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Surfaces of Solids XV

First-Order Phase Changes of Adsorbed Films on the Surfaces of Solids: The Film of *n*-Heptane on Ferric Oxide

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Two-dimensional first-order changes, in which a gaseous film of normal heptane is transformed into another phase of lower molecular area with evolution of heat, have been discovered on subphases of ferric oxide, silver, and graphite. All of the critical phenomena observed in three-dimensional systems are found to be duplicated. For *n*-heptane on ferric oxide the critical constants are: σ_c (area) 900\AA^2 per molecule; π (film pressure) 0.45 dyne cm^{-1} ; and T_c , 29°C . The critical constants are found to depend on the nature of the solid as well as on that of the vapor. The heat of transformation at 25°C is estimated to be $12,000 \pm 5000\text{ cal. mole}^{-1}$. This value appears to be considerably higher than the $6150\text{ cal. mole}^{-1}$ required for the formation of three-dimensional liquid *n*-heptane from its vapor at the same temperature. The volume-pressure relations are considered for the adsorption isotherm in the case in which a second- or third-order phase change occurs.

I. INTRODUCTION

IN recent papers from this laboratory the point of view has been adopted that the phases and phase changes of films on solids are similar to those of monolayers on the surface of water. It has been found that those changes which are first order in three dimensions are apt to be second order on either solids or water in two dimensions. One exception to this is in the reversible vaporization-condensation in monolayers of oil on the surface of water, which is usually first order, even though it is in some cases second order.¹

* The writers wish to acknowledge the helpful cooperation in this work of Dr. Orlan M. Arnold of the Chrysler Corporation. This is a part of a larger research project under the general direction of William D. Harkins.

¹ For an illustration of such a second-order change, see N. K. Adam and G. Jessop, *Proc. Roy. Soc. A* **110**, 423 (1926)

The earliest first-order change to be found on a solid was that of *n*-heptane on silver.² However, that of the same vapor on crystalline ferric oxide, as reported here, has been investigated in much more detail and exhibits at temperature from 15° to 30°C the same general phenomena as those of three-dimensional gases in the vicinity of the critical point.

II. THEORY

Most changes of phase in three dimensions are of the first order, i.e., possess a latent heat of transformation and a discontinuous change in volume. Many transformations, however, are of the second order. The criteria for the order of changes of phase in three dimensions were first

² G. Jura, E. H. Loeser, W. D. Harkins, and P. R. Basford, *J. Chem. Phys.* **13**, 535 (1945).

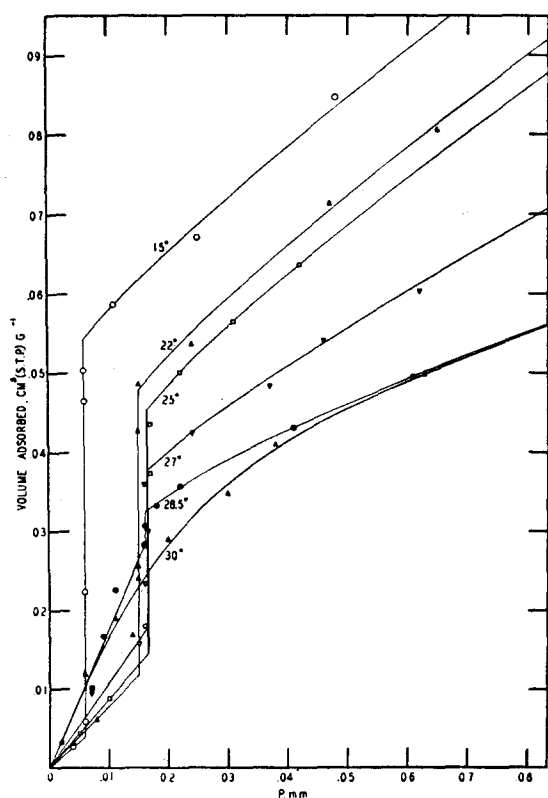


FIG. 1. Low pressure isotherms of *n*-heptane on ferric oxide. The curves at 15°, 22°, 25°, 27°, 28.5°C exhibit a finite discontinuity of v as a function of p .

