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DETERMINATION OF ADSORPTION ISOTHERMS OF THE COMPONENTS OF BINARY GAS MIXTURES BY GAS CHROMATOGRAPHY

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SUMMARY

A method is described for calculating the adsorption isotherms of the components of a binary gas mixture as a polynomial function of their partial pressures.

The method is applied to the adsorption of oxygen-nitrogen mixtures on Linde Molecular Sieve 5A at temperatures from 10 to 50 °C and a total pressure of 1 atm.

INTRODUCTION

The determination of adsorption isotherms in binary gas mixtures has been described in only a few publications. The early investigators used stationary volumetric or gravimetric adsorption equipment^{1,2}, which led to complicated methods for obtaining data at a constant total pressure. Recent investigators have used gas chromatographic (GC) procedures. These methods can be subdivided into frontal chromatography³ and tracer pulse chromatography^{4,5}.

In frontal chromatography, low gas velocities are used in order to ensure the complete establishment of local equilibrium.

Tracer pulse chromatography was developed by PETERSON AND HELFRICH^{6,7} and was used for both single-component⁸ and multi-component^{4,5} adsorption. This method gives excellent results but it requires a special detection system for the radioactive isotopes. In a modified arrangement, stable isotopes could be used together with a mass spectrometer as detector. Special apparatus and isotopes must be available.

This contribution shows the possibility of determining adsorption isotherms in binary gas mixtures by using ordinary GC equipment. The principle of the method consists of measuring the retention volume, V_r , of a concentration perturbation (caused by the injection of a small pulse of one of the components) as a function of the partial pressure, p_1 , of component 1 by using a binary mixture of different compositions, p_1 , p_2 , as a carrier gas (at constant total pressure p and temperature). When this V_r - p_1 relationship is expressed as a polynomial function of p_1 of degree k , the isotherms of the components will also be polynomials of their partial pressure, generally of degree k . The coefficients of the polynomial isotherms can be calculated

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for $k = N + 1$, where N is the number of additional data on the adsorption of the components. For example, when the amount of each component adsorbed at $p_1 = p$ and $p_2 = p$ is known, $N = 2$ and the isotherms are obtained as third-degree polynomials. The adsorption of oxygen-nitrogen mixtures on Linde Molecular Sieve 5A was used as an example because of our recent studies on the separation of these mixtures by cycling zone adsorption⁹. Here the amount adsorbed of oxygen and nitrogen at $p_1 = 1$ and $p_2 = 1$ is obtained from the V_r-p_1 relationships in the mixtures oxygen-helium and nitrogen-helium, assuming that helium is not adsorbed. Together with the V_r-p_1 relationship of oxygen-nitrogen mixtures, they are used to calculate the oxygen and nitrogen isotherms in the binary oxygen-nitrogen mixture as third-degree polynomials.

THEORETICAL

Starting from the original chromatographic equation of MARTIN AND SYNGE¹⁰, HAYDEL AND KOBAYASHI⁵ derived a relationship between the retention volume of a concentration perturbation in a binary gas mixture at fixed composition and the slopes of the individual isotherms of the components. They used the equation

$$V_r = V_0 + \frac{m}{c} \left(c_2 \frac{dw_1}{dc_1} + c_1 \frac{dw_2}{dc_2} \right)$$

where

- V_r = retention volume (cm³).
- V_0 = free gas volume (cm³).
- m = mass of adsorbent in the column (g).
- $c = c_1 + c_2$ = total gas phase concentration (moles/cm³).
- c_1, c_2 = gas phase concentration of components 1 and 2 (moles/cm³).
- w_1, w_2 = specific amounts of components 1 and 2 adsorbed (moles/g).
- $dw_1/dc_1, dw_2/dc_2$ = slopes of the individual isotherms at the composition c_1, c_2 .

This equation, which can also be obtained from mass balances, is valid under the usually assumed conditions of constant temperature and pressure, homogeneously packed columns and negligible gas phase diffusion and radial effects.

By inserting partial pressures, p_1 and $p_2 = p - p_1$, for the concentrations and rearranging, we obtain:

$$\frac{(V_r - V_0)}{mRT} p = (p - p_1) \frac{dw_1}{dp_1} + p_1 \frac{dw_2}{dp_2} \equiv G(p_1) \quad (1)$$

Experimentally, V_r is determined as the retention volume of a concentration perturbation at different gas phase compositions. V_0 is the retention volume of an unadsorbed perturbation (He pulse in N₂ or O₂ as a carrier gas). Thus $G(p_1)$ is known through the experiments as a function of p_1 at a constant temperature.

