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Surfaces of Solids XVII

A First- and a Second-Order Phase Change in the Adsorbed Film of *n*-Heptane on Graphite*

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The films of *n*-heptane formed by adsorption on the surface of graphite between 25° and 40°C exhibit a first- and a second-order phase transition. The first-order transition occurs between the gaseous and liquid expanded phases. The second-order transition occurs between the liquid expanded and liquid intermediate phases, and between the gaseous and liquid intermediate phases above the critical temperature. Since the behavior of the film is the same as that observed with insoluble films on aqueous subphases, the nomenclature for the latter is used. The critical constants for the gaseous film were determined as: temperature, 31°C; area, 400Å² per molecule; and film pressure, 1.05 dyne cm⁻¹. These values are different from those found for *n*-heptane on ferric oxide, which shows that the solid as well as the gas plays an important role in the determination of the adsorption isotherm. The heat of transition for the first-order change is estimated as 13,000 ± 5000 cal. mole⁻¹ at 25°C. It is found at corresponding temperatures, within this large experimental error, that the heat evolved in the first-order transition is the same on graphite and ferric oxide.

I. INTRODUCTION

RECENTLY, the writers have presented experimental evidence which shows that films formed by adsorption on the surfaces of

solids may undergo first-order phase transitions on increase of pressure from the gas phase. These are analogous to those which occur in insoluble films on an aqueous subphase. Data were presented for two systems: *n*-heptane on silver¹ and *n*-heptane on ferric oxide.²

Of the two systems, that which involves ferric oxide was the more extensively investigated. The system exhibited all the critical temperature phenomena in the film pressure (π)-area (σ) relationships associated in general with a first-order transition. It was also shown that the compressibility κ of the film formed by adsorption on the surface of the solid is

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

where V_M is molar gas volume at standard temperature and pressure; Σ , the specific area of the solid; R , the gas constant; T , the absolute temperature; v , the volume of gas adsorbed per gram of solid; and p , the equilibrium pressure. From the criteria for phase changes in films presented by Dervichian³ and by Harkins and

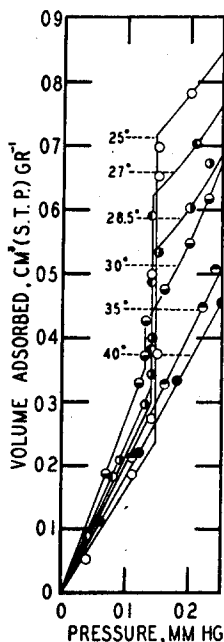


FIG. 1. The isotherms between 25° and 40°C of *n*-heptane on oxygen-free graphite with less than 0.004 percent ash to pressures of 0.025 mm. At 25°, 27°, 28.5°, and 30°C the isotherms exhibit a discontinuity in the volume adsorbed as a function of the pressure. This indicates a first-order phase transition of the film.

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

² G. Jura, E. H. Loeser, P. R. Basford, and W. D. Harkins, *J. Chem. Phys.* **14**, 117 (1946).

³ D. G. Dervichian, *J. Chem. Phys.* **7**, 931 (1939).

Boyd⁴ it also was shown that for a first-order transition $(\partial v/\partial \ln p)_{T,z}$ becomes infinite, while for a second-order transition there is a finite discontinuity in the derivative.

In the present paper, which considers the adsorption of *n*-heptane on graphite at low relative pressures, the experimental data indicate that both a first- and a second-order transition occur at pressures below 0.040 mm at temperatures between 25° and 40°C.

II. EXPERIMENTAL METHODS AND MATERIALS

The experimental procedures and materials used have been fully described in previous papers.^{5,6} The graphite used is that which contains less than 0.004 percent ash. It was furnished by the courtesy of Dr. Lester L. Winter of the National Carbon Company. As in the previous paper, 4.22 m²g⁻¹ was used as the area of the sample, as obtained from an absorption isotherm of nitrogen at -195.6°C, and calculated by the relative method of Harkins and Jura.

