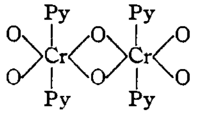
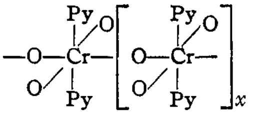
throughout the reaction. The analytical methods have already been described.[2] The percentages of chromium reduced in the various reactions are listed in Table I.

Discussion

If we were to consider the addition compounds of the type $CrO_3 \cdot 2\beta$ (β = pyridine or some similar nitrogen base) prepared in this study to be monomeric, and to be formed by the sharing of electrons between the nitrogen and chromium atoms, it must be assumed that the chromium atom has the unusual coördination number of five. Such an assumption is not necessary, however, if we consider the possibility of molecules containing more than one molecule of chromic anhydride. Two possibilities which immediately suggest themselves are





To obtain additional information as to the molecular structure of these complexes, X-ray diffraction studies of these compounds are contemplated. Cryoscopic studies on solutions of the various addition compounds in an excess of the corresponding nitrogen base are also indicated, and it is expected that such studies will be carried out in this Laboratory.

The percentages of chromium reduced in the reactions of the chromium anhydride addition compounds of pyridine, β-picoline, and γ-picoline, with liquid ammonia do not differ greatly from those obtained in the reaction of chromic anhydride itself.[2] These results may be taken to indicate in a rough way that the reduction of only about 25% of the chromium is not explainable in terms of the arrangement of the CrO_3 units in the crystal lattice.

It is interesting to note the marked difference in the behavior of α-picoline toward chromic anhydride and that of β- and γ-picoline. The former amine apparently has a much less tendency to coördinate with chromic anhydride and a much greater tendency to be oxidized by that substance than do the β- and γ-picolines. The latter effect is to be expected for it is a well known fact that an α-methyl group on a pyridine ring is of the activated type and is, therefore, more susceptible to oxidation than are β- or γ-methyl groups. The lesser tendency of α-picoline toward coördination with chromic anhydride may result, in part at least, from the steric interference of the methyl group with a CrO_3 molecule approaching the neighboring nitrogen atom.

Summary

The reactions of chromic anhydride with pyridine, α-picoline, β-picoline, γ-picoline, quinoline and isoquinoline have been studied. The compounds $CrO_3 \cdot 2C_5H_5N$, $CrO_3 \cdot 2C_6H_7N(\beta)$, $CrO_3 \cdot 2C_6H_7N(\gamma)$ and $CrO_3 \cdot 2$ quinoline have been prepared.

Chromic anhydride is almost completely reduced by isoquinoline at room temperature. α-Picoline is more easily oxidized by chromic anhydride than is β- or γ-picoline or pyridine, and has a lesser tendency to coördinate with chromic anhydride than the latter substances.

The reactions of $CrO_3 \cdot 2C_5H_5N$, $CrO_3 \cdot 2C_6H_7N(\beta)$ and $CrO_3 \cdot 2C_6H_7N(\gamma)$ with liquid ammonia at $-33°$ were carried out. These substances react with liquid ammonia in a manner similar to chromic anhydride itself and give a similar percentage of reduced chromium (about 25%).

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

On Physical Adsorption.[1] II. A Comparison of Methods of Estimating Surface Areas of Crystalline Solids by Gas Adsorption[2]

BY SYDNEY ROSS[3]

Introduction

The adsorption isotherms of ethane at $-183°$ on cube crystals of sodium chloride and potassium chloride have been reported.[4] The results obtained were interpreted as indicative of a two-dimensional phase transition of ethane. The nature of these isotherms makes it possible to compare some of the methods that have been proposed for estimating the surface area of crystalline solids by means of gas adsorption. The great practical utility of the methods involved is proffered as justification for the subject of this report.

The BET[5] method of obtaining the surface area

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(1) The first paper of this series (see ref. 4) will be published within the next few months.

(2) This document is based on work performed under Contract No. W-35-058, eng 71 for the Atomic Energy Project at the Clinton Laboratories (now Oak Ridge National Laboratory). Presented before the Division of Colloid Chemistry at the 113th national meeting of the American Chemical Society, Chicago, Illinois, April 19–23, 1948.

(3) Present address: Department of Chemical Engineering and Chemistry, Walker Laboratory, Rensselaer Polytechnic Institute, Troy, New York.

(4) S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena." Presented at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April 14–18, 1947. See Abstracts of Papers, p. 33P, No. 52. Also see MDDC 864 (Office of Technical Services, Department of Commerce, Washington, D. C.).

(5) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938); P. H. Emmett, "Advances in Colloid Science," Vol. I, New York, 1942, pp. 1-36.

of a solid by the adsorption of a gas at a constant temperature has already been so widely applied that it is generally familiar. Not as well known is the method proposed by Gregg,[6] which is essentially a simple carry-over of a method from the more fully developed field of adsorption on liquid surfaces to gas adsorption on solids.

Gregg's Method.—Gregg follows Bangham's[7] procedure in integrating the Gibbs adsorption equation

$$\Gamma = (1/RT)\, d\pi/d \ln p$$

in order to get the relation

$$\pi\Sigma = kT \int_0^p x\, d \ln p \qquad (1)$$

where π is a two-dimensional pressure analogous to the surface pressure of films on water and x is the number of molecules adsorbed per gram of adsorbent, having Σ square centimeters per gram. k is the Boltzmann constant, R/N.

