single crystal zinc surface at 78.1 K (Fig. 3) [Rhodin, 1950], (2) water vapor on annealed quartz silica at 15 °C and 25 °C (Fig. 4) [Hackerman et al., 1958], (3) nitrogen on polyethylene and nylon at the temperature of liquid nitrogen (Fig. 5) [Zettlemoyer et al., 1950], (4) argon on reduced polycrystalline copper at 78.1 K and 89.2 K (Fig. 6) [Rhodin, 1950], and (5) nitrogen, oxygen and argon on rutile at 75 K and 85 K (Fig.

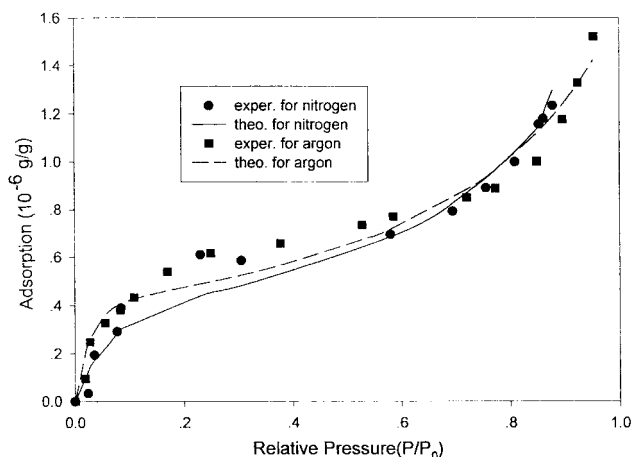


Fig. 3. Experimental adsorption isotherms of nitrogen and argon on crystal single zinc at 78.1 K compared with theoretical two group sites adsorption isotherms Eq. (16); ( $\beta_1=.03$ ,  $f_1=.15$ ,  $M_1=.55$ ,  $c_{s1}=.8$ ) for nitrogen and ( $\beta_1=.0062$ ,  $f_1=.18$ ,  $M_1=.6$ ,  $c_{s1}=.75$ ) for argon [Rhodin, 1953].

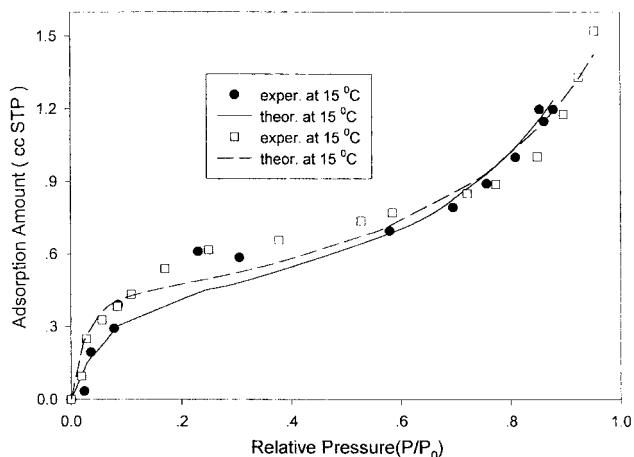


Fig. 4. Experimental adsorption isotherms of water on annealed and unannealed at 15 °C quartz silica compared with theoretical two group sites adsorption isotherms Eq. (16); ( $\beta_1=.0071$ ,  $f_1=.16$ ,  $M_1=.8$ ,  $c_{s1}=.89$ ) for annealed at 15 °C and ( $\beta_1=.0011$ ,  $f_1=.16$ ,  $M_1=.98$ ,  $c_{s1}=.88$ ) for unannealed at 15 °C [Hackerman et al., 1958].

7) [Drain et al., 1952, 1953], (6)  $H_2O$  on anatase treated by  $Al_2O_3$  at 25 °C (Fig. 8) [Harkins et al., 1944]. (7) nitrogen at 78 K and benzene 20 °C on graphitized thermal blacks (Fig. 9) [Isirikyan et al., 1961], (8) n-propyl alcohol and n-heptane on reduced iron at 25 °C (Fig. 10) [Loeser et al., 1953].

For the experimental isotherms shown in Fig. 3 the weight monolayers are also calculated. All of the above experimental data are fitted by minimizing the standard error between the experimental data and the theoretical adsorption isotherm Eq. (16). Then the standard error is calculated as follows:

$$\text{standard error} = \sqrt{\frac{\sum_{i=1}^n (\text{experimental data} - \theta)_i^2}{n}}$$