III. EXPERIMENTAL RESULTS

The adsorption isotherms of *n*-heptane on graphite are exhibited in Fig. 1. These were obtained at pressures up to 0.025 mm at 25.00° ± 0.02, 27.00° ± 0.02, 28.50° ± 0.02, 30.00° ± 0.02, 35.00° ± 0.05, and 40.00° ± 0.05°C. At 25°, 27°, 28.5°, and 30°C, the isotherms exhibit a first-order phase change at a pressure of 0.014 mm Hg. The behavior of the isotherms in this region is exactly analogous to that of those observed when ferric oxide is the subphase. The best values for the critical constants on graphite are: $T=31^\circ\text{C}$, $\sigma=400\text{A}^2$ per molecule, and $\pi=1.05$ dyne cm⁻¹. The corresponding values for ferric oxide are: $T=29^\circ\text{C}$, $\sigma=900\text{A}^2$ per molecule, and $\pi=0.45$ dyne cm⁻¹. These two sets of values show the dependence of the critical constants on the nature of the subphase. Obviously, the critical constants must depend also on the nature of the gas.

The heat evolved in the first-order transformation of the film of *n*-heptane on graphite

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

⁵ G. Jura and W. D. Harkins, J. Am. Chem. Soc. **66**, 1356 (1944).

⁶ W. D. Harkins, G. Jura, and E. H. Loeser, J. Am. Chem. Soc. **68**, 554 (1946).

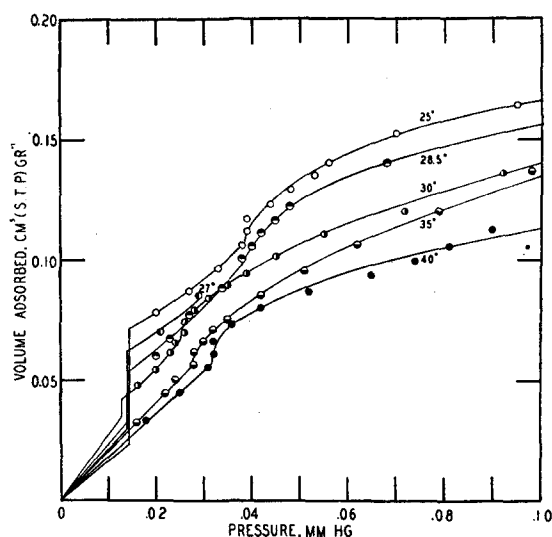


FIG. 2. The same as Fig. 1, but to pressures of 0.100 mm Hg. These curves exhibit at pressures above 0.025 mm a second-order phase transition of the film.

at 25°C is estimated at $13,000 \pm 5000$ cal. mole⁻¹, which is practically the same as that on ferric oxide at the same temperature: $12,000 \pm 5000$ cal. mole⁻¹. If the comparison were made at corresponding temperatures for the film on graphite and ferric oxide, the heats evolved in the phase transformation would be the same. The experimental facts seem to indicate that the gas-gas interaction cannot be neglected, even when the adsorbed molecules are separated by comparatively large distances.

Figure 2 exhibits the isotherms to a pressure of 0.100 mm. The experimental points for the discontinuity and lower pressures have been omitted, since they are shown in Fig. 1. Each of these curves (except that at 27°C, where the data are insufficient) exhibits a sudden increase in $(\partial v/\partial p)_{T,z}$ at pressures decreasing from 0.038 mm at 25°C to 0.025 mm at 30°C and then again increasing to 0.032 mm at 40°C. The data in this region are completely reproducible, and the values do not change with time. In several of the determinations in this region two consecutive points are found at the same pressure. It is apparent that this rapid change in $(\partial v/\partial p)_{T,z}$ represents a second-phase change in the film. The isotherms below the critical temperature ($T \leq 30^\circ\text{C}$) cannot be used to decide this point, since too few experimental points can be ob-

