RICE UNIVERSITY

The Adsorption of Gases on Solids

by

Frederick Specht

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS

Houston, Texas
May, 1962
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I. INTRODUCTION

With the advent of the Brunauer-Emmett-Teller multilayer adsorption equation the process of gas-adsorption on solids was successfully described in terms of a simple model. This equation was not intended to explain all phases of gas-solid adsorption, but it described reasonably well those cases for which it was derived. The simplifying feature of this equation lies in the assumption concerning the nature of the surface of the solid, viz. the surface is assumed to consist of uniformly distributed, stationary sites on which the gas molecules may be adsorbed. Each site is assumed capable of accommodating one gas molecule. The multilayer nature of the equation is obtained by assuming that each adsorbed molecule in the first layer creates a new site on which a second molecule may be adsorbed, and so on for higher layers. With its simple model of site-adsorption this equation has been able to explain a large number of multilayer gas adsorption processes.

Since the introduction of the BET equation some twenty years ago, a number of generalizations have been attempted by various authors. (See Appendix IV.) A good number of these generalizations departed from the original simplicity of the BET theory and resulted in somewhat unmanageable mathematical expressions.
The work explained here deals with a generalization which retains the stationary site picture and thus loses none of the basic simplicity of the BET theory. This treatment gives an extra degree of freedom to the nature of the sites over that of the BET and an equation with three parameters is obtained.

A least squares fitting of this three constant equation to a large and varied set of adsorption data was done, the results of which are given in tabular form in the appendices.
II. Derivation of a New Three Constant Adsorption Equation

The noteworthy success of the Brunauer, Emmett, and Teller\textsuperscript{(1)} adsorption equation, especially at partial pressures up to about 0.35 and from the point of view of practical application, has engendered many attempts at modification, so that the effective working range may be extended towards higher values of the partial pressure of the adsorbate. Newer modifications, usually resulting in one or more additional constants, have involved primarily (a) no longer assuming that the heat of adsorption in all layers after the first is equal to the heat of liquefaction of the adsorbate, and (b) assuming certain horizontal interactions between adsorbed molecules. Departures arising from (a) were considered by deBoer\textsuperscript{(2)}, Cook\textsuperscript{(3)}, Dole\textsuperscript{(4)}, Anderson\textsuperscript{(5)}, Pickett\textsuperscript{(6)}, and others. Halsey\textsuperscript{(7)} derived a new multilayer adsorption equation by considering a distribution of energy sites. Hütting and Pietzka\textsuperscript{(8,9)} modified the assumptions concerning vertical interactions, but Keii\textsuperscript{(10)} has objected to the method of derivation. More recently Kiselev\textsuperscript{(11)} has suggested a more general equation, involving an additional constant, which becomes the standard Brunauer, Emmett, and Teller equation when this new third constant becomes zero. (See Appendix III.) The third constant takes into account horizontal interactions.

It is the purpose here to consider another approach,
which involves a change in some of the original assumptions concerning the specific nature of the surface.

Let us consider an adsorbent consisting of a surface containing uniformly distributed adsorption sites which can accommodate one and only one gas molecule. Let \( \Delta H_M \) be the heat of adsorption of a molecule adsorbed on such a site. In all that follows any \( \Delta H \) is associated with the reaction: vapor \( \to \) adsorbed phase, and in general is a negative quantity. Denote by \( a \) the total number of such sites. So far, our assumptions are identical with those of Langmuir and of Brunauer, Emmett, and Teller. Now let us assume that on a certain fraction, \( d \), of the surface, each adsorbed molecule creates a new site on which a second molecule can be adsorbed with a heat of adsorption \( \Delta H_L \). Furthermore, each molecule in the second layer creates a new site on which a third layer may form, and so on for higher layers. The heat of adsorption for each molecule in all layers after the first is assumed to be \( \Delta H_L \), the heat of liquefaction. The remaining fraction of the surface, \( (1-d) \), is assumed to be only capable of monolayer adsorption. These new assumptions amount to stating that the original surface actually consists of two kinds of sites. One kind of sites, \( (1-d) \), corresponds to pure Langmuir adsorption, while the second kind of sites, \( d \), corresponds to pure Brunauer-Emmett-Teller adsorption. (See Appendix III.) The fraction \( d \) is assumed to be an in-
trinsic parameter of the surface of the adsorbent and does not depend on parameters of the gas such as temperature and pressure. The only interactions considered here are the lateral interactions between stacked molecules in a given column of adsorbed molecules, and the interactions between the first adsorbed molecule and the adsorption site. Horizontal interactions, if present, are neglected. The only adsorbed molecules that are free to evaporate are those on the top of each column, in contrast to the assumption of Hütting (8) that each molecule within a given column can freely evaporate. (See Appendix III.)

The theoretical isotherm corresponding to such a surface in contact with an ideal gas may be obtained by constructing the grand partition function. Since the monolayer and multilayer fraction of the surface are considered to be independent, we may treat them temporarily as separate systems.

A site on the monolayer fraction can exist in two states with zero and one adsorbed molecules respectively. The canonical partition functions for these two states are:

\[
Q(0) = 1 \quad (1)
\]

\[
Q(1) = \mathcal{J}_i \quad (2)
\]

where

\[
\mathcal{J}_i = \exp\left(-\frac{\Delta H_m}{kT} - \frac{5}{2}\right)
\]
This expression for $Q(l)$ is obtained by considering the energy required to transport a molecule from the adsorbed to the gas phase. If $E_1$ is the binding energy between the molecule and the site, then the energy of the adsorbed molecule is $-E_1$. The energy required to transport a molecule from the adsorbed to the gas phase is $E_1$, the binding energy, plus $3/2$ kT, the kinetic energy per molecule of an ideal gas, plus $kT$, the energy per molecule required to expand an ideal gas at temperature $T$ from a volume zero to a volume $V$. (We are neglecting the volume of the adsorbed phase.) Thus,

$$-E_1 = \Delta H_m + \frac{3}{2} kT$$

(3)

from which Equation (2) follows. Equation (3) relates the standard energy state between the gas and adsorbed phase.

