tion heat of dilution work by Bertetti and McCabe. The heat of neutralization at standard conditions was taken as −13,321 defined calories per mole.[3]

To obtain relative enthalpies at round concentrations the heats of neutralization at these concentrations were interpolated from the experimental data. These heats of neutralization are given in Table II. Table II also includes the values of ϕ_L and $\bar{L}_2$ for hydrobromic acid, together with the sodium bromide and sodium hydroxide enthalpy data used in their computation. $\bar{L}_2$ was computed in the conventional fashion by the expression of ϕ_L(HBr) as a function of molality. Combination of the several sets of data limits the accuracy of the apparent relative enthalpies of hydrobromic acid to about ±30 calories/mole.

Discussion

Comparison of the apparent relative enthalpies of hydrobromic acid solutions with equivalent values for hydrochloric acid solutions computed from the data of Akerlof and Teare[12] shows the close resemblance anticipated. If the relative enthalpies of the two solutions are plotted against molality the hydrobromic acid plot shows somewhat greater curvature, and the relative enthalpy curve of hydrobromic acid is displaced from a few calories at lower concentrations to a maximum of about 250 calories lower at higher concentrations. Interpretation of this comparison will be deferred until a later paper.

[12] G. C. Akerlof and J. Teare, THIS JOURNAL, 59, 1855 (1937).

WINNIPEG, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

On Physical Adsorption. VI. Two-dimensional Critical Phenomena of Xenon, Methane and Ethane Adsorbed Separately on Sodium Chloride[1]

BY SYDNEY ROSS AND HADDEN CLARK

RECEIVED APRIL 27, 1954

Xenon, methane and ethane when adsorbed separately on {100} surface planes of sodium chloride show two-dimensional condensation and typical critical temperature phenomena as the temperature is raised. The two-dimensional critical temperatures are observed at *ca.* 104°K. for xenon, *ca.* 90°K. for methane, and *ca.* 132°K. for ethane. The isosteric heats of adsorption are calculated from the isotherms, and their variation with degree of surface coverage is interpreted.

The previous paper of this series[2] reported the two-dimensional condensation of ethane when adsorbed as a monolayer on a variety of homotattic solid surfaces, and set forth the conditions required for two-dimensional condensation of an adsorbate. These conditions were used to discover suitable adsorbates that would demonstrate this phenomenon on the uniform crystallographic surface, the {100} planes, of sodium chloride. The phenomenon was investigated, however, only at a single temperature, and hence its interpretation as a genuine monolayer condensation did not carry the authority that could be conferred on it, if it were shown (by observing the behavior of the system at different temperatures) to have a heat of transition and a critical temperature for the transition. The present paper reports the results obtained with xenon, methane and ethane adsorbed separately on the same sample of sodium chloride at different temperatures. These systems were selected, according to the principles stated by Ross and Winkler,[2] as likely to display the phenomenon of two-dimensional condensation on a solid surface. The predicted effects were actually observed, and it was found that, for each system, there exists a critical temperature, analogous to the normal critical temperature of liquefaction of a gas, above which the condensation does not occur. The purpose of this paper is to find the region of the two-dimensional critical temperature, as an important step in elucidating the mechanism of adsorption of non-polar adsorbates on an ionic adsorbent.

Apparatus and Materials

The adsorption system is a volumetric type, generally similar to that of Wooten and Brown,[3] using mercury stock valves to avoid the presence of stopcock grease in the system. The stock-valves and the buret are surrounded by an ice–water-bath while the apparatus is in use. The pressures are read with a cathetometer and a mercury manometer of 12-mm. internal diameter.

The cryostat consists of an aluminum block, hollowed out to hold the adsorption bulb and the bulb of the vapor pressure thermometer. The block is wound with electrical heating coils of constantan wire, which are used to balance the cooling of the liquid nitrogen bath and so provide temperature control. This assembly is suspended inside a brass can, which is evacuated during the determination of an adsorption isotherm. A large Dewar flask containing liquid nitrogen encloses the brass can. Figure 1 is a diagram of the arrangement of the cryostat.

The glass tubing that is not enclosed by the aluminum block would be cooler than the adsorption bulb were it not provided with a heater, the lead heater of Fig. 1. Two copper–constantan thermocouples are placed in the cryostat; one measures the stability of the temperature of the aluminum block, and the other detects any differences in temperature between the leads and the block, which difference need not be made to disappear since it is enough to make sure that the lead heater is warmer than the block, by adjusting the current through the heater.

The authors are indebted to Dr. J. A. Morrison, National Research Council, Ottawa, for the original design of the cryostat.[4] In its present slightly modified form, temperature fluctuations are restrained to within 0.02°.

The temperature of adsorption is obtained from the vapor-pressure thermometer, which has its bulb inside the cryo-

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[1] This paper is based on a portion of a Thesis submitted by Hadden Clark to the faculty of Rensselaer Polytechnic Institute, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1954.

[2] S. Ross and W. Winkler, THIS JOURNAL, 76, 2637 (1954).

[3] L. A. Wooten and J. R. C. Brown, *ibid.*, 65, 113 (1943).

