

tion in the cycloheptatrienone and cyclopentadienone rings is given by Brown's calculation<sup>12</sup> of the number of  $\pi$ -electrons per atom by the method of Coulson and Longuet-Higgins.<sup>13</sup> From the charge distribution and the dimensions of the tropolone ring given by X-ray analysis,<sup>14</sup> a dipole moment value  $9.5 \times 10^{-18}$  may be calculated for cycloheptatrienone. A similar calculation gives  $5.6 \times 10^{-18}$  for the hypothetical cyclopentadienone, irrespective of whether the ring is taken as a symmetrical pentagon or as resembling that of cyclopentadiene. The calculated moments greatly

(12) R. D. Brown, *J. Chem. Soc.*, 2670 (1951).

(13) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(14) J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

exceed the observed much as the values calculated for ionic structures tend to exceed such as may be observed,<sup>15</sup> but show that the molecular moments should be greater than those of ordinary aliphatic and aromatic ketones. The moment of the tetracyclone molecule is, presumably, increased above that of cyclopentadienone by the resonance contributions from the twelve polar structures with positive charge on a phenyl group. This would account for the fact that the tetracyclone moment is not as far below the value calculated for the cyclopentadienone ring as is the cycloheptatrienone moment below its calculated value.

(15) Cf. C. P. Smyth, *THIS JOURNAL*, **63**, 57 (1941).

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

## Heat Capacity of Methane Adsorbed on Titanium Dioxide between 55 and 90°K.

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Some features in the construction and operation of a low-temperature adiabatic calorimeter for the study of gas-solid systems are described briefly. The heat capacity of methane adsorbed on titanium dioxide (rutile) has been determined between 55 and 90°K. at four coverages ranging from 0.2 to 1.0 monolayer. The heat capacity of the adsorbed methane is greater than that of solid methane and, at 89°K., exceeds the value for liquid methane. The heat capacity-temperature curves point to the absence of any first-order phase transitions in the range of temperatures and concentrations studied. It is suggested that the relatively high heat capacity of the adsorbed methane may be due in part to a contribution to the heat capacity resulting from a transition from localized to mobile adsorption. Additional experimental data and theoretical considerations are necessary before a complete model for the adsorption can be proposed.

Many investigations have been directed toward the determination of the state of the adsorbate and the nature of phase transitions in the adsorbate for systems of gases adsorbed on a finely divided solid. The isotherm measurements of the *n*-heptane-silver, *n*-heptane-ferric oxide, *n*-heptane-graphite systems<sup>1-3</sup> by Jura, Harkins and co-workers are particularly relevant to the present work. Analysis of the isotherms showed the presence of a first-order two-dimensional condensation in the adsorbed film. The two-dimensional critical temperature was found to be approximately 0.5 of the three-dimensional critical temperature, a value in rough agreement with theory utilizing a simple model<sup>4</sup> for the adsorbed gas. It was a purpose of the present investigation to observe directly and evaluate quantitatively a two-dimensional condensation by using a low-temperature adiabatic calorimeter in measurements of the heat capacity of the adsorbed film in the 50 to 90°K. temperature range. Such a transition would appear as a discontinuity in the heat capacity-temperature curve. The choice of methane as a suitable adsorbate was based on the following considerations. Its three-dimensional critical temperature of 190°K. made it reasonably probable that a two-dimensional condensation of the type observed by Jura and co-workers would occur in the temperature range to be studied. In addition,

(1) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **13**, 535 (1945).

(2) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

(3) G. Jura, W. D. Harkins and E. H. Loeser, *ibid.*, **14**, 344 (1946).

(4) T. L. Hill, *ibid.*, **14**, 441 (1946).

Hill<sup>4</sup> had pointed out that transitions from localized to mobile adsorption should occur at low temperatures. The spherical symmetry of the methane molecule was a desirable feature if any interpretation of the results in terms of structure was to be made. Titanium dioxide in the rutile form was selected as an adsorbent after a preliminary study of the adsorption isotherms indicated that it was satisfactory from the standpoint of surface area, non-porosity, and reversibility of adsorption.

The only comparable measurements are those of Simon and Swain<sup>5</sup> with the argon-charcoal system, Morrison and Szasz<sup>6</sup> with the nitrogen-rutile system, and Morrison, *et al.*,<sup>7</sup> with the argon-rutile system.