To obtain from eqn. 1 the isotherms w_1 and w_2 as a function of their partial pressure, an integration procedure is required. If $G(p_1)$ is expressed as a polynomial function of p_1 of degree k , at least one of the isotherms must be a polynomial of degree k , and the other isotherm is a polynomial of equal or lower degree. In general:

$$G(p_1) = G_0 + G_1 p_1 + G_2 p_1^2 + \dots + G_k p_1^k$$

$$w_1 = a_1 p_1 + a_2 p_1^2 + a_3 p_1^3 \dots + a_k p_1^k$$

$$w_2 = b_1 p_2 + b_2 p_2^2 + b_3 p_2^3 \dots + b_k p_2^k$$

By curve fitting, the $k + 1$ coefficients G_j can be found. Substitution of the polynomial representation of $G(p_1)$, w_1 and w_2 in eqn. 1 gives $k + 1$ equations for the $2k$ unknown coefficients a_j, b_j . This system can be solved if $k + 1 = 2k$, and therefore for $k = 1$ only. When additional data are available, higher degree polynomials can be used. Experimentally well accessible are the "end-points" of the isotherms, viz., $(w_1)_{p_1=p}$ and $(w_2)_{p_2=p}$. Then there are $k + 3$ equations with $2k$ unknown coefficients, which means that the isotherms can be described in terms of third-degree polynomials. If a total of N independent additional reference points are known, the degree of the isotherm polynomials will be $N + 1$.

Using our experimental data, we have fitted each set of experimental retention volumes at a constant temperature into a third-degree polynomial of p_1 . The accuracy of this curve fitting is better than 5%, which is within experimental error limits.

From the V_r -polynomials the $G(p_1)$ -polynomials are calculated. The single component isotherms are determined from O_2 -He and N_2 -He experiments in which He is assumed to be unadsorbed (for these mixtures, $w_2 = 0$ and the coefficients a_j are calculated directly from $G(p_1)$). From these single-component isotherms, the end-points $(w_1)_{p_1=p}$ and $(w_2)_{p_2=p}$ are obtained. Working at a total pressure of 1 atm, the coefficients of the third-degree polynomial isotherms in the mixture can be calculated as follows:

$$a_1 = G_0$$

$$b_1 = G_0 + G_1 + G_2 + G_3$$

$$a_2 = (G_1 - 2(w_2)_{p_2=1} + a_1 + b_1) / 2$$

$$a_3 = (w_1)_{p_1=1} - a_2 - a_1$$

$$b_3 = G_3 + 3a_3$$

$$b_2 = (w_2)_{p_2=1} - b_3 - b_1$$

The detailed calculation of the coefficients is shown in APPENDIX I.

EXPERIMENTAL

Fig. 1 shows the experimental apparatus, which consists of two parts. The upper part is a gas handling system, in which the inlet pressures are controlled by double-stage pressure regulators (Dräger, Type Zwerg-Regulus I, 100-650 mm of water). The gases are purified by passing them over a deoxygenating catalyst (BASF, Type R 3-11) (not for oxygen) and over Linde Molecular Sieve 4A as a drying agent. The total gas flow-rate is kept constant by a mass flow controller (Brooks, Type 8843). The inlet and outlet pressures of the chromatographic column are measured with open U-tube mercury manometers. The individual flow-rates of the gas components are measured by capillary flow meters. These flow meters, shown in detail in Fig. 2, have exchangeable capillaries.

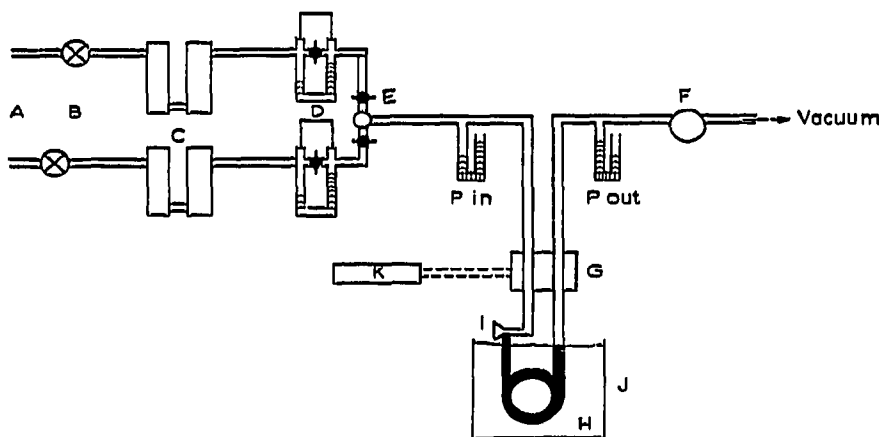


Fig. 1. Experimental apparatus. A = Gas feed; B = double-stage pressure regulator; C = gas purification; D = capillary flow meter; E = mixing chamber; F = mass flow controller; G = detector; H = column; I = injection point; J = thermostat; K = potentiometric recorder.