set down by Ehrenfest.³ Harkins and Boyd⁴ and Dervichian⁵ have both developed the criteria for phase changes in two-dimensional films. For films it develops that the compressibility, k , defined by the equation, is sufficient to determine the order of the change.

$$k = \frac{1}{-\sigma} \left(\frac{\partial \sigma}{\partial \pi} \right)_T \quad (1)$$

For a first-order change, k becomes infinite for those values of σ for which the transition occurs; for a second-order change there is a *finite* discontinuity in k , while for a third-order change there is a finite discontinuity in $(\partial k / \partial \sigma)_T$.

The observed pressure (p), volume (v) adsorption data can be put into the π - σ form if π is

³ P. Ehrenfest, Proc. Acad. Sci. (Amsterdam) **36**, 115 (1933).

⁴ W. D. Harkins and G. E. Boyd, J. Phys. Chem. **45**, 20 (1941).

⁵ D. G. Dervichian, J. Chem. Phys. **7**, 932 (1939).

obtained by the integration of the Gibbs adsorption equation as suggested by Bangham.⁶⁻⁸

The area of the surface available per molecule can be calculated from the specific area, Σ , and the volume of gas adsorbed. Likewise, it is possible to express the compressibility as a function of the quantities directly measured in adsorption. This transformation can be carried out by use of the Gibbs adsorption equation. The compressibility is then found to be

$$k = \frac{V_M \Sigma}{RT v^2} \left(\frac{\partial v}{\partial \ln p} \right)_{T, \Sigma} \quad (2)$$

where V_M is the molar gas volume, Σ , the specific area, R the gas constant, T the absolute temperature, v the volume of gas adsorbed per gram, and p the equilibrium pressure. Thus, in a first-order change, the volume must vary, without any change in pressure, in a second-order change there is a discontinuity in $(\partial v / \partial p)_T$, and in a

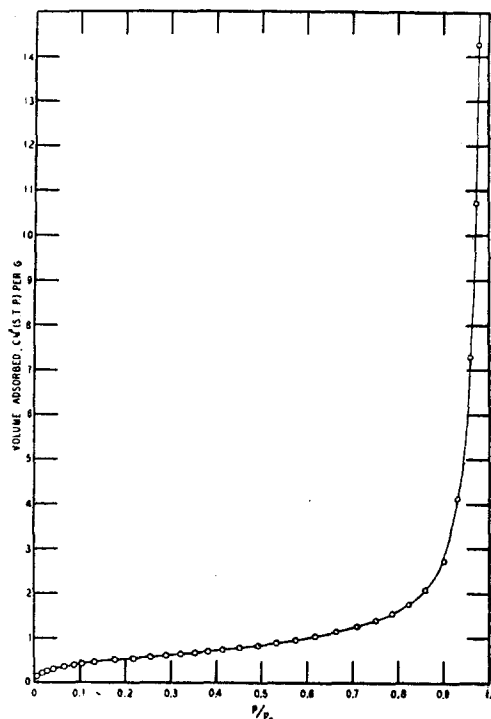


FIG. 2. The complete isotherm of *n*-heptane on ferric oxide at 25°C. $p_0 = 45.77$ mm.

⁶ D. H. Bangham, Trans. Faraday Soc. **33**, 805 (1937).

⁷ D. H. Bangham and R. I. Razouk, Trans. Faraday Soc. **33**, 1463 (1937).

⁸ D. H. Bangham and R. I. Razouk, Proc. Roy. Soc. (London) **A166**, 572 (1938).

third-order change there is a discontinuity in $(\partial^2 v / \partial p^2)_T$. Thus, it is possible to determine if in a film a phase change occurs and the order of the phase change directly from the observed experimental data.