### Experimental

**Apparatus.**—The low temperature adiabatic calorimeter used in the experimental measurements followed essentially the same relative arrangement of cold reservoirs, radiation shields and calorimeter vessel as employed by Yost, *et al.*,<sup>8</sup> in calorimetric studies of condensable gas systems. Because the activation of the adsorbent required the use of elevated temperatures with the calorimeter vessel containing the solid adsorbent, the construction of the calorimeter and the arrangement of the electrical leads, difference thermocouples, etc., was accomplished in such a manner as to allow convenient disassembly of the apparatus. Morrison and Los<sup>9</sup> have utilized a calorimeter of similar design in a study of the argon-rutile system.

(5) F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

(6) J. A. Morrison and G. J. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

(7) J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

(8) D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, Jr., *THIS JOURNAL*, **63**, 3488 (1941).

(9) J. A. Morrison and J. M. Los, *Discussions Faraday Soc.*, No. 8, 321 (1950).

In order to control accurately the temperature of the gas sample admitted to the solid adsorbent, a portion of the moel filling tube 60 cm. in length was cast in solder between two brass plates. The plates were supported by three No. 25 B and S gage copper wires, 5 cm. in length, which were soldered both to the plates and the bottom of the liquid hydrogen container. In the normal operation of the calorimeter, the cold drift along these wire supports was compensated by the heat conducted from the room along the tube or generated by constantan heaters attached to the plates and the filling tube. Difference thermocouples, constructed of copper and constantan wire, were appropriately located to show temperature differences between the filling tube and calorimeter vessel. These temperature differences were carefully adjusted during the admission of the gas sample or during actual thermal measurements in order to prevent condensation of the gas outside the calorimeter vessel.

The calorimeter vessel was maintained in an adiabatic environment by means of a copper shield which totally enclosed it. The construction and operation of this shield was similar to that of Scott, *et al.*<sup>10</sup> The critical temperature differences existing between the top and side of the calorimeter vessel and the shield were indicated by four-junction, copper-constantan thermocouples connected to Leeds and Northrup Type R galvanometers. Temperature differences as small as 0.002° were readily observable.

The measurement of energy input to the calorimeter vessel containing the gas-solid system during a heat capacity determination and of the equilibrium temperature was accomplished by appropriate electrical circuits utilizing a White double potentiometer. The time of the heater period was measured with a synchronous interval timer operated with an accurately controlled 60-cycle source. The temperature of the system was read with a four-lead strain-free platinum resistance thermometer, constructed and encased in a platinum thimble by the Leeds and Northrup Company, and calibrated in the 11 to 90°K. interval by the National Bureau of Standards. Its ice-point resistance was approximately 25.5 ohms.

The quantity of gas was measured with the usual volumetric and manometric apparatus. Pressures were determined with a Gaertner high-precision cathetometer.

**Materials.**—The adsorbent used in the investigation was a 48.5-g. portion of a 200-g. sample of high area rutile (TiO<sub>2</sub>) provided by the National Lead Company. The monolayer concentration as determined by the BET method was approximately 18 ml. (STP) of methane per gram.

The adsorbate was Research Grade methane of 99.5% purity obtained from the Phillips Petroleum Company. This methane was further purified by condensation in a liquid air trap and rejection of the first and last fractions.

**Method.**—The heat capacity of the titanium dioxide (rutile) and of the methane-titanium dioxide system was established with a pressure of helium in the calorimeter vessel of 0.5 mm. in order to hasten the distribution of energy. Thermal equilibrium was thus obtained in about ten minutes after the input of energy. No significant adsorption of helium by the titanium dioxide nor measurable change in the heat capacity of the titanium dioxide could be detected with helium pressures as high as 3 mm. of mercury. Therefore, it was assumed that the use of helium for this purpose introduced no error in the measurements.

