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3/17/65
SUBMONOLAYER PHYSICAL ADSORPTION; INTERACTION OF KRYPTON
WITH THE \((1,1,1)\) FACE OF COPPER

A THESIS
Presented to
The Faculty of the Graduate Division
by
James John McAlpin

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

Georgia Institute of Technology
October, 1966
SUBMONOLAYER PHYSICAL ADSORPTION; INTERACTION OF KRYPTON

WITH THE (1,1,1) FACE OF COPPER

Approved:

Chairman

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LIST OF SYMBOLS AND ABBREVIATIONS

\( a \) = the parameter characterizing the strain energy in Eyring's approach; also the cell size parameter in the Lennard-Jones and Devonshire cell model.

\( a_f \) = the free area available to a molecule.

\( A \) = the area of a two-dimensional system; also the area per molecule in the significant structure partition function.

\( A_m^o \) = the area per molecule at monolayer coverage.

\( A_s \) = the area per molecule of a two-dimensional solid.

\( A_t \) = the total area of a surface.

\( B \) = a mathematical collection defined on page 25 and redefined on page 30.

\( B_{2d} \) = the second two-dimensional virial coefficient.

\( C \) = a mathematical collection defined on page 25.

\( C' \) = a mathematical collection defined on page 39.

\( D \) = a mathematical collection defined on page 25.

\( e \) = the base of the natural logarithms.

\( E_s \) = the energy of sublimation of a solid.

\( f \) = the partition function for a single molecule.

\( f_{\text{rg}} \) = the rotational partition function in the gas phase.

\( f_{\text{rs}} \) = the rotational partition function on the surface.

\( f_{tt} \) = thermal transpiration correction factor.

\( F \) = the Helmholtz free energy of a system.

\( h \) = Planck's constant.

\( I_x \) = the moment of inertia of a molecule about the x axis.
LIST OF SYMBOLS AND ABBREVIATIONS (Continued)

$I_y$ = the moment of inertia of a molecule about the $y$ axis.
$I_z$ = the moment of inertia of a molecule about the $z$ axis.
$j$ = the number of degrees of freedom assumed to change from rotations to vibrations on adsorption.
$k$ = Boltzmann's constant.
$K$ = the force constant in the harmonic oscillator potential.
$K_h$ = the Henry's law constant for adsorption.
$K_v$ = the integration constant in the application of the Gibbs' adsorption isotherm technique.
$m$ = the mass of a molecule.
$M$ = the molecular weight of a substance.
$n_h$ = the number of nearest neighbor holes in Eyring's approach.
$N$ = the number of molecules in a system.
$N_{av}$ = Avogadro's number.
$N_m$ = the number of molecules on the surface at monolayer coverage.
$q_i$ = the generalized momentum conjugate to $q_i$.
$P$ = the pressure.
$P_{di}$ = the dose pressure for the $i^{th}$ isotherm point.
$P_{ei}$ = the measured equilibrium pressure of the $i^{th}$ isotherm point.
$P_{si}$ = the equilibrium pressure in the sample cell for the $i^{th}$ isotherm point.
$q_i$ = the $i^{th}$ generalized coordinate associated with a representative point in phase space.
$q_j$ = the vector which specifies the position of the $j^{th}$ molecule in a system.
$q_{st}$ = the isosteric heat of adsorption.
LIST OF SYMBOLS AND ABBREVIATIONS (Continued)

\( r \) = the distance from the center of the cell to the molecule in the Lennard-Jones and Devonshire cell model.

\( r_{ij} \) = the distance between the \( i^{th} \) and \( j^{th} \) molecules in a system.

\( R \) = the gas constant; also the range of a surface-gas interaction.

\( T \) = the absolute temperature.

\( T(p_{xi}, p_{yi}) \) = the contribution to the kinetic energy of a system by the \( i^{th} \) molecule due to its motion in the \((x, y)\) plane.

\( T(p_{zj}) \) = the contribution to the kinetic energy of a system by the \( j^{th} \) molecule due to its motion in the \( z \) direction.

\( U_0 \) = the surface-gas interaction parameter.

\( U_01 \) = the value of the surface-gas interaction parameter corresponding to the "hot spots" on the surface.

\( U_02 \) = the value of \( U_0 \) corresponding to the uncontaminated surface.

\( U_i(z) \) = the potential energy of interaction of a molecule with a surface when they are separated by a distance \( z \).

\( U'(q_j) \) = the function which gives the potential energy of the \( j^{th} \) molecule in a system.

\( v_a \) = the volume adsorbed.

\( v_b \) = the volume of the gas burette.

\( v_c \) = the cold volume of the system.

\( v_{ds} \) = the dead space volume.

\( v_g \) = the volume of gas remaining in the gas phase.

\( v_h \) = the hot volume of the system.

\( v_t \) = the volume of gas added to the system.

\( v_{cell} \) = the volume adsorbed on the cell.

\( v_{geo} \) = the volume of a monolayer based on the geometric area of the sample.

\( v_{ss} \) = the volume of a monolayer from the significant structure theory fit of the data.
LIST OF SYMBOLS AND ABBREVIATIONS (Continued)

\( V \) = the volume of a system.

\( V_m \) = the molar volume of a liquid.

\( V_s \) = the molar volume of a solid at its melting point.

\( V(\{x_r, y_r\}) \) = the potential energy of a system due to interactions among molecules on the surface.

\( W \) = the lattice energy of the two-dimensional solid.

\( x \) = one of the Cartesian coordinates.

\( (x, y) \) = Cartesian coordinates of a molecule in the plane of a surface.

\( \{x_r, y_r\} \) = the set of position coordinates in the \((x, y)\) plane of all the molecules in a system.

\( y \) = one of the Cartesian coordinates; also the reduced distance parameter in the Lennard-Jones and Devonshire model.

\( z \) = one of the Cartesian coordinates.

\( Z \) = the partition function for a system.

\( Z_c \) = the compressibility factor.

\( Z_n \) = the coordination number of a solid.

Greek symbols:

\( \alpha \) = the analog of the Van der Waals "a" for a two-dimensional system.

\( \beta \) = the analog of the Van der Waals "b" for a two-dimensional system.

\( \gamma \) = fraction of the surface characterized by \( U_{01} \).

\( \delta(U_{01}) \) = a Dirac delta function centered at \( U_{01} \).

\( \epsilon \) = the Lennard-Jones interaction parameter.

\( \epsilon_{LJ} \) = the Lennard-Jones interaction parameter.

\( \zeta \) = the coordination number of a two-dimensional lattice.
LIST OF SYMBOLS AND ABBREVIATIONS (Continued)

\( \theta \) = the fractional coverage of a surface.

\( \theta_E \) = the Einstein temperature of a solid.

\( \theta_{ss}(P;U,\omega) \) = the isotherm equation computed for the parameter \( U_{oi} \) from the significant structure theory.

\( \mu \) = the chemical potential of a system.

\( \mu_g \) = the chemical potential of a gas in its standard state.

\( \nu \) = the frequency of a vibration.

\( \nu_x \) = the frequency of the rocking vibration about the x axis.

\( \nu_y \) = the frequency of the rocking vibration about the y axis.

\( \Pi \) = the spreading pressure of a two-dimensional system.

\( \rho(U,\omega) \) = function which gives the fraction of the surface with surface-gas interaction parameter between \( U \) and \( U_{oi} dU \).

\( \sigma \) = the internuclear distance in the Lennard-Jones potential function; also the symmetry number of a molecule.

\( \sigma_g \) = the symmetry number of a gas phase molecule.

\( \sigma_0 \) = the internuclear distance at which the interaction energy becomes zero (in the Lennard-Jones function).

\( \sigma_s \) = the symmetry number of a molecule on the surface.

Subscripts:

\( z \) = a two-dimensional system.

\( 3 \) = a three-dimensional system.

\( a \) = adsorbed.

\( c \) = critical.

\( g \) = gas phase.

\( i \) = an integer.

\( j \) = an integer.
LIST OF SYMBOLS AND ABBREVIATIONS (Concluded)

\[ r \quad = \quad \text{an integer.} \]
\[ s \quad = \quad \text{surface or solid.} \]
\[ \text{sol.} \quad = \quad \text{solid.} \]
\[ \text{ss} \quad = \quad \text{significant structure.} \]
\[ x \quad = \quad \text{the coordinate} \ x. \]
\[ y \quad = \quad \text{the coordinate} \ y. \]
\[ z \quad = \quad \text{the coordinate} \ z. \]
SUMMARY

The significant structure theory of the liquid state has been applied to the description of the physical adsorption of gases on solids. The theory has been applied to several systems for which data have been reported. The agreement has been found to be excellent.

The significant structure partition function for \( N \) molecules in an area \( A_t \) (a two-dimensional system) is

\[
Z_2 = (f_s(1 + n_h e^{-s/n_h RT}))(N/A_s) (f_g e/N)^N((A-A_s)/A)
\]

where \( f_s \) and \( f_g \) are the partition functions for a two-dimensional solid and gas respectively. The symbol \( n_h \) is the average number of holes around a "lattice" site in the liquid, and \( a \) is a parameter characteristic of the strain in the solid due to the presence of a large number of holes. The symbols \( A \) and \( A_s \) are the areas per molecule at the condition of interest, and at a state where the two-dimensional phase is a solid, respectively.

The partition function has been used with three different modifications. The first (Approximation I in what follows) amounted to setting \( a \) equal to zero and taking \( n_h = \zeta((A - A_s)/A) \) where \( \zeta \) is the coordination number of the lattice. In this approximation, an Einstein solid was used to compute \( f_s \). The system treated with this approximation was the argon-graphite system. The parameters used in the treatment of the data were obtained from various sources, and the agreement achieved was excellent.
The values of the parameters are: $U_0 = 2200 \text{ cal/mole}$, $\nu = 1.2 \times 10^{12} \text{ sec}^{-1}$ and $\epsilon/k = 101^\circ \text{K}$. The first two parameters are the depth of the potential well in which an adsorbed molecule resides, and the frequency with which it vibrates in this well. The other parameter is the interaction parameter characterizing the argon-argon interaction on the surface.

The next change (Approximation II) was the introduction of the cell model of Lennard-Jones and Devonshire into the theory in place of the Einstein solid. Everything else remained the same, and again good agreement was obtained; the systems treated being argon-graphite and argon-boron nitride. The parameters here were: argon-graphite: $U_0 = 2200 \text{ cal/mole}$, $\nu = 1.2 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 106^\circ \text{K}$; argon-boron nitride: $U_0 = 1950 \text{ cal/mole}$, $\nu = 0.95 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 108^\circ \text{K}$. Here the parameter $\epsilon/k$ was determined to fit the data, the others being obtained from outside sources.

The last modification (Approximation III in what follows) amounted to the use of the expression $n_s = \xi(A - A_s)/A_s$ which is essentially the one used by Eyring. The cell model was retained as the solid-like partition function in this treatment. A fitting technique was devised, and the adsorption parameters of a number of interesting systems determined. The values of the parameters were: argon-graphite: $U_0 = 2204 \text{ cal/mole}$, $\nu = 2.13 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 110^\circ \text{K}$; argon-boron nitride: $U_0 = 1960 \text{ cal/mole}$, $\nu = 1.16 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 112^\circ \text{K}$; CO$_2$-graphite: $U_0 = 9031 \text{ cal/mole}$, $\nu = 0.66 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 395^\circ \text{K}$; krypton-boron nitride: $U_0 = 2625 \text{ cal/mole}$, $\nu = 1.0 \times 10^{12} \text{ sec}^{-1}$, $\epsilon/k = 118^\circ \text{K}$.

The adsorption of krypton on the (1,1,1) face of copper was studied. Large areas of this face were grown and polished to a mirror finish. They were placed inside a nickel cell and hydrogen treated. Then isotherms
were measured on the copper using a volumetric technique. The significant structure theory was applied to the data to extract parameters characteristic of the surface-gas interaction. These parameters were: \( U_0 = 3500 \) cal/mole, \( v = 0.6 \times 10^{12} \) sec\(^{-1}\), \( \epsilon/k = 100^\circ K \). Due to the surprisingly high value of \( U_0 \), the adsorption fell in a region of the thermodynamic variables which taxed the capabilities of the apparatus to measure. Thus, there is considerable uncertainty in the parameters above. The parameter of most interest is \( U_0 \), and the uncertainty in this parameter is probably of the order of 50 cal/mole.
CHAPTER I

INTRODUCTION

Physical Adsorption-General Theory

Gibbs has shown that in the vicinity of the boundary between two phases, there are thermodynamic reasons for expecting considerable deviations from bulk phase values for certain variables. The class of phenomena which result from this sort of deviation is generally lumped together under the name "adsorption."

When the boundary is the interface between a solid and a gas, the effect of the interface on the gas can be characterized in terms of the density of the gas. In most cases, the observation is made that the density of the gas in the immediate vicinity of the surface is higher than that in the remainder of the gas phase. By choosing the proper range of thermodynamic variables, one can sometimes measure the surface excess density quite accurately. It is usually true that the measurements are made under conditions such that the surface density is many orders of magnitude greater than the gas phase value; thus it becomes convenient to think of the region in the immediate vicinity of the surface as a separate phase. Ross and Olivier give a detailed account of this formal modification of the system.

Having made the formal modification just described, it can be shown that a meaningful way to express the thermodynamics of a pure gas phase in equilibrium with a single type of solid surface is to give the
number of molecules in the surface phase as a function of the temperature and the gas phase pressure. Traditionally, the data of gas adsorption are reported in terms of this relation; the usual approach being to report the number of molecules in the surface phase as a function of pressure at constant temperature for a number of different temperatures. These isothermal relationships are the "adsorption isotherms."

A distinction is generally made between "physical" and "chemical" adsorption. The implication of the titles chosen to describe the two cases is that in one case the forces holding molecules near the surface are of a physical nature (e.g., Van der Waals forces), while in the other case the forces are chemical in nature (e.g., exchange forces). In practice, the criteria used to characterize a system as being in one or the other of the above cases have only a tenuous connection with the implications of the title. These criteria usually have to do with the strength of the "bond" between the solid and the adsorbed molecule. One such criterion would be to require that the heat of adsorption be less than twice the heat of vaporization of the adsorbed species. In the following work, the models are of systems in which the adsorption is "physical" in the literal sense of the term.

It happens that, for many systems, the results of adsorption measurements may be explained on the basis of the idea that the adsorbed molecules form a film on the surface that is essentially one molecule thick. As molecules are added, this film is thought to become more and more dense, until finally additional molecules are forced to reside on top of this film, thus forming another layer. It is this interpretation of adsorption measurements which leads to the ability to measure the sur-
face of a powder, for instance. The study of the adsorption process in the region of thermodynamic variables where no second layer formation has commenced is called the study of "submonolayer adsorption." Systems which fit this description are the type treated in this work.

Physical adsorption also affords one the opportunity to study intermolecular interactions within a very interesting framework. One may study the interaction between a gas molecule and a solid with this tool, or one may be able to study the adsorbed phase under conditions which render it essentially a two-dimensional liquid. The effect of the solid on the interactions in the two-dimensional phase can thus be determined. This is one of the few places where a third order interaction effect can be studied with relative ease. Whatever one wishes to study, the deduction of intermolecular interaction information from the data of adsorption requires the use of statistical mechanics. The next section contains an introduction to the statistical theory of the surface problem.

**Statistical Theory**

It will now be shown that it is possible to relate the adsorption data for a certain simple system to the parameters of a potential function which is a fundamental representation of the interaction of a gas molecule with a solid. It will also be shown what assumptions are necessary to reduce a more complex problem to a tractable state. The treatments described in this section apply only to monatomic molecules.

Consider a system made up of a container with volume "V," and suppose that there is an internal area "A" of surface associated with the container. Further, suppose that a molecule of gas inside the container
experiences an excess of potential energy "$U(z)$" due to its residence at a distance "$z$" from the nearest point of the surface. Also, suppose that it is possible to neglect "corner effects": that is that a molecule never finds itself in a position where two surfaces are able to interact with it at once. Under these conditions, it is possible to write the partition function for $N$ molecules in the volume $V$; assuming the laws of classical mechanics are applicable, and that the molecules do not interact with one another, this partition function is

$$Z = \left(\frac{1}{\hbar^3 N!}\right) \int_V \frac{3N}{h^3} dq_i \int_{-\infty}^{\infty} \frac{3N}{h^3} dp_i \left[ \exp \left(-\frac{1}{kT} \sum_{i=1}^{3N} \frac{p_i^2}{2m} \right) \right]$$

$$+ \sum_{j=1}^{N} U'(\bar{q}_j))$$

where

$Z$ is the partition function of interest

$h$ is Planck's constant

$N$ is the number of molecules in the volume $V$

$q_i$ is the $i^{th}$ generalized coordinate associated with a particular representative point in the phase space of the problem

$p_i$ is the $i^{th}$ generalized momentum (conjugate to $q_i$)

$m$ is the mass of a molecule

$k$ is Boltzmann's constant

$T$ is the absolute temperature
$U'$ is the function which gives the potential energy of the $j^{th}$ molecule as a function of the components of the vector $\mathbf{q}_j$.