In the above equation  $n$  is the number of the possible experimen-

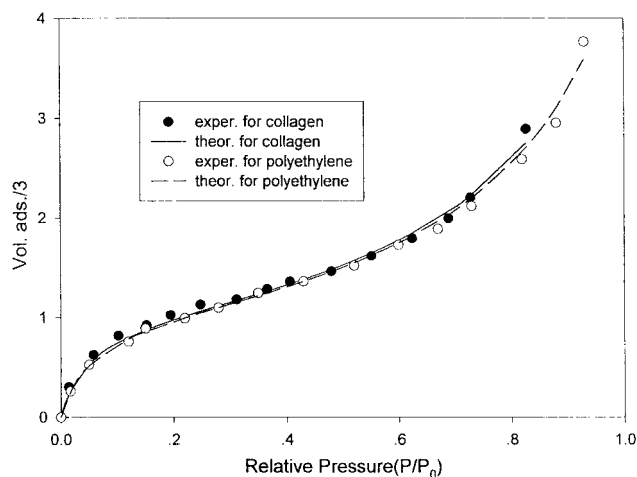


Fig. 5. Experimental adsorption isotherms of nitrogen on polyethylene and collagen at 78 K compared with theoretical two group sites adsorption isotherms Eq. (16); ( $\beta_1=.0026$ ,  $f_1=1$ ,  $M_1=.84$ ,  $c_{s1}=.8$ ) for polyethylene and ( $\beta_1=.0021$ ,  $f_1=1$ ,  $M_1=.87$ ,  $c_{s1}=.8$ ) for collagen [Zettlemoyer et al., 1950].

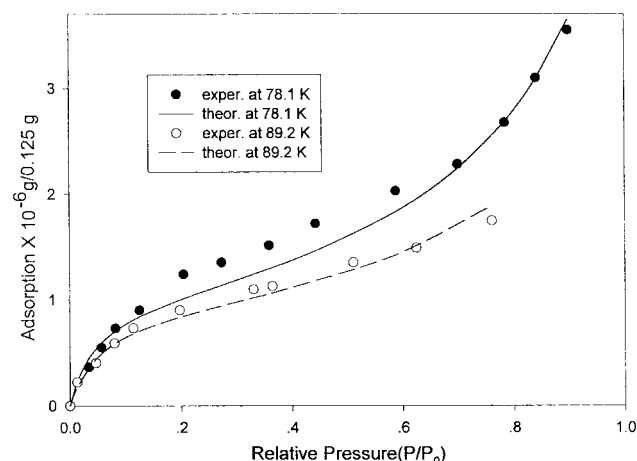


Fig. 6. Experimental adsorption isotherms of argon on reduced polycrystalline copper at 78.1 K and 89.2 K compared with theoretical two group sites adsorption isotherms Eq. (16); ( $\beta_1=.002$ ,  $f_1=.92$ ,  $M_1=.852$ ,  $c_{s1}=.82$ ) for at 78.1 K and ( $\beta_1=.008$ ,  $f_1=.8$ ,  $M_1=.422$ ,  $c_{s1}=.76$ ) for at 89.2 K [Rhodin, 1950].

tal data to calculate.

When  $f_1 > M_1$ , the adsorption sites of group 1 have stronger adsorption force than those of group 2 (Figs. 5-7, 9 and 10). When  $f_1 < M_1$ , the above adsorption force balance between groups is reversed (Figs. 3 and 4). When  $f_1 = M_1$ , the adsorption force balance between groups becomes the same. As we see in Fig. 6 and from the standard error in the Table 1 the disagreement between the theoretical isotherm and the experimental isotherm of argon adsorption on the reduced polycrystalline copper at 78.1 K is large. While at 89.2 K, its agreement is fair. This may imply that as the temperature of the adsorption system decreases to 78.1 K from 89.2 K, the surface charges of argon and copper of a transition metal affect the statistical distribution abnormally. In Fig. 9 the experimental data for the isotherm of benzene on graphitized thermal black agree with the theoretical isotherm of two group site Eq. (16), but those

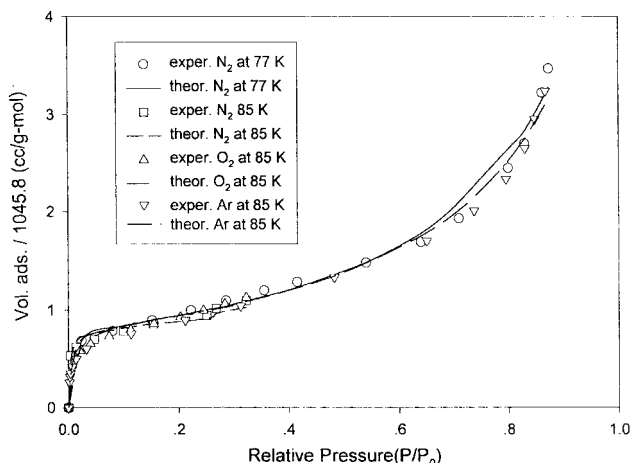


Fig. 7. Theoretical two groups sites isotherms [Eq. (16)] for  $N_2$  at 77 K ( $\beta_1=.0004$ ,  $f_1=.98$ ,  $M_1=.557$ ,  $c_{s1}=.87$ ),  $N_2$  at 85 K ( $\beta_1=.00015$ ,  $f_1=.98$ ,  $M_1=.487$ ,  $c_{s1}=.83$ ),  $O_2$  ( $\beta_1=.00055$ ,  $f_1=.98$ ,  $M_1=.587$ ,  $c_{s1}=.79$ ) and Ar ( $\beta_1=.00035$ ,  $f_1=.98$ ,  $M_1=.557$ ,  $c_{s1}=.86$ ) at 85 K compared with their experimental data on rutile [Drain et al., 1952, 1953].