TABLE I

THIRD-DEGREE CURVE FITTING OF V_r AND STANDARD DEVIATION OF THE FITTING (D)

$$V_r = (a + bp_1 + cp_1^2 + dp_1^3) \text{ cm}^3 \text{ (column conditions).}$$

$$D = \sqrt{\frac{\sum_{i=1}^N (V_{ri} - a_1 - bp_1 - cp_1^2 - dp_1^3)^2}{N - 4}} \text{ cm}^3 \text{ (column cond.).}$$

where N = number of experimental points;

V_{ri} = experimental value of measurement no. i .

Mixture	Temp. (K)	a	b	c	d	D
O ₂ -He	283.4	+ 65.586	- 45.096	+ 22.081	- 18.256	0.96
	293.0	+ 59.521	- 29.496	- 8.742	+ 2.831	1.25
	302.9	+ 55.562	- 37.801	+ 21.823	- 15.208	0.69
	313.9	+ 51.174	- 30.274	+ 7.410	- 3.383	0.68
	323.5	+ 46.347	- 12.874	- 21.673	+ 13.895	0.63
N ₂ -He	283.5	+ 210.10	- 385.49	+ 320.70	- 122.29	1.39
	293.1	+ 172.10	- 263.32	+ 164.07	- 49.833	1.73
	302.9	+ 138.02	- 172.53	+ 66.821	- 8.676	1.09
	314.0	+ 109.08	- 111.95	+ 21.541	+ 4.870	0.61
	323.5	+ 92.103	- 77.541	- 6.236	+ 15.054	0.75
O ₂ -N ₂	283.6	+ 59.668	+ 68.983	+ 4.868	+ 72.105	1.27
	293.1	+ 57.343	+ 64.652	- 6.624	+ 49.204	1.07
	304.1	+ 53.449	+ 47.688	+ 0.053	+ 31.813	1.14
	313.7	+ 49.230	+ 45.978	- 1.588	+ 16.509	0.69
	323.5	+ 46.656	+ 36.329	- 1.399	+ 11.122	0.78

TABLE II

THIRD-DEGREE ISOTHERMS OF PURE COMPONENTS

$$w = (a_1 p_1 + a_2 p_1^2 + a_3 p_1^3) 10^{-6} \text{mole/g.}$$

Compound	Temp. (K)	a_1	a_2	a_3
O ₂	283.4	+ 118	- 5.5	+ 17.4
	293.0	+ 98.1	+ 8.2	- 2.6
	302.9	+ 83.6	- 8.9	+ 13.6
	313.9	+ 67.9	- 5.2	+ 2.9
	323.5	+ 51.8	+ 9.8	- 11.6
N ₂	283.5	+ 536	- 284	+ 117
	293.1	+ 413	- 158	+ 46.0
	302.9	+ 307	- 78.0	+ 7.8
	314.0	+ 221	- 34.1	- 4.2
	323.5	+ 173	- 11.0	- 12.6

Each capillary has its own flow region where, at pressure differences up to 10 cm of silicone oil, the flow-rate depends linearly on the pressure difference. The flow meters are calibrated by means of a bubble flow meter and checked with a thermal mass flow meter (Hastings, Model E ALL-50X).

The lower part of the apparatus in Fig. 1 contains the GC column immersed in a 45-l water thermostat controlled to within 0.02 °C. The detector is a liquid immersion thermistor-type thermal conductivity detector (Gow Mac, Type 10-677) installed in a Dewar flask containing ice-water.

The GC column is 200 cm long, I.D. 0.4 cm, and contains 15.0 g of Linde Molecular Sieve 5A, particle size 45-60 mesh. The sieve is previously activated by heating at 400 °C for 24 h in a stream of helium. The total flow-rate in the experiments varied from 15 to 20 cm³ (NTP)/min, depending on the pressure drop and on the composition of the mixture. The maximum pressure drop was about 10 cm of mercury, $P_{in} = +5$ cm Hg and $P_{out} = -5$ cm Hg, and the mean pressure was taken as 1 atm. The gas phase composition is controlled by the pressure regulators and was determined from the observed individual gas flow-rates. Samples of 50, 25 and 10 μ l of one or both components are introduced through the injection point. The retention times are measured with a chronometer and extrapolated to zero sample size. The experiments are carried out with the mixtures O₂-He, N₂-He and O₂-N₂ at temperatures of 10, 20, 30, 40 and 50 °C. The free gas volume is taken as the retention volume of a helium pulse, which is assumed to be unadsorbed, and using N₂ and O₂ as the carrier gas.

