Adsorption of Methane on Silica at Temperatures to 121° C. and Pressures to 650 Atmospheres

T. DON STACY,[1] ELDRED W. HOUGH,[2] and WILLIAM D. McCAIN, Jr.
College of Engineering, Mississippi State University, State College, Miss. 39762

Adsorption isotherms and isobars of a gas-solid system were obtained for conditions ranging from 37.8° to 121.1° C. and pressures up to 650 atm. The adsorbent was Linde silica, having a surface area of 145 sq. meters per gram. The system utilized was a high-pressure constant-temperature volumetric apparatus.

FUNDAMENTAL data on gas adsorption for systems at low pressure are readily found in the literature. Published data on high-pressure gas adsorption are rare. Gilmer and Kobayashi (*3*) have published data on adsorption of methane on silica at pressures up to 135 atm. Cadogan (*2*) has published data on adsorption of hydrocarbon gases and their mixtures on silica up to 20 atm. Lewis *et al.* (*4*, *5*) reported similar data for the adsorption of hydrocarbons on silica at temperatures up to 250° C. and pressures up to 20 atm. All reported isotherms take the shape of the classical Type I isotherm, as classified by Brunauer (*1*).

This paper discusses gas adsorption at temperatures and pressures above the critical point of methane in the methane-silica system.

EXPERIMENTAL

Materials. Silica, manufactured by the Linde Division, Union Carbide Corp., was used as the solid phase for all isotherms included in this study. The manufacturer did not report the density of the adsorbent. However, bulk density was determined by use of a volumetric pycnometer to be 1.98 gram per cc. The surface area measured 145 sq. meters per gram, determined by the classical BET low-temperature adsorption of nitrogen, where monomolecular adsorption was assumed. The adsorbate was research-grade methane, having a stated purity of at least 99.65%. The dead-space volume of the sample and adsorption chamber was determined by expansion of helium into the high-pressure side of the apparatus. Volume was calculated assuming no helium was adsorbed.

Equipment and Methods. The apparatus used in this research is the same apparatus used to gather data on the methane-carbon system reported by Stacy *et al.* (*7*). The adsorbent was enclosed in a high-pressure cell where methane gas was compressed at constant temperature until the desired pressure was obtained. Measurements were taken during the desorption cycle, after temperature equilibrium had been obtained. Construction of the apparatus to allow for work at high pressures precluded the taking of data during the adsorption portion of the cycle. The low-pressure cells were evacuated and the pressure was recorded immediately. Gas was then expanded from the adsorbent chamber until a pressure of approximately 1 atm. in the low-pressure system was reached. After temperature and pressure were noted in both systems, the low-pressure system was evacuated and the process repeated. Withdrawal of gas was continued in a stepwise manner until expansion of gas from the adsorption cell into the low-pressure system caused no change in the manometer reading. A complete description of the apparatus and experimental procedure can be found elsewhere (*8*).

Calculation of the adsorbed quantity of gas requires that the quantity of gas contained in the dead-space volume, $\bar{V}$, be subtracted from the summation of gas withdrawn into the low-pressure system during all desorption steps. This equation, expressed mathematically, is

$$N_k = -\frac{P_k\bar{V}}{Z_kRT} + \frac{V}{RT}\sum_{i=k}^{i=n}\left(\frac{P_i}{Z_i}\right)$$

where $1 < k < n$.

This expression describes Gibbs' adsorption according to the thermodynamic definition—that is, dead-space volume, $\bar{V}$, includes the volume of free gas space in the adsorption cell, as well as the volume of the adsorbed layers.

Compressibility factors were determined by taking a desorption isotherm with no adsorbent in the sample chamber. The amount of gas in the sample chamber was calculated at each pressure increment by using the ideal gas law. The ratio of the calculated quantity of gas in the cell to the measured quantity was taken as the compressibility factor. These data agreed to within ±0.3% with smoothed values reported by Sage and Lacey (*6*).

Adsorption data reported here were gathered with a single adsorbent bed weighing 12.9 grams. Dead-space volume in the apparatus, including high-pressure lines and pore space, totaled 66.4 cc. The sample was thoroughly outgassed between runs.

