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# Gas/Solid Interaction at Various Degrees of Surface Coverage

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## ABSTRACT

Adsorption and desorption studies of gas/solid interfaces have been, in the past, mainly concerned with considerations of mass balance. A strong effort is now being made to define the initial state of the adsorbing surface in terms of solid state structure and composition and to identify the adsorbent-adsorbate complex. The most important experimental parameter in current researches is probably the influence of the pretreatment of the solid before measurements. The properties of some surfaces may change with time as the strain-stress relationships set up in forming the solid adjust slowly toward minimum surface free energy. The pretreatment may include some combination of thermal, electrical, and chemical methods.

It is increasingly relevant to report a surface property in terms of unit surface. The physical adsorption of nitrogen and krypton at low temperatures may be used to obtain the necessary data for a surface area evaluation. The determination of  $v_m$  (the volume of nitrogen at STP required to form a monolayer of adsorbed gas) can be accomplished by the point B method or by the BET procedure, the latter requiring fewer data. In special cases, other adsorbates such as ethane and carbon dioxide have proved useful.

Multilayer adsorption presents many unsolved problems; the theoretical difficulties are similar to those encountered in studies of the liquid state. Current researches at fractional surface coverage attempt to express the surface nonuniformity in terms of an energy distribution as a function of surface coverage. Considerable interest is now being expressed in the field of "high-temperature" physical adsorption. At the corresponding low surface coverage, there is minimum interaction between adsorbate molecules.

Development of modern gas chromatography and mass spectrometry make it possible to follow the partial pressures of all gaseous reactants and products of a gas/solid system. Facility of data collection makes possible more elaborate experimental designs. The ability to analyze complicated gas mixtures enables new studies to be made of selective adsorption in multiple-component systems.

High-vacuum technology is rapidly being applied to researches at low surface coverage. Surface properties are very sensitive to adsorbed impurities (mobile and immobile) that originate either in the environment or as decomposition products from sample preparation. Only in ultrahigh vacuum systems can one minimize the impurity and study its influence systematically. There is an increasing use of evaporated films or otherwise vacuum-formed deposits in order to study fundamental surface properties. A greater insight into the nature of the gas/solid interaction is thus possible which holds great promise for the growth and development of this phase of surface chemistry.

## PROBLEM STATUS

This is an interim report; work on the problem is continuing.

## AUTHORIZATION

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## GAS/SOLID INTERACTION AT VARIOUS DEGREES OF SURFACE COVERAGE

### INTRODUCTION

The experimental effort in adsorption at the gas/solid interface is very extensive. In this report it is proposed to (a) survey recent researches of interest to surface chemistry, (b) mention some of the important current trends in their broader aspects, and (c) present the material from the point of view of surface coverage.

Grouping of adsorption phenomena by coverage (denoted by  $\theta$ ) has practical value. A realistic view of the boundary of a solid is never the mathematical plane that must be assumed in theoretical models. On an atomic scale the boundary includes crystal faces of a composition, extent, and orientation that are fixed during the formation and pretreatment of the solid. The residual reactants and products of side reactions are among the debris that accumulates in the boundary in trace and larger quantities. These and other imperfections of the boundary become more significant with decreasing coverage at the gas/solid interface and as experimental techniques attain greater sensitivity to cope with properties of the decreased coverage.

Four classifications of coverage are:

1. Completion of the monolayer
2. Multilayer formation
3. Fractional monolayer
4. Sparsely covered surfaces

The BET model (19) has furnished the required estimate of monolayer coverage (usually designated by  $v_m$ , the volume adsorbed at STP), and the coverage is then given by the ratio of the actual adsorbed volume  $v$  to that required for monolayer coverage ( $\theta = v/v_m$ ). Fractional coverage is, of course, a calculated quantity since molecular clusters having both width and depth may exist at isolated sites to a limited extent. The sparsely covered surface has attained considerable importance as a result of its accessibility via the new ultrahigh vacuum techniques.

The many applications of adsorption in research and technology involve approximately a range of  $10^6$  in surface coverage corresponding to a range of  $10^{12}$  in pressure, although this may not have been observed for any one gas/solid system. Some examples are given in Table 1 for a number of physical adsorption and chemisorption operations. It is quite an accomplishment to reach a level where the absolute total surface coverage is about  $10^{-5}$ . In order to gain a feeling for this magnitude, consider the area of clean surface ascribed to the tungsten tip of the field-emission microscope; this has been given as approximately  $10^{-10}$  cm<sup>2</sup> or  $10^6$  Å<sup>2</sup>. When only three molecules, each about  $10$  Å<sup>2</sup> in cross section, are on this surface,  $\theta$  is about  $10^{-5}$ . A surface of  $10^4$  Å<sup>2</sup> having one percent of a monolayer (either adsorbed or as replaced surface atoms) would contain ten such molecules. Solid state investigators have used this practical level as a definition of "an atomically clean surface" (1), and this degree of coverage is readily attained in ultrahigh

Table 1  
Some Adsorption Phenomena as a Function  
of Surface Coverage

Coverage	Phenomenon or Application
Physical Adsorption	
0.9 to 1.1	Surface area estimates
0.1 to condensation	Industrial separations Solvent recovery Water vapor removal
0.001 to 0.1	Gas phase chromatography
0.0001 to 0.01	Retention of toxic gases
0.0001	Inert gas adsorbed at $10^{-10}$ torr
0.00001 to 0.01	After outgassing to $10^{-6}$ torr
Chemisorption (behavior very specific)	
1.0	Completion of monolayer
0.01 to 0.10	Commercial catalytic processes
0.0001 to 0.001	Coverage with oxidation gases on hot carbon
<0.00001	After gettering action and high temperature in ultrahigh vacua ( $<10^{-7}$ torr)

vacuum systems. The lowest coverages estimated in Table 1 for special systems are based on a consideration of coverage calculated for a specified partial pressure and to a surface of high area such as evaporated films.

The overall reaction at a gas/solid interface may be written:



This formulation emphasizes the need to characterize both the starting material and the adsorption complex. It also provides a division of researches into those concerned with the adsorption complex and those attempting to give to a large degree the properties of the initial adsorbing surface. The thermodynamic activity of both complex and solid in Eq. (1) cannot be taken as unity, and it is usually the solid in its standard state that is considered as having unit activity. The experimenter must, of course, be alert to the possibility that the formation of the adsorption complex may modify or deform on an atomic scale the original surface of the solid. Hence, the main problem of the experimental investigator is to characterize the initial and the final states of a gas/solid interaction to a degree that is consistent with the objective of the study.

Information concerning the adsorbent itself has been obtained by a variety of techniques. The relatively recent techniques developed for experimentation in ultrahigh vacuums are essential to an understanding of the detailed structure of a surface, and

these are being used to attain the desired level of reproducibility. The interface can be modified by a variety of pretreatments, intentional or otherwise. Knowing how sharply intermolecular forces decrease with increase in separation, it is not surprising that a knowledge to the chemical composition in the gas/solid interface, i.e., the impurity defects, is of prime importance. Many researches have sought to define the surface in terms of the known underlying crystal structure. Geometric or steric factors are then evoked to bring out the close fit or misfit between atomic separations of the adsorbate and surface.

Finally, the chemical reactivity of groups in the gas/solid interface has for a long time occupied the attention of scientists and technologists, encompassing as it does the field of heterogeneous catalysis. The complexity of surface structure and the amazing range of surface properties will require decades of research to unravel. Studies in the semiconductor field have introduced new experimental techniques, but these have added another magnitude of new problems to the surface chemistry and physics of solids. The task of the experimental investigator today is to make the pertinent observations needed to define the initial and final states of the gas/solid process in terms of atomic structure and energy levels in addition to mass balance, which has dominated research studies previously.

## THE ADSORBATE COMPLEX

### Completion of the Monolayer ( $\theta = 1$ )

Measurements of nitrogen physically adsorbed on the sample in the relative pressure range of approximately 0.05 to 0.25 are used to determine the monolayer capacity. The available methods have been recently reviewed by Young and Crowell (122).

A general procedure for determining surface area is the "point B" method, which when combined with the BET model is used to estimate the monolayer coverage of a solid. Figure 1, used by Brunauer and Emmett (18) in their pioneering studies of iron catalysts, summarizes the typical behavior of nitrogen adsorption isotherms at  $-195^{\circ}\text{C}$ . The point B is associated with that adsorption where the first layer of nitrogen is completed. This "knee" in the isotherms is frequently followed by an almost linear portion BD. The position where the linear portion breaks away from the observed isotherm is used to determine the point B. The surface area is calculated from the number of molecules in one

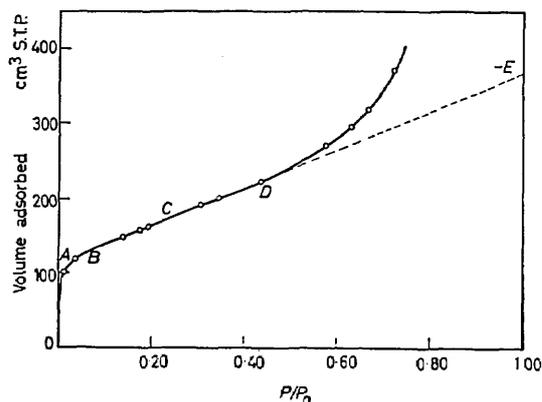


Fig. 1 - Brunauer and Emmett's (18) analysis of the adsorption isotherm of nitrogen on an iron catalyst at  $-195.8^{\circ}\text{C}$ . Point B is the beginning of the linear portion of the isotherm.

layer of adsorbed gas. The number of moles adsorbed at point B is multiplied by Avogadro's number and the area per nitrogen molecule ( $16.2\text{\AA}^2$ ). The other positions noted on the curve have not correlated with actual surface area as well, nor have they proved to be of theoretical interest.

The point B is now identified with  $v_m$  of the BET theory (19), and the equations of this theory have been viewed as analytical methods of locating point B. The relationship most generally used in calculating  $v_m$  is

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_o} \quad (2)$$

where  $p$  = pressure,  $v$  = volume adsorbed,  $p_o$  = saturation pressure,  $v_m$  = monolayer coverage, and  $c$  = a constant characteristic of the particular interaction at the gas/solid interface. The slope  $m$  and intercept  $i$  of the linear plot of  $p/v(p_o - p)$  against  $p/p_o$  are used to determine the  $v_m$ , ( $v_m = 1/(m + i)$ ). The  $c$  value of Eq. (2) may likewise be obtained, ( $c = 1 + (m/i)$ ).

The practical advantage of the BET procedure over the point B method is that fewer experimental points are required, and thus the economics of laboratory operations favor the BET procedure. However, with commercial instruments now available to record the complete adsorption and desorption isotherms automatically, the point B method is becoming more useful.

Usually, a volumetric method is used with nitrogen gas as the adsorbate and liquid nitrogen at atmospheric pressure as the refrigerant. For materials of small surface area, it is necessary to use large samples and, hence, to employ sample containers with comparatively large dead space. It is important to estimate the experimental error inherent in conventional volumetric apparatus. Assuming ideal gas laws, the number of moles  $n$  of gas adsorbed for the initial adsorption measurement is

$$n = \frac{P_i v_b}{300 R} - \frac{P_e v_b}{300 R} - \frac{P_e v_d}{78 R} \quad (3)$$

where  $p_i$  = initial pressure of nitrogen introduced into the buret system at room temperature (300°K),

$p_e$  = equilibrium pressure after contact with the sample at 78°K,

$v_b$  = volume of nitrogen (STP) in the buret space,

$v_d$  = dead space, and

$R$  = gas constant.

The variation in the number of moles adsorbed  $\delta n$  can be used to express the percentage error (80). The values of  $\delta p_i$  and  $\delta p_e$  are no greater than 0.1 since an accuracy in pressure of  $\pm 0.1$  torr may be readily attained. Also, a value of  $\delta v_b = 0.1$  is possible, since the calibration of the buret space with mercury is conveniently made before the apparatus is assembled. A reasonable value for the accuracy of the dead space volume (calibration with helium) is one percent; hence,  $\delta v_d$  is  $0.01 v_d$ . This analysis has been applied to the first points for a number of measurements, and the results are given in Table 2. The error in obtaining subsequent adsorption points is cumulative; nevertheless, the treatment given indicates the dependence of accuracy on the magnitude of adsorption.