Using the definition of the grand partition function

$$\Xi = \sum_{N} \left[ \exp(\mu N/kT) \cdot Q(N) \right]$$

(4)

$\Xi$ for one monolayer site may be written as

$$\Xi = 1 + J_1 \exp(\mu/kT)$$

With $a(l - d)$ such sites $\Xi$ for the entire monolayer fraction is

$$\Xi(a, d, \mu, T) = \left[ 1 + J_1 \exp(\mu/kT) \right]^{a(l - d)}$$

(5)
The values of $Q(N)$ for a site on the multilayer fraction of the surface may be enumerated as follows:

\[
Q(0) = 1 \\
Q(1) = J_1 \\
Q(2) = J_1 J_2 \\
\vdots \\
Q(N) = J_1^N J_2^{(N-1)} \quad (N \neq 0)
\]

where $N$ is the number of molecules adsorbed, and

\[
J_2 = \exp \left( -\frac{\Delta H_1}{kT} - \frac{5}{2} \right)
\]

Again using (4) $\Xi$ for one multilayer site is

\[
\Xi = 1 + J_1 \exp(\mu/kT) \sum_{N=0}^{\infty} \left[ J_2 \exp(\mu/kT) \right]^N
\]

(6)

If

\[
J_2 \exp(\mu/kT) < 1
\]

(7)

then (6) becomes

\[
\Xi = 1 + \frac{J_1 \exp(\mu/kT)}{1 - J_2 \exp(\mu/kT)}
\]
With ad such sites \( \Xi \) for the entire multilayer fraction is

\[
\Xi(a, d, \mu, T) = \left[ 1 + \frac{J_1 \exp(\mu/kT)}{1 - J_2 \exp(\mu/kT)} \right]^{ad}
\]  

Since the two parts of the surface are independent, the complete grand partition function is the product of the partition function for each portion. Thus

\[
\Xi(a, d, \mu, T) = \left[ 1 + J_1 \exp(\mu/kT) \right]^{a(1-d)}
\]

\[
\times \left[ 1 + \frac{J_1 \exp(\mu/kT)}{1 - J_2 \exp(\mu/kT)} \right]^{ad}
\]

(9)

The isotherm may be obtained from the relation

\[
N = kT \left[ \frac{d \ln \Xi}{d\mu} \right]_{a, d, T}
\]

(10)

Substituting (9) into (10) we have

\[
N = \left[ a(1-d) J_1 \exp(\mu/kT) \right]/\left[ 1 + J_1 \exp(\mu/kT) \right] + ad \left[ (J_1 - J_2) \exp(\mu/kT) \right]/\left[ 1 + (J_1 - J_2) \exp(\mu/kT) \right] + ad \left[ J_2 \exp(\mu/kT) \right]/\left[ 1 - J_2 \exp(\mu/kT) \right]
\]

(11)
The exponential functions may be related to the pressure of the gas by considering the thermodynamic equation

\[ S \, dT - V \, dP + N \, d\mu = 0 \]

For an adsorption isotherm \( dT = 0 \), and for a perfect gas \( PV = NkT \). Thus

\[ d\mu = kT \, \frac{dP}{P} \]

Integrating we have

\[ \frac{P}{P_0} = \exp(-\mu_0/kT) \exp(\mu/kT) \]  \hspace{1cm} (12)

where \( P_0 \) is saturation pressure, and \( \mu_0 \) is the chemical potential at saturation. Since the partial pressure is proportional to \( \exp(\mu/kT) \), and since an infinite number of layers are free to form on the multilayer fraction at saturation, Equation (11) requires that

\[ \frac{P}{P_0} = J_2 \exp(\mu/kT) \]

Thus

\[ J_1 \exp(\mu/kT) = b \frac{P}{P_0} \]

where

\[ b = \frac{J_1}{J_2} = \exp\left[-(\Delta H_m - \Delta H_L)/kT\right] \]

It will be noted that \( (\Delta H_m - \Delta H_L) \) corresponds to the net heat of adsorption. Letting \( p = P/P_0 \) equation (11) becomes
\[ N = \frac{a(i-d)bp}{1 + bp} + \frac{ad(b-1)p}{1 + (b-1)p} + \frac{adp}{1 - p} \]  

(13)

This equation may be written in the form

\[ \chi = \frac{a(i-d)bp}{1 + bp} + \frac{ad(b-1)}{1 + (b-1)p} + \frac{adp}{1 - p} \]  

(14)

where \( \chi \) is the number of grams of adsorbate per gram adsorbent with an appropriate change in meaning of \( a \).

For \( b \gg 1 \), (14) reduces to

\[ \chi = \frac{abp}{1 + bp} + \frac{adp}{1 - p} \]  

(15)

Equation (15) has been employed in this laboratory on an experimental basis for over six years. It has been observed that numerous adsorption isotherms of water on various individual and dual oxides follow this equation up to partial pressures of 0.8 or more. Most of the isotherms show a sharp rise at small partial pressures, (0-0.15), corresponding to a very high value of \( b \), followed by a relatively flat region at intermediate partial pressures, (0.15 - 0.5), and finally a rapid rise nearer saturation, (0.5 - 1.0). Under these conditions, \( b \gg 1 \), the reduced form of Equation (14), i.e., Equation (15) can represent many isotherms in a very satisfactory manner.
In Appendix I is given the results of a least squares fitting of Equation (15) to 190 water isotherms which were taken at Rice during the past several years. The isotherms are arranged in increasing order of standard deviation, which was taken as the criterion for a good fit.