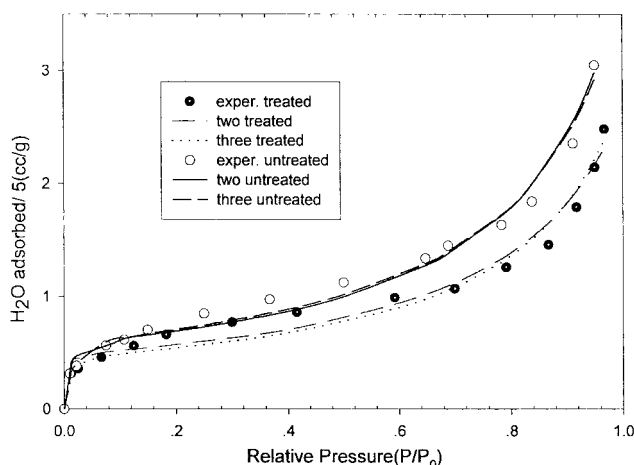


Fig. 8. Theoretical two groups sites isotherms [Eq. (16)] ( $\beta_1=.00011$ ,  $f_1=.299$ ,  $M_1=.93$ ,  $c_{s1}=.82$  for treated cat. by  $Al_2O_3$  and  $\beta_1=.00021$ ,  $f_1=.385$ ,  $M_1=.94$ ,  $c_{s1}=.85$  for untreated cat.) and three groups sites isotherms [Eq. (37)] compared with their experimental data of  $H_2O$  adsorbed on anatase at 25 °C [Harkins et al., 1994].

Three groups sites isotherms [Eq. (37)]:  $\beta_3=.00020$ ,  $f_1=.289$ ,  $f_2=.132$ ,  $M_1=.950$ ,  $M_2=.137$ ,  $c_{s3}=.84$  for treated cat. by  $Al_2O_3$ ,  $\beta_3=.00017$ ,  $f_1=.129$ ,  $f_2=.382$ ,  $M_1=.25$ ,  $M_2=.917$ ,  $c_{s3}=.84$  for untreated cat.

for the isotherm of nitrogen on graphitized thermal black do not agree well with it. The standard error of benzene is around 0.1, but that of nitrogen around 0.2. The isotherm of benzene is type II according to the classification of BDDT. The isotherm of nitrogen is classified as belonging to type II, but strangely, in it there are tiny three inflection points. So there is pore condensation [Kim, 2000]. Since the adsorption rate increases after the third inflection point, there is free surface condensation to the saturated pressure axis. In Fig. 10 the abnormal large standard error of n-heptane on reduced iron between the experimental data and the theoretical two

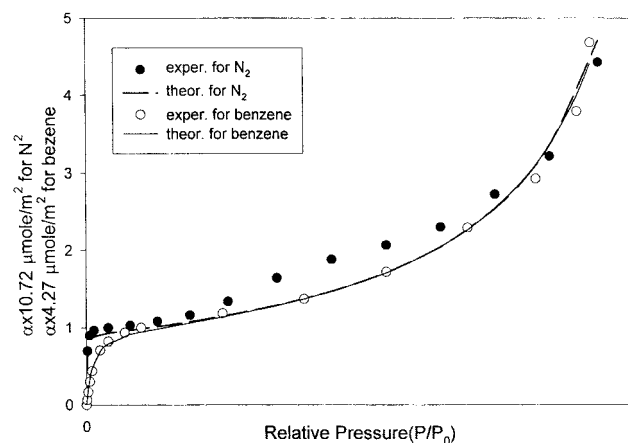


Fig. 9. Adsorption isotherms for vapors on graphitized thermal blacks at  $-195^\circ C$  compared with theoretical isotherm Eq. (16): ( $\beta_1=.000004$ ,  $f_1=.94$ ,  $M_1=.75$ ,  $c_{s1}=.86$ ) for nitrogen and ( $\beta_1=.000204$ ,  $f_1=.94$ ,  $M_1=.75$ ,  $c_{s1}=.86$ ) for benzene vapor [Isirikyan, 1961].