When the amount adsorbed is small, the determination depends on a small difference between the relatively large amounts introduced and those left in the gas phase. This experimental difficulty has been partly overcome by reducing the temperature and hence

Table 2  
Experimental Error in Nitrogen  
Adsorption at 78 K°(80)

	Weight	BET Area	Dead Space	Error
	g	m <sup>2</sup> /g	ml	δn/n %
Titanium Oxide	1.08	9.9	4.1	2.1
Coconut Charcoal	0.71	1700	5.7	0.1
Glass Spheres	12.29	0.93	16.3	1.9
Bone Char	1.92	120	7.0	0.3
Cotton	31.1	0.7	121	10.4

$p_0$  so that the same relative pressures can be realized at smaller absolute pressures. As a result, the residual gas not adsorbed at equilibrium is smaller. In addition, the dead space need not be reduced to a minimum to achieve the desired precision nor does the volume of the pressure gage. Table 3 lists a few gas/solid systems which have been used in such a procedure.

It is not known how far the strategy of decreasing  $p_0$  can be pushed in order to measure yet smaller surface coverages. Clarke (24) has determined adsorbed krypton ( $Kr^{85}$ ) directly by counting the  $\gamma$  emission of the sample in liquid nitrogen. A thermistor pressure gage was used to determine the pressure of the equilibrating gas. This method is applicable over a wide range of surface areas (10 cm<sup>2</sup> to 10 m<sup>2</sup>/g) and to sample sizes of 0.5 g or less. The precision is given as two percent for  $8 \times 10^3$  counts in five minutes when the background count is less than  $10^3$ /minute. The above procedure, however, is not without some complications.

It is necessary to correct observations at low pressures for the change in pressure due to thermal transpiration. In the Knudsen range (mean free path several times the tube diameter) the ratio of pressures in the reaction vessel at two temperatures is  $p_2/p_1 = \sqrt{T_2/T_1}$ . Figure 2 illustrates the pressure ratio for the Knudsen effect above and

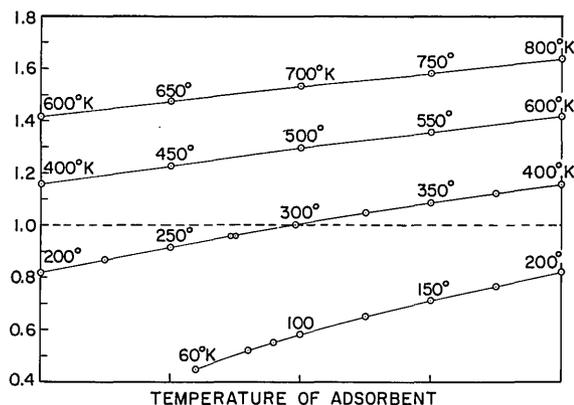


Fig. 2 - The ratio of pressure in the adsorbent vessel at various temperatures to that measured at 25°C. All pressures are in the Knudsen region.

Table 3  
Adsorbates Used for the Determination of BET Monolayer Coverage

Adsorbate	Temp.	$p_0$ (torr)	Solid	Pressure Gage	Ref.
Nitrogen	-195°C -183.1°C	760 2700	Fe Catalyst	Hg Manometer	19
n-Butane	-116°C	0.17	Coated	McLeod	120
Ethylene	-183°C	0.0305	Cathode		
Ethylene	-183°C		Al Foil	McLeod	38
Ethylene	-183°C	0.033 0.021			20
Ethane	90°K	0.010	NaCl KCl	McLeod	101
	122.9°K 136.0°K	3.92 19.00		Manometer	
Ethane	-183°C	$10^{-2}$	Cu Films	Pirani	2
Krypton	-195°C	2.63 to 3.72	Anatase, porous glass, etc.	McLeod	13
Krypton	77.8°K	Super- cooled liquid	Ge Powder	Thermistor	100
Krypton (85)	-195°C	Super- cooled liquid	Graphite	Thermistor $\gamma$ -counter	24

below 25°C, the temperature assumed for the pressure measurement. In the intermediate pressure range where  $p_2/p_1$  is between the Knudsen values and unity, a correction must be made. A number of procedures are available, that of Takaishi and Sensui (110) being the most recent. There is some uncertainty as to the exact lower limit for the thermal transpiration ratio of hydrogen and neon (92a) and helium (66a).

There are solids for which the BET plots are not sufficiently linear to give an acceptable value for  $v_m$ . These are characterized by small values of the constant  $c$ . In some of these cases the original point B method may be used, and then more experimental points are needed. An interesting exception is the Type III isotherm of the Brunauer classification (17), where there is nothing in the isotherm that indicates the completion of a monolayer. In these cases the BET theory with the parameter  $c = 1$  furnishes an acceptable value of  $v_m$ . The completion of the first layer before appreciable formation of the second layer is valid only for large values of  $c$ . Hill (61) has shown that for small values of  $c$  the adsorption takes place at  $v = v_m$  by the adsorbing molecules interacting with adsorbate molecules rather than with the bare surface. Examples of such low-energy surfaces will be given in a later paragraph.

The adsorption of nitrogen on coconut shell charcoal has been represented by the Langmuir equation, and the calculated  $v_m$  corresponds to adsorption near saturation pressure. However, in this case it is reasonable to discount the Langmuir behavior and use a value based on point B. Ross and Olivier (103) have demonstrated that an apparent Langmuir behavior can occur by a special distribution of the energy of the sites for mobile physical adsorption. A careful experimental study of the nitrogen isotherm on coconut shell charcoal (50) has shown that the Langmuir equation actually does not hold

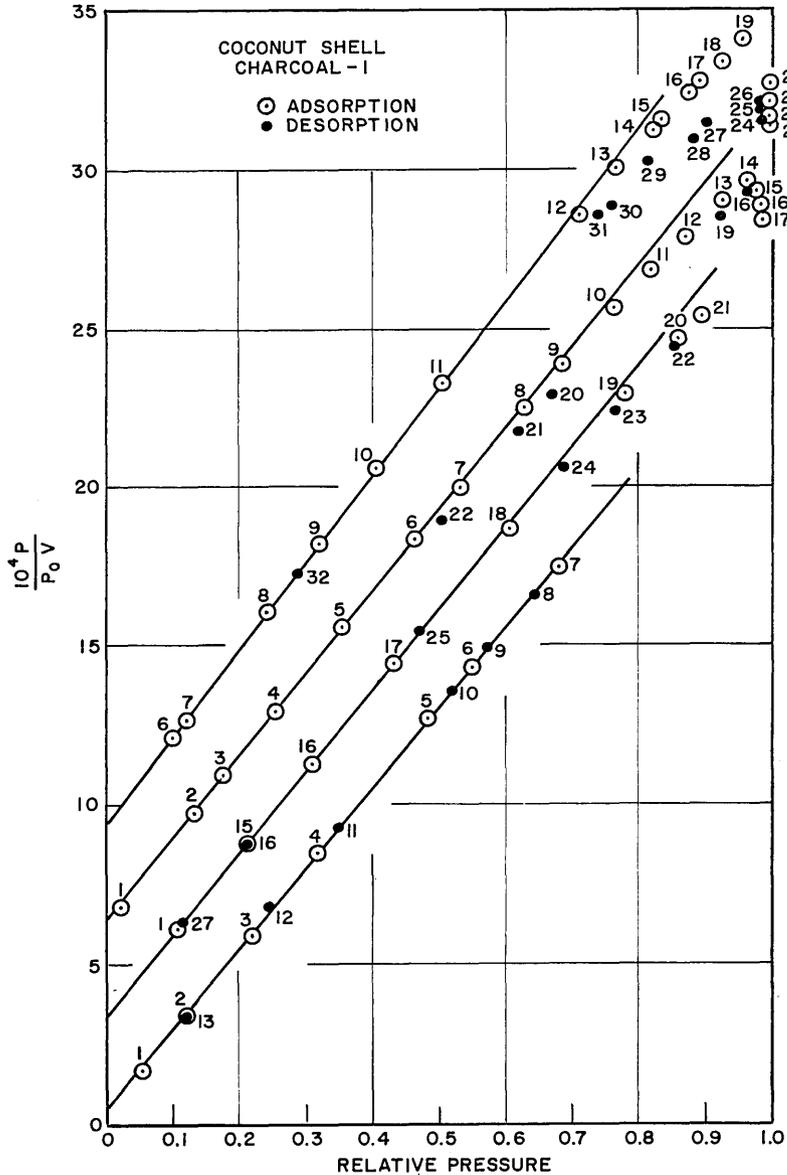


Fig. 3 - Langmuir plots of nitrogen adsorbed on coconut shell charcoal at 78°K illustrating hysteresis at high relative pressures

at relative pressures above 0.7. Figure 3 gives the plots of  $p/p_0 v$  versus  $p/p_0$  and demonstrates that a small hysteresis may take place. Nitrogen adsorption on other gas adsorbent charcoals obeys the three-constant BET equation in which the parameter  $n$  is a measure of the restricted number of adsorbed layers at saturation. In these cases  $v_m$  is located close to point B.

The BET surface area measurement may be used for a variety of purposes; one is to estimate the entrapped surface in the closed voids within a solid. Particle size diminution increases the surface area per unit weight to a greater extent than can be attributed to the decrease in particle size alone. The boundary area on 1 g of cubes (density  $2 \text{ g/cm}^3$ ) varies with size of the cubes as shown in Table 4. The opening of the internal voids in several basic calcium phosphates was shown by Hendricks and Hill (57); the BET area is shown in Fig. 4 to vary linearly with boundary area. The total surface area increases 20 times faster than the boundary area. Recently, Clarke (24) has demonstrated the presence of internal closed voids in nuclear graphites, and Fig. 4 also shows the surface area of graphite plotted against the corresponding geometrical boundary. In the case of graphite the total area increased 200 times faster than the boundary area. The linear nature of the dependence could indicate a uniform distribution of very small closed voids within these solids. The technique may be applied to a number of solids as a test for homogeneity, but as Savage (105,106) has shown, it is necessary to be alert to chemisorption effects with the environments during the grinding process.

Table 4

Increase of Boundary Area  
with Particle Diminution

Size	Particles/g	Area ( $\text{cm}^2/\text{g}$ )
(Cubic particle of density $2 \text{ g/cm}^3$ )		
1 mm	500	30
$149 \mu$	150,000	200
$44 \mu$	$6 \times 10^6$	700
$10 \mu$	$500 \times 10^6$	3,000
$1 \mu$	$500 \times 10^9$	30,000
$100 \text{ m}\mu$	$500 \times 10^{12}$	300,000

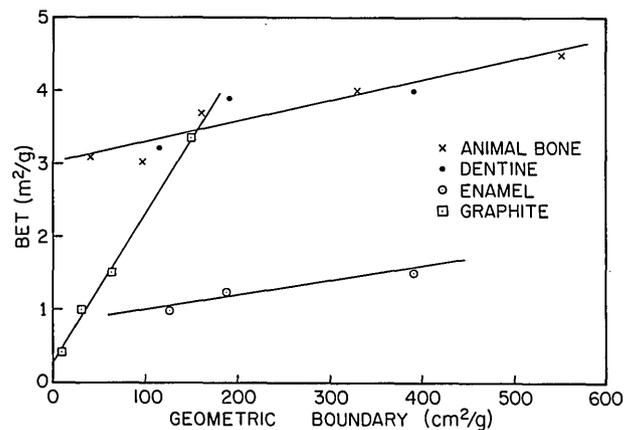


Fig. 4 - Evidence of the entrapped surface associated with closed voids within a solid and exposed by particle diminution

It is preferred, when possible, to define the monolayer in terms of changes in several adsorption characteristics rather than base it on some one particular system. The physical adsorption of nitrogen at liquid nitrogen temperatures, however, appears to have unique correlation with other adsorption phenomena associated with monolayer coverage and comes close to being a universal technique. The heat of adsorption is usually sufficiently high to give a value of  $c$  that furnishes a well-defined point B.

#### Multilayer Region ( $\theta > 1$ )

The study of multilayer adsorption has developed in several directions since Brunauer's classic volume (17). Up to that time the main objective was to predict the shapes of

adsorption isotherms, which was accomplished by the BET theory with good success. Later developments include, (a) calculation of the thermodynamic properties of carefully selected systems, (b) extension to a variety of adsorbates and solids, and (c) influence of molecular structure on the properties of the adsorption complex. Other than demonstrated the great complexity of the problem, there has been no real breakthrough since the BET theory was formulated.