RESULTS

Fig. 3 shows plots of the retention volume as a function of the gas phase composition for the mixtures O₂-He, N₂-He and O₂-N₂. The coefficients of the corresponding third-degree polynomial isotherms are given in Table II.

The end-points required for the calculation of the isotherms in the O₂-N₂ mixtures are taken from the isobars at 1 atm of the pure components shown in Fig. 5.

In Fig. 6 the third-degree polynomial isotherms of the components in the binary

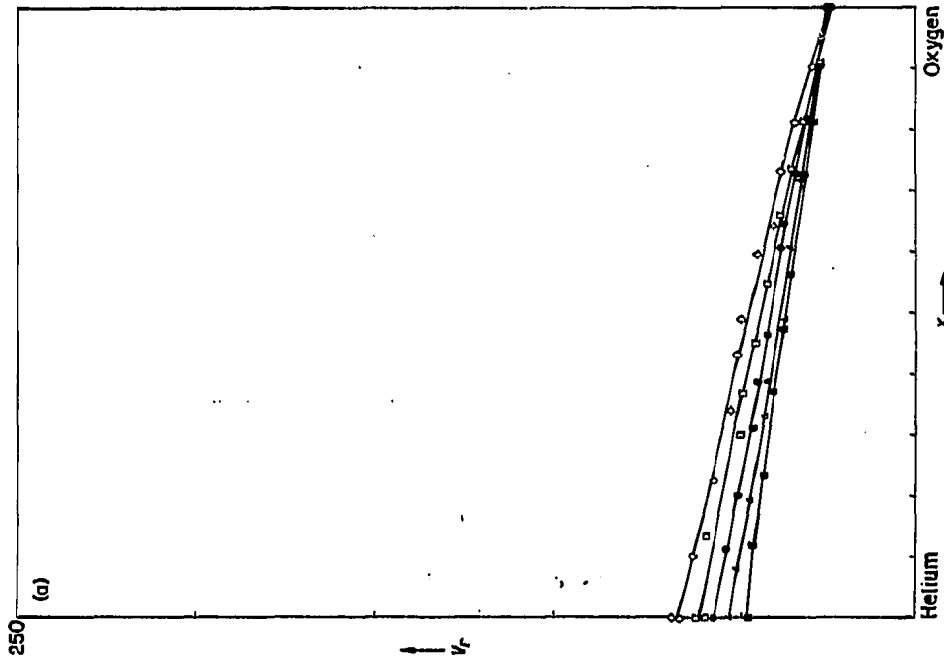


Fig. 3a.

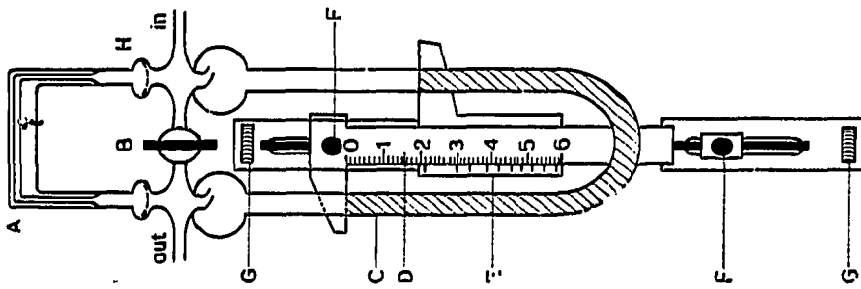


Fig. 2. Capillary flow meter. A = capillary; B = bypass valve; C = silicone oil; D = ruler; E = Vernier; F = coarse regulation; G = fine regulation; H = spherical glass joint.