$\mathbf{q}_j$ is the vector which specifies the position of the $j^{th}$ molecule in the system.

The function $U'$ contains implicitly all the information contained in the conditions of the problem which relate to potential energy. That is, it is essentially $U(z)$ transformed to the generalized coordinates of the problem. Performing the integration over the momenta

$$Z = \frac{(1/N!) (2\pi mkT/h^2)^{3N/2}}{V} \int_{V} \frac{N}{j=1} \exp \left( -\frac{1}{kT} \sum_{j=1}^{N} U'(\mathbf{q}_j) \right)$$

where the integral is the well known "configuration integral" of classical statistical mechanics.

If the further assumption is made that the surface gas interaction is short range, the problem can be reduced to an understandable state. Say the effective range of the interaction is $R$, that is $U(z) = 0$ for $z > R$, and further specify that $R$ is much smaller than any dimension of the container. Under these conditions, equation 2 becomes

$$Z = \frac{(1/N!) (2\pi mkT/h^2)^{3N/2}}{V} \int_{0}^{R} \left[ \exp \left( -\frac{U(z)}{kT} \right) - 1 \right] dz$$

where, if the interaction is short range, the integration may be extended to infinity, thus rendering it identical to the integral involved in the computation of second virial coefficients. The deduction of an equation
of state from equation 3 yields

\[ \frac{PV}{NKT} = 1 - \frac{(P/kT)A}{\exp \left(- \frac{U(z)}{kT} \right) - 1} \int_{0}^{\infty} dz \]

(4)

which, since \( P/kT \) is very nearly equal to \( N/V \) in the weakly interacting case, is almost identical to the first two terms in a virial expansion. Hence, if either the area is large or the surface gas interaction is strong, apparent deviations from gas phase ideality may be expected even in regions of the thermodynamic variables where the gas is, in fact, ideal.

Although the above treatment is a simplified version of a popular approach, only recently have Sams, Constabaris, and Halsey applied the theory to real systems with an eye to determining details concerning the function \( U(z) \). Their success has led a number of investigators to adopt the approach.

While the approach described above has great conceptual value and is becoming more popular for practical purposes, the following approach is still the more widely used. The system is the same as described in the foregoing treatment, except that the requirement of the absence of interaction among the gas molecules (either on the surface or in the gas phase) has been relaxed. It is now visualized that the surface gas interaction is of a nature such that it can be thought of as affecting only those molecules in the immediate vicinity of the surface. Suppose it is again assumed that the range of such influence is "R." This divides the volume \( V \) of the system into two distinct regions: one in which the surface can be ignored and whose extent is \( (V - R \cdot A) \), and one in which the
effect of the surface must be considered and whose extent is $R \cdot A$. These two regions are now considered as comprising two separate phases. Although this seems a rather artificial way of looking at the problem, it simplifies considerably the treatment of strongly interacting systems. Further, it is a thermodynamically valid approach, since the conditions of thermal, mechanical, and chemical equilibrium between the "phases" result in the same number of degrees of freedom as a straightforward application of the phase rule to the undivided system yields.

After the problem has been simplified in this manner, it often happens that the gas phase left over when the surface layer is deleted from the volume of the system can be treated as an ideal gas. Hence the thermodynamics of one phase can be treated with great ease. There remains then only the task of treating the region in close proximity to the surface. It often occurs that systems of interest admit of an even greater degree of simplification. This is due to the fact that, at the temperature where the adsorption may be measured with convenience, the potential energy in the vicinity of the surface is of such a character as to yield a "bound" state, and, further, the excursions of a "bound" molecule about its equilibrium position are extremely small. Hence, at least when the number of molecules in the region of the surface is small, almost all of them may be treated as if they are in a bound state. That is, one may treat the adsorbed phase as if all the molecules in it had the same equilibrium distance from the surface and were executing slight vibrations about this equilibrium position. As soon as the surface becomes "crowded," however, an appreciable number of molecules begin to reside at larger distances from the surface, and the treatment breaks down and must be modified.
The adsorption considered in what follows will always be of the type which conforms to the surface dilution criterion required for the application of the approach just described. This type of adsorption is called "submonolayer adsorption."

Having restricted the systems considered to those in which the surface may be viewed as just described, it will now be shown that, under certain conditions, the problem reduces neatly to one of the classic problems of statistical mechanics. The conditions necessary to effect the further reduction are the following. If \( x \) and \( y \) are Cartesian coordinates in the plane of the surface, and \( z \) is the coordinate measuring the vertical distance from the surface, it will be assumed that the interaction of a single gas molecule with the surface may be represented by a potential function \( U(z) \) which is independent of \( x \) and \( y \). This restriction has been implicit in the earlier development, but it must be pointed out here that it is a very difficult task to find real systems which satisfy this condition sufficiently well to allow the application of the results of the following development. Consideration of the fact that the surface of a solid will always have a structure corresponding to its bulk lattice indicates that the surface will always have molecular scale irregularities. Thus the condition above can never be rigorously fulfilled, but certain systems allow successful application of the theory resulting from the imposition of the condition. The other new condition which is to be imposed is that the Hamiltonian of a system of \( N \) molecules is assumed to be expressible in the form

\[
H(x_1, \ldots, P_{x_1}, \ldots) = \sum_{i=1}^{N} T(P_{x_i}, P_{y_i}) + V(\{x_{y_i}, y_{x_i}\})
\]  

(5a)
\[ + \sum_{j=1}^{N} \left( T(p_{z,j}) + U(z_j) \right) \]

where

- \( T(p_{x_i', y_{y_i'}}) \) is the contribution to the kinetic energy of the system due to motion in the \((x, y)\) plane by the \(i^{th}\) molecule.
- \( \{x_r, y_r\} \) is the set of position coordinates in the \((x, y)\) plane of all the molecules in the system.
- \( V(\{x_r, y_r\}) \) is a function which gives the potential energy of the system due to interactions among molecules on the surface.
- \( T(p_{z,j}) \) is the contribution to the kinetic energy of the system by the \(j^{th}\) molecule due to its motion in the \(z\) direction.
- \( U(z_j) \) is the potential energy of the \(j^{th}\) molecule due to its interaction with the surface.

The separation of the kinetic energy is routine in all cases of interest; the key restriction expressed by equation 5 concerns the term \( V(\{x_r, y_r\}) \).

Without considering the exact form of the term, one can use the following line of reasoning to aid in understanding the meaning of the approximation. It is well known that the function depends only on distances between pairs of molecules in the first order approach. The formula for the distance between two molecules is

\[ r_{ij} = ((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2)^{\frac{1}{2}} \]

But the condition states that the function depends only on \(x\) and \(y\), hence the condition must be equivalent to the requirement...
where \( q \) stands for either \( x \) or \( y \). Hence the approximation to reality will be good if the excursions of the molecules in the \( z \) direction are small, or if the surface phase is so dilute that distances between molecules are great on the average.

Having restricted attention to systems conforming to the above conditions, it follows that the partition function may be written as

\[
Z = \left(\frac{1}{h^3 n!}\right) \int_{-\infty}^{\infty} \prod_{i=1}^{N} dp_{x_i} dp_{y_i} \int_{-\infty}^{\infty} \prod_{i=1}^{A} dx_i dy_i \left[ \exp \left( -\frac{1}{kT} \left( \sum_{i=1}^{N} T(p_{x_i}, p_{y_i}) + V(x_i, y_i) \right) \right) \right] \\
\times \int_{-\infty}^{\infty} \prod_{i=1}^{N} dp_{z_i} \int_{-\infty}^{\infty} \prod_{j=1}^{N} dz_j \left[ \exp \left( -\frac{1}{kT} \left( \sum_{j=1}^{N} T(p_{z_j}) + U(z_j) \right) \right) \right]
\]

where the symbols have all been explained previously. If one deletes \( 1/h \) times the part depending on \( z \) from equation 6, the remainder is just the partition function for a two-dimensional interacting system of molecules. This problem has been studied in detail for a number of types of systems. It has usually been the case that considerably better results are obtained for two-dimensional systems than for their three-dimensional analogues. For example, Onsager was able to solve the two-dimensional Ising problem analytically, while the three-dimensional case has not been solved.
yet. At any rate, the approach has reduced a very complex situation to one in which there is a wealth of experience to draw on.

Once a system has been chosen and it has been decided that it satisfies the conditions of the two-phase treatment, one proceeds as follows. The gas phase is treated by a statistical model (usually the ideal gas assumption is valid), and the thermodynamics of this phase deduced. Then the surface phase is modeled by some tractable theory of dense gases, and its thermodynamics derived. At this stage one has expressions for the free energy of both phases; it is then a simple matter to differentiate both expressions with respect to the number of molecules in the phase. This yields the chemical potentials, and the condition of equilibrium is then expressed by equating these two results. Since one is a function of the number density of molecules on the surface and the other may be expressed as a function of the pressure in the gas phase, this process leads to an "isotherm equation." Although the above comments have been made for monatomic molecules, the treatment is valid for more complex systems.

It sometimes happens that the model of the surface phase to be used is based on an approximation made at the "equation of state level," that is, no partition function is written. An example of this would be the application of the Van der Waals equation to the surface phase. In this case, it is convenient to derive the isotherm equation by using the "Gibbs' adsorption isotherm." This relates the spreading pressure to the pressure in the gas phase and is derived from classical thermodynamics. One form of the relation is

\[ \Pi = \left( \frac{kT}{A_m^0} \right) \int_0^P \Theta d\ln p \] (7)
where

- $\Pi$ is the spreading pressure
- $A_m^0$ is the area per molecule at monolayer coverage
- $\theta$ is the fractional surface coverage (defined as the ratio of $A_m^0$ to the area per molecule at the state of interest)
- $P$ is the pressure in the gas phase (assumed a pure phase)

and the other symbols are as defined previously. Thus, if one has information in the form of a two-dimensional equation of state, say $\Pi(\theta)$, then manipulation of equation 7 can lead to $\theta(P)$, the isotherm equation.

Special Cases of the Theory

As illustrations of the two-phase approach to the problem of the adsorption of gases on solids, two special cases of the theory will now be considered. One will illustrate the technique of starting with a partition function and equating chemical potentials, and the other will illustrate the application of the Gibbs' adsorption isotherm to a model equation of state.

The first case considered will be that in which both the gas phase and the adsorbed phase may be considered as ideal gases. Partition functions will be written, and the appropriate thermodynamic functions will be computed.

For the three-dimensional ideal gas, the partition function is

$$Z_3 = \left( \frac{(2\pi m k T/\hbar^2)^{3/2} eV_3/N_3}{(2\pi m k T/\hbar^2)^{3/2} eV_3/N_3} \right)^{N_3}$$

while that for the two-dimensional case is
\[ Z_2 = \left( \frac{(2\pi mkT/h^2)}{eA_2/N_2} \right)^{N_2} \]  

(9)

where

- \( V_3 \) is the volume of the three-dimensional phase
- \( N_3 \) is the number of molecules in the three-dimensional phase
- \( A_2 \) is the area of the two-dimensional phase
- \( N_2 \) is the number of molecules in the two-dimensional phase

and the other symbols have been defined previously.

Having now the partition function describing the two phases, there remains only the problem of dealing with the \( z \) coordinate of the surface phase. Since a key assumption in the reduction of the problem was that the excursions of bound molecules from their equilibrium positions are small, a logical model of the \( z \) degree of freedom would be a harmonic oscillator. If the excursions of the molecules are small, the potential function may be approximated by a parabola. The model which will be used, then, is that of a molecule executing vibratory motion in a parabolic potential well, the bottom of which is \( U_0 \) calories per mole below the zero of energy. This zero is again taken as a molecule at rest infinitely far removed from the surface and from any field, for that matter. The only other parameter needed to characterize the model is the second derivative of the potential with respect to displacement evaluated at the potential minimum. This is the familiar "force constant" which determines the frequency of vibration according to the formula

\[ \nu = \left( \frac{1}{2\pi} \right) \left( \frac{K}{m} \right)^{1/2} \]
where \( \nu \) is the frequency with which a molecule of mass \( m \) vibrates in a well whose force constant is \( K \). Up to this point in the development, classical statistical mechanics has been used, but here the application of classical theory would run counter to the assumptions made. That is, the assumption of small excursions amounts to assuming the oscillator is only slightly excited, while the classical treatment is only valid for highly excited oscillators. Hence, for the \( z \) coordinate, the quantum mechanical partition function for the model just described is used; for one molecule this is

\[
f_z = \left( \frac{e^{-\frac{\nu \hbar}{2kT}}}{1 - e^{-\frac{\nu \hbar}{kT}}} \right) e^{\frac{U_0}{RT}} \tag{10}
\]

where the symbols have been defined earlier. Combining equations 9 and 10, one can arrive at the partition function for \( N_s \) molecules on the surface. The result is

\[
Z_s = Z_2(\nu_s) \cdot (f_z)^{N_s} = \left( \frac{2\pi mkT/\hbar^2}{e^{\nu \hbar/kT}} \cdot \frac{\nu_s}{N_s} \right)^{N_s} \tag{11}
\]

\[
\times \left( \frac{e^{-\frac{\nu \hbar}{2kT}}}{1 - e^{-\frac{\nu \hbar}{kT}}} \right) e^{\frac{U_0}{RT}} \right)^{N_s}
\]

where \( A_s \) is now the area of the surface.

Equations 8 and 11 along with the appropriate relations from statistical thermodynamics allow the calculation of the chemical potentials in each phase. As an example, the result for the gas phase is

\[
\frac{\mu_g}{kT} = -\ln\left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} kT + \ln(P) \tag{12}
\]
where \( \mu_g \) is the chemical potential in the gas phase, and \( P \) is the pressure of the gas in the gas phase. After equating the chemical potentials and making certain simplifications, one obtains the equation

\[
\theta = P \cdot e^{\frac{U_0}{RT}} \cdot \exp \left( \left( \frac{2 \pi m k T}{h^2} \right)^{\frac{1}{2}} A_m^0 f_a / kT \right)
\]

(13)

where

\( \theta \) is the fractional coverage of the surface (number of molecules on the surface divided by the number on the surface at monolayer coverage)

\( A_m^0 \) is the area per molecule on the surface at monolayer coverage.

Equation 13 is just the familiar "Henry's law" isotherm equation. The advantage of the derivation just presented is that the explicit temperature dependence of the constant in the equation \( \theta = K_n P \) is exhibited in terms of the fundamental parameters of the model. As will now be shown, the transformation of a two-dimensional equation of state (empirical) by the Gibbs' adsorption isotherm does not lead to a connection with the fundamental properties of the molecular system.

The system chosen for the illustration of the use of the Gibbs' isotherm method will be a system in which the surface phase obeys the Van der Waals equation of state. This is a very important case, since the resulting equation, the "Hill-deBoer" equation, is widely used in the treatment of mobile adsorption. Although it is possible to relate the Van der Waals parameters to the constants of an intermolecular potential function, the form of this function is rather unrealistic, and
thus the Van der Waals constants are almost never used to arrive at values for fundamental molecular parameters. Therefore, the Hill-deBoer equation is derived from the two-dimensional equation of state. This is

\[ \Pi = \left( \frac{kT}{\beta} \right) \left( \frac{\theta}{1 - \theta} \right) - \alpha \theta^2 / kT \beta \]  

(14)

where

\( \Pi \) is the spreading pressure
\( \beta \) is the analogue of "b," the covolume constant in the three-dimensional case
\( \alpha \) is the analogue of "a" in the three-dimensional case and has to do with the interactions of the molecules
\( \theta \) is the fractional surface coverage

and the other symbols are as previously defined.

Now by the use of equation 7, it is possible to derive the isotherm equation for this sort of a surface phase. One proceeds as follows: at a given temperature, \( \Pi \) is a function of only one variable, and either \( P \) or \( \theta \) may be chosen as the pertinent variable. Equation 7 is \( \Pi(P) \), while equation 14 is \( \Pi(\theta) \). By differentiating both of these relations, two expressions for \( d\Pi \) are obtained. Equating these expressions leads to

\[ \left( \frac{kT \theta}{A_m^0 P} \right) dP = \left( \frac{kT}{\beta} \right) \left( \frac{1}{1 - \theta^2} \right) - 2\alpha \, \theta / (kT \beta) \, d\theta \]  

(15)

where all the symbols have been defined previously. Equation 15, when integrated, yields
\[ P = K_v\left(\frac{\theta}{(1 - \theta)}\right) \exp\left(\left(\frac{\theta}{(1 - \theta)}\right) - \frac{2\alpha \theta}{(kT^*)}\right) \] (16)

where \( K_v \) is a constant depending on the surface gas interaction, and the other symbols have been previously defined. Equation 16 is the well known Hill-deBoer equation. So it is seen to be a simple matter to convert a two-dimensional equation of state to an isotherm equation.

As mentioned earlier, this method has its greatest utility in treating approximations which are not made at the molecular level, but rather at the macro-thermodynamic level. In the work that follows, this method will not be used since a model with molecular level approximations is to be used.