The area per molecule, σ, is Σ/x, so

$$\pi\sigma = \pi\Sigma/x \qquad (2)$$

Following Bangham's procedure, Gregg calculated $\pi\Sigma$ by plotting x against $\ln p$ and taking the area under the curve from zero up to any pressure p $\pi\sigma$ is then found from Equation 2, and plotted against $\pi\Sigma$.

Graphical integration at the lower limit of the integral is accomplished by using a two-dimensional analogy to Henry's law for the solubility of gas in liquids, $x = mp$. Then

$$\int_0^{p_1} x\, d \ln p = mp_1 = x_1$$

where x_1 is the value of x when p equals p_1. This is equivalent to assuming the ideal gas law ($\pi\sigma = kT$) to describe the behavior of the surface film at low pressures, up to the lowest pressure (p_1) at which the experimental points occur. It may well be that the first experimental point is not at a pressure sufficiently low that the assumption of a linear isotherm extending from that point to zero pressure is fully justified. For insoluble films on water it is known that in many cases extremely low surface pressures must be achieved before one has a perfect gas. The detailed course of the $\pi\sigma$–$\pi\Sigma$ diagram for the region of low adsorption is therefore uncertain but in the range of medium and high adsorptions it is not much affected by uncertainties in the isotherm at low adsorptions, and so can still be drawn even if low-pressure data are scanty.[6]

The data of Ross and Boyd[4] for the adsorption of ethane at −183° on cube crystals of sodium chloride and potassium chloride are used in this paper to illustrate the connection between Gregg's method of estimating surface areas and the well-known BET method. The argument is dependent on the validity of the assumption that the preponderant surface of the sodium chloride and potassium chloride crystals is the (100) surface. The crystals were carefully prepared using the technique recommended by Fitz-Hugh Marshall[8] for the production of cube crystals of sodium chloride of uniform size. Photomicrographs of the samples used revealed defects in the uniformity of size but each separate crystal was clearly seen to be a perfect cube with no visible indication of any octahedral or other faces.

The ethane isotherms of sodium chloride and potassium chloride at −183° were treated as described, and the $\pi\sigma$–$\pi\Sigma$ curves so obtained are shown in Figs. 1 and 2. By analogy with the $\pi\sigma$–$\pi\Sigma$ graphs for films of insoluble substances on water, Gregg interprets such $\pi\sigma$–$\pi\Sigma$ graphs as those in Figs. 1 and 2 as descriptive of a transformation from an adsorbed gaseous or vaporous state to a condensed state of the adsorbed film. The linear portions of these curves are described by the two-dimensional analog of Amagat's equation for highly compressed gases and liquids

$$\pi(\sigma - \sigma_0) = ikT \qquad (3)$$

in which σ_0 is the limiting area of the adsorbed molecules and $1/i$ is a measure of the lateral molecular cohesion.[9]

The slopes of the linear portions of the curve are numerically equal to σ_0/Σ. If appropriate values can be assigned to σ_0, the specific surface Σ can be calculated. Assignment of a value of σ_0 must be made with reference to the manner of orientation proper to the state of the film, whether gaseous or condensed.

In Fig. 1 there are two linear portions of the curve. The slope of both portions can be measured, giving σ_0/Σ, although it is not to be expected that the same value of σ_0 will be applicable to both cases. The first linear portion represents a gaseous film where the molecules are considerably further apart than they are in the condensed film that is represented by the second linear portion. As is therefore to be expected, the first slope is greater than the second.

In Figure 2, ethane adsorbed on potassium chloride, there are only a few data at low pressures from which to evaluate the slope of the $\pi\sigma$–$\pi\Sigma$ curve for the gaseous film. The method of least squares was used to draw the line shown in the figure. It may be used to provide an approximate result. For the condensed film a linear portion is again obtained and is sufficiently marked to determine its slope.

We are now required to make decisions about appropriate values for σ_0 for adsorbed ethane films, where both the physical state of aggregation and the solid substrates are capable of variation. In trying to derive suitable values of σ_0 two courses of procedure are possible. We can assume that

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(6) S. J. Gregg, *J. Chem. Soc.*, 696 (1942).

(7) (a) Bangham and Fakhoury, *J. Chem. Soc.*, 1324 (1931); (b) Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc.* (*London*), **138A**, 177(1932); (c) D. H. Bangham, *J. Chem. Phys.*, **14**, 352 (1946).

(8) Fitz-Hugh Marshall, *Phys. Rev.*, **58**, 642 (1940).

(9) E. K. Rideal, "An Introduction to Surface Chemistry," Cambridge, 1930, p. 66.

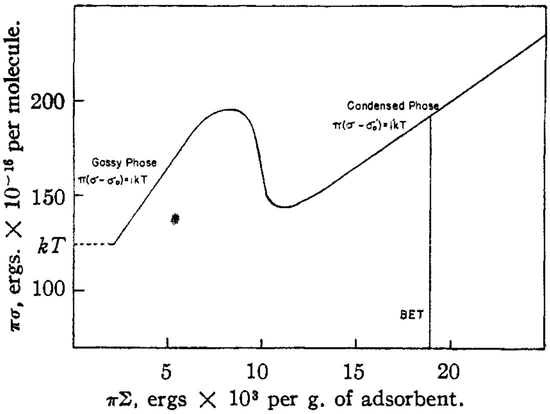

Fig. 1.—$\pi\sigma$–$\pi\Sigma$ diagram for ethane adsorbed on (100) surfaces of sodium chloride, from data of Ross and Boyd.[4] The course of the experimental observations is indicated by the full line; the broken line indicates the perfect gas isotherm, $\pi\sigma = kT$, assumed at low pressures. The vertical line labelled BET cuts the isotherm at σ = 23 Å.^{2}, corresponding to the adsorption of an amount of vapor enough to produce a single layer of molecules on the surface at 23 Å.^{2}/molecule.