III. MATERIALS AND APPARATUS

The ferric oxide used was Baker and Adamson's reagent grade. The *n*-heptane, apparatus, and method of making the measurements have been described by Jura and Harkins.⁹ Temperatures were determined with a mercury thermometer graduated to 0.1°C which had been compared with a similar thermometer calibrated by the Bureau of Standards.

IV. EXPERIMENTAL RESULTS

The isotherms at 15.00°±0.05°, 22.00°±0.02°, 25.00°±0.02°, 27.00°±0.02°, 28.50°±0.02°, and 30.00°±0.02°C up to a pressure of 0.080 mm are exhibited in Fig. 1, while the entire isotherm at 25°C from $p/p_0 = 0$ to $p/p_0 = 1$ is shown in Fig. 2. The area of the sample was 7.46 m² g⁻¹ as determined by the relative method of Harkins and Jura.¹⁰ The study of the isotherm in the region of high relative pressures indicates that the sample has some pores, although the small area exhibited indicates that the porosity is of minor importance. The data indicate also that the few pores that are present are large compared to the size of the *n*-heptane molecule. Assuming that the macroscopic constants of *n*-heptane can be used and that the Kelvin equation is valid, the isotherm shows that only a negligible fraction of the area is present in pores whose diameters are less than 200 Å.

Figure 2 shows that as judged by previous standards the isotherm is "normal." The main interest of this paper, however, lies in Fig. 1.

The important feature of the isotherms shown in Fig. 1 is that *all* the isotherms, except that at 30°, exhibit a finite discontinuity of *v* as a function of *p*. The discontinuity becomes smaller as the temperature is increased, and there is a concomitant increase in the value of the pressure from 0.006 mm at 15° to 0.016 mm at 28.5°, at

TABLE I. The values of *v* and *p* at the discontinuity in the adsorption of *n*-heptane on ferric oxide.

<i>t</i> , °C	<i>p</i> , mm Hg	cc ads. g ⁻¹ at low <i>p</i>	cc ads. g ⁻¹ at high <i>p</i>
15.00	0.006	0.00396	0.0545
22.00	0.014	0.0119	0.0479
25.00	0.016	0.0144	0.0453
27.00	0.016	0.0173	0.0383
28.50	0.016	0.0283	0.0324

which the discontinuity occurs. *The above are the experimentally observed facts.* Table I lists the pressures at which the discontinuity occurs and the volume of gas adsorbed at the end of each branch of the curve at the discontinuity.

Obviously, the values of the volume adsorbed per gram at the point of discontinuity are not very precise since they are obtained by the extrapolation of each branch of the curve. This is especially true of the extrapolation of the branch of the curve from zero pressure. In Fig. 1 the curves on the low pressure side of the discontinuity are shown as straight lines. There is evidence, as illustrated by the 30° isotherm and the later discussion, that the lines are not straight but curved. However, sufficiently accurate data cannot be obtained with the present apparatus to determine the curvature.

Three questions concerning the discontinuity are raised by the experimental work: (1) the reproducibility of the values; (2) do they represent equilibrium? and (3) is the isotherm reversible? As to (1) it was found that the reproducibility of the discontinuity is within the limits of error of the determination of the pressure. For example, the discontinuity shown at 27°C occurs at a pressure of 0.017 mm Hg. A repetition of the experiment on a different sample of the ferric oxide showed the discontinuity to take place at the same pressure. The maximum observed difference of the pressure of the flat was found to be 0.002 mm.

From the experiments on adsorption alone it was not possible to prove without question that the observed values represent equilibrium. It can be shown only that the values do not change with time. After the time when the constancy of the pressure seemed to indicate that equilibrium had been established, it was found that there was no further change on standing for another 24 hours,

⁹ G. Jura and W. D. Harkins, J. Am. Chem. Soc. **66**, 1356 (1944).