**Discussion of Significant Structure Theory**

Eyring, Ree, and Hirai have set forth a theory of the liquid state. This theory has come to be called "the significant structure theory of the liquid state." It is based on intuitive reasoning partly supported by experiment. The theory has been applied to a large number of systems with generally good success.

The intuitive basis of the theory is the assumption that the differences in properties of liquids and solids may be explained by considering that the melting process introduces a large number of molecular-size holes into the solid thus producing the liquid. It is further assumed that the entire volume change on melting is due to these molecular-size holes. Eyring, et al. refer to the theory as the vacancy theory, the implication being that a liquid has some of the characteristics of the solid lattice, the prime difference being that some sites are vacant. The experimental
evidence to support this idea is somewhat limited; the greatest support coming from diffraction studies of the liquid in which nearest neighbor distances are found to be essentially the same as in the solid. This seems to indicate that during a part of its life, a liquid molecule experiences an environment not greatly different from the one it experienced in the solid state. Of course, there may be a smaller number of these nearest neighbors, but their proximity is about the same as in the solid.

Having now made the key assumption in the theory, one must next decide how to treat the vacancies. It is not unreasonable to expect that the energetics of a liquid might be predicted rather well on the basis of what has gone before, but the entropics are another matter. The entropics hinge on the properties which the holes assume. For example, the mobility of the holes, the effect on vibrations in a neighboring site due to the existence of a hole, etc. Eyring's approach is roughly as follows: the liquid is treated as being a highly degenerate and strained solid, with holes which are thought of as moving perfectly freely through the bulk of this strained structure. The partition function is thus written as the product of the partition function for a degenerate, strained solid and the partition function of an ideal gas (to represent the motion of the holes), each weighted to take into account their relative proportions in the liquid. The concept of a hole moving is convenient, but it must be realized that the motion is really the exchange of a molecule from a molecular site into a neighboring vacancy. Hence, the gas-like partition function makes use of the molecular parameters of the molecules and does not depend on any further assignment of properties to the holes. Mathematically the partition function is represented as
\[
Z = \left( (1 - e^{-\frac{E_s}{RT}}) \right)^{-3} e^{\frac{E_s}{RT}} (1 + n_h e^{-a/n_h RT}) \frac{N V_s}{V_m} \]

where

\( \theta_E \) is the Einstein temperature of the solid
\( T \) is the absolute temperature
\( E_s \) is the energy of sublimation of the solid
\( R \) is the universal gas constant
\( n_h \) is the average number of vacant sites adjacent to a filled site
\( a \) is a parameter characteristic of the strain in the solid
\( N \) is the total number of molecules involved
\( V_s \) is the molar volume of the solid at the melting point
\( V_m \) is the molar volume of the liquid
\( e \) is the base of the natural logarithms
\( N_{av} \) is Avogadro's number

and the remainder of the symbols are as defined earlier in this chapter.

This partition function applies only to monatomic molecules. Taking the terms in order, it is seen that \( (1 - e^{-\frac{E_s}{RT}})^{-3} \) is just the partition function of an Einstein solid, while \( e^{\frac{E_s}{RT}} \) is a correction to the zero of energy made necessary by having chosen the zero as a molecule in free space at rest. The next term is associated with the degeneracy and strain energy of the solid and will be examined in detail later. The group of
terms up to the exponential \( NV_g / V_m \) comprise the solid-like partition function, and the exponent weights it as the ratio of the volume of the solid to the volume of the liquid. The other term is the familiar ideal gas partition function and is weighted by the ratio of the melting volume change to the volume of the liquid.

The parameters \( n_h \) and \( a \) are not molecular properties which can be obtained from other experiments, and hence must be termed "empirical," although Eyring claims to be able to guess \( n_h \) quite accurately. All the rest of the parameters are available from thermodynamic measurements and are thus not adjustable. The theory may thus be regarded as a "two parameter" theory.

The partition function just arrived at is formally the same as one would write for a system composed of a gas which experiences no resistance to diffusion and which moves through the body of a strained solid. Eyring objects to this view, his opinion being: "It should be stressed that our theory does not regard the liquid state as a mixture of solid and gas. A molecule has solid-like properties for the short time it vibrates about an equilibrium position, then it instantly transforms to gas-like behavior as it jumps into the neighboring vacancy." Whatever view the individual takes of the derivation, it is true that Eyring, et al. have experienced remarkable success in treating real systems.

**Statement of the Problem**

The work which will be presented in the following pages will be partly theoretical and partly experimental. The developments of the theory will be used to extract from the results of the experiment the desired in-
The theoretical part of the work will consist of the application of the significant structure theory to the physical adsorption problem. An attempt to render the connection between molecular parameters and thermodynamic measurement more direct will be made. The results of the treatment will be compared with experiment.

The experimental part of the work will consist of an attempt to characterize the interaction of krypton with the (1,1,1) face of copper. The approach used will be to measure adsorption isotherms and use the theoretical results to extract the interaction parameters from the data. Interactions within the adsorbed phase will also be investigated.
CHAPTER II

APPLICATION OF SIGNIFICANT STRUCTURE THEORY
TO THE SURFACE PROBLEM

Introduction

This chapter contains a detailed description of the application of the significant structure partition function to the surface phase. Three cases are discussed. Two of them have to do with the physical adsorption of monatomic molecules and differ only in the details of the partition function, while the third is the application of the theory to the physical adsorption of polyatomic molecules.

The first case discussed involves the direct application of Eyring's partition function to the current problem. The only change being a slight difference in the manner in which the number of holes is assumed to vary with density. The thermodynamic functions of interest are derived, and an isotherm equation arrived at.

The second case discussed involves the changing of the solid state part of the partition function to that of a classical cell model. This has the advantage of giving the thermodynamics of the solid in terms of a fundamental interaction parameter, \( \epsilon \), instead of the Einstein parameters. Further, it removes more of the quantum mechanical character of the Eyring function, thus rendering the partition function conceptually more satisfying. In this case, two types of variation of the number of holes with density will be tried. First, the same approach as above will be tried.
Then Eyring's approach will be used. The thermodynamic functions are computed, and an isotherm equation is derived for the case of the changed variation in the number of holes.

The third case is that of adsorption of polyatomic molecules. Several possibilities for the action of the added degrees of freedom are mentioned, and the partition function derived for a particular case.

Direct Application of Eyring's Partition Function:

Approximation I

Equation 17 is the partition function for a monatomic liquid (or dense gas). Eyring and Ree have specified the form of \( n_h \) as \( Z_n (v_m - v_s)/v_m \), where \( Z_n \) is the number of nearest neighbors in the solid. This amounts to a random distribution assumption. Eyring does not use this expression, however, but uses instead \( n(v_m - v_s)/v_s \), where \( n \) is a parameter characteristic of the liquid. As will be demonstrated later, the former expression leads to certain anomalies which the latter avoids. In the initial work reported here, this difficulty was not recognized. Thus the random distribution approximation is used in this section. Since most of the systems of interest have surface phases which are more nearly analogous to a dense gas than to a liquid and since it was also felt that the effect of strain on the two-dimensional structure would be less than on the three-dimensional structure, it was decided that the approximation \( a/n_h = 0 \) would be used. This simplifies the treatment and does not seem to reduce the effectiveness of the theory materially. The approach based on the above assumptions will be referred to as "Approximation I."

Using the above assumptions, the surface partition function becomes
\[ Z_{2s} = \left( \frac{e^{-\theta E_s/2T}}{1 - e^{-\theta E_s/T}} \right)^2 e^{W/RT} \left( 1 + \frac{\zeta(A - A_s)/A}{\zeta(A - A_s)/A} \right)^{N_s A_s/A} \]

\[ \times \left( \frac{2\pi m kT/h^2}{e A} \right)^{N_s (A - A_s)/A} \times f_z^s \]

where

- \( Z_{2s} \) is the required partition function
- \( W \) is the two-dimensional lattice energy (obtained by summing the potential energy of interaction over the assumed lattice geometry)
- \( A \) is the area per molecule of the adsorbed phase
- \( A_s \) is the area per molecule of the adsorbed phase if it were all in the hypothetical "solid" form
- \( N_s \) is the number of molecules on the surface

and the other symbols are as defined earlier. Equation 18 now can be used to derive the free energy of the adsorbed phase as a function of \( N_s, A, \) and \( T \). It will prove convenient, however, to have this free energy expressed as a function of \( \theta \), \( T \), and \( N_m \), the number of molecules on the surface at monolayer coverage.

In order to transform equation 18 to the variables of interest, one need only recall that \( \theta = N_s/N_m \) and also that \( \theta \) may be expressed as \( A_m^0/A \). In this work, it is assumed that \( A_s \) and \( A_m^0 \) are the same. Making use of these facts and the relation \( F = -kT \ln Z \), one may derive the following expression for the Helmholtz free energy \( F_s \) of the adsorbed phase
\[ F_s = -kT(\theta^mN_m \ln \left[ \frac{E^0}{C} (1 + \xi(1 - \theta)) \right] + \theta N_m \ln(C/\theta)) \] (19)

where

\[ B = D(\left( e^{-\frac{E^0}{2T}} \right)/(1 - e^{-\frac{E^0}{T}})) e^{W/RT} \]

\[ C = D(\left( 2\pi mkT/h^2 \right) e A^m_o) \]

and \( D \) is defined by

\[ D = \left( \left( e^{-\frac{\nu}{2kT}} \right)/(1 - e^{-\frac{\nu}{kT}}) \right) e^{U_o/RT} \]

and the other symbols have been previously defined. The chemical potential follows directly from this, the result being

\[ -\mu^o_s/kT = 2\theta \ln [(B\theta/C)(1 + \xi(1 - \theta))] + \frac{\theta(1 + \xi - 2\xi\theta)}{(1 + \xi(1 - \theta))} \]

\[ + \ln(C/\theta) - 1 \] (20)

where the symbols have all been previously defined.

The chemical potential of the gas phase (under the assumption that it behaves ideally) is given by equation 12 which is usually written

\[ \mu^o_g = \mu^o_g + kT \ln(P). \]

The exact form of \( \mu^o_g \) is clear from equation 12.

Equating this expression to equation 20, one obtains

\[ \ln(P) = -\frac{\mu^o_g}{kT} - 2\theta \ln [(B\theta/C)(1 + \xi(1 - \theta))] - \frac{\theta((1 + \xi - 2\xi\theta)}{(1 + \xi(1 - \theta))} \]

\[ - \ln(C/\theta) + 1 \] (21)

where the symbols are as defined earlier.
Equation 20 is the isotherm equation which is the main point of interest in the treatment of adsorption data. Another interesting relationship is that of the isosteric heat to the coverage. This heat quantity is defined by the expression

\[ q_{st} = RT^2 \left( \frac{3 \ln(p)}{\beta T} \right) N_s \]  

(22)

where \( q_{st} \) is the isosteric heat of adsorption, and the other symbols are as defined previously. The application of the operation described by equation 21 to equation 22 yields

\[ q_{st}(\theta, T) = \left( 2W - 2R\theta + 2RT - 3RT \right) \left( e^{-\theta E/T} \right) \]  

\[ \frac{1}{(1 - e^{-\theta E/T})} \theta \]  

(23)

which shows a linear dependence on the coverage. This is expected because experience has shown that the random distribution approximation leads to this sort of dependence in vacancy theories of adsorption.

In light of the increasing importance of the treatment of adsorption data in terms of a virial expansion, it was decided that it would be of interest to compute two-dimensional second virial coefficients for the model. When the virial coefficient was computed, it was found that the limit involved in the computation was undefined. In effect, the second virial coefficient for this treatment was infinite.
The other interesting thermodynamic quantities are the two-dimensional critical properties. These are calculated according to the normal criteria, which are the disappearance of the first and second derivatives of the pressure with respect to the coverage at constant temperature at the critical point. The results for this model are

\[ \theta_c = 0.3834 \] (24)

\[ T_c = \frac{(4.93 \times 10^9)/(M \alpha_n^0)}{(e^{-\frac{W-R\theta_c}{RT_c}} \theta_c)/(1 - e^{-\frac{\theta_c}{T}})^2} \]

where

- \( \theta_c \) is the critical value of the coverage
- \( T_c \) is the critical temperature
- \( M \) is the molecular weight of the gas

and the other symbols are as defined previously. The critical pressure may be obtained from \( \theta_c \) and \( T_c \) by application of the isotherm equation (equation 21).

**Modifications of Eyring's Partition Function**

**Approximation II**

The first modification to be discussed is the change to a classical cell solid. This modification seemed desirable because of the difficulty in predicting the value of the Einstein temperature. As mentioned earlier, the surface has the effect of modifying the interactions in the adsorbed phase. Sinanoglu and Pitzer\(^9\) have treated this effect, and in the treatment of data with Approximation I, their expression was used to correct
for the effect. A Lennard-Jones potential

\[ \varepsilon_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{\sigma_0} \right)^{12} - \left( \frac{\sigma}{\sigma_0} \right)^{6} \right] \]

where \( \varepsilon \) is the depth of the potential minimum, \( \sigma \) is the internuclear distance, and \( \sigma_0 \) is the internuclear distance where the interaction energy becomes zero, was used to compute the quantity \( W \). The Sinanoglu-Pitzer theory gives \( \varepsilon \) in terms of the surface gas interaction parameter \( U_0 \). Thus the corrected value of \( \varepsilon \) was used, and the above equation summed over all the lattice points of a close packed plane to get \( W \). The quantity \( \varepsilon_0 \) could be deduced with difficulty from the form of the above mentioned lattice sum in the neighborhood of the equilibrium lattice site. It was decided that a model which gave the thermodynamics directly in terms of the parameters \( \varepsilon \) and perhaps a characteristic distance would be preferable to trying to relate \( \varepsilon_0 \) to \( \varepsilon \).

A model which fits this description is the cell model of Lennard-Jones and Devonshire. In this approach, a molecule in the solid is treated as if it resided in a cell whose boundaries are defined by the nearest neighbors in the solid. The interaction of a molecule in a cell and each of its nearest neighbors is assumed to be expressed by a Lennard-Jones potential. This interaction is then averaged over the nearest neighbors (each assumed to reside at its equilibrium position). The result is a potential well in which the molecule of interest can be thought of as residing. This potential function is then used in the classical formulation to derive the thermodynamics of the system. The partition function of a two-dimensional solid is then
\[ Z_{2\text{sol}} = \left( \frac{2\pi mkT}{h^2} \right) a^2 \int_0^\infty \exp \left( \frac{(6e/kT)(2m_s(y) - 1_s(y))}{2} \right) dy \right)^{N_s \frac{W}{RT}} \]

where

- \( a \) is the diameter of the cell in which the molecule resides
- \( e \) is the Lennard-Jones interaction parameter
- \( m_s \) and \( 1_s \) are polynomials whose form is given by Lennard-Jones and Devonshire
- \( y \) is defined as \((r/a)^2\) where \( r \) is the distance from the center of the cell to the molecule
- \( W \) is the two-dimensional lattice energy (obtained by summing the Lennard-Jones function over the assumed lattice).

This assumed lattice is here taken as a close packed plane. This amounts to assigning the value of six to the parameter \( \zeta \). The term \( \pi a^2 \) times the integral in equation 25 is the free area and will be symbolized by \( a_f \) in the following work.

Having decided on this model for the representation of the solid-like degrees of freedom, the partition function for the adsorbed phase becomes

\[ Z_{2s} = \left( \frac{2\pi mkT}{h^2} \right) (c^{\frac{-\hbar v/2kT}{1-e}}/1-e) \left( U_0/RT N_s \right) \]

\[ \times \frac{W/RT}{N_s A_s/A} \left( \frac{N_s A_s/A}{\left( A_m^c e/\theta \right)^{\frac{N_s(A-A_s)}{A}}} \right) \]

where all the symbols have been defined previously. From this expression,
the adsorption isotherm may be derived, the result being the same as equation 21 except that the constant B assumes the form $D(2\pi mTk/h^2)_{\text{av}}\exp^{W/RT}$ where $D$ is defined as in equation 20. The expression for $q_{\text{st}}$ is the same as equation 23 except that the term multiplying $\theta$ becomes

$$[-2W - 12(x_eN_{\text{av}} a^2/a_f) \int_0^{1/4} (2m_s(y) - l_s(y)) \, dy]$$

where $N_{\text{av}}$ is Avogadro's number, and the other symbols have been defined previously. The critical properties are given by

$$\theta_c = 0.3834$$

$$\left(\frac{a_f(T_c/A_m^0)}{W/RT_c} \right) e^{\frac{W/RT_c}{c}} = 3.726$$

where the $c$ subscripts refer to the critical values of the quantities.

It should be pointed out here that the use of the cell model has resulted in the effective reduction of the number of parameters necessary to characterize the solid-like degrees of freedom. This is due to the fact that it is assumed in this work that the parameter $a$ should be chosen so that the area of the cell is the same as $A_m^0$. As shown above, $W$ is calculable from the value of $e$ used and knowledge of the lattice involved. Hence, the only parameter used to characterize the solid-like degrees of
freedom is \( e \). Also, \( e \) is the parameter one is interested in for the determination of the effect of the solid on the intermolecular interactions in the adsorbed phase. Hence the treatment using this model of the solid is operationally and conceptually more attractive than the treatment which involves the Einstein solid.

