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THE ADSORPTION OF n-HEPTANE ON SOLIDS AT LOW PRESSURES

by

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SUMMARY

Adsorption isotherms have been measured for n-heptane on graphite, ferric oxide and on reduced silver powder at low pressures. The rate of attainment of adsorption equilibrium has been studied in detail; the results suggest that the discontinuities in the isotherms for the above systems claimed by earlier workers were in fact due to inadequate time being allowed for the establishment of equilibrium.

The isotherms reported by Jura, Harkins and Loeser¹ for the adsorption of n-heptane on graphite at room temperatures exhibit some features for which there is little precedence. A vertical portion or 'step' was observed at a pressure of 0.014 ± 0.001 mm. in the isotherms measured below 35°C. As the temperature was increased the height of the step appeared to decrease until at 35° and above, the isotherms were found to be continuous. These authors interpret the step as evidence for the occurrence of a first-order phase transition in the adsorbed film. There was also evidence for the existence of a second-order phase change in the pressure range 0.02 to 0.05 mm. at all the temperatures studied. The third and perhaps the most striking observation was that the isotherms at different temperatures intersected in the pressure range 0.014 ± 0.001 mm., indicating that the adsorption process is endothermic at pressures below 0.014 and exothermic thereafter. On the other hand the isotherms measured at 35° and 40° suggest that the adsorption process is exothermic over the entire range of the measurements. A family of isotherms with similarly anomalous properties was also measured for the adsorption of n-heptane on ferric oxide at room temperatures², but the second order phase transition was not observed. A single adsorption isotherm for n-heptane on reduced silver powder at 15°C. was found to exhibit a first-order transition; the isotherm at 25°, however, was reported to be smooth.

It was decided to re-examine the adsorption of n-heptane on these three adsorbents using a more sensitive method for detecting small changes in pressure. Since this work was started there has appeared a paper by Smith³

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describing some careful measurements of the adsorption of n-heptane on graphite and on ferric oxide at room temperatures. Using a McLeod gauge to measure pressures and a sensitive gravimetric technique to measure the amount adsorbed, Smith has found that adsorption was exothermic under the conditions studied and that the isotherms were all smooth and of a general shape commonly encountered in adsorption studies. The subject cannot be regarded as closed, however, until the adsorption of n-heptane on reduced silver has been re-examined and until a satisfactory explanation of the results of Harkins, Jura et al. has been proposed.

EXPERIMENTAL

MATERIALS

NC-1 graphite made by the National Carbon Company was obtained through the courtesy of Professor Conway Pierce. It is similar to, though not identical with, the sample used by Smith³, which was "thought to be like the sample for which Harkins, Jura and Loeser report their phase transitions." In the present experiments 7.07 g. of graphite were used. Reagent grade ferric oxide was supplied by Baker and Adamson; 18.48 g. were used. Silver powder was supplied by the Hanovia Chemical and Manufacturing Company, designated "silver precipitate No. 20". 27.47 g. of this material were reduced in situ as follows. Electrolytic hydrogen, purified by passing through a "Deoxo" catalytic purifier, over NaOH pellets, over P₂O₅, and finally through a trap cooled in liquid nitrogen, was allowed to stream over the adsorbent for 24 h. The adsorbent bulb was then surrounded by a furnace maintained at 160°C. and the passage of hydrogen maintained for a further 24 h. The hydrogen inlet and outlet tubes were then sealed off and the adsorbent evacuated.

Pure grade n-heptane (99 mole % minimum) supplied by the Phillips Petroleum Company was shaken with concentrated H₂SO₄ until no coloration appeared. It was then washed with water, dried over metallic sodium and fractionated, the middle fraction boiling in a range not exceeding 0.1° being collected ($n_D^{20} = 1.3840$). This fraction was introduced into the adsorption apparatus and stored over metallic sodium. Bulb-to-bulb distillations were carried out until the vapour pressure was constant (11.47 ± 0.01 mm. at 0°C.), indicating that all the dissolved air had been removed. Spectroscopically pure helium supplied by the Air Reduction Company was used without further purification.