¹⁰ W. D. Harkins and G. Jura, J. Am. Chem. Soc. **66**, 1366 (1944).

regardless of the position of the point in the isotherm, as follows: at the last point in the lower branch before entering the flat; at the first, middle, and end points in the flat; and in the first point on the upper branch of the curve. All of these remained constant, within experimental error, for a 24-hour period.

The results obtained by desorption at 25°C are exhibited in Fig. 3. The solid line represents the adsorption curve at the same temperature. Because of the low pressures, less than 2×10^{-3} cc of gas could be desorbed at one time. Since as much as 10 grams was used for the determination of the adsorption, it was not feasible to determine the desorption curve on the same sample as that used for adsorption. For the determination of the desorption 8×10^{-3} cc of gas was adsorbed on a

sample weighing 0.16 gram. This point is shown as a circle in Fig. 3 at a pressure of 0.022 mm. The points obtained by desorption are shown as rectangles, whose size represents the possible error in the determination. The error in the volume desorbed was estimated on the assumption that the pressure reading could be in error by 0.001 mm. The time test applied to the adsorption was also used for desorption. In desorption the discontinuity occurred at a pressure of 0.014 mm, whereas in adsorption it occurred at 0.016 mm. Equal discrepancies in the pressure of the discontinuity have been observed for duplicate determinations of adsorption. Thus, within experimental error, the isotherm is reversible in the region of the discontinuity.

Both the fact that the values do not change with time and the reversibility of the process indicate that the curves given in Fig. 1 represent equilibrium values. Similar discontinuities have been observed with other systems: *n*-heptane on reduced silver at 15° and other solids at 25°C; nitrogen on several solids at -195.8° to -195.0°C; water on graphite at 25°C; and triptane on silver at 0°C. The above systems have not been investigated in as great detail as that on ferric oxide. Work on other systems indicates that similar discontinuities exist. For example, there is an exceedingly long vertical region in the $p-v$ plot at 0.006 mm when *n*-heptane is adsorbed on graphite containing 0.46 percent ash by weight.

With the exception of the discontinuity of water on graphite, all take place at very low relative pressures. For example, the isotherms of nitrogen were determined on six solids in the low pressure region. The discontinuity was observed on three of them at relative pressures of 0.8, 1.1, and 1.4×10^{-3} . These three solids were alumina-silica cracking catalysts whose areas varied from 120 to $485 \text{ m}^2 \text{ g}^{-1}$.

Wooten and Brown¹¹ have observed and reported discontinuities which bear some resemblance to those reported here when ethylene is adsorbed on alkaline earth oxide-coated cathodes. The discontinuities they observed occur at relative pressures of 0.25 to 0.4. Apart from the difference in the relative pressure at which the discontinu-