**Approximation III**

The other modification which has been made is not really a modification but is the conversion of the original treatment presented here to the formula of Eyring for the variation of the number of holes. This conversion was made because of the discovery that the thermodynamics predicted by the initial treatment broke down at \( \theta = 0 \). That is, as mentioned earlier, the second virial coefficient did not exist.

The approach used in the initial treatment presented here amounts to the random distribution approximation for the variation in numbers of holes. Eyring's approach, on the other hand, seems rather artificial. He\(^7\) presents the following rationalization of his formula

\[
\frac{Z_n (V_m - V_s)}{V_m} = \left( \frac{Z_n V_s}{V_m} \right) \left( \frac{(V_m - V_s)}{V_s} \right) = n \left( \frac{(V_m - V_s)}{V_s} \right) \quad (29)
\]

where \( n \) is just \( \left( \frac{Z_n V_s}{V_m} \right) \). With only slight justification, Eyring assumes that \( n \) is independent of \( V_m \) and \( T \). This seems strange, but the fact is that it removes the difficulty with the virial coefficient, and it also seems to allow the fitting of data with as good results as with the other approach. Recently, Pierotti\(^{11}\) has been able to show that the functional dependence on the volume exemplified by equation 29 is identical to that
obtained from a free volume theory of liquids. The assumption necessary
to make the connection was that the free volume of the liquid varied
linearly with density.

Assuming \( n \) from equation 29 is equal to \( \xi \) for the surface, the
present approach amounts to \( n_h = \xi(1 - \theta) / \theta \). Thus it is seen that the
new approach will result in a major modification of the functional form
of the isotherm equation.

The derivation of the isotherm equation proceeds as before, the
result being

\[
\ln(P) = -\mu^0/kT - 2\theta \ln((B\theta/C)(1 + \xi((1 - \theta)/\theta))) + \frac{5\theta^2}{(\xi - (\xi - 1)\theta)} (30)
\]

\[ - \ln(C/\theta) + 1 \]

where the constants \( B \) and \( C \) are identical to those which are found in the
cell approach previously set forth. The expression for the isosteric
heat is the same as in the case just discussed. This is due to the fact
that the constants \( B \) and \( C \) are the same as in Approximation II. The
critical properties should change, and this is indeed the case. The cri­
tical properties are

\[
\theta_c = 0.322 \quad (31)
\]

\[
(a^{m}(m_c/A^{m}) e^{W/RT})_c = 6.517
\]
where the symbols are as defined earlier. The critical pressure can again
be found from the isotherm equation. The expression for the second two-
dimensional virial coefficient is

$$B_{2d}(T) = A_m^0 [\ln (A_m^0 (a_f e^{W/RT})) - \ln (\xi) - 1]$$  \(32\)

where the symbols have all been defined earlier.

**Modification to Include Non-Spherical Molecules**

If the theory developed here is to be of practical value, it must
be applicable to systems which are more complex than monatomic gases. In
this regard, the significant structure theory is particularly strong. In
the following development, it will be shown that a molecule which can be
modeled as a rigid body may be treated by the theory.

Consider a molecule which is essentially rigid and whose moments
of inertia are $I_x$, $I_y$, and $I_z$, where the $x$, $y$, $z$ refer to the principal
axes of the molecule. Suppose further that the molecule has $n_v$ internal
vibrations characterized by the frequencies $\nu_1, \nu_2, \ldots, \nu_{n_v}$. The gas
phase partition function for such a molecule is

$$f_g = \left( \frac{(2\pi^2 kT)^{3/2}}{(\pi \sigma^2)^{3/2}} \right)^{n_v} \left( \prod_{i=1}^{n_v} (1 - e^{-h\nu_i/kT})^{-1} \right) \times (2\pi mkT/h^2)^{3/2} V_g$$  \(33\)

where $\sigma$ is the symmetry number of the molecule, and $V_g$ is the volume of
the gas phase in which the molecule resides. Having decided on this expres-

sion, one must next decide (based on intuition) what the state of
motion of the molecule in the adsorbed phase is. Suppose it is decided
that the degrees of freedom corresponding to the rotation about the x and
y axes will be modified to the extent that they will appear as vibrations
(a rocking motion). This would be typified by the assumption that a mole-
cule such as benzene was lying flat on the surface and never flipped over
but continued to rotate about the axis normal to the surface. Under these
assumptions, the partition function for the adsorbed phase becomes

\[
Z_s = \left( \prod_{i=1}^{n_v} \frac{1}{(8\pi kT)^{3/2}} \right) \left( \prod_{i=1}^{N_s} (1 - e^{-\frac{\hbar v_i}{kT}})^{-1} \right) Z_{ssl}
\]

where \( Z_{ssl} \) is the significant structure partition function for a monatomic
molecule characterized by the appropriate parameters of the molecule of
interest. The parameters \( v_x \) and \( v_y \) are the frequencies associated with
the vibrations which have been assumed to have replaced the x and y rota-
tion. Here the standard assumption that the presence of the surface does
not perturb the internal vibrations appreciably has been made.

Inspection of equations 33 and 34 in the light of the way that the
isotherm equation is derived reveals that terms corresponding to degrees
of freedom which are unaltered by the surface will cancel out, and hence
they do not need to be included in the partition function. The net effect
of including consideration of the complexities of the molecule is to yield
the following isotherm equation

\[
\ln(p) = \ln(p)' + \ln \left( \left( \frac{\sigma (g^2 kT)(I_x I_y)}{x^2} \right) / e (1 \cdot e^{-\frac{h\nu}{kT}} \right) \right) \tag{35}
\]

where \( \ln(p)' \) is the expression obtained by the direct application of equation 30. The other term is the logarithm of the ratio of the partition function representing the changing degree of freedom in the gas phase to the partition function representing this degree of freedom on the surface. Hence the treatment of the complexities is fairly easy.

Since the entropy is the one thermodynamic variable which best reflects the hindrance or freedom of a given state, it is generally used to test the validity of an assumed surface state. The procedure is to compute the entropy change on adsorption from the assumed model and then to measure the entropy change. The comparison of these figures then leads to a conclusion concerning the validity of the assumed surface state.

It has been assumed in the foregoing that the geometry of the molecule had no effect on the thermodynamics of the condensed phase. This allowed the separation symbolized by equation 34. If for instance the rotation of our model system about the axis normal to the surface is quenched by the crowding of molecules onto the surface, the treatment described is invalid. A first order attempt may be made at accounting for this effect by describing the condensed phase partition function as a hybrid of a torsional vibration in the solid-like part of the overall
partition function and as free rotation in the gas-like part. Eyring et al. have done this in treating the liquid state of chlorine. This might allow more success in the prediction of the effect of coverage on the entropy of adsorption. It is clear that the details of the isotherm equation become more complex, but this case will not be treated here since it is not used in any of the subsequent work.
CHAPTER III

APPLICATION OF THE THEORY TO SELECTED DATA

Development of a Fitting Technique

In attempting to test the theory by comparison with data, it was found that a systematic approach to the determination of parameters was needed. At first the parameters had been determined by computing a large number of isotherms corresponding to a range of all the parameters and comparing these directly with the data. This was a laborious and costly procedure even in cases where approximate values were known. In the case of more complex systems, it was felt that the difficulties would prove intolerable, so the following approach was devised.

The technique set forth here applies only to Approximation III; that is, Eyring's expression for the variation in the number of holes with coverage is used. The cell solid is also used. Using this approximation, the isotherm equation is obtained by rewriting equation 35 in the light of equation 30; the result is

\[
\ln(p) = -\frac{\mu^0}{kT} - 2\theta \ln\left(6 - 5\theta\right)\left(c'/c\right) + \frac{\theta^2}{(6 - 5\theta)} - \ln\left(c'/\theta\right) + 1 \quad (36)
\]

\[
+ \ln\left(f_{rg}/f_{rs}\right)
\]

where

\( f_{rg} \) is the rotational partition function of the molecule in the
gas phase

\( f_{rs} \) is the rotational partition function of the molecule on the surface.

\( C' \) is the same as the constant \( C \) in earlier forms of this equation except that it contains the effect of the newly introduced vibrations and the other symbols are as defined earlier. In deriving equation 36, one important assumption has been made. This is that the constant \( \xi \) in equation 30 has the value six; this is equivalent to assuming that the monolayer is a close packed layer of molecules. For simple molecules, this is reasonable, and it is the assumption used in all the treatments described here.

To a person interested in the gas solid interaction, the effect of interaction in the adsorbed phase often appears as an undesirable complication which disguises the character of the interaction of interest. This point of view will be adopted here, and the technique is thus solely directed at extracting the parameters \( U_0 \) and \( v \). The other interaction parameter, \( \epsilon \), which is often of interest also, will be determined by the technique of scanning the range of its values and comparing computed isotherms directly with data.

Consideration of equation 36 shows that it may be written in the form

\[
\ln(P) + g(\theta) = -2\theta \ln(B/C') - \frac{\mu^0}{kT} \ln(C') + \ln(f_{rg} / f_{rs}) \quad (37)
\]

where
and the other symbols are as defined earlier. From what has gone before, 
$\mu_E^0/kT$ and $\ln(f_{rg}/f_{rs})$ are functions of the temperature whose form is
known. Hence plotting the left side of equation 37 against $\theta$ should yield
a straight line, and the intercept should be the sum of the two tempera-
ture dependent terms just mentioned and the quantity $-\ln(C')$. Since it
is possible to compute the exact value of the two terms above, the inter-
cept gives a value of the logarithm of the constant $C'$. It will now be
shown that the evaluation of this constant for a number of different tem-
peratures can lead to a determination of the parameters $U_0$ and $\nu$.

It will prove convenient to make the following assumptions. It
will be assumed that all of the vibrations on the surface may be charac-
terized by the same frequency $\nu$. It will also be assumed that these os-
cillatory degrees of freedom may be described as classical oscillators.
This last assumption will only be used in the extraction of parameters.
Having made these assumptions, the expression for the logarithm of $C'$ be-
comes

$$\ln(C') = (2 + j) \ln(T) + (1 + j) \ln(k/\nu)$$

$$+ \ln(2\pi m k a_0^0 e/h^2) + U_0/RT$$

(38)

where $j$ is the number of rotational degrees of freedom which are changed
to vibrations on the surface.

Careful consideration of equation 38 reveals that, if values of
ln(C') are available at a number of temperatures, then a plot of the quantity ln(C') - (2 + j) ln(T) versus 1/T will yield a straight line with slope $U_0/R$. The frequency may be calculated from the intercept, since it is the only quantity remaining which is not known. When the available data consist of isotherms at only two temperatures, the following expression for $U_0$ proves useful.

$$U_0 = \frac{R T_1 T_2}{(T_2 - T_1)} \ln \left[ (T_2/T_1)^{2+j(C_1/C_2)} \right]$$

where the 1 and 2 distinguish between the two isotherms, and the other symbols are defined earlier.

**Treatment of Data with Approximation I**

Before the results of fitting data with the theory are presented, a word is in order concerning the parameters for the different treatments. In Approximation I, the approach was to use parameters available from other sources. Some discrimination was exercised, but the values selected were always within the range of literature values. In Approximation II, the values of ε were adjusted, while the other values were selected. In Approximation III, the interaction parameters were all determined by fitting the data; the values were then compared with those from other sources. In every case, the source of a parameter appears in footnotes to the tables.

Approximation I, as its name implies, was the first approach used in the treatment of adsorption data. As mentioned earlier, the variation in the number of holes with coverage is given by an expression of the form

$$n_h = \xi (1 - \theta)$$

The parameters used for the treatments described in this...
section were selected from the literature. As mentioned earlier, where there was a range of reported values, the parameter was adjusted within this range to give the best fit. The value of \( \epsilon \) was determined from the theory of Sinanoglu and Pitzer.\(^9\)

The first systems considered were the adsorption of argon on a highly graphitized carbon black (P-33), and the adsorption of krypton on the same black. This work was reported,\(^{13}\) but subsequently the work of Levy\(^{14}\) has cast grave doubt on the validity of the data used for the krypton case. Hence, the krypton case is not included in this work. The results for the argon system appear in Figure 1 and Figure 2. Figure 3 shows a comparison of the experimental and calculated isosteric heat of adsorption. The data are from Ross and Olivier,\(^{15}\) and the parameters derived here appear in Table 1 under the appropriate heading. It is clear from this comparison that the theory has great promise. In evaluating the theory, it must be remembered that the temperature range over which the theory has achieved the fit shown corresponds to a large fractional change in a term of the sort \( \text{energy}/kT \). Because of the difficulties discussed previously, this was the only system treated using the Einstein Function to describe the solid-like degrees of freedom.

**Treatment of Data with Approximation II**

The transition to the cell model of the solid was tested\(^{16}\) on the same argon-graphite system, and on the similar system, argon on boron nitride.\(^{17}\) The results of this treatment appear in Figure 4, and the applicable values of the parameters in Table 1 under the appropriate heading. Again it is seen that the agreement is very good, and also that the para-
Figure 1. Adsorption of Argon on Graphite at 77.6°K; Approximation I
Figure 2. Adsorption of Argon on Graphite at 90.1°K; Approximation II
Figure 3. Isosteric Heat of Adsorption of Argon on Graphite
Table 1. Adsorption Parameters for Approximations I and II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ar-C System Approximation I</th>
<th>Ar-C System Approximation II</th>
<th>Ar-BN System Approximation II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_0$ (cal/mole)</td>
<td>2200$^a$</td>
<td>2200$^a$</td>
<td>1950$^b$</td>
</tr>
<tr>
<td>$vX \times 10^{-12}$ (sec$^{-1}$)</td>
<td>1.2$^c$</td>
<td>1.2$^c$</td>
<td>0.95$^d$</td>
</tr>
<tr>
<td>$\epsilon/k$ ($^\circ K$)</td>
<td>101$^e$</td>
<td>106$^f$</td>
<td>108$^f$</td>
</tr>
<tr>
<td>$\theta_B$ ($^\circ K$)</td>
<td>45.0$^h$</td>
<td>...$^g$</td>
<td>...$^g$</td>
</tr>
<tr>
<td>$A_m^0$ ($\AA^2$/molecule)</td>
<td>(14.8$^i$)</td>
<td>(14.8$^i$)</td>
<td>(14.8$^i$ - (77.6$^0K$)</td>
</tr>
<tr>
<td>$a$ ($\AA$)</td>
<td>...$^g$</td>
<td>3.84$^j$</td>
<td>3.84$^j$</td>
</tr>
<tr>
<td>$v_m$ (cc(STP)/gm)</td>
<td>3.66$^k$</td>
<td>3.66$^k$</td>
<td>(5.06$^l$</td>
</tr>
</tbody>
</table>

$^a$ Obtained from reference 18
$^b$ Obtained from reference 19
$^c$ An average of theoretical estimates
$^d$ Obtained from reference 20
$^e$ Literature value corrected for third order effect by theory of Sinanoglu and Pitzer
$^f$ Determined for best fit of data
$^g$ Not applicable in this approximation
$^h$ Literature value adjusted for third order effect
$^i$ Calculated from liquid densities
$^j$ Taken as nearest neighbor distance in solid (reference 21)
$^k$ References 22 and 15
$^l$ Reference 17
Figure 4. Adsorption of Argon on Graphite and Boron Nitride; Approximation II
meters used here are in fair agreement with those of the other treatment.

After having treated these cases with the original theory, it was decided to try to fit the data of Sams, et al. for the second two-dimensional virial coefficient of argon on P-33. This led to the discovery of the anomaly previously described and to the decision to change to the other method of variation of the number of holes with density.

**Treatment of Data with Approximation III**

Approximation III has been applied to several systems for which data have been reported in the literature. The results of this application appear in this section. It should be mentioned here that the data available for systems which conform to the conditions set down in the derivation are very limited. This is mainly due to the requirement on the solid that it be energetically homogeneous. Levy has measured isotherms for the system krypton on boron nitride which have an interesting ambivalent character. The treatment of that system will be included in this section as an example of the potential utility of the model in treating heterogeneous solids. Since, with the $\xi(1 - \theta)/\theta$ type variation function, it becomes possible to compute two-dimensional second virial coefficients, a comparison of the data of Halsey, et al. with the theory is also included here.