In the period after World War II, careful measurements of reversible adsorption isotherms were made which enabled the thermodynamic properties of the adsorbed phase to be determined. The desired precision of volumetric gas analysis and the determination of the amount adsorbed gravimetrically made special demands on manometers and microbalances. It may be noted that many of these components are now available on a commercial basis. For example, the entire adsorption and desorption isotherms may be determined volumetrically in a completely automated apparatus (5).

Early investigators in multimolecular adsorption were still concerned with monolayer coverage and studied the availability of a surface to molecules of increasing size and complexity. An example for a porous adsorbent (bone char) is shown in Fig. 5. The adsorption of hydrogen and that of n-butane differ by a factor of almost eight at the same relative pressure. The homologous series  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{C}_4\text{H}_{10}$  indicated a progressive decrease in BET area of 115, 90, 76, and 66  $\text{m}^2/\text{g}$ , respectively. The sequence is not proportional with  $v^{2/3}$  ( $v$  = molar volume of adsorbate species as a liquid) nor could it be correlated with any obvious packing arrangement on the surface. The situation was found to be the same for nine other carbon adsorbents. Recently, Kini (72), using two carbon adsorbents with Ar,  $\text{CO}_2$ , Kr, Xe, and  $\text{CH}_3\text{OH}$ , has shown that the BET theory in its original form gave good agreement for surface area. This problem is also treated by a technique known as "high-temperature" adsorption, which will be discussed below. The monolayer coverage deals with an important phase of the multilayer problem. The packing of adsorbate molecules in multilayers and the corresponding entropy changes present problems of even greater complexity than for the completion of the monolayer.

The theoretical treatments of multilayer formation, recently reviewed by Young and Crowell (122), indicate that the theoretical difficulties are similar to those encountered with problems of liquid state. Multilayer adsorption has been considered as the precursor to the condensed phase. The packing of adsorbate molecules has raised the problem of values for the density of the adsorbed phase at different coverage relative to that of the condensed phase. Several careful attempts using helium as the displaced fluid have been reported (30,86,113), and while no absolute values for density are given, the results have a definite trend. At surface coverages up to a monolayer, the density is close to the normal value of the liquid. In the multilayer region a more dilute type of coverage forms which then increases gradually until the normal density is reached at saturation. More work is required to establish the concept of "holes" in the multilayer structure. The structure of the multilayer appears compatible with the original BET model of a random vertical stacking of adsorbed molecules, although an alternative cluster model would behave similarly.

The adsorption isostere is particularly useful for expressing experimental results. An example is the system methane/charcoal taken from the work of Kidnay and Hiza (71), shown in Fig. 6. It is important, of course, that the data be reversible in order to calculate the heats of adsorption. Figure 6 brings out a marked curvature (slope increases with temperature) and, moreover, shows that the heats of adsorption for this system may be less than the heats of condensation. Other systems have shown a similar behavior: argon with graphitized carbon black (93), nitrogen or argon with diamond or mineralogical graphite (81), and nitrogen or argon with polypropylene and polytetrafluoroethylene (51). Calorimetric measurements to verify these findings would be interesting. It is important

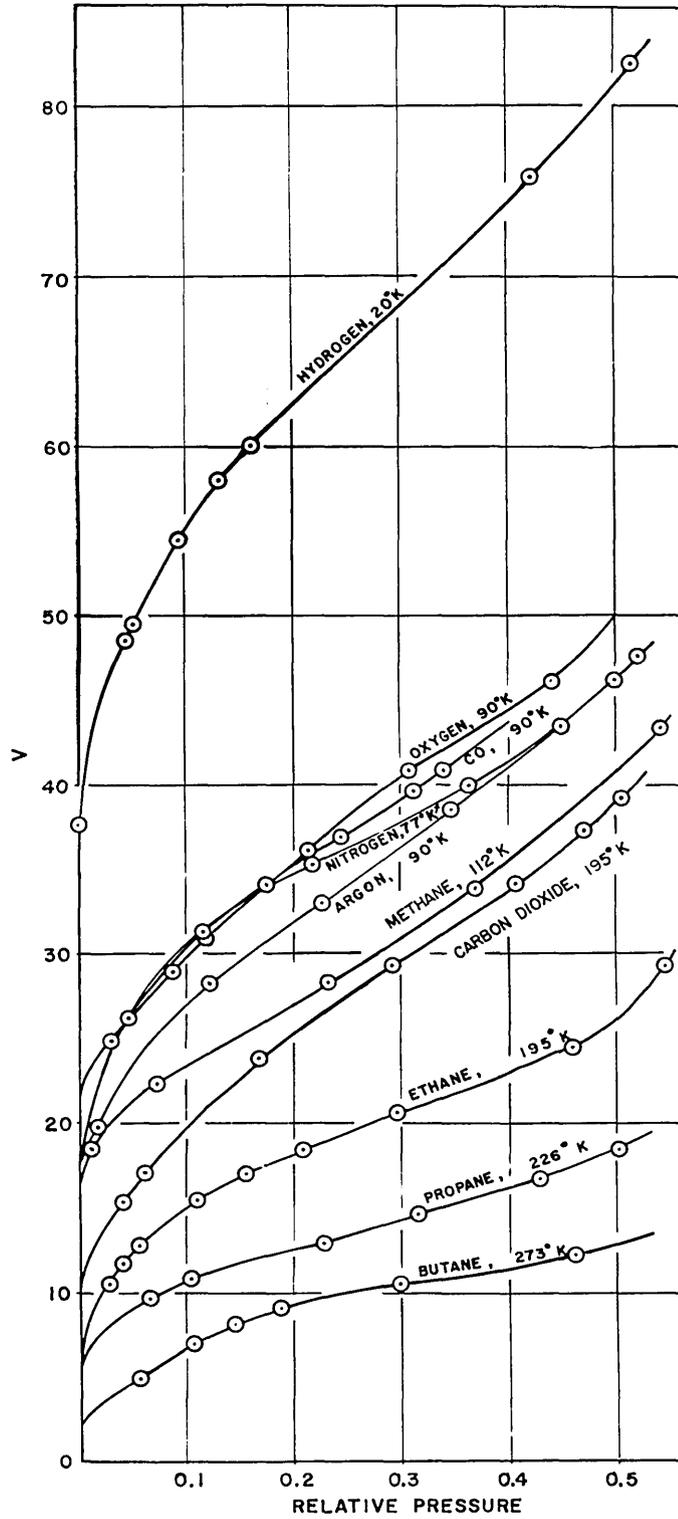
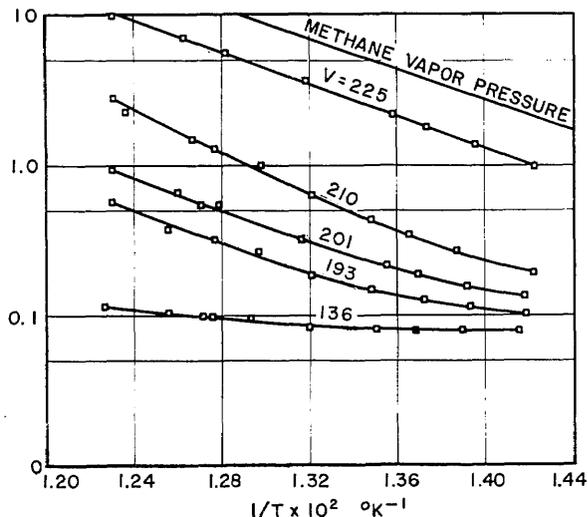


Fig. 5 - The physical adsorption of ten gases on a sample of new bone char at the designated temperatures (34)

Fig. 6 - The adsorption isosteres of methane on a charcoal (Kidnay and Hiza (71)) presented as a plot of  $\log p$  vs  $1/T$



to obtain data at close temperature intervals in order to bring out fine-structure behavior. Experimentally, there is a need for a simple cryostat not tied too strongly to normal boiling points and melting points of the available refrigerants.

Hill in a series of theoretical papers (62) developed a thermodynamic model in which the adsorbent was assumed inert and the presence of the surface provided an attractive force field for the adsorbate molecules. This one-component model presents all the measured heat and entropy changes as taking place in the adsorbate. In addition to affording a simplicity in theory, the model has provided new information. For example, Hill, Emmett, and Joyner (64), independent of the BET theory, were able to locate the point of monolayer coverage by calculating the position of minimum integral entropy for the system nitrogen/graphitized carbon black. Their results are shown in Fig. 7.

One aspect of physical adsorption that delineates it from chemisorption is the absence of strong specificity between the interacting gas and solid. This, however, is true to only a moderate degree. Actually, multilayer formation does sense the structure of the bare solid. Singleton and Halsey (108), using argon isotherms on graphitized carbon black, showed progressive change in the shape of the isotherms as the thickness of preadsorbed xenon layers increased (up to 6 layers). The heats of adsorption determined from isotherms of hydrogen, deuterium, and helium on graphon agree with calorimetric values (92). The calorimetric studies of Morrison et al. (37,87,88) on the systems argon, oxygen, and nitrogen with titanium dioxide (rutile) were very valuable and showed the great experimental difficulties inherent in the measurements.

A strong motivation for such measurements is the information sought for the uniformity, or lack thereof, of the surface. The data are evaluated in terms of statistical models that place restrictions on rotational, translational, and vibrational degrees of freedom ascribed to a free molecule.

The extremes of gas/solid interaction are those of a strictly localized bond to the surface site and a completely mobile adsorbate where the bond to the surface is completely degenerate. The careful studies of Morrison showed that argon adsorbed on rutile at 14-25°K was localized. At the higher temperatures the results could not be accounted for on the basis of any simple model but did suggest some degree of mobility of the adsorbed argon. The "melting" process in multilayer adsorption of nitrogen on rutile is completely reversible and takes place at temperatures well below the normal melting point of nitrogen.

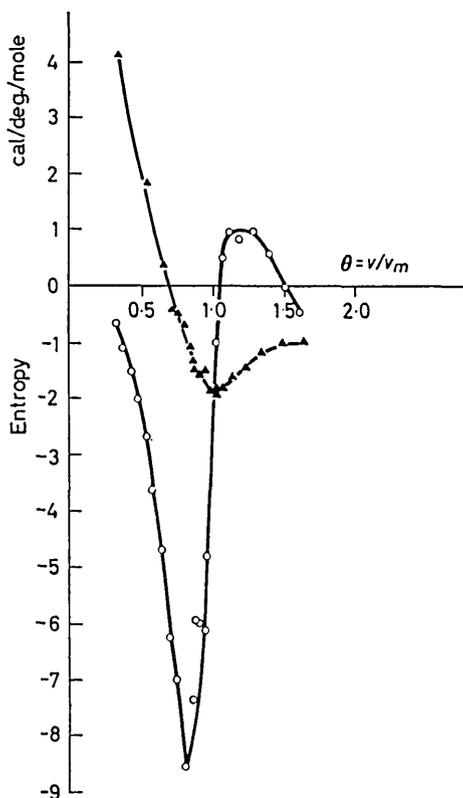


Fig. 7 - The criterion of minimum molar entropy to locate monolayer coverage in the physical adsorption of nitrogen on graphitized carbon black (64). Upper curve is the integral entropy of adsorption calculated from spreading pressures, and the lower curve is the differential (isosteric) entropy.

OH groups of porous glass. Galkin, Kiselev, and Lygin (49) have recently shown for aromatic molecules/silica systems that there is an interesting dependence of the adsorption on both molecular structure and surface coverage. Specifically, the interaction is between the  $\pi$ -electron system of the aromatic molecule and the OH group of the surface.

The electrical properties of gas/solid systems have been studied widely with relatively little success. In the multilayer region, there are sufficient numbers of surface groups to affect the nuclear magnetic resonance spectra of certain nuclei, which fortunately includes hydrogen. Recently, nuclear magnetic resonance relaxation times (97) were observed for water adsorbed on a hardwood gas charcoal. The observations were compatible with a model of supercooled water in the capillaries of the charcoal. The dielectric properties (91,124) of surface hydrates and other polar adsorbates have been recorded, but there is considerable difficulty in factoring out the particular electrical properties of the adsorbate.

