

Studies on Adsorption of Oxygen on γ -Alumina. Nature of Adsorbed Species¹

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Adsorption of oxygen on γ -alumina has been studied over a temperature range from 77 to 129°K. and the results have been analyzed in terms of an equilibrium constant K_x for $2O_2 \rightleftharpoons O_4$, proposed previously on the basis of magnetic susceptibility data. The adsorption isotherms and isosteres have been resolved into component curves showing contributions from both O_2 and O_4 species. From the component isotherms and isosteres for O_2 and O_4 , the heats of adsorption for these species have been evaluated; the difference, ΔQ_s (~ -552 cal./mole), between these heats of adsorption is seen to correspond to the heat of dimerization ΔH (~ -500 cal./mole) obtained separately from K_x values based on the magnetic data for the singlet O_4 state. Similarly, the assumption of a triplet state leads to a difference (~ -713 cal./mole) between the heats of adsorption, which corresponds to a ΔH of ~ -700 cal./mole found from the magnetic data. This correspondence between Q_s and ΔH values indicates that the proposed dimerization equilibrium is established in the adsorbed state of oxygen.

Introduction

A number of studies on physical adsorption and chemisorption of oxygen on various supports have been reported in the literature during the past decade. These cover areas ranging from changes in conductivity³⁻⁵ photochemistry,⁶⁻⁸ spectroscopy,^{9,10} to kinetic studies.¹¹ Very few of these studies and those reported prior to 1950 have been oriented toward an investigation of the nature of the molecular species formed during physical adsorption. While some magnetic investigations of oxygen adsorbed on silica gel, titania, and carbon have been reported, very few of these attempted to correlate the changes in magnetic susceptibility with the state of the adsorbed species.^{12-14a} This paper reports

studies of adsorption of oxygen on γ -alumina, which were undertaken to elucidate the nature of the adsorbed species. The magnetic susceptibility studies have been reported separately,¹⁵ which indicate the formation of dimeric species, O_4 . This work involved a careful determination of changes in magnetic susceptibility during the course of adsorption and also involved a detailed study of physical adsorption itself.

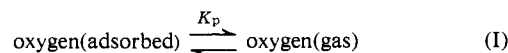
Experimental

The adsorption spring microbalance utilized in making these investigations has been described elsewhere.¹⁶ The adsorbent γ - Al_2O_3 was obtained through the courtesy of Dr. R. B. Emerson, Kaiser Aluminum and Chemical Corp., Baton Rouge, La., and had a surface area of 361 m.²/g. as determined by the B.E.T. method. A sample (~ 0.05 g.) was degassed to 10^{-7} mm. for 10 hr. at about 120° prior to each experiment. This has been shown to be sufficient for removing any physically adsorbed water vapor.¹⁷ The final isotherms obtained represent the average of three separate runs, with a maximum variation of 5%, using different amounts of alumina at each temperature. Equilibrium was seen to be attained at each pressure when there was no further increase in the amount of oxygen adsorbed. The oxygen used was obtained from General Dynamics and was 99.5% pure. It was passed over anhydrous magnesium perchlorate to remove any traces of water. The isotherms were obtained at 77, 90, 100, 113, and 129°K. using a specially designed cryostat.¹⁸

Results and Discussion

In this paper we shall use the term "oxygen" to represent the bulk adsorbate and the symbols " O_2 " and " O_4 " to represent the specific components of this bulk adsorbate. Here we propose to depict, on the following premises, the adsorption of oxygen on the surface of γ -alumina in terms of the initial formation of an O_2 layer which after reaching a certain critical concentration begins to dimerize to O_4 and thereafter continues to remain in equilibrium with it in all phases. The reader must note that the entire discussion on the dimer formation in the adsorbed layers must be contrasted from the usual studies on multilayer adsorption in inert gases, such as nitrogen, argon, etc., where there is no chemical interaction between the layers.

(1) The equilibrium



fessor, Princeton University) pointed out his comments on various multiplet states for dimeric oxygen (*Discussions Faraday Soc.*, **22**, 17 (1956)). The author (L. N. M.) wishes to thank them for their communications.

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(16) L. N. Mulay and L. K. Keys, *Anal. Chem.*, **36**, 2383 (1964).

