cm.$^{-1}$ very probably corresponds to the ground state vibrational frequency of 494 to 509 cm.$^{-1}$ which has been deduced from the vibrational analysis, which in turn correlates with the polarized Raman band or bands appearing in the region 450–490 cm.$^{-1}$ in liquid $(ClCO)_2$. ZMCD[3] and SK[4] do not agree about the number of bands or the assignments in this region of the Raman spectrum. All workers agree that the Raman bands in this region are polarized. Nevertheless, ZMCD have assigned a B_g fundamental at 483 cm.$^{-1}$, basing their conclusions principally on the results of a normal coördinate analysis. Saksena, Kagarise and Rank,[12] have discussed this and other shortcomings of ZMCD's interpretations, and it appears that this aspect of ZMCD's assignment is untenable. This vibration has been assigned by SK to an A_g COCl deformation.

The intervals 77 and −85 cm.$^{-1}$ deduced from the vibrational analysis probably correspond to 1–1 transitions of low vibration frequencies of $(ClCO)_2$. The A_u torsional frequency, which has not been located with certainty in the infrared spectrum, and the A_g COCl rocking (276 cm.$^{-1}$) may be the vibrations which are responsible for these difference frequencies.

e. Comparison with Biacetyl and Glyoxal.—In the n—π^* transitions in glyoxal, biacetyl, and oxalyl chloride, an electron is excited from a nonbonding orbital localized on the O atom to a π^* antibonding orbital which extends over the OCCO skeleton.[8,10] Although the transition may be formally allowed by symmetry, as is definitely the case in $(CH_3CO)_2$ and $(CHO)_2$, the intensity is nevertheless low. The reasons for the low intensity of n—π^* transitions of azines have been discussed by Orgel,[13] and similar considerations apply to the OCCO chromophore.

The I^1A_u—^1A_g transition in $(ClCO)_2$ is shifted approximately 4000 cm.$^{-1}$ to higher frequencies relative to the corresponding transitions in $(CHO)_2$ and $(CH_3CO)_2$. This is to be expected in an n—π^* transition, as has been discussed by Orgel.[13]

SK[5] have noted the greater length of the C–C bond in $(ClCO)_2$ relative to $(CHO)_2$ and $(CH_3CO)_2$, and have correlated this with the smaller double bond character and greater degree of freedom of rotation around the central bond. As expected, the ground state C–C stretching frequency is considerably lower in $(ClCO)_2$ (1078 cm.$^{-1}$ [4]) than in $(CHO)_2$ (1205 cm.$^{-1}$ [7]) or in $(CH_3CO)_2$ (1280–1300 cm.$^{-1}$ [8]).

In summation, both the similarities and the differences in the spectra of these molecules appear to be explicable in terms of their molecular structure, and the spectroscopic properties of the OCCO chromophoric group support the predictions of the simple LCAO–MO theory.

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[12] B. D. Saksena, R. E. Kagarise and D. H. Rank, *J. Chem. Phys.*, **21**, 1613 (1953).

[13] L. E. Orgel, *J. Chem. Soc.*, 121 (1955).

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

Entropy of Krypton Adsorbed on Titanium Dioxide (Anatase)

BY E. L. PACE, W. T. BERG AND A. R. SIEBERT

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Calorimetric measurements of the heat capacity, adsorption isotherms and heat of adsorption between 12 and 140°K. have been used to determine the zero point entropy of krypton adsorbed on titanium dioxide of the anatase form. The zero point entropy for 0.00765, 0.01396 and 0.02421 mole of adsorbed gas corresponding to the monolayer fractions 0.13, 0.23 and 0.40 are, respectively, 1.1 ± 1.1, 1.5 ± 0.6 and 1.3 ± 0.3 cal. deg.$^{-1}$ mole^{-1}. The results indicate strongly that thermodynamic equilibrium has not been attained between the surface and the adsorbed gas. The experimental procedure which was used as well as theoretical consideration leads one to believe that most of the randomness in the system existing at approximately 50°K. was preserved at temperatures below this value.

In recent years, some investigations have been carried out in which calorimetric measurements of adsorption isotherms, heats of adsorption and heat capacity have been used to determine the entropy of a gas adsorbed physically on a solid surface. Morrison, *et al.*,[1] have carried out such a study with the argon–rutile system and Aston and co-workers[2] with the neon–rutile system. In both cases, the conclusion was reached that the zero point entropy of the adsorbed gas was zero within the experimental error, thus indicating adsorption processes in thermodynamic equilibrium.