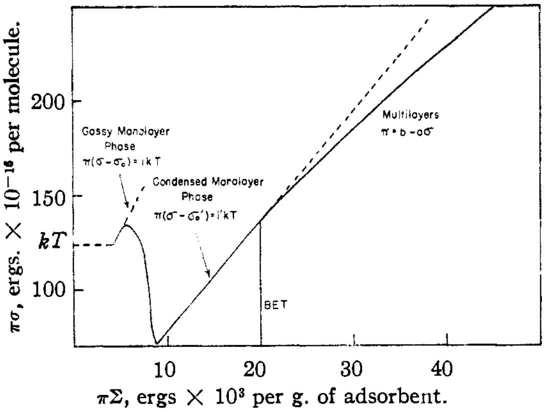

Fig. 2.—$\pi\sigma$–$\pi\Sigma$ diagram of ethane adsorbed on (100) surfaces of potassium chloride from data of Ross and Boyd.[4] The course of the experimental observations is indicated by the full line; the broken lines indicate the ideal gas at low pressures and the Amagat equation for the gassy and condensed phases, respectively. The vertical line labelled BET cuts the isotherm at σ = 23 Å.^{2}, corresponding to the adsorption of an amount of vapor enough to produce a layer of molecules on the surface at 23 Å.^{2}/molecule.

the value of Σ, the specific surface of the solid, is determined correctly by the BET method, and then calculate backward to find out what values of σ_0 would have to be used to give an agreement with the BET Σ. The values of σ_0 thus obtained could then be examined to see if they give any information about the film or the substrate.

An alternative mode of presentation is first to examine the nature of the substrate and the adsorbed film and attempt to deduce the incompressible area of the molecule therefrom. This is the more direct and hence preferable method, although it may affect the reader unpleasantly by directing his attention to matters not customarily taken into consideration in evaluating molecular areas.

Area Occupied by Adsorbed Ethane Molecules

Lennard-Jones and Dent[10] have considered the total cohesive force in the field outside a (100) plane on a crystal of the rock salt type, between the crystalline solid and an external atom or ion. They have shown that the work required to separate a charge *e* from the crystal is a maximum immediately above the lattice points on the surface, because of the influence of the electrostatic field outside the crystal. The energy of adsorption, however, also takes into account the van der Waals attraction between the molecules of the gas and the crystal, which force they found to be of greater importance at long distances than the electrostatic field. The *total* energy of adsorption is greatest above a point equidistant from the four ions, and where the electrostatic force is zero.

The most extensive calculations of the energy of attraction of molecules to sodium chloride type crystals were done by Orr,[11] based on the method of reasoning outlined by Lennard-Jones. For argon adsorbed on cesium iodide the concept of adsorption in preferred positions above lattice centers leads to a square packed arrangement which is actually more stable than the close-packed hexagonal array pictured by disregarding preferred adsorption sites. For argon adsorbed on potassium chloride, on the other hand, while the atoms are adsorbed initially above centers of lattice squares, the final more stable arrangement at high adsorptions is the hexagonal close-packed, which disregards the preferred adsorption sites. For our present purpose, the course of the initial adsorption is the important consideration as that is decisive in determining the initial slope of the linear portion of the curve, and whether or not the arrangement in the first layer is ultimately close-packed or square-packed (*i. e.*, whether or not the concept of preferred adsorption sites is still relevant at high adsorptions), it is not in dispute that the early stages of adsorption on a sodium chloride type of crystal are conditioned by the existence of preferred adsorption sites.

These considerations are used in the construction of a model representing ethane molecules adsorbed on the surface (100) planes of a sodium chloride-type crystal. In the gaseous film the ethane molecules are considered to be flat on the surface.[12] When the variation of adsorption energy over the surface is taken into account, as a localizing restriction on the probable positions of the adsorbed molecules, two alternative arrange-

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[10] J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.*, **24**, 92 (1928); J. E. Lennard-Jones, *ibid.*, **28**, 333 (1932); J. E. Lennard-Jones and C. Strachan, *Proc. Roy. Soc.* (*London*), **150A**, 442 (1935).

[11] W. J. C. Orr, *Trans. Faraday Soc.*, **35**, 1247 (1939).

[12] Irving Langmuir, THIS JOURNAL, **39**, 1858 (1917); N. K. Adam, *J. Phys. Chem.*, **29**, 97 (1925).

ments appear. The center of symmetry of the ethane molecule may be placed over the most probable site or, with perhaps greater likelihood, each methyl group may be considered separately as most probably located over sites of maximum adsorption energy. Fortunately, it is not necessary to decide between alternative arrangements, as the value of σ_0 turns out to be the same by either choice. The size of the lattice and the existence of a localizing restriction are sufficient to define the limiting area of the molecule.