The measurement of heat capacity involves experimentally the concurrent measurement of an energy input,  $\Delta E$ , and a temperature rise,  $\Delta T$ . The method of calculating the true total heat capacity,  $dE/dT$ , from the experimentally determined average,  $\Delta E/\Delta T$ , has been discussed elsewhere.<sup>10</sup> For the calorimeter vessel containing the adsorbent and adsorbate, the true total heat capacity is given by the expression<sup>7</sup>

$$dE/dT = C_{pg} + C_{peal} + C_{Ns} - q_{ht} \cdot (dN_s/dT)_{\text{expt.}} + V_G (dP/dT)_{\text{expt.}} \quad (1)$$

The heat capacity of the gas in the deadspace volume of the calorimeter vessel,  $C_{pg}$  was negligible for all practical purposes. The heat capacity of the calorimeter vessel plus adsorbent was read from a smoothed plot based on thermal measurements made prior to the admission of any methane. For the highest coverage,  $\theta = 1.0$ ,  $(dP/dT)_{\text{expt.}}$  was of the

order of 2 mm. deg.<sup>-1</sup>. The deadspace volume of the calorimeter,  $V_G$ , was 60 ml. The maximum value of the heat of compression term,  $V_G(dP/dT)_{\text{expt.}}$ , was less than 1% of  $C_{Ns}$ , the heat capacity at constant coverage, and consequently, it was neglected in the calculations. The desorption term,  $q_{ht}(dN_s/dT)_{\text{expt.}}$ , was evaluated from isosteric heats,  $q_{ht}$ , determined from a  $\log P$  vs.  $1/T$  plot. The pressures were observed in the equilibrium periods following the heat capacity measurements. This term amounted to as much as 10% of  $C_{Ns}$  at the highest coverages and temperatures.

The energy input to the calorimeter was measured with an uncertainty of less than  $\pm 0.01\%$ . Therefore, the precision of the calorimeter was essentially dependent on the precision with which the temperature rise was measured. The fact that the shields were maintained manually at the same temperature as the calorimeter vessel introduced an additional uncertainty. With satisfactory operation of the shields, the average deviation of the total heat capacity from a smooth curve was less than  $\pm 0.03\%$  in the range from 55 to 90°K. when temperature increments of approximately six degrees were used. In terms of the adsorbed methane, this means that the heat capacity was determined with a precision ranging from about 3% for a coverage of 0.2 monolayer to slightly better than 1% for the monolayer. However, there was an added uncertainty of not more than 2% at the high coverages and temperatures arising from desorption and compression effects in the calorimeter.

## Results and Discussion

The heat capacity was determined for methane adsorbed on titanium dioxide at concentrations of 0.00884, 0.01566, 0.03048 and 0.03834 mole of methane corresponding to approximate coverages of 0.2, 0.4, 0.8 and 1.0 monolayer. The methane was introduced into the calorimeter vessel at the concentration of 0.01566 mole at a temperature of about 100° K. The system was then cooled to 50° K. and measurements of the heat capacity were made to 90° K. For the measurements at the concentrations of 0.03048 and 0.03834 mole, the methane was added cumulatively without reactivating the adsorbent. The measurements were then repeated in a similar manner. The concentration of 0.00884 mole was obtained by desorbing the proper amount of methane after the completion of the measurements at the highest concentration. At each concentration, the measurements were repeated three or more times over a period of several days.

A graph of the molar heat capacity at constant coverage (coverage assumed independent of temperature) versus the temperature is presented in Fig. 1. Because the data obtained in successive runs over the temperature range agreed within the experimental error, no attempt has been made to associate individual points in the graph with the respective runs.

No discontinuities appear in the heat capacity-temperature curve. Consequently, it is believed that no first-order phase transitions have occurred in the range of concentrations and temperatures covered in the investigation.

Gaseous methane has a heat capacity of 8 cal. per mole and liquid methane a heat capacity of 13 cal. per mole at 89°K., the melting point of methane. The stable phase of methane in the range from 50° to 85°K. is the solid.<sup>11</sup> The observed heat capacity of the adsorbed methane is greater at all coverages than that of solid methane and, at 89°K., exceeds the value for liquid methane. As the coverage is increased, one would expect the properties of the adsorbed phases to approach those of liquid meth-

(10) R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945).

(11) K. Clusius, *Z. physik. Chem.*, **B3**, 41 (1929).

ane in the temperature range immediately above 89°K. and those of solid methane for temperatures below 89°K. However, in the range of temperatures covered by the work, there does not appear to be any significant trend in the value of the heat capacity as the coverage is increased from 0.2 to 1.0 monolayer. The fact that the heat capacity of the adsorbed methane is greater than that of solid methane may be due in part to the effect of a phase transition from localized to mobile adsorption. Hill<sup>4</sup> has shown for a simple theoretical model which neglects the interaction of the molecules and the effect of the heterogeneity of the surface that such a transition would occur at temperatures below 90°K. In this case, the contribution to the heat capacity by the transition is determined by the shape and magnitude of the potential barrier restricting the movement of the molecules over the surface of the solid.