(17) D. S. MacIver, H. H. Tobin, and R. T. Barth, *J. Catalysis*, **2**, 485 (1963).

(18) S. R. Butler and W. R. Buessem, *J. Appl. Phys.*, **34**, 1754 (1963).

(1) Paper to be presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) Laboratory for interdisciplinary research in chemistry, physics, planetary science, etc., participating in a graduate program in solid-state science.

(3) H. Uchida and Y. Ogino, *Bull. Chem. Soc. Japan*, **29**, 174 (1956).

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(5) J. O. Butler, *Trans. Faraday Soc.*, **56**, 1842 (1960).

(6) Y. Fujita and T. Kwan, *Bull. Chem. Soc. Japan*, **31**, 379 (1958).

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(10) K. Klier, *Kinetika i Kataliz*, **3**, 65 (1962).

(11) R. L. Pearson and M. E. Wadsworth, *Trans. AIME*, **212**, 294 (1958).

(12) J. Aharoni and F. Simon, *Z. physik. Chem. (Leipzig)*, **B4**, 175 (1929).

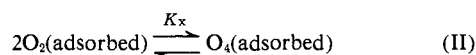
(13) A. W. Czanderna and J. M. Honig, *J. Phys. Chem.*, **63**, 620 (1959).

(14) R. Juza and F. Grazenick, *Z. Elektrochem.*, **54**, 145 (1950).

(14a) NOTE ADDED IN PROOF. Professor K. Hirota called our attention to his recent work suggesting the formation of O_4^- species on ZnO (*J. Catalysis*, **3**, 196 (1964)) and Dr. A. D. Buckingham (visiting Pro-

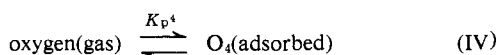
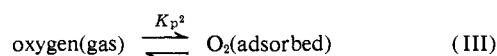
can be described by a pressure-type equilibrium constant K_p which is easily related to the pressure, p , observed under conditions of equilibrium.¹⁹

(2) However, the equilibrium



is better described by a concentration-type equilibrium constant, K_x , in view of the condensed or the quasi-liquid phase of the two species as considered in an earlier publication.¹⁵

(3) On the basis of the above premises one could then imagine separate equilibria between the gaseous oxygen and adsorbed O_2 , on the one hand, and gaseous oxygen and adsorbed O_4 , on the other.



(4) It should be further possible to think of separate equilibria similar to those described above based on assumptions that all dimer exists either in the singlet or in the triplet state for which two different sets of K_x values (and also heats of dimerization ΔH) were established previously.¹⁵

We shall first evaluate the isosteric heats of adsorption for oxygen based on premise 1 and later outline the consequences of assuming an equilibrium between oxygen gas and the adsorbed dimer O_4 according to equilibrium IV in premise 3. For the sake of simplicity the relationships pertaining to the dimer in the singlet state will be presented in some detail and the analogous inferences for the triplet state will be given.

Figure 1 shows the adsorption isotherms based on the experimental data for the amount of oxygen adsorbed at different pressures and temperatures. The surface area of the oxygen molecule²⁰ is 12.9 \AA^2 . Since the surface area of the γ -alumina is about $361 \text{ m}^2/\text{g}$, 1 g. of the sample is expected to adsorb 2.8×10^{21} molecules of oxygen corresponding to a monolayer capacity of 150 mg. Saturation (maximum) adsorption of alumina at 77°K . occurs with about 340 mg. of oxygen, which therefore represents a statistical coverage of 2.3θ . This coverage decreases with increasing temperature to about 0.7θ at 129°K .

Table I. Amount of Oxygen Adsorbed As a Function of Temperature ($^\circ\text{K}$.) at Constant Pressures

P , mm.	M , mg./g. of γ -alumina				
	77°	90°	100°	113°	129°
20	100	48	26	11	15
100	227	86	60	39	36
150	312	107	73	50	45
300		155	104	78	62
600		243	148	120	86
740		330	187	151	109

The data in Table I were obtained from the isotherms shown in Figure 1 and were used to obtain the isobars in Figure 2. For the convenience of showing all the isotherms clearly, the pressure P is used instead of the

(19) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(20) H. K. Livingston, *J. Colloid Sci.*, **4**, 484 (1954).