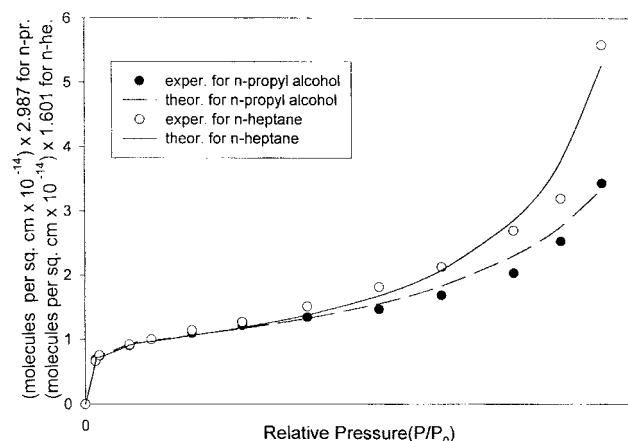


Fig. 10. Adsorption isotherms for vapors on reduced iron at 25 °C compared with theoretical isotherm Eq. (16): ( $\beta_1=.000094$ ,  $f_1=.94$ ,  $M_1=.77$ ,  $c_{s1}=.77$ ) for n-propyl alcohol and ( $\beta_1=.000284$ ,  $f_1=.84$ ,  $M_1=.63$ ,  $c_{s1}=.88$ ) for n-heptane [Loeser et al., 1953].

group site isotherm Eq. (16) comes from with no donating of non-bonding electrons of the normal heptane, or the large difference of the last two data.

Fig. 3 of the literature [Isirikyan et al., 1961] represents well that the adsorbent has two group of sites for benzene adsorption on the reduced iron because the differential heat has two clear slopes of which one is almost horizontal. Bose-Condensation heat is ca. 820 cal/mol.

And some consistent differences between the theoretical and the experimental isotherms of the adsorbents are attributed to the assumption of the maximum term method in getting the total partition functions of the systems [McQuarrie, 1973]. But this assumption is considered trivial.

The surface monolayer sites of the solid adsorbent can be obtained from the relationship of  $\theta$  and the amount of experimentally adsorbed molecules at a given relative pressure as follows:

$$(\text{No. of monolayer sites})_{\text{experiment}}/\text{g of adsorbent}$$



$$\begin{aligned}
 &= (\text{No. of monolayer sites})_{\text{theoretical eq.}} \\
 &\times \frac{\text{No. of adsorbed molecules experimentally/g of adsorbent}}{\text{No. of adsorbed molecules theoretically}} \\
 &= \frac{\text{No. of experimentally adsorbed molecules/g of adsorbent}}{\theta} \quad (39)
 \end{aligned}$$

At each relative pressure we can get the experimental surface monolayer sites per gram of the adsorbent by dividing the amount of the experimentally adsorbed molecules by  $\theta$  values obtained from Eq. (16), of which values should minimize the standard error. Then the number of the monolayer sites ( $B_1+B_2$ ) over the whole range of the relative pressure should be averaged arithmetically. The surface monolayer sites are compared with  $v_m$  calculated by using the BET isotherm in Table 1. If the theoretical isotherm is fitted well with the experimental isotherm, the averaged number

of the surface monolayer sites become near one with the unit of amount of the experimentally adsorbed molecules per the weight of the adsorbent. Its fairness depends on the value of the standard error which should be small as far as possible. These results are shown in Tabel 1. All the surface monlayer sites ( $B_1+B_2$ ) calculated by the two-group isotherm Eq. (16) are a little larger than those ( $v_m$ s) calculated by BET isotherm as presented in Table 1.

And it is found that even if Rhodin [Rhodin, 1950] has shown the surface monolayer sites calculated with BET isotherm for argon adsorption on the reduced polycrystalline copper larger than that of Eq. (16) as shown in Table 1, in fact it is smaller than that calculated with the two-group isotherm Eq. (16) over the given range of the relative vapor pressure.

In Table 1 all the surface areas of the adsorbents are calculated by using Eq. (39) and the weight monolayers are also compar-

**Table 1. Monolayer sites, surface areas, weight monolayers etc. obtained from two groups isotherm [Eq. (16)] through Eq. (39) for various experimental data**