The first systems studied with the fitting technique were the previously treated argon-graphite and argon-boron nitride systems. Figures 5 and 6 illustrate the plot suggested by equation 37. The treatment is seen to linearize the data rather nicely for the coverages used. The values of $\ln(C')$ were determined from the intercepts, and equation 39 was used to compute $U_0$. The value of "j" in that equation is clearly zero for
Figure 5. Plot of $g(\theta)$ for Argon-Graphite System

Note: Lines are drawn for best fit of data.
Figure 6. Plot of $g(\theta)$ for Argon-Boron Nitride System

Note: Lines are drawn for best fit of data.
these monatomic molecules. The parameter \( \nu \) was obtained from equation 38. The determination of this parameter seems to depend strongly on the determination of the correct \( \ln(C') \) values. It can be seen from the parameters for the graphite system (see Table 2) that the value of \( U_0 \) is in line with those determined by Approximations I and II. The value of \( \nu \) is seen to be out of line, however. This is reflected in the slightly less satisfactory agreement obtained; compare Figures 7 and 8 with Figures 1, 2, and 4. The reason for the disagreement is probably that only a few data points were used in the fitting technique. The fact that the BN fit is not as good as the P-33 fit may be because the system is not as ideal as required for the applicability of the theory. The parameter \( \epsilon \) used in the computation of the isotherm was determined by trial and error using the 90.1°C data for the P-33 and the 77.6°C data for the boron nitride.

The next system studied was carbon tetrachloride on P-33. The data of Ross and Machin for this system represent the most complete study available for a system which may reasonably be expected to satisfy the requirements for the application of the present treatment. This system is also interesting because it represents the "first order of complexity" above the monatomic case. This system has been studied theoretically by Kiselev, with particular interest being given to the question of the state of motion of the molecule on a plain surface. By computing the traditional lattice sums, Kiselev finds that on a solid such as P-33, one can expect a large energy barrier (many times as large as \( kT \) at the temperatures of interest) to the process of flipping from one of the stable states of a tetrahedron resting on a plane to another such state. This indicates that the assumption that the adsorption process might be accom-
Table 2. Adsorption Parameters for Approximation III; Comparison with Existing Values.

<table>
<thead>
<tr>
<th>System</th>
<th>(U_0) (cal/mole)</th>
<th>(v \times 10^{-12}) (sec(^{-1}))</th>
<th>(\sigma/k) (°K(^{-1}))</th>
<th>(A_m^0) (Å(^2)/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-C</td>
<td>2204(^a)</td>
<td>2.13(^a)</td>
<td>110(^a)</td>
<td>14.6(^e)</td>
</tr>
<tr>
<td></td>
<td>2200(^b)</td>
<td>1.28(^c)</td>
<td>96(^b)</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>2120(^c)</td>
<td>2.3-2.7(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar-BN</td>
<td>1900(^a)</td>
<td>1.16(^a)</td>
<td>112(^a)</td>
<td>14.6(^e)</td>
</tr>
<tr>
<td></td>
<td>1950(^d)</td>
<td></td>
<td></td>
<td>15.4</td>
</tr>
<tr>
<td>CCl(_4)-C</td>
<td>9031(^a)</td>
<td>0.66(^a)</td>
<td>395(^a)</td>
<td>25.5(^f)</td>
</tr>
<tr>
<td>Kr-BN</td>
<td>2629(^a)</td>
<td>1.00(^a)</td>
<td>118(^a)</td>
<td>19.5(^g)</td>
</tr>
</tbody>
</table>

\(^a\) Determined as described in the text
\(^b\) Obtained from reference 18
\(^c\) Obtained from reference 25
\(^d\) Obtained from reference 19
\(^e\) Determined from liquid densities
\(^f\) Estimated from data of reference 26
\(^g\) Obtained from reference 27
\(^h\) The value of the parameter \(a\) was chosen to make the area of the cell equal to \(A_m^0\)
Figure 7. Data Comparison for Argon on Graphite and Boron Nitride at 90.1°K; Approximation III
Figure 8. Data Comparison for Argon on Graphite and Boron Nitride at 77.6°K; Approximation III
panied by the loss of two degrees of rotational freedom and the introduc-
tion of two degrees of vibrational freedom in their place might be a good
one. Thus it was decided to attempt to fit the entire range of the data
on the basis of these assumptions.

Ross and Machin report data corresponding to isotherms at nine
temperatures between 231.2°K and 323.8°K. It was decided to fit the data
at three intermediate temperatures, and then let the theory "predict" the
data at the other temperatures. For the fitting treatment, the isotherms
at 296°K, 288.4°K, and 278.2°K were chosen. The plot of ln(P) + g(θ) ver-
sus θ appears in Figure 9. Again the linearizing effect of the treatment
is evident. The values of the parameters determined from the data appear
in Table 2, along with the value of θ determined to give the best fit for
the isotherm at 278.2°K. In this case, there is enough data to justify
plotting ln(C') - (2 + j) ln(T) versus 1/T as suggested following equa-
tion 38. The result of this operation appears in Figure 10, where j is
now two. Figure 11 illustrates the fit obtained for the isotherms used
in the fitting technique. Figure 12 shows the agreement obtained at the
higher temperature. The fit is good when it is recalled that the agree-
ment corresponds to a prediction based on the treatment of data which is
50 to 65°K removed from the temperature of the data. Figures 13 and 14
demonstrate the prediction of the data at lower temperatures. The agree-
ment here is very good; it is so good that one is tempted to question the
validity of the data at 265.8°K at a value of ten on the ordinate where
it behaves peculiarly. The fact that the theory predicts the isotherm
at 231.2°K so precisely is probably somewhat fortuitous, but the fact that
Note: Lines are drawn for best fit to data.

Figure 9. Plot of $g(\theta)$ for CCl$_4$ on Graphite
Figure 10. Plot of $\ln(C') - (2 + j) \ln(T)$ versus $1/T$ for the CCl₄-Graphite System.

Note: Line is drawn for the best fit of the data.
Figure 11. Data Comparison for CCl₄ on Graphite in the Intermediate Temperature Range; Approximation III.
Figure 12. Data Comparison for CCl\textsubscript{4} on Graphite in the High Temperature Range; Approximation III
Figure 13. Data Comparison for CCl₄ on Graphite in the Low Temperature Range; Approximation III
Figure 14. Data Comparison for CCl$_4$ on Graphite in the Lowest Temperature Range; Approximation III
the computed isotherm demonstrates a vertical riser of the same character as the experimental one is very significant. This indicates that the significant structure theory is predicting the properties of the two-dimensional phase over a temperature range of more than 50°K. This must be viewed as a virtually unqualified success for the significant structure theory.

The data of Sams, et al. appear in Figure 15 along with the predictions of the present theory. It is clear that the virial coefficient is still a property which the theory is ill equipped to deal with. This has been observed in the three-dimensional case by Henderson who was able to predict the overall thermodynamics of a system of hard spheres rather well, but found considerable discrepancies in the virial coefficients. Wang, Ree, Ree, and Eyring have treated a system of two-dimensional hard "discs" and have likewise encountered difficulties in the prediction of virial coefficients. Ree, Ree, and Eyring, on the other hand, have modified the theory to treat dense gases, and are able to obtain good agreement in certain systems. It was felt that the desirability of keeping the theory as simple as possible outweighed the increased ability to predict virial coefficients gained by extensive modifications.

An interesting and highly successful application of Approximation III has been made by Levy. Levy investigated the adsorption of krypton on hexagonal boron nitride which he thought was energetically homogeneous. The data, however, indicated that some adsorbing impurity existed on the surface. Using an approach suggested by Ross and Olivier, Levy was able to extract from the data parameters characteristic of the BN-krypton interaction.
Figure 15. Two-Dimensional Virial Coefficient Comparison; Argon-Argon on Graphite; Approximation III
The assumption was made that the surface consisted of two distinct regions, and that the distribution function characterizing the surface gas interaction could be written

\[ \rho(U_0) = \gamma \delta(U_{01}) + (1 - \gamma) \delta(U_{02}) \]  \hspace{1cm} (40)

where

- \( \rho(U_0) \) is the fraction of the surface with surface gas interaction parameter between \( U_0 \) and \( U_0 + dU_0 \)
- \( \gamma \) is a constant between zero and one, and which corresponds to the fraction of the surface characterized by \( U_{01} \)
- \( \delta(U_{01}) \) is the Dirac delta function centered at \( U_{01} \)
- \( U_{01} \) is the value of the interaction parameter corresponding to the hot spots
- \( U_{02} \) is the value of the interaction parameter corresponding to the milder adsorption potential (presumably the BN).

It was then assumed that both of the regions of the surface could be modeled by the significant structure theory, and, using the distribution function above, this led to the isotherm equation

\[ \theta(P) = \gamma \theta_{SS}(P;U_{01}) + (1 - \gamma) \theta_{SS}(P;U_{02}) \]  \hspace{1cm} (41)

where

- \( \theta(P) \) is the isotherm of the composite system
- \( \theta_{SS}(P;U_{01}) \) is the isotherm computed from significant structure
theory for the parameter $U_{01}$
and the other symbols have been defined previously. The result of applying
this equation to the data is illustrated in Figure 16, and the applicable parameters are given in Table 2. The parameter $\gamma$ was found to be 0.2, but this is not of interest here as is the case with $U_{01}$. The agreement with the high $\theta$ part of the data is very good and is to be considered as further evidence that the theory shows great promise in dealing with two-dimensional liquids.

**Discussion of Results**

The results of the treatment of adsorption data are contained in Tables 1 and 2 and are self explanatory to a large degree. The values with which the parameters are compared are a hybrid collection of both experimental and theoretical values. The experimental values depend on some other model, and as such are no more experimental than the ones of the present treatment.

A word is in order about the values of $\epsilon/k$. The values of this parameter for the argon and krypton systems show the expected behavior; that is a decrease in the value of $\epsilon/k$, from the gas phase value, as predicted by Sinanoglu and Pitzer.$^9$ The value of the parameter $\epsilon/k$ for carbon tetrachloride is larger than the one reported in the literature$^{33}$ ($327^\circ K$). This latter figure is obtained from viscosity data; this fact, along with the complexity of the molecule, is probably sufficient to render comparisons meaningless.
Figure 16. Data Comparison for Krypton on Boron Nitride; Approximation III
CHAPTER IV

THE ADSORPTION OF KRYPTON ON THE (1,1,1) FACE OF COPPER

Introduction

The nature of the metallic surface has been of interest for many years; the catalytic activity of some metals has been partly responsible for this interest. Most of the adsorption studies which have been made on metals have been done on rather poorly characterized, polycrystalline surfaces. Because of this fact, very little is understood about the fundamentals of the interaction of gases with the metallic surface. In recent years, the advent of low energy electron diffraction has allowed the investigation of certain systems at a very fundamental level; in every case, however, the systems studied by this technique are those in which the adsorption must be characterized as "chemisorption."

The study of the physical interaction of a gas with an energetically homogeneous metallic surface should be very interesting. The existence of the conduction electrons must lead to a somewhat different type interaction than in the case of an insulator. Also, the theory of Sinanoglu and Pitzer\textsuperscript{9} indicates that dramatic decreases in the interaction between molecules on the surface are to be expected for certain metallic systems.

In one of the few attempts to study physical adsorption on well characterized metallic surfaces, Rhodin\textsuperscript{34} looked at the adsorption of nitrogen and argon on single crystals of copper. He was trying to charac-
terize the anisotropy of interaction of the various crystal faces with the gas. Many other studies \(^{35,36}\) have been made on deposited metal films, but usually in the multilayer region. Where studies have encompassed the submonolayer region, \(^{37}\) the data seem to indicate energetically heterogeneous surfaces.

Rhodin's work encompasses the submonolayer region, but his data, while giving some information, are not sufficiently precise to allow detailed conclusions about the interaction. Rhodin made use of a microbalance in his work. Pierotti, \(^{36}\) in his study of deposited metal films, had been able to measure isotherms on small surfaces quite accurately by a volumetric technique. It was thus thought that, if a method of obtaining an area of around 100 square centimeters or so of single crystal surface could be found, more accurate measurements than those of Rhodin could be made. Further, it was hoped that by applying the significant structure model, parameters could be deduced in more detail than is possible using only classical thermodynamical methods.

It was found that Dr. F. W. Young, in his laboratory at Oak Ridge National Laboratory, had developed a method for growing large, flat, single crystals of copper with a particular crystallographic plane on the flat sides. The crystals are rectangular slabs whose dimensions are \(1 \text{ mm} \times 1 \text{ cm} \times 8 \text{ cm}\). Hence, a single one of these crystals can supply \(16 \text{ cm}^2\) of area of a given face, while introducing only one square centimeter of "edge." Also, the shape of these crystals lends itself to the placing of a number of them in a chamber.

The availability of a method for the growth of large areas of a particular plane of copper along with the feeling that volumetric adsorp-
tion studies could be made more precise than the microbalance work led to the decision to try to repeat the measurements of Rhodin. Because of its more favorable properties, it was decided to use krypton instead of the gases studied by Rhodin. The experimental work reported here is on the development of techniques for the preparation of single crystal faces of sufficient area for study and on the measurement of isotherms on a particular face, the (1,1,1) face.

Experimental Apparatus

Introduction

The various pieces of experimental apparatus used in the performance of this work fall into two distinct classifications. The first such class is that of equipment used in the preparation of samples of a quality consistent with the overall aims of the experiment. The second class is that of apparatus used in the actual experiment; this includes equipment used in the thermal and chemical treatment of the sample as well as in the isotherm measurement. In what follows, the first class will be referred to as "sample preparative apparatus," and the second class as "adsorption apparatus."

Sample Preparative Apparatus

Included in this class of apparatus are all those pieces of equipment associated with the treatment of the sample during the period prior to its introduction into the vacuum system for the isotherm measurement.

The first "treatment" given the sample is the growth of the single crystal. The furnace used for this process is shown in Figure 17. The design is of the standard Bridgeman type. The outer wall of the furnace
Figure 17: Crystal Growth Furnace
is a ten-inch diameter transite pipe; this surrounds the insulating space which is filled with fibrous potassium titanate. The furnace core is a threaded alundum cylinder which is wound with Kanthal resistance wire. The top and bottom of the furnace are transite backed with steel. The "mullite tube" in Figure 17 is a two-inch diameter cylinder with the bottom end closed and a Pyrex glass tube fused to the top. A side arm of the glass tube goes to vacuum, while a 54/40 ground glass joint on the top allows the introduction and removal of the crystal growth crucible. The vacuum is produced by a Welch model 1400 mechanical vacuum pump. The furnace may be raised along the mullite tube by the spool arrangement illustrated in Figure 17. The motor powering the raising apparatus is a one revolution per hour gear motor. The furnace rides up on ball bearing wheels which run in two slots milled in the vertical square bars. Careful counterbalancing of the furnace allows the raising operation to be performed by a small motor. The power for the furnace is supplied by a ten ampere rated Powerstat.

The previously mentioned crystal growth crucible is illustrated in Figure 18. It was machined from high purity graphite obtained from Union Carbide Corporation. The slots shown on the left hand piece in the figure are one millimeter deep and one centimeter wide. The overall length of the piece is about 25 centimeters. The matching chamfer on the top cap and the base of the threads at the top allow sealing force to be applied, thus preventing any of the melt from leaking out through the crack. The constriction in the middle of the slots serves to terminate any low angle grain boundaries generated in the initial propagation process. The design is identical to that used by Dr. F. W. Young in his
Figure 18. Crystal Growth Crucible
laboratory at Oak Ridge National Laboratory. The top of the crucible is machined so that a molybdenum wire may be attached; this wire is used to lower the crucible into the millite tube and to raise it out of the tube after a crystal growth cycle.

The next operation performed on the crystal is that of characterization. The apparatus for this is a Phillips X-ray machine with a back reflection camera. Another method of characterization was used which depended on the observation of etch pits; the apparatus for this technique was a Zeiss "standard model metal microscope."

The final operation of the sample preparative phase was the polishing of the sample. The polishing technique used is essentially that of Powers. Figure 19 illustrates the electropolishing bath. The pyrex jar is approximately eight inches in diameter and contains the polishing solution. The electrochemical anode is a three-inch by five-inch piece of copper bus bar about one-fourth inch thick. The cathode has sides of the same material, and these sides are separated by Teflon bars. The area marked "place of residence of the sample" is coated with Hazel Bishop nail polish. The crystal is laid flat on this coat with one end making contact with the bus bar. The anode is then placed on the bottom of the jar, and the cathode positioned around the anode. Power is supplied by an Electro model D-612T filtered DC power supply. The cell voltage is monitored with a Triplett model 850 vacuum tube voltmeter.

The washing and drying operations that followed electropolishing required no special equipment.
Figure 19. Polishing Apparatus
**Adsorption Apparatus**

**Introduction.** Figure 20 is a schematic diagram of the adsorption apparatus. In Figure 20 the dashed lines divide the system into its four general categories. The line labeled "A" contains that portion of the system which will hereafter be designated "high vacuum pumping system." The line labeled "B" encloses the section of the system which will be referred to as the "clean system." Line "C" traverses that fraction of the system which will be called "pressure measuring system." Finally, line "D" which passes through the area within line "B," partitions off that area of the system which will be termed "sample cell and cryostat assembly." These categories will now be examined in detail.

