[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Effect of Sorption on the Structure of Surfaces of Solids. II. Sorption of NO_2–N_2O_4 on Rutile[1]

BY L. H. REYERSON AND J. M. HONIG

RECEIVED DECEMBER 3, 1952

The sorption of NO_2–N_2O_4 on rutile differs markedly from the usual physical adsorption isotherms reported in the literature. An interpretation of these isotherms is given in terms of the deviation of the solid from the stoichiometric composition. The applicability of adsorption experiments for obtaining information on the chemical properties of solids is discussed.

Introduction

This investigation deals with the system nitrogen dioxide–tetroxide sorbed on rutile. Special emphasis will be placed on the differences between the adsorption isotherm reported here and those generally encountered in the literature. The object of this work is to show, on the basis of these differences, how information concerning the chemical properties of some solids may be obtained from a study of adsorption phenomena.

Experimental

The rutile was taken from the same source material as was used in earlier experiments on the adsorption of N_2, O_2 and A.[2] The NO_2–N_2O_4 was fractionally distilled in an all glass vacuum line until the condensate appeared snow white by comparison to a color chart. The first and last fractions were discarded and the volatile impurities removed after each fractional distillation by pumping to pressures of the order of 10^{-5} mm. A sensitive quartz spiral balance was used to study the uptake of gas as a function of pressure. The entire vacuum line was suspended on a rigid steel tower frame so designed that vibration in a high vacuum was reduced to a minimum. The cryostats necessary for precise temperature control (to be described later) were set on an independent base inside the tower frame. The spring and coaxial reference rods were suspended from a double hook, held on a "vibrationless mount" which itself was set on the steel frame. The spring was thermostated by circulating water through a surrounding jacket; this was found to be essential since the spring extension changed noticeably with temperature changes.

The sample was maintained at constant temperature by use of cryostats similar in design to that employed by Scott and Brickwedde.[3] Temperature regulation to ±0.02° was achieved by use of a standard thyratron phase shift circuit.[4] A platinum resistance thermometer, forming one arm of a Wheatstone bridge, was used as the temperature detecting element. It controlled the light intensity falling on the photocell of the phase shift circuit. In case of failure of this device rough (±2°) temperature regulation could be maintained by use of micromax potentiometer connected to a five junction copper–constantan thermocouple. Pressure regulation of the gas was achieved by cryostating the condensed phase in a U-tube, using an arrangement similar to that just described.

The cryostat temperatures were determined by measuring the e.m.f. developed by a copper–constantan thermocouple. Readings of the spring position with respect to the reference rod were taken with a Gaertner travelling telescope to within ±2 microns.

Procedure and Calculations.—In order to prevent contamination by pump oil, the samples were heated to the outgassing temperature before beginning the evacuation. The entire system was flamed 10–20 times to free the glass walls from adsorbed gases until the pressure during heating did not exceed 10^{-5} mm. The spring envelope was blackened with an acetylene torch (burning no oxygen); a bank of six infrared lamps was trained on the envelope and the whole assembly was enclosed in an aluminum radiation shield. After pumping two weeks the vacuum line was finally isolated from the pumps. The run was started by shattering the septum separating the N_2O_4 reservoir and the vacuum line.

Due to the corrosive nature of NO_2, none of the conventional pressure measuring devices could be included in the vacuum line. It was felt that by measuring the temperature of the condensed phase and then using the Antoine equation for calculating the vapor pressure, sufficiently accurate values would be obtained. The necessary equations were specified by Reyerson and Wertz[5] who fitted the Antoine equation[6,7] to the data of Giauque and Kemp.[8] The calculated vapor pressures are in excellent agreement with those determined in the last 50 years by several authors[9–13] over the range of temperatures from −60° to +35°.

Unfortunately this method does not allow corrections to be made for the changes in pressure which result from the small amounts of NO, N_2O_3 and NOCl that were observed to be present at the conclusion of the runs. The adsorption curves for these runs are, therefore, subject to experimental error in their location along the pressure axis. However, the conclusions which are drawn in the later sections were based solely on the over-all appearance of these curves and are thus not likely to be in error.