The phenomenon of hysteresis remains an intriguing and largely unexplained behavior in the region of multilayer coverage. When an adsorbent contains microscopic open voids, the process of "capillary condensation" occurs (17). This structural model has been the basis of attempts to understand hysteresis, and many publications have been based on it.

Current researches in multilayers attempt to express the surface nonuniformity in terms of energy distribution as a function of surface coverage. On an atomic scale there may be a distribution of crystal faces, each having different atomic spacings. There is certainly in many cases a distribution of defects (impurities, etc.) over the boundary surface which varies with the techniques employed to pretreat the surface. Finally, it has been shown (27) that the properties of the surface may change with time as the strain-stress relationships set up in forming of the solid adjust slowly toward a minimum surface free energy.

The dimensional changes that take place in the physical adsorption in carefully selected gas/solid systems demonstrate that the adsorbent is definitely not inert in these cases. Yates (121) developed a vacuum interferometer and measured the length changes upon adsorption of several gases on porous glass. Some of these results are shown in Figs. 8a and 8b. The general phenomena are very complex with interesting temperature effects and fair reproducibility; these take place in systems free of chemisorption possibilities.

Many current researches in this field are concerned with the interaction among the molecular groups located in the gas/solid interface. The infrared absorption technique has been applied rapidly to many systems (40). In chemisorption systems, new molecular species are formed; in physical adsorption, there are significant changes in the normal vibrational modes of the free molecule, and forbidden frequencies appear in the perturbation field of the surface

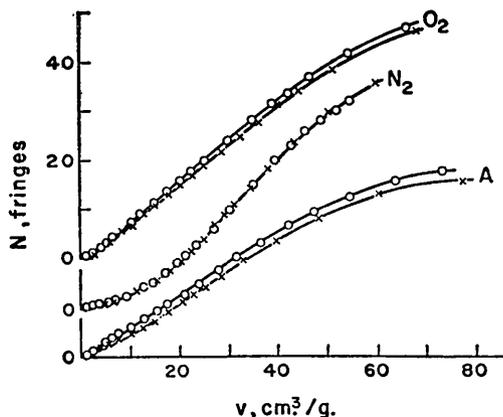


Fig. 8a - Expansion of porous glass (interference fringes) after the adsorption of argon, oxygen, and nitrogen at 90°K (o) and 79°K (x) (121)

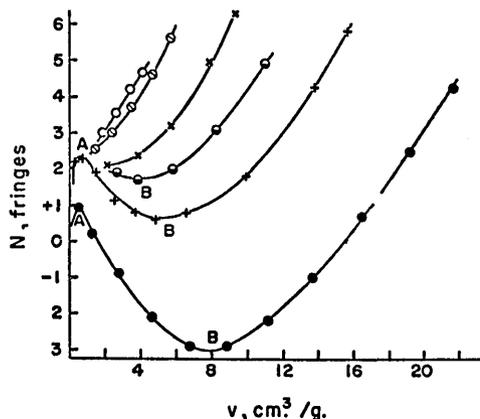


Fig. 8b - Length changes of porous glass upon the adsorption of sulfur dioxide at -78°, 0°, 24°, 50°, 75°, and 100°C (121)

The hypothetical cylindrical capillary and the realistic texture based on crystal structure constitute an anomaly that has yet to be resolved. An alternate explanation of hysteresis may be found in some low-energy modification of the adsorbent surface during the adsorption process (see the domain concept of D.H. Everett (42a) and J.A. Enderby (42b)). There may be steric factors that influence the orientation of surface groups in which only the weaker bending forces of the surface bonds are involved. A cooperative orientation effect may be a function of the amount adsorbed in a manner similar to adsorbed films on liquids. It is interesting that hysteresis of a surface film of ovalbumin on several buffer solutions has recently been reported (67). Thus, for each orientation of the bonds in the surface, there is a different gas/solid system to study, and it would be interesting if experimental means were found to freeze each for individual study.

#### Fractional Surface Coverage ( $0.1 < \theta < 1$ )

Only a fraction of the total gas/solid interface is covered by physical adsorption at temperatures above the critical temperature of the gas and at relative pressures below 0.05 to 0.10. Chemisorption processes usually involve only a fractional part of the BET surface. The importance of the BET theory, and also the constructive criticism that has followed, should again be appreciated. Only after this development was a general means available for ascertaining fractional coverage.

Analyses of the Gas Phase - The experimenter today has a tremendous advantage over his colleagues of only five to ten years ago. With the development of modern gas chromatography and mass spectrometry procedures, the means are available to follow the partial pressures of all reactants and products. In fact, facility of data collection makes possible more elaborate experimental designs so as to include binary, ternary, and multiple gas mixtures. Adsorption studies with multiple gas component systems were first reported with commercial adsorbents (78); and with the introduction of gas phase chromatography, many studies have followed (8,9).

Reliability of gas/solid studies in the past has sometimes been questioned because of possible competitive gaseous impurities. Although the means have been available to start with high-purity gases, it was not known to what degree the solid and stopcock manipulations might introduce gaseous contaminations. Now, a continuous monitoring of the gas

phase with built-in components permits greater attention to be given to this factor. Systems involving fractional surface coverages, in general, are concerned with experimental procedures that are more demanding.

Pretreatment of the Solid - The pretreatment of the solid is probably the most important experimental parameter in current researches. The usual degassing in vacuum at some specified temperature has generally been selected for convenience and expediency. For many commercial adsorbents this may contribute effectively to the subsequent adsorption, and in some cases the treatment may generate an adsorption site on the solid. The recipes employed in the manufacture of some solid state devices have depended upon the generation of special sites at the surface and junction of the crystallites, and only recently has some rationality replaced uncertainty.

The extent of outgassing may be monitored by measuring the rate of gas formation at an elevated temperature. Deitz and Carpenter (32) recorded pressure-time curves after the heated sample was isolated, and a typical record is shown in Fig. 9. A memory effect is indicated in the time evacuated at the elevated temperature. Curves AB and EF are typical of successful operation. Point C indicated that a back-diffusion of oxygen to the heated sample had taken place, but subsequent degassing gradually progressed to the initial rate of decay. This study raises questions as to the advantages and disadvantages to be gained by some high-temperature pretreatments. The impurities removed from the surface may be renewed by the volatile products of decomposition originating in the bulk of the solid. A poorly defined substrate such as glass spheres can hardly be expected to give a better defined surface by thermal pretreatment alone. Liang (79) showed that such glass surfaces are quite heterogenous and that the gas/glass interface is nonreproducible (90 hours at 300°C) in the adsorption of krypton at 77.6°K at low coverage (<0.05). The cleaning of a solid surface is really a three-dimensional problem. The two-dimensional concentration of impurities has been recognized, but the concentration changes on moving inward from the surface must also be considered. For the present, however, much interesting work can be done with surface impurities depleted to a level knowingly set by the design of the experiment.

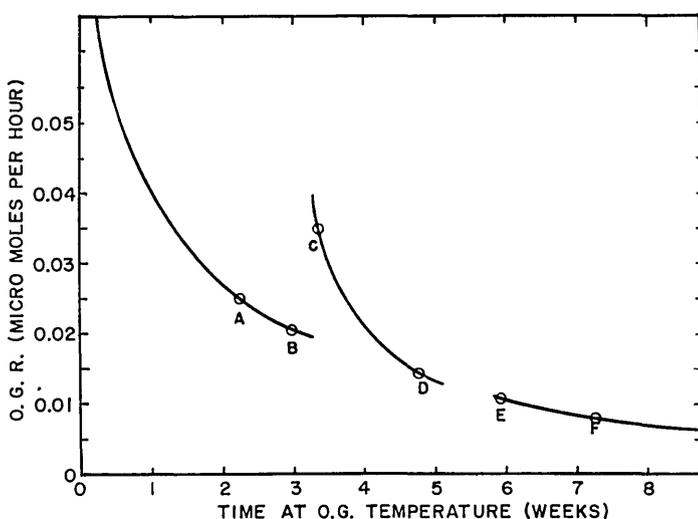


Fig. 9 - The outgassing behavior of a diamond powder at 600°C in terms of the rate of gas formation (micro-moles per hour)

The thermal treatment in vacuum may be supplemented by chemical treatments. Examples are the reaction of hydrogen chloride or chlorine with sodium chloride crystals to restore the anion vacancy (7), of oxygen with oxides to restore the stoichiometric balance desired (119), and of hydrogen with some metals to eliminate trace oxygen and nitrogen (73). Adequate pumping must always be available to assure that the desorption process dominates over the potential simultaneous adsorption process.

The flushing of a solid by repeated adsorption and desorption with the gas of interest has long been advocated (84,85). High-purity gases are obviously required for such a procedure. Special techniques are available to pretreat metals: (a) atomic hydrogen treatment, (b) rare gas ion bombardment, (c) filament flashing, etc. Organic solids require very special care so as not to introduce decomposition impurities.

The objectives sought in a pretreatment process are (a) reproducibility, (b) known chemical composition of the interface, and (c) known structure of the boundary planes at an atomic level. Not all of these objectives are achieved, although good progress has been made toward reproducibility in a number of cases.

"High-Temperature" Adsorption - Considerable interest is now being expressed in the field of "high-temperature" physical adsorption. The significant factor at the low fractional surface coverage is the minimum interaction between adsorbate molecules.

The Steele-Halsey (S-H) model (109,46,26) is concerned with an integration of the gas/solid interaction given by an interatomic energy potential over a structureless semi-infinite solid. The Ross-Olivier (R-O) model (103,102) applies the de Boer-Hill isotherm (16) for a two-dimensional mobile film interacting with a surface having a Gaussian distribution of adsorption energies. The experimental data used in applications of the S-H model have been obtained at 0° to 50°C and correspond to fractional coverages of 0.01 to 0.02. The application of the R-O model have been to coverages between 0.1 and 0.6. The objectives of this work are (a) an independent method of determining surface area, (b) a technique for dealing with heterogeneous surfaces, and (c) a physical adsorption process independent of adsorbate and temperature. The definitions of physical adsorption involved in these considerations have been discussed by Hill (63).

Barker and Everett (6) have expressed the Steele-Halsey model in terms of conventional adsorption theory, and their simplified presentation will now be given. The potential energy of the molecule varies with the normal distance  $z$  to the plane in the usual way, and the average concentration  $c$  in the potential field  $\epsilon$  varies according to a Boltzmann distribution (Fig. 10)

$$c = c_o e^{-\epsilon/kT} \quad (4)$$

where  $c_o$  is the bulk phase concentration at  $\epsilon = 0$ . Using the Gibbs definition of adsorption and dividing line at  $z_o$  ( $z = z_o$  when  $\epsilon = 0$ ),

$$dn_a = dx dy \int_{z_o}^{\infty} (c - c_o) dz. \quad (5)$$

Substituting (4) in (5)

$$n_a = c_o \int_x \int_y \int_{z_o}^{\infty} (e^{-\epsilon/kT} - 1) dz dy dx. \quad (6)$$

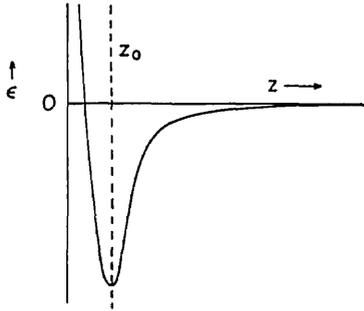


Fig. 10a - Dependence of the potential energy of the molecule on the normal distance to the plane of the surface

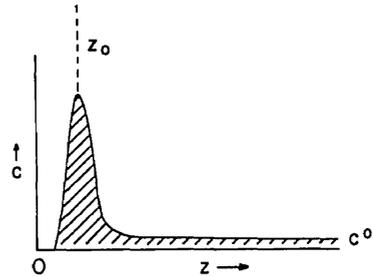


Fig. 10b - Dependence of the coverage concentration in the potential field on the normal distance to the plane of the surface

For a uniform surface and an ideal gas ( $c_0 = p/RT$ )

$$n_a = Ap/RT \int_{z_0}^{\infty} [e^{-\epsilon/kT} - 1] dz$$

$$n_a = Ap(k_h). \quad (7)$$

If  $\epsilon$  is a known function of  $z$ , then  $k_h$  can be calculated. When  $n_a/p$  is found experimentally, the area  $A$  can be found.