APPARATUS

The apparatus was of the constant volume type and contained no stopcocks or ground joints. The helium and n-heptane reservoirs were isolated from the rest of the system by metal diaphragm valves supplied by Hoke Incorporated; they were opened and closed by applying a torque not exceeding 40 inch-pounds as indicated by a "Torqometer". Elsewhere, mercury cut-offs were used instead of stopcocks. Increments of n-heptane or helium were measured using a doser specially designed for this work⁴, a 25 mm. bore mercury manometer and a travelling microscope. By this means doses as small as 0.01 c.c. at N.T.P. could conveniently be measured and admitted to the adsorption system. The adsorbent was spread out on twenty copper shelves one inch in diameter, the whole being sealed into a glass tube. This type of arrangement has been advocated by Jura and Criddle⁵, who find that the rate of attainment of adsorption equilibrium for argon on graphite at low pressures is thereby markedly increased. It has the further advantage that the heat capacity of the adsorbent bulb is greatly increased by the presence of this large mass (80 g.) of copper, so that the effect of any temperature fluctuations in the surrounding thermostat bath is minimized. During experiments the adsorbent bulb was immersed in a water bath whose temperature was maintained constant to within 0.01°C.

The pressure of heptane vapour in equilibrium with the adsorbed phase was measured by a Pirani gauge. For this purpose a gauge of high stability was required, since it was often necessary to leave an experiment overnight and continue it the next day. This stability was achieved by allowing a constant current to flow through the Wheatstone bridge circuit, which type of control has the further advantage that it partially overcomes the drop in sensitivity of the gauge with increasing pressure. The Pirani tubes were a matched pair (Sylvania Electric No. R 111 M) connected to a Wheatstone bridge circuit consisting of a 1000 ohm fixed resistance and a four decade resistance box reading to 0.1 ohm; the balance of the bridge was indicated by a Leeds and Northrup galvanometer, sensitivity 0.1 μ V/mm. at one metre. The bridge was connected in series with a 2 v. accumulator, a rheostat and a milliammeter. During measurements the total current through the bridge was maintained constant at 70 ± 0.1 ma. The two Pirani tubes were immersed in an ice bath which was stirred continuously. This arrangement proved satisfactory, as indicated by the zero readings of the gauge which

did not vary by more than 0.1 ohm over a period of several days; similar stability was observed with low pressures of n-heptane.

The Pirani gauge was calibrated for n-heptane using a manometer of the type described by Puddington⁶, modified as follows⁷. The bulb at the upper end of the calibrated capillary was moved to the lower end; this obviated the necessity of passing a large volume of mercury through the long capillary, thus enabling the measurements to be made more rapidly. The two mercury-sealed stopcocks were lubricated with a thin coating of "Aquadag" colloidal graphite. The wide manometer tubes were of 48 mm. bore, their cross-sectional areas being determined by calibration with mercury before the inside surfaces were ground with carborundum powder. The capillary was a metre length of 0.78 mm. precision bore capillary tubing with ground internal surface. The magnification factor was thus 1868 and the maximum measurable pressure 0.45 mm. The whole manometer was rigidly clamped and enclosed in an air thermostat constant to within $\pm 0.01^\circ\text{C}$. Readings of the position of the mercury thread in the capillary were accurate to ± 1 mm., so that the maximum absolute error in the measured pressures was ± 0.001 mm., assuming that the mercury-glass contact angle did not vary with the pressure of n-heptane over the range of pressures studied.

At the lowest pressures ($\sim 4 \times 10^{-3}$ mm.) the sensitivity of the Pirani gauge for n-heptane vapour was 2×10^{-6} mm., decreasing to 5×10^{-4} mm. as the pressure approached 0.1 mm., the highest pressure at which adsorption measurements were made.

PROCEDURE

Initially the adsorbent was outgassed for several days at 300°C . ($\leq 160^\circ\text{C}$. for the silver powder adsorbent) in a vacuum of less than 10^{-3} mm., as indicated by a roughly calibrated McLeod gauge; between each experiment it was outgassed overnight under the same conditions. After removing the furnace, the adsorbent bulb was allowed to cool for one hour in the presence of a small pressure (≤ 1 mm.) of helium, after which time it was surrounded by the thermostat bath. The helium was then pumped out for a further hour; meanwhile the Pirani tubes were surrounded by an ice bath, and zero readings recorded at regular intervals until a constant value was obtained. The first dose of n-heptane vapour was measured and introduced to the adsorption system as previously described⁵. Pirani gauge readings were taken every five minutes

until three consecutive readings varied by less than 0.1 ohm; as soon as the first dose had come to equilibrium (as indicated by the above criterion), the next dose was introduced. That equilibrium had actually been attained was shown by the fact that the Pirani gauge readings would remain constant (± 0.1 ohm) if the system were left for several days.