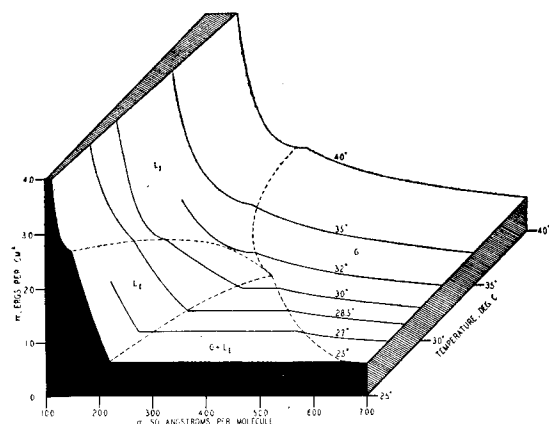


FIG. 3. A cabinet projection of the π - σ - T surface of the film of *n*-heptane on graphite. In this projection the correct π - σ relations are maintained. The temperature axis is drawn at 45° . Thus, an increase of 5°C causes an apparent increase of molecular area of 100\AA^2 per molecule and an apparent increase of 1 dyne cm^{-1} in the film pressure. The surface shows four regions: (1) the gas, G ; (2) the "liquid expanded," L_E ; (3) the "liquid intermediate," L_I ; (4) the two-phase region, gas + "liquid expanded."

tained between the identified first-order transition at 0.014 mm and the possible second transition. At 35° and 40°C , however, a definite decision can be made. At these temperatures a study of the data shows that a transition does occur, the question being solely one of order, i.e., first or second. The fact that in some cases two points are observed at the same pressure might indicate a first-order change with an exceedingly small change of area. A study of the pressure (π)-area (σ) curves indicates, however, that the only reasonable assumption is that a second-order change occurs. If the transition were first order, the compressibility of the phase formed by the transition would at first decrease and then increase as the pressure is increased. This behavior is unreasonable from both the two- and three-dimensional behavior of matter under pressure. This difficulty is obviated if it is assumed that order of the change is second rather than first. The π - σ curves are exhibited in Fig. 3.

If the second transition is considered as first order, the heat relations on this basis are peculiar. The ΔH for the second transition on the assumption that the change is first order, becomes positive below the critical temperature and negative above this temperature. Also, at 25° $\Delta H = 300$ cal. mole^{-1} , which increases to $27,000$ cal. mole^{-1} at 30°C and decreases to -700 cal. mole at 35°

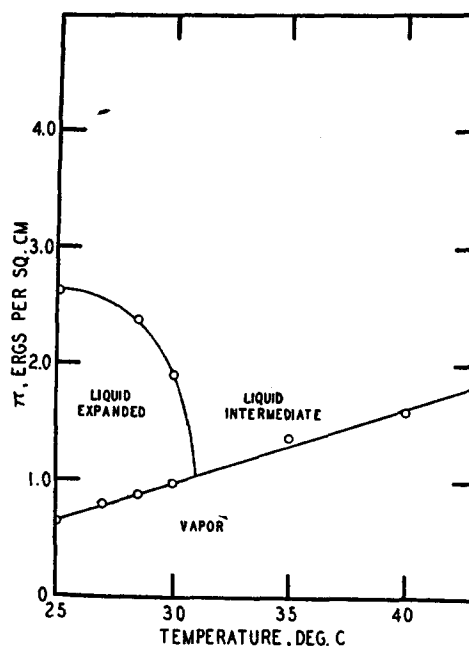


FIG. 4. The π - T phase diagram of the film of *n*-heptane on graphite. The triple point is placed at the critical temperature and critical film pressure.

and 40° . The ΔH for the process of transforming the vapor to the third phase that appears would be $-12,000$ cal. mole^{-1} at 25°C , which would increase to $26,000$ cal. mole^{-1} at 30°C and then at above the critical temperature change to -700 cal. mole^{-1} . This behavior is also unlikely. Thus, it is almost certain that the phase change under consideration is of the second order. The fact that this change exhibits an appearance somewhat analogous to a change of the first order is presumably due to an insufficient sensitivity of the pressure measurements.

