Lucite, were used. Samples containing approximately 20% high-purity rock crystal quartz as an internal standard were scanned from 2° to 63° 2 θ at a rate of 0.2°/min, which permitted measurement of 2 θ values to the nearest 0.01°. Samples containing no internal standard were then scanned, following alignment on the (020) line of the bromide, to provide complete interplanar spacing and intensity data. Integrated intensities were obtained from the diffractometer recording chart by counting squares.

Sample Preparation

All measurements were made with Fisher ACS certified $MgBr_2 \cdot 6H_2O$ crystals. Attempts to grind the crystals to a sufficiently fine powder to obtain reproducible intensities were not successful. The crystals were completely dehydrated, therefore, at 300°C and then allowed to rehydrate at 50°C. After one week at 50°C, the very fine powder was packed in the X-ray sample holder and covered with plastic wrap (Dow Handi-Wrap) to prevent absorption of water during X-ray scanning.

Density Measurements

Densities of rehydrated powder and the crystals were measured by suspension in liquid mixtures at 22°C, as described previously (*4*). Difficulty was encountered in both cases. It proved to be impossible to grind the crystals sufficiently to remove all included air bubbles, and the powder tended to form a static suspension, presumably because of the very small crystallites (approximately 1 μm, as measured by X-ray line broadening).

Results

Measured diffraction angles, 2 θ, interplanar spacings, d_{obs}, and relative intensities, I/I_1, are given in Table I. The indexing procedure used was as described previously (*4*). For the bromide, however, it was necessary to estimate the 2 θ angles of the key lines, (001), (200), (020), (40$\bar{1}$), and (401), to the nearest 0.005° to obtain acceptable agreement between calculated and observed interplanar spacings. The revised lattice parameters are a = 10.290 ± 0.001 Å; b = 7.334 ± 0.001 Å; c = 6.211 ± 0.001 Å; β = 93° 25′ ± 10′.

Indexing is in agreement with the reported space group, C2/m, in that $h + k = 2n$ for all lines. The unit cell volume is 467.89 Å^3, and the calculated density, ρ_x, is 2.074 g/cm^3. The best value that can be placed on the measured density is 2.07 ± 0.01 g/cm^3, in agreement with the calculated value and considerably higher than that obtained from the X-ray data of Andress and Gundermann (*1*), 2.035, or that reported in the "Handbook of Chemistry and Physics" (*5*), 2.00.

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Vapor Pressure of Methanol from 288.15 to 337.65K

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Forty-two measurements of the vapor pressure of methanol are made at 5K intervals from 288.15 to 337.65K with a new static vapor-pressure apparatus. The estimated uncertainties in the experimental temperature and pressure are ±0.002K and ±1 Pa, respectively. The measurements are represented by the equation: $\ln (P/\text{kPa}) = 15.76129944 - 2.845920984 \times 10^3 K/T - 3.743415457 \times 10^5 K^2/T^2 + 2.188669828 \times 10^7 K^3/T^3$. This equation is compared with the best previous measurements, with agreement generally within the experimental uncertainties reported by other workers.

As part of a study of the vapor pressures of solutions of several nonvolatile solutes in methanol (*4*), we have measured the vapor pressure of pure methanol. The methanol used was of the highest purity; it contained less than 0.005 mol % water and even less of any other volatile impurity. Our new static vapor-pressure apparatus operates with a precision of ±0.002K in the temperature (temperatures in this paper are expressed as International Practical Kelvin Temperatures T_{68}, which for most purposes are indistinguishable from thermodynamic temperatures T) and ±1 Pa in the pressure. No previous measurements of this precision have been reported for methanol.

Materials

The methanol used as a starting material was Fisher certified reagent grade, rated by the manufacturer as 99.9 mol % pure. This material was distilled through a 1-m vacuum-jacketed column filled with 0.6-cm glass helices into a degassing apparatus similar to that of Taylor (*15*). This methanol contained less than 0.001 wt % water by Karl Fischer titration (*9*) and less than 0.003% acetone and formaldehyde by the test of Morton and Mark (*10*). A second batch of methanol, prepared by addition of potassium hydroxide and dimethyl phthalate to methanol and distillation of the mixture, contained 0.025 wt % water.

Apparatus

The static vapor-pressure apparatus contains an oil thermostat, regulated at ±0.001K, for the vapor-pressure cell, and an air thermostat, regulated to ±0.01K, for the null manometer. The vapor-pressure cell is similar to the one used by Scatchard et al. (*13*); it is fitted with the de-

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gassing valve described by Gibbard and Scatchard (5). The large, external mercury manometer is similar to that used by Scatchard and Raymond (*12*); measurements of the pressure were made with the same Societe Genevoise comparator and scale used by them. The null manometer is an MKS Baratron Model 90 H3 capacitance-diaphragm instrument with a sensitivity of 2 × 10^{-6} kPa.