The volume of the dead space (~ 250 cm.³) was determined by calibration with helium, using the Puddington manometer to measure the pressure of helium in the adsorption system. In designing the apparatus, however, no attempt was made to limit the volume of the dead space since, even at the highest pressures studied, the volume of unadsorbed vapour was less than 2% of the total volume admitted (less than 10% in the case of the silver powder adsorbent).

RESULTS AND DISCUSSION

The main interest lay in discovering whether or not the isotherms followed a smooth curve. No attempt was made to secure results of great absolute accuracy, it being more relevant to show that, at all values of V , the addition of ΔV cm.³ of the vapour to the adsorption system was accompanied by an increase in the equilibrium pressure. It was not necessary, therefore, to follow the usual practice of limiting the number of successive increments of vapour admitted to the system in order to avoid cumulative errors. Nor was it necessary to calibrate the Pirani gauge with great accuracy. Finally, it was not necessary to obtain an exactly reproducible surface, since each isotherm could be measured in a single experiment lasting several days; the three isotherms on which this paper is based therefore represent three complete experiments.

The isotherm measured for n-heptane on graphite at 25.0°C is shown in Fig. 1, in which the amount adsorbed (in cm.³g.⁻¹ at N.T.P.) is plotted against the equilibrium pressure (in mm. of Hg). On the same graph are shown the isotherm interpolated at 25.0°C from isosteres constructed from Smith's results⁴ and the isotherm at 25.0°C reported by Jura, Harkins and Loeser¹. Fig. 2 shows a similar comparison of the results of Smith⁴, of Jura, Loeser, Basford and Harkins² and of the writers for the system n-heptane on ferric oxide at 15.0°C. In Fig. 3 are plotted the results of the present work, alongside those of Jura, Loeser, Basford and Harkins³ for n-heptane on reduced silver powder at 14.9°C.

The closeness of the isotherms shown in Fig. 1 suggests that the samples of graphite used by the three groups of workers were indeed similar. The only significant difference between these results is that Jura, Harkins and Loeser¹ find evidence for a first-order and for a second-order transition. It will be noted that the middle portion of the writers' isotherm is linear, but little significance should be attached to this in view of the low absolute accuracy of the pressure measurements. The agreement between Smith's and the present workers' isotherms in Fig. 2 is remarkable when it is considered that the two samples, though both of the same quality and obtained from the same source, were drawn from different batches. These curves are entirely different from that of Jura, Loeser, Basford and Harkins², in which the isotherm consists of three linear portions, the second of which evidences a first-order transition. Again, in Fig. 3, there is no evidence for a first-order transition, in contrast to the findings of Jura *et al.*³, although the slight wave in the isotherm at $p \approx 0.10$ mm. might be regarded as evidence for a second-order transition. Whether the observed wave is real or due to experimental error is a matter for conjecture and lies outside the scope of the present paper, which is principally concerned with first-order phase changes. It is curious that the isotherm of Jura *et al.* should lie so much higher than the authors' when it is recalled that the two samples were supposed to be identical.

The Pirani gauge used in these experiments facilitated a detailed study of the rate of adsorption. It was found that the first increment of n-heptane admitted to the graphite adsorbent required approximately 2 h. to attain equilibrium, at both 25° and 30°C. Subsequent doses came to equilibrium within 15 min. or less. On the ferric oxide adsorbent at 15°C, the first increment of vapour required 4 h. 15 min. to come to equilibrium, the second required 2 h. 45 min., the time taken by the subsequent doses to reach equilibrium decreasing until only 10 min. was required at the 15th dose. These observations are consistent with the suggestion² that ferric oxide may have some pores. The first dose of vapour admitted to the silver powder adsorbent came to equilibrium within 2 h. at 15°C and within 50 min. at 25°C. The latter is the only system for which definite evidence has been obtained for a temperature coefficient of the rate of attainment of equilibrium. It may be noted in parentheses that if helium were not admitted to the adsorbent

bulb before the start of the experiment, the time taken for the first dose to come to equilibrium was increased by approximately 1 h.