By analogy with the behavior of insoluble films on water, the phase formed from the gas by the first-order change would be the liquid expanded (L_e), while that formed by the second-order change from the gas and the analog of the liquid expanded would be considered the liquid intermediate (L_i) phase. The phase diagram of this system is given in Fig. 4. The diagram is in complete accord with our present knowledge of the behavior of films and also of matter in three dimensions, when the pressure, temperature, area (or volume) relations are considered.

Figure 4 does not represent all of the phases which appear in this system. At 25°C , where the

entire isotherm has been determined, the "liquid intermediate" phase transforms into a condensed phase at a film pressure of about 20 dyne cm⁻¹. The nature of this transition has not as yet been determined.

The second-order change reported here has also been found with other solids when *n*-heptane is the adsorbate, and also with *n*-butane and triptane at 0°C on several solids. The work done to date with *n*-butane indicates that the observed phenomena are the same as those found for graphite above the critical temperature. The work of Orr⁷ strongly suggests that similar transformations take place when argon, nitrogen, and oxygen are adsorbed on ionic solids at temperatures in the neighborhood of 77°K. The writers are planning to repeat his work and, by

⁷ W. J. C. Orr, Proc. Roy. Soc. London **173A**, 349 (1939).

taking more points, to determine whether or not these are phase transitions of the second order in the low pressure region. First-order transitions with nitrogen at these temperatures have been observed.

The results with graphite show, even when the adsorbed film is above the critical temperature of the liquid expanded film, that the increase of the pressure of the film transforms the gas into a phase which, below the critical temperature, does not appear until much higher pressures are attained. This behavior has its counterpart in the solidification of helium and other gases above their critical temperatures. Thus, in films formed on the surfaces of solids by adsorption, phase transformations from the gas are possible, even above the critical temperature of the liquid expanded.

Errata: Statistical Mechanics of Transport Processes

I. General Theory

[J. Chem. Phys. **14**, 180 (1946)]

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IN this article an important distinction was made between the distribution function $f^{(n)}(\mathbf{p}, \mathbf{q}; t)$ at time t and its time average $\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$ over an interval τ subsequent to the instant t . The two functions are related in the following manner,

$$\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) = \frac{1}{\tau} \int_0^\tau f^{(n)}(\mathbf{p}, \mathbf{q}, t+s) ds.$$

Unfortunately, serious confusion was caused by a series of typographical errors introduced between galley and page proof, in which the bar was omitted at random from the functions $\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$. These errors are to be corrected as follows:

1. $\bar{f}^{(N)}$ to replace $f^{(N)}$ on the left side of the second of Eqs. (14).
2. $\bar{f}^{(n)}$ to replace $f^{(n)}$:
 - (a) On left side of second of Eqs. (20).
 - (b) In integrand of Eq. (21).
 - (c) On left side of the third of Eqs. (46).

- (d) On left side of the differential equation, Eq. (47).
 - (e) On right side of the first of Eqs. (48).
3. $\bar{f}^{(1)}$ to replace $f^{(1)}$:
 - (a) In the integrands on the right sides of Eqs. (23), (24), (25), (26), and the second of Eqs. (60).
 - (b) On the left side of the differential equation, Eq. (49).
 - (c) On both sides of the differential equation, Eq. (59).
 - (d) First sentence, last paragraph, page 194.

Two additional errors of a minor character are also to be noted:

4. In the first of Eqs. (70), C_i , the concentrations in moles/cm³ should replace C_l , the concentrations in molecules/cm³.
5. The expression $6\pi\eta\mathbf{p}_i/m_i$ should replace $6\pi\eta m_i\mathbf{p}_i$ at the end of the eighteenth line from the bottom of the second column, page 198.