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# Physical Adsorption of Gases on Anatase

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Physical adsorption data on anatase for the gases $N_2$, Kr, A and CO at both −195 and −183° and for $CO_2$ at −78° are reported. From these data are calculated molecule cross-sectional area values for the BET area method and *k*-values for the H–J relative area method. The cross-sectional area values in general are in poor agreement with those obtained from liquid adsorbate density data. A simple relation is obtained between the BET cross-sectional area values and the H–J *k*-values for adsorption on anatase. For a number of adsorption data for $N_2$ and Kr at −195° the variation in the ratio of the BET and H–J area values with BET *C*-value is found to be similar to that calculated by P. H. Emmett.

## Introduction

The purpose of this paper is to present the results of an investigation of the physical adsorption of a number of gases on a sample of non-porous titanium dioxide whose specific surface area has been measured by the Harkins–Jura absolute method.[1] The adsorption results have been analyzed by the Brunauer, Emmett and Teller[2] (BET) method and the Harkins–Jura[3] (H–J) relative method of calculation. From these analyses, constants for the H–J relative area method are evaluated at −195 and −183° for nitrogen, krypton, argon and carbon monoxide and at −78° for carbon dioxide. Standardized cross-sectional areas per molecule were calculated by the method proposed by Loeser and Harkins.[4] Also presented are data showing the effect of the BET *C*-value on the agreement between area values as determined by the BET and H–J methods for a large number of experiments using nitrogen and krypton as adsorbates.

## Experimental

**Equipment.**—The apparatus and procedure for the determination of the adsorption isotherms for nitrogen, argon, carbon monoxide and carbon dioxide were very similar to those described by Harkins and Jura.[3] The apparatus used for the krypton measurements is shown in Fig. 1. The bulb of the McLeod gage and the calibrated line volumes were used for volumetric measurements of the krypton. Tubing diameter through the bath–room temperature gradient was such that thermal transpiration corrections were negligible in the krypton pressure region in which the BET and H–J theories were applicable.

Conventional temperature baths were used, and corrections for deviations of gases from ideality were made where necessary. Carefully purified adsorbates were used throughout.

**Materials.**—The titanium dioxide sample was supplied by Dr. George Jura and was a sample of the anatase used by Harkins and Jura in their absolute method of area measurement.[1] Before adsorption measurements, the sample was evacuated overnight at 100° at 1 × $10^{-5}$ mm.

Electron micrographs of a sample of this anatase were obtained at a magnification of 30,000 diameters. A particle diameter was measured for each of about 500 individual particles. The average particle diameter (surface–volume basis assuming cubes) was found to be 0.188 microns corresponding to a surface area of 13.1 sq. m./g., which is 5% lower than that obtained by Harkins and Jura.[1]

## Results

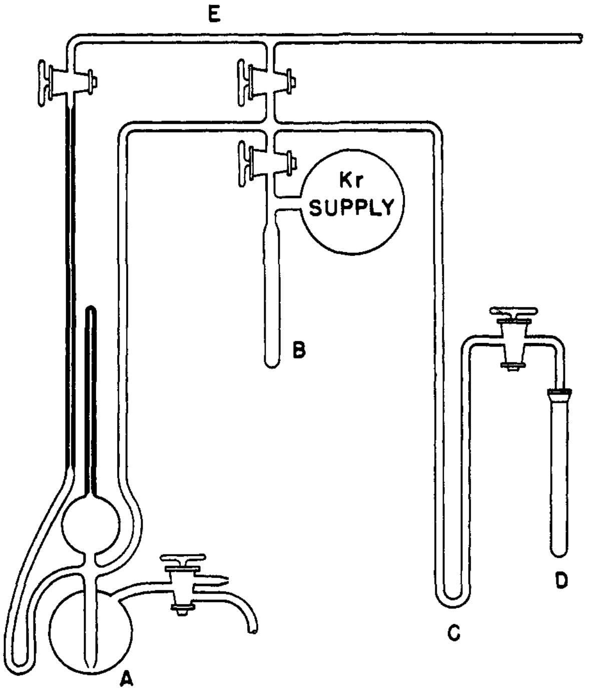

Fig. 1.—Krypton adsorption apparatus: A, McLeod gage; B, Kr trap; C, vapor trap; D, adsorption cell; E, high vacuum line.