The first-order phase transitions reported by Jura and his collaborators may be due to an inadequate time interval being allowed between the admission of the first and second doses. No mention is made in their papers ¹⁻³ of the slow attainment of adsorption equilibrium after admitting the first increment of vapour. They may have been unable to detect a slow drift in the pressure with time since the manometer which they used for these observations was comparatively insensitive. On the other hand, some work published a few years later by Harkins and Loeser⁹ on the adsorption of n-heptane on metal surfaces revealed a very slow adsorption process at low pressures. Harkins and Loeser state that "the attainment of equilibrium, especially at the lowest and highest pressures, is very slow, so a single isotherm requires from two to three weeks for its completion."

The effect, on the shape of the isotherm, of adding the second dose of vapour before the first had come to equilibrium would be as follows. The first point on the observed isotherm would occur at too high a pressure; the second point would also occur at too high a pressure, but the system would be nearer equilibrium than at the first point since a longer time interval would have elapsed. As the experiment proceeds and more time elapses, the system will approach equilibrium. Thus the slope of the observed isotherm from the first point onwards will be greater than that of the true equilibrium isotherm. This argument is based on the assumption that the time taken for the first dose to reach equilibrium is longer than the time allowed, while the time taken for subsequent doses to reach equilibrium is commensurate with the time interval allowed between the admission of each dose. If the total surface area of the adsorbent is large and the volume of the "dead space" is small, the effect predicted above will be very marked; a slight change in the volume adsorbed per unit surface area will greatly alter the observed pressure. The above hypotheses could account in part for the observations of Jura and his collaborators.

On general grounds it might be supposed that the time taken for the first dose to reach equilibrium would decrease with increasing temperature, as has been found experimentally for the silver powder adsorbent (*vide infra*). Thus, if the above explanation of the observed 'steps' is substantially correct, one would expect the height of the step to diminish as the temperature

increases. This effect is noted in practice, indeed, the isotherms reported for n-heptane on graphite at 35° and 40°, on ferric oxide at 30° and on silver powder at 25°C exhibit no first-order phase transitions.¹⁻³

These ideas are supported by some work, recently carried out by Ballou¹⁰ at Rensselaer Polytechnic Institute, in which an apparatus similar to that of Jura *et al.* was used to study the adsorption of a number of vapours on activated MoS₂. First-order phase transitions, similar to those reported by Jura and his co-workers, were observed, found to be reproducible and to coincide with transitions in the desorption isotherms. But if a longer time interval were allowed after the admission (or withdrawal, for the desorption isotherms) of each dose, the isotherms exhibited no discontinuities. Ballou concludes that "a careful worker might report such discontinuities as entirely reproducible if he repeated experiments with the same doses and time intervals."

The authors are indebted to Dr. I. E. Puddington for his advice on the construction of the low pressure manometer, to Drs. R. N. Smith and E. V. Ballou for helpful discussions and for making available their experimental results before publication, and to Mr. J. H. Fuller for technical assistance.