[4] Dr. J. A. Morrison intends to publish a more extensive account of this cryostat, which makes a fuller description in this place unnecessary.

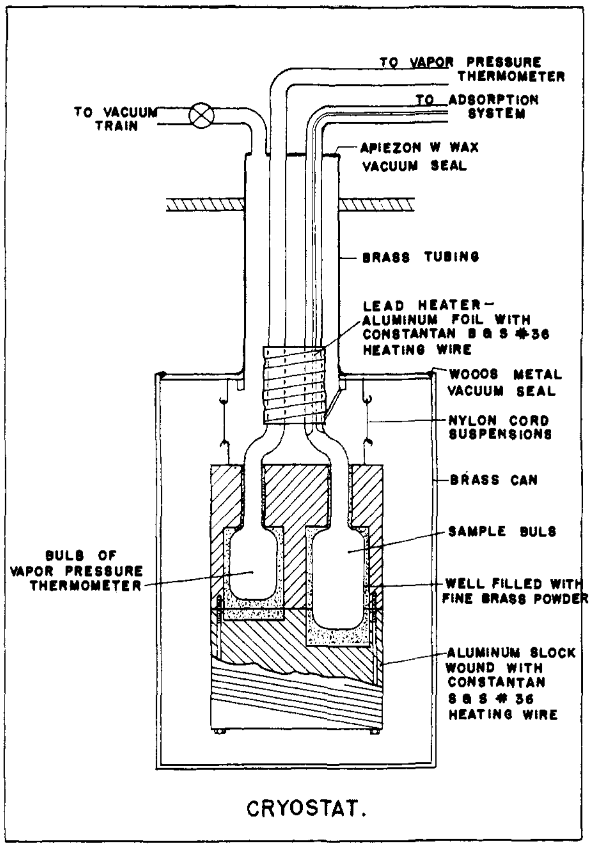

Fig. 1.—Low temperature thermostat, based on a design of J. A. Morrison.

stat, and which is filled with the same gas as that used as adsorbate in the adsorption bulb. The manometer of the vapor pressure thermometer is read with a cathetometer. The temperatures are calculated from published vapor pressure data, using the Antoine equation for methane and ethane.[5] The temperatures of the xenon adsorption isotherms were obtained from the thermocouple, which had been calibrated previously with a methane vapor pressure thermometer.

The sodium chloride crystals were prepared by the sublimation method of Craig and McIntosh.[6] The surface area, calculated by means of the BET equation from nitrogen gas adsorption, is 4.64 m.^{2}/g. The xenon was a sample of reagent grade of the Air Reduction Sales Company. It was stored in a freezing mixture while in use to prevent any contamination by water vapor, which was reported by the manufacturer as present as 0.07 mole per cent. or less. The methane gas was Matheson lecture bottle grade fractionated at 78°K. and passed through a liquid oxygen trap into a storage bulb. The ethane gas was Matheson research grade. It was passed through Ascarite and concd. H_2SO_4, and then fractionated twice, back and forth, into a storage bulb.

Experimental Results

The experimental observations are reported in Figs. 2, 3 and 4. The pressures given are those actually measured. Any correction for thermal transpiration at these relatively high pressures is small. Crowell and Young[7] quote values of about 0.01 mm. at 0.1 mm. for 200° gradient, and 0.02 mm. at 2 mm. Even assuming errors of this order of magnitude in the present work, these values are comparable to the limits of experimental precision, and hardly affect the results save for the isotherms at the lowest temperatures.

The xenon isotherm at 103.8°K. (Fig. 2) was determined by both adsorption and desorption, and their coincidence establishes it as a description of equilibrium conditions. An effort was made to obtain xenon isotherms at even lower temperatures, but the low value of p_0 severely restricts the range within which measurements can be obtained. The time for reaching equilibrium with xenon adsorption is also prolonged at lower temperatures. Since the precision of this low pressure isotherm is not satisfactory, it is not reported. It demonstrated, nevertheless, the existence of a vertical discontinuity at a value of p/p_0 above 0.5.

Adsorption isotherms of methane on sodium chloride at temperatures between 77.7 and 92.8°K. are reported in Fig. 3. The time required for equilibrium at the lower temperatures was too long for a ready determination of desorption points. The isotherms 83.0, 89.6, 90.4 and 92.8°K., however, were all determined by both adsorption and desorption points. The vertical discontinuity present at low temperatures is seen to disappear gradually as the temperature is raised.

Adsorption isotherms of ethane on sodium chloride at temperatures between 122.9 and 147.6°K. are reported in Fig. 4. The measured vapor pressures of ethane are also reported in Fig. 4. These isotherms, with one exception, are determined by both adsorption and desorption, thus ensuring equilibrium conditions throughout. The vertical discontinuity present at low temperatures disappears as the temperature is raised above 131.2°K.