Temperature was measured with a Leeds and Northrup-type ER resistance bridge and 8164B platinum resistance element, which fits into a well inside the vapor-pressure cell. This element was calibrated against a Leeds and Northrup 8163B platinum resistance thermometer which had been calibrated in 1971 by the manufacturer on the IPTS-68 scale at the oxygen, ice, steam, and sulfur points.

The air thermostat was maintained 2.0K hotter than the oil thermostat to prevent condensation in the null manometer. The temperature difference between the two thermostats had no measurable effect on the vapor pressure.

Procedure

Before each measurement, vapor was expanded from the equilibrium cell until the noncondensible gas pressure was less than 2 × 10^{-6} kPa. The cell was then allowed 30–60 min to return to the thermostat temperature. The null manometer pressure difference and thermometer resistance were monitored for a period of 30 min, during which the temperature always remained constant within 0.001K. Then, while the nulling pressure was read from the 90-dm^3 manostat connected to the system, the thermostat was heated to the next temperature at which measurements were to be made.

During one series of measurements, the volume of methanol in the cell was reduced by expansion through the degassing valve from 12 to 8 cm^3. The vapor-pressure measurements during this change at constant temperature deviated by less than one part in 10,000. This confirms our opinion of the purity of the methanol used in this study.

Table I. Vapor Pressures of Methanol

T, K	P, kPa	$10^3 (P - P_{\text{calcd}})$, kPa	T, K	P, kPa	$10^3 (P - P_{\text{calcd}})$, kPa
288.1506	9.8844	−1.6	313.1504	35.4695[a]	1.2
288.1508	9.8858[a]	−0.3	313.1504	35.4714[a]	3.1
288.1511	9.8889[a]	2.6	313.1520	35.4654[a]	−5.6
288.1515	9.8867	0.2	318.1475	44.5814	0.7
293.1361	13.0023	1.7	318.1477	44.5799	−1.2
293.1443	13.0119[a]	2.2	318.1483	44.5829[a]	0.6
293.1507	13.0109[a]	−3.3	318.1506	44.5833[a]	−3.6
293.1628	13.0228	0.0	323.1420	55.5900	1.8
298.1478	16.9558	0.3	323.1460	55.5996[a]	1.8
298.1498	16.9562[a]	−1.1	323.1490	55.5972[a]	−7.9
298.1500	16.9578	0.3	328.1436	68.8187	1.8
298.1505	16.9584[a]	0.5	328.1442	68.8158[a]	−2.8
298.1517	16.9594	0.4	328.1476	68.8278[a]	−0.6
303.1427	21.8743	−0.9	328.1517	68.8450[a]	4.7
303.1464	21.8782	−1.0	333.1417	84.5761	1.4
303.1494	21.8823[a]	−0.2	333.1466	84.5907	−0.8
303.1503	21.8859[a]	2.4	333.1468	84.5859[a]	−6.3
308.1459	27.9763	0.6	333.1471	84.5940[a]	0.7
308.1509	27.9844[a]	1.9	337.6452	101.2523[a]	3.4
308.1521	27.9871[a]	3.0	337.6456	101.2526	2.1
313.1500	35.4685	0.8	337.6514	101.2742[a]	0.6

[a] Vapor pressure corrected by Raoult's law for the presence of 0.043 mol % water.

Results

Our results for methanol are shown in Table I. The first column is the temperature, and the second is the measured vapor pressure. The third column gives the difference between the experimental vapor pressure and that calculated from the equation:

$$\ln (P/\text{kPa}) = 15.76129944 - 2.84592098 \times 10^3\, K/T - 3.743415457 \times 10^5\, K^2/T^2 + 2.188669828 \times 10^7\, K^3/T^3 \quad (1)$$

determined from our measurements by the method of least squares.

Figure 1 shows the deviations from Equation 1 of the measurements of Dever et al. (2), plotted as the triangles, and of the equation of Scatchard et al. (*14*), represented by the unbroken curve. The circles represent our own measurements; fewer circles are plotted than the number of measurements because of the frequent overlap of the plotting symbols on a graph of this scale. This occurs most notably at 298.15K, where four of the five measurements lie within a spread of 0.2 Pa. The scatter of the measurements of Dever et al. shows their results to be about an order of magnitude less precise than ours. Their consistently positive deviations at the lowest temperatures suggest incomplete degassing of the solutions, which is a major source of error in static measurements. The single measurement of Polak et al. (*11*) at 298.14K, plotted as a square in Figure 1, is in good agreement with Equation 1.