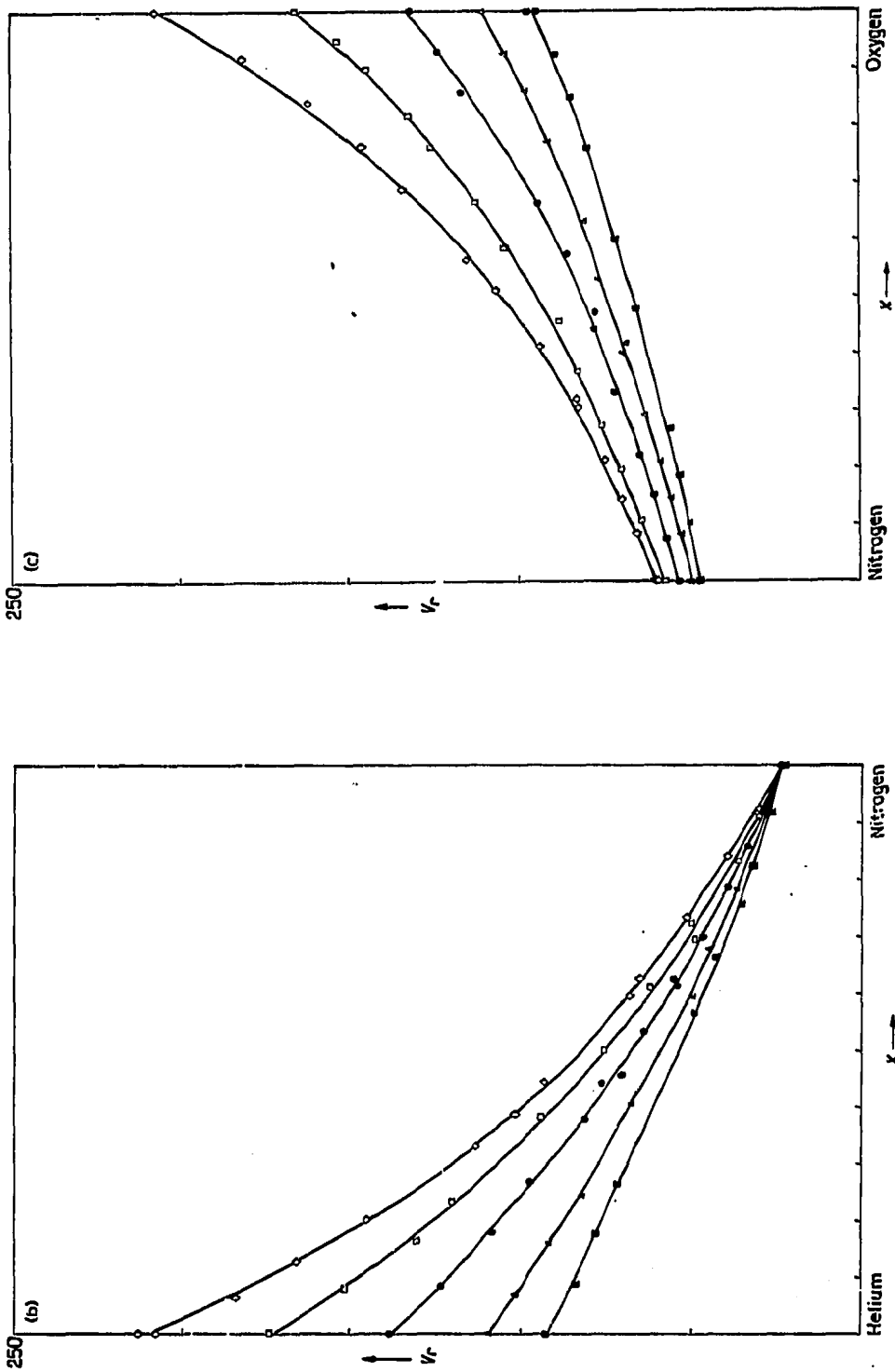


Fig. 3. Retention volume V_r (cm^3) as a function of the mole fraction x for (a) O_2 -He, (b) N_2 -He and (c) O_2 - N_2 mixtures. Total pressure 1 atm. Experimental points \blacksquare , \triangle , \bullet , \square , \diamond and \diamond determined at 283.5, 293, 314 and 323.5 K, respectively (see Table I). Solid lines represent the third-degree polynomial curve fitting.