The small adsorption may be readily measured by gas chromatography procedures. Hanlan and Freeman (55) have shown that the gas/solid interaction coefficient can be obtained from the retention volumes calculated under the given set of experimental conditions. The potential energy of the interaction can then be found from the temperature dependence of the retention volumes. The necessary experimental results are readily obtained on a routine basis and the calculations, although involved, may be handled by computers with dispatch. The method may, therefore, prove to be a research tool of considerable value.

Ross and Olivier (102,103) deal with adsorbed mobile films with an interaction given by the two-dimensional van der Waals gas constants. The de Boer-Hill isotherm (16) is used

$$p = K_i \frac{\theta_i}{1 - \theta_i} \exp \left[ \frac{\theta_i}{1 - \theta_i} - \frac{2a \theta_i}{\beta kT} \right] \quad (8)$$

where

$K_i$  = a term giving the adsorbate-adsorbent interaction,

$\theta_i$  = coverage of a given patch of energy  $U_0$  at pressure  $p$ , and

$\alpha, \beta$  = 2 dimensional van der Waals constants (assumed independent of surface heterogeneity).

A Gaussian distribution of adsorption energies is assumed and a series of model isotherms are computed for particular adsorbates and temperature expressing the total coverage by

$$\theta = \int \Phi(U_o) \Psi(p, U_o) dU_o. \quad (9)$$

Actually, a machine summation is made over 50 patches instead of an integration. The experimental isotherm is compared with the model isotherms, and four results are immediately obtained: (a) the monolayer capacity is determined, (b) a quantitative measure of heterogeneity is given by the constants of a particular Gaussian curve, (c) a value of the mean energy of adsorption is given which can be related to the isosteric heat of adsorption, and (d) the theory predicts a temperature-coefficient of adsorption.

There is a need to provide the experimental isotherms for a large variety of solids and adsorbates to test these two aspects of gas/solid interaction. The means are available to record the isotherms in pressure regions desired, namely  $10^{-4}$  to  $10^3$  torr, and the temperatures selected to cover a wide range in close intervals.

Materials - Powders, films, and filaments have been studied in a variety of fundamental investigations, each requiring a different experimental technique. Only a few solids have been studied in all three forms; a well-known example is tungsten. To these forms must be added the tungsten point used so successfully in the field-emission microscope.

Table 5 presents some of the relative advantages and disadvantages in pursuing investigations at the gas/solid interface by the three techniques. Such an analysis may have value when viewing the gas/solid interface in its broadest aspects. Actually, each system has its own share of individual idiosyncrasies. All solids can be studied as powders or crystals, and a relatively few (metals) can be studied as filaments. Films can be formed of any substance that has a finite vapor pressure or that can be formed from volatile reactants. De Boer (31) obtained films of calcium, strontium, and barium fluorides by sublimation and studied the interesting surface chemistry of these films. Continuation of such studies would be extremely valuable.

The study of films has the major advantage of large surface to volume ratio. Consequently, the amount adsorbed per unit weight of material is greatest for films, next for powders, and least for filaments. Moreover, films share with filaments the capability of being studied in ultrahigh vacuums. Since the sublimation process in itself may be used as a purification step, films obtained by sublimation may be of high chemical purity.

Rate of Adsorption - The rates of adsorption vary in magnitude from extremely rapid values for physical adsorption to much slower values for diffusion-controlled adsorption. Recently, various solid state sensors have been devised for monitoring very fast reactions at solid surfaces (115).

Modern methods of investigation began with the studies on clean filaments (98) and with evaporated metal films (15). Trapnell (112) has reviewed the status of the field in his volume published in 1955 and 1964; Ehrlich (39) has recently given an account of current work on clean surfaces. In the last decade the emphasis has been on the rates of mass transfer at solid/solid and gas/solid interfaces using isotope tracers. Evaporated films under ultrahigh vacuum conditions are finding preference because the surface boundary can be defined with more certainty.

Table 5  
Advantages of Solid Surfaces in Different Forms

	Powders or Crystals	Metal Filaments	Films
General Applicability	1	3	2
Cleanness	3	1	2
Surface/Volume	2	3	1
Amount Adsorbed	2	3	1
Thermal Stability	2	1	3
Ultrahigh Vacuum	3	1	2
Chemical Purity	3	1,2	2,1
Structure Determination	1	2,3	3,2
Calorimetric Measurements	1	3	2
Electrical Measurements	3	1	2
Heat Transfer	3	2	1

The factors that influenced rates of adsorption are given by functions in which the variables are assumed separable. The following expressions for the rates of adsorption  $\mu_a$  and desorption  $\mu_d$  are typical:

$$\mu_a = \frac{P}{\sqrt{2\pi m k T}} \sum n_i \sigma_i f(\theta_i) e^{-E_i/RT} \quad (10)$$

and

$$\mu_d = \sum n_i K_i f'(\theta_i) e^{-E_i/RT} \quad (11)$$

where there are  $n_i$  sites of type  $i$  each of an energy  $E_i$  and coverage  $\theta_i$ . The four factors are:

- (1) the number of collisions with a surface  $\left(\sim P / \sqrt{2\pi m k T}\right)$ ,
- (2) the condensation probability  $\sigma$ ,
- (3) the activation energy  $E$ , and
- (4) the fraction of the surface covered  $\theta$ .

When surfaces are heterogeneous, these four factors are applied to each type of site available. Experimental procedures are selected in an attempt to simplify interpretation of the data; the selection of constant pressure and constant temperature permits an analysis in terms of distribution of surface sites.

Gas phase chromatography lends itself readily to many studies in physical adsorption in which the adsorbates on various column materials are maintained at fractional surface

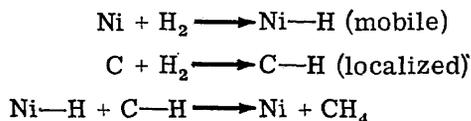
coverage. Molecular exchange on carefully conditioned surfaces is the basis of the gas chromatographic process, and the delicate interaction at the numerous gas/solid interfaces in the chromatographic column presents a very difficult system to analyze on a fundamental basis.

Surface Migration – The extremes of surface migration are readily apparent experimentally. The early observations of Volmer on the migration of benzophenone on glass and mercury surfaces proved that adsorbed molecules move many thousands of atomic distances. There are today scores of examples of crystal growth from the gas phase that involve adsorption and surface diffusion (65).

The complete absence of surface migration has been shown for strongly chemisorbed species. The classical example is oxygen on tungsten which was demonstrated by Langmuir (77) to have a heat desorption of atomic oxygen of 160 kcal/gram atom. It is now known that at elevated temperatures surface migration in this system can be detected. Becker (12) has directly observed in the field-emission microscope mobility of oxygen on tungsten at temperatures lower than those required for evaporation. The mobility was observed to vary with the different planes of the tungsten crystal and with the fields applied. Between 650° and 800°K some oxygen is desorbed, and the first layer is stable between 800° and 1400°K. Above 1400°K some planes begin to desorb, and at about 2200° the oxygen is completely desorbed.

This direct observation of surface migration by field emission contrasts strongly with the many indirect means that have been used in the past. However, indirect means are still required in order to work with a greater variety of surfaces. Migration on boundary surfaces is an essential step in crystal growth, as already mentioned. It has been necessary to assume diffusion along a surface in order to account for the migration of gas molecules through porous packings (11). The intriguing mechanism of the "hopping molecules" has been proposed by de Boer (16), but has not as yet been demonstrated experimentally. Dacey (29) has shown that surface diffusion through systems in which the dimensions of the internal voids are smaller than the mean free path at subatmospheric pressures can be by both Knudsen and surface flow.

The mobility of hydrogen atoms on nickel films has been used by Deitz and McFarlane (35) to account for the low-temperature formation of methane when hydrogen was contacted with stacked films of carbon and nickel. All of the carbon in methane had to come from the carbon film. In their proposed model



hydrogen is chemisorbed to carbon, and the multiple hydrogenation to form methane is favored by the ready transport of H atoms to a site located at the Ni/C interface.

Heat of Adsorption – The simplest indirect measure of gas adsorption is the temperature change of the solid. Adsorption takes place with a decrease in free energy  $\Delta F$  and a decrease in entropy  $\Delta S$ . Since these are related for reversible adsorption by the equation

$$\Delta F = \Delta H - T\Delta S$$

it follows that  $\Delta H$  must decrease; in other words, adsorption is always exothermic.

The heats of physical adsorption have been measured with good precision, and, in general, good reproducibility is found when the surface is well defined. An outstanding case is the adsorption of argon on titanium dioxide in the work of Morrison, Los, and

Drain (88). Approximate values may be estimated from the parameter  $c$  of the BET equation, the values of which range from 1 to 250. The heats are obtained as follows:

$$c = e^{q_1 - E_\ell / RT}$$

where  $q_1$  is the heat of adsorption in the first layer and  $E_\ell$  is the heat of liquefaction.

In recent developments the technique of gas chromatography has been applied to the determination of heats of adsorption (Habgood and Hanlan (54); Hanlan and Freeman (55); Beebe and Emmett (14); Ross, Saelens, and Olivier (104)). Gale and Beebe (48) have made a number of comparisons with heats of adsorption determined by calorimetric measurements at low coverage and report good agreement with their chromatographic data. The accuracy, simplicity, and speed of chromatography may be expected to expedite the accumulation of heat of adsorption data for gas/solid systems at very low surface coverage. The application of these techniques to surface area determinations has been pursued recently by Hansen, Murphy, and McGee (56) and by Freeman and Kolb (47), as mentioned in a previous paragraph.

The heats of chemisorption have a considerably greater range because of the specific interaction of chemical bonds in the gas/solid interface. Reproducibility is difficult to attain in many such systems, as adequately documented by Trapnell (112).

Multiple Gas Phase/Single Solid - The experimental procedures now receiving attention in current studies are (a) simultaneous adsorption of two or more gases at one solid boundary and (b) the replacement of one adsorbed gas by the introduction of another. The latter is always observed with a bulk sample, since it is extremely difficult to evacuate a powder and attain an ultrahigh vacuum. Raising the temperature of outgassing almost always increases the adsorptive capacity when the sample is cooled.

Observations with binary gaseous reactants on a given solid frequently show a dependence of rate on the order of admission of gases. In the ethylene hydrogenation on evaporated nickel and iron films it has been shown (75) that the relative rates were in the following descending order: (a)  $H_2$  first,  $C_2H_4$  second; (b) simultaneous addition; (c)  $C_2H_4$  first,  $H_2$  second. There is obviously an urgent need to observe a property of the surface that demonstrates the surface interaction along with measurements of gas phase composition.

One such study is the adsorption of ethylene at  $-195^\circ$  and at  $25^\circ C$  by evaporated nickel films which were followed (28) with determinations of BET area (Kr at  $-195^\circ C$ ). The results in Table 6 show a reduction in area as a result of the ethylene adsorption; no reduction in area was reported for hydrogen adsorption at either  $-195^\circ$  or  $25^\circ C$ .

Table 6  
Changes in BET Area (Kr at  $-195^\circ C$ )  
Caused by the Adsorption of  $C_2H_4$  at  
 $-80^\circ C$  on Ni Films (28)

Temp. ( $^\circ C$ )	Surface Area ( $m^2/g$ )		$C_2H_4$ Adsorbed ( $\mu l$ at STP)
	Initial	After Adsorption	
0	0.232	0.128	20
25	0.196	0.110	12
100	0.134	0.078	8

Sparsely Covered Surfaces ( $\theta < 0.1$ )

Ultrahigh vacuum techniques are required to prepare and maintain a surface at very low coverage. Commercial equipment to do this has reached a satisfactory working level, and experimentation in this field often has the choice of alternative procedures (3,22,96,99). The pumping facilities have reached a high level of performance, which appears to be limited only by the means of observing residual pressures. The principles of the various pumping techniques are:

Diffusion pumps: kinetic theory

Cold traps: condensation to low vapor pressure

Cryogenic: physical adsorption

Getter action: chemisorption and chemical reactivity

Sputter-ion pumps: gas-ion impact.

The pressure measurement depends on the region of experimentation. A resumé is given in Table 7.