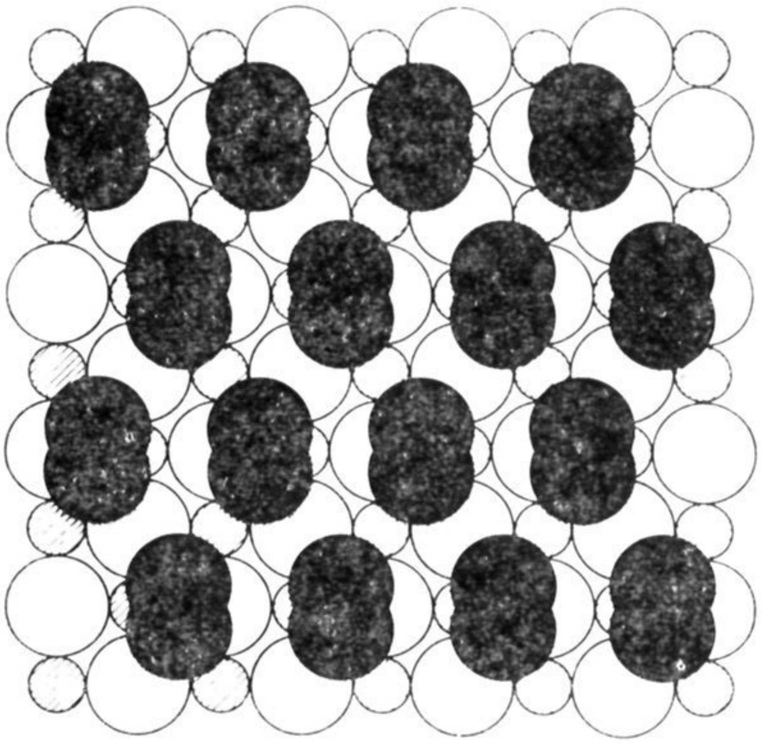

Fig. 3.—Limiting arrangement of ethane molecules adsorbed on sodium chloride surface (gaseous film):

Chart of Dimensions

	Å.
Na$^+$ radius	0.98
Cl$^-$ radius	1.83
Long dimension of C_2H_6	5.3
Short dimension of C_2H_6	3.7

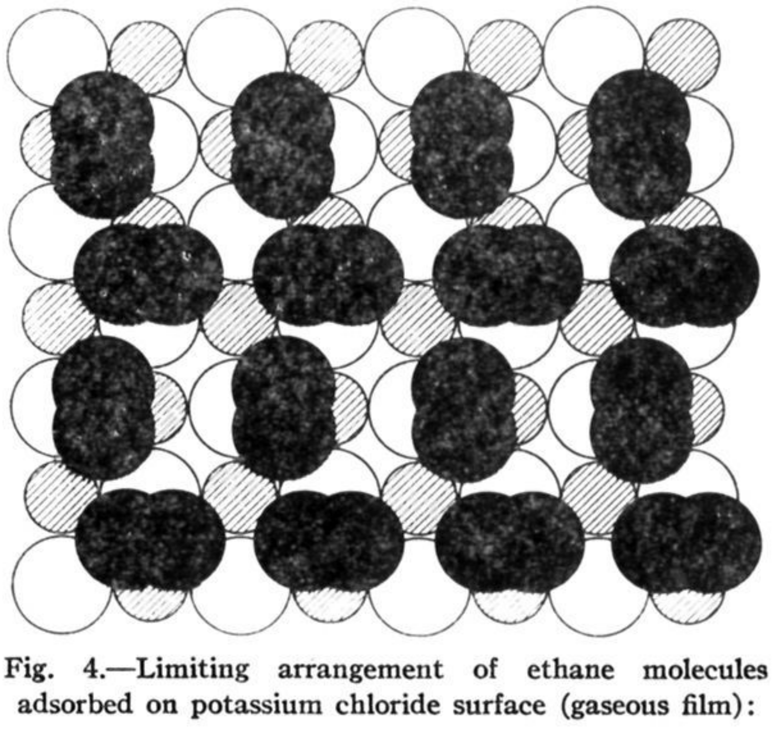

Fig. 4.—Limiting arrangement of ethane molecules adsorbed on potassium chloride surface (gaseous film):

Chart of Dimensions

	Å.
K$^+$ radius	1.31
Cl$^-$ radius	1.83
Long dimension of C_2H_6	5.3
Short dimension of C_2H_6	3.7

Figures 3 and 4, for sodium chloride and potassium chloride substrates, respectively, show arrangements for the gaseous film where the localizing restriction is that the methyl groups are each as close as possible to a site of maximum adsorption energy. The dimensions of the ethane molecule are taken from the X-ray crystallography of solid ethane.[13] A theoretically derived contraction of the crystal lattice at the surface, of about six per cent.,[14] as well as its contraction caused by cooling, are not taken into account in these figures, as experimental results for surface area determinations by ethane adsorption have a variation of 10%. For ethane on the surface of sodium chloride the closest packing of the molecules in the gaseous film is one molecule per unit surface cell (Fig. 3). The larger unit surface cell of potassium chloride would permit an arrangement of ethane molecules having one and one-third molecules per unit surface cell. Figure 4 shows the arrangement with the same localizing condition.