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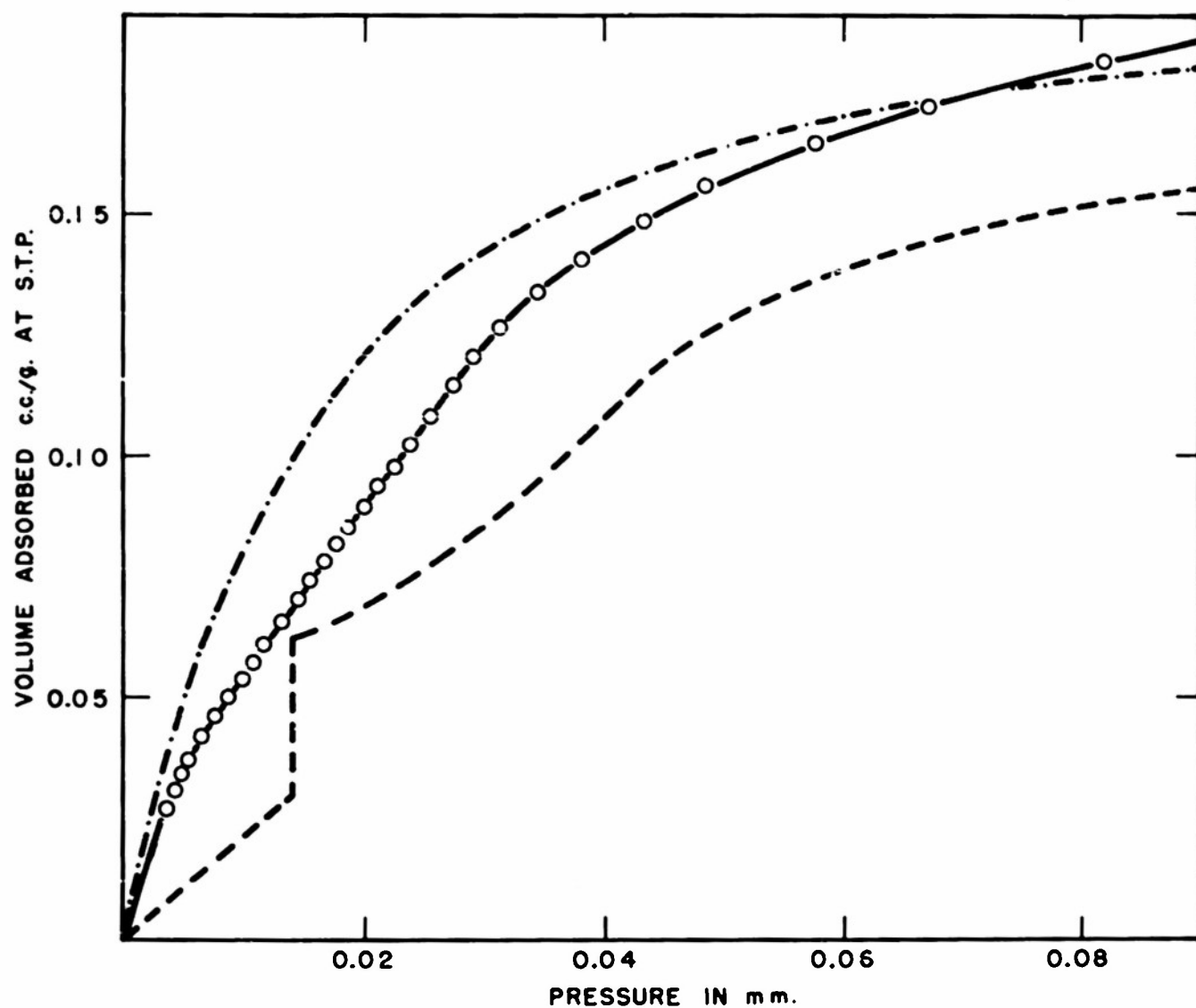


FIG. 1
ADSORPTION OF N-HEPTANE ON GRAPHITE AT 25.0 °C.

