This difference can be accounted for by the difference between the heats of neutralization of catechol by $HPO_4^{=}$ and OH^-, respectively.

BERKELEY, CALIFORNIA RECEIVED MAY 22, 1935

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL SCIENCES OF WEST VIRGINIA UNIVERSITY]

The Adsorption of Methane by Coal[1]

BY J. BARTLETT SUTTON AND EARL C. H. DAVIES

Introduction

To determine the adsorption equilibrium between a highly adsorptive coal and methane, we have recently used an apparatus which contains a variable volume unit, by means of which the total system volume can be varied through four stages, enabling one to obtain adsorption values for four pressures with each gas sample and to check such values on both the adsorption and desorption side of the equilibrium point. The fact that approximately twenty-four hours were required for equilibrium conditions to be attained led us to enclose, in an electric refrigerator at constant temperature (± 0.1°), not only the adsorption bulb but the entire apparatus.

Materials and Apparatus

The coal was obtained from the Carreta, West Virginia, mine of the Carter Coal Company, which is the most gassy mine in the world. It was of semibituminous rank and from the Pocahontas No. 4 seam. A ton sample, collected from all over the mine, was passed through a jaw crusher and then quartered several times to obtain a representative sample of fifty pounds. A portion of this was then ground in a "coffee mill" to approximately 100-mesh average size.

The analysis of this coal[2] as given by the Bureau of Mines was H, 4.4; C, 88.7; N, 1.3; O, 2.2; S, 0.5; H_2O, 0.4 and ash, 2.9. After refluxing with water for two weeks, we found the average density (nine determinations) to be 1.3521. The range of particle sizes, in the coal sample, as determined by the application of Stokes' equation to sedimentation data, was: 63.0%, 0.132 mm.; 10.0%, 0.045 mm.; 10.8%, 0.030 mm.; 10.2%, 0.021 mm.; 1.7%, 0.016 mm. and 4.3%, 0.007 mm. The coal received no preliminary heat treatment but was evacuated to 10^{-4} mm. for a period of seventy-two hours.

The methane was obtained from the Bureau of Mines at Pittsburgh, Pennsylvania. The higher hydrocarbons[3] had been removed from natural gas by passing it through 117 cm. of activated coconut charcoal.

The analysis of the methane[4] supplied by the Bureau of Mines was: CH_4, 97.8–98.0%; C_2H_6, 0.05%; O, 0.10% and N, 1.85%. The density found by the Regnault method was 0.7196. Traces of moisture were removed from the methane, before it was admitted to the system, by passing through a coil submerged in an ether–solid carbon dioxide mixture.

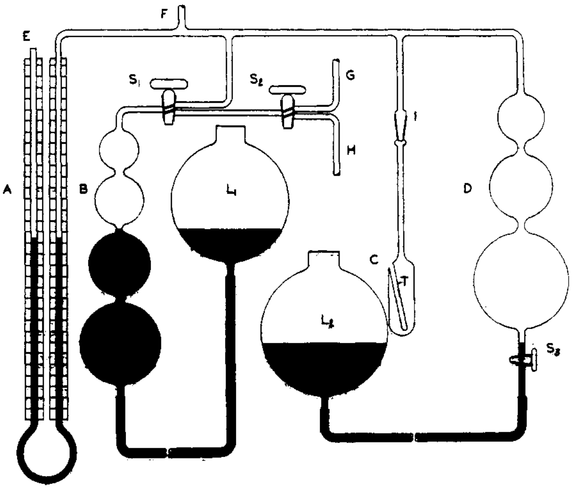

Fig. 1.—Adsorption apparatus with variable volume unit.

The apparatus (Fig. 1), designed and constructed in this Laboratory, consists essentially of the four units, A, B, C and D. A is the manometer, B the gasometer, C the adsorption bulb and D the variable volume unit. The volumes, between constricted portions, of both the gasometer and variable volume unit, as well as the total system volume, were accurately measured by the use of mercury. The temperature was determined by means of two ten-junction copper–constantan thermocouples, the hot junctions of which were en-

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[1] This paper is from a dissertation submitted in June, 1935, by J. Bartlett Sutton to the Faculty of the Graduate School of West Virginia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] R. S. Selden. R. I-3233; U. S. B. M., June, 1934.

[3] H. H. Storch and P. L. Golden, THIS JOURNAL, 54, 4662 (1932).

[4] H. H. Storch, Bureau of Mines, personal communication.

closed in a paraffin-filled glass tube, embedded in the adsorbing material, while the cold junctions were enclosed in a glass tube immersed in a water-ice mixture, contained in a Dewar flask.

