per and include here only the results (Table II) obtained in this paper together with a comparison of

## TABLE II

RELATIVE SPEEDS OF ELEMENTARY REACTIONS			
$CH_3 + CH_3CHO$	$\longrightarrow CH_4$	+ CH₃CO	(1)
$CD_3 + CD_3CDO$	$\longrightarrow CD_4$	$+ CD_{3}CO$	(2)
$CH_3 + C_2D_6$	→ CH₃D	$+ C_2 D_5$	(3)
$CD_3 + C_2H_6$	$- \rightarrow CD_3H$	$+ C_2H_5$	(4)
$CD_3 + CH_3CH = CH_2 \longrightarrow CD_3H + CH_2 = CH = CH_2 (5)$			
		va	Lit. 1. ref. 12
$k_1/k_3 = \mathrm{CH}_4/\mathrm{O}_4$	$CH_3D = 39.$	2	71.2
$k_2/k_4 = \mathrm{CD}_4/9$	$CD_3H = 4.$	75	11.7
$b_0/b_r = CD_t/0$	9	75	2.0
$\kappa_{2}/\kappa_{5} = CD_{4}/$	$CD_3H = 2.$	10	5.9

published results. The published results for reactions 1, 4 and 5 are taken from a recent review by Trotman-Dickenson.<sup>12</sup> In the case of reactions 2 and 3 we have assumed that the activation energy is 1.8 kcal. greater than that of reactions 1 and 4, respectively. Since the literature values were obtained at lower temperatures using a very different technique, the differences from our values are not too surprising.

We would like to express our thanks to Dr. E. W. R. Steacie and to Dr. James R. McNesby for helpful discussion and suggestions in connection with this paper.

(12) F. A. Trotman-Dickenson, Quart. Rev., VII, 198 (1953).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

### The Viscosity of Vapor Mixtures of Hydrogen Peroxide and Water

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The viscosity of hydrogen peroxide-water mixtures in the vapor state, containing up to 65 mole % hydrogen peroxide, was measured by a capillary flow method at one atmosphere total pressure and at a temperature of 170°. By extrapolation, the viscosity of anhydrous hydrogen peroxide vapor at 170° was found to be 144 micropoises. A few studies also were made at 200 and 240° to provide a basis for estimating the effect of temperature. The results of this work may be expressed by the following equation:  $\mu = 134 + 0.35(t - 100) - 14y$ ; where  $\mu =$  viscosity, micropoises; t = temperature, and y = vapor composition, mole fraction hydrogen peroxide. This equation is recommended for the calculation of the viscosity of vapor mixtures of hydrogen peroxide and water over the temperature range of about 100 to 300°, and has a precision of within  $\pm 2\%$ . The results provide a measure of the viscous forces in a highly polar gaseous mixture; few such systems have been studied previously.

The viscosity of vapor mixtures of hydrogen peroxide and water is of interest for at least two reasons: (a) The use of hydrogen peroxide as an energy source requires knowledge of such physical properties as vapor viscosity in the design of power producing devices. (b) Relatively little information is available on the transport properties of mixtures of two highly polar gases. No information previously has been published on the viscosity of this system in the vapor phase.

The method used here was that of measurement of the pressure drop occurring upon flowing hydrogen peroxide vapor through a capillary tube at constant temperature. The mathematical relation between the viscosity,  $\mu$ , the measured pressure drop,  $\Delta p$ , and the volumetric flow rate, q, is given by the Poiseuille equation

$$\mu = 10^6 \pi r^4 (\Delta p) / 8qL \tag{1}$$

Equation 1 is valid only when the flow is streamlined in a tube of radius, r, and length, L. In practice the measured pressure drop will include contributions from energy losses at the entrance and exit of the tube. These must be minimized and corrected for to obtain the pressure drop due to viscous flow only, which is required for use in equation 1. The apparatus was therefore calibrated with gases of known viscosity.

The following alterations to equation 1 must be made in order that the viscosity may be calculated from the experimentally determined pressure difference,  $p_1 - p_2$ , and mass rate of flow, w: (a) Since the fluid under measurement is compressible, equation 1 must be integrated to allow for the changing value of the volumetric rate of flow as the fluid of molecular weight M having a compressibility factor z passes through the capillary tube. This results in the equation<sup>1</sup>

$$\mu = 10^6 \pi r^4 M (p_1^2 - p_2^2) / 16 L w R T z$$
 (2)

(b) A correction factor,  $K_{\rm E}$ , which allows for kinetic energy losses, must be introduced in equation 2.