**High Vacuum-Pumping System.** This portion of the system has only three elements. They are: a small mechanical vacuum pump, an oil diffusion pump, and a cold trap. Also in this section are two stopcocks. Both are Corning high vacuum stopcocks greased with Apiezon "N" stopcock grease. The mechanical pump is a Welch model 1405 pump which is capable of producing a vacuum of 0.010 Torr on the downstream side of the diffusion pump, while the diffusion pump is operating under normal load. The diffusion pump is a Consolidated Vacuum Corporation model GF-20 fractionating diffusion pump. It has two diffusion stages, is water cooled, uses oil as a pump fluid, is constructed of pyrex glass, and is capable of producing vacuums of $10^{-8}$ Torr routinely. The oil used in this pump is Octoil-S; it is marketed by the pump manufacturer and recommended by them for high vacuum use. The third element in this section of the system is a cold trap. This trap is of a standard con-
Figure 20. Adsorption System
centric tube design and is kept at about 78°K during the course of the experiment by keeping the trap in liquid nitrogen.

Clean System. This section of the system includes the sample cell and all the equipment which is used to supply gases to the sample. It also includes an ionization gauge for monitoring vacuum and the sensing head of a capacitance manometer. This last is used to measure the equilibrium pressure in the experiment. Also included in this region is a cold trap whose design is identical to that of the one described in the "high vacuum pumping system" section. All of the elements of this section are arranged so that they may be baked at a temperature of about 300°C. This accelerates the pumpdown procedure and allows the achievement of better ultimate vacuum. The sample cell is included in the category "sample cell and cryostat assembly" and will be discussed in that section. The gas handling apparatus consists of pyrex glass tubing connecting the various valves which control the flow of gases. These valves are bakeable, as was mentioned earlier, and are of a diaphragm design using a metal-to-metal seal in the closed position. They are of two types, metering and on-off. The first type is obtained from Granville-Phillips Company and is designated "variable leak" by the company. The second type is obtained from the same source and is designated "type C ultra high vacuum" by the company. Valves 1, 3, and 4 are of the metering variety, while valves 2, 5, 6, and 7 are of the on-off variety. The line connecting valves 2 and 3 with the sample cell is not of glass but is a composite of stainless steel tubing and copper tubing (one-eighth inch). The tubes are joined by a silver braze.
Pressure Measuring System. This section of the systems has basically two types of equipment. First comes those instruments concerned directly with the measurement of pressure and second comes those pieces of equipment involved in the handling of gases on this side of the system. Into the first category falls the capacitance manometer described in the previous section. The "dirty" side of the diaphragm is included in this part of the system, although the head is included in the bakeable portion of the system. A Consolidated Vacuum Corporation type GM-100 McLeod gauge is the other element whose purpose is the direct measurement of pressure. This instrument has associated with it a vacuum pump and an atmospheric bleed for adjusting the height of the mercury in the gauge.

The vacuum pump is a Welch model 1400 mechanical pump, while the atmospheric bleed valve is a Fisher-Porter glass needle valve. A Corning three-way stopcock also is used here. Into the second category fall the various valves represented schematically in Figure 20. Valves 9 and 10 are Eck & Krebs 2 mm high stopcocks. They serve to isolate the trap when the system is not in operation. Valve 11 is a Fisher-Porter needle valve which is used to admit helium (the balancing gas) to the system. Valve 13 is a Corning 2 mm high vacuum stopcock which isolates the needle valve when high vacuum is desired. Valve 8 is a Granville-Phillips variable leak valve which connects this part of the system to high vacuum and which permits the accurate adjustment of pressure necessary to the successful use of the capacitance manometer. All stopcocks are greased with Apiezon N grease. The trap which separates the McLeod gauge from the capacitance manometer head and from the high vacuum system is a U-tube with symmetrical arms. It is kept in dry ice whenever valves 9 and 10 are open.
Sample Cell and Cryostat Assembly. This part of the system consists of a cell into which the sample is placed for study and those pieces of equipment whose function is to control and measure the temperature in the region of the sample cell.

The cell itself is constructed of nickel; a drawing of it appears in Figure 21. The design of the seal is (with slight modifications) taken from Steckelmacher. It was chosen because of its wide range of operating temperatures. The tube connecting the top of the cell to the system is one-eighth inch copper refrigeration tubing. It is brazed to the nickel piece with gold-nickel eutectic brazing alloy. The brazing was done in a furnace under a hydrogen atmosphere. A gasket is employed in the demountable seal, and copper was used as the gasket material. The cell was electropolished before installation. A solution of 25 percent perchloric acid and 75 percent glacial acetic acid was the electrolyte.

The cryostatic assembly makes use of a method recently set forth by Lytle and Stoner. A Dewar flask contains a boiling liquid in which the sample cell resides. Also in the liquid is a vapor pressure thermometer; this thermometer is attached to a U-tube filled with mercury and having a number of contacts spaced along one arm of the U-tube. When a temperature lower than the normal boiling point of the cryostatic fluid is desired, helium is bubbled through the fluid. This reduces the partial pressure of the cryostatic fluid, inducing more of it to evaporate. This results in a lowering of the temperature. The vapor pressure thermometer then causes the mercury in the U-tube to break contact between two of the aforementioned contacts. This activates a solenoid which shuts off the helium. Then as the temperature rises, the contact is re-made, and helium
Figure 21. Sample Cell

body of cell

cap of cell

gold-nickel brazed joint

copper tube to system

material: nickel except where otherwise noted
flows again. At the temperatures of the experiment, argon is used in the vapor pressure thermometer, while mixtures of liquid nitrogen and liquid oxygen are used as the cryostatic fluid. Also in this section of the system is the apparatus for the measurement of the experimental temperature. A copper-constantan thermocouple in conjunction with a Leeds and Northrop type K-1 potentiometer serves to measure this temperature. The thermocouples were welded under hydrogen and calibrated against a platinum resistance thermometer. The resistance thermometer was calibrated by the National Bureau of Standards; its serial number is 1593183.

During the treatment of the sample just prior to measurement, it is necessary to heat the sample cell to a temperature of 750°C. This temperature is obtained by use of an alundum furnace tube wound with chromel wire and wrapped in asbestos cloth. The temperature in this phase of the experiment is measured with a chromel-alumel thermocouple.

Experimental Procedures

Introduction

As in the preceding chapter, this chapter divides into two distinct types of procedures. First there are those procedures associated with the growth of the single crystals and with their subsequent polishing. Following the precedent of the preceding chapter, these will be referred to as "sample preparative procedures." Then there are those procedures necessary for the thermal and chemical treatment of the sample and for the measurement of the adsorption isotherm. These will be referred to as "adsorption procedures." Each of these types will be examined in detail in what follows.
Sample Preparative Procedures

Proceeding chronologically, the growth of the single crystal must be considered first. As mentioned earlier, a Bridgeman furnace is used; the crucible which contains the seed and raw copper is illustrated in Figure 18. The seed crystal (for which we are indebted to Dr. F. W. Young of Oak Ridge National Laboratory) is placed in the lower section of the crucible as indicated in the figure. The upper portion of the slot is filled with raw copper which has been machined to close tolerance and etched vigorously with nitric acid. The copper and seed are then sealed into the crucible by means of the screwed ends. The crucible is then lowered into the mullite furnace tube with a molybednum wire. The mullite tube has a 54/40 pyrex glass joint attached to the top of the tube, and this is now sealed with Apiezon L grease and the vacuum pump turned on. The movable furnace is adjusted to a height on the tube such that the melt line in the crucible will be in the region where the seed resides. Power is then applied, and the temperature is monitored with a chromel-alumel thermocouple in the region between the mullite tube and the furnace core. There is no temperature sensor in the crucible itself, so, by trial and error, a suitable outside temperature is determined. Once this temperature is obtained, a small one revolution per hour gear motor is energized and, through a pulley system, the furnace is raised at the rate of one inch per hour. Again by trial and error, it is determined how high the furnace must rise before the melt line clears the crucible. When this height is reached, the furnace is switched off and the system allowed to cool overnight under vacuum. The crucible is then removed, and the copper taken out with great care. The seed, now represented by
everything below the waist in the slot (see Figure 18), is detached from
the newly grown crystal by sawing with a jewelers saw. The seed is put
back into the crucible, and the new crystal enters the characterization
phase of its life.

The job of crystal characterization amounts to answering the fol­
lowing questions: are there any grain boundaries in the sample and, if
not, is the orientation of the broad face of the crystal within about
two degrees of the desired orientation ((1,1,1, here). Two methods are
used to answer these questions. The most obvious one is, of course, back
reflection X-ray diffraction. This method was employed exclusively in
the early stages of the work, but, due to the laboriousness of the tech­
nique, it gave way to the simple etch pit technique. The original crys­
tals were X-rayed in from five to seven spots on both sides. This took
an entire day's work and involved the use of borrowed facilities. Fi­
nally, it was decided that the symmetry, orientation, and density on the
surface of the etch pits caused by the action of nitric acid on the
crystal were sufficiently good indications of the quality of the crys­
tal. This was suggested by the work of Young. This method was used
exclusively in the characterization of the last five or six crystals
prepared. An acceptable crystal shows no grain boundaries on etching
with nitric acid and has etch pits which do not deviate visibly from tri­
angular symmetry. In the X-ray work, it was determined from the data
that orientations were always within about two degrees of (1,1,1).

Once the crystal had been characterized as single, the next step
was the polishing of the crystal. The procedures used in this phase of
the work were almost identical to those of Powers. The job of polish­
The essence of Powers' method is that the polishing action on the top of the piece of interest is superior to that on any other side. Hence, only one side of a piece may be polished at once. The piece resides on the bottom of a container in which the electrolyte is placed. The piece is the electrochemical anode, or at least part of it, and the cathode is a strip of copper foil wrapped around the inside of the container. Since the samples to be used in this study must have both sides prepared, the following scheme was devised. One side of the crystal was coated with Hazel Bishop fingernail polish, and the other side electropolished as Powers described; then the nail polish was removed and the electropolished side coated. Then the second side was polished. It was found that acetone did a very thorough job of removing the nail polish. During the polishing operation, the sample lay flat on a rather large piece (three inches by five inches) of copper bus bar. This was done to reduce rounding of the edges of the sample during polishing. Powers seems to have had difficulty making electrical contact between the sample (when it was delicate and could not be soldered) and the leads from the power supply. It was found in this study that the application of a generous coating of Vaseline petroleum jelly between the sample and the bus bar gave very good, reproducible contacts. This was done on one end of each crystal, and the resulting unpolished area was subsequently removed by snipping with a pair of diagonal pliers.

The cathode in this work consisted of two pieces of copper bar separated by Teflon spacers, and the container was a pyrex animal jar of eight-inch diameter. The solution was 50 percent ortho-phosphoric acid.
originally, but after operation, some of the hydrogen ion is replaced by copper ions.

During the early stages of the work, a stirred bath was experimented with for electropolishing. Although the crystals were brightened by this technique, macro scale roughness was not removed. In fact, the polishing seemed to result in a wavy surface. The advantage of Powers' method is that it reduces macro roughness and leads to a flattening of the surface. This eliminates the need for the mechanical polishing steps usually required in sample preparation. It was found that eight hours of polishing on each side of the crystal led to a surface which was free of the wavy character observed in the stirred polishing technique.

After the crystals were prepared by the technique described, a small hole was drilled in one end of each crystal. A wire looped through this hole was the contact in subsequent polishing operations. The crystals were next cleaned in acetone, etched lightly in concentrated nitric acid, and polished electrically in a vertical position in an unstirred bath until the brightness removed by the nitric acid treatment was restored. The solution used was the same as in the other polishing scheme. This last treatment had as its primary goal the complete removal of any traces of residue remaining from the dissolution of the fingernail polish. After the final polish, the crystals were washed (with the voltage still applied) in ten percent ortho-phosphoric acid for 20 to 30 seconds and then in distilled water for five minutes. They were then dried in a stream of trapped (-78°C) helium.

Adsorption Procedures

This category of procedures includes every operation performed on
the crystals subsequent to their polishing. The procedures described in what follows are described for the case of an isotherm on the sample.

It was also necessary to measure a blank isotherm, that is, an isotherm on the nickel cell without the sample. This was done exactly as the isotherm on the sample except that the steps concerning the placement of the crystals in the cell are obviously not applicable.

The first operation is the placing of the sample in the cell. As mentioned in the previous section, each crystal has a small hole (one-eighth inch diameter) in one end. A one-eighth inch diameter bar was machined out of the same copper that the crystals were grown from, and the crystals (nine in all) were gently slipped onto this bar. The crystals were then lowered into the sample cell, and the bar was fitted into the grooves on either side of the cell (see Figure 21). The crystals hung loosely without contacting the nickel. Previously, a gasket had been formed and annealed, and this was now placed in position and the top bolted to the body of the cell. The gasket material was, as previously mentioned, copper (electrolytic grade) in the form of a sheet 0.010 inch thick initially. The bolts employed were one-fourth inch stainless steel (type 316) cap screws. The nuts were of the same material.

As indicated in Figure 21, eight bolts were employed on a one and one-half inch bolt circle. It was found that even with this many bolts, much effort was required in the making of a tight seal. Once the seal was made, however, no difficulties were ever encountered even under temperature cycling from 71°K to 1075°K. This was in spite of the fact that the coefficient of linear thermal expansion of the steel is appreciably
different from the nickel.

Once the seal was made, it could be leak tested in the following way. Valves 2 and 4 (see Figure 20) were closed and kept closed for a period of time consistent with the magnitude of leak expected. Then valve 4 was opened, and the resulting movement of the needle on the capacitance manometer recorded. Since the system could not be baked before the seal was tight, a part of this deflection was due to virtual leaks. In order to differentiate between real and virtual leaks, the cryostatic Dewar flask was attached, and the region around the cell was evacuated. This removed whatever component of the observed leak was due to real leaks in the sample cell. Using this method, it was possible to observe leaks of about $10^{-7}$ micron liters per second.

When the cell was vacuum tight, the bake-out oven was installed and the heaters energized. The trap in the high vacuum pumping system was kept at liquid nitrogen temperatures throughout the bake. The trap in the clean system was heated to about 200°C during the bake. The bake typically lasted about ten hours, with the pressure in the hot part of the system falling to about $10^{-4}$ Torr toward the end of the bake. On cooling, this pressure fell below $10^{-7}$ Torr and on further pumping, decreased to $1-5 \times 10^{-8}$ Torr. The trap in the clean system was refrigerated when the pressure fell to $10^{-6}$ Torr or so. This prevented the trapping of great quantities of water in this trap and rendered the vacuum fairly insensitive to the liquid level. The other trap was also kept cold in all the subsequent operations. Having removed the oven, the valve drivers and other hardware were installed on the system.

With the establishment of high vacuum in the system, the sample was
ready for the reduction treatment. The tube heater, which was left in place from the bake out, was energized and the temperature in the vicinity of the sample adjusted to 525 ± 25°C. The adjustment was accomplished by use of chromel-alumel thermocouple. Valve 5 was then closed and the break seal on the hydrogen bottle broken. Valves 4, 6, and 7 were then closed and valve 5 opened and then closed. This established a pressure of about 0.9 atmospheres of hydrogen in the sealed off portion of the system. Valve 2 was then closed and valve 4 opened (valve 3 was open at the time). This last expansion was calculated to give a pressure of one-half to two-thirds of an atmosphere in the sample cell. Valve 3 was then closed, and the hydrogen allowed to reside in the cell for a period of from five to twenty minutes. Valve 2 was opened at the end of this period and the hydrogen pumped out for about five minutes. This procedure was iterated until a total treatment time of about one to two hours was achieved.

The cell was heated to 750 ± 25°C after the treatment and maintained at this temperature until a pressure of 10^{-4} mm was obtained in the sample cell. The evolution of solution hydrogen is responsible for this residual pressure. Although some hydrogen is quenched in by the cooling of the sample before high vacuum is obtained, it is felt that in the physically interacting system under study the presence of small amounts of dissolved material will not affect the results. After the cell is cooled, the pressure falls rapidly to 10^{-6} mm. At this time the system is deemed ready for measurement. The total time from the commencement of hydrogen treatment to the beginning of a measurement is of the order of six to seven hours.

Following the cooling period described above, the cell is refrig-
erated in an appropriate bath. In the temperature range of interest, this consists of a Dewar of liquid nitrogen and oxygen mixed together. The mixture should be rich in the higher boiling component (oxygen here) since the control mechanism can only adjust the temperature downward. Once the controller is actuated and a temperature of interest has been established in the bath, a pressure of about 100 mili-Torr of hydrogen is admitted to the cell. This is to speed the thermal equilibration of the crystals with the walls of the cell. It was found that this was necessary, and it is reasonable that this would be so, since the extreme brightness of the two surfaces results in the elimination of any radiative heat transfer between the two surfaces. There was found no evidence that any irreversible absorption of hydrogen occurred at the temperatures of the experiment. After the cell had been cooled for two hours, it was found that reproducible measurements could be made, and this was taken to mean that the temperature of the bath was also the temperature of the sample. The bath temperature was measured with a copper-constantan thermocouple.