Adsorbent	Adsorbate (Tem.)	$v_m$ from Eq. (16)	$A_m$ (sq Å)	SN (Sw, SAr, SO) (m <sup>2</sup> /g)	Standard error	Weight monolyer $\times 10^8$ g/cm <sup>2</sup>
Single crystal zinc [Rhodin,1953]	N <sub>2</sub> (78.1 K)	$1.03 \times 10^{-6}$ g/g	16.1 <sup>a</sup>	.0036	.0704	2.87(3.32 <sup>a</sup> )
Single crystal zinc [Rhodin, 1953]	Ar(78.1 K)	$.98 \times 10^{-6}$ g/g	14.2 <sup>a</sup>	.0021	.0716	4.69(5.19)
Annealed quartz silica [Hackerman et al., 1958]	H <sub>2</sub> O(25 °C)	1.206 cc/g	11.7 <sup>b</sup>	3.8	.0459	
Annealed quartz silica [Hackerman et al., 1958]	H <sub>2</sub> O(25 °C)	1.119 cc/g	14.8 <sup>a</sup>	4.80(4.2 <sup>b</sup> )	.0705	
Polyethylene [Zettlemoyer et al., 1950]	N <sub>2</sub> (78.1 K)	3.1(2.6 <sup>a</sup> ) cc/g	16.2 <sup>a</sup>	13.8(11.3 <sup>a</sup> )	.0639	
Nylon [Zettlemoyer et al., 1950]	N <sub>2</sub> (78.1 K)	3.0(2.5 <sup>a</sup> ) cc/g	16.2 <sup>a</sup>	13.0(10.8 <sup>a</sup> )	.0709	
Reduced polycrystalline copper [Rhodin, 1950]	Ar(78.1 K)	$8.39 \times 10^{-6}$ g/g ( $9.2 \times 10^{-6}$ g/g <sup>a</sup> )	15.2 <sup>a</sup>	.0192(.0220)	.1411	
Reduced polycrystalline copper [Rhodin, 1950]	Ar(89.2 K)	$8.37 \times 10^{-6}$ g/g ( $9.0 \times 10^{-6}$ g/g <sup>a</sup> )	15.2 <sup>a</sup>	.0191(.0214)	.0663	
Rutile [Drain et al., 1953]	N <sub>2</sub> (75 K)	13.1 cc/g	16.2 <sup>c</sup>	56.9(66 <sup>b</sup> )	.1017	
Rutile [Drain et al., 1953]	N <sub>2</sub> (85 K)	13.4(9.9 <sup>a</sup> ) cc/g	16.8 <sup>c</sup>	60.4	.0617	
Rutile [Drain et al., 1953]	O <sub>2</sub> (85 K)	12.7(10.1 <sup>a</sup> ) cc/g	13.7 <sup>c</sup>	46.6	.0476	
Rutile [Drain et al., 1953]	Ar(85 K)	12.8(9.4 <sup>a</sup> ) cc/g	14.3 <sup>c</sup>	49.1	.0920	
MT(3100 <sup>b</sup> ) [Isirikyan et al., 1961]	N <sub>2</sub> (78 K)	1.11 $\mu$ mol/g	16.2 <sup>a</sup>	8.88(6.51 <sup>a</sup> )	.2146	2.87(3.32 <sup>a</sup> )
MT-1(3100 <sup>b</sup> ) [Isirikyan et al., 1961]	C <sub>6</sub> H <sub>6</sub> (78.1 K)	.972 $\mu$ mol/g	40 <sup>a</sup>	7.65(7.68 <sup>a</sup> )	.1032	4.69(5.19 <sup>a</sup> )
Reduced iron [Loeser et al., 1953]	n-propyl alcohol (25 °C)	.000163 $\mu$ mol/g	37.2 <sup>b</sup>	1.089	.1106	
Reduced iron [Loeser et al., 1953]	n-heptane (25 °C)	.000170 $\mu$ mol/g	64 <sup>a</sup>	1.05(.187 <sup>a</sup> )	.2085	

1. The values of superscript a are in their corresponding papers.

2. The values of superscript b are in the present reference [Gregg et al., 1969].

3. The values of superscript c are calculated by  $A_m = 1.091(M/pN)^{2/3} \times 10^{16}$  in the present reference [Gregg et al., 1969].

**Table 2. Monolayer sites, surface areas and etc. obtained from two [Eq. (16)] and three [Eq. (37)] groups isotherms through Eq. (39) for Harkins and Jura's study [Harkins et al., 1944]**

Adsorbent	Adsorbate (Temp. °C)	Groups or calorimetric method	$v_m$ through eq (16) and eq (37)	$A_m$ (sq Å)	So (m <sup>2</sup> /g)	Standard error
Untreated anatase	H <sub>2</sub> O (25 °C)	2	5.06 cc/g	14.8	20.08	.0999
	H <sub>2</sub> O (25 °C)	3	5.18 cc/g	14.8	20.10	.0947
		calorimetric method			13.8	
Treated anatase	H <sub>2</sub> O (25 °C)	2	4.97 cc/g	14.8	19.78	.1037
	H <sub>2</sub> O (25 °C)	3	4.83 cc/g	14.8	23.04	.1089
by Al <sub>2</sub> O <sub>3</sub>		calorimetric method			8.9	

ed with the values in the original literature.

As shown in Table 2 it seems that the surface of the untreated anatase adsorbent has two groups of adsorption sites by judging from almost the same magnitude of the standard error calculated by our best fit for the isotherms of two and three groups of adsorption sites. But the anatase treated with  $\text{Al}_2\text{O}_3$  might have three rather than two groups of adsorption sites to the extent that it may not be ignored. But we should not ignore that it may have four groups of adsorption sites because the  $\text{Al}_2\text{O}_3$  itself has two groups of adsorption sites confirmed. In Table 2 the number of the adsorption sites of the untreated anatase per unit weight is larger than that of the treated anatase as shown in Fig. 8. The large standard error calculated by Eq. (16) for the experimental argon adsorption data on the reduced polycrystalline copper at 78.1 K was not reduced when we calculated it through three-group isotherm Eq. (37). Therefore, the reduced polycrystalline copper has two groups of adsorption sites. Its deviation from Eq. (16) may come from the d-orbital of copper.

Many experimental amounts of the adsorbed molecules near the saturated vapor pressures are larger than those calculated by two-group isotherms [Eq. (16)]. The reason might be that near the saturated vapor pressure a lot of adsorbents adsorb abnormally because the cohesion forces among adsorbates dominate in the adsorption. Near the saturated vapor pressure the free gas molecules approach the adsorbed molecules very closely and the tiny electronic field of the sites may affect the free gas molecules to the adsorption.