In performing the least squares calculation Equation (15) was written in the form

\[ \frac{E_p}{x} + \frac{F}{x} + b(1-p) + \frac{1}{p} - 1 = 0 \]

where

\[ E = ab(1-d) \]

and

\[ F = -a(b+d) \]

The usual standard deviation was used, i.e.

\[ S.D. = \sqrt{\frac{\sum_{i=1}^{n} (x_{EXP} - x_{CAL})^2}{n}} \]

In Appendix II is given the results of a least squares fitting of Equation (15) to a set of 94 experimental isotherms taken from the literature. The set consisted of 28 different adsorbates. The same procedure described above for Appendix I was used for Appendix II.
REFERENCES TO SECTION II


(8) G. Hütting and G. Pietzka, Monatsh., 78, 185 (1948).


APPENDIX I

Water Isotherms taken at Rice
for which good fits were obtained by
The Three Constant Equation
\[ x = \frac{abp}{1+bp} + \frac{adp}{1-p} \]
(All isotherms were taken at 12.00°C)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Parameters</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a, b, d</td>
<td></td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_3 )</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.6028</td>
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</tr>
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</tr>
<tr>
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<td>0.3186</td>
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13.
## APPENDIX I, 2

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<tr>
<th>Adsorbent</th>
<th>Parameters a, b, d</th>
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<tr>
<td>40% NiO, 60% Cr$_2$O$_3$ Heated at 600°C</td>
<td>0.0009901, 15526, 0.4562</td>
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<td>0.02411, 39376, 0.2419</td>
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<td>0.2684, 15068, 0.4316</td>
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<td>30% NiO, 70% Al$_2$O$_3$</td>
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<td>20% NiO, 80% Al$_2$O$_3$</td>
<td>0.1195, 34263, 0.2816</td>
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<td>0.007237, 15917, 0.4307</td>
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<tr>
<td>10% ZrO$_2$, 90% Cr$_2$O$_3$ Heated 2 hrs. at 400°C</td>
<td>0.02265, 21257, 0.3589</td>
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### APPENDIX I, 3

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<td>20% ZrO$_2$, 80% Cr$_2$O$_3$ Heated 2 hrs. at 400°C</td>
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<td>50% NiO, 50% Cr$_2$O$_3$ Heated at 500°C</td>
<td>0.04120 0.2297, 0.01081</td>
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<td>10% NiO, 90% Al$_2$O$_3$</td>
<td>0.1402 0.2989, 0.01163</td>
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<td>50% NiO, 50% Al$_2$O$_3$</td>
<td>0.2705 0.1592, 0.01197</td>
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<td>Cr$_2$O$_3$ Heated at 500°C</td>
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## APPENDIX I, 4

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<tr>
<td>20% NiO, 80% Cr₂O₃ Heated at 500°C</td>
<td>0.02010 30600 0.3397</td>
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<td>30% NiO, 70% Cr₂O₃ Heated at 600°C</td>
<td>0.01581 19605 0.5039</td>
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<td>0.3169 43050 0.1282</td>
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<td>0.02832 35210 0.2236</td>
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<td>0.1063 23791 0.3620</td>
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<td>70% Cr₂O₃, 30% Fe₂O₃ Heated 2 hrs. at 200°C</td>
<td>0.3029 76720 0.03131</td>
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<td>0.1643 26909 0.06396</td>
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<td>NiO, heated 2 hrs. at 300°C</td>
<td>0.1236 30597 0.3226</td>
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<td>40% NiO, 60% Cr₂O₃ Heated at 500°C</td>
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<td>0.09518 18032 0.3361</td>
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### APPENDIX I, 5

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## APPENDIX I, 6

<table>
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<th>Adsorbent</th>
<th>Parameters a, b, d</th>
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<td>NiO, Heated at 400°C</td>
<td>0.04689 18822 0.3903</td>
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<tr>
<td>10% NiO, 90% Al₂O₃ Heated 2 hrs. at 500°C</td>
<td>0.3155 38853 0.1489</td>
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<tr>
<td>Cr₂O₃, heated 2 hrs. at 300°C</td>
<td>0.1955 39780 0.2237</td>
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<tr>
<td>80% Cr₂O₃, 20% Fe₂O₃ Heated 2 hrs. at 200°C</td>
<td>0.2599 47192 0.05459</td>
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<tr>
<td>30% ZrO₂, 70% Cr₂O₃ Heated 2 hrs. at 400°C</td>
<td>0.08864 25972 0.4266</td>
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</tr>
<tr>
<td>60% NiO, 40% Cr₂O₃ Heated 2 hrs. at 300°C</td>
<td>0.2738 25338 0.08477</td>
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<tr>
<td>30% Cr₂O₃, 70% Fe₂O₃ Heated 2 hrs. at 200°C</td>
<td>0.1627 26612 0.1024</td>
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<td>80% NiO, 20% Cr₂O₃ Heated 2 hrs. at 600°C</td>
<td>0.02891 41101 0.3308</td>
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<tr>
<td>20% Cr₂O₃, 80% Fe₂O₃ Heated 2 hrs. at 200°C</td>
<td>0.1471 23296 0.1371</td>
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<tr>
<td>90% ZrO₂, 10% Cr₂O₃ Heated 2 hrs. at 400°C</td>
<td>0.06796 11928 0.3092</td>
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<tr>
<td>Cr₂O₃, heated 2 hrs. at 200°C</td>
<td>0.3657 77001 0.07596</td>
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## APPENDIX I, 7