Experimental Procedure

By means of blank determinations, we found that the glass and mercury surfaces within the apparatus did not adsorb a measurable amount of methane. The procedure followed was similar to that used in other investigations of the same nature except for the use of the variable volume unit, by means of which the pressure was varied through four stages by changing the mercury level within the unit.

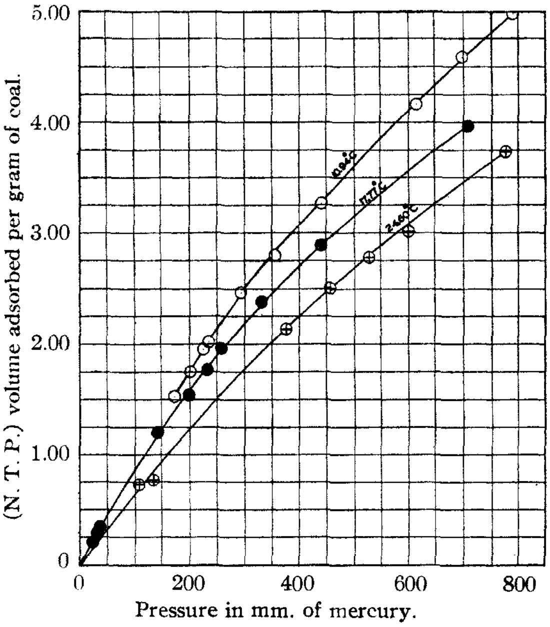

Fig. 2.—Adsorption isotherms.

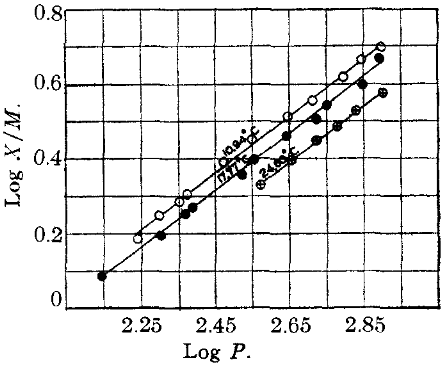

Fig. 3.—Log isotherms.

A weighed sample of coal was then placed in C and the manipulations carried out as before. After adsorption values had been determined and checked at four different pressures, more gas was then added and the above procedure repeated. The volume of gas adsorbed is $V_a = (273/760\ T_1)(P_1V_1 - P_2V_2)$, where T_1 is the temperature of the system, V_1 the volume of gas introduced, P_1 the atmospheric pressure, V_2 the volume of the system and P_2 the pressure produced by the gas introduced into the system.

Data and Graphical Interpretations

The relationships between adsorption and pressure for temperatures of 10.94, 17.77 and 24.60° are represented graphically in Fig. 2.

The Freundlich equation has been found to be applicable to the data, as shown by the straight line curves in Fig. 3. Here the log of x/m has been plotted against the log of P. A straight line is obtained, because the Freundlich equation in the form $\log x/m = \log k + 1/n \log P$ yields a straight line if it is applicable to the data. The slope of this line is equal to $1/n$ and its intercept with the $\log x/m$ axis is equal to $\log k$.

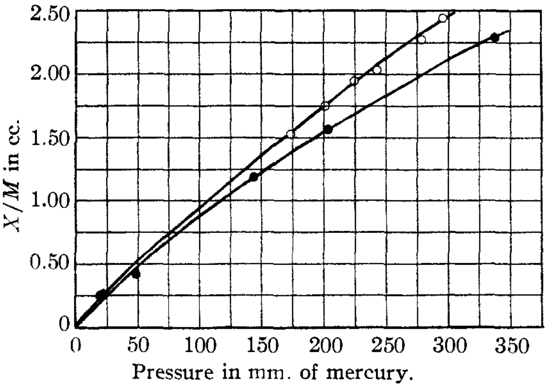

Fig. 4.—Effect of moisture in decreasing adsorption.

The effect of traces of moisture in lowering the adsorption of methane is shown in Fig. 4. The data for these curves were obtained at 10.94°.

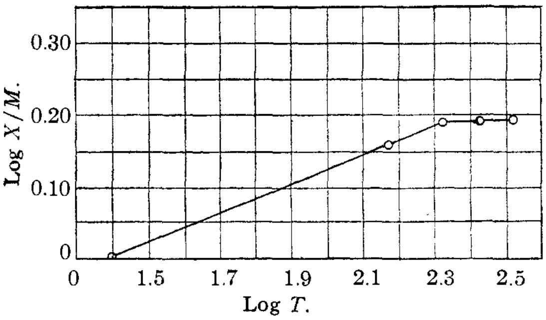

Fig. 5.—Log rate curve.

Figure 5 gives a log rate curve, the values for which were obtained at 17.77°.