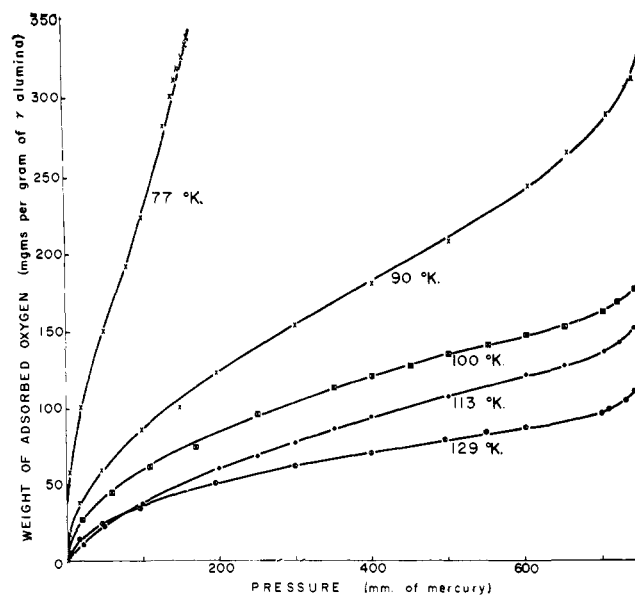


Figure 1. Adsorption isotherms for oxygen on γ -alumina at different temperatures.

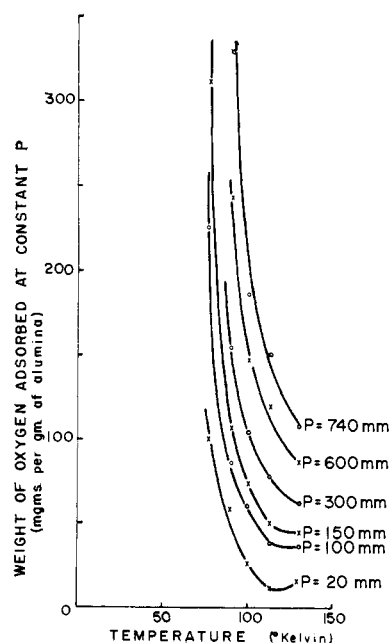


Figure 2. Adsorption isobars for oxygen on γ -alumina.

fraction P/P_0 , where P_0 is the saturation pressure corresponding to a particular temperature. This procedure spreads the curves out, giving a sharper separation, and leads directly to the $\ln P$ coordinate used in later figures. This approach does not change our interpretations in any way and was chosen to make them more apparent. The isosteric heat of adsorption based on premise 1 is obtained through the use of the derived Clausius-Clapeyron relation

$$\left(\frac{d \ln P}{dT}\right)_{n_{\text{ox}}} = \frac{Q_s}{R_0 T^2}$$

giving on integration

$$(\ln P)_{n_{\text{ox}}} = -\frac{Q_s}{R_0 T} + C$$

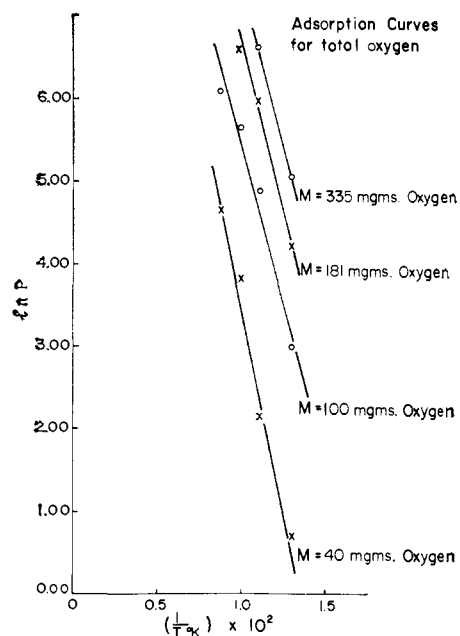


Figure 3. Plot of $\ln P$ vs. reciprocal temperature for oxygen on γ -alumina.

where Q_s is the isosteric heat of adsorption, P is the pressure in mm., R_0 is the gas constant, T is the temperature in $^{\circ}\text{K}$., C is an integration constant, and n_{O_x} refers to conditions of constant amount of oxygen adsorbed.