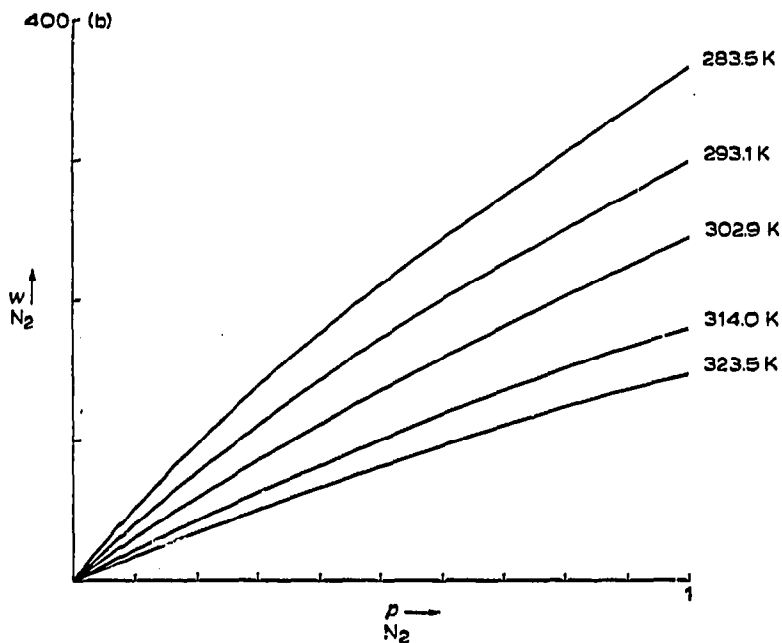
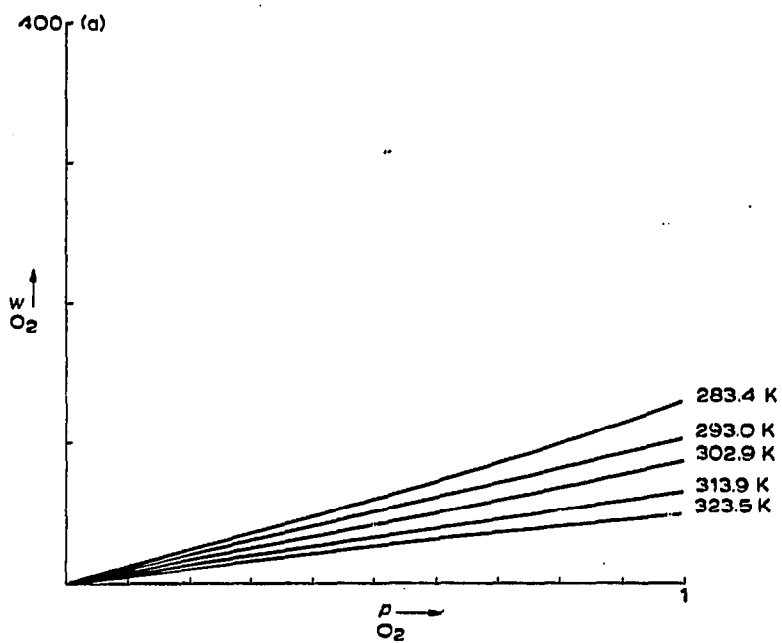


Fig. 4. Single-component isotherms for (a) oxygen and (b) nitrogen, with w in 10^{-6} mole/g and p in atmospheres (from measurements with He).

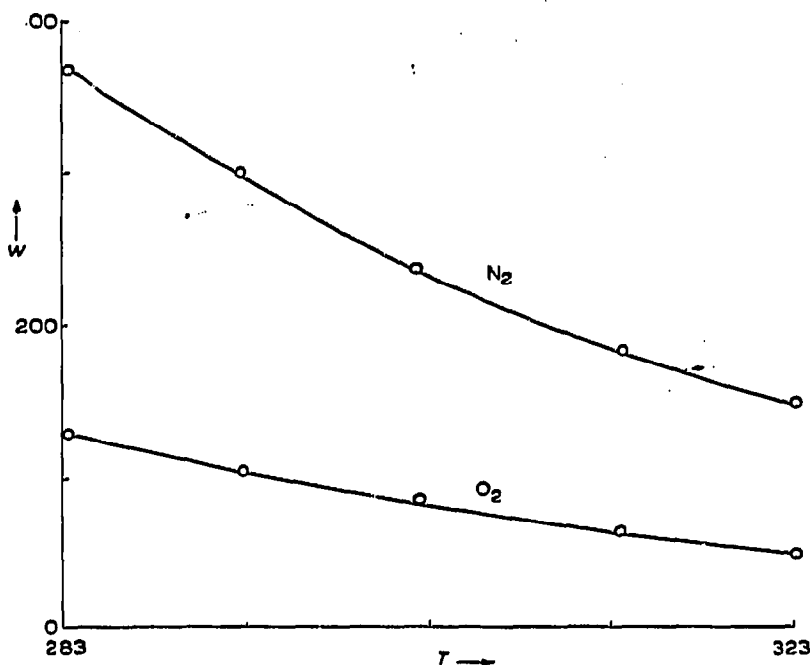


Fig. 5. Isobars of oxygen and nitrogen at 1 atm, with w in 10^{-6} moles/g and T in K.

O_2 - N_2 mixtures are plotted. Table III contains the coefficients of the polynomial mixture isotherms.

DISCUSSION

The experimental accuracy of the retention volume is about 5%, and the accuracy of the curve fitting is better than 5%. Fitting to a higher degree polynomial (we tried up to $k = 5$) did not produce a significant decrease in the standard deviation.

A rough estimation of the accuracy of the isotherms can be made by calculating the relative error in $G(p_1)$ at $p_1 = 0$. This gives the error in the initial slope of the isotherms, which can be considered to represent the error in the isotherms because the latter are only slightly curved. The error will be large when the retention volume is small. Thus the maximum error, 14%, is found for the O_2 single-component isotherm at the highest temperature, 323.5 K.