BET plots which are typical of those obtained in this work are shown in Fig. 2. The constants $v_m$ and *C* of the BET multilayer theory equation are shown in columns 3 and 4 of Table I for all the systems investigated. They were obtained by a least-squares treatment of the data over the linear range of the BET plots. In those cases where the adsorption temperature was below the normal freezing point of the bulk adsorbate ($CO_2$ at −78°, Kr at −183° and −195° and A at −195°), the adsorbed layer was presumed to be liquid-like, and the value of $p_0$ used was obtained by extrapolation of liquid vapor pressure data into the unstable temperature region. This method of calculation is in accord with that indicated by the results of Brunauer, Emmett and Teller for $CO_2$ adsorption at −78°[2] and by Beebe,

TABLE I

| Gas[a] | Temp., °C. | $v_m$, ml./g. | *C* | Molecule cross-sectional area, Å.$^2$ This work | Molecule cross-sectional area, Å.$^2$ Liquid density | $A^{1/2}$ | *k* |
|---|---|---|---|---|---|---|---|
| $N_2$(2) | −195.4 | 3.156 | 136 | 16.27 | 16.2 | 3.387 | 4.08 |
| $N_2$ | −183.0 | 2.898 | 136 | 17.72 | 17.0 | 3.187 | 4.33 |
| Kr(3) | −195.5 | 2.357 | 143 | 21.78 | 15.2 | 2.727 | 5.06 |
| Kr(3) | −183.2 | 2.363 | 86 | 21.73 | .. | 2.23 | 6.28 |
| A | −195.7 | 3.041 | 82 | 16.88 | 14.2 | 3.059 | 4.51 |
| A | −183.3 | 2.824 | 62 | 18.19 | 14.4 | 2.661 | 5.18 |
| CO(2) | −195.7 | 3.471 | 111 | 14.73 | 16.0 | 3.778 | 3.66 |
| CO | −183.3 | 3.149 | 122 | 16.25 | 16.9 | 3.395 | 4.07 |
| $CO_2$(2) | − 79.0 | 2.096 | 84 | 24.39 | 17.0 | 2.195 | 6.29 |

[a] Numbers in parentheses indicate data are averages for that number of experiments.

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[1] G. Jura and W. D. Harkins, THIS JOURNAL, **66**, 1362 (1944).

[2] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

[3] W. D. Harkins and G. Jura, *ibid.*, **66**, 1366 (1944).

[4] E. H. Loeser and W. D. Harkins, *ibid.*, **72**, 3427 (1950).

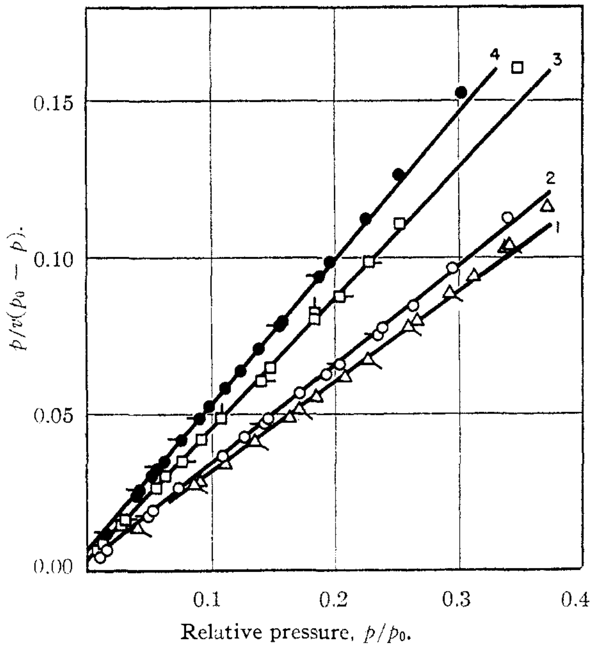

Fig. 2.—BET plots for adsorption on anatase: curve 1, CO at −195.7°; curve 2, $N_2$ at −195.4°; curve 3, Kr at −195.5°; curve 4, $CO_2$ at −79.0°.

Beckwith and Honig for Kr adsorption at −195°.[5] The molecule cross-sectional areas shown in column 5 of Table I were calculated from the corresponding $v_m$ values by assuming the correct area for the anatase to be 13.8 sq. m./g.[1] and using the values for the Avogadro number and the molar volume of a perfect gas recommended by Dumond and Cohen.[6]

H-J plots which are typical of those which were obtained in this work are shown in Fig. 3. The values of $A^{1/2}$ and $k$ from the H-J equation[3] (for $v$ expressed in ml. of gas at S.T.P.) are shown in columns 7 and 8 of Table I. These values were obtained by a least-squares treatment of the data over the linear range of the H-J plots assuming the anatase area to be 13.8 sq. m./g. The values for krypton at −183.2° may be somewhat in error since the highest relative pressure which could be measured was 0.13.