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Parameters a, b, d</th>
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<tr>
<td>90% Cr$_2$O$_3$, 10% Fe$_2$O$_3$ Heated 2 hrs. at 200°C</td>
<td>0.3023 51823 0.08779</td>
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<td>30% NiO, 70% Cr$_2$O$_3$ Heated at 400°C</td>
<td>0.05232 31426 0.2286</td>
<td>0.05343</td>
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<tr>
<td>Cr$_2$O$_3$, heated 2 hrs. at 200°C</td>
<td>0.3805 66733 0.07755</td>
<td>0.05361</td>
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<tr>
<td>ZrO$_2$, heated 2 hrs. at 400°C</td>
<td>0.03926 14785 0.7709</td>
<td>0.05511</td>
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<tr>
<td>50% ZrO$_2$, 50% Cr$_2$O$_3$ Heated 2 hrs. at 400°C</td>
<td>0.1634 22893 0.1975</td>
<td>0.06159</td>
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<tr>
<td>Fe$_2$O$_3$, heated 2 hrs. at 200°C</td>
<td>0.1386 18362 0.1433</td>
<td>0.06265</td>
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<tr>
<td>50% NiO, 50% Cr$_2$O$_3$ Heated 2 hrs. at 300°C</td>
<td>0.2562 21983 0.1672</td>
<td>0.06274</td>
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<tr>
<td>40% ZrO$_2$, 60% Cr$_2$O$_3$ Heated 2 hrs. at 400°C</td>
<td>0.1202 29758 0.3769</td>
<td>0.06637</td>
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<tr>
<td>70% NiO, 30% Cr$_2$O$_3$ Heated at 250°C</td>
<td>0.3178 46309 0.04315</td>
<td>0.06848</td>
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<td>Al$_2$O$_3$</td>
<td>0.1375 33643 0.4146</td>
<td>0.07363</td>
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<td>Fe$_3$O$_4$ + K$_2$O Coprecipitate</td>
<td>0.005434 3261 0.4245</td>
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## APPENDIX I, 8

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<td>10% NiO, 90% Cr₂O₃</td>
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<td>0.07659</td>
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<td>Heated 2 hrs. at 300°C</td>
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<tr>
<td>Cr₂O₃</td>
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<td>Fe₃O₄ + K₂O Coprecipitate</td>
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<td>Cr₂O₃</td>
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<td>50% Cr₂O₃, 50% Fe₂O₃</td>
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<td>40% Cr₂O₃, 60% Fe₂O₃</td>
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<td>60% Cr₂O₃, 40% Fe₂O₃</td>
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<td>Heated 2 hrs. at 300°C</td>
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<td>30% Cr₂O₃, 70% Fe₂O₃</td>
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<td>70% Cr₂O₃, 30% Fe₂O₃</td>
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<td>20% Cr₂O₃, 80% Fe₂O₃</td>
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<td>0.09422</td>
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<tr>
<td>Al₂O₃</td>
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<td>0.05180</td>
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### APPENDIX I, 9

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<td>50% NiO, 50% (\text{Cr}_2\text{O}_3)</td>
<td>0.07313, 41827, 0.3400</td>
<td>0.09493</td>
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<td>Heated at 450°C</td>
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<tr>
<td>40% NiO, 60% (\text{Cr}_2\text{O}_3)</td>
<td>0.2700, 22794, 0.2339</td>
<td>0.09513</td>
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<tr>
<td>Heated 2 hrs. at 300°C</td>
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<tr>
<td>10% (\text{Cr}_2\text{O}_3), 90% (\text{Fe}_2\text{O}_3)</td>
<td>0.2255, 13514, 0.09461</td>
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<td>90% NiO, 10% (\text{Cr}_2\text{O}_3)</td>
<td>0.03254, 22056, 0.4943</td>
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<td>Heated at 600°C</td>
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<tr>
<td>70% NiO, 30% (\text{Cr}_2\text{O}_3)</td>
<td>0.05835, 32166, 0.2974</td>
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<td>Heated at 600°C</td>
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<tr>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>0.2206, 12936, 0.08977</td>
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<td>80% NiO, 20% (\text{Cr}_2\text{O}_3)</td>
<td>0.1889, 21132, 0.1258</td>
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<td>Heated at 350°C</td>
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<td>20% NiO, 80% (\text{Al}_2\text{O}_3)</td>
<td>0.2071, 18499, 0.05085</td>
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<td>60% NiO, 40% (\text{Cr}_2\text{O}_3)</td>
<td>0.09401, 32226, 0.2474</td>
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<td>Heated at 500°C</td>
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<td>90% NiO, 10% (\text{Cr}_2\text{O}_3)</td>
<td>0.1584, 16742, 0.1369</td>
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<tr>
<td>80% (\text{Cr}_2\text{O}_3), 20% (\text{Fe}_2\text{O}_3)</td>
<td>0.5307, 31032, 0.05291</td>
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### APPENDIX I, 10

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<th>Parameters</th>
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<tr>
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<td>a, b, d</td>
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<tr>
<td>Fe$_3$O$_4$ pigment + 1% K$_2$O + 1% Al$_2$O$_3$</td>
<td>0.04144 23948</td>
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<td>Fe$_3$O$_4$ + K$_2$O Coprecipitate</td>
<td>0.04611 9649</td>
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<td>70% NiO, 30% Cr$_2$O$_3$</td>
<td>0.1051 22377</td>
<td>0.1292</td>
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<tr>
<td>30% NiO, 70% Cr$_2$O$_3$ Heated 2 hrs. at 300°C</td>
<td>0.2386 27532</td>
<td>0.1301</td>
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<td>90% NiO, 10% Cr$_2$O$_3$ Heated at 500°C</td>
<td>0.08276 19990</td>
<td>0.1319</td>
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<tr>
<td>90% NiO, 10% Cr$_2$O$_3$ Heated at 400°C</td>
<td>0.1440 15112</td>
<td>0.1367</td>
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<tr>
<td>60% NiO, 40% Cr$_2$O$_3$ Heated at 400°C</td>
<td>0.1800 21542</td>
<td>0.1425</td>
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<tr>
<td>40% NiO, 60% Cr$_2$O$_3$ Heated at 400°C</td>
<td>0.1050 25790</td>
<td>0.1506</td>
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<tr>
<td>50% NiO, 50% Cr$_2$O$_3$ Heated at 250°C</td>
<td>0.2885 21498</td>
<td>0.1624</td>
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<tr>
<td>50% NiO, 50% Cr$_2$O$_3$ Heated at 400°C</td>
<td>0.2042 20570</td>
<td>0.1850</td>
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<tr>
<td>Wyodak</td>
<td>0.1037 6581</td>
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### APPENDIX I, 11