Comparison of the single-component isotherms with the isotherms in the binary mixture at 293 and 323.5 K shows that the adsorbates in the N_2 - O_2 mixture behave in an essentially similar manner to those of the pure components. There is no effect of mutual exclusion or hindrance. From B.E.T. measurements (adsorption of N_2 at liquid N_2 temperature), it is known that the monolayer volume at liquid nitrogen temperature is about $60 \text{ cm}^3 \text{ (NTP)/g}$ or $2700 \cdot 10^{-6} \text{ mole/g}$. When the monolayer volume at room temperature is the same, the maximum fraction of the surface covered by nitrogen is about 14%. The maximum fraction covered by oxygen

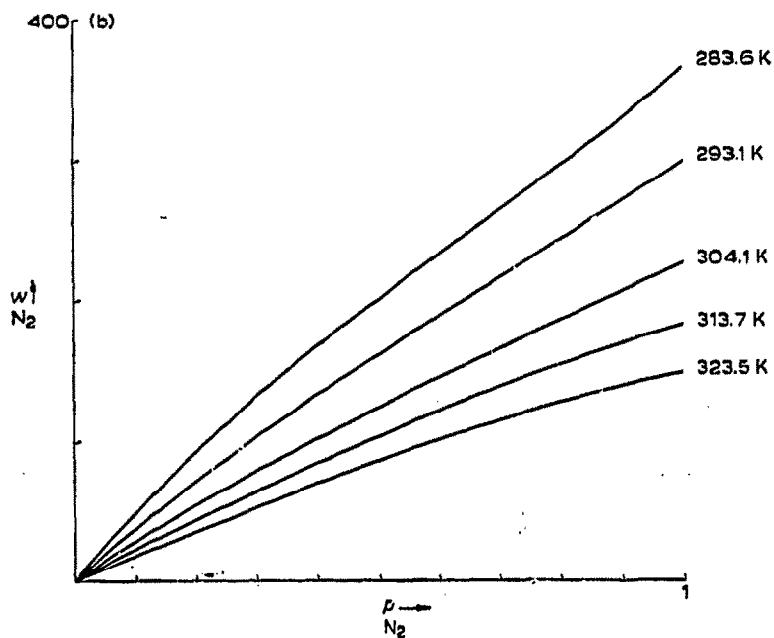
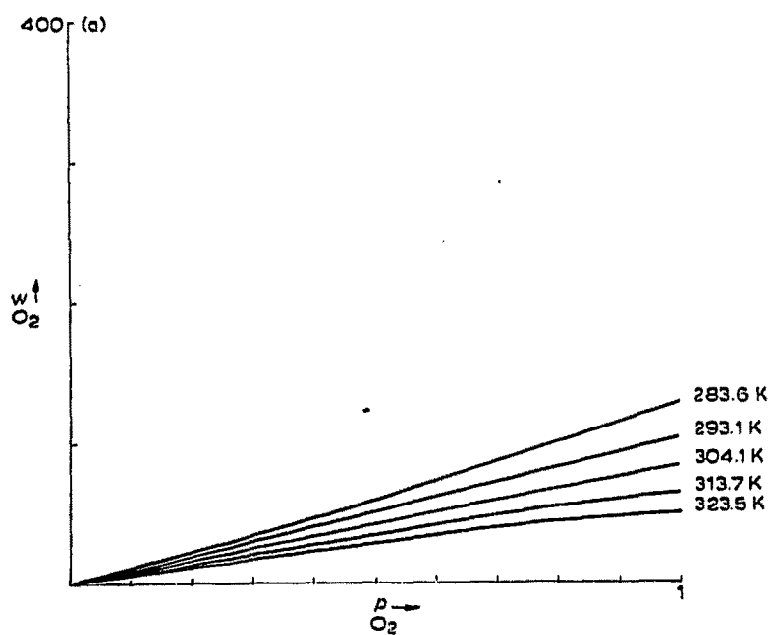


Fig. 6. Individual isotherms of (a) O_2 and (b) N_2 in the binary O_2 - N_2 mixture, with w in 10^{-6} moles/g and p in atmospheres. Total pressure 1 atm.

TABLE III

THIRD-DEGREE ISOTHERMS IN THE BINARY MIXTURE

$$w_{O_2} = (a_1 p_1 + a_2 p_1^2 + a_3 p_1^3) 10^{-6} \text{ mole/g.}$$

$$w_{N_2} = (b_1 p_2 + b_2 p_2^2 + b_3 p_2^3) 10^{-6} \text{ mole/g.}$$

Temp. (K)	a_1	a_2	a_3	b_1	b_2	b_3
283.6	+102	+41.8	-14.9	+520	-314	+162
293.1	+92.4	+29.4	-17.8	+389	-171	+83.0
304.1	+78.6	+20.5	-15.1	+291	-103	+39.6
313.7	+65.3	+19.7	-20.0	+223	-21.8	-17.2
323.5	+56.9	+13.7	-20.6	+179	-4.44	-33.9

is about 5%. Here the molecular area of oxygen was assumed to be 17.5 \AA^2 and of nitrogen 16.2 \AA^2 . Thus, no effects such as hindrance or exclusion of one of the components is to be expected. Heats of adsorption, determined by application of the Clapeyron relationship, are 3.0 and 4.5 kcal/mole for oxygen and nitrogen, respectively.