Table 7  
Gages for Use in Various Pressure Ranges

Pressure Range	Pressure (torr)	Instrument
Subatmospheric	1-760	Manometers
Conventional vacuum	$10^{-4}$ - 1	Bourdon gage Membrane gage McLeod gage Thermocouple Thermistor Pirani Thermal conductivity
High vacuum	$10^{-7}$ - $10^{-4}$	McLeod gage Ionization
Ultrahigh vacuum	$10^{-7}$ - $10^{-11}$ $10^{-16}$ - $10^{-5}$ $10^{-13}$ - $10^{-5}$	Ionization Mass spectrometers Cold cathode ionization

The outstanding device below  $1 \mu$  pressure is the mass spectrometer. Not only can it span a tremendous pressure range, but it also has the selectivity required to determine the partial pressures of a gas mixture.

Adsorption isotherms in ultrahigh vacuums are obtained essentially from pressure measurements and the accuracy realized depends on several factors: (a) calibration procedure, (b) background gas, (c) container wall, and (d) interaction with the pressure gage. The calibration is usually based on the McLeod gage in the range  $10^{-3}$  to  $10^{-5}$  torr. Linearity of a Bayer-Alpert ionization gage between ion current and pressure is then checked by the calculated pressure drop across apertures of known conductance. Because of the background gas and the degassing of the sample and container wall, the partial pressure of the gas of interest may be uncertain. The use of mass spectrometry is, therefore, a necessity in such cases.

Experimentation in ultrahigh vacuums has several unique advantages to the surface chemist. The interface maintained at  $10^{-9}$  torr may be held for several hours under a given set of conditions without fear of contamination by adsorbed gases. In building up to higher pressure, the impurities in the gas phase are critical, since clean surfaces exhibit a high affinity for chemically reactive gases such as oxygen and water if present. The stability of surfaces in ultrahigh vacuum offers an opportunity to define the structure of the solid/vacuum interface unperturbed by an adsorbed phase. Significant advances in this regard have been made with tungsten, silicon, nickel, platinum, cuprous oxide and a few other solids. A reaction at the gas/solid interface can be studied with no lateral interaction of adsorbate molecules. Ultrahigh vacuums permit work in pressure regions where the thermal diffusion is independent of pressure ( $<10^{-6}$  torr). The correction factors when the observations are made at  $25^{\circ}\text{C}$  are shown in Fig. 2.

The early adsorption data in high vacuums were concerned with pressure-time experimentation. The observed reversible sorption phenomena are superimposed with phenomena resulting from the pumping action of ionization gages. The latter can be minimized, but not avoided, by intermittent operation for short intervals and by reduction of the electronic current so as to reduce the pumping action. Many specific factors influence the results, such as the kind of gas, the nature and temperature of the adsorbing surface, and gas leakage and gas emission by impurities. The surface chemist, aware of the complexity of these systems, is in a position to make a significant contribution.

Henry's Law - One important requirement for all models of adsorption is that the isotherm simplify to Henry's law at low coverage:

$$v = \frac{bap}{1 + ap} \simeq bap.$$

In this respect, experimentation in ultrahigh vacuums is very pertinent. Linear adsorption isotherms have been observed for many systems, and good examples are the rare gases on graphitized carbon black, P-33 (25), and carbon dioxide on graphitized carbon black (FT); the latter is shown in Fig. 11 (33) at coverages of 0.01 to 0.05. However, linear

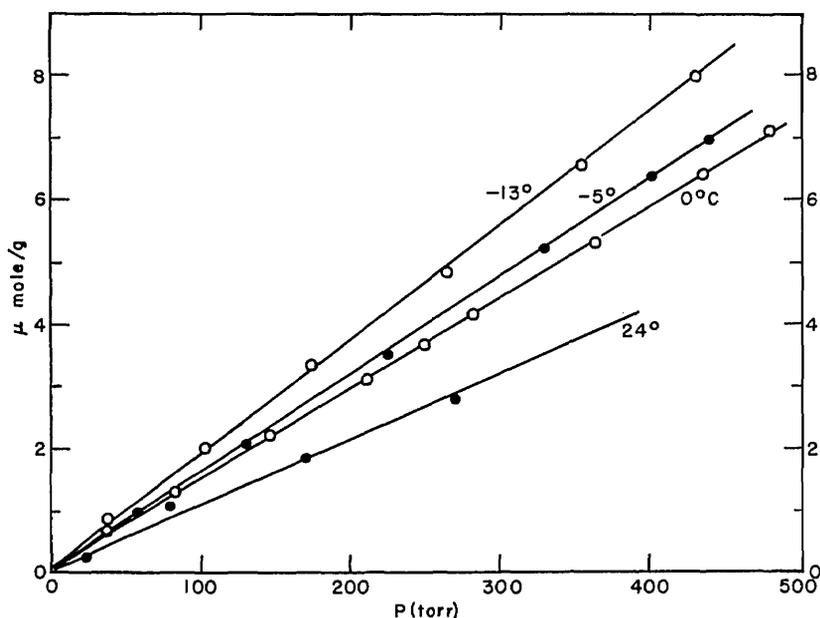


Fig. 11 - Linear adsorption isotherms of carbon dioxide on a graphitized carbon black, FT (33)

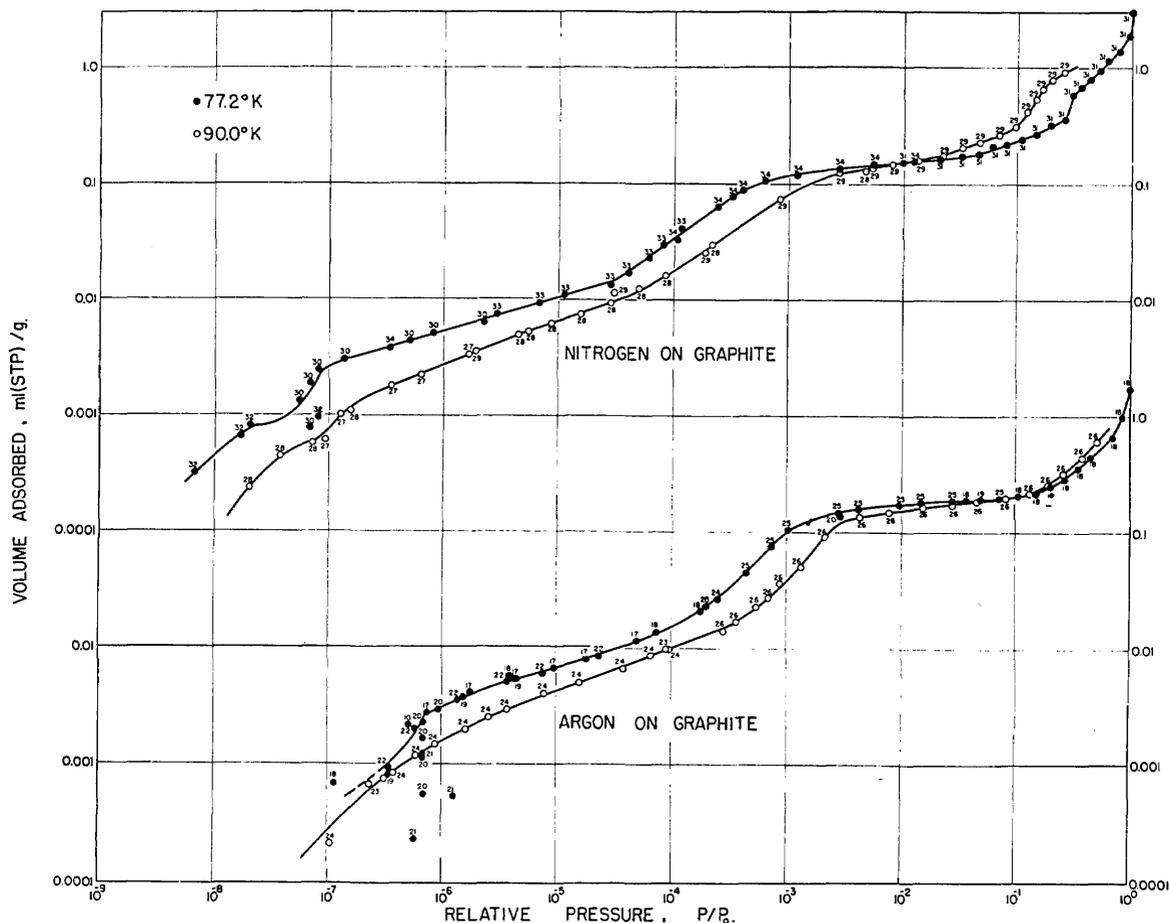


Fig. 12 - Adsorption isotherms of nitrogen and argon on graphite at low relative pressures (81)

isotherms at 273°K have also been reported for nonuniform energy surfaces such as porous glass, some nongraphitized carbon black, and an alumina-silica cracking catalyst (10).

Henry's law behavior is a necessary but not sufficient condition of surface uniformity. Lopez-Gonzalez, Carpenter, and Deitz (81) showed that adsorption isotherms of nitrogen and argon at 77° and 90°K on mineralogical graphite obeyed Henry's law between  $10^{-3}$  and  $10^{-4}$  relative pressure but were definitely nonlinear at lower pressures. These results are shown in Fig. 12. Hobson and Armstrong (66) observed nonlinear isotherms of nitrogen and argon at 78°K on Pyrex glass to absolute pressures of  $10^{-9}$  torr and to coverages of  $10^{-4}$ ; some of their results are shown in Fig. 13. Fedorova (44) has reported nonlinear adsorption isotherms of hydrogen and deuterium on several adsorbent charcoals over a pressure range of  $10^{-3}$  to  $10^{-8}$  at 4°, 20.4°, and 80°K. It is estimated that  $\theta = 0.10$  at  $10^{-6}$  torr for this material. The isotherms for hydrogen at 20.4° and 80°K are given in Fig. 14.

The failure to obtain Henry's law at low coverages may be due to the fact that a sufficiently low coverage has not been attained to realize a residual uniform surface. However, Henry's law behavior for known heterogeneous surfaces at low coverage appears to be another matter. Barrer and Rees (10) concluded that this is due to an approximate linear relationship that exists between  $T\Delta S_0$  and  $\Delta E$  (where  $\Delta S_0$  is the thermal entropy of adsorption and  $\Delta E$  the energy of adsorption), which may occur only at highly dilute coverage. A

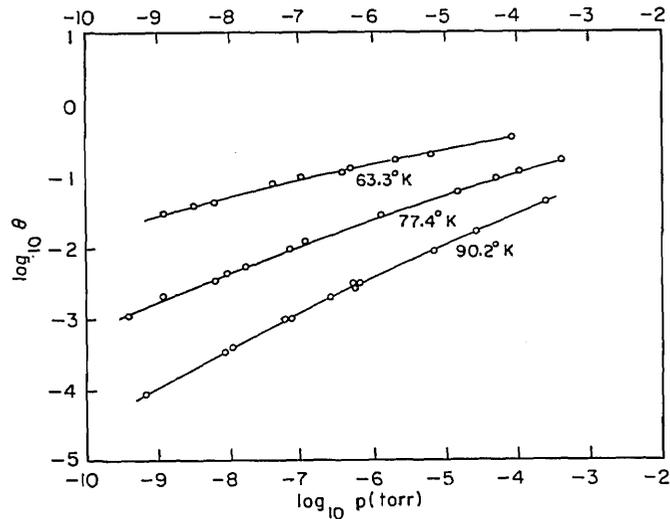


Fig. 13 - Physical adsorption of nitrogen on Pyrex glass at 78°K (66)

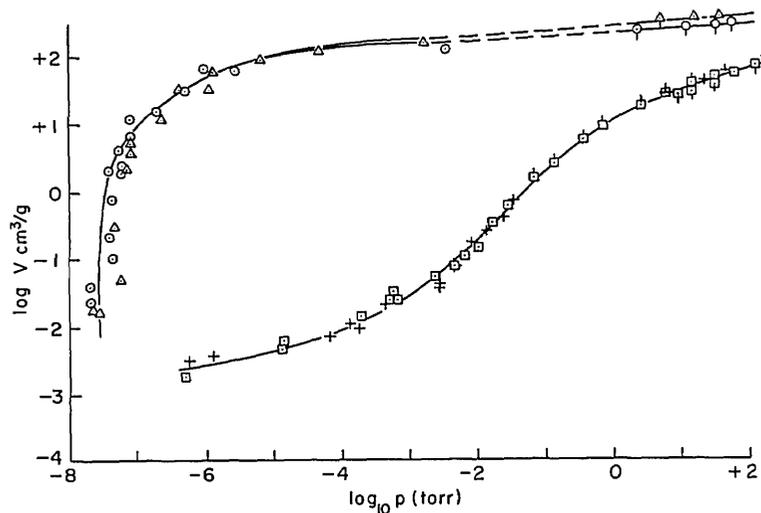


Fig. 14 - The adsorption of hydrogen on a charcoal at 20.4°K (top curve) and 80°K (bottom curve) (44)

similar conclusion was reached by Everett (42) and Barker and Everett (6), who related the linear behavior to a constant value of  $\Delta S_{\text{ad}} / (T\Delta C_p + RT)$ , where  $\Delta C_p$  is the differential heat capacity of adsorption. Thus,  $\Delta E$  at low surface coverage may depend on temperature and not on coverage, but at the lower temperatures, where the adsorption may cease to follow Henry's law,  $\Delta E$  becomes dependent on coverage.