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<th>Adsorbent</th>
<th>Parameters a, b, d</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>90% NiO, 10% Al₂O₃</td>
<td>0.1265 10698 0.2433</td>
<td>0.1939</td>
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<td>Fe₂O₃  H₂O</td>
<td>0.1280 28487 0.07143</td>
<td>0.1949</td>
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<td>Cr₂O₃, heated at 250°C</td>
<td>0.2594 27295 0.2010</td>
<td>0.2091</td>
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<tr>
<td>NiO, Heated at 250°C</td>
<td>0.1639 30567 0.3230</td>
<td>0.2191</td>
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<tr>
<td>10% NiO, 90% Al₂O₃</td>
<td>0.2434 23808 0.04984</td>
<td>0.2437</td>
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<td>10% NiO, 90% Cr₂O₃, heated at 350°C</td>
<td>0.1931 29526 0.3330</td>
<td>0.2554</td>
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<tr>
<td>20% NiO, 80% Cr₂O₃, heated at 250°C</td>
<td>0.2494 26280 0.2708</td>
<td>0.2692</td>
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<tr>
<td>20% NiO, 80% Cr₂O₃, heated at 350°C</td>
<td>0.1163 19031 0.5805</td>
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<td>Fe₃O₄ + 10.0% K₂O</td>
<td>0.07916 10496 0.2007</td>
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<td>Cr₂O₃</td>
<td>0.1892 29347 0.08475</td>
<td>0.3109</td>
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<td>30% NiO, 70% Cr₂O₃, heated at 350°C</td>
<td>0.1411 21842 0.5225</td>
<td>0.3280</td>
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<td>Adsorbent</td>
<td>Parameters a, b, d</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>---------------------------------</td>
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<td>-------------------</td>
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<tr>
<td>Bentonite Clay</td>
<td>0.1643 8258 0.1316</td>
<td>0.3395</td>
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<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.7886 53916 0.03026</td>
<td>0.4172</td>
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<tr>
<td>$30% \text{Cr}_2\text{O}_3, 70% \text{Fe}_2\text{O}_3$ Heated at 200°C</td>
<td>0.1409 19580 0.1544</td>
<td>0.5301</td>
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<td>$\text{Fe}_3\text{O}_4$</td>
<td>0.1887 17061 0.1517</td>
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<td>$\text{TiO}_2$</td>
<td>0.2406 8713 0.1327</td>
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<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>0.2960 11630 0.1420</td>
<td>0.9219</td>
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APPENDIX II

Isotherms from the Literature for which good fits were obtained by the Three Constant Equation
\[ x = \frac{abp}{l+bp} + \frac{adp}{l-p} \]

<table>
<thead>
<tr>
<th>Adsorbate &amp; Adsorbent</th>
<th>Temp.</th>
<th>Ref.</th>
<th>Parameters a, b, d</th>
<th>Standard Deviation</th>
</tr>
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<tbody>
<tr>
<td>Water on TiO₂</td>
<td>99.4°C</td>
<td>(1)</td>
<td>0.08257 94.68 9.938</td>
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<tr>
<td>Sulphur Dioxide on Gel of Silica Acid</td>
<td>100°C</td>
<td>(2)</td>
<td>0.2229 57.70 14.22</td>
<td>0.001558</td>
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<tr>
<td>Ethyl Alcohol on ThO₂</td>
<td>99.4°C</td>
<td>(1)</td>
<td>0.7715 314.5 1.290</td>
<td>0.002148</td>
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<td>Nitrogen on Aluminum Oxide</td>
<td>77.3°C</td>
<td>(3)</td>
<td>0.2594 79.04 75.40</td>
<td>0.002334</td>
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<tr>
<td>Sulphur Dioxide on Gel of Silica Acid</td>
<td>57°C</td>
<td>(2)</td>
<td>0.07788 103.1 9.279</td>
<td>0.003099</td>
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<tr>
<td>Cyclo hexane on Charcoal</td>
<td>100°C</td>
<td>(4)</td>
<td>0.02108 109.9 0.2931</td>
<td>0.003812</td>
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<tr>
<td>Chlorine on Activated Charcoal</td>
<td>35.5°C</td>
<td>(5)</td>
<td>0.3655 663.7 1.192</td>
<td>0.004021</td>
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<tr>
<td>Chlorine on Activated Charcoal</td>
<td>73.5°C</td>
<td>(5)</td>
<td>0.3381 3773 2.734</td>
<td>0.004068</td>
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<tr>
<td>Water on Silica</td>
<td>28°C</td>
<td>(6)</td>
<td>0.06425 10.47 0.8258</td>
<td>0.004406</td>
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25.
<table>
<thead>
<tr>
<th>Adsorbate &amp; Adsorbent</th>
<th>Temp.</th>
<th>Ref.</th>
<th>Parameters a, b, d</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>Oxygen on Charcoal (Desorex B)</td>
<td>90.18°K</td>
<td>(7)</td>
<td>0.09460 54679 617.2</td>
<td>0.004547</td>
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<td>Oxygen on Charcoal (Desorex B)</td>
<td>85.20°K</td>
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<td>0.1176 41410 311.5</td>
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<td>Oxygen on Charcoal</td>
<td>65.85°K</td>
<td>(7)</td>
<td>0.2981 448.3 10.07</td>
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<td>Benzene on Charcoal</td>
<td>100°C</td>
<td>(4)</td>
<td>0.2922 116.7 0.2027</td>
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<td>Chlorine on Activated Charcoal</td>
<td>51.0°C</td>
<td>(5)</td>
<td>0.3468 5941 2.119</td>
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<td>Sulphur Dioxide on Gel of Silica Acid</td>
<td>0°C</td>
<td>(2)</td>
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<td>Ethylene on Gel</td>
<td>194.5°K</td>
<td>(8)</td>
<td>0.02085 1000 1.558</td>
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<td>Benzene on Activated Charcoal</td>
<td>35°C</td>
<td>(9)</td>
<td>0.2006 938.4 0.003339</td>
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<tr>
<td>Oxygen on Charcoal</td>
<td>60.82°K</td>
<td>(7)</td>
<td>0.3810 1460 2.793</td>
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<td>Oxygen on Charcoal (Desorex B)</td>
<td>75.55°K</td>
<td>(7)</td>
<td>0.1851 28861 67.93</td>
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<tr>
<td>Cyclohexane on Charcoal</td>
<td>77°C</td>
<td>(4)</td>
<td>0.02181 163.8 0.09156</td>
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## APPENDIX II, 3