These are suggested arrangements for maximum packing and give rise to the following values for the incompressible molecular area of the gaseous film

(1) On NaCl surface, $\sigma_0 = (5.63)^2 = 31.7$ Å.^{2}

(2) On KCl surface, $\sigma_0 = 3 \times (6.28)^2/4 = 29.5$ Å.^{2}

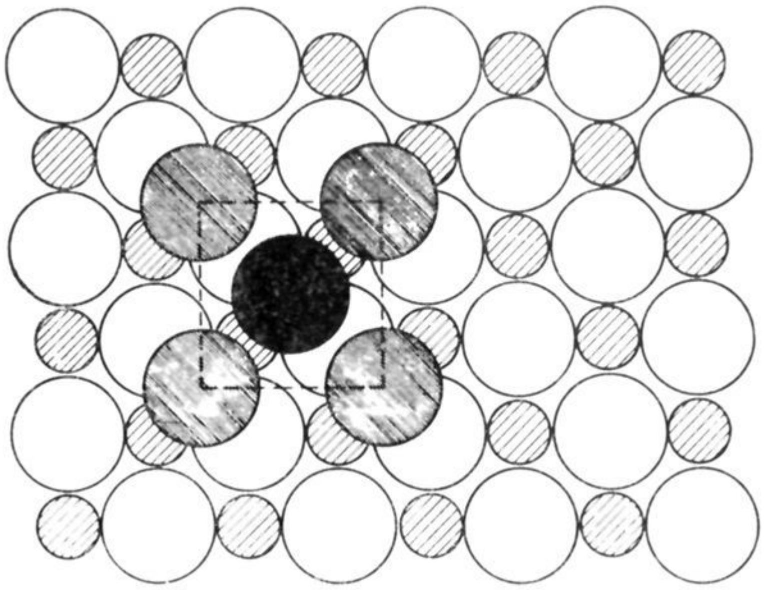

Fig. 5.—Closest approach of molecules of ethane in condensed film on sodium chloride substrate:

Chart of Dimensions

	Å.
Na$^+$ radius	0.98
Cl$^-$ radius	1.83
Long dimension of C_2H_6	5.3
Short dimension of C_2H_6	3.7

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(13) "Strukturbericht," Collected Volume for 1913–1928, 1931, p. 658.

(14) J. E. Lennard-Jones and B. M. Dent, *Proc. Roy. Soc.* (*London*), **121A**, 247 (1928).

A condensed film begins to form while the adsorption is still in the monolayer region. Ethane molecules in a gaseous film are flat on the surface, but in the condensed film intermolecular forces become more significant. More sites of maximum adsorption energy are made available, and hence closer packing of the condensed film is possible, by the ethane molecules becoming oriented vertically above the surface. If the localizing condition is still that a methyl group is most probably found above a site of maximum adsorption energy, then the arrangement for closest packing in the condensed film is as shown in Fig. 5. There are now two gas molecules in each unit surface cell; and so the incompressible area per molecule for the condensed phase is:

(1) On NaCl surace, $\sigma_0' = {}^1/_2(5.63)^2 = 15.8$ Å.^{2}, and

(2) On KCl surface, $\sigma_0' = {}^1/_2(6.28)^2 = 19.7$ Å.^{2}

In the diagrams molecules are shown in every available site, to make clear the limiting arrangement. In picturing the states to himself the reader should imagine the existence of many empty sites on the surface. The completed condensed monolayer is never actually achieved as the building of the second layer of molecules becomes sufficiently pronounced (at about the BET point[15]) to obscure the observation of what is taking place on the first layer.

Comparison of Results

Using the values of σ_0 elicited by the previous argument, the specific surface can be calculated by Gregg's method and compared with the result obtained by the application of the BET equation to the same data. The results of this calculation are shown in Table I.

The use of the BET method for obtaining surface areas likewise requires an estimate of the area of the adsorbed molecule. This estimate is usually based either on the crystallographic data for the solidified gas, or the density of the liquefied gas. It is not uncommon to find that after an area has been so selected it is necessary to increase it empirically. Thus, for example, Brown and Uhlig[16] use 20 Å.^{2} for the area of the ethane molecule in an application of the BET method. This value is taken from X-ray crystallography. A value of 23 A.^{2} has been used in this Laboratory for ethane, established empirically by comparison with nitrogen adsorption.[17]

As nitrogen adsorption has been most extensively investigated and the area of the nitrogen molecule most securely determined for BET purposes, it is reasonable to use it as a standard of reference. In any series of comparisons of methods, such as the present report, it is convenient to be thus able to refer the BET method to nitrogen adsorption.

The difficulty that here presents itself to the reader is the propriety of using two different areas for the limiting area/molecule on the first layer. The ambiguity is apparent rather than real. At the initiation of the condensed phase the concept of preferred adsorption sites leads to a picture of molecules adsorbed on the surface in such a way that at infinite compression the area for each molecule would be about 15 Å.^{2}. The BET theory adds to this picture the further, not contradictory but additional, information that this degree of compression is never achieved on the first layer, even at saturation pressure, and that the smallest area per molecule actually encountered at infinite adsorption is still only about 23 Å.^{2}. The concept is that the preferred adsorption sites guide the initial course of the adsorption while the molecules are separated from one another by relatively large distances, but that the influence of the surface becomes less pronounced at greater adsorptions where the surface adsorptive forces are offset by forces between molecules.