In the experimental literature [Joyner et al., 1948] which Joyner and Emmett have executed, the adsorption of nitrogen on the adsorbent of Grade 6 Spheron the isotherm of Fig. 1 agrees a little unsatisfactorily with the two-group isotherm Eq. (16). But we cannot say by calculation that the isotherm belongs to the BET equation. When in the isotherm the Bose-Condensation energy ( $D_m$ ) is fixed as 1,400 cal/mol with  $(j_m/j_1)(j_m/j_2)^{M_1}=1$ ,  $D_1=2,304$  cal/mol and  $D_2=0.9D_1$ ,  $D_2$  becomes 2,103 cal/mol. Thus the site adsorption energies between groups in the first layer are almost the same in magnitude and the Bose-Condensation energy is not much smaller than them. As shown in Fig. 5 in that paper [Joyner et al., 1948], the similar magnitude of the adsorption energies between groups or layers may occur for the simple linear decrease of the differential heat vs.  $v/v_m$  without a hump or a saddle. But the latter always comes from the former; the occurrence of a hump or a saddle needs the combined results of the starting of the Bose-Condensation with the adsorption energies of each group. In Fig. 6 of the paper [Joyner et al., 1948] the adsorption energies between two groups are different from each other. And the differential heat has a hump and a saddle. And a type of pore condensation [Kim, 2000] and free surface Bose-Condensation exist in the adsorption. There are three inflection points as shown in Fig. 2 of the paper [Joyner et al., 1948]. In Fig. 6 of the paper [Joyner et al., 1948] the third inflection point ( $v/v_m=1$ ) is coincident with the second inflection point ( $p/p_0=0.3$ ) of Fig. 2 of the paper [Joyner et al., 1948]. Then the point to start the Bose-Condensation to occur is somewhere between 0.1 and 0.2 of the  $p/p_0$  value and  $p/p_0=0.3$  is approximated to be the inflection point formed by the pore condensation [Kim, 2000] and the middle point of the pore condensation. After this point the pore is filled completely by the Bose-Condensation until

the third inflection point. In this interval (from the second to third inflection point) of the relative vapor pressure, the adsorption rate vs.  $p/p_0$  decreases. After the third inflection point the adsorption rate increases again because of the Bose-Condensation on the free surface. Then the cause of the Bose-Condensation is that the condensation on the free surface is easier than that on the pore. The meaning of the easiness relies on the strongness of the adsorption sites, the easy elimination of the adsorption heat and the geometric balance. At that time we cannot say that the pore condensation stops entirely. From Fig. 6 of the paper [Joyner et al., 1948] the Bose-Condensation heat for nitrogen adsorbed on Graphon adsorbent is read to be ca. 1,600 cal/mol.

In Fig. 7 of the experimental literature of Zettlemoyer et al.'s [1950],  $-\Delta H$  vs.  $v/v_m$  can be called as the differential heat vs.  $v/v_m$ . Since it has a hump and a saddle, the adsorbent is composed of two groups of sites as explained in the above paragraph. The decreasing tendency of the differential heat with its steep slope shows that the strength (electronegativity) to adsorb gas molecules is reduced swiftly as the strong group of sites is occupied by the gas molecules. It is supposed that the other weak group of sites is adsorbed by gas molecules before the strong group of sites is occupied completely and then the Bose-Condensation occurs in the higher than second layers of the strong group of sites before the weak group of sites is occupied. These combined results bring a hump and a saddle in the figure of the differential heat vs.  $v/v_m$ . The maximum point of the adsorption by the weak group of sites becomes 1.5 of  $v/v_m$ . After that point the Bose-Condensation occurs simultaneously on both groups of sites and the differential heat decreases steeply. The Bose-Condensation occurs to the saturated vapor pressure with the remaining surface sites being occupied as completely as possible. The Bose-Condensation heat for nitrogen adsorbed on polyethylene is read to be ca. 1,450 cal/mol.

When we see in Fig. 1 of the experimental literature by Drain and Morrison [Drain et al., 1953] and as we explain in the Table