#### Apparatus and Procedure

Working with hydrogen peroxide vapor introduces several experimental difficulties: (a) Hydrogen peroxide vapor is highly reactive. Furthermore, at atmospheric pressure mixtures with inert gases containing above about 26 mole % hydrogen peroxide vapor will explode readily on contact with a wide variety of substances which are catalytically active,<sup>2</sup> particularly the metals of relatively high atomic weight. (b) Being a condensable vapor, care must be taken to avoid condensation and the presence of mist. (c) Decomposition of hydrogen peroxide into water and oxygen in the apparatus changes the composition of the system, introduces a third component, oxygen, and causes difficulty in temperature control.

The apparatus used in this work consisted of a boiler for producing hydrogen peroxide vapor, a separator and superheater for mist removal and temperature regulation, a capillary tube, and auxiliary equipment for the measurement of pressure, temperature and rate of flow. A rather complicated boiler is required to deliver at atmospheric pressure concentrated hydrogen peroxide vapor of a desired concentration and at a steady flow rate, and at the same time to minimize decomposition and to avoid explosions. Such a

(1) G. Barr, "A Monograph of Viscometry," Oxford University Press, London, 1931, p. 153.

(2) C. N. Satterfield, G. M. Kavanagh and H. Resnick, Ind. Eng. Chem., 43, 2507 (1951).

boiler is described elsewhere.<sup>2</sup> The usual flow rate of vapor from the boiler was equivalent to about 7 cc./min. of condensed liquid.

Simple insulation carrying an electrical heating winding cannot be depended upon to maintain constant temperature in a capillary tube of the dimensions used; the necessarily slow mass flow rate at which the vapor passes through the capillary makes it sensitive to heat loss or gain. To meet this problem the arrangement shown in Fig. 1 was devellarge flow rate passed through an annulus about the capil-lary in countercurrent flow. The temperature of this larger stream could be maintained constant and this in turn ensured that the portion of the stream which was subsequently allowed to flow through the capillary was also maintained at constant temperature. Thus the stream passed a thermocouple well, travelled along the outside of the capillary tube, and reached a bulb of 2000-cc. capacity. This bulb carried a pressure tap which led to a manometer and a sample tap which allowed the withdrawal through a condenser of the greater portion of the stream. A thermo-couple well was inserted in the bulb. The relatively large volume of the bulb provided an additional opportunity for settling and/or vaporization of mist, if any were present, and constituted a reservoir of vapor in a state of near stagna-tion. A small proportion of the vapor stream, about 100th of that entering the bulb, then passed into the capillarv tube.



#### Fig. 1.-Capillary assembly.

The measurement of the radius of the "Trn-Bore" capillary tube was carried ont by determining the weight of and length occupied by a thread of mercury introduced into the capillary. Such a measurement was carried ont, using a Zeiss Focometer, with threads of about 1.4 and 6.6 cm. length and moved to different positions along the length of the capillary. The precision of these measurements, about one part in 2000, was of the same magnitude as the maximum difference found between radii of the capillary at six positions of the 1.4 cm. mercury thread along the length of the capillary. The arithmetic average radius found was  $0.02594 \pm 0.00004$  cm. The accuracy of the figure obtained is sufficient to allow the evaluation by measurement on a gas of known viscosity of the magnitude of the energy loss due to causes other than pressure drop in the tube. Once it was thus determined that this energy loss was of such low magnitude under the conditions of experiment that the precision of the determination of the pressure drop in the tube was satisfactory, the knowledge of the tube radius was, strictly speaking, no longer necessary. By measurement with a cathetometer the length of the capillary was found to be  $28.53 \pm 0.04$  cm. The capillary was sealed at its downstream end to the outer tube which served as a vapor jacket. Particular care was taken that this sealing procedure did not distort the end of the tube. After leaving the end of the capillary tube, the stream passed into a sample bulb as shown in the insert in Fig. 1. No condenser was needed at this point since the small samples readily condensed in the uninsulated bulbs. The amount of decomposition occurring in the apparatus was determined by analysis, with standardized potassium permanganate solution, of condensate samples at the two sampling points. The amount of oxygen present in the exit stream from the apparatus was determined by measuring by water displacement the volume of non-condensable gas leaving the condenser.