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APPENDIX I

Calculation of the coefficients of the third-degree polynomial isotherms at a total pressure of 1 atm.

$$G(p_1) = (1 - p_1) \frac{dw_1}{dp_1} + p_1 \frac{dw_2}{dp_2} \quad (1)$$

$$w_1 = a_1 p_1 + a_2 p_1^2 + a_3 p_1^3 \quad (2)$$

$$w_2 = b_1 p_2 + b_2 p_2^2 + b_3 p_2^3 \quad (3)$$

From eqns. 2 and 3:

$$\frac{dw_1}{dp_1} = a_1 + 2a_2 p_1 + 3a_3 p_1^2 \quad (4)$$

$$\frac{dw_2}{dp_2} = b_1 + 2b_2(1 - p_1) + 3b_3(1 - p_1)^2 \quad (5)$$

Inserting eqns. 4 and 5 in eqn. 1:

$$G(p_1) = (1 - p_1)(a_1 + 2a_2p_1 + 3a_3p_1^2) + p_1[b_1 + 2b_2(1 - p_1) + 3b_3(1 - p_1)^2]$$

or, after rearranging:

$$G(p_1) = a_1 + p_1(-a_1 + 2a_2 + b_1 + 2b_2 + 3b_3) + p_1^2(-2a_2 + 3a_3 - 2b_2 - 6b_3) + p_1^3(-3a_3 + 3b_3) \quad (6)$$

$G(p_1)$ is known from the curve fitting as:

$$G(p_1) = G_0 + G_1p_1 + G_2p_1^2 + G_3p_1^3 \quad (7)$$

Substitution of eqn. 6 in eqn. 7 leads to:

$$G_0 = a_1$$

$$G_1 = (-a_1 + 2a_2 + b_1 + 2b_2 + 3b_3)$$

$$G_2 = (-2a_2 + 3a_3 - 2b_2 - 6b_3)$$

$$G_3 = (-3a_3 + 3b_3)$$

Together with the known end-points of the single-component isotherms:

$$(w_1)_{p_1=1} = a_1 + a_2 + a_3$$

$$(w_2)_{p_2=1} = b_1 + b_2 + b_3$$

we have a set of six linear equations with six unknowns, which has the following solution:

$$a_1 = G_0$$

$$b_1 = G_0 + G_1 + G_2 + G_3$$

$$a_2 = (G_1 - 2(w_2)_{p_2=1} + a_1 + b_1)/2$$

$$a_3 = (w_1)_{p_1=1} - a_2 - a_1$$

$$b_3 = G_3 + 3a_3$$

$$b_2 = (w_2)_{p_2=1} - b_3 - b_1$$

In the case of the O_2 -He and N_2 -He mixtures, we assumed that He is not adsorbed. Now, b_1 , b_2 , b_3 and $(w_2)_{p_2=1}$ are zero and a_1 , a_2 and a_3 are directly obtained from $G(p_1)$ as:

$$a_1 = G_0$$

$$a_2 = (G_1 + a_1)/2$$

$$a_3 = -G_3/3.$$

REFERENCES

- 1 E. C. MARKHAM AND A. F. BENTON, *J. Amer. Chem. Soc.*, 53 (1931) 497.
- 2 G. DAMKOLER, *Z. Phys. Chem. (Leipzig)*, 23B (1933) 69.
- 3 G. SCHAY, GY. SZÉKELY AND G. SZIGETVÁRY, *Acta Chim. Acad. Sci. Hung.*, 12 (1957) 299 and 309.
- 4 H. B. GILMER AND R. KOBAYASHI, *Amer. Inst. Chem. Eng. J.*, 11 (1965) 702.
- 5 J. J. HAYDEL AND R. KOBAYASHI, *Ind. Eng. Chem., Fundam.*, 6 (1967) 546.
- 6 F. HELFRICH AND D. L. PETERSON, *Science*, 142 (1963) 661.
- 7 D. L. PETERSON AND F. HELFRICH, *J. Phys. Chem.*, 69 (1965) 1283.
- 8 D. L. PETERSON, F. HELFRICH AND R. J. CARR, *Amer. Inst. Chem. Eng. J.*, 12 (1966) 903.
- 9 E. VAN DER VLIST, *Separ. Sci.*, 6 (1971) 727.
- 10 A. J. P. MARTIN AND R. L. M. SYNGE, *Biochem. J.*, 35 (1941) 1358.