The present investigation is concerned with krypton adsorbed on titanium dioxide of the anatase form. Considering the fact that at the same temperature the mobility of krypton on a solid surface is lower than argon and neon, the question naturally arises as to whether the adsorbed krypton would attain thermodynamic equilibrium with the surface under experimental conditions similar to those employed in the studies with argon and neon.

Experimental

The krypton was purchased from the Air Reduction Sales Company, Jersey City, New Jersey. Mass spectrographic analyses furnished with the gas indicated a purity of more than 99.9%.

The anatase used in the research was obtained from Dr. W. K. Nelson of the National Lead Company, South Amboy,

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

[2] R. J. Tykodi, J. G. Aston and G. D. L. Schreiner, THIS JOURNAL, **77**, 2168 (1955).

New Jersey. It was stated to be 84.7% titanium dioxide with the remainder water, either adsorbed or coördinately bound. The anatase was activated at 185° by evacuation at a pressure of 10^{-5} mm. for three days.

The calorimeter vessel was filled with approximately 50 g. of anatase with a monolayer capacity of 0.05977 mole as determined by the BET method.

The apparatus[3] and general experimental procedures[1,4] which were employed have been described previously in the literature.

The samples of krypton were added to the anatase at temperatures above the normal boiling point of krypton. For the heat capacity measurements above 50°K., the calorimeter was cooled to 77°K. over a period of about 24 hours. After remaining at 77°K. for two or three days, the calorimeter was finally cooled to 50°K. over an additional 24-hour period. Temperature differences between the calorimeter vessel and the surroundings were carefully maintained to ensure no condensation of the adsorbate outside the vessel. For the heat capacity measurements below 50°K., the preceding routine was repeated to 50°K., and then the final step to 12°K. was carried out in approximately two hours.

The operating characteristics of the calorimeter appeared to be the same both with and without the adsorbed gas, and anomalous heat effects were not observed.

The heat capacity of the adsorbed krypton was measured between 12 and 140°K. at surface concentrations of 0.00765, 0.01396 and 0.02421 mole. These quantities corresponded, respectively, to the fractions 0.13, 0.23 and 0.40 of the monolayer capacity. The results are shown in Fig. 1.

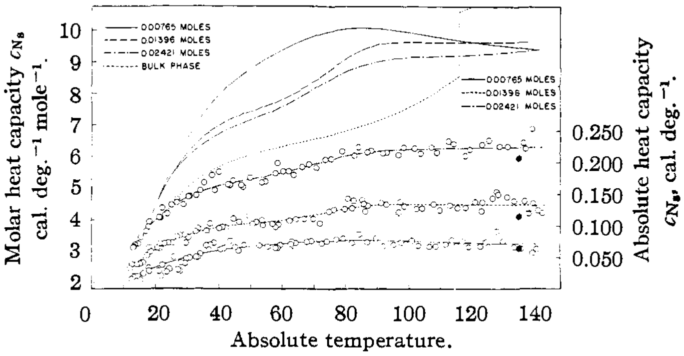

Fig. 1.—Heat capacity of krypton adsorbed on anatase.

Differential heats of adsorption were obtained at 130 and 140°K. By making use of the heat capacity data, the results were reduced to the single curve at 130°K. shown in Fig. 2.

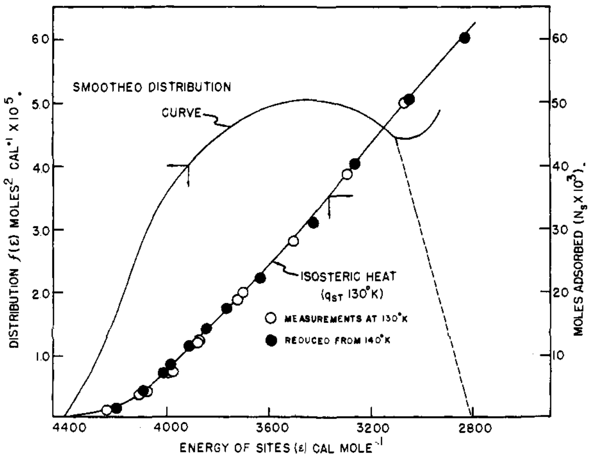

Fig. 2.—Isosteric heat and energy distribution for krypton adsorbed on anatase.