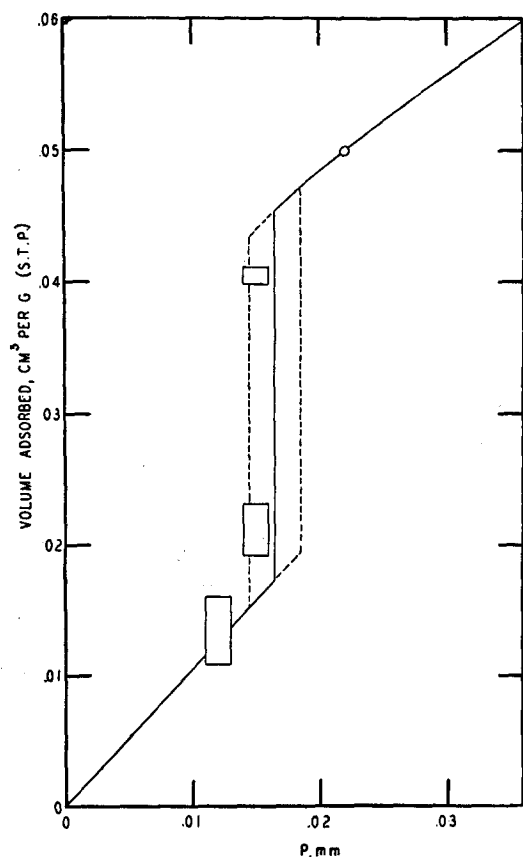
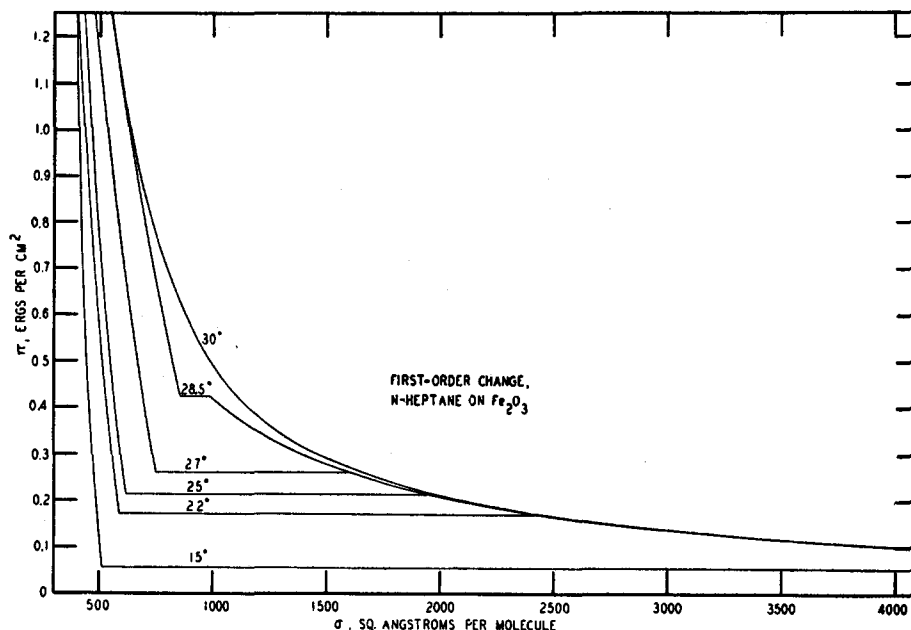


FIG. 3. The reversibility of the adsorption at the discontinuity at 25°C. The solid line represents the adsorption curve. The dotted lines indicate the maximum observed pressure of the "flat" in repeat experiments. The circle represents the adsorption point taken on the small sample for the desorption. The rectangles, whose sizes represent the possible experimental error, are the desorption points.

¹¹ L. A. Wooten and C. Brown, J. Am. Chem. Soc. 65, 113 (1945).

FIG. 4. The pressure-area curves for the films of *n*-heptane on ferric oxide at various temperatures as calculated from the adsorption values of Fig. 1.



ities occur, there are two other differences in their work and the results reported in this paper: (1) their films are polymolecular when the discontinuity occurs, while those reported here exhibit the discontinuity when only a fraction of a monolayer has been adsorbed; and (2) the effect of temperature appears to be in the opposite direction from that observed by the writers. The results of Wooten and Brown strongly suggest a phase transition between two of the non-gaseous phases of films. At least, the behavior observed by them is not incompatible with this idea.

V. DISCUSSION

In the previous section the experimental facts concerning the discontinuity have been presented. The only reasonable explanation which adequately explains the observed facts is that the discontinuity represents a first-order phase change of the film adsorbed from the gas phase. The phase formed by the condensation of the vapor phase of the monolayer probably corresponds to the liquid expanded phase of insoluble films on the surface of water.

The most striking evidence that a first-order change is taking place can be seen in Fig. 4, where the film pressure, π , area, σ , curves have been plotted. Figure 4 exhibits all the charac-

teristics of the three-dimensional pressure-area relationships of gases in the neighborhood of the critical temperature. The isotherms at 15°, 22°, 25°, 27°, and 28.5° lie below the critical temperature, while that at 30° is above. There is present the typical van der Waal's area for this transformation, characteristic of this type of transformation in both two and three dimensions.