Hydrogen peroxide vapor was prevented from reaching the manometer by a special technique involving the use of a buffer gas. For additional safety, Fluorolube FS, a fluorinated hydrocarbon product of the Hooker Electrochemical Co., which is compatible with hydrogen peroxide, was used as the manometer fluid. Density measurements of this fluid were made at several temperatures with a pycnoneter, *e.g.*, at 25° the density was found to be 1.887 g./cc. The height of the fluid in the manometer, of which the low pressure leg was open to the atmosphere, was measured with two 40-cm. cathetometers. Thermocouple voltages were measured with a potentiometer, using a Rubicon galvanometer.

#### Experimental Results

Calibration with Water Vapor.—The magnitude of the correction factor for end losses,  $K_{\rm E}$ , was determined for this apparatus by measuring the apparent viscosity of water vapor as calculated by equation 2. The correction factor is then  $K_{\rm E}$  = (established viscosity)/(observed viscosity).

Surprisingly enough, a rather large uncertainty appears to exist regarding the viscosity of water vapor near 200° at one atmosphere. The values for the viscosity of water vapor used in this work were calculated from equations recommended by Keyes<sup>3</sup> and based on the data of Hawkins, Solberg and Potter.<sup>4,5</sup>

Other evaluations of the literature dealing with the viscosity of water vapor have appeared recently: one by Jaumotte<sup>6</sup> agrees with Keyes<sup>3</sup>; ones by Richter,<sup>7</sup> Silgardo and Storrow<sup>8</sup> and Granet and Kass<sup>9</sup> have preferred viscosity values for one atmosphere pressure which are lower than those recommended by Keyes.<sup>3</sup> There is no doubt that the experimental data of Hawkins, Solberg and Potter<sup>4</sup> are to be preferred for establishing the viscosity of water vapor over a wide range of temperature and pressure. However, it is necessary to make an extrapolation of their data to the region of pressure and temperature which is of interest here, and it must be concluded that an uncertainty of not less than  $\pm 1\%$  exists regarding the viscosity of water vapor at one atmosphere pressure near 200°. Should improved values become available, however, the results reported here may be converted to the new basis by application of a simple ratio.

At a pressure of one atmosphere and at temperatures of 170, 200 and 240°, then, the values 158.4,

(3) F. G. Keyes, THIS JOURNAL, 72, 433 (1950).

(4) G. A. Hawkins, H. L. Solberg and A. A. Potter, *Trans. ASME*, 57, 395 (1935).

(5) G. A. Hawkins, W. L. Sibbitt and H. L. Solberg, *ibid.*, **70**, 19 1948).

(6) A. fauthofte, Rev. universells mines, [9] 7, 213 (1951).

(7) H. Richter, Brennstoff-Wärme-Kraft. 3, 147 (1951).

(8) R. B. Silgardo and J. A. Storrow, J. Soc. Chem. Ind., 69, 261 (1950).

(9) I. Granet and P. Kass, Petroleum Refiner, 32, No. 5, 179 (1953).

168.9 and 182.6 micropoises, respectively, have been calculated to be the established values for the viscosity of water vapor and have been used in this work. Over this limited range of temperature the viscosity-temperature relationship may be considered to be linear, and the viscosity change to be 0.35 micropoise/°C. The value of this slope may also be changed slightly by more accurate viscosity determinations.

In calculating the correction factor for the steam calibration through use of equation 2 a value for the compressibility factor of 0.995 was used at all temperatures. The accuracy of this value is uncertain; however, it appears as a constant factor and was applied to calibration with steam-oxygen mixtures and hydrogen peroxide experiments as well.