The scope of the present measurements is too limited to propose a complete model for the adsorption. Hill<sup>12</sup> has considered the case of a molecule localized on a heterogeneous surface. The energy of such a molecule is dependent on (1) the partition function for the three vibrational degrees of freedom of the center of mass plus the usual internal degrees of freedom, (2) the distribution of energy at the solid sites, (3) the lateral interaction of the adsorbed molecules. The heat capacity of the adsorbed phase is determined by the temperature dependence of all these factors. The distribution of energy at the solid sites, evaluated from measurements of adsorption isotherms and heats of adsorption, as well as theoretical considerations such as

(12) T. L. Hill, *J. Chem. Phys.*, **17**, 762 (1949).

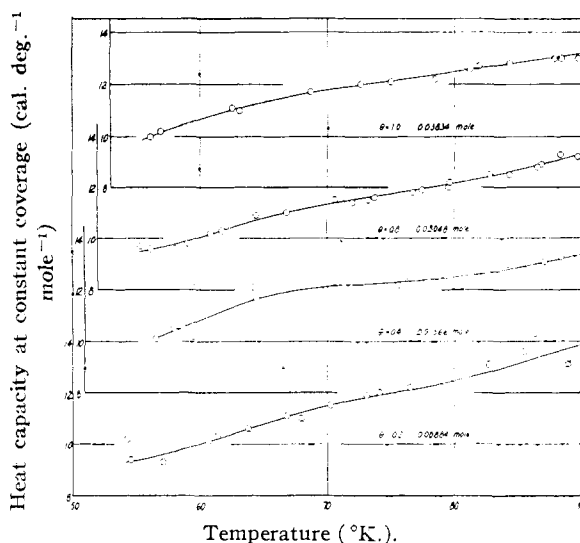


Fig. 1.—Molar heat capacity of methane adsorbed on titanium dioxide (rutile) at various coverages.

the variation of the internal partition function with the energy of the sites are necessary for the description of the complete model.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISUS COLLEGE]

## The Radiation Decolorization of Dilute Dye Solutions; Chlor Phenol Red<sup>1,2</sup>

BY EDWARD N. WEBER AND ROBERT H. SCHULER

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The kinetics of the decolorization processes induced in dilute aqueous solutions of chlor phenol red by X-radiation of 120 kev. energy has been investigated. The reactions are secondary to the absorption of the radiation by the water and subsequent formation of active intermediates. The molecule, which results from the initial decolorization has a susceptibility for further reaction approximately equal to that of the original species. The relatively low yield for decolorization suggests that reaction of the dye molecule does not necessarily result in decolorization. The properties of this system are such as to provide a good model for the radiation chemistry of enzyme and related systems. Competition of thiourea for the radiation intermediate has been observed.

Application of X-ray decolorization of solutions of methylene blue in radiation dosimetry has been previously discussed<sup>3-5</sup> and the X-ray induced reactions of numerous other colored organic materials have also been qualitatively described.<sup>6</sup> We have had occasion, in an examination of chemical actin-

ometers for radiation decomposition studies in progress, to study the kinetics of the decolorization reactions of dilute aqueous solutions of chlor phenol red. The results of this investigation, although indicating that these decolorization reactions are not suitable for accurate actinometric purposes, do have a bearing on the radiation chemistry of aqueous systems. Because of the low concentrations involved, aspects may be regarded as quite analogous to certain radio-biological processes.

### Experimental

The unfiltered radiation from an industrial 60-140 kev. X-ray unit was used as the source of activation. The instrument was operated at constant intensity characterized by a current of 5 ma. at 120 kev. energy, the effective

(1) Presented at the 119th National Meeting of the American Chemical Society, Cleveland, Ohio, April 8-12, 1951.

(2) This work was supported, in part, under contract AT(30-1)-1084 with the U. S. Atomic Energy Commission.

(3) W. Stenstrom and H. R. Street, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1498 (1935).

(4) W. Stenstrom and A. Lohman, *Radiology*, **16**, 322 (1931); **22**, 304 (1934).

(5) S. A. Goldblith, B. E. Proctor and O. A. Hammerle, *Ind. Eng. Chem.*, **44**, 310 (1952).

(6) G. L. Clark and K. R. Fitch, *Radiology*, **17**, 285 (1931).