The isotherm measurement was carried out according to the following scheme. Valves 2 and 3 were closed, thus isolating the cell from the rest of the system. Valves 4 and 7 were closed, and valve 6 opened, thus allowing krypton into the volume between them. Then valve 6 was closed. Now valve 4 was opened until krypton bled into the volume between valves 3 and 4. The amount of krypton added was monitored by following the needle of the capacitance manometer during the process. When a suitable amount had been added, valve 4 was closed and the krypton pumped out of the space between valves 4 and 7 by opening valve 7 (valve 1 was open also). Having trapped a prospective dose of gas in the gas burette, its
pressure was measured by allowing helium to leak into the "dirty" side of the capacitance manometer through valve 11 (valve 13 being open). With valve 8 closed, soon the pressure of helium became such that the capacitance manometer indicated a zero pressure differential across the diaphragm. At this point, the mercury was raised in the McLeod gauge, trapping helium at the pressure of the dose. Valve 3 was then opened, allowing the dose to expand into the sample cell. After this was done, the pressure of the trapped helium was measured and recorded as the dose pressure.

After a period of time sufficient for the attainment of equilibrium, the equilibrium pressure was obtained in the following way. The reading of the capacitance manometer was recorded (with the instrument on the most sensitive scale), and valve 3 was closed; then valve 4 was opened, thus evacuating the gas burette. The final reading of the manometer was then recorded and the difference in these readings taken as being proportional to the pressure. The "dirty" side of the manometer had previously been evacuated. The procedure was then repeated for each isotherm point.

The proportionality to the pressure of the aforementioned difference in readings had been determined by calibration, and calibration points were determined at intervals during a measurement to insure that the instrument was functioning properly. The calibration only applied to the most sensitive scale, and a calibration point was determined exactly as a dose pressure was measured with the exception that the amount of krypton added was usually less than a typical dose and the meter reading after the addition was recorded. The procedure of taking differences was
necessitated by the fact that the zero of the instrument drifted somewhat during the period of an isotherm point. This was thought to be due to temperature fluctuations in the room. The period of an isotherm point was about 25 minutes; it is felt that the slight instability does not endanger the measurement of dose pressure, since this was measured within five minutes of having zeroed the instrument.

**Calibration Procedures**

One other type of procedure needs to be discussed; this is that type of procedure employed in the calibration of certain pieces of equipment. One such procedure has already been discussed, that is, the calibration of the capacitance manometer. In this section, calibration procedures will be discussed for the following pieces of equipment: the gas burette (the volume between valves 3 and 4 in Figure 20); the copper constantan thermocouples; and the McLeod gauge.

The calibration of the volume of the gas burette was accomplished by the following technique. A glass vessel with a high vacuum stopcock was attached to the system through two millimeter capillary tubing. The volume of the vessel had been previously determined by measuring the weight of mercury contained by the vessel. In the same manner, the volume of the capillary tube was determined. The stopcock was opened and the whole system evacuated. Then the stopcock was closed and a dose of gas added to the gas burette; this pressure was then measured as described in the section on the measurement of dose pressure. The stopcock was opened, allowing the gas to expand into a known volume, and the pressure was measured after the expansion. From these data and the gas law, it was possible to calculate the volume of the gas burette. At this point, the calibrating
vessel was removed from the system, and the volume previously determined was corrected for the removal of a length of capillary. Now, knowing the volume of the gas burette, the dead space of the system was determined using the burette as the known volume.

The copper-constantan thermocouples were calibrated with the help of a platinum resistance thermometer which was previously calibrated by the National Bureau of Standards. The thermocouples and the thermometer were emersed in a liquid oxygen bath. After emersion, the value of the resistance and of the EMF (relative to an ice bath) was recorded. It was found that the EMF measured was in disagreement with the published value by around a degree. In order to correct for this difficulty, it was assumed that the difference in the measured value and the literature value varied linearly with temperature. Since at zero degrees (the ice bath temperature) the two values had to agree, only one other point was required for the calibration. This was the oxygen point mentioned above. The linear approximation for the variation of the difference in the experimental and literature values has been suggested and used previously. The bridge used to measure the resistance was a Leeds & Northrop type G-2 Mueller bridge, and the potentiometer used was a Leeds & Northrop model K-2.

The McLeod gauge used was, as previously pointed out, a commercial instrument. Dr. R. A. Pierotti has constructed and calibrated a McLeod gauge, and this gauge was used to check the calibration which the manufacturer supplies. The gauges were found to agree over their entire ranges. Having observed this, the supplied calibration was accepted and used in all the measurements.
Discussion of Results

The results of the measurements are summarized by Figures 22 and 23. Figure 22 presents the data for the adsorption on the nickel cell. These were used to subtract from the total adsorption to give the net adsorption on the copper. The nickel cell was treated exactly as it was to be treated in the final measurement. Values of the nickel adsorption at the temperatures of interest were obtained by extrapolation of the data shown by means of the Clapeyron relation. Although this introduces some additional uncertainty, it was felt that since the effect of the nickel adsorption is very small, the additional uncertainty was unimportant.

Figure 23 illustrates the adsorption on the copper computed by the difference technique described above. The solid lines are isotherms computed from the significant structure theory for the parameters listed in Table 3. It is seen that the theory does a good job of fitting the data through the region of the knee, but the isotherm does not flatten out at higher pressure as predicted by the theory. This may be due to the beginnings of second layer formation.

Table 3. Interaction Parameters for the Copper-Krypton System

<table>
<thead>
<tr>
<th>$U_0$ (cal/mole)</th>
<th>$v \times 10^{-12}$ (sec$^{-1}$)</th>
<th>$\epsilon/k$ (°K)</th>
<th>$A_m$ ($\AA^2$/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3500^a$</td>
<td>$0.6^a$</td>
<td>$100^a$</td>
<td>$19.5^b$</td>
</tr>
</tbody>
</table>

$^a$ Determined as described in the text

$^b$ Obtained from reference 44
Figure 22. Adsorption of Krypton on Polycrystalline Nickel

Note: Lines are drawn to fit data.

- ○ 77.1°C ± 0.1°C
- ○ 80.4°C ± 0.1°C
- ○ 82.67°C ± 0.05°C
Figure 23. Adsorption of Krypton on (1,1,1) Copper
The major area of disagreement between the theory and the data is in the case of the 90.10°K isotherm. The disagreement is of the type which could be explained by errors inherent in the correction for thermal transpiration. The method used to correct for this effect is based on the work of Miller. This approach utilizes an approximate solution to Weber's equation to derive a correlation between the pertinent variables. Then the available data for a given system are used to derive an empirical formula. This formula then can be used to estimate the effect at conditions other than those at which the data were measured. The correlation for krypton was based on the work of Rosenberg. This work used 78°K as the cold temperature. Miller's method has been applied by Levy, and it has led to good consistency in the application of thermodynamic relations to the corrected data. Levy's work was done at temperatures below 78°K, and also closer to 78°K than the measurements at 90.10°K are. Thus it may be that the method of Miller is being pressed too hard; that the range of effective applicability of the method is smaller than the 12°K demanded of it here. This may or may not be the correct explanation, but it is felt that the data at 90.10°K are somewhat faulty and the indications are that the problem is probably systematic in nature.

Whatever the case may be, it is felt that the fit is rather good considering the experimental uncertainty involved. The shapes of the isotherms are predicted well by the theory, and this lends support to the notion that the surface is energetically homogeneous and also supports the contention that the adsorption is mobile. Interestingly, it appears that the nickel adsorption does not conform to one or perhaps either of these requirements. The nickel is polycrystalline, and the heterogeneity
arising from this fact may be responsible for this behavior.

The parameters for the copper adsorption (see Table 3) are interesting. The value of $U_0$ is exceedingly high. No value this high has ever been reported for the adsorption of krypton on a solid. In light of this high interaction, it is rather difficult to understand the low value of $\nu$ required for the fit. Although the parameters have considerable uncertainty, it is felt that the strange combination of $U_0$ and $\nu$ necessary to achieve a fit may indicate that the metal-gas interaction is of a fundamentally different nature than the traditional Van der Waals derived forces.

The parameter $\epsilon/k$ for krypton is $171^\circ K$, while from Table 3 the surface value is $100^\circ K$. This sort of decrease is qualitatively in agreement with the predictions of the Sinanoglu-Pitzer theory.

It should be noted that after the conclusion of the second measurement at $87.7^\circ K$, the system changed character radically. The adsorption became stronger, and the apparent area somewhat higher. The cell was taken down and the sample examined visually. No trace of contamination could be detected. The crystals seemed to possess the same mirror finish which they had when they were introduced into the system. However, when the crystals were again subjected to the normal electropolishing treatment, a small area at what had been the top in the sample cell was etched instead of polished. The remainder of the crystal polished normally. This indicated that some impurity had coated the upper regions of the crystals. There was a silver solder joint in the line, above the cell, and it was concluded that a speck of flux residue had fallen into the cell and caused the radical behavior observed. The joint had been cleaned with steam when it was installed, and it has been observed that this removes all traces of
flux residue. It has also been observed, however, that, on heating, a spongy white material accumulates in the region of a fluxed silver solder seal even if it has been steam cleaned. It was this material to which the impurity was ascribed. The data obtained previous to the contamination was taken to be characteristic of the copper. The main evidence supporting this contention is the shape of the isotherms which indicated a homogeneous surface, not one partially contaminated. Also, it can be seen from the figure that the values of $v_{geo}$ and $v_{ss}$ are similar, the roughness factor being about 1.6, a typical value in a system of this sort.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Significant Structure Theory

It is concluded that the significant structure theory as applied to physical adsorption in the monolayer region has great potential as a method of treating the surface gas interaction parameters. The theory also has promise in the investigation of the interactions in the adsorbed phase, at least as a comparative method. It is further concluded that the values of the interaction parameters in Table 3 are as trustworthy as any existing values.

Copper-Krypton System

A technique for the measurement of adsorption data on small area samples has been developed. It is concluded that with certain modifications the system will allow the accurate determination of surface gas adsorption parameters. It is also concluded that the copper-krypton system is an extremely interesting one; that copper apparently exhibits a very strong attraction for krypton, and that the magnitude of this interaction is in the neighborhood of 3500 calories per mole. The krypton-krypton interaction on the surface appears to be characterized by a value of $\epsilon/k$ of about 100°K compared to 171°K for the gas phase value. It is also concluded that the methods of crystal preparation described are effective in producing an energetically homogeneous surface.
Recommendations

Significant Structure Theory

It is recommended that the theory be tested on large amounts of data as they become available. It is further recommended that the theory be extended to include the case of multilayer adsorption.

Copper-Krypton System

It is recommended that the system be investigated in greater detail. The construction of a cryostat allowing the attainment of higher temperatures will lead to increased precision in the data. It is further recommended that a system be constructed which is free from the presence of silver solder joints. These two modifications will, it is felt, result in much more meaningful measurements on this interesting system.
It is seen that the transformation from the variables $A$, $N_s$, and $T$ to the variables $\theta$, $N_m$, and $T$ occurs throughout the theoretical sections and deserves some attention here. It is first encountered in the change from equation 18 to equation 19. The transformation is represented by

$$A = A^0_m/\theta \quad (A-1)$$

$$N_s = \theta N_m$$

$$T = T$$

where the symbols have the same meaning as in equations 18 and 19.

The thermodynamics of a two-dimensional system may be expressed by the differential relationship

$$dF_s = -\Pi dA_t - S_s dT + \mu_s dN_s \quad (A-2)$$

where $A_t$ is the total area of the surface, and the other symbols have their same meanings as earlier. Remembering that $A_t = A\cdot N_s$, and substituting from equation A-1 into equation A-2, one obtains
\[ dF = (\mu_s N_m) \, d\theta - S_s \, dT + (\mu_s - \Pi A_m^{\theta}) \, \theta dN_m \] 

(A-3)

where the symbols are all defined earlier. Thus, after making substitutions from equation A-1 into equation 18 to obtain equation 19, equation 20 follows from the relation

\[ \mu_s = \frac{1}{N_m} \left( \frac{\partial F}{\partial \theta} \right)_{T, N_m} \]

This expression is obtained from the first term on the right side of equation A-3; one sees that the third term would also yield an expression for \( \mu_s \).

For the calculation of the critical properties, use is made of the criteria

\[ (\partial P/\partial \theta)_{T, N_m} = 0 \] 

(A-4)

\[ (\partial^2 P/\partial \theta^2)_{T, N_m} = 0 \]

where the symbols have been previously defined. These relationships are the experimental criteria for detecting a two-dimensional condensation by adsorption work.

In the calculation of the virial coefficients, use was made of the relationship

\[ dF_s = - \Pi N_s dA - S_s dT + (\mu_s - \Pi A) dN_s \] 

(A-5)
where the symbols are the same as before. This relation is an intermediate in the transition from equation A-2 to equation A-3. Thus, the free energy was written in terms of $A$, $T$, and $N_s$, and the equation of state derived from $\Pi = -(1/N_s)(\partial F_s/\partial A)_T, N_s$. Then the virial coefficient was extracted using $B_{sd} = \lim_{A \to 0} (\partial Z_c/\partial A)_T, N_s$. The symbol $Z_c$ here refers to the compressibility factor $(k_A/kT)$.

These methods of calculating the thermodynamic relations are common to all the approximations used.

The Fitting Technique

The developments of the first part of Chapter III will be set forth in more detail in this section.

The main point where elaboration is required is in the transition from equation 37 to equation 38. In equation 37, the constant $C'$ is defined by

$$C' = ((2\pi mkT/h^2) e^{A_0^o} f_z (1+j) U_0/RT \tag{A-6}$$

where $j$ is the number of degrees of freedom which are changed to vibrations from rotations on adsorption. The assumption has been made that the new vibrations can be characterized by the same frequency as the old. The function $f_z$ is the quantum mechanical partition function for a harmonic oscillator. Taking the logarithm of both sides of equation A-6 and rearranging
\[
\ln(\mathcal{C}') - \ln((2\pi mk/h^2) e^{A_m^0} T_{fZ}^{(1+j)}) = \frac{U_0}{RT}
\]  

(A-7)

where the symbols have been defined previously. Inspection of equation A-7 reveals that the form of \( f_z \) is going to complicate any subsequent manipulations. Thus, it was decided to insert the classical oscillator partition function for convenience. Substituting \( f_z = (kT/h\nu) \) into equation A-7 and rearranging

\[
\ln(\mathcal{C}') - (2 + j) \ln(T) = \frac{U_0}{RT} + \ln(2\pi mkA_m^0 e/h^2) + (1 + j) \ln(\kappa/h)
\]

which is equation 38. Equation 39 is then derived by writing equation A-8 for two temperatures (\( T_1 \) and \( T_2 \)) and subtracting. The result of this subtraction is

\[
\ln(C_f') - \ln(C_f) - (2 + j) \ln(T_1/T_2) = (U_0/R)((1/T_1) - (1/T_2))
\]

(A-9)

where the symbols have been defined previously. Rearrangement of equation A-9 yields

\[
U_0 = \left(\frac{RT_1T_2}{(T_2 - T_1)}\right) \ln((C_f'/C_f)(T_2/T_1)^{2+j})
\]

(A-10)

which is equation 39.

The following compilation of values of \( g(\theta) \) may prove useful.
Table 4. Tabulated Values of the Function \( g(\theta) \)

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( g(\theta) )</th>
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<tbody>
<tr>
<td>0.02</td>
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<tr>
<td>0.04</td>
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<td>0.20</td>
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<td>1.006</td>
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<tr>
<td>0.50</td>
<td>0.589</td>
</tr>
<tr>
<td>0.60</td>
<td>0.229</td>
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<tr>
<td>0.70</td>
<td>-0.341</td>
</tr>
<tr>
<td>0.80</td>
<td>-1.268</td>
</tr>
<tr>
<td>0.90</td>
<td>-2.865</td>
</tr>
</tbody>
</table>
APPENDIX B

EXPERIMENTAL DATA

The raw data associated with the $i$th isotherm point consist of the pressure of the dose, $P_{d1}$, the equilibrium pressure measured at the capacitance manometer, $P_{e1}$, and the temperature of the sample, $T_e$. These quantities along with the various known volumes of the system allow the computation of an isotherm.