Equilibrium pressure data for use in the entropy calculation were obtained at both 130 and 140°K.

Discussion of Results

The molar entropy $S_G(T, P_0)$ of N_s moles of adsorbed gas taken from the adsorbed state at 0°K. to the gaseous state at a temperature T and adsorbate equilibrium pressure P_0 is given by the expression

$$S_G(T,P_0) = S_0 + \int_0^T C_{N_s}/T\,dT + Q_{N_s}/T + R/N_s \int_0^{N_s} \ln P/P_0\,dN_s \quad (1)$$

in which S_0 is the zero point entropy; C_{N_s}, the molar heat capacity of the adsorbate; Q_{N_s}, the integral molar heat of adsorption.

The molar entropy $S_G(T, P_0)$ was calculated from the Sackur–Tetrode equation. The integral $\int_0^T C_{N_s}/T\,dT$ was evaluated between 0 and 12°K. for coverages of 0.13 and 0.23 monolayer and between 0 and 14°K. for 0.40 monolayer assuming the adsorbed phase to be an assembly of independent, isotropic, three-dimensional harmonic oscillators. The frequency of the oscillators was determined from the lowest measured values of the molar heat capacity. The entropy contributions were then calculated from a table of Einstein functions. The remainder of the above integral was evaluated directly from the experimental data by the use of Simpson's rule. The last term in expression (1) was computed by graphical integration of plots of ln P/P_0 *vs.* N_s. The zero point entropy calculations for 0.00765, 0.01396 and 0.02421 mole of adsorbed krypton are summarized in Table I. The values of the zero point entropy for the fractions 0.13, 0.23 and 0.40 of the monolayer are, respectively, 1.1, 1.5 and 1.3 cal. deg.$^{-1}$ mole^{-1}.

Table I

Zero Point Entropies of Krypton Adsorbed on Anatase at 130°K.

Moles adsorbed	0.00765 $\theta = 0.13$	0.01396 $\theta = 0.23$	0.02421 $\theta = 0.40$
$\int_0^{12} C_{osc}/T\,dT$, cal./deg./mole	0.6	0.8	1.2[a]
$\int_{12}^{130} C_{N_s}/T\,dT$	17.0	15.8	14.9
$Q_{N_s}/130$	31.6	30.9	29.9
$R/N_s \int_0^{N_s} \ln P/P_0\,dN_s$	−2.2	−2.7	−3.3
S_G (130, P_0) (Sackur–Tetrode)	48.1	46.3	44.0
S_0	1.1 ± 1.1	1.5 ± 0.6	1.3 ± 0.3

[a] Extrapolated from 14°K.

The heat capacity, adsorption isotherm and heat of adsorption data between 130 and 140°K. are internally consistent to within ±10 cal. per mole in the molar integral heat of adsorption. The uncertainty in the heat capacity results approaches a value of about ±0.004 cal. deg.$^{-1}$ independent of coverage and temperature. The uncertainty in the entropy has been estimated as ±1.1 cal. deg.$^{-1}$

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(3) E. L. Pace, L. Pierce and K. S. Dennis, *Rev. Sci. Instr.*, **26**, 20 (1955).

(4) E. L. Pace, D. J. Sasmor and E. L. Heric, This Journal, **74**, 4413 (1952).

mole^{-1} for $\theta = 0.13$, ±0.6 cal. deg.$^{-1}$ mole^{-1} for $\theta = 0.23$ and ±0.3 cal. deg.$^{-1}$ mole^{-1} for $\theta = 0.40$. Most of this uncertainty comes from the heat capacity measurements.

The results indicate strongly that thermodynamic equilibrium has not been attained between the surface and the adsorbed krypton. The experimental procedure which was used as well as theoretical considerations lead one to believe that most of the randomness in the system existing at approximately 50°K. was preserved at temperatures below this value. From the standpoint of the experimental procedure in cooling which was followed, the relatively rapid cooling of the calorimeter from 50 to 12°K. prior to heat capacity measurements appears to be the most likely step during which equilibrium may not have been attained. If we accept as a reasonable model for the adsorbed gas one for which the molecules are adsorbed in monomolecular fashion on a heterogeneous surface and molecular interaction is neglected, it is possible to calculate the configurational entropy by the theoretical method developed by Hill.[5] Drain and Morrison[6] have utilized this method in their interpretation of the results of the argon–rutile system. Following essentially the same method as Drain and Morrison, we have used the continuous distribution of energy at the adsorption sites shown in Fig. 2 to compute values of the configurational entropy at 60°K. For coverages of 0.23 and 0.40 monolayers, these are 1.27 and 1.06 cal. deg.$^{-1}$ mole^{-1}. These theoretical results appear to be consistent with the experimental picture.

