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ADSORPTION OF GASES AND VAPORS ON GLASS SPHERES. II. TWO-DIMENSIONAL CONDENSATION OF OXYGEN¹

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Received February 24, 1956

Two-dimensional phase formation is described for oxygen on glass spheres at liquid air temperature. This phase formation was found absent at -78° . A supersaturated adsorbed phase is also described. The pressure of two-dimensional condensation is discussed in relation to surface activation and the van der Waals equation of state for surfaces.

In connection with studies in this Laboratory on the relationship of porosity of the adsorbent to adsorption the phenomenon of two-dimensional condensation was observed for nitrogen and oxygen. Also, it was found that supersaturation of the adsorbed phase may precede the formation of the two-dimensional two-phase system. In recent years, after the work on nitrogen² was published, a considerable amount of research has been done on this subject and a great deal more is known of the phenomenon.³ It is our object to present the research on the two-phase formation of the adsorbed phase of oxygen on glass spheres.

Experimental Details

Apparatus.—The adsorption system was of the volumetric type, and because of experimental low pressure requirements, the different parts of the system were separated by mercury cut-offs, and stopcocks were used only in the least sensitive areas.

One branch of the system included an adsorption vessel, a low temperature trap, a manometer, a buret and a McLeod gage. The adsorption vessel was a Pyrex flask of known volume with a graduated neck. The volume occupied by the adsorbent under different packings was measured by its position in the neck. The buret was used for calibrating the volumes of the different parts of the systems and for precise measurements of quantities of gas. Another part of the system was the evacuation branch. It included a vapor diffusion pump and a Hyvac oil pump connected in series. A third branch consisted of a vessel for storing the purified gas, a dosing stopcock for delivering approximate quantities of gas, and a purification train.

Materials.—Five thousand glass spheres which constituted the adsorbent and were approximately 3 mm. in diameter were cleaned with chromic and nitric acids, washed with distilled water and dried in an oven. Glass spheres treated in this manner showed by methylene blue⁴ adsorption to possess a real surface which was 54.5 times as large as the geometrical surface.

The oxygen was prepared by heating potassium permanganate in an evacuated system, and purified by passage through glass wool and potassium hydroxide. It was stored over phosphorus pentoxide. The helium used for calibration was purified by passage through activated charcoal at liquid air temperature.

Activation of Adsorbent.—The spheres were activated for adsorption measurements by heating and pumping at 250° in a high vacuum until a pressure less than 10^{-5} mm. of mercury was reached. The length of time that was required to attain this varied from 24 to 60 hours.

Thermal Flow Corrections.—The liquid air temperature and low experimental pressures required that the equilibrium pressures be corrected for transpiration. These corrections were made in accordance with the calibrations reported elsewhere.² No corrections were necessary in the isotherms at the temperature of carbon dioxide snow and ether.

Procedure.—A desired quantity of oxygen was introduced into the fore-chamber of the adsorption branch of the apparatus and its pressure determined on the manometer by means of a cathetometer reading to 0.01 mm. It was allowed to expand into the adsorption chamber by lowering the mercury cut-off separating these two parts of the adsorption branch. The pressure was measured at brief intervals on the McLeod gage until no further decrease in pressure occurred. This gage was of three stages, allowing the measuring of pressures in the ranges of from 10^{-5} to 10^{-3} , from 10^{-4} to 10^{-2} , and from 10^{-3} to 10^{-2} mm. of mercury. In making further additions of gas to the adsorbent, the mercury in the cut-off was raised to separate the adsorption vessel from the fore-chamber, a quantity of gas was introduced into the fore-chamber, its pressure measured, and allowed to expand into the adsorption chamber. The adsorption at any point n is given by the equation

$$A = \frac{V_1}{RT_1}(P_n - P_n^1) - \frac{V_2}{RT_2}P_n^1 \quad (1)$$

where V_1 and V_2 are the volumes of the fore-chamber and the adsorption vessel, respectively; P and P^1 are the pressures in the fore-chamber before expansion and at equilibrium after expansion, respectively, P_n^1 is the pressure in the cold adsorption chamber as corrected for transpiration; T_1 and T_2 are the absolute temperatures of the room and cold adsorption vessel, respectively.