PRECISION

Several measurements of dead-space volume agreed within 1%. Volume was the most critical parameter determined. Error in the density of the adsorbent would be well within the 1% possible error in dead-space volume. Maximum error arising from erroneous volume measurement could amount to 10% of the gas adsorbed. Temperature was measured to within ±0.05° C. during any isotherm. This variation could result in a maximum absolute error of 0.2% of the gas adsorbed. This error

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[1] Present address, Pan American Petroleum Corp., Houston, Tex. 77001

[2] Present address, Southern Illinois University, Carbondale, Ill.

would occur at maximum pressure on the low-temperature isotherm. At the highest pressure, this would amount to 5 p.s.i., causing an error of 0.63%. High-pressure measurements were taken with an accuracy of 0.05%. Low-pressure readings were taken with a cathetometer reported to be precise at 0.02 mm. These pressure measurements were sufficient to limit errors to within 1% of the amount adsorbed.

RESULTS

Figures 1 and 2 illustrate isotherms and isobars for the solid-gas system. The isotherms take the classical Type I shape, indicating increasing adsorption with steadily increasing pressure. The curves also show decreasing adsorption with increasing temperature.

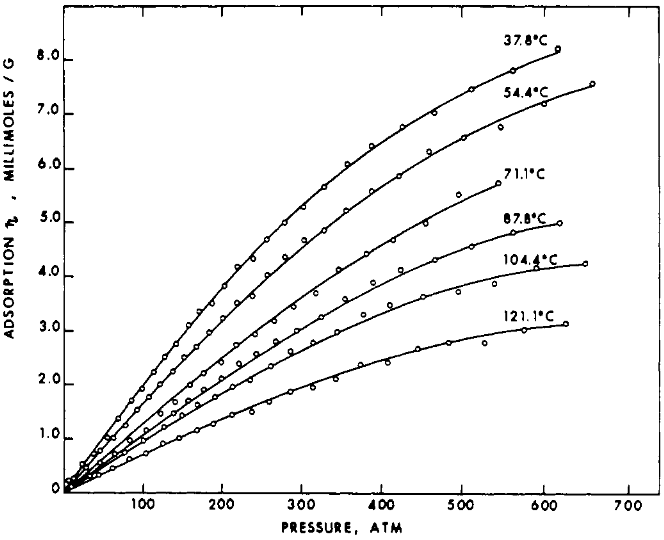

Figure 1. Adsorption isotherms of methane on Linde silica

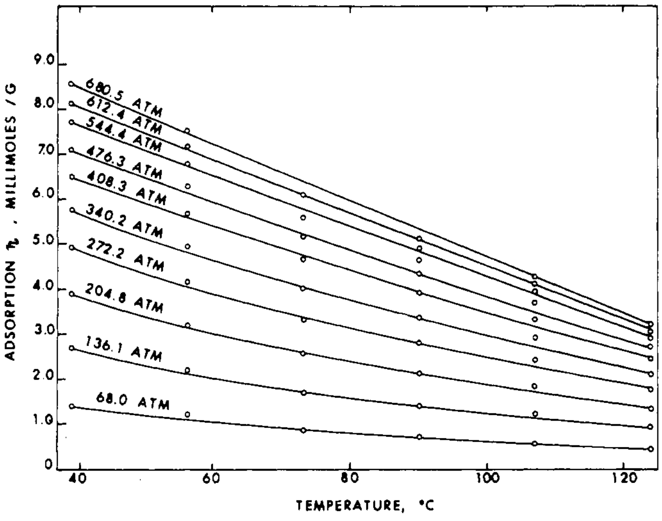

Figure 2. Absorption isobars of methane on Linde silica

Complete tabular data have been deposited with ASIS; however, an example of the raw data is as follows:

Pressure, Atm.	Temperature, ° C.	Quantity, Moles/1000 Grams
155.66	37.8	3.09
152.39	54.5	2.54
159.53	71.1	1.98
156.61	87.8	1.71
147.70	104.5	1.45
145.72	121.1	1.03

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NOMENCLATURE

N_k = amount adsorbed at P_k, gram-mole
P_i = pressure in low-pressure system for the ith step, atm.
V = volume of low-pressure system, cc.
P_k = pressure in adsorption cell at step k, atm.
$\overline{V}$ = dead-space volume, cc.
Z_i = compressibility factor at P_i
Z_k = compressibility factor at P_k
R = gas constant, cc. atm./(° K.) (gram-mole)
T = adsorption temperature, ° K.

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