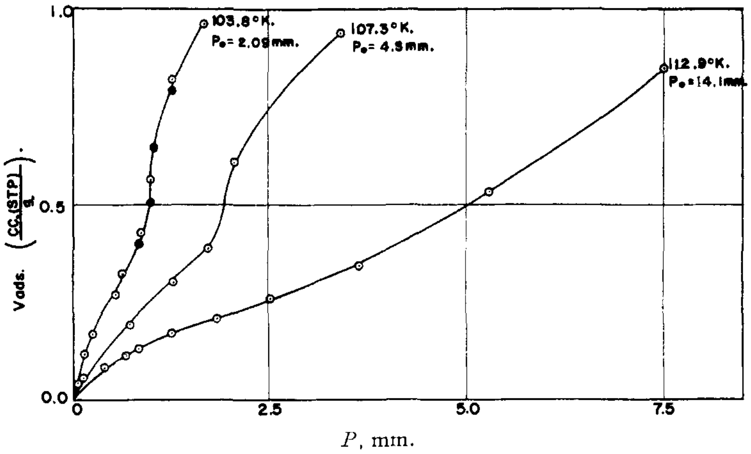

Fig. 2.—Adsorption isotherms of xenon on sodium chloride. Open circles represent adsorption points and closed circles represent desorption points.

Discussion of Results

1. Critical Phenomena of Absorption.—The general shape of the isotherms and their variation with temperature show that two-dimensional critical

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(5) "Selected Values of Properties of Hydrocarbons," NBS C.461, U. S. Dept. of Commerce, Washington, D. C., 1947.

(6) A. Craig and R. McIntosh, *Can. J. Chem.*, **30**, 448 (1952).

(7) A. D. Crowell and D. M. Young, *Trans. Faraday Soc.*, **49**, 1080 (1953).

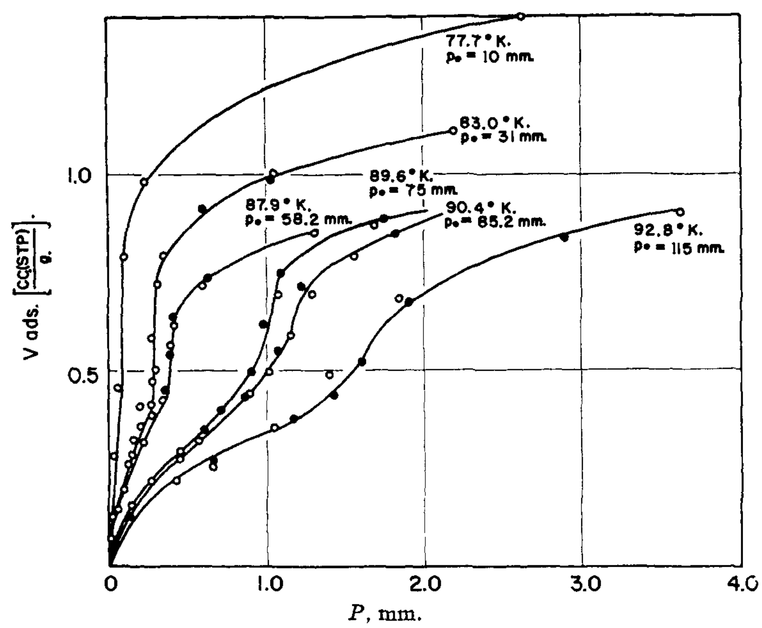

Fig. 3.—Adsorption isotherms of methane on sodium chloride. Open circles represent adsorption and closed circles desorption points.

phenomena are being observed. A general discussion of the adsorption isotherm that shows two-dimensional condensation has been published recently by de Boer.[8] An application of a two-dimensional van der Waals equation to spherical, isotropic, molecules leads to the result that the two-dimensional critical temperature is only half the normal three-dimensional one, or

$$T_{c_2} = 0.5T_c \quad (1)$$

where T_{c_2} is the two-dimensional critical temperature and T_c is the normal critical temperature.[9] For xenon, T_c is 289.7°K.,[10] and T_{c_2} is *ca.* 104°K., as determined by a visual inspection of Fig. 2. The two-dimensional critical temperature is therefore about 41° below the value predicted by eq. 1. This lowering may be ascribed to the effect of the solid substrate, which is not taken into account in the derivation of eq. 1. The ionic lattice at the surface induces a dipole on the atoms of xenon, and if these induced dipoles are directed parallel to each other by the influence of the underlying lattice, there arises a mutual dipole-repulsion. This repulsive force between the adsorbed atoms is introduced by de Boer[11] as a third constant (a_2') in the two-dimensional van der Waals equation

$$\left[\pi + \frac{(a_2 + a_2')}{\sigma^2}\right](\sigma - b_2) = kT \quad (2)$$

where π is the two-dimensional pressure in dynes/cm. and σ is the area occupied by each molecule adsorbed on the solid. The constants are based on units per molecule; k is the ideal gas constant per molecule, equal to R/N. The relation between a_2' and μ, the induced dipole moment, is given by the expression

$$a_2' = -\frac{1}{2}\int_d^\infty \frac{\mu^2}{r^3}2\pi r\,dr = \frac{-\pi\mu^2}{d} \quad (3)$$

where r is the variable distance between the dipoles, and d is the diameter of the molecules.