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

(6) L. E. Drain and J. A. Morrison, *Trans. Faraday Soc.*, **48**, 316 (1952).

CLEVELAND, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY[1]]

Low Temperature Heat Capacity and Entropy of Molybdenum Trioxide and Molybdenum Disulfide

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The heat capacities of crystalline MoS_2 and MoO_3 have been measured down to about 18°K. Both substances have layer-lattice structure and exhibit approximately T^2 dependence of C_p between 20 and 60°K. Because of the T^2 behavior prior extrapolations by the T^3 law below 50°K. are in error. Corrected values are given for S^0 and $\Delta H^0{}_f$.

A number of anisotropic substances which crystallize with so-called layer-lattice structure have been shown to exhibit a T^2 dependence of their heat capacity in the approximate range 15 to 60°K.[4–6] Theories concerning this behavior have been published by Tarassov,[7] Komatsu and Nagamiya,[8] Krumhansl and Brooks,[9] Rosenstock[10] and Newell.[11] The detailed interpretation of the observed approximate T^2 behavior in the low temperature range is still the subject of controversy. We therefore chose for study several additional compounds with layer structure. It has been shown by several of us[12] that the anisotropy in the cadmium iodide layer structure is insufficient to cause T^2 behavior of the heat capacity above 15°K., below which the measurements did not extend.

Two molybdenum compounds, the disulfide and trioxide, are good examples of layer lattice structures in polyatomic compounds and are, therefore, well suited to low temperature heat capacity investigations in connection with T^2 behavior. Molybdenum disulfide, MoS_2, the "moly" of commerce, has so marked a layer structure that it is slippery to the touch. This is true of both the natural mineral (molybdenite) and artificial preparations. MoS_2 and probably WS_2 are the only examples of sixfold coördinated layer structure in which the coördination is not octahedral; molybdenum disulfide is hexagonal with elongated bimolecular[13] units. Sulfur atoms lie at corners of right equilateral trigonal prisms which share vertical edges to build up MoS_2 layers normal to the C-axis. Molybdenum trioxide, MoO_3, is a white orthorhombic substance possessing fewer layer properties on the macroscopic scale, although it does cleave well parallel to certain

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(3) Department of Physical Sciences, Arizona State College, Tempe, Arizona; Summer Participant 1954, Oak Ridge National Laboratory.

(4) W. DeSorbo and W. W. Tyler, *Phys. Rev.*, **83**, 878 (1951); *J. Chem. Phys.*, **21**, 1660 (1953), graphite; W. DeSorbo, *ibid.*, **21**, 168 (1953), gallium.

(5) A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *ibid.*, **21**, 954 (1953); **22**, 837 (1954), boron nitride.

(6) E. F. Westrum and J. J. McBride, *Bull. Am. Phys. Soc.*, **29**, No. 8, 22 (1954), boron nitride and molybdenum disulfide.

(7) V. V. Tarassov, *Compt. rend. acad. sci. U.R.S.S.*, **46**, 20, 110 (1954); **54**, 795 (1946); *Doklady Akad. Nauk U.R.S.S.*, **58**, 577 (1947); *Zhur. Fiz. Khim.*, **24**, 111 (1950).

(8) K. Komatsu and T. Nagamiya, *J. Phys. Soc. Japan*, **6**, 438 (1951); K. Komatsu, *ibid.*, **10**, 346 (1955).

(9) J. Krumhansl and H. Brooks, *J. Chem. Phys.*, **21**, 1663 (1953).

(10) H. B. Rosenstock, *ibid.*, **21**, 2064 (1953).

(11) G. F. Newell, "Specific Heat of Lamellar Crystals," Technical Report from Brown University to Office of Naval Research, Physics Branch, December 15, 1954.

(12) A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, THIS JOURNAL, **77**, 1305 (1955).

(13) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, Chap. IV, Text p. 9.