Column 5 of Table I compares the V_m, or the monolayer capacity, as obtained by the BET equation with the monolayer capacities obtained by the Gregg method from the slopes of the linear portions of the $\pi\sigma - \pi\Sigma$ curves.

$$\text{Slope} = \sigma_0/\Sigma = 1/x_0 \qquad (4)$$

where V_m is expressed in millimoles/g., then $V_m = 1000\ x_0/N$.

Referred back to the original isotherm it is found that the condensed film is not a completed monolayer until a relative pressure (p/p_0) of about 0.6 has been reached. That is at a point considerably beyond the BET monolayer value. Let us call it the Gregg monolayer value. It is defined as the quantity of gas that would be adsorbed if the entire surface were imagined as covered by a monomolecular layer at its limiting compression (in this case, about 15 Å.^{2} per molecule). It is recognized that the actual situation never corresponds to such a concept, as multilayers begin to form before the required degree of compression is achieved. The slope of the Gregg plot for the condensed film is descriptive then of only the beginning of the course of the condensed film which, before it is completed, is covered by a second molecular layer, as evidenced by a deviation of the $\pi\sigma - \pi\Sigma$ curve from its initial linear course.

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[15] The BET point is defined as the point on the isotherm where, by an application of the BET theory,[5] the amount of vapor adsorbed is equivalent to covering the complete surface with a monomolecular layer. The B point is defined as the point on the isotherm which is determined visually to be the beginning of the linear portion on a plot of amount adsorbed against relative pressure. For many isotherms these two points are found to be very close together.

[16] C. Brown and H. H. Uhlig, THIS JOURNAL, **69**, 462 (1947).

[17] A comparison of the results of ethane adsorption with an absolute method of determining surface area has been made by Dr. J. R. C. Brown, formerly of the Bell Telephone Laboratories, working in the group led by Dr. L. A. Wooten. He used the low pressure adsorption method described by Wooten and Brown, THIS JOURNAL, **65**, 113 (1943). In a private communication, Dr. Wooten writes: "We have tested Harkins' sample of anatase of specific surface 13.8 sq. m. per g. determined by his absolute method and obtain a straight line (BET plot) in the lower pressure region. It is necessary to use a coverage factor of 24 Å.^{2} for the ethane molecule to obtain agreement in area with ethane on this TiO_2" (quoted by permission).

TABLE I

COMPARISON OF SURFACE AREAS OBTAINED BY METHODS PROPOSED BY VARIOUS AUTHORS FROM THE VAPOR ADSORPTION ISOTHERMS OF ETHANE ON NaCl AND KCl CRYSTALS AT −183°

		Portion of isotherm used				
Author	Description	Lower limit of p/p_0	Upper limit of p/p_0	Monolayer capacity in millimoles/g.	Incompressible area per molecule in sq. Å.	Specific surface in sq. cm./g.
No. 1, CUBE CRYSTALS OF SODIUM CHLORIDE						
Gregg	Gaseous phase	0.007	0.027	1.17	31.7	2250
Gregg	Condensed phase	.07	.165	2.55	15.8	2433
BET	Condensed phase and multilayers	.06	.22	1.63	23.0	2260
Harkins and Jura	Multilayers	.11	.77	..	..	2350
No. 2, CUBE CRYSTALS OF POTASSIUM CHLORIDE						
Gregg	Gaseous phase	0.020	0.025	1.80	29.5	3190
Gregg	Condensed phase	.04	.11	2.88	19.7	3416
BET	Condensed phase and multilayers	.04	.14	2.48	23.0	3430
Harkins and Jura	Multilayers	.08	.38	..	..	3930

Yet another method of determining specific surface of a solid from the vapor adsorption isotherm has been developed by W. D. Harkins and George Jura.[18] This method is independent of any assigned value for molecular areas, once the specified gas and temperature have been "calibrated" by the use of a material whose specific surface has been obtained by an absolute method. When such a material is lacking, use can be made of TiO_2, since Harkins and Jura have shown it to give the same result by the BET method and by the method of Harkins and Jura.

A sample of TiO_2 (rutile)[19] was used. The value of its specific surface by ethane adsorption, using the BET method and a molecular area of 23 Å.², thus referring it in effect to nitrogen adsorption is $\Sigma = 65{,}600$ sq. cm./g. The value of the slope of the line obtained by plotting log p/p_0 against $1/v^2$—where v is the amount of gas adsorbed in cc.-mm. per g.—was obtained by the method of least squares. From this slope, represented by $-A$, a value for K is obtained, using the relation

$$K = \Sigma A^{-1/2} \qquad (5)$$

where K is taken as constant for a given adsorbate at a given temperature. From the sample of titanium dioxide that I used, the K for ethane at −183° is found to be 73.5 (amount adsorbed measured in cc.-mm. per g., area in sq. cm. per g.).

The Harkins and Jura plots for the ethane isotherms of sodium chloride and potassium chloride were constructed and the slopes of the linear portions of the curves obtained by the method of least squares. The surface areas of sodium chloride and of potassium chloride were calculated from Equation (5), and they are included for comparison in Table I. Figure 6 shows the Harkins and Jura plot for potassium chloride.