By developing to the fullest extent the analogy between the van der Waals equation and its two-dimensional equivalent, de Boer arrives at the following equations

$$a_2 = 3a/8d \quad (4)$$
$$b_2 = 3b/4d \quad (5)$$
$$T_{c_2} = 8a_2/27kb_2 = {}^1/_2T_c \quad (6)$$

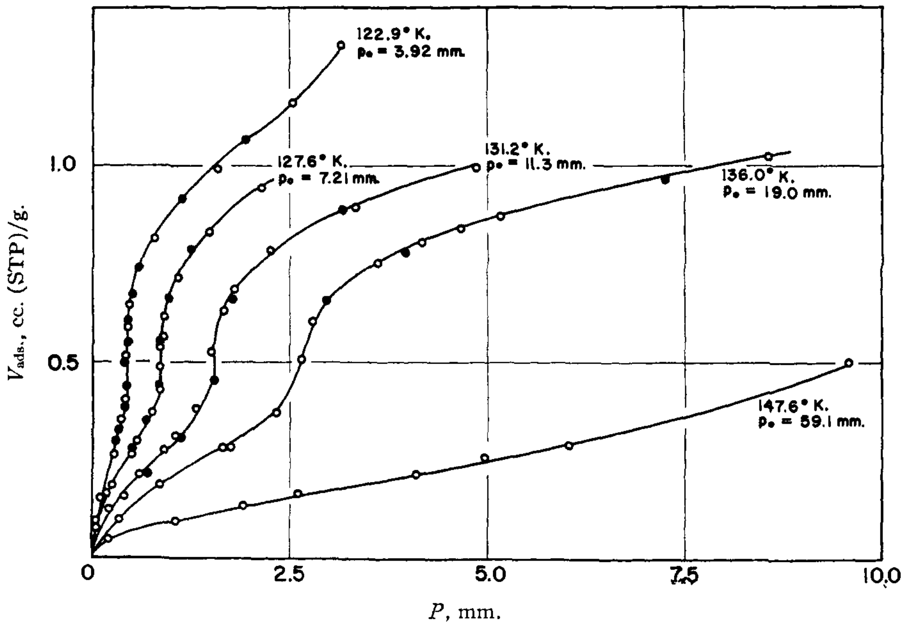

Fig. 4.—Adsorption isotherms of ethane on {100} surfaces of sodium chloride. Open circles represent adsorption and closed circles desorption points.

If, instead of a_2 we now have $(a_2 + a_2')$, eq. 6 becomes

$$T_{c_2} = 8(a_2 + a_2')/27kb_2 = \frac{1}{2}T_c - \Delta T \quad (7)$$

where ΔT is the lowering of the two-dimensional critical temperature below 50% of the normal critical temperature. Hence

$$\Delta T = -8a_2'/27kb_2 \quad (8)$$

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[8] J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, pp. 123-199.

[9] An equation similar to eq. 1 was first developed by D. Devonshire, *Proc. Roy. Soc.* (*London*), **A163**, 132 (1937).

[10] K. A. Kobe, *Chem. Revs.*, **52**, 117 (1953).

[11] J. H. de Boer, ref. 8, p. 134.

Combining eq. 3, 5 and 8, we get

$$\mu^2 = 0.806kb\Delta T \qquad (9)$$

Equation 9 can be used to obtain a value of the induced dipole-moment of xenon on a sodium chloride surface. It is found to be 0.62×10^{-18} e.s.u. cm. (0.62 debye). An argument developed by de Boer[12] leads to an estimate of the dipole moment induced on xenon by its approach to a mercury surface. The value thereby calculated is 0.74 debye, which is comparable to the value elicited here from the foregoing reasoning.

For methane, Fig. 3 enables a visual estimate of the two-dimensional critical temperature to be set at 90°K. The normal critical temperature of methane is 191.1°K.,[13] half of which is 95.6°K. The two-dimensional critical temperature is therefore 5.5°K. below one-half the normal critical temperature ($-\Delta T$). For an isometric molecule this difference can be ascribed to an induced dipole of the methane molecule brought about by the ionic surface, and related by eq. 9 to the value of ΔT. The value of μ calculated from eq. 9 is 0.21×10^{-18} e.s.u. cm. (0.21 debye).

An estimate of the induced dipole moment on a methyl group can be obtained by comparing the dipole moments of methyl chloride and ethyl chloride. The dipole moment of methyl chloride is 1.87 debyes.[14] Let us suppose that the dipole moment of ethyl chloride can be estimated by adding together the dipole moment of the chloromethyl group and the dipole moment induced on the methyl group by the chloromethyl group. If the value of 1.87 debyes is given to the chloromethyl group then, since the total dipole moment of ethyl chloride is 2.07 debyes,[14] the dipole induced on the methyl group by the $-CH_2Cl$ adjacent to it is 0.20 debye. This is comparable to the value estimated above for the induced dipole of methane by the sodium chloride surface lattice. The dipole moments of the higher alkyl chlorides are the same as that of ethyl chloride, indicating that induced dipole effects on the third and successive carbon atoms are negligible.