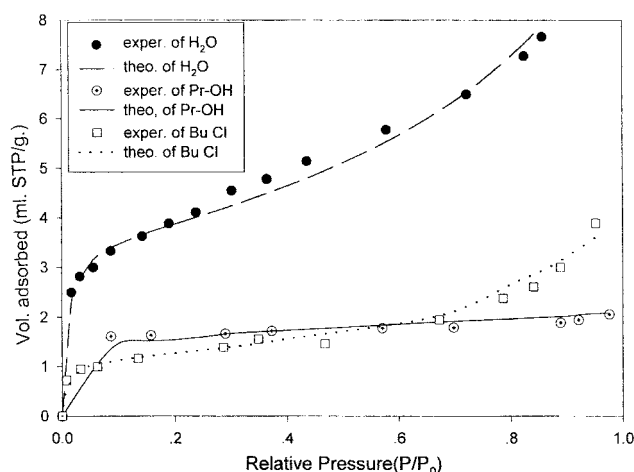
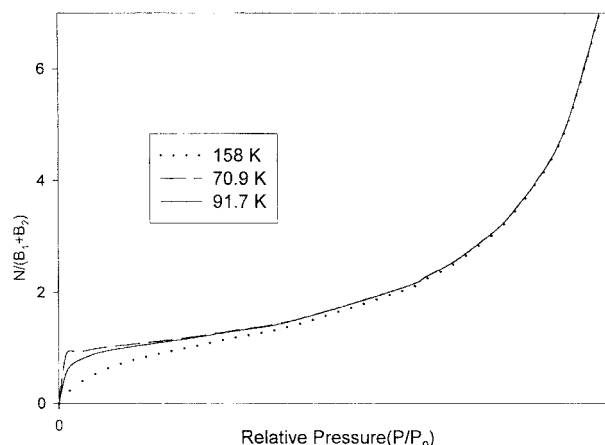


Fig. 11. Adsorption isotherms for the adsorption of vapors on rutile ( $\text{TiO}_2$ ) at 26 °C after activation at 450 °C compared with theoretical isotherm Eq. (16): ( $\beta_1=.000001$ ,  $f_1=1.45$ ,  $M_1=1.68$ ,  $c_{s1}=.66$ ) for  $\text{H}_2\text{O}$ , ( $\beta_1=.000001$ ,  $f_1=1.45$ ,  $M_1=1.53$ ,  $c_{s1}=.23$ ) for n-propyl alcohol and ( $\beta_1=.000001$ ,  $f_1=1.45$ ,  $M_1=1.68$ ,  $c_{s1}=.73$ ) for n-butyl chloride [Hollabaugh et al., 1961].

2 and the above two paragraphs, we can say that the adsorbent of  $\text{TiO}_2$  has two groups of adsorption sites. The reason is that although the isosteric heat as a function of the volume adsorbed does not have a hump or a saddle, it has two respective different slopes. Concerning these types of slopes, the stronger group of sites is occupied first and then the weaker group of sites is occupied. Lastly, the Bose-Condensation occurs continuously to the end of the relative vapor pressure. That is, a coincidence of the adsorption between groups and sites does not happen. Therefore, their results bring good agreement between the theoretical data and the experimental data in the adsorption isotherm as shown in Fig. 5. The Bose-Condensation heat for nitrogen adsorbed in  $\text{TiO}_2$  is ca. 555 cal/mol.

The isotherm data belonging to experiment 1 among the adsorption isotherms which Hollaraugh and Chessick [Hollaraugh et al., 1961] executed is fitted through Eq. (16) and represented in Fig. 11. As we see in the compared isotherms of Fig. 11, the experimental data of  $\text{H}_2\text{O}$  and n-propyl alcohol agree well with the



**Fig. 12. Temperature dependence of theoretical two groups adsorption isotherms (type II) Eq. (16):  $(j_m/j_1)(j_m/j_2)^{M_1}=1$ ,  $D_m-D_1=-1,200$  cal/g-mol,  $D_m-D_2=-938$  cal/g-mol,  $f_1=4$ ,  $M_1=.32$ ,  $c_1=.88$ ) on non-porous adsorbent.**

**Table 3. Bose condensation energies ( $D_m$ ) vs. various parameters of  $\beta_1$ , temperature,  $M_1$ ,  $(j_m/j_1)(j_m/j_2)^{M_1}$ ,  $D_1$  and  $D_2$**