A comparison of BET and H-J area values for a number of nitrogen adsorption experiments at −195° on Fischer-Tropsch iron-type catalyst samples is shown in Fig. 4. In this figure, the ratio of the H-J area to the BET area is plotted against the BET $C$-value using 16.2 Å.$^2$ for the cross-sectional area of the nitrogen molecule and 4.06 for the H-J $k$-value. A similar comparison for a number of krypton adsorption experiments at −195° is also shown in Fig. 4. In this case the area ratios were obtained by using the molecule cross-sectional area and H-J constant shown in Table I.

## Discussion

Emmett and Brunauer[7] have proposed that, in calculating surface areas from $v_m$ values, the cross-sectional area, $\sigma$, of adsorbed molecules was related to the density of bulk adsorbate, $\rho$, by the equation

$$\sigma = 1.091\,(M/N\rho)^{2/3} \qquad (1)$$

where $M$ is the molecular weight of adsorbate and $N$ is the Avogadro number. The values for $\sigma$ from equation (1) and liquid-density data are compared with cross-sectional area values obtained in this work in columns 5 and 6 of Table I. In general, the agreement between the cross-sectional area values from equation (1) and those from this work is poor, ranging from −8.1% for CO at −195.7° to +43.5% for $CO_2$ at −79°.

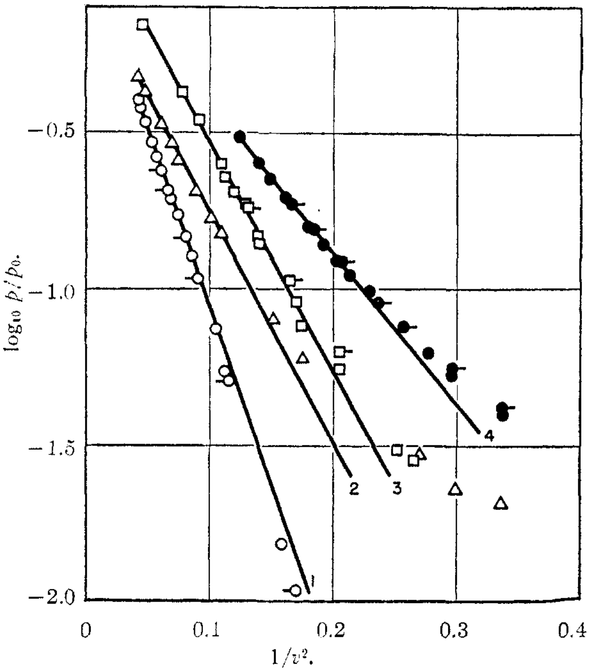

Fig. 3.—H-J plots for adsorption on anatase: curve 1, $N_2$ at −195.4°; curve 2, A at −183.3°; curve 3, Kr at −195.5°; curve 4, $CO_2$ at −79.0°.

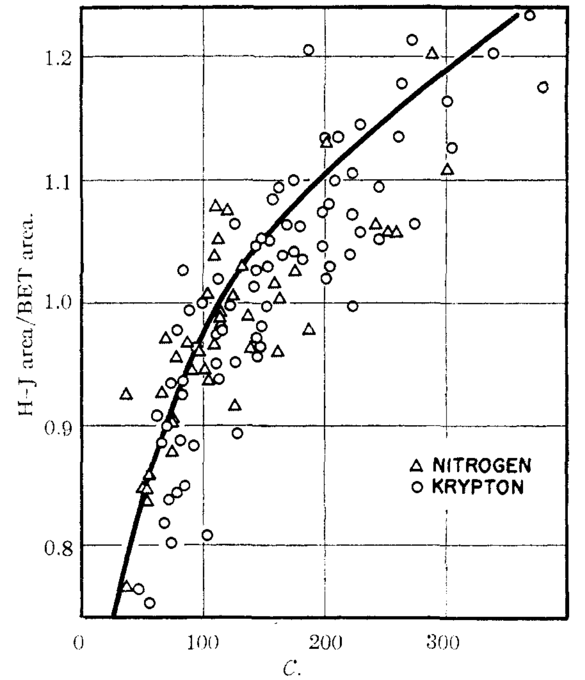

Fig. 4.—Comparison of area values from nitrogen and krypton adsorption data at −195° for BET and H-J methods of calculation, Emmett's calculated curve.

For nitrogen at −195°, the present cross-sectional area value of 16.27 Å.$^2$/molecule is in good

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(5) R. A. Beebe, J. B. Beckwith and J. M. Honig, This Journal, **67**, 1554 (1945).

(6) J. W. M. Dumond and E. R. Cohen, *Revs. Modern Phys.*, **20**, 106 (1948).