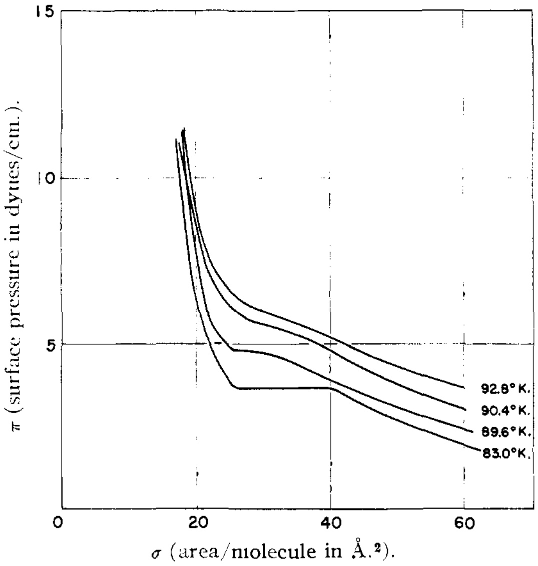

Fig. 5.—Surface pressure in dynes/cm. *vs.* area per molecule in Å.², for methane adsorbed on sodium chloride, obtained by graphical integration of Gibbs' adsorption equation.

2. **Integration of the Gibbs Equation.**—The data of the original isotherms can be converted into corresponding two-dimensional π–σ–T diagrams by introducing the Gibbs adsorption equation

$$\Gamma = (1/RT)\,\mathrm{d}\pi/\mathrm{d}\ln p \qquad (11)$$

where Γ is the amount adsorbed in moles per sq. cm. at an equilibrium pressure p, and π is a two-dimensional pressure in dynes/cm., analogous to the surface pressure of insoluble films on aqueous surfaces. The integration of eq. 1 is expressed as

$$\pi = \frac{RT}{V\Sigma}\int_0^p \frac{v}{p}\,\mathrm{d}p \qquad (12)$$

where R is the gas constant, V the molar volume of the gas, Σ the specific area of the solid, and p and v represent the adsorption data. The graphical integration of eq. 2 is described by Harkins.[15]

The data for the adsorption of methane on sodium chloride when converted to the corresponding π–σ–T form are represented in Fig. 5. The points are derived from smoothed curves made from the original data. Figure 5 has a general resemblance to the curves for surface pressure against area for insoluble films on aqueous substrates, in the region of the transition from gaseous to coherent films.[16] The two-dimensional pressures are here much greater, and the limiting area per molecule slightly less, than were found for 12- to 18-carbon atom fatty acids on water. A result of this sort is to be expected for methane. At the same time, it is of course possible that the portions of the curves of Fig. 5 that lie at high values of π and low values of σ no longer represent true unimolecular adsorption on the solid surface.

The π–σ–T relations for methane adsorbed on sodium chloride (Fig. 5) show that the two-dimensional condensation process is exothermic. An approximate value of ΔH_c, the two-dimensional heat of condensation, can be obtained by the use of the equation

$$\log\left(\frac{\pi_2}{\pi_1}\right) = \frac{\Delta H_c}{2.303R} \times \frac{T_2 - T_1}{T_2T_1} \qquad (13)$$

where π_1 and π_2 are the surface pressures of the first-order phase transition at temperatures T_1 and T_2. From Fig. 5 the values of $\pi_{1,2}$ are 3.68 and 4.75 dynes/cm. at 83.0 and 89.6°K., respectively. The value of ΔH_c calculated by eq. 13 is 570 cal./mole. The two-dimensional critical temperature is close to 90°K.

The π–σ–T integration for the present data for the adsorption of ethane on sodium chloride are presented in Fig. 6. The areas per molecule shown in this diagram are of the correct order of magnitude for a unimolecular adsorbed film. Since it has

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[12] J. H. de Boer, ref. 8, pp. 168–169.

[13] K. A. Kobe, *Chem. Revs.*, **52**, 117 (1953).

[14] A. A. Maryott and F. Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," N.B.S. Circular 537, U. S. Dept. of Commerce, Washington, D. C., 1953.

[15] W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952, pp. 211, *et seq.*

[16] N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, London, 1941, pp. 43–46.

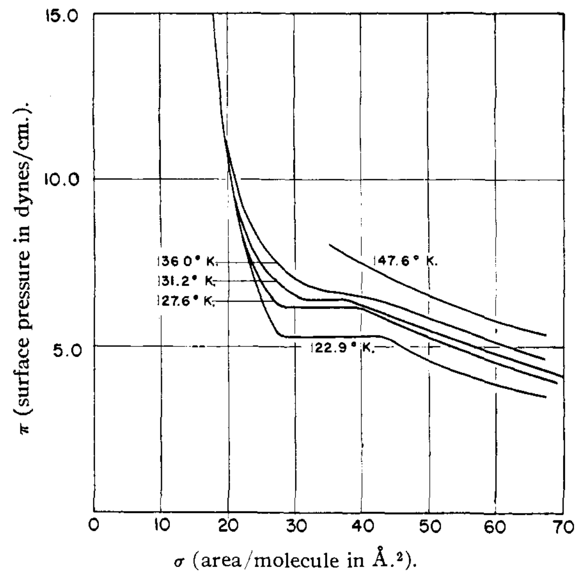

Fig. 6.—Surface pressure in dynes/cm. *vs.* area per molecule in Å.², for ethane adsorbed on sodium chloride, obtained by graphical integration of Gibbs' adsorption equation.

been shown[17] that complete monolayer coverage by ethane corresponds to an area per molecule of 22.5 Å.², the portions of the curves of Fig. 6 that occur to the left of this value presumably lie in the multilayer region.