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<th>Ref.</th>
<th>Parameters a, b, d</th>
<th>Standard Deviation</th>
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<tr>
<td>Sulphur Dioxide on Gel of Silica Acid</td>
<td>40°C</td>
<td>(2)</td>
<td>0.3262 129.3 10.00</td>
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<td>Oxygen on Charcoal</td>
<td>57.95°K</td>
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<td>0.4650 682.7 1.327</td>
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<td>Nitrogen on Aluminum Oxide</td>
<td>77.3°K</td>
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<td>0.3607 4396 3.822</td>
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<tr>
<td>Benzene on Activated Charcoal</td>
<td>20°C</td>
<td>(9)</td>
<td>0.1879 1057 0.04797</td>
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<tr>
<td>Sulphur Dioxide on Gel of Silica Acid</td>
<td>30°C</td>
<td>(2)</td>
<td>0.3966 137.3 6.674</td>
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<td>Benzene on Charcoal</td>
<td>77°C</td>
<td>(4)</td>
<td>0.2859 2520 0.08618</td>
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<td>Benzene on Activated Charcoal</td>
<td>25°C</td>
<td>(9)</td>
<td>0.1660 55011 0.02518</td>
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<td>Iodine on Activated Charcoal</td>
<td>178.4°C</td>
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<td>0.6445 8353 0.2222</td>
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<td>Water on Silica</td>
<td>20°C</td>
<td>(6)</td>
<td>0.09466 6.096 0.1465</td>
<td>0.04618</td>
</tr>
<tr>
<td>Benzene on Activated Charcoal</td>
<td>25°C</td>
<td>(9)</td>
<td>0.2073 442.7 0.007417</td>
<td>0.07374</td>
</tr>
<tr>
<td>Water on Silica</td>
<td>23°C</td>
<td>(6)</td>
<td>0.1538 2.610 0.1101</td>
<td>0.08254</td>
</tr>
</tbody>
</table>
## APPENDIX II, 4

<table>
<thead>
<tr>
<th>Adsorbate &amp; Adsorbent</th>
<th>Temp.</th>
<th>Ref.</th>
<th>Parameters a, b, d</th>
<th>Standard Deviation</th>
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</thead>
<tbody>
<tr>
<td>Benzene on Activated Charcoal</td>
<td>35°C</td>
<td>(9)</td>
<td>0.3964 333.0 0.04356</td>
<td>0.1042</td>
</tr>
<tr>
<td>Water on Barium Sulphate</td>
<td>20°C</td>
<td>(11)</td>
<td>0.6572 155.9 0.3681</td>
<td>0.1720</td>
</tr>
</tbody>
</table>
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(2) McGavack and Patrick, J. Am. Chem. Soc., 946, 42 (1920)
(3) Kreiger, J. Am. Chem. Soc., 2712, 63 (1941)
(7) Itterbeck and Dingenen, Physica, 1169, 4 (1937)
(8) Howard and Taylor, J. Am. Chem. Soc., 2259, 56 (1934)
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APPENDIX III

Derivation of Five Standard Adsorption Equations

In the derivation of Langmuir's, the BET, and Hüttig's Equation, the gas is assumed to be ideal, and the surface is assumed to consist of uniformly distributed stationary sites on which the gas molecules are adsorbed. A molecule adsorbed on a given site is assumed to remain there for the duration of its stay on the surface, i.e., there are no horizontal adsorbate-adsorbate interactions. The surface and the corresponding equation are distinguished by the assumed characteristics of the sites.