The available data give for the critical constants: area, 900Å² per molecule; temperature, 29°C; and film pressure, 0.5 dynes cm⁻¹. The values for the critical constants depend on the nature of the surface of the solid as well as on that of the gas. For example, the critical temperature of a similar transformation on reduced silver has been found by us to lie between 15° and 25°C. The evidence also indicates that the critical area is lower than that on ferric oxide.²

The values for the critical constants are of the order of magnitude to be expected, except that for the area, 900Å² per molecule, which appears high. The *n*-heptane molecule lies flat on the surface at these concentrations of the film. If the corresponding area is calculated for the three-dimensional gas at its critical temperature, it is found to be 110Å² per molecule. The interaction with the strong surface field should condense the film before it reaches this low area. No explanation has been found as yet for the

TABLE II. The critical constants for *n*-heptane on silver, ferric oxide, and graphite.*

	$\pi\sigma$ (dyne cm ⁻¹)	$\sigma\sigma$ (Å ² per molecule)	T_c (°C)
Silver	over 0.18	310 < σ_c < 2200	15° < T_c < 25°
Ferric oxide	0.5	900	29
Graphite*	over 0.6	200 < σ_c < 600	over 25°

* Ash less than 0.004 percent.

high molecular area (Fig. 4) at which the transition to a lower area phase is completed. With *n*-heptane on graphite this area is much smaller. It is possible, though there is no evidence for this, that different crystal faces are present and that the first-order transition occurs on only one of these.

Sufficient data are now available to demonstrate that the values of the critical constants are dependent on the nature of the solid as well as that of the vapor. Values of the constants for ferric oxide, with limits of variation for silver and graphite, are given in Table II.

The heat of transformation may in theory be calculated from the Clausius-Clapeyron equation as applied to surfaces:

$$d\pi/dT = \Delta H/T\Delta\sigma,$$

where π is the film pressure of the transition, ΔH the heat of transformation in ergs per molecule, and $\Delta\sigma$ the change in molecular area during the transition. Unfortunately, the data are not sufficiently accurate or sufficiently extensive to make possible an accurate estimate of the heat liberated. At 25°C the heat evolved is 12,000 \pm 5000 cal. mole⁻¹, while at 28.5° it is 1000 \pm 400 cal. mole⁻¹. The variation of the heat of adsorption in this region is exceedingly interesting and will be considered in a later paper.

The inaccuracy of the heat of transition is due to the inability to determine π and $\Delta\sigma$ more accurately. In obtaining the value of π it has been assumed that the film is a perfect gas before the transition. However, the work at 30°C shows that the film begins to deviate appreciably from the perfect gas law when the molecular area is reduced to 1800 Å² per molecule. The equilibrium vapor pressure cannot be determined sufficiently accurately to determine the curvature of the low pressure branch of the isotherm. Thus, the values for σ on the high area side are probably too low. The probable effect on the value of π is to make

it too high. This can be seen from the equation used for integrating the function.

From the statistical point of view Devonshire¹² has calculated for the rare gases, with a number of simplifying assumptions, the ratio of the critical temperature of a two-dimensional film to that of the gas in three dimensions. Although his calculation is in theory not applicable to the present system, a comparison with the experimental values is made below, since this is the first time any experimental values of the ratio have been obtained. He calculated that

$$T_c \text{ of film} / T_c \text{ of gas} = 0.53.$$

For the transition of *n*-heptane on ferric oxide this ratio is found to be 0.56 or only 6 percent higher than his value. For *n*-heptane on silver this ratio lies between 0.53 and 0.55. It is not possible to state at the present time how general the above agreement is.

The discussion has shown that the observed experimental facts are in complete accord with the idea that the discontinuity is a first-order transition: (1) the compressibility becomes infinite; (2) there is a ΔH not equal to zero; (3) the results at various temperatures exhibit critical temperature phenomena; and (4) the critical temperature is in agreement with that calculated theoretically. The last of these, (4), is, however, of doubtful significance.