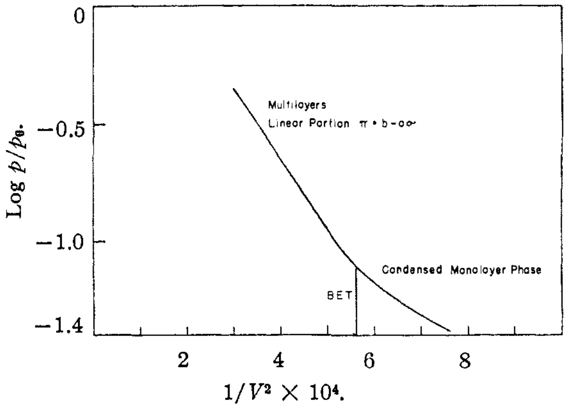

Fig. 6.—Harkins and Jura plot for ethane adsorbed on potassium chloride at −183°. The vertical line marked BET marks the position on the isotherm where enough is adsorbed to produce a single layer of molecules on the surface at 23 Å.²/molecule. The condensed monolayer phase, defined in the text, is described by the equation $\pi(\sigma - \sigma_0') = i'kt$ and the multilayer portion is described by the equation $\pi = b - a\sigma$.

Discussion

Terminology.—Jura and Harkins have followed Gregg in boldly transferring the complete terminology used for insoluble oil films on water to the study of solid surfaces. Justification for this decision is based on the use of the same empirical equations to describe the state of films on both types of substrate. This is to place complete reliance on mathematical coincidence while ignoring a gross physical difference between the two types of film, namely, that all the states of insoluble films on water refer to a monomolecular layer whereas films on solid substrates are usually multimolecular for about 80% of the range of the isotherm. Jura and Harkins apparently have no objection to placing not only their "condensed film" in the multilayer region, but also the "liquid intermediate" and "liquid ex-

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[18] W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431 (1943); THIS JOURNAL, **66**, 1366 (1944).

[19] I am indebted to Dr. M. Bredig for X-ray identification of my sample of TiO_2 as rutile. Harkins and Jura used TiO_2 (anatase) rather than rutile. A sample of anatase was not immediately available. It was not considered that the difference is sufficiently great to invalidate the argument, a conclusion supported by the outcome.

panded" phase.[20] When these phase relations are postulated in the region of multilayers the analogy with monomolecular oil films on water becomes a poor one, and hence misleading.

It seems preferable to keep the terminology vague and general at the present state of the subject. Accordingly, I use the terms gaseous and condensed phases only, without more precise specification, and have restricted their application to the portion of the isotherm where the film is monomolecular. There is a sharp distinction between this usage and that of Harkins and Jura, who have defined a condensed film for a solid substrate, as for an aqueous one, as existing where the π–σ relation is found to be linear. This is in conformity with their practice of using the form of an empirical equation to define phases.

The portion of the isotherm beyond the BET point I have called the multilayer region, whether it follows a linear π–σ relation or not. Harkins and Jura claimed the existence of phase transitions within this region, although the nature of the phases concerned still remains uncertain.

Comparison of BET and Gregg Theory.—The treatment published by Gregg[6] is insufficient to be described as a theory, yet by his insistence on the similarity of films on solids to films on water, which leads him to use a two-dimensional Amagat equation to describe part of the isotherm, he has introduced a theoretical equation which presupposes a theoretical basis. I have applied the term Gregg theory to this theoretical basis.

Both Gregg and Brunauer, Emmett and Teller employ monolayer values—*i. e.*, the volume of gas adsorbed equivalent to covering the entire adsorbent surface with a complete monomolecular layer. The two theories do not lead to the same value. Gregg's value for the amount adsorbed equivalent to a monolayer occurs at a relative pressure of about 0.6, and the corresponding BET value occurs at a relative pressure of 0.1.

This difference is caused by a difference in viewpoint of the two theories. Gregg's theory introduces as variables only the limiting area of the molecule on the monolayer and the lateral cohesion between molecules. The energy of adsorption is not introduced as a parameter. Consequently, the Amagat equation is incapable of following the isotherm when multilayer formation takes place.

On the other hand, the degree of compression of the film on the surface is not introduced as a parameter in the BET equation. As we have seen, the Gregg monolayer value specifies that the monomolecular layer is at *limiting* compression. The BET monolayer has no precise specification.

Some idea of the state of the film in a BET monolayer can, however, be obtained for those isotherms where there is a large energy of adsorption of the first layer. One might there expect that virtually a complete monolayer is produced on the first layer before multilayer formation becomes significant. Such a situation can be correlated with isotherms having a large value for the BET constant C. And for such isotherms there is a close correspondence of the BET value of V_m with the point B, the lower extremity of the long linear part of the S-shaped isotherm.[15] The change of slope of the isotherm at the point B may be a reflection of a physical change on the surface. The point B is then interpreted as the point where multilayer adsorption becomes sufficiently significant to obscure the direct observation of what is taking place on the first adsorbed layer. That point should therefore be found to come close to the point where, on a Gregg plot, the curve for the condensed phase begins to bend away from its initial linear course, as the building of a second layer will inevitably disrupt the simplicity of the π–σ relation existing during the formation of a condensed phase on a monolayer.

Although the ethane molecules in a condensed phase could theoretically be squeezed sufficiently close so that they would be as represented in Fig. 5, occupying an area of only about 15 Å.^{2} each, it appears that multilayer formation becomes significant long before that point is reached. Even at the saturation pressure, the average area per molecule on the first layer is only 23 Å.^{2} The wideness of application of the BET method to many different substrates indicates that this area per molecule on the first layer at saturation pressure is virtually independent of the substrate, and hence of the arrangement of the adsorbed molecules in the condensed monolayer phase. The Gregg method, however, which differentiates phases of the adsorbed vapor, as the BET theory does *not*, requires for *its* application some knowledge of the arrangement of the vapor molecules in each state of aggregation. For the method of Harkins and Jura, which is independent of any assumption about molecular areas and which is often applied to the isotherm in regions of multimolecular adsorption, it is hard to find any kinetic model.