In deriving these three equations we shall use the notation.

\[ \begin{align*}
    n_0 & = \text{total number of adsorption sites} \\
    n & = \text{total number of adsorbed molecules} \\
    p & = \text{partial pressure of the gas}
\end{align*} \]

The assumed characteristics of the sites and the derivation of the corresponding equation are given as follows:

**Langmuir's Equation.** Each site may accommodate one and only one gas molecule. The heat of adsorption for all sites are equal. Equilibrium between the gas and adsorbed phase may be written as:

\[
    A \rho (n_0 - n) = B n
\]

30.
Thus

\[ n = \frac{n_0 bp}{1 + bp} \]

where

\[ b = \frac{A}{B} \]

**B.E.T. Equation.** Each site may accommodate a column of unlimited number of molecules. The heat of adsorption of a molecule in the first layer is \( w_1 \), while the heat of adsorption of a molecule in each of the higher layers is \( w_2 \). Only the top molecule in each column is free to return to the gas phase. Letting \( n_i \) denote the number of molecules in the \( i \)'th layer, equilibrium for each layer may be written as:

\[
\begin{align*}
A_1 p(n_0 - n_1) &= B_1 (n_1 - n_2) & \text{1st Layer} \\
A_2 p(n_1 - n_2) &= B_2 (n_2 - n_3) & \text{2nd Layer} \\
A_3 p(n_2 - n_3) &= B_3 (n_3 - n_4) & \text{3rd Layer} \\
& \vdots \\
A_i p(n_{i-1} - n_i) &= B_i (n_i - n_{i+1}) & \text{\( i \)'th Layer}
\end{align*}
\]

Solving for \( n \) where \( n = n_1 + n_2 + n_3 + \cdots \) we have

\[
n = \frac{n_0 cp}{[1 + (c-1)p][1 - p]}
\]

where

\[
\frac{A_i}{B_i} = c
\]
and the assumption
\[ \frac{A_i}{B_i} = 1 \quad (i = 2, 3, 4, \ldots) \]
has been made.

Hättig's Equation. This equation is derived identically as the B.E.T. Equation with one assumption modified: Any molecule is free to return to the gas phase, regardless of the number of molecules adsorbed above it. The modified equilibrium conditions become:

\[
\begin{align*}
A_1 p(n_0 - n_1) &= B_1 n_1 & \text{1st Layer} \\
A_2 p(n_1 - n_2) &= B_2 n_2 & \text{2nd Layer} \\
A_i p(n_{i-1} - n_i) &= B_i n_i & \text{i th Layer}
\end{align*}
\]

Thus
\[
n = \frac{n_0 b p(1+p)}{1 + b p}
\]

where
\[ A_1 / B_1 = b \]
and
\[ A_i / B_i = 1 \quad (i = 2, 3, 4, \ldots) \]

Kiselev Approximate Equation. In deriving this equation all assumptions concerning the nature of the gas and the surface are identical to those used in deriving Langmuir's Equation, with the exception of one additional assumption. In addition
to the adsorbate-adsorbent interaction of a Langmuir surface, there is an adsorbate-adsorbate interaction of the form

Unitary complex + Unitary complex ⇄ Binary horizontal complex
Unitary complex + Binary horizontal complex ⇄ Ternary horizontal complex etc.

Letting \( T_i \) denote the total fraction of the surface covered by a complex of degree \( i \) (\( T_0 \) is the fraction of the surface remaining free), then the primary adsorbate-adsorbent interaction may be expressed by

\[
K_i = \frac{T_i}{\rho T_0}
\]  
(1)

and the adsorbate-adsorbate interactions by

\[
K_i^* = \frac{T_i}{T_i T_{i-1}} \quad (i = 2, 3, 4, \ldots)
\]  
(2)

Assuming \( K_1 = K_n \) (\( i = 2, 3, 4, \ldots \)), then Equations (2) yield

\[
T_i = \frac{T}{1 + K_n T}
\]  
(3)

where \( T \) is the total fraction of the surface covered by all complexes, i.e.,

\[
T = T_1 + T_2 + T_3 + \cdots
\]

Substituting (3) into (1) and using \( T_0 = (1 - T) \), we obtain the Kiselev Approximate Equation:

\[
p = \frac{T}{K_i (1 - T)(1 + K_n T)}
\]  
(4)
If $K_n = 0$, this equation reduces to Langmuir's Equation. The Complete Equation. This equation is generalized from the approximate equation by admitting multilayer adsorption. We assume that only the uncovered unitary complexes take part in the reaction given by (1). Then the notation used in (1) must be modified, and we write

$$K_i = \frac{U_i}{\rho T_0}$$

(5)

where $U_i$ is the concentration of the uncovered complexes of degree $i$. We further assume that in the reaction

\[ \text{Vapor} + \text{Uncovered complexes of first layer} \rightarrow \text{Binary vertical complexes} \]

the adsorbate molecules are uniformly distributed among the different types of uncovered complexes, i.e.,

$$\frac{U}{T} = \frac{U_i}{T_i} = \frac{U_2}{T_2} = \cdots$$

(6)

where $U$ is the total concentration of uncovered complexes, i.e.,

$$U = U_1 + U_2 + U_3 + \cdots$$

and $T$ is the same as given above (concentration of all complexes).

Let us assume that the horizontal interactions in the first layer do not depend on the presence of molecules in the higher layers. Therefore (3) remains valid. Substituting (3) and (6) into (5) and using $T_0 = (1 - T)$ we obtain
\[ p = \frac{U}{K_i(1-T)(1+K_nT)} \quad (7) \]

Next we consider the total fraction \( R \) of the surface covered in multimolecular adsorption. We assume that the equilibrium constants for the formation of multiple vertical complexes are equal, i.e.,

\[ \frac{R_2}{p R_1} = \frac{R_3}{p R_2} = \cdots = K_L \quad (8) \]

where \( K_L \) is assumed to be one, and \( R_1 \) is the fraction of the surface covered by a vertical complex of degree \( 1 \). Thus

\[ R = R_1 + 2R_2 + 3R_3 + \cdots \quad (9) \]

Substituting Equations (8) into (9), we obtain

\[ R = R_1 / (1-p)^2 \]

But \( R_1 = U \). Hence

\[ U = R(1-p)^2 \quad (10) \]

Noting that

\[ T = R_1 + R_2 + R_3 + \cdots \quad (11) \]

and substituting Equations (8) into (11) we have

\[ T = \frac{R_1}{(1-p)} = \frac{U}{(1-p)} \quad (12) \]
Combining (10) and (12) we obtain

\[ T = R(1-p) \]  \hspace{1cm} (13)

Substituting (10) and (13) into (7), the Kiselev Complete Equation follows, i.e.,

\[ p = \frac{R(1-p)^2}{K_i[1-(1-p)R][1+K_n(1-p)R]} \]  \hspace{1cm} (14)

If \( K_n = 0 \), (14) reduces to the B.E.T. Equation.
APPENDIX IV

VI. Brief Description of Generalizations of the BET Equation

The B.E.T. Equation has been found to be in agreement with experimental data for relative pressures in the range 0.05 to 0.35. A number of generalizations of the B.E.T. Equation have been proposed to increase this range.