The refinement of these pieces of information into an isotherm proceeds according to the following scheme. First, the equilibrium pressure in the sample cell, $P_{e1}'$, is obtained by the use of the method of Miller to correct for thermal transpiration. This is then the proper pressure for the particular isotherm point. The amount of krypton on the surface is deduced by computing the total amount added and subtracting the amount necessary to produce the observed pressure in the gas phase. For the $j$th isotherm point, the total amount of krypton added is given by

$$v_t = \left( \sum_{i=1}^{j-1} (P_{d1} - P_{e1}) + P_{d1}' \right) \cdot \frac{v_b}{760} \cdot \frac{273.15}{296}$$  \hspace{1cm} (B-1)$$

where $v_t$ is the amount added expressed in cc (S.T.P.), and $v_b$ is the volume of the gas burette in cc. The $i$ and $j$ refer to the different isotherm points, and the pressures are in Torr. The last term is the correction of the room temperature to standard temperature and pressure. In order to
compute the amount on the surface, one must be able to compute the amount of krypton remaining in the gas phase. At the low pressures of the experiment, departures from gas phase ideality for krypton are negligible. Thus, for the $j^{th}$ point, the amount of krypton in the gas phase is just

$$v_g = \left( \frac{P_{ej}}{760} \right) \cdot v_{ds} \cdot \left( \frac{273.15}{296} \right)$$  \hspace{1cm} (B-2)$$

where $v_{ds}$ is the effective dead space of the system, and the pressure is in Torr. The dimensions of $v_g$ are cc (S.T.P.). The value of $v_{ds}$ is arrived at in the following manner. If $v_h$ is the volume in cc of the system which resides at room temperature during a measurement, and $v_c$ is that volume which resides at $T_e$, then the effective dead space is

$$v_{ds} = v_h + v_c \left( \frac{296}{T_e} \right) \cdot f_{tt}$$  \hspace{1cm} (B-3)$$

where $f_{tt}$ is the ratio of the pressure in the cold region to that in the hot region. This quantity is obtained using Miller's method as described earlier. The quantity $v_b$ is determined by an expansion technique, and the total volume of the system is determined similarly. The quantity $v_c$ is computed from the dimensions of the sample cell, the density of copper, and the weight of copper added. The density of copper used was 8.92 gm/cc. Then $v_h$ is obtained by a difference method. Using equations B-1, B-2, and B-3, one may then compute the volume adsorbed by use of the following expression

$$v_a = v_t - v_g - v_{cell}$$  \hspace{1cm} (B-4)$$
where $v_a$ is in S.T.P. cc, and $v_{cell}$ is the volume adsorbed on the nickel. A plot of $v_a$ versus $P_{si}$ is the isotherm equation.

In the following data compilation, the quantities are calculated as described above with the following values for the pertinent volumes: $v_c = 16.7$ cc $\pm$ 0.5 cc; $v_h = 20.0$ cc $\pm$ 0.5 cc; and $v_b = 14.3$ cc $\pm$ 0.1 cc. The diameter of the tube between the hot and cold volumes was 1.32 mm. This quantity was used in the thermal transpiration correction.

Table 5. Experimental Data for the Copper-Krypton System

<table>
<thead>
<tr>
<th>$P_{ei} \times 10^3$ (Torr)</th>
<th>$P_{si} \times 10^3$ (Torr)</th>
<th>$v_a$ (STP cc) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16$^b$</td>
<td>0.09$^c$</td>
<td>0.55$^d$</td>
</tr>
<tr>
<td>0.27</td>
<td>0.14</td>
<td>1.35</td>
</tr>
<tr>
<td>0.43</td>
<td>0.23</td>
<td>2.07</td>
</tr>
<tr>
<td>0.88</td>
<td>0.48</td>
<td>2.82</td>
</tr>
<tr>
<td>2.21</td>
<td>1.26</td>
<td>3.32</td>
</tr>
<tr>
<td>4.92</td>
<td>2.96</td>
<td>4.00</td>
</tr>
</tbody>
</table>

$^a$The limit of error in this quantity is approximately $\pm$ 0.05°K.
$^b$The limits of error in this column are approximately $\pm$ 0.05 $\times 10^{-3}$ Torr.
$^c$The limits of error in this column are approximately $\pm$ 0.05 $\times 10^{-3}$ Torr, but the values depend on the thermal transpiration correction, and no limit of reliability can be placed on this correction.
$^d$The limits of error in this column are approximately $\pm$ 2 percent of the value.
### Table 6. Experimental Data for the Copper-Krypton System\(^a\)
87.70°K--Run 1

<table>
<thead>
<tr>
<th>(P_{ei} \times 10^3) (Torr)</th>
<th>(P_{si} \times 10^3) (Torr)</th>
<th>(v_a) (STP cc) (\times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>0.15</td>
<td>1.13</td>
</tr>
<tr>
<td>0.94</td>
<td>0.53</td>
<td>2.27</td>
</tr>
<tr>
<td>2.91</td>
<td>1.71</td>
<td>3.05</td>
</tr>
<tr>
<td>6.50</td>
<td>4.03</td>
<td>3.91</td>
</tr>
<tr>
<td>11.0 (^b)</td>
<td>7.17</td>
<td>4.90</td>
</tr>
</tbody>
</table>

\(^a\)The limits of error applicable to these data are the same as those given in the footnotes to Table 5.

\(^b\)This point is not included in the figure because it is at too high a pressure.

---

### Table 7. Experimental Data for the Copper-Krypton System\(^a\)
87.70°K--Run 2

<table>
<thead>
<tr>
<th>(P_{ei} \times 10^3) (Torr)</th>
<th>(P_{si} \times 10^3) (Torr)</th>
<th>(v_a) (STP cc) (\times 10^3)</th>
</tr>
</thead>
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<tr>
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<tr>
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<td>0.78</td>
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</tr>
<tr>
<td>4.30</td>
<td>2.61</td>
<td>3.36</td>
</tr>
</tbody>
</table>

\(^a\)The error limits applicable to these data are the same as those given in the footnotes to Table 5.
Table 8. Experimental Data for the Copper-Krypton System$^a$
90.10°K

<table>
<thead>
<tr>
<th>$P_{ei} \times 10^3$ (Torr)</th>
<th>$P_{si} \times 10^3$ (Torr)</th>
<th>$v_a$ (STP cc) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43</td>
<td>0.24</td>
<td>0.78</td>
</tr>
<tr>
<td>0.77</td>
<td>0.43</td>
<td>1.58</td>
</tr>
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<td>1.62</td>
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<td>2.31</td>
</tr>
<tr>
<td>5.80</td>
<td>3.61</td>
<td>3.16</td>
</tr>
</tbody>
</table>

$^a$The error limits applicable to this table are the same as those given in the footnotes to Table 5.

The adsorption on the nickel cell was measured exactly as the copper adsorption, except that the value of $v_c$ was 20.0 cc $\pm$ 0.5 cc. This was due to the fact that the copper had not been added to the cell. The data are presented in the following tables.
Table 9. Experimental Data for the Nickel-Krypton System
77.1 K\textsuperscript{a}

<table>
<thead>
<tr>
<th>$P_{ei} \times 10^{3}$ (Torr)$^{b}$</th>
<th>$P_{si} \times 10^{3}$ (Torr)$^{b}$</th>
<th>$V_{cell}$ (STP cc)$^{b} \times 10^{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>0.27</td>
<td>0.39</td>
</tr>
<tr>
<td>1.10</td>
<td>0.59</td>
<td>0.64</td>
</tr>
<tr>
<td>1.90</td>
<td>1.00</td>
<td>0.81</td>
</tr>
<tr>
<td>3.80</td>
<td>2.20</td>
<td>0.94</td>
</tr>
<tr>
<td>6.40</td>
<td>3.90</td>
<td>1.03</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The error limit applicable to this quantity is ± 0.1 K.

\textsuperscript{b}The error limits applicable to these data are the same as those given in Table 5 for the corresponding quantities.
### Table 10. Experimental Data for the Nickel-Krypton System
80.5°K

<table>
<thead>
<tr>
<th>$P_{ei} \times 10^3$ (Torr)</th>
<th>$P_{si} \times 10^3$ (Torr)</th>
<th>$V_{cell}$ (STP cc) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>0.31</td>
<td>0.22</td>
</tr>
<tr>
<td>1.14</td>
<td>0.62</td>
<td>0.46</td>
</tr>
<tr>
<td>2.10</td>
<td>1.18</td>
<td>0.66</td>
</tr>
<tr>
<td>10.2</td>
<td>6.60</td>
<td>1.02</td>
</tr>
</tbody>
</table>

*a The error limit applicable to this quantity is ± 0.1°K.

*b The error limits applicable to these data are the same as those given in Table 5 for the corresponding quantities.

---

### Table 11. Experimental Data for the Nickel-Krypton System
82.7°K

<table>
<thead>
<tr>
<th>$P_{ei} \times 10^3$ (Torr)</th>
<th>$P_{si} \times 10^3$ (Torr)</th>
<th>$V_{cell}$ (STP cc) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94</td>
<td>0.52</td>
<td>0.21</td>
</tr>
<tr>
<td>2.15</td>
<td>1.23</td>
<td>0.46</td>
</tr>
<tr>
<td>4.93</td>
<td>3.02</td>
<td>0.62</td>
</tr>
<tr>
<td>10.0</td>
<td>6.48</td>
<td>0.80</td>
</tr>
</tbody>
</table>

*a The error limit applicable to this quantity is ± 0.1°K.

*b The error limits applicable to these data are the same as those given in Table 5 for the corresponding quantities.
APPENDIX C

DISCUSSION OF UNCERTAINTIES IN PARAMETERS

The task of assigning a meaningful error limit to a parameter arrived at by the methods of this work is a difficult one. Whatever estimate of the uncertainty is made, one must always view it in the light of the model. For this reason, no error limits were included in the tables of derived parameters. The following remarks are meant to give an overall picture of the kind of uncertainties involved in the extraction of the parameters.

The parameters of greatest interest are the surface-gas interaction parameter, $U_Q$, and the adsorbate-adsorbate interaction parameter, $\epsilon$. The effect of variation in these parameters on the isotherms will be investigated here. Figure 24 shows the effect of varying $U_Q$. The point in the figure is of a size representative of the experimental uncertainties in the experimental work reported earlier. The dashed lines correspond to values of $U_Q$ of 3550 and 3650 calories per mole; the solid curve corresponds to $U_Q = 3600$ calories per mole. The values of all other parameters are the same for the three curves. The figure indicates that uncertainties of about 50 calories per mole are to be expected for the parameter $U_Q$. One must bear in mind that this uncertainty refers to the ability of the model to fit the data and is not an estimate of the nearness of the value of the parameter to physical reality. In the cases treated in Chapter III of this work, the data are somewhat more reliable than the
A typical experimental point

- $U_0 = 3550$ cal/mole
- $U_0 = 3600$ cal/mole
- $U_0 = 3650$ cal/mole

Figure 24. The Effect of Variation of $U_0$ on the Isotherm

$T = 87.3^\circ K$
point in Figure 24 indicates. Thus, the values of $U_0$ reported in Tables 1 and 2 are probably more precise than ± 50 calories per mole.

The parameter $\epsilon$ exercises a strong effect on the position as well as on the shape of the isotherm. Figure 25 shows the effect on the position; the curves all correspond to a value of 3600 calories per mole for $U_0$. As indicated, $\epsilon$ varies over a ten calorie per mole range. If one uses the fitting technique to arrive at values of $U_0$ and $\nu$, then the positioning effect of $\epsilon$ may be used to determine its best value. If, on the other hand, one evaluates parameters by simply scanning ranges of all parameters and comparing computed isotherms with experiment, one must rely on the shape of the isotherm to determine $\epsilon$, since $U_0$ and $\epsilon$ interfere with each other in the positioning of the isotherm. Figure 26 shows the effect of $\epsilon$ on the shape of the isotherm. The two curves have had their values of $U_0$ adjusted to yield the demonstrated coincidence. The curves correspond to $\epsilon/k = 100^\circ K$ and $\epsilon/k = 110^\circ K$. The point is again of a typical size for a datum point in the experimental work reported earlier. It appears that ± 5$^\circ K$ is a somewhat optimistic estimate of the uncertainty, but ± 10$^\circ K$ is perhaps somewhat pessimistic. Perhaps ± 7$^\circ K$ is a realistic estimate. It is clear that the parameters are interrelated, and that no unique set of values can be derived from one isotherm; in general, data exist at several temperatures, and this removes the ambiguity.

The effect of the parameter $\nu$ is greatest on the temperature variation of the isotherm. In other words, it affects the heat of adsorption. Uncertainties in this parameter are large because of its rather weak effect on the isotherm. A rough estimate of this uncertainty might be ± 0.25 x $10^{12}$ sec$^{-1}$. 
Figure 25. The Effect of Variation of $\epsilon$ on the Position of the Isotherm
Figure 26. The Effect of Variation of $\epsilon$ on the Shape of the Isotherm
It should again be stressed that the error limits given above refer to the parameter in the model and not to reality. Whether or not the parameter is close to the value of some analogous physical property depends, of course, on the merit of the model as a representation of the physical system.

In cases where values of the parameters $U_0$ and $\nu$ are available from other treatments (see Table 2), the agreement with the present theory is generally good. This indicates that the significant structure model is a good representation of adsorption on homogeneous solids.
APPENDIX D

DETAILS OF SOME EXPERIMENTAL DIFFICULTIES

During the course of the experiment reported in this work, numerous difficulties were encountered; some of these were of sufficient interest to be reported here.

In the early stages of the work, a sample cell was built from a magnetic stainless steel, the number of which was not known. The steel was probably in the 400 series. The cell was polished and mounted on the system. It initially exhibited a roughness factor of about three. On hydrogen treatment, however, the roughness factor increased to about ten or more. At the time, the hydrogen treatment was being done with tank grade hydrogen which was advertised as having a dew point of -78°C. On disassembly, the steel cell was found to be coated with a bluish film which was evidently the source of the dramatic increase in surface area. Calculation of the thermodynamics of the system indicated that the chromium which was probably present in the steel was capable of decomposing water to yield chromic oxide and hydrogen in an atmosphere whose dew point was -78°C. It was to this effect that the film was attributed.

The obvious solution to the problem was to use reagent grade gases and thus avoid the troublesome reaction. However, in order to improve the roughness mentioned before, it was decided to construct a cell of copper (which could be electropolished with ease). In order to facilitate the opening of the seal, it was decided to make the top out of type 304
stainless steel which has the same coefficient of linear expansion as the
copper but which will not diffusion weld at the seal. The composite cell
was found to be vacuum tight over the range of operation of the apparatus,
but, on hydrogen treatment, the same bluish film was observed on the steel
top. This again gave rise to a non-reproducible blank isotherm. Here it
was concluded that the water which produced the interfering oxide was
the product water from the reduction of the copper oxides.

After the repeated difficulties with the stainless steels, it was
decided that the nickel cell would probably solve the problems. The oxides
of nickel are unstable at the conditions of the hydrogen treatment, and
the material has good machinability and mechanical properties. The nickel
cell did solve the problems and was used in the experiment.

During one attempt at measurement, a very interesting thing occurred.
The cell contained the copper, and after hydrogen treatment, an isotherm
measurement was commenced. The adsorption was found to be much weaker than
had been previously observed. On disassembly, the cell was found to be
coated with a dark (almost black) film, and the crystals were coated to
some extent with a whitish film. Both of these films proved resistant to
chemical attack. There had been one difference in the experimental pro­
cedure for this experiment; that was that during the bake-out of the sys­
tem, the trap in the high vacuum pumping system had been kept at dry ice
temperature instead of the normal liquid nitrogen temperature. From this
and the extreme inertness of the films, it was concluded that the contami­
nation had its origin in the diffusion pump oil. The film on the nickel
would thus be carbon because of the cracking activity of nickel toward
hydrocarbons, and the film on the copper might be some intermediate decom­
position product. At any rate, this difficulty was never encountered in any other experiment.

Another interesting though not unexpected phenomenon occurred during the measurement of isotherms on the copper crystals. The crystals, as mentioned earlier, were suspended loosely in the cell. It was observed that at any point of contact between two crystals, a rather strong diffusion weld occurred. Since these were very small (typically 0.1 mm in diameter), they had no effect on the experiment.
APPENDIX E

DISCUSSION OF THE ETCH PIT TECHNIQUE
FOR CRYSTAL CHARACTERIZATION

Young has been able to demonstrate the existence of an intimate relationship between the properties of copper single crystals and the characteristics of the pits formed on them by the action of certain chemical agents. In particular, he was able to show that, under certain conditions, the quality of a crystal (in terms of its defect structure) was inversely related to the number density of the etch pits formed by the action of a certain etching solution. In the work reported here, the relationship between the geometry of the etch pit and the orientation of the crystal has been used to characterize the orientation of a crystal face.

The etching conditions used in this work are very easy to achieve. The crystal is dipped in nitric acid (concentrated) for about two seconds and then rinsed in distilled water. On the (1,1,1) face, this produces the triangular etch pits illustrated in Figure 27. The micrographs were taken at a magnification of approximately 150X.
Figure 27. Photomicrographs of Typical (1,1,1) Etch Pits (150X)
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5. Hill, p. 287.


*The abbreviations used here follow the form used by Chemical Abstracts (vol. 55, pt. 9, p. 123).*
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32. Ross and Olivier, p. 124.


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James John McAlpin was born October 28, 1939, in Memphis, Tennessee, to Martha Phillips and Malcolm McAlpin. He was reared in Memphis and graduated from the Elizabeth Messick High School there in June, 1957. He entered the Georgia Institute of Technology in September, 1957, and received the degree Bachelor of Chemical Engineering in June, 1962. While an undergraduate, he participated in the co-operative program in engineering, working for seven quarters in the Field Research Laboratory of the then Socony-Mobil Oil Company. After completing his undergraduate work, he entered the graduate division of Georgia Tech to study for the Doctor of Philosophy in the School of Chemistry. During his graduate work, he held two National Science Foundation co-operative fellowships, and one National Science Foundation regular fellowship.