—○— PRESENT WORK
- · - · - SMITH
- - - JURA, LOESER & HARKINS

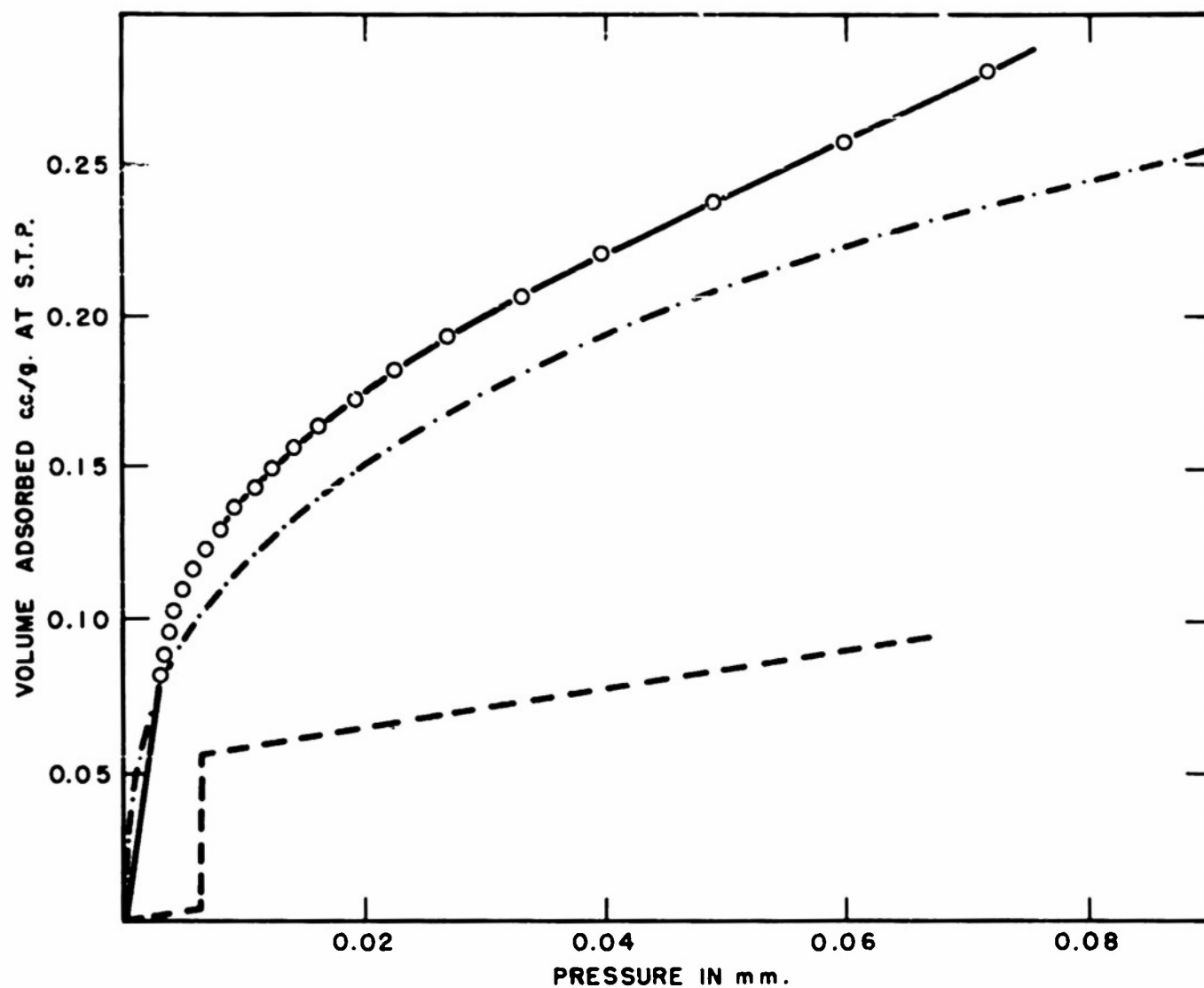


FIG. 2
ADSORPTION OF N-HEPTANE ON FERRIC OXIDE AT 15.0°C.