G. Pickett has derived two such equations. In his first equation he assumes a decrease in probability of escape from a site covered with \( n \) layers (the number of layers is restricted to \( n \)) as the adjacent sites become covered with \( n \) layers, and derives an equation similar to the B.E.T. Equation of restricted adsorption. (In the B.E.T. Equation this probability is constant.) Viz.,

Pickett Equation:

\[
\frac{n_r}{n_m} = \frac{c \chi (1 - \chi^n)}{(1 - \chi)(1 - \chi + c \chi)}
\]

B.E.T. Equation:

\[
\frac{n_r}{n_m} = \frac{c \chi}{1 - \chi} \left[ \frac{l - (n+1) \chi^n + n \chi^{n+1}}{1 + (c-1) \chi - c \chi^{n+1}} \right]
\]

In the derivation of his second equation he adds two more assumptions: (1) on a fraction, \( \beta \), of the total surface a maximum of \( n \) layers can be accommodated. (2) \( dA/di \) is proportional to \( e^{-ai} \) for the remaining surface where \( dA \) is the portion of the surface on which from \( i \) to \( i+1 \)
+ di layers can be built, and \( \alpha \) is a constant such that the total volume of the adsorbate is accounted for.

With these assumptions he derives the equation

\[
\frac{N_r}{N_m} = \frac{c\alpha}{(1-\alpha)(1-\alpha+c\alpha)} \left\{ \beta (1-\alpha^n) \right\} + (1-\beta) \left[ 1 - \frac{1 - \left( n_{av} - n \right) \ln \chi}{1 - 1/\left( [1-\beta] \right)} \right]
\]

where

\[
\eta_{av} = \frac{N_{max}}{N_m}
\]

R. B. Anderson has proposed two generalizations of the B.E.T. Equation. In his first equation he modifies the B.E.T. formulation by assuming the heat of adsorption in the 2nd through 9th layers is

\[
E_{2 \text{ to } 9} = E_L + d
\]

where \( E_L \) is the heat of liquefaction, and obtains the equation

\[
\frac{N_r}{N_m} = \frac{c\kappa\chi}{(1-\kappa\chi)(1+(c-1)\kappa\chi)}
\]

In his second equation he assumes that the surface area available to the \((1 + 1)\)th layer, \( A_{1+1} \), is \( JA_1 \), where \( j \) is less than one and obtains the equation

\[
\frac{N_r}{N_m} = \frac{c\chi}{(1-j\chi)(1+(c-1)\chi)}
\]
G. D. Halsey has derived a multilayer adsorption equation by considering the distribution function of sites-energy. He makes the following assumptions:

1. The source of van der Waals energy, $\Delta E$, has its origin one adsorbate diameter below the center of the first layer.
2. $\Delta E$ decays with the third power of the distance from the surface.
3. Regions of equal $\Delta E$ are localized into large enough patches so that edge effects may be neglected.

With these assumptions he derives the equation

$$\theta = \exp \left\{ \frac{\Delta E_0}{\Delta E_m} \right\} \sum_{n=1}^{\infty} \frac{Z}{n^3}$$

where $\theta$ is the amount of adsorbed gas, $\Delta E_0$ is the energy of the weakest site on the first layer, $\Delta E_m$ is the modulus of the distribution, and

$$Z = \left( \frac{p}{p_0} \right)^{RT/\Delta E_m}$$

W. K. Hall has criticized this equation by pointing out that the first two assumptions are incompatible.

In the theory presented by M. A. Cook an attempt is made to describe more accurately the adsorption forces by introducing terms expressing (1) the interaction forces of adsorbed molecules with the adsorbent, and (2) the adsorbate
interaction forces, the latter being introduced, however, largely on an empirical basis. He obtains the equation

\[
\frac{n}{n_m} = \left\{ \sum_{i=1}^{q} i \chi^i \exp \left[ E_i (1 + \frac{1}{8} + \cdots + \frac{1}{i^3}) \right] + \right. \\
E_L \left[ (c_1 + c_2 + \cdots + c_i - i) \right] \left/ \left( RT \right) \right. + \left. k \sum_{i=1}^{q+1} i \chi^i \right\} \right. \\
\left. \left\{ 1 + \sum_{i=1}^{q} \chi^i \exp \left[ E_i (1 + \frac{1}{8} + \cdots + \frac{1}{i^3}) \right] + \right. \\
E_L \left[ (c_1 + c_2 + \cdots + c_i - i) \right] \left/ \left( RT \right) \right. + \left. k \sum_{i=1}^{q+1} \chi^i \right\} \right. \\
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where

\[
c_i = \left( c_i + i - 1 \right) / i
\]

and \( x \) is the partial pressure.

M. Dole modifies the B.E.T. Equation by assuming the equilibrium constants obey the relations
\[ \frac{A_n}{B_n} = \frac{C}{n} \quad (n = 1, 2, 3, 4, \ldots) \]

(see derivation of B.E.T. Equation in Appendix III) and obtains a linear adsorption equation

\[ \frac{n}{n_0} = c \rho \]

Dole points out, however, that this equation is probably without physical significance.