The results of the calibration runs indicated that with the chosen dimensions of the capillary and at the rates of flow permitted, the error due to the occurrence of energy losses other than those caused by flow in the capillary ranged between -1 and +3%. Experiments with air and helium showed that the magnitude of the correction factor was unchanged by large variations in flow rate, temperature and physical properties. The correction factor chosen to be applied to the hydrogen peroxide vapor runs was based only on the correction factors determined with water vapor. A small difference was found between the correction factors determined with steam at 170 and  $200^{\circ}$  and at  $240^{\circ}$ . The values found and applied to the results of the hydrogen peroxide vapor runs are: at 170 and  $200^\circ$ ,  $\check{K_{\rm E}}$  = 1.023; at 240°,  $K_{\rm E}$  = 0.993. Additional evidence that the correction factor varies with temperature was found in the results of the hydrogen peroxide vapor measurements and measurements in which oxygen was mixed with steam. In both of these cases a correction factor varying with temperature is required to maintain consistency of results.

Viscosity of Oxygen-Water Vapor Mixtures.-Since the object of this work was limited to the determination of the viscosity of hydrogen peroxide-water mixtures, it was necessary to adopt some method for correcting the experimental results for the presence in the stream of small proportions of oxygen. The soundest basis for determining the effect of oxygen appeared to be the direct measurement of the effect of the presence of oxygen on the viscosity of water vapor. Steam runs were accordingly conducted in which pure oxygen was introduced at various rates, constant for each run. It was found that the viscosity of mixtures of oxygen and water vapor was higher than that of water vapor alone, but that the presence of less than one mole % of oxygen is without significant effect upon the measured viscosity. Thus, only the results of measurements of the viscosity of hydrogen peroxide vapor in which the oxygen content was less than one mole % were retained, and no correction was made for the oxygen present.

Measurements on Hydrogen Peroxide.—The results of 62 runs with hydrogen peroxide vapor were judged to have been obtained under conditions allowing precise calculation of the viscosity. All

runs were discarded in which temperature and pressure drop did not remain constant, in which the oxygen content was greater than 1%, and in which decomposition in the capillary tube caused the downstream concentration to be less than 9/10of the upstream concentration.

These results are shown in Fig. 2 where the viscosity of the hydrogen peroxide-water-oxygen mixture at 170, 200 and 240° is plotted as a function of the mole fraction hydrogen peroxide based on the complete stream composition. These viscosities were calculated using the mole fraction average molecular weight calculated for the mid-point of the capillary tube. It was often not possible to attain the desired stream temperature exactly, but it was possible to maintain the temperature constant at a level within a few degrees of the desired temperature. In order to bring the results to a common temperature it was assumed that the variation of viscosity with temperature amounted to 0.35 micropoise per degree, the value found for steam at this temperature level.



Fig. 2.—Viscosity of hydrogen peroxide vapor.

From the evidence of Fig. 2 it is apparent that some small factor, not accounted for by the correction applied, influenced the measurements on hydrogen peroxide vapor to produce low results. Although the slopes of the curves are well established, the intercepts of the best curves through the hydrogen peroxide viscosity data fail to occur at the accepted value for water vapor. Because this effect becomes larger with increasing temperature it is believed to have been caused by the small amount of decomposition occurring in the capillary during the experiments. This decomposition undoubtedly affects the flow to a small degree in a manner which the Poiseuille equation cannot account for, or, in other words, introduces a correction factor which the water vapor calibration runs could not have represented. There is some indication that the slopes increase with temperature, but the precision of the results is not sufficient to establish this. The curves therefore have been drawn parallel with a slope of 14 micropoises per unit mole fraction.

By extrapolation, the values for the viscosity of anhydrous hydrogen peroxide vapor at the temperatures investigated given by these curves are:  $170^{\circ}$ , 144 micropoises; 200°, 154; 240°, 167. At the normal boiling point of hydrogen peroxide (150°) the vapor viscosity is estimated to be 136 micropoises. These results may be expressed by the following equation

$$\mu = 134 + 0.35(t - 100) - 14\gamma \tag{3}$$

This equation has a precision of  $\pm 2\%$  at temperatures between 100 and 300° at pressures near one atmosphere.