Experimental Results

The isotherms obtained at liquid air temperature are shown in Fig. 1. Each isotherm was obtained on newly activated glass spheres packed at a different porosity and a different average number of contacts per sphere.⁵

Every isotherm in this figure, as in the case of nitrogen,² shows a sudden drop in pressure and a corresponding increase in adsorption, after a period of low linear adsorption that follows Henry's law. This behavior is strikingly illustrated in Fig. 2, where the equilibrium pressure is plotted as abscissa and, as the ordinate, is plotted the pressure that would prevail were the gas not adsorbed. In this plot the points of the initial linear adsorption process almost coincide with a linear curve representing the adsorption isotherm carried out at the same temperature in a blank vessel of volume equal to the void space in the adsorption flask.

The adsorption isotherms at the temperature of carbon dioxide snow and ether are given in Fig. 3. The number of contacts per sphere for the isotherms is different. These isotherms coincide, follow a linear course, and show no sudden pressure drop and no sudden adsorption increase.

The process following the sudden pressure drop in the low temperature isotherms was found to proceed slowly, in distinction to the rapid attainment of equilibrium at adsorption higher than that corresponding to the minimum pressure point.

(5) W. O. Smith, P. D. Foote and P. F. Busang, *Phys. Rev.*, **34**, 1271 (1929).

(1) Based on a M.S. thesis of Charles E. Weir.

(2) J. L. Shereshefsky and C. E. Weir, *J. Am. Chem. Soc.*, **58**, 2022 (1936).

(3) S. Ross and W. Winkler, *ibid.*, **76**, 2637 (1954); *J. Colloid Sci.*, **10**, 330 (1955).

(4) F. Paneth and A. Radu, *Ber.*, **57B**, 1221 (1924).

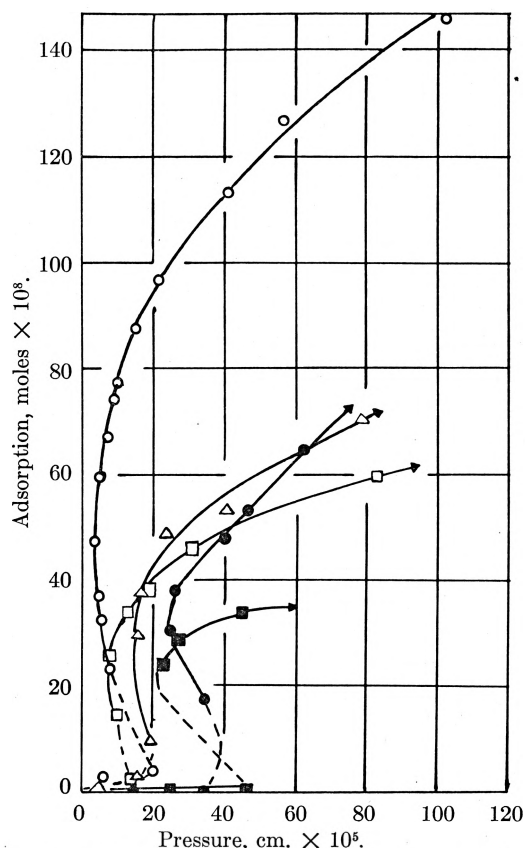


Fig. 1.—Adsorption of oxygen on glass spheres at liquid air temperature: ●, 8.5; ○, 9.3; ■, 8.0; □, 8.8; △, 9.0; contacts per sphere.

The pressure-time curves obtained in the broken line sections followed the equation

$$\ln (P/P_0) = kt \quad (2)$$

where P is the pressure at time t and P_0 is the initial pressure at $t = 0$. The value of the rate constant k for oxygen was found to equal that for nitrogen.²

Discussion

The phenomenon observed in this and the nitrogen studies, of a sudden drop in pressure accompanied by a rapid rise in adsorption, is considered by us to be due to the formation of a condensed two-dimensional phase. The sudden appearance of this phase is preceded by a labile supersaturated adsorbed phase, in which the adsorption varies linearly with pressure, in accordance with Henry's law. This interpretation is now amply corroborated.^{3,6} The transition of the labile adsorbed gas phase to the stable condensed phase is a slow process, taking place in accordance with equation 2 and following the paths indicated by the broken lines in Fig. 1.

According to the van der Waals type equation 3 for an adsorbed phase derived independently by DeBoer⁷ and Hill,⁸ condensation and the

$$P/P_0 = K_2 \theta / (1 - \theta) \exp(\theta/1 - \theta) \exp(-K_1\theta) \quad (3)$$

pressure at which it takes place are dependent on

(6) E. Weingaertner, *Z. Elektrochem.*, **42**, 599 (1936).

(7) J. H. DeBoer, "The Dynamical Character of Adsorption," Oxford, 1953, p. 170.