Buoyancy corrections were made in order to correct for the forces acting on the sample, container, fibers and spring. The corrections for the first three were calculated by the use of Archimedes' principle. The buoyancy force acting on the spring was obtained experimentally by noting the change in spring extension (spring supporting its full load) per unit change in air pressure. The computations require evaluation of the degree of dissociation, α, of N_2O_4 into NO_2 at the various temperatures. The quantity α was obtained from the equilibrium constant of the reaction $N_2O_4 = 2NO_2$ the latter being computed according to values of the quantity $\Delta(F^0 - H^0_0)/T$ listed by Giauque and Kemp[8] at various temperatures. Their values were fitted by least squares calculations to the equation

$$-\Delta\left(\frac{F^0 - H^0_0}{T}\right) = \frac{1172}{T} - 2.496 \log T + 49.40$$

from which K could be readily computed, using H^0_0 = 12,870 cal./mole.

It was verified that neglect of gas imperfections did not introduce any appreciable error.

Experimental Results

Adsorption data for NO_2-N_2O_4 on rutile were obtained in the range from −16 to 29°. A presentation of all the isotherm data does not seem to be justified because the various curves differ from

---

[1] This investigation was supported by funds from the Office of Naval Research and from the Graduate School of the University of Minnesota.

[2] J. M. Honig and L. H. Reyerson, *J. Phys. Chem.*, **56**, 140 (1952).

[3] R. B. Scott and F. G. Brickwedde, *J. Res. Natl. Bur. Standards*, **6**, 401 (1931).

[4] R. H. Müller, R. L. Garman and M. E. Droz, "Experimental Electronics," Prentice–Hall, Inc., New York, N. Y., 1942.

[5] L. H. Reyerson and J. E. Wertz, *J. Phys. Colloid Chem.*, **53**, 234 (1949).

[6] C. Antoine, *Compt. rend.*, **107**, 681 (1888).

[7] G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

[8] W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

[9] A. G. C. Egerton, *J. Chem. Soc.*, **105**, 647 (1914).

[10] P. A. Guye and G. Drouginine, *J. chim. phys.*, **8**, 473 (1910).

[11] A. Mittasch, E. Kuss and H. Schlueter, *Z. anorg. allg. Chem.*, **159**, 1 (1926).

[12] (a) F. Russ, *Z. physik. Chem.*, **82**, 217 (1913); (b) F. Scheffer and J. Treub, *ibid.*, **81**, 308 (1912).

[13] J. W. Smith, *J. Chem. Soc.*, **130**, 867 (1927).

each other only very slightly. Therefore, only a typical isotherm obtained at −16° is shown here (see Fig. 1, curves A and B); the remaining data can be found elsewhere[14] in full detail. Although the BET theory[15] is not applicable to these data the BET plots are still linear in the usual range of surface coverage. Note that the points in Fig. 1 were obtained in three separate runs.

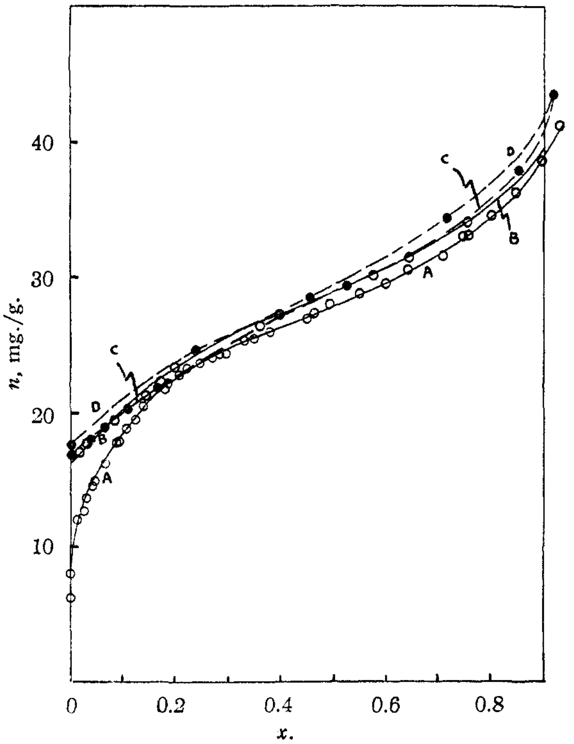

Fig. 1.—Adsorption of NO_2-N_2O_4 on rutile at −16°: A, B, original adsorption-desorption cycle; C, D, second adsorption-desorption cycle (full circles).