At very low fractional coverage the isosteric heats of adsorption may be quite large. A well-known example is the oxygen/charcoal system for which values of 70 to 80 kcal/mole have been reported for the first increment of gas introduced (70,82). Recently, the differential heats of adsorption of oxygen on a purified mineralogical graphite ("evacuated for a long time and degassed at  $10^{-5}$  mm Hg") (43) were determined calorimetrically.

Very large heats of adsorption ( $\sim 100$  kcal/mole) were observed up to  $0.3 \mu\text{mole}/\text{m}^2$ ; thereafter, the heat decreased steadily with oxygen adsorption ( $\sim 50$  kcal/mole at  $1.4 \mu\text{mole oxygen}/\text{m}^2$ ). Such magnitudes are doubtlessly to be associated with chemisorption processes. Cook, Pack, and Oblad (27) raised the question of whether physical adsorption typified by the Type II isotherm can exist in the low-pressure region. These authors suggested that a mechanical strain exists at the surface of the solid and the first amounts adsorbed are associated with the relief of this strain. To this may be added a chemical aspect. When the first aliquot of gas is added to an intensively outgassed solid, the rate of adsorption is definitely slower than for succeeding doses. This behavior is associated with chemical changes that are apparent in the composition of the gas phase as revealed by mass spectrometry techniques. Bursts of gas have been observed when a crystal is cleaved under ultrahigh vacuum conditions (116). From the surface chemist's point of view, part of the "strain" located at the surface may be associated with surface impurities that are known to concentrate at the interface and which may be released by desorption or by a molecular exchange brought about in the first introduction of the adsorbed gas under study.

The interaction of surface atoms and the adsorbate atoms or molecules to minimize the surface energy leads in general to ordered arrangements. This is readily accomplished, given a sufficient degree of surface mobility. In the preparation of commercial solid adsorbents and catalysts, however, much effort is made to avoid minimization of surface energy. Here, disordered structures and high surface energies are sought. Fundamental knowledge of the sparsely covered surface can, therefore, indicate the direction to go to attain either goal.

The thermal desorption of gases in ultrahigh vacuum has been widely studied by the "flash-filament" technique to determine the reaction order and the dependence of activation energy on surface coverage (94). When applied to gases chemisorbed on the refractory metals, the results indicate that there are several adsorbed states on the same surface. Nitrogen has three states on tungsten and two on molybdenum (90). Oxygen adsorbed at  $300^\circ\text{K}$  on polycrystalline molybdenum in two states has been shown by Redhead (95) to desorb by electron bombardment (0-300 eV) into neutral atoms and  $\text{O}^+$  ions in the ratio of 50 to 1. The surface chemistry and physics of even these well-defined surfaces entails, therefore, fundamental atomic processes that require the application of several available techniques simultaneously for further elucidation.

## THE ADSORBENT SURFACE

### Chemical Composition of the Boundary

The useful properties of commercial solid adsorbents and catalysts normally depend on the presence of chemical groups possibly extraneous to the bulk composition. These serve to prevent an otherwise self-minimization of the surface energy of the solid. One requirement essential to research investigations is the ability to approach an ideal surface as closely as possible and then study the effect of an applied change. The composition of the boundary of a solid can only be controlled to a limited degree during its formation. The impurities in the reactants may be adsorbed or desorbed at the interface; and although constituting a relatively small fraction of the total solid, this segregation of impurities can involve a significant fraction of the boundary. In addition, the environment may contribute adsorbed species or decomposition products, unless very special precautions are taken.

The importance of surface composition was recently demonstrated in a study of sodium chloride crystals containing 2.2% calcium chloride (74) prepared from fused mixtures. The higher catalytic activity of the mixture toward ethyl chloride dehydrohalogenation than that of sodium chloride alone was accounted for by the preferential adsorption of calcium ions at the interface. Repeated extracts with acetone, in which both salts are only

slightly soluble, showed a large difference between bulk and surface concentration of calcium and reflected the greater ease of making a cation vacancy in the surface of the sodium chloride than doing so in the interior. In general, the "active centers" originally conceived by the surface chemist are now interpreted as vacancies, interstitial atoms, dislocation, and occluded impurities by the solid state physicist. The nonstoichiometric behavior of some materials is based on the composition of the total sample; the well-known laws of combining proportions for macrostructures need revision where applied to surface structures (76).

Adsorbed impurities have long been known to influence the growth, topography, and evaporation of crystals. The complexity of the problem is paced by the great variations possible in the chemical environment. For example, sodium chloride crystals react readily with water vapor and oxygen (7). The reaction with water vapor displaces chlorine by hydrolysis, and this can be reversed by a treatment with hydrogen chloride. The oxygen ( $O_2$  or  $O_3$ ) reaction with sodium chloride forms an anion species, probably  $O_2^-$ , and an appreciable amount can be introduced by normal handling and annealing in the laboratory atmosphere. A value for the  $OH^-$  concentration in sodium chloride of  $10^{-4}$  to  $10^{-5}$  mole fraction was found at 1% R.H. (7).

The importance of adsorption impurities in a study of the gas/solid interface cannot be overemphasized (21). Figure 15 shows schematically some of the simple defects that are possible in a surface. As early as 1927 Kossel postulated that a growth process involved surface adsorption, diffusion to a step, diffusion along a step to a point defect (active site) and incorporation into the crystal. Much later, Frank (45) proposed that crystal dislocations provided a source of molecular steps required for the growth step. Very small amounts of impurities change the surface diffusion and the time of residence on a surface. Obviously there is need to collect systematic information on individual systems prepared in the particular way of interest to the investigator.

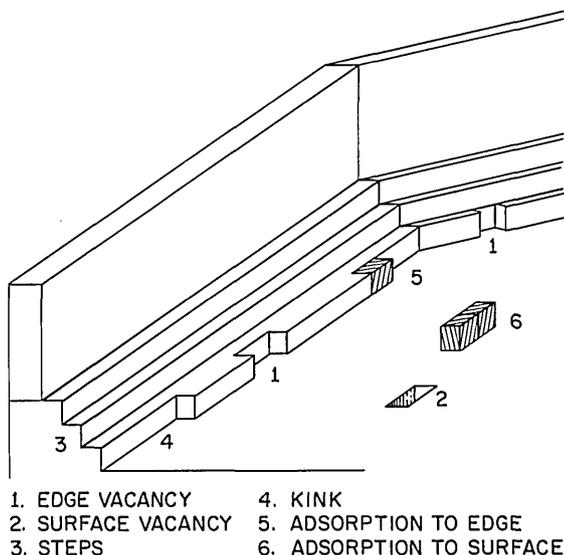


Fig. 15.- Simple defects ascribed to the boundary surfaces of crystals

There appear to be two limiting cases that the surface chemist might consider: (a) immobile adsorbed impurities and (b) completely mobile impurities. In the first case, the adsorbed layer must squeeze around the impurity and thus incorporate the impurity into the adsorption complex. The degree to which this takes place depends on the concentration of impurity; it may build to an extent that stops all growth.

In the second case, the mobile-impurity concentration along the step is in equilibrium with its gaseous concentration, and the principal effect is then to maintain the impurity concentration at the active site. This lowers the rate of adsorption by direct poisoning or by an exchange process. Mobile adsorbed impurities lower the edge energy, and this raises the chemical activity of the adsorption site, i.e., a dislocation or nucleation. One current view of whisker growth from the vapor is (1) adsorption of atoms on perfect sidewalls of the whisker, (2) surface diffusion to the tip, and (3) incorporation at a step in the tip.

The whisker growth of silicon crystals, however, has been ascribed to the essential presence of an impurity (53). This has led to a vapor-liquid-solid mechanism of single crystal growth (117) in which the impurity forms a droplet having a relatively low freezing temperature. This is a preferred site of vapor deposition and causes the liquid to become supersaturated. The whisker grows by precipitation of the solid from the droplet. The proposed mechanism has many applications in which controlled growth can be obtained by appropriate use of impurities.

Semiconductors are examples in which "impurities" can actually be termed the essential ingredient. Oxygen adsorption on atomically clean surfaces has shown the importance of specifying the surface condition of each crystal face (36), since differences in behavior are in some cases due to contamination alone and in other cases to crystal face orientation produced in a degassing followed by subsequent annealing. Some surface properties of the gas/germanium system have been reported by Zettlemyer et al. (123). The adsorption isotherms of argon and propanol were determined after treating the germanium 15 hours at  $10^{-5}$  torr and temperatures ranging from  $25^{\circ}$  to  $500^{\circ}\text{C}$ . The interaction (chemisorption) of propanol with oxide- and/or hydroxide-covered germanium single crystals could be correlated with the electrical conductivity. This is an example of the need for simultaneous measurements of adsorption and some independent property, in this case, an electronic behavior of the germanium single crystal (68).

It is well appreciated that chemical groups in the gas/solid interface can be modified and thus bring about pronounced changes. In recent years a start has been made in relating the observed adsorption with changes in the molecular spectra of the adsorbate. One example is the infrared absorption spectra in the OH region observed for various silicates before and after the adsorption of various organic compounds (111). A narrow band at  $3750\text{ cm}^{-1}$  (the position for the free stretching frequency) is unchanged in position, but the adjacent wide absorption band (hydrogen-bonded surface OH groups) is sensitive to the thermal treatment of the silicate and to the adsorbate employed. Galkin, Kiselev, and Lygin (49) examined the changes in spectra of a silicate surface with adsorbed aromatic hydrocarbons. The shift in the OH absorption band was related to the heat of adsorption of the hydrocarbon. Removing the OH from the surface (dehydration and methylation) lowers the adsorption and the heat of adsorption for polar, quadrupolar, and  $\pi$ -electron-bond molecules; the intensity of the absorption bands for CH out-of-plane modes of vibration is also lowered. A complete understanding of the spectra of the adsorption complex will require experimental data of high resolution, and a satisfactory theoretical treatment has yet to be formulated.

#### The Geometric Factor in Gas/Solid Interaction

The terminal planes of a solid are generally considered different than the substrate planes where the forces between constituents have the symmetry of the crystal. Actually, the boundary planes may be bonded to the substrate quite differently. Either there may be strong interactions in the z-direction, or the interaction may be strong in the xy plane (assumed to be in the surface). Ionic crystals and graphite are examples, respectively. In all likelihood there are intermediate degrees of interaction possible in other types of surface structures where, in addition to symmetry considerations, the steric factors of fit and misfit contribute to the distance of closest approach.

Regions of low and high surface activity are in all likelihood accompanied by corresponding differences in atomic structure of the surface. Correlations between the geometry of the surface and catalytic activity have been sought by many investigators (Balandin (4), Beeck (15), Rideal (60,114), and Maxted (83)), and definite evidence has been obtained with the field-emission microscope by Müller and Drechsler (89) and others. The activity of individual crystal faces in catalysis has been reviewed by Gwathmey and Cunningham (52); and although the activity does depend on the particular lattice spacing exposed, there are regions within any one face which differ in activity. These differences must now, of course, be related to imperfections in the crystal.