#### Discussion

Precision of the Measurements .-- With the exception of the oxygen rate, the precision of the recorded data such as pressure drop, temperature and flow rate was at least one part in 500 or better. The precision of estimation of the oxygen flow rate was about one part in 200. If decomposition in the capillary tube could have been avoided entirely, these limits of precision would have applied in estimating the precision of the results. However, decomposition of hydrogen peroxide in the capillary may introduce significant changes in the composition and temperature of the stream. With a change in composition the results must be taken to represent the viscosity of a stream of some average composition. The rejection of runs in which the downstream hydrogen peroxide concentration was less than 9/10 of the concentration entering the capillary placed an upper limit of 1% on the magnitude of the possible variation in average molecular weight of the stream. The change in weight composition is relatively much larger, as much as 5%in some runs. It seems unlikely, however, that an uncertainty of  $\pm 2.5\%$  must therefore be placed on the concentration which the calculated viscosity is taken to represent. If the decomposition in the capillary is a linear function of the distance travelled through the capillary it is reasonable to assume that the viscosity calculated for the average molecular weight represents that of the average concentration.

The effect of the release of the heat of decomposition in the capillary upon the temperature measured is difficult to estimate. However, a temperature difference of one degree centigrade between the stream in the capillary and the stream in the surrounding annulus where temperatures were measured appears to be more than adequate to dissipate the heat of decomposition.

Estimates of the precision are: steam calibration runs,  $\pm 0.5\%$ ; hydrogen peroxide runs,  $\pm 1\%$ . Inspection of the data showed the actual precision to have been about 1% or better in both the steam calibration runs and the hydrogen peroxide runs. The absolute accuracy of the data is of course dependent upon the accuracy of the accepted viscosity of water vapor. As the earlier discussion indicated, a change of as much as 2% in this value may be warranted.

Theoretical Considerations.-It is of interest to test the reliability of relationships which have been proposed for predicting the viscosity of pure gases and gas mixtures with a system of highly polar constituents such as has been studied here. The empirical methods of Licht and Stechert19 and Uyehara and Watson,11 which are based chiefly upon the theory of corresponding states, were found to predict the extrapolated values of the viscosity of anhydrous hydrogen peroxide within a few %. Calculation of the viscosity by estimation of the collision diameter and maximum energy of attraction between molecules, using the procedure described by Bromley and Wilke<sup>19</sup> was successful within similar precision. An attempt to carry out the reverse procedure, *i.e.*, calculation of the values of the collision diameter and intermolecular attractive energy from experimental data without recourse to the approximations used is not warranted. Such a procedure requires the knowledge of the variation of viscosity with temperature. The small range of temperature investigated and the uncertainty involved in the extrapolation used to obtain the viscosity of anhydrous hydrogen peroxide do not permit the differentiation of the temperature coefficient of viscosity of hydrogen peroxide from that of water. It should also be pointed out that the uncertainty of the magnitude of about 1% which exists regarding the accurate viscosity of the vapors of water and hydrogen peroxide would allow considerable latitude in the choice of the form of an equation for the energy of interaction.

The results obtained in this work may also be used to test various mixture rules which have been proposed. If the values for the viscosity of anhydrous hydrogen peroxide obtained by linear extrapolation are accepted, then the mixture rule proposed by Wilke<sup>12</sup> predicts in turn a linear composition relationship exactly.

The prediction of the viscosity of a pure substance or of the composition-dependence of viscosity, on the simple basis of molecular weight and general structure, is uncertain even in a qualitative way. The present results bear out the generalization that (a) gas viscosity decreases as molecular structure becomes more complicated, <sup>10</sup> e.g., compare the series  $\mu_{0_2} > \mu_{S0_2} > \mu_{H_2O} > \mu_{H_2O_2} > \mu_{S_8}$  and (b) that the variation of viscosity of mixtures from simple additivity is least when the mass, structure and interaction potentials of molecules are most alike.<sup>13</sup> The nearest analog to the system studied here among polar systems for which data are available appears to be that of alcohol and

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<sup>(13)</sup> J. S. Rowlinson and J. R. Townley, Trans. Faraday Soc., 49, 20 (1953).

water, studied by Silgardo and Storrow.<sup>8</sup> Here, however, there appears to exist sufficient difference in polarity, mass and structure for the viscosity of the mixtures to vary significantly from additivity.