The positive variation of the surface pressure of the transition with temperature is proof that the monolayer condensation is exothermic. The heat of transition, estimated by the Clausius–Clapeyron equation, is 680 cal./mole, which is slightly greater than a similarly estimated value for methane of 570 cal./mole. The three-dimensional heat of condensation of ethane in the same temperature range is 3960 cal./mole (calculated from the observed vapor pressures by the Clausius–Clapeyron equation).

The two-dimensional critical temperature is close to 132°K.

3. Isosteric Heat of Adsorption.—The isosteric heats of adsorption of xenon on sodium chloride are calculated from the isotherms at 103.8 and 107.3°K., by means of a procedure outlined by Joyner and Emmett.[18] The variation of the isosteric heat as a function of the degree of surface coverage, θ, is represented in Fig. 7A. The value of θ is obtained from the equation $\theta = V/V_m$, where $V_m = 0.918$ cc. of xenon at STP.[19]

The isosteric heat curve of Fig. 7A shows a raised portion corresponding to the region of two-dimensional condensation. The height of this portion above the general level of the isosteric heat curve corresponds approximately to the value of ΔH_c, the two-dimensional heat of condensation, which is thus superimposed on the adsorption heat. Since one of the two isotherms used to estimate the isosteric heats lies above the critical temperature, a maximum rather than a plateau is obtained in Fig. 7A, and the value of ΔH_c must be regarded as approximate. That it should be only a few hundred calories per mole and hence considerably less than three-dimensional molar latent heats is not surprising.

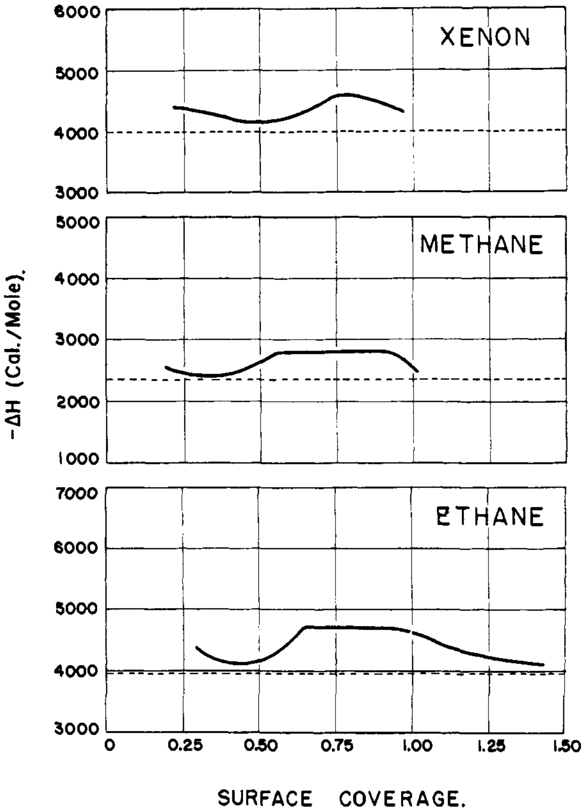

Fig. 7-A.—The isosteric heats of adsorption of xenon on sodium chloride, as derived from two adsorption isotherms at 103.8 and 107.3°K. The horizontal dotted line represents the heat of sublimation of xenon, as derived from the vapor pressures measured at 103.8 and 107.3°K.

Fig. 7-B.—The isosteric heat of adsorption of methane on sodium chloride, calculated from adsorption isotherms at 83.0 and 89.6°K. The dotted line represents the normal three-dimensional heat of sublimation of methane, 2330 cal./mole, for the same temperature range.

Fig. 7-C.—The isosteric heat of adsorption of ethane on sodium chloride, calculated from adsorption isotherms at 122.9, 127.6 and 131.2°K. The horizontal dotted line represents the heat of liquefaction of ethane, 3960 cal./mole, for the same temperature range.

The calculation of other thermodynamic functions for the process of the adsorption of xenon on sodium chloride requires data at temperatures far below the critical temperature, where the distinction between the two surface phases is more pronounced.

The isosteric heats of adsorption of methane on sodium chloride were calculated, following the procedure of Joyner and Emmett, from the isotherms at 83.0 and 89.6°K., and are reported in Fig. 7B. The values for surface coverage, V/V_m, are derived from $V_m = 1.07$ cc. of methane at STP per gram of adsorbent, which is an average value obtained by an application of the BET equation to the methane adsorption isotherms.

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[17] H. K. Livingstone, *J. Colloid Sci.*, **4**, 447 (1949).

[18] L. G. Joyner and P. H. Emmett, THIS JOURNAL, **70**, 2353 (1948).