I do not intend to claim any more generality than is covered by the present isotherms for restricting the application of the Harkins and Jura method to the multilayer region of the isotherm. The surfaces here employed, however, are closer to homogeneous than many of the solid substrates that have previously been used. It is therefore worth consideration that the nature of a heterogeneous substance is such as to smear out distinctions that appear so clearly at the BET point in this treatment of the sodium chloride and potassium chloride isotherms.

Comparison of Methods of Estimating Specific Surface

Comparison of the theoretical isotherm of Brunauer, Emmett and Teller with that of Harkins

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[20] G. Jura and W. D. Harkins, THIS JOURNAL, **68**, 1941 (1946), see Fig. 9. In this same figure the transition from gaseous to "liquid expanded" shows no first order discontinuity, as would be expected by analogy with an oil film on water.

and Jura has been made by Harkins and Jura,[18] by Emmett[21] and by Livingston[22]—Livingston finally concluding that the two equations are substantially alike in describing experimental observations. The validity of this conclusion remains open to question, as in many cases the two equations are found to agree in regions where the BET equation is rarely found capable of describing experimental observations. Nor does Livingston's treatment rule out the possibility that the experimental points may lie in a region of the isotherm where the coincidence of the two equations does not occur. Table I shows, for example, that the BET equation covers a range of the isotherm including at least two portions that have different π–σ relations.

The discrepancy of the Harkins–Jura value for potassium chloride may be partially caused by my use of TiO_2 (rutile), taken as the standard for the Harkins–Jura method. Livingston[22] claims that if the BET constant C for the standard substance is very different from that of the substance being measured, discrepancies may be found in the Harkins–Jura results. The values for this constant for the substances here involved are:

TiO_2 $C = 34$
NaCl $C = 60$
KCl $C = 108$

These relatively low values for C are in the region where the variation of the Harkins–Jura K with C is greatest. A considerable lessening of the discrepancy for Σ_{KCl} can be effected if a value of K is used based on the sodium chloride isotherm instead of the TiO_2.

The large deviation of the result for specific surface obtained from the gaseous film on potassium chloride is not surprising considering the few data from which it is derived. This result is worth including, however, to show that it is in line with the general reasoning.

The use of equation 3 brings up another point of interest. As used by Schofield and Rideal,[23] the reciprocal of the constant i is a measure of the lateral molecular cohesion. The equation is used four times and so gives four values of σ_0 and i for ethane. These are

σ_0 in Å.^{2}	15.8	19.7	29.5	31.7
i	0.49	0.16	0.67	0.76
$1/i$	2.04	6.25	1.49	1.32

The values of i for the gaseous films are close to those found for the same constant when Amagat's equation is applied to gaseous films on water. The variation of $1/i$ with σ_0 is in line with the modern theory of the specific heats of solids, which visualizes a specific distance between the centers of gravity of molecules where the resultant force between them is zero. Closer approach produces a repellent force, increasing in magnitude as the distance apart decreases; greater separation produces an attractive force which, *at first*, increases as the distance increases. At further separation, however, this attractive force is found to be rapidly diminishing with the distance apart.[24] If sufficient data were available it should be possible, by plotting $1/i$ *vs.* $\sigma_0^{1/2}$, to show the shape of the potential curve between molecules adsorbed on a solid surface.

The experimental comparison of Gregg's method with the other two methods has not been made before. The methods give concordant results only if certain assumptions are made about the way in which the molecules of a monolayer are placed on solid substrate when in different states of aggregation. There are undoubtedly other crystals that will give similar isotherms to those obtained with sodium chloride and potassium chloride, but pending their discovery it seemed worthwhile to present the results so far achieved.

Summary

Low temperature ethane adsorption isotherms on NaCl and KCl crystals, showing a first-order phase transition, are described in the monolayer region by two equations of the form $\pi(\sigma - \sigma_0) = ikT$, where σ_0 is the incompressible area per molecule for each of the two phases and i is an inverse function of the lateral molecular cohesion in each of the two phases. It is found that an agreement in the values for the specific surface of the solid with the specific surface obtained by the BET method can be obtained when σ_0 has a simple dependence on the underlying crystal lattice and the state of the adsorbed monolayer. The nature of this dependence is illustrated for the isotherms in question. The relation between the values of σ_0 thus deduced and the cross-sectional area required for use with the BET method is pointed out. A comparison of results obtained for specific surface by various ways that have been proposed for treating vapor adsorption data is included, and the significance of the findings discussed.

OAK RIDGE, TENN. RECEIVED MARCH 10, 1948

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[21] P. H. Emmett, THIS JOURNAL, **68**, 1784 (1946).

[22] H. K. Livingston, *J. Chem. Phys.*, **12**, 466 (1944); THIS JOURNAL, **66**, 569 (1944); *J. Chem. Phys.*, **15**, 617 (1947).

[23] R. K. Schofield and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A109**, 57 (1925); **A110**, 617 (1926); also see ref. 9.

[24] L. J. Hudleston, *Trans. Faraday Soc.*, **33**, 97 (1937).