(8) Terrell L. Hill, *J. Chem. Phys.*, **14**, 441 (1946).

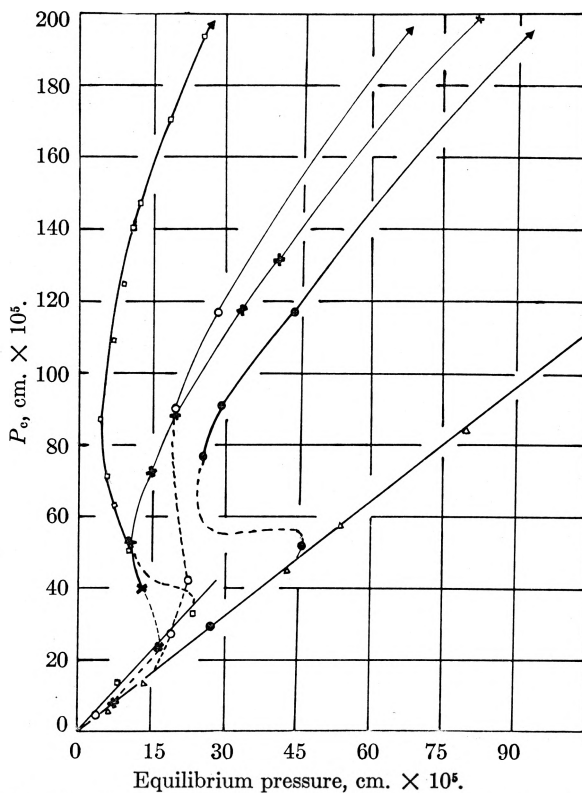


Fig. 2.—Transition of adsorbed oxygen phase: Δ, blank.

the values of the constants K_1 and K_2 . In this equation P/P_0 is the relative pressure and θ is the degree of surface population. The constant K_1 depends on temperature and the van der Waals

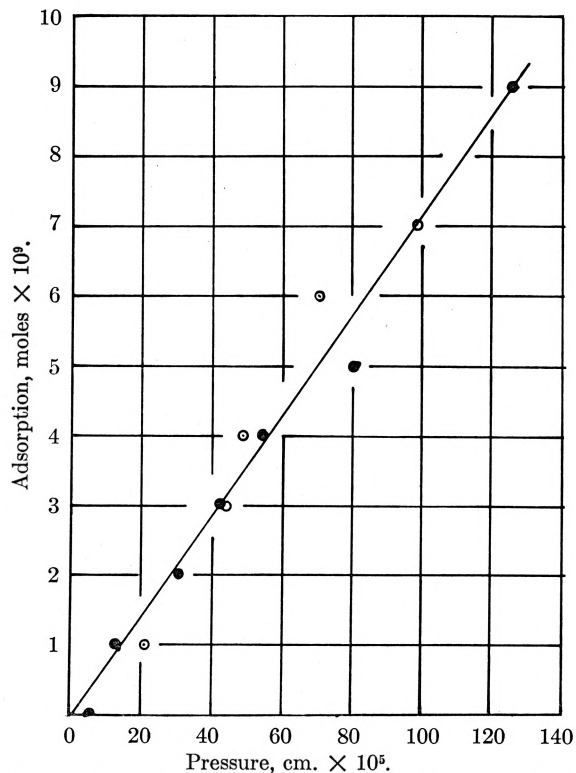


Fig. 3.—Adsorption of oxygen on glass spheres at -78° : ●, 8.8; ○, 9.3 contacts per sphere.

two-dimensional constants a and b . This constant depends only on the properties of the molecules of the adsorbate, which was the same in the several isotherms shown in Fig. 1. The constant K_2 , on the other hand, is related to the heat of adsorption, and measures mainly the strength with which the molecules are adsorbed on the surface. It appears therefore that the different minimum equilibrium pressures at which condensation takes place in the several isotherms are given rise by the variation in the energetic factors of the surface, and hence the variations in the constant K_2 .

The several isotherms presented here were obtained with the same spheres, but at different pack-

ings. In this connection, it is of interest to point out that there appears to be a correspondence between the amount of adsorption, the condensation pressure and the number of contacts per sphere. Since the sequence of obtaining the isotherms, and hence of the activation, was other than that of obtaining the different packings, the observed correspondence in the above properties cannot be ascribed to a successive change in activation of the adsorbent. It seems to us, therefore, that this relationship between the amount of adsorption, condensation pressure and the number of contacts per sphere is indicative of a greater probability of surface activity in the area of contact between two spheres.