[19] This value is derived from the BET equation applied to the nitrogen adsorption isotherm, which gives $V_m = 1.06$ cc. of nitrogen at STP. The ratio of the areas of the nitrogen and xenon molecules is taken as 16.2/18.7.

The isosteric heat curve (Fig. 7B) shows a raised plateau corresponding to the region of two-dimensional condensation. The height of this plateau above the general level of the isosteric heat curve corresponds to the value of ΔH_c, the two-dimensional heat of condensation, which is thus superimposed on the heat of adsorption.

Figure 7B shows that the end of the phase transition takes place at about 90% surface coverage. It is worth noting that when V_m is calculated from the nitrogen adsorption isotherm, and then converted by the appropriate factor to the corresponding volume of methane, the end of the phase transition takes place closer to 100% surface coverage.

The isosteric heats of adsorption of ethane on sodium chloride are calculated from the three isotherms obtained below the critical temperature, and are reported in Fig. 7C. The variation of the isosteric heats with temperature is so slight that the reported values, shown in Fig. 7C, are the results of averaging. An application of the BET equation to the same three ethane isotherms, at pressures above the transition, gives values of V_m that are close to the same. The average V_m is 0.70 cc. of ethane at STP per gram. The surface coverage, $\theta = V/V_m$, given in Fig. 7C is based on this value.

The heat of adsorption decreases to a minimum before 50% surface coverage, indicating an "ideal" adsorption, *i.e.*, free of molecular interaction at low coverages. The same effect is observed with methane and xenon. The state of lowest energy occurring soon after one-third coverage suggests a mechanism of adsorption in which, at low surface coverage, there is a distribution of adsorbed molecules in a mobile film, such that each molecule precludes occupation of neighboring sites. The grouping of sites on the {100} surfaces of sodium chloride is in an hexagonal array,[20] and for such an array it is possible to arrange molecules on the surface so far apart that, up to one-third coverage, the interaction energy is zero. Diagrams that show the geometrical proof of this statement, developed for the {100} surface planes of tungsten, which are also an hexagonal surface array, have been published by Miller.[21]

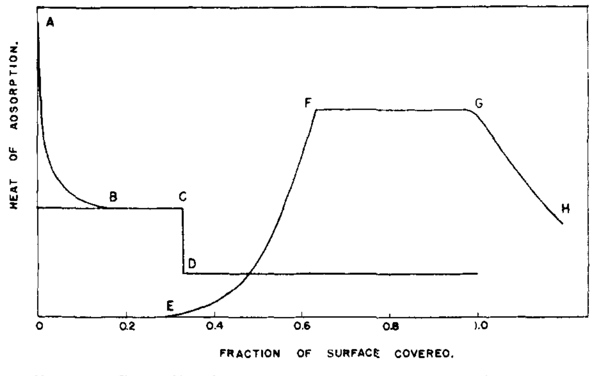

Fig. 8.—Contributions to the heat of adsorption by surface heterogeneity (AB), adsorption on homotattic surface (BC), repulsion of induced dipoles on homotattic surface (CD), molecular interaction (EF), two-dimensional condensation (FG) and adsorption on second layer (GH). The relative values are suppositional.

Such a model for the adsorption mechanism, since it postulates preclusion of adsorption on certain sites, implies repulsive intermolecular forces, brought about by mutually oriented induced dipoles of the adsorbed molecules. This interpretation is supported, for xenon, methane and ethane, by the occurrence of the two-dimensional critical temperature below 50% of the normal critical temperature, an effect which is also ascribed to the effect of repulsive intermolecular forces.[22] The model also implies that all the adsorption sites are equivalent, in spite of the alternation of positive and negative ions on the surface. This situation is actually met on a sodium chloride lattice, as the maximum adsorption energy occurs at lattice centers, equidistant from the four ions, and adjoining lattice centers are too close together to accommodate adsorbent molecules. *Available* lattice centers are therefore found to be equivalent and in an hexagonal array.[20]

Above one-third surface coverage, further adsorption can only occur by molecules taking up the adjacent sites previously shunned. Since the dipole induced by each of these sites is oriented to cause a force of repulsion between adsorbed molecules, the net heat of adsorption is greatly reduced. However, as those sites are filled up the molecules become more closely packed, so that the normal attractive interaction begins to operate between them. The intermolecular attractive energy now causes the net heat of adsorption to rise, overcoming the repulsive energy of the mutually oriented induced dipoles, and ultimately becoming sufficiently great to produce a phase transition of the adsorbed molecules.

Figure 8 is a representation of all the factors that have been mentioned as contributing to the observed heat of adsorption. It is supposed that surface heterogeneity extends to 15% of total coverage, as found by Orr[23] for his crystals of potassium chloride, and that the repulsive effect of induced dipoles begins at 33.3% coverage. Actual isosteric heat curves are combined from these component factors, and may have a variety of shapes depending on the strength of the adsorption, polarizability of the adsorbate, heterogeneity of the adsorbent, form of interaction curve, heat of two-dimensional condensation, etc.