The abscissa values, *i.e.*, the "relative pressures" $x = p/p_0$ were computed by dividing the vapor pressure corresponding to the temperature of the reservoir cryostat by the vapor pressure corresponding to the temperature of the sample cryostat. This procedure has no real theoretical justification because in these experiments we deal with adsorption from a mixture of gases. The procedure merely offers a convenient method for reducing all pressure values to the same scale in all runs.

Discussion of Results

The adsorption of NO_2–N_2O_4 on rutile presents several features of interest.

1. The runs required between three weeks and two months each for completion. In passing from one point of the isotherm to the next there occurred a very rapid initial uptake for 5–10 minutes, followed by a slow adsorption process lasting from two hours to several weeks, depending on the sample temperature and the region of the isotherm.
2. The isotherms taken at different temperatures differ only very slightly in the appearance of their initial portions, contrary to what is normally encountered in physical adsorption. There is no shifting of the isotherms to smaller ordinate values with increasing sample temperature.
3. The weight changes are only partially reversible, in that all desorption curves such as curve B, Fig. 1, lie well above the adsorption curves such as curve A, Fig. 1. This is not the usual "hysteresis phenomenon" often encountered in the literature, since the discrepancy between the adsorption and desorption isotherms is accentuated at low surface coverage.
4. Upon completion of the desorption cycle in each experiment, the adsorbate–adsorbent system suspended from the spring showed a net weight increase of 16 mg. per gram of sample. To get back to the original sample weight it was found necessary to heat the sample to 400° while keeping the NO_2–N_2O_4 condensed phase at Dry Ice temperature.
5. Most of the initial weight increase of the adsorbent–adsorbate system occurred in the remarkably low pressure range of 40–500 microns. Evidently a strong interaction between adsorbate and adsorbent must have taken place to account for the large weight changes at such low pressures.
6. The adsorption and desorption isotherms obtained with a rutile sample which had not been heated during outgassing remained consistently below the corresponding curves obtained with the outgassed samples. In other respects the two types of isotherms are closely similar; observations 1–5 as well as 8 are equally applicable to isotherms obtained with the unheated rutile sample.
7. Upon repeating an adsorption run using the same rutile sample as in the original run the second curves were found to lie considerably above the original isotherm (compare curves C, D to A, B in Fig. 1). A similar experiment was carried out on the sample which had already been used in obtaining the 16° isotherms. This sample was again outgassed; using a freshly prepared quantity of NO_2–N_2O_4 an isotherm was then run at −7.6°. This isotherm lay much higher than all others; evidently, the rutile surfaces were markedly altered in the course of the first adsorption–desorption cycle.
8. After beginning the runs there was evidence of N_2O_3 formation as indicated by the presence of a blue ring in the cryostat. The condensed phase obtained in the N_2O_4 reservoir after chilling the latter to −78° at the conclusion of the run showed a distinct bluish-green tinge, as contrasted to the snow white appearance of the condensate prior to adsorption. In "dry runs" during which purified NO_2–N_2O_4 was allowed to circulate through the all-glass system in the absence of the sample, no contamination of the gas was observed.

These visual observations were confirmed by an infrared analysis of the adsorbate. At the conclusion of a run at 29° the reservoir was sealed off from the adsorption line and connected to a fluorite absorption cell which had been evacuated. The infrared spectral region in the range from 1200 to 3500 cm.$^{-1}$ was scanned several times while raising the reservoir temperature from −78 to 0°.

---

[14] J. M. Honig, Ph.D. Thesis, University of Minnesota, Minneapolis, 1952.

[15] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 390 (1938).

Careful comparisons of the infrared spectrum with the spectra cited in the literature were made; the presence of NO, NO_2, N_2O_3, N_2O_4 and NOCl in the gas phase was established on the basis of these comparisons.

9. Prior to degassing, the rutile sample was white. During the heating the sample darkened considerably, but at the conclusion of each run the solid once again had reverted to its original appearance.

Interpretation of Results

The evidence presented in the two preceding sections shows that the adsorption of NO_2–N_2O_4 on rutile is an exceedingly complicated process.