To prove definitely that the observed discontinuity is a first-order change it is necessary to show that other explanations are not satisfactory. Another possible explanation is that capillary condensation is the cause of the discontinuity. On the basis of the theory of capillary condensation the solid would need to possess pores of exactly the same diameters, which are then filled at the pressure of the discontinuity. The application of this idea would then require that the top branch of the curve should depend on the temperature in such a manner that the volume of condensed material is constant, i.e., for the short temperature range covered, 15° to 28.5°, all of the volumes at the top of the flat should be the same within the limits of experimental error. There is a variation from .0545 cc gas at 15°C to .0324 cc gas at 28.5°C. This

¹² A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 132 (1937).

variation is entirely too large to be accounted for by a change in density of condensed liquid. Also the condensation process cannot explain the disappearance of the discontinuity at 30°. Thus, the results obtained cannot be explained by the assumption of capillary condensation.

It might be assumed that a first-order change does not occur, but that the phenomena are due to the presence on the crystals of more than one type of surface, some of which are more effective than others. This can be shown to be improbable. Each surface would have its own isotherm. If the discontinuity were to take place on only one of the surfaces, then under equilibrium conditions a discontinuity would be observed as a mean of the effects. All of the experimental data, the constancy with time, and the reversibility indicate that the data are equilibrium values. Therefore, the observed discontinuity must be due to a discontinuity on at least *one* of the surfaces present. Therefore, the existence of different types of surfaces does not explain the observed discontinuity.

Other possible explanations are equally as im-

probable. Thus, the interpretation that the observed discontinuities are due to a first-order change appears certain. What has been designated as *stepwise adsorption* exhibits no obvious relationship to the change considered here.¹³ (See Fig. 2.) The discontinuity in the low pressure region is the only one found, and the data do not indicate the presence of any other first-order change.

If the interpretation that the irregularities in stepwise adsorption are due to phase transitions, then it is possible to explain their existence in two ways. For a homogeneous surface each discontinuity would represent a new surface phase. This would lead to an inordinately large number of phases, so many that such an explanation is unreasonable. The other possible explanation from this point of view is that there are present a large number of individual surfaces for which the transitions take place at different pressures. However, the problem of stepwise adsorption has not been studied in sufficient detail to show what is involved.

¹³ For a brief review, see: S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943), pp. 346-348.

Absorption Spectrum of Fluorobenzene in the Near Ultraviolet*

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Department of Physics, Duke University, Durham, North Carolina

(December 28, 1945)

The absorption spectrum of C_6H_5F at 2750-2380Å was photographed in the first order of a three-meter grating spectrograph. As in C_6H_5Cl the band system corresponds to an electronic transition A_1, B_1 . This is an allowed transition and the 0,0 band is stronger than in C_6H_5Cl because of the greater perturbation by the fluorine. Several progressions of totally symmetric vibrations are observed. The vibration whose excitation brings the corresponding benzene spectrum into appearance, and which shows up relatively intensely in C_6H_5Cl , appears in C_6H_5F but is not particularly prominent. In contrast to C_6H_5Cl , transitions to the carbon-halogen vibration in the upper electronic state are quite strong.

INTRODUCTION

THE near ultraviolet absorption spectrum of chlorobenzene has been interpreted¹ as

* Based on a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1941.

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¹ H. Sponer and S. H. Wollman, *J. Chem. Phys.* **9**, 816 (1941).

having its origin in two types of transitions, each made possible by a different perturbation of the hexagonally symmetric potential field of benzene's planar carbon ring: a weak transition permitted because of the destruction of the sixfold symmetry by a non-totally symmetric vibration of symmetry β_1 , and a somewhat stronger transition permitted because of the destruction of the sixfold symmetry by the presence of the electro-