The broken curves in Figure 1 show the limits of error in the pressure for an uncertainty of ±0.01K in the tem-

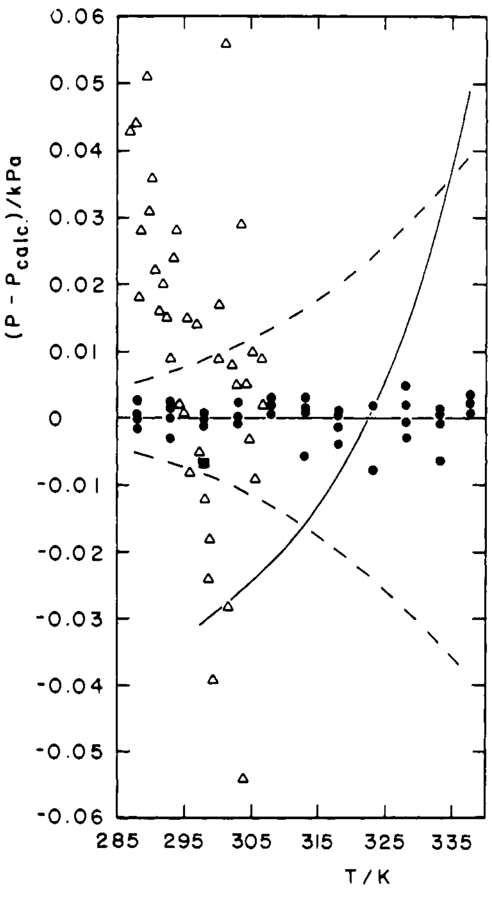

Figure 1. Deviations of methanol vapor pressures from Equation 1

● This work; △ Dever et al. (2); ■ Polak et al. (*11*); —— Scatchard et al. (*14*); - - - limits of error in P for ±0.01K in T

perature. Over most of the temperature range, the deviation curve for Scatchard et al., who estimated their temperature uncertainty as ±0.01K, falls within these limits. The systematic difference between our results and theirs probably lies in the calibration of their 20-junction thermopile. The same comparator and scale were used in both studies.

The normal boiling temperature calculated from Equation 1 is 337.664K. This is in excellent agreement with the value calculated from the equation of Scatchard et al. (*14*), 337.65 on the current temperature scale. Wojciechowski (*16*) also obtained 337.65K in a careful study of the boiling temperature of methanol. Many other investigators have obtained higher boiling temperatures for methanol. We attribute higher boiling temperatures to higher water content in the methanol samples studied by these workers.

Ambrose and Sprake (*1*) have reported precise vapor-pressure measurements for a number of aliphatic alcohols. Their vapor pressures for methanol, obtained by comparative ebulliometry, are consistently lower than ours. The differences between the two sets of measurements can be explained, over the temperature range of the present work, by a water content of 0.07 wt % in their methanol. This explanation seems reasonable in view of the difficulty expressed by Ambrose and Sprake in removing the last traces of water from their samples.

Through the use of the Clapeyron equation, Dever et al. (*2*) attempted to show thermodynamic consistency of their vapor pressures with the precise calorimetric enthalpies of vaporization of Fiock et al. (*3*). Dever et al. calculated the volume of the vapor from the virial coefficients of Kretschmer and Wiebe (*7*). This procedure is unsatisfactory both because it requires at least a twofold extrapolation of Kretschmer and Wiebe's results to reach the saturation pressure, and because Kretschmer and Wiebe omitted the third virial coefficient but included the fourth in their equation of state. This unusual equation has recently been criticized by Kell and McLaurin (*6*) in a study of the *PVT* behavior of methanol at high temperatures.

We have found that reasonable values for the third virial coefficients for methanol vapor can be calculated from the vapor-pressure measurements reported here, the enthalpy of vaporization (*3*) and literature values of the second virial coefficient (6–8). These calculations will be published elsewhere.

Acknowledgment

This work would not have been possible without the kind donation of the comparator and scale to the senior author by George Scatchard (now deceased) of the Massachusetts Institute of Technology.

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Adsorption of Hydrocarbons on Carbon Molecular Sieve

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The adsorption equilibria for methane, ethylene, ethane, propylene, propane, *n*-butane, *n*-pentane, benzene, and cyclohexane on commercially available carbon molecular sieve were obtained by a gravimetric technique. Isotherms were measured for the pure gases in the temperature range from 5.4° to 50°C and pressures up to 1 atm. The isotherms show the Type I shape according to the classification by Brunauer et al., which is usually observed at adsorption on microporous adsorbents. The molecular sieving effect was clearly observed by the adsorption showing the strong discrimination of cyclohexane from benzene.

The data presented were obtained as a first part of a continuing study of adsorption of gases and vapors on microporous solids. The carbonaceous molecular sieve materials are interesting as a separation medium in which zeolite sieves are not suitable. The carbon sieves are more stable at high temperatures than zeolite sieves and are quite stable in strong acid solutions. They also exhibit much less hydrophilic character than the zeolites (*6*).

The carbon molecular sieve used in this work is the Molecular Sieving Carbon-5A (MSC-5A) (a product of Takeda Chemical Industrial Co.) which has micropores of approximately 5 Å. The hydrocarbon adsorption on this material was reported by Kawazoe et al. (5) for ethylene, ethane, and benzene at several temperatures. But the raw data which made it possible to compare with our data were limited only to ethane adsorption data at 0° and 30°C.

Experimental Apparatus and Procedure

Adsorbent. A carbon molecular sieve sample was crushed into 28–42 mesh, which originally consisted of

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