Figure 7C tells us that the drop in the heat of adsorption that follows the termination of the phase transition is caused by the adsorption of a second layer. The same interpretation could also be made of the corresponding drop in the isosteric heat curve for methane on sodium chloride (Fig. 7B). The consideration of this aspect of these diagrams reveals an unresolved question, the answer to which hinges on the proper fixing of V_m. It was shown by Ross[20] that two different equations of state described the adsorbed film of ethane on sodium chloride at 90°K., one before and the other after the phase transition. Each of those equations included a term that referred to the limiting

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(20) S. Ross, THIS JOURNAL, **70**, 3830 (1948).

(21) A. R. Miller, "The Adsorption of Gases on Solids," Cambridge University Press, New York, N. Y., 1949, pp. 87–88.

(22) J. H. de Boer, ref. 8, p. 155.

(23) W. J. C. Orr, *Proc. Roy. Soc.* (*London*), **A173**, 349 (1939).

area of the molecule in an infinitely compressed film. The limiting area per molecule before the transition is exactly twice that of the film after the transition. This finding is capable of two interpretations: (a) The monolayer is completed simultaneously with the completion of the transition, and there is no difference in the orientation of the molecules during the course of the transition. The limiting area per molecule then *apparently* drops to half its former value because the data refer to *two* molecular layers. (b) The condensed surface phase produced after the transition is still a monolayer, and is capable of further compression by adsorption of more molecules. The limiting area per molecule drops to one half its former value because the molecules erect themselves during the transition. The condensed monolayer phase is therefore composed of ethane molecules standing perpendicular to the surface.

Figure 7C, with 100% surface coverage at the end of the transition, is in accord with the first of these interpretations. Yet it is based on nothing more than the fixing of V_m by the BET equation applied to the ethane adsorption and to nitrogen adsorption data. More fundamental arguments and evidence are desirable.[24]

Ross[20] in 1948, and de Boer,[8] have favored the second interpretation. The question is still open and its answer is not only of interest to pure science; the nature of the orientation of adsorbed molecules affects the mechanism of catalytic and heterogeneous reactions.

(24) Dr. Donald Graham (E. I. du Pont de Nemours and Company, Inc.) has outlined an argument that includes more fundamental considerations. "The erection of the molecules would require lateral interaction between the adsorbed molecules sufficiently strong to overcome the energy holding the molecules flat on the surface. The activation energy for this shift would be approximately equal to the difference between the heats of adsorption of ethane and methane plus a small localization term. If this energy were available, it would still be necessary for the system with the molecules interacting from positions flat on the surface to be higher in energy than a system in which the adsorbed molecules are erect." Private communication.

TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

On Physical Adsorption. VII. Two-dimensional Critical Phenomena of Diborane Adsorbed on Sodium Chloride[1]

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RECEIVED MARCH 4, 1954

Diborane adsorbed on {100} surface planes of sodium chloride shows two-dimensional condensation and critical temperature phenomena at about 133°K. The isosteric heat of adsorption is reported as a function of surface coverage, and shows a large increase in the heat of adsorption after the completion of the phase transition. The effect is interpreted as a polymerization reaction in the adsorbed surface film.

Although it has been known for thirty years that unimolecular films of insoluble substances on aqueous surfaces can show phase transitions analogous to the normal condensation of vapor, there has been no convincing demonstration of the same phenomenon on solid surfaces. The reports by Jura, *et al.*, of a first-order phase transition of *n*-heptane on graphite,[2] ferric oxide[3] and reduced silver powder,[4] have not been confirmed by other independent investigators.[5–7] Certain internal peculiarities of the reported transitions had, in any case, raised doubts about them.

The present series of reports on physical adsorption is an attempt to demonstrate unequivocally that monolayer phase transitions do take place on solid surfaces. This demonstration is the more convincing the greater the variety of adsorbate vapors that are shown to exhibit the phenomenon. Xenon, methane and ethane have been shown to undergo two-dimensional condensation on the surface of sodium chloride, and to exhibit the characteristic behavior that usually describes a critical temperature for condensation.[8] The present paper reports the behavior of diborane vapor adsorbed on the same solid surface. This substance also displays a monolayer phase transition and typical critical temperature behavior.

Apparatus and Materials

The adsorption apparatus and the cryostat have been described previously.[8] The temperature of the adsorption was measured with an ethane vapor pressure thermometer, calibrated by the Antoine equation for ethane.[9] The vapor pressures of diborane were not measured directly, but obtained from the temperature by means of the vapor pressure data of Clarke, Rifkin and Johnston.[10]

The sodium chloride is the same sample that was used for the adsorption experiments with xenon, methane and ethane.[8] It has a surface area of 4.64 m.^{2}/g., determined by an application of the BET equation to the nitrogen adsorption isotherm.

The diborane gas was prepared by Mr. G. Stridde, in this Laboratory, by the method of Shapiro, *et al.*[11] The BF_3-$(C_2H_5)_2O$ was added to the ether solution of $LiAlH_4$ for convenience. Purification was by distillation at the melting point of CS_2. Infrared spectra showed no bands for ethyl ether or bands extraneous to diborane. Immediately be-

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(1) This paper is based on a portion of a Thesis submitted by Hadden Clark to the faculty of Rensselaer Polytechnic Institute, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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