Observations 1–9 of the previous section are consistent with the concept that we are not dealing with a simple physical adsorption process but that a chemical interaction between rutile and nitrogen dioxide–tetroxide has occurred. The slow rate of approach to equilibrium infers the presence of an activated process. The very steep rise of the adsorption isotherm at low pressures and the alteration of the surface upon adsorption discussed in observations 5 and 7 are also indicative of strong adsorbate–adsorbent interaction. For this reason the usual theories concerning physical adsorption on inert surfaces are obviously not applicable. On the other hand, the existence of an initially rapid adsorption rate and of partial reversibility in desorption indicates that physical adsorption also occurs to some extent. The effect of raising the sample temperature is to enhance chemisorption and to diminish physical adsorption; these two opposing effects are undoubtedly responsible for observation 2.

In order to account for the chemical reaction that appears to take place between NO_2–N_2O_4 and rutile we propose the following working hypothesis: The rutile samples which were supplied for this investigation were deficient in oxygen, this oxygen deficiency being further accentuated by subjecting the sample to an outgassing temperature of 400° for two weeks at pressures below 10^{-5} mm. Upon adsorption of NO_2–N_2O_4, the oxygen deficient sites were reoxidized, resulting in a partial reduction of the adsorbate.

The plausibility of this hypothesis will now be examined in the light of its consistency with the above observations. Further evidence in favor of this hypothesis will be presented in the succeeding paper. In the first place, the formation of NO and of N_2O_3 is explained by this mechanism. The hypothesis is also substantiated in part by observation 9: it is known[16–18] that oxygen deficient rutile is dark in appearance. Observations 3–6 can also be interpreted on this basis. It is evident that during reoxidation the sample weight increased. The "isotherms" such as presented in Fig. 1, therefore, include a contribution arising from the weight increase of the sample. In the absence of further information it is difficult to correct for this contribution and such a correction will not be attempted here. It is clear, however, that the large weight increase at low relative pressure (see observation 5), as well as the behavior of the system in the desorption cycle (see observation 3 and 4), is due in large measure to the progressive increase of the sample weight during reoxidation. The slow oxidation rate and the long time intervals required for oxygen diffusion from exterior points to oxygen deficient sites inside the lattice were in all probability responsible for the slow rate at which the system reached equilibrium.

Finally, in order to account for the formation of NOCl it must be noted that the rutile samples used here were prepared commercially by hydrolysis of $TiCl_4$. Some of the $TiCl_4$ undoubtedly coprecipitated during hydrolysis. It is known[19] that a vigorous reaction between NO_2 and $TiCl_4$ occurs at room temperature, resulting in the formation of NOCl.

Conclusion

If the above working hypothesis is correct then the adsorption of NO_2–N_2O_4 can be used to obtain information on the physical properties of rutile. For example, an analysis for NO formed during adsorption would give an estimate on the number of surface defect sites in the lattice, and this value can then be compared to information obtained by such studies as conductivity, dielectric loss, or magnetic susceptibility measurements.

The present experiments indicate that the Ti:O ratio may vary over a wide range in rutile and that oxygen is easily removed from the lattice even under mild heating in a non-oxidizing atmosphere. Conversely, one finds that NO_2 may be used as a suitable oxidizing agent to replace oxygen lost from the lattice.

Finally, it is evident that the difficulties encountered in assays for titanium in rutile or anatase may be traced in part to the fact that these crystals readily form a lattice having a defective structure. Thus the sorption of NO_2 on rutile is a complicated chemical and physical process.

Acknowledgment.—The authors gratefully acknowledge the aid of Professor Dana Young and Mr. Jack Stevens for their coöperation in demonstrating the use of the IBM computers in calculations involving buoyancy corrections. They are indebted to Professor Bryce Crawford, Messrs. Ed. Meyers, Bert Zaslow and Dave Rotenberg for help in the infrared analysis. They also wish to acknowledge the part time help of Jerry Ulrich, Lowell Peterson, Louis Nidus, Art Dickson and the kind assistance of Gertrude Honig on the project.

MINNEAPOLIS, MINNESOTA

---

[16] P. Ehrlich, *Z. Elektrochem.*, **45**, 362 (1939).

[17] O. Ruff, *Z. inorg. Chem.*, **82**, 377 (1913).

[18] E. J. W. Verwey, *Philips Tech. Rev.*, **9**, 46 (1947).

[19] J. R. Partington and A. L. Whynes, *J. Chem. Soc.*, 3135 (1949).