—○— PRESENT WORK
 - · - · - SMITH
 - - - JURA, LOESER, BASFORD & HARKINS

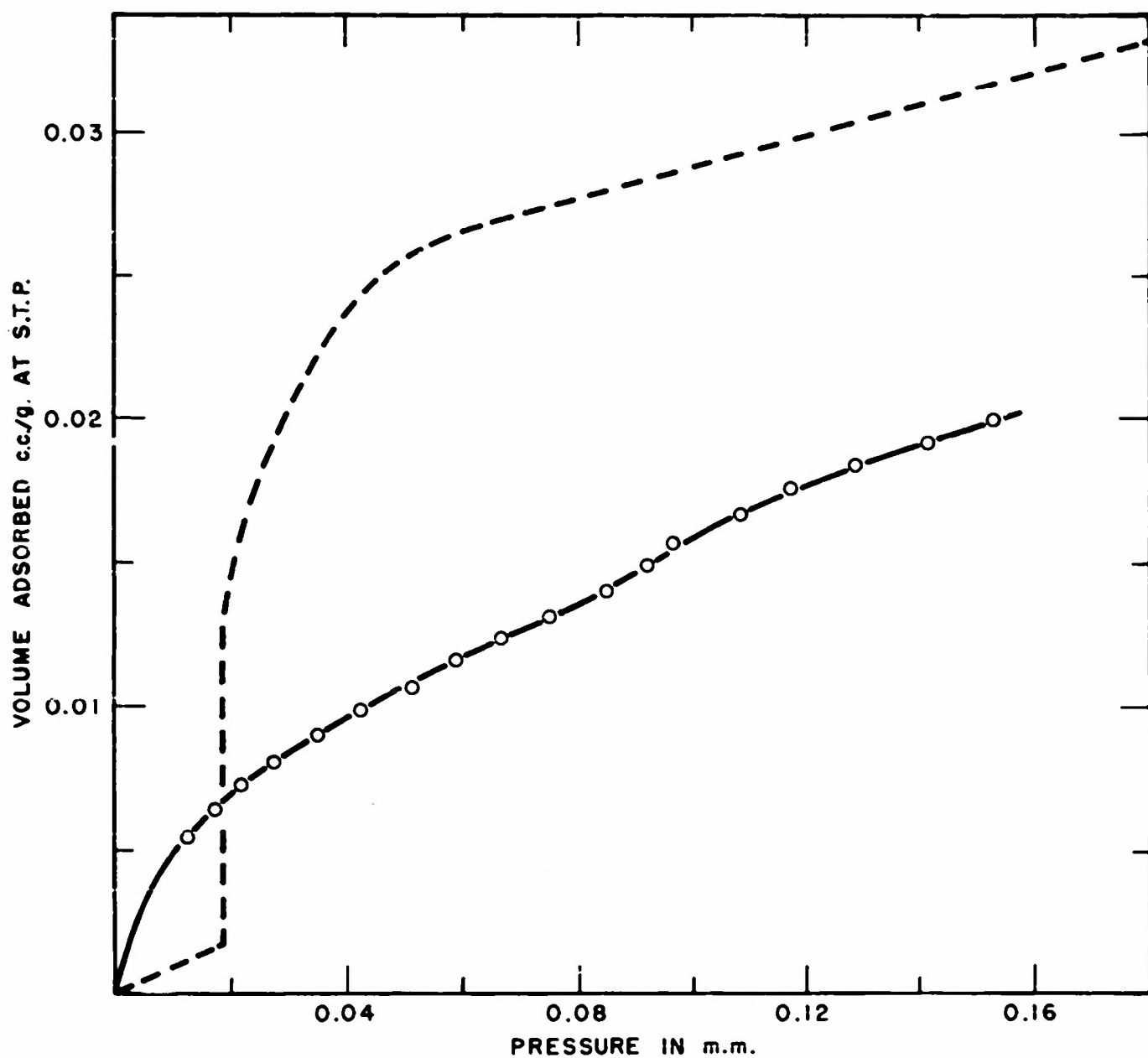


FIG. 3

ADSORPTION OF N-HEPTANE ON REDUCED SILVER POWDER AT 14.9 °C.

—○— PRESENT WORK
- - - JURA, LOESER, BASFORD & HARKINS

APPENDIX

A DOSER FOR ADMITTING MEASURED AMOUNTS OF VAPOR*

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Measured amounts of gas are conventionally admitted to a reaction vessel by means of a gas buret¹ or doser.² In order to use the above devices for admitting condensible vapors, considerable modification is required, for the stopcocks should be replaced by mercury or glass cutoffs. Wendell³ has described a greaseless gas buret employing an all-glass hypodermic syringe. The present note outlines a method whereby the doser technique may be modified to permit the handling of vapors.

The apparatus is shown diagrammatically in Fig. 1. The lower part of the doser terminates in a conventional mercury cutoff B; to the upper end is sealed a fritted-glass disk surrounded by a wider tube A into which mercury may be admitted. The method of operation is as follows: Mercury is admitted into A so that the fritted disk is covered, and the mercury in B is adjusted until the meniscus is just below the cutoff (as illustrated). Vapor is then admitted via the sidearm of B, its pressure measured on a manometer, and the temperature of the doser recorded. The head of mercury above the fritted disk must, of course, be greater than the pressure of vapor admitted. The doser is isolated by closing the cutoff B. The mercury in A is lowered and the charge of vapor expelled through the fritted disk by completely filling the doser with mercury. Subsequent doses are admitted by covering the fritted disk with mercury, withdrawing mercury from the doser to its original level in B, and repeating the above cycle.

This arrangement has proved useful in some studies, currently in progress in this laboratory, of the adsorption of n-heptane vapor at low pressures. The volume of the doser determined by calibration with mercury was 19.84 cc and the volume of the pore space in the fritted disk taken as 0.04 cc (mean of several independent estimates). Pressures of n-heptane vapor between 0.5 and 20 mm of Hg, measured on a 25-mm bore mercury manometer using a traveling microscope, have been admitted to the doser. Thus, volumes of vapor as small as 0.01 cc at STP may conveniently be handled. The device is simple to operate since, unlike the conventional gas buret or gas doser, it requires no exact adjustment of mercury levels.