(7) P. H. Emmett and S. Brunauer, This Journal, **59**, 1553 (1937).

agreement with the value 16.2 obtained from equation (1) and generally adopted for surface-area measurements. For krypton at −195°, the present cross-sectional area value of 21.78 Å.$^2$/atom is 11.8% higher than that reported by Beebe, Beckwith and Honig[5] for the same system and 8.6% above that recommended by Davis, DeWitt and Emmett.[8] However, it is in good agreement with the average value of 21.8Å.$^2$/atom which would have to be assigned to make BET nitrogen and krypton area values agree for a series of six Fischer–Tropsch iron-type catalyst samples which have been studied in this Laboratory.

The adsorption of the several gases on anatase has also made it possible to evaluate the constant $k$ of the relative area method of Harkins and Jura for those gases (see Table I, column 8). For nitrogen at −195° the $k$-value is in good agreement with that reported by Harkins and Jura.[3] For krypton at −195° the $k$-value of 5.06 is 20.5% larger than that estimated by Beebe, Beckwith and Honig[5] for the same system.

The experimental relationship between the constant $v_m$ from the BET equation and the constant $A$ from the H–J equation for a number of adsorbates on samples of the same anatase is shown in Fig. 5. The square root of $A$ is plotted against $v_m$ for the systems investigated in this work as well as for $n$-hexane at 0°,[4] $n$-heptane at 25°,[4] $n$-butane at 0°,[3] and water at 25°.[3] An approximately linear relation exists with a best line having a slope of 1.07. This leads to the approximate relation

$$k = 0.251\sigma \qquad (2)$$

where $k$ is the H–J constant (for volumes in ml. at S.T.P.) and $\sigma$ is the molecular cross-sectional area (in Å.$^2$) as measured by the BET $v_m$. Equation (2) is valid for the several gases involved when adsorbed on the anatase and indicates a one-to-one correspondence between the parameter $A^{1/2}$ of the H–J equation and $v_m$ of the BET equation for these systems.

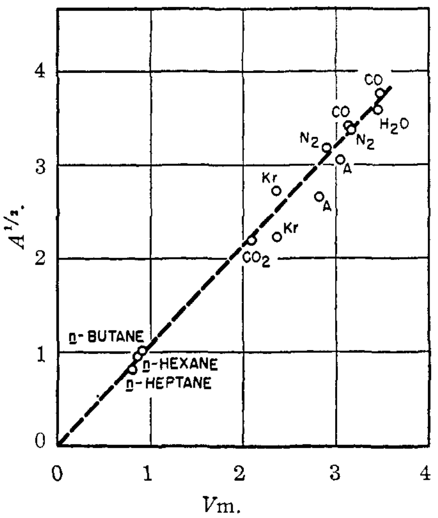

Fig. 5.—Comparison of the BET parameter $V_m$ with the H–J parameter $A^{1/2}$ for several gases adsorbed on standard anatase.

Emmett[9] has shown that, for a surface of constant $v_m$ on which a given gas is adsorbed according to the BET equation, the constant $A$ varies with the value of $C$. He has calculated the variation of molecule cross-sectional area with $C$ for $N_2$ adsorption at −195° and found experimentally about the same effect. In Fig. 4, a similar comparison is made for nitrogen adsorption experiments made in this Laboratory on Fischer–Tropsch iron-type catalyst samples except that the ratio of H–J to BET areas is plotted against $C$. The corresponding ratios according to Emmett's calculation are shown as a continuous curve, and these were obtained from his calculated cross-sectional area values by dividing by the factor 16.2 Å.$^2$/molecule. Many of the points were obtained from experiments in which relatively few adsorption data were available so that the precision on the $C$ values is rather poor; however, the data tend to follow the calculated curve.

A comparison for a large number of krypton adsorption experiments at −195° between H–J and BET areas on iron-type Fischer–Tropsch catalyst samples has been made and is also shown in Fig. 4. Again, the ratio of the areas by the two methods tend to follow the curve calculated by Emmett. Although the data for nitrogen and krypton adsorption at −195° show the expected variation of H–J/BET area ratio with BET $C$-value, this does not seem to be always the case; *e.g.*, the data of Loeser and Harkins[4] for $n$-heptane adsorption on twenty-one powders at 25° show only a very slight trend in the direction calculated by Emmett.

**Acknowledgment.**—We wish to acknowledge the coöperation of Professor George Jura in providing the sample of anatase used in this investigation and of Mr. Garst of this Laboratory for the electron micrographs.

TULSA, OKLAHOMA

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[8] R. T. Davis, Jr., T. W. DeWitt and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1232 (1947).

[9] P. H. Emmett, THIS JOURNAL, **68**, 1784 (1946).