$\beta_1=.0002$ , 77 K and $M_1=.8$										
		$D_1=3500$ cal/g-mol			$D_1=3000$ cal/g-mol			$D_1=2500$ cal/g-mol		
	$D_2 \rightarrow$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$
$(j_m/j_1)(j_m/j_2)^{M_1} =$	.5	1413	1746	2057	1134	1401	1668	835	1057	1279
	1.0	1376	1746	2057	1076	1342	1609	776	998	1220
	1.5	1341	1652	1962	1041	1308	1574	741	964	1186
	2.0	1317	1628	1939	1017	1283	1550	717	939	1161
$\beta_1=.002$ , 77 K and $M_1=.8$										
		$D_1=3500$ cal/g-mol			$D_1=3000$ cal/g-mol			$D_1=2500$ cal/g-mol		
	$D_2 \rightarrow$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$
$(j_m/j_1)(j_m/j_2)^{M_1} =$	.5	1630	1941	2252	1330	1597	1864	1030	1254	1475
	1.0	1571	1882	2139	1271	1538	1805	971	1193	1461
	1.5	1537	1848	2159	1237	1504	1770	937	1461	1381
	2.0	1512	1823	2135	1212	1479	1746	913	1135	1357
$\beta_1=.2$ , 77 K and $M_1=.8$										
		$D_1=3500$ cal/g-mol			$D_1=3000$ cal/g-mol			$D_1=2500$ cal/g-mol		
	$D_2 \rightarrow$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$
$(j_m/j_1)(j_m/j_2)^{M_1} =$	.5	2022	2333	2644	1722	1983	2255	1422	1644	1866
	1.0	1963	2274	2585	1663	1929	2196	1363	1585	1807
	1.5	1928	2239	2550	1495	1895	2162	1328	1550	1773
	2.0	1904	2215	2526	1604	1870	2137	1304	1526	1748
$\beta_1=2$ , 77 K and $M_1=.8$										
		$D_1=3500$ cal/g-mol			$D_1=3000$ cal/g-mol			$D_1=2500$ cal/g-mol		
	$D_2 \rightarrow$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$
$(j_m/j_1)(j_m/j_2)^{M_1} =$	.5	2217	2528	2840	1917	2184	2451	1617	1840	2062
	1.0	2158	2470	2781	1857	2125	2392	1558	1781	2003
	1.5	2124	2435	2746	1824	2191	2524	1552	1830	2107
	2.0	2138	2527	2916	1833	2166	2500	1527	1805	2083
$\beta_1=22$ , 77 K and $M_1=.8$										
		$D_1=3500$ cal/g-mol			$D_1=3000$ cal/g-mol			$D_1=2500$ cal/g-mol		
	$D_2 \rightarrow$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$	$.1D_1$	$.3D_1$	$.5D_1$
$(j_m/j_1)(j_m/j_2)^{M_1} =$	.5	2460	2849	3238	2154	2488	2821	1849	2127	2404
	1.0	2401	2790	3179	2096	2429	2762	1790	2062	2346
	1.5	2367	2756	3144	2061	2394	2728	1756	2033	2311
	2.0	2342	2731	3120	2037	2370	2703	1731	2009	2287

\*unit: cal/g-mol

theoretical isotherms. But the experimental data for the n-butyl alcohol agree a little unsatisfactorily with the theoretical isotherm Eq. (16). As we see in Fig. 3 of the literature [Hollaraugh et al., 1961], the adsorbent truly has two groups of sites and the differential heat of each group is constant with respect to  $v/v_m$  until each group of the sites is occupied almost completely. The constants of the differential heat vs.  $v/v_m$  represent the constants  $D_1$  and  $D_2$  of  $\beta_1$  in Eq. (16). Hence this fact is already assumed in deriving the statistical isotherm Eq. (16) first. The reasons which bring almost the constant values for  $D_1$  and  $D_2$  rely on the scarce adsorption sites of the rutile adsorbent for the adsorption of the above given adsorbates; thus the scarce repulsion among the adsorbed molecules and that the electronegativity of the adsorbent is not reduced since the non-bonding electrons of Ti-O-Ti are donated to the rutile as the sites are occupied by the molecules. But in the Ti-Cl-Ti and Ti-Cl bondings of n-butyl chloride the bondings are weak since it is large and the degree of the electron donation of Cl to the adsorbent is small. These facts result in the steep slopes of the differential heat vs. the adsorbed volume of n-butyl chloride.

Fig. 12 shows the adsorption isotherms [Eq. (16)] which represent the amount of the adsorbed gas molecules according to temperature. The adsorption isotherm of type II represents the increase of the amount of the adsorbed molecules as the temperature increases. It rules the beginning adsorption with respect to the relative vapor pressure.

From various values of  $\beta_1$  in Eq. (16) we have calculated  $D_m$ ,  $D_1$  and  $D_2$  at 77 °K and  $M_1=0.8$  with four differential values of the local molecular partition function ratios between groups,  $(j_m/j_1)(j_m/j_2)^{M_1}$ , as an example in Table 3 to get the their unknown values easily when some of them are known and the rest of them are not known. And the table is made to represent and to rely on that the Bose-Condensation heat of CO gas on particular chromia catalyst is ca. 1,400 cal/mol [Gregg et al., 1969].

## CONCLUSION

It is considered that the present two groups isotherm is fitted well to appropriately selected experimental data and we have found that almost all the surfaces of the adsorbents have two and rarely more than two groups of the heterogeneous adsorption sites. The monolayer sites ( $v_m$ ) of any group over the whole range of the relative pressure can be obtained as easily as that obtained by the BET isotherm over the limited range of the relative pressure.

When the BET isotherm and our two groups isotherm have the same maximum adsorption energy differences between the first layer and the higher layer with the same localized partition function, the latter isotherm necessitates more adsorption sites than the former isotherm to adsorb the same amount of the molecules. It is found that as temperature decreases to 78 K or so, the surface charges of the reduced polycrystalline copper and rutile adsorbents may affect the distribution of the adsorbed molecules much differently from our derived isotherms. Near saturated vapor pressure the cohesion force may dominate in the adsorption. It is found that the differential heat vs.  $v/v_m$  describes well the characteristics of the groups of adsorption sites, the mechanism of the adsorption of the meeting point of the surface adsorption layer and the higher than second layers, the Bose-Condensation heat and its characteristics.

The Bose-Condensation heat depends on the kind of adsorbent.

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