Figure 3 shows a plot of $\ln P$ vs. $1/T$ for oxygen, from which the physical heat of adsorption can be derived; however, since our major interest is to derive heats of adsorption for the O_2 and O_4 components, no special effort will be made here to derive the heat for total oxygen. The straight lines in Figure 3 (and also 5 and 7) involving more than two points represent the results obtained from a least-squares fit giving the best straight line.

The over-all adsorption isotherms for oxygen (shown in Figure 1) have been resolved into their component parts (Figures 4 and 6) corresponding to the respective contributions from the O_2 and O_4 species on the basis of the magnetic susceptibility data¹⁵ which helped to establish their concentrations as reported previously on the basis of the singlet (and also the triplet) states of O_4 . Extending premise 3 to the Clausius-Clapeyron relation we have

$$n_{\text{O}_x} = n_{\text{O}_2} + n_{\text{O}_4}$$

Thus isosteres for the O_2 and O_4 (singlet) components are obtainable from the relationships

$$(\ln P)_{n_{\text{O}_2}} = \frac{Q_{\text{O}_2}}{R_0 T} + C_1$$

$$(\ln P)_{n_{\text{O}_4}} = \frac{Q_{\text{O}_4}}{R_0 T} + C_2$$

Figure 5 gives the plot of $\ln P$ vs. $1/T$ for O_2 and O_4 (singlet), the data for which were obtained from Figure 4. It is interesting to note from Figure 5 that at low coverages the component curves for O_2 and O_4 give straight lines with almost identical slopes, and this yields a value of -2300 cal./mole for the heat of

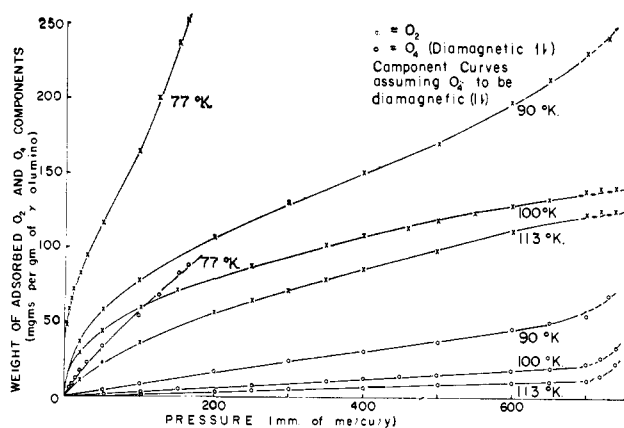


Figure 4. Isotherms for O_2 and O_4 (singlet) components adsorbed on γ -alumina (resolved from Figure 1 for total oxygen on the basis of magnetic data¹⁶).

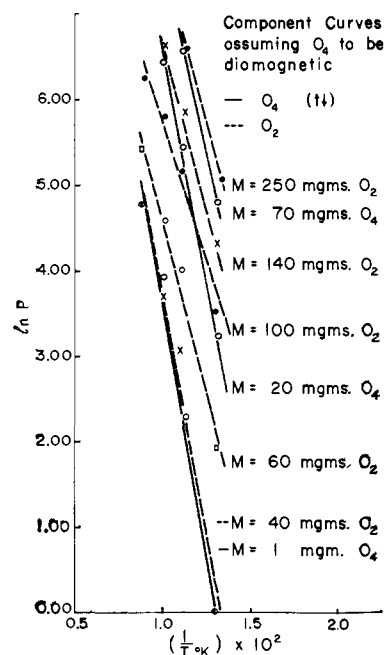


Figure 5. Plot of $\ln P$ vs. reciprocal temperature for O_2 and O_4 (singlet) components adsorbed on γ -alumina (obtained from Figure 4).