*This note was published in the Review of Scientific Instruments 24, 76 (1953).

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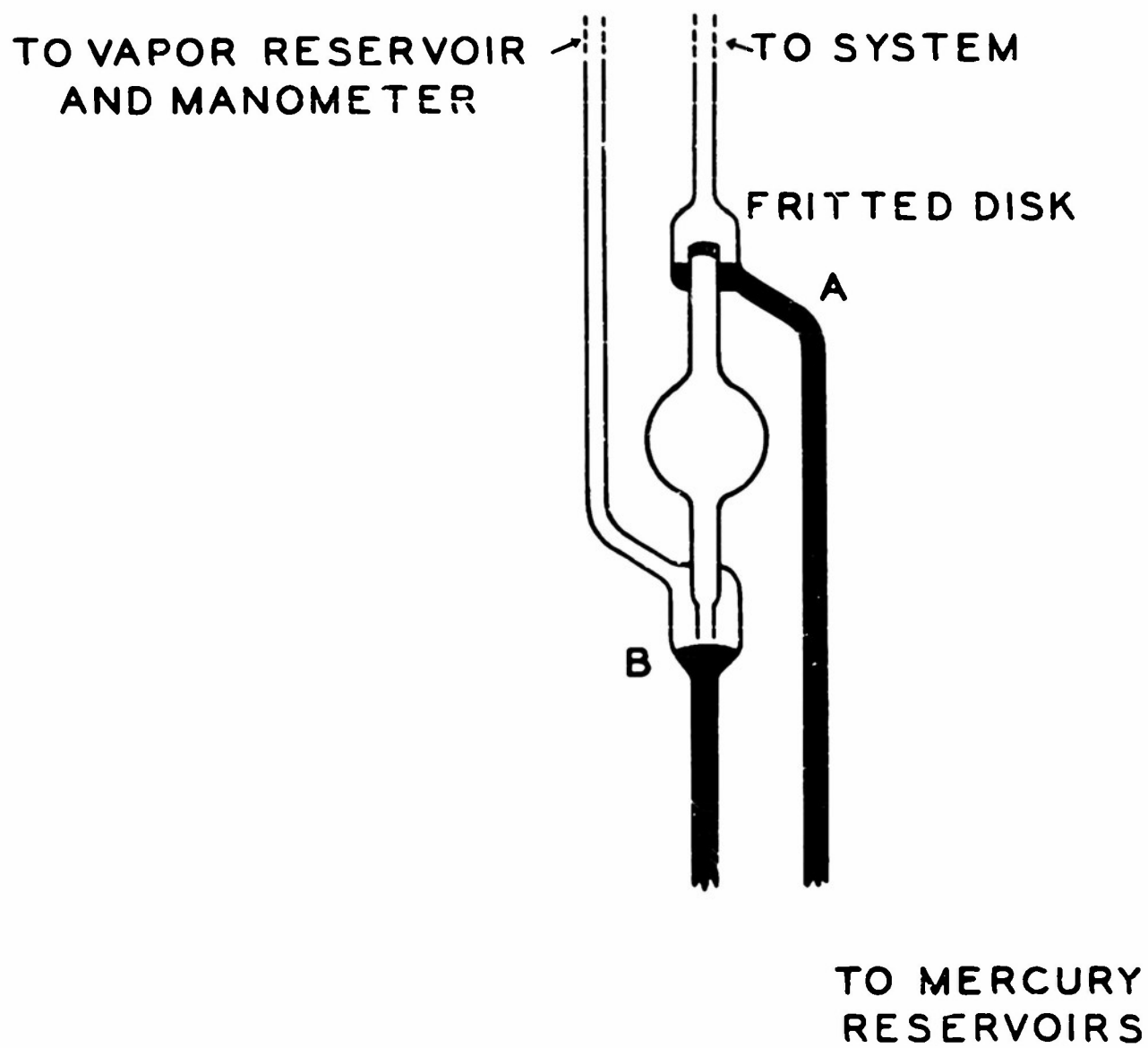


FIG. 4