The heats evolved per mole of gas adsorbed, as obtained by the application of the Clausius–Clapeyron equation to pressure and temperature readings taken from adsorption isosteres (Fig. 6), are plotted against amounts of gas adsorbed in Fig. 7.

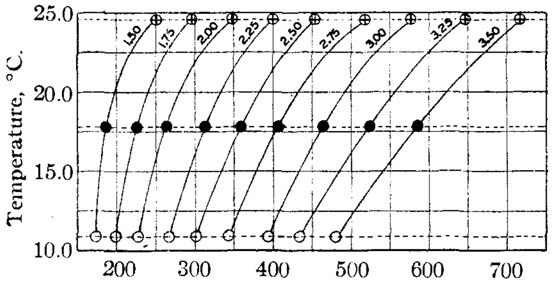

Fig. 6.—Adsorption isosteres.

Summary

1. It has been shown that an apparatus equipped with a variable volume unit offers an accurate means of checking adsorption equilibrium on both the adsorption and desorption side of the equilibrium point.

2. The maintenance of the total adsorption system at constant temperature has been found to offer advantages of accuracy of measurement and simplicity of calculation.

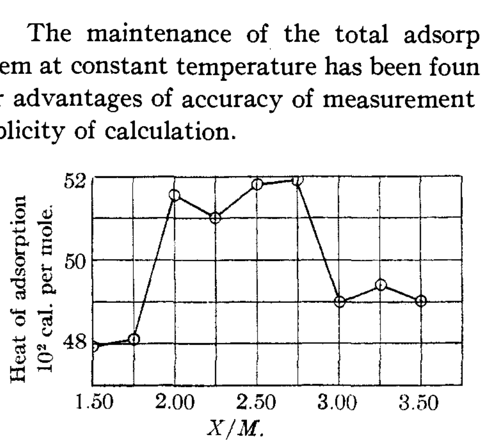

Fig. 7.—Heats of adsorption of methane on coal at 17.77°.

3. A successful application of the Freundlich equation, to data found for the adsorption of methane by coal, has been made.

4. The calculated heats of adsorption of methane on coal have been found to be between 4700 and 5200 calories per mole for x/m values between 1.5 and 3.5.

MORGANTOWN, W. VA.

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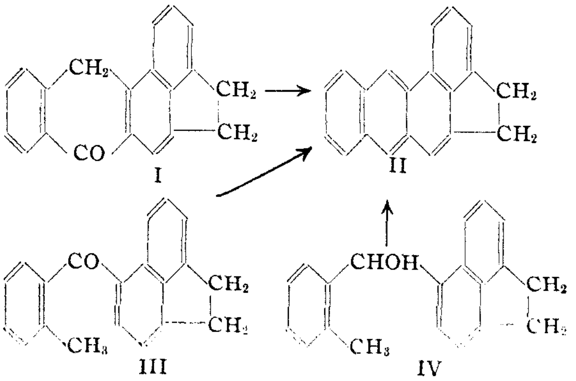
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHEASTERN UNIVERSITY]

A Pyrolytic Synthesis of 2,3-(Naphtho-2',3')-acenaphthene[1]

BY BRADFORD P. GEYER AND SAVERIO ZUFFANTI

2,3-(Naphtho-2',3')-acenaphthene (II) has been synthesized by Cook[2] by reduction of the anthrone (I), and, according to the statements in some patents,[3] the hydrocarbon also can be obtained by the pyrolysis of 3-*o*-toluylacenaphthene (III) or 3-acenaphthyl-*o*-tolylcarbinol (IV) in the presence of a dehydrating catalyst. These intermediates have not been described in the literature, however, and there is no evidence to indicate that a catalyst is required in their pyrolysis. It appeared a matter of interest, therefore, to synthesize 3-*o*-toluylacenaphthene and then, by subjecting this ketone to the conditions ordinarily employed for effecting the Elbs reaction, to prepare the hydrocarbon II.

The ketone III was obtained from *o*-toluyl chloride and acenaphthene by the Friedel–Crafts reaction. When pyrolyzed at 400–410°, it was converted smoothly into a hydrocarbon having the composition and the properties of the substance described by Cook.[2]



The authors are greatly indebted to Professor Louis F. Fieser of Harvard University for much helpful advice.

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[1] A thesis submitted in June, 1935, by Bradford P. Geyer in partial fulfilment of the requirements for the degree of Bachelor of Science at Northeastern University.

[2] Cook, *J. Chem. Soc.*, 1087 (1930).

[3] O. Nicodemus, German Patent 481,819 (1929); O. Nicodemus and W. Berndt, U. S. Patent 1,776,925 (1930).