adsorption for each species. However, at relatively high coverages, the component curves separate out with different slopes. The heats of adsorption give an average value of -1651 cal./mole for O_2 and -2103 cal./mole for O_4 . Considering that both species exist in equilibrium at all times and that O_2 molecules are very likely to be adsorbed prior to the formation of O_4 species on the surface, any excess heat of adsorption for O_4 and O_2 obtained under conditions of maximum adsorption may be attributed to the heat of formation of O_4 from O_2 . This average excess ΔQ_s for O_4 [$-2103 - (-1651)$] is equal to -452 cal./mole, which is seen to correspond quite well with the average heat of dimerization ΔH of about -500 cal./mole obtained independently¹⁵ from an entirely different approach in which the $\log K_x$ from magnetic data were plotted against $1/T$. It should be noted that the magnetic susceptibilities observed for oxygen at low coverages (*i.e.*, less than a monolayer) correspond generally to its

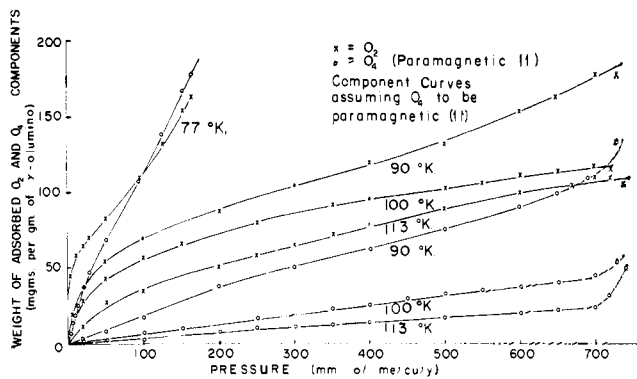


Figure 6. Isotherms for O_2 and O_4 (triplet) components adsorbed on γ -alumina (resolved from Figure 1 and on the basis of magnetic data¹⁵).

paramagnetism, whereas the susceptibilities at higher coverages (from less than a monolayer to greater than two layers) corresponds to polymeric oxygen in the singlet and/or triplet states. Some of the aspects of magnetic interaction in the O_4 species have been discussed previously,¹⁵ and a complete account of this based on e.p.r. studies, etc., will be published separately.

The agreement discussed above between the heats of formation for the dimer obtained from the isosteric heat data for O_2 and O_4 (in which interactions of the species with the surface are involved as a function of temperature) and from the dependence of the equilibrium constant K_x for the $2O_2 \rightleftharpoons O_4$ equilibrium on temperature leads to a significant conclusion, namely that the O_4 molecules are formed from the O_2 species which already have been adsorbed on the surface. The assumption of an O_4 triplet state gives us the component isotherm curves shown in Figure 6. This assumption gives $\ln P$ vs. $1/T$ curves for the components in Figure 7, which yield an average ΔQ_s value of about -713 cal./mole, in good agreement with the heat of formation ΔH (~ -700 cal./mole), obtained from the

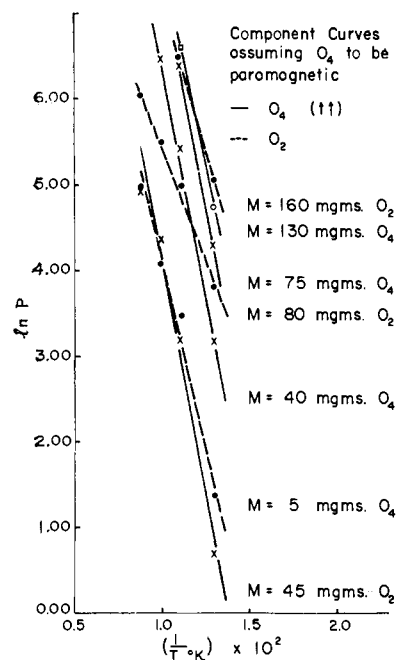


Figure 7. Plot of $\ln P$ vs. reciprocal temperature for O_2 and O_4 (triplet) components adsorbed on γ -alumina (obtained from Figure 6).

corresponding equilibrium constants obtained previously¹⁵ for the triplet state.

Acknowledgment. We wish to thank Mrs. Beth Porter and Mr. Raymond Kunz for their help with the Fortran IBM computer program for the least-squares analysis of our data. L. K. K. wishes to acknowledge the benefit derived from a predoctoral fellowship sponsored by the Paint Research Institute for basic research in an area of our choice. We are also thankful to the U. S. Atomic Energy Commission (Contract AT(30-1)-2581) for a grant which partially permitted the instrumentation described here.