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[Contribution from the Departments of Chemistry and of Chemical Engineering, Rensselaer Polytechnic Institute]

# On Physical Adsorption. V. Two-Dimensional Condensation of Ethane on Surfaces of Solids at 90°K.<sup>1</sup>

By Sydney Ross and Werner Winkler

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The conditions for two-dimensional condensation of an adsorbed monomolecular vapor on a solid surface are postulated, and shown to be met when ethane at 90 °K. is adsorbed by a solid having a large proportion of a single, unique, and uniform surface (*homotallic* surface). Previous reports of two-dimensional condensation of ethane adsorbed on cube crystals of NaCl and KCl are confirmed, using crystals of smaller dimensions prepared by sublimation. The same phenomenon is demonstrated on a sample of asbestos, described by independent investigators as having a relatively uniform surface, and on a sample of calcium fluoride. Supersaturation phenomena, and the effect of extensive supersaturation on the BET surfacearea determination, are described. The value of two-dimensional condensation as a tool for the investigation of solid surfaces is pointed out.

#### Introduction

In previous papers of this series by Ross, et al.,<sup>2-5</sup> discontinuities in the low pressure adsorption isotherms of ethane at  $90^{\circ}$ K. on the  $\{100\}$  and  $\{111\}$ faces of sodium chloride and potassium chloride were reported, and were attributed to the condensation of a unimolecular layer of ethane from a twodimensional gaseous phase to a two-dimensional condensed phase. Harkins, Jura and others, who had previously investigated similar discontinuities, used *n*-heptane as adsorbate and reduced silver powder,<sup>6</sup> ferric oxide<sup>7</sup> and graphite<sup>8</sup> as adsorbents. The failure of recent efforts to reproduce Harkins and Jura's results<sup>9-11</sup> may perhaps be attributable to the difficulty of finding identical surfaces of these adsorbents. We have accordingly considered it advisable, in preparation for further development of this topic, to verify the existence of the effect described, using surfaces whose nature would be independent of their history.

This paper (a) reproduces, with sodium chloride and potassium chloride prepared by sublimation, the results earlier reported for the adsorption of ethane on the same substances prepared by rapid

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 S. Ross and G. E. Boyd, "New Observations on Two-Dimen-

(2) S. Ross and G. E. Boyd. "New Observations on Two-Dimensional Condensation Phenomena," MDDC Report No. 864, 1947.

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(11) M. L. Corrin, THIS JOURNAL, 75, 4623 (1953).

precipitation; and (b) presents low-pressure adsorption isotherms of ethane on other surfaces deemed likely to provide conditions required to demonstrate the two-dimensional phase transition.

#### Apparatus and Materials

The apparatus is based on the design of Wooten and Brown<sup>12</sup> and, save for details of dimensions, is the same as that used by Ross and Boyd<sup>2</sup> for the original ethane isotherms on sodium and potassium chlorides. The authors are obliged to Dr. E. V. Ballou who first set up this apparatus in this Laboratory. Pressure measurements are made with a McLeod gage and mercury cut-offs are used to preclude the presence of stopcock grease in the adsorption portion of the apparatus. The adsorption temperature of 90°K. is maintained by a liquid oxygen bath. An oxygen gas thermometer is used to measure the temperature of the bath.

The sodium chloride (Baker and Adamson, reagent grade) and potassium chloride (Fisher Scientific Company, special buffer salt) were sublimed in a stream of prepurified nitrogen gas (Matheson Company) and collected by electrostatic discharge, as described by Craig and McIntosh.<sup>13</sup> The calcium fluoride (Baker and Adamson, reagent grade) was used without any further treatment than the initial desorption of air before the experiment. The ethane gas was Matheson research grade, treated by passing through Ascarite and concd. H<sub>2</sub>SO<sub>4</sub> before being collected in the storage bulb. The asbestos, described as 7-R fiber, Canadian Johns-Manville Company, was furnished by courtesy of Prof. A. C. Zettlemoyer of Lehigh University. Some of its adsorption characteristics already have been published.<sup>14</sup>

#### Experimental Results

**Isotherms.**—The isotherms were determined volumetrically. The final equilibrium pressures were so low that the ideal gas law is valid for the unadsorbed gas. The observed pressures have not been corrected for thermal transpiration, as the existence of the discontinuity, or its relative position on the pressure axis, is not thereby affected.

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