As discussed in a previous section, the simplest method of varying the geometry of a solid surface is by evaporation onto a suitable substrate. The evaporated film may range from a random array of small crystallites to one with a well-organized structure. The surface area of a fresh deposit demonstrates that evaporated films are particularly sensitive to thermal treatment, the reduction in area depending on time, temperature, and the weight of the film. This appears to be particularly true for films that are free of serious chemical contamination. The sintering has been ascribed to the mobility of metal atoms on their own surface. According to Tammann's rule (118) the mobility of the atoms of a solid attains an observable rate in solid-solid reactions within a temperature range one-half below the normal melting point expressed in °K. This approximate rule would limit the sintering of nickel to temperatures above 600°C; actually, it takes place at a considerably lower temperature as shown in Table 8. With more sensitive methods based on radioactive tracers, the mobility of constituent atoms far below the melting point has been detected in numerous self-diffusion measurements for a large number of metals and alloys.

Table 8  
Sintering of Some Evaporated Films

Copper*		Nickel†		Carbon‡	
(10 mg weight)		(10 mg weight)		(3.23 mg weight)	
Temp. (°C)	A (m <sup>2</sup> /g)	Temp. (°C)	A (m <sup>2</sup> /g)	Temp. (°C)	A (m <sup>2</sup> /g)
-183	39				
-183 to 18	12	25	0.19	24	730
18	6	100	0.12	400	730
100	4	200	0.084		
		300	0.064		
		400	0.050		

\* Ref. 2.

† Ref. 28.

‡ Ref. 35.

Films of copper show a similar sintering behavior. The BET areas (ethane at -183°C) of thin films of evaporated copper were determined by Allen, Evans, and Mitchell (2), and the oxygen adsorption was also observed. Typical isotherms are shown in Fig. 16. For films deposited at -183°C, the surface areas (39 m<sup>2</sup>/g) were linearly proportional to the mass of copper in the films. These facts were interpreted in terms of a uniformly porous structure. The decrease in area on annealing and the accompanying decrease in the resistance (prevented by the admission of oxygen) suggest a structure change by a surface migration of copper atoms. As in the case of nickel, the temperatures were considerably below the melting point of copper.

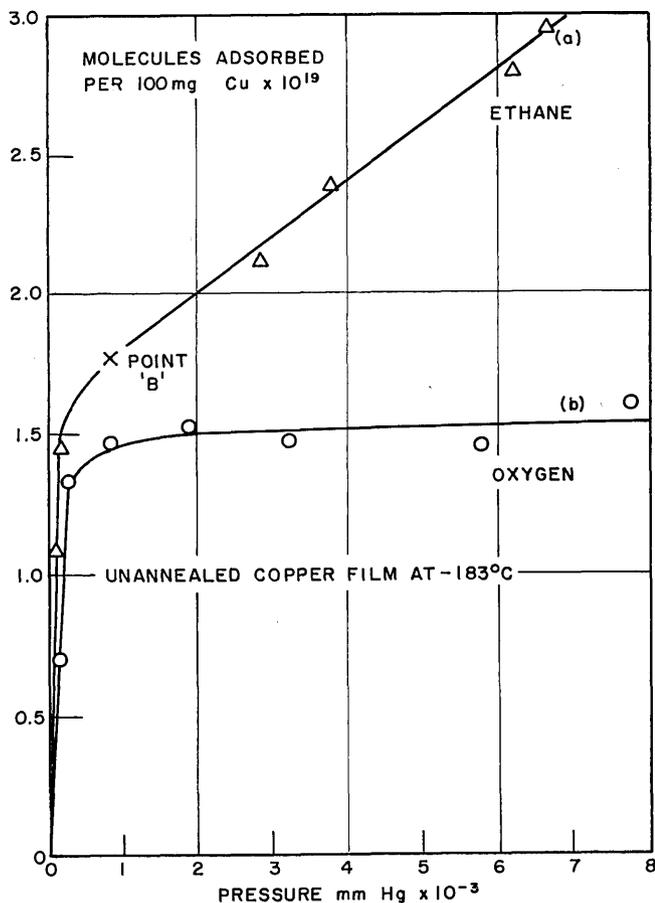


Fig. 16 - Adsorption isotherms of ethane (a) and oxygen (b) on copper films at  $-183^{\circ}\text{C}$  (Allen, Evans, Mitchell (2))

In contrast to the behavior of metal films, carbon films deposited at  $78^{\circ}\text{K}$  show no sintering effect up to  $400^{\circ}\text{C}$ . In view of the very high melting point of carbon ( $\sim 4000^{\circ}\text{K}$ ) this may be expected. Working with stacked films of carbon and nickel, Deitz and McFarlane (35) have shown that the observed sintering may be attributed solely to the nickel content. This is shown in Fig. 17.

The sintering behavior of some metal films may depend on factors other than mobility of the constituent atoms. Caswell and Budo (23) observed that tin films deposited at  $78^{\circ}\text{K}$  were continuous (electron micrograph) but agglomerated into separate islands in vacuums of  $\sim 10^{-8}$  torr when warmed to room temperature. However, any stage in the agglomeration process could be stabilized by admitting oxygen ( $10^{-4}$  torr) and warming to room temperature. A surface oxide monolayer was formed with no appreciable diffusion of oxygen into the bulk of the film. It has been proposed that oxygen be used to freeze a low-temperature kinetic process (69) so that it may be examined at room temperature. This technique could be useful in certain problems, and the value of ultrahigh vacuum procedures is self-evident for maintaining good control of a desired impurity.

Using a "decoration" technique with evaporated gold and graphite surfaces (in quantities only sufficient to form less than a monolayer), Hennig (58,59) showed that the gold aggregated preferentially at surface irregularities which were thus rendered visible under electron microscopy. Adsorbed impurities caused a considerable increase in the background

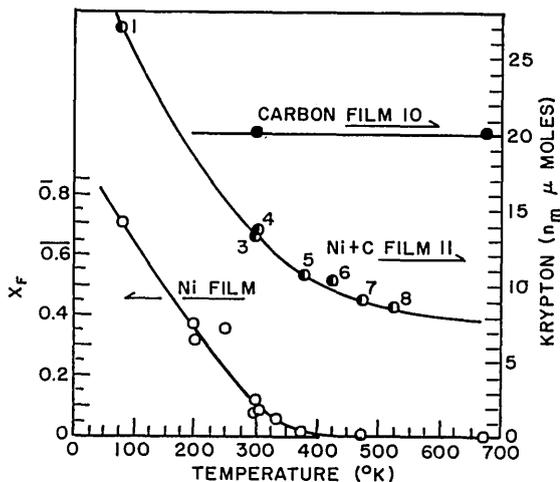


Fig. 17 - Area changes of nickel and of nickel-on-carbon produced on heating to progressively higher temperatures (35)

Table 9  
Aggregation of Gold Observed by Hennig (58)  
on Cleaved Graphite Crystals

	Aggregates/ $10^{-10} \text{ cm}^2$
Freshly cleaved	0.1
Cleaved, heated to 900°C	0.02
Adsorbed $\text{Cl}_2$	1
Adsorbed $\text{I}_2$	20
Adsorbed Acetone	190
Reacted with Ozone	60

number of gold aggregates either uniformly or in patches—atomic H produced patches within seconds at room temperature and molecular  $\text{H}_2$  only above 850°C. Hennig's results, given in Table 9, show that surface compounds were surprisingly stable after heat treatment. Water could be removed below 300°C, but acetone appeared only partly removed in vacuum at 500°C, leaving residues that became "decorated" by gold.

#### Chemical Reactivity at the Gas/Solid Interface

An enhanced chemical reactivity is generally found when the reactants are made part of a particular gas/solid interface. As a consequence, the temperature range in which a reaction rate becomes appreciable is significantly lowered relative to the reaction between the condensed phases. The enhancement is not due only to the increase in surface area but takes place under conditions thought to be preliminary to actual catalytic activity. One or more chemisorption processes involving adsorption complexes are generally acknowledged to be involved as intermediate steps.

Many techniques are being used to study the intermediate complexes. These include infrared spectroscopy, high-vacuum techniques, field-emission microscopy, nuclear magnetic and electron spin resonance, contact potential measurements, and measurements of the geometric structure of the surface and substrate (41). The evidence for the existence

of "hot spot" adsorption, or the adsorption bond, has been reviewed by Schuit and Reijen (107) for metal-on-silica catalysts. In this case the bonds are covalent although slightly polarized.

In addition to the formation of chemical bonds with constituents in the surface, a more subtle interaction involves the bending of chemical bonds and the formation of oriented adsorbates. In regard to the adsorbate, the gas/solid interaction must be accompanied by decrease in entropy of the system. The cooperative orientation of surface-adsorbate bonds furnishes a further entropy decrease that can be quite significant in special systems. In fact, this mechanism would be a plausible one to explain relocation of the atoms and groups in a surface and the relief of strain distributed over the surface without transmitting it through the solid. The experimental approach to this aspect of adsorption is through the anisotropy of optical and magnetic measurements.

### CONCLUDING REMARKS

This report presents many interesting trends in current researches at the gas/solid interface. It is increasingly relevant to report surface reactivity in terms of unit surface. The physical adsorption of nitrogen at low temperatures may be used with only a few exceptions as a general measurement of surface area. Furthermore, it now appears desirable in the determination of adsorption or desorption to make a simultaneous measurement of some additional property of the adsorbate/adsorbent complex. In this way a greater insight is possible as to the nature of the gas/solid interaction. Obviously, a primary observation of fundamental significance is preferred.

A serious effort is now being made to define the initial states of the adsorbent solid and the adsorbing surface in terms of atomic structure. This has led to an increasingly closer tie between the surface chemist and the solid state physicist. It would be very helpful to resolve some aspects of the apparently different vocabularies used by these two disciplines.

There is an increasing use of evaporated or otherwise vacuum-deposited films to study fundamental surface properties. In so doing, many new aspects of individual solids without their normal bulk impurities have been discovered. The advances in high-vacuum technology have furnished commercial equipment to do this. The various film-forming techniques are capable of producing surfaces of a high degree of definition. With gas phase chromatography and mass spectrometry available to analyze complicated gas mixtures, the adsorption of mixed gases has taken on an added interest. One may look forward to considerable progress using multiple-component gases at both multilayer- and fractional-layer coverages.

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13. ABSTRACT <p>Adsorption and desorption studies of gas/solid interfaces have been, in the past, mainly concerned with considerations of mass balance. A strong effort is now being made to define the initial state of the adsorbing surface in terms of solid state structure and composition and to identify the adsorbent-adsorbate complex. The most important experimental parameter in current researches is probably the influence of the pretreatment of the solid before measurements. The properties of some surfaces may change with time as the strain-stress relationships set up in forming the solid adjust slowly toward minimum surface free energy. The pretreatment may include some combination of thermal, electrical, and chemical methods.</p> <p>It is increasingly relevant to report a surface property in terms of unit surface. The physical adsorption of nitrogen and krypton at low temperatures may be used to obtain the necessary data for a surface area evaluation. The determination of <math>v_m</math> (the volume of nitrogen at STP required to form a monolayer of adsorbed gas) can be accomplished by the point B method or by the BET procedure, the latter requiring fewer data. In special cases, other adsorbates such as ethane and carbon dioxide have proved useful.</p> <p>Multilayer adsorption presents many unsolved problems; the theoretical difficulties are similar to those encountered in studies of the liquid state. Current researches at fractional surface coverage attempt to express the surface nonuniformity in terms of an energy distribution as a function of surface coverage. Considerable interest is now being expressed in the field of "high-temperature" physical adsorption. At the corresponding low surface coverage, there is minimum interaction between adsorbate molecules.</p> <p>Development of modern gas chromatography and mass spectrometry make it possible to follow the partial pressures of all gaseous reactants and products of a gas/solid system. Facility of data collection makes possible more elaborate experimental designs. The ability to analyze complicated gas mixtures enables new studies to be made of selective adsorption in multiple-component systems.</p> <p>High-vacuum technology is rapidly being applied to researches at low surface coverage. Surface properties are very sensitive to adsorbed impurities (mobile and immobile) that originate either in the environment or as decomposition products from sample preparation. Only in ultrahigh vacuum systems can one minimize the impurity and study its influence systematically. There is an increasing use of evaporated films or otherwise vacuum-formed deposits in order to study fundamental surface properties. A greater insight into the nature of the gas/solid interaction is thus possible which holds great promise for the growth and development of this phase of surface chemistry.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Adsorption Desorption Gas/solid interface Adsorbate - adsorbent complex BET theory Point B method Monolayer Multilayer Coverage Fractional surface coverage Adsorbed impurities Ultrahigh vacuum Surface area						

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