

Binary Adsorption Equilibrium on 4A Molecular Sieves

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ABSTRACT. Adsorption equilibria in the oxygen-nitrogen-4A molecular sieve pellets system are determined at two pressures of 1.7 and 4.4. bar and three temperatures 278.15, 293.15 and 303.15 K. The corresponding pure component isotherms for both gases are also determined at the same temperatures and at pressures up to 8 bar. The binary experimental data have been found to be predicted within a good accuracy by the ideal adsorbed solution theory of Myers and Prausnitz, Cooks and Bamadjian model and the statistical thermodynamic model of Ruthven *et al.* Fair agreement was obtained with the vacancy solution model of Suwanayuen and Danner.

The use of zeolite molecular sieve adsorbents as a means of separating or purifying gas mixtures is becoming increasingly popular as improved technology comes on the market (Breck 1973). Adsorption equilibrium for pure component systems have been extensively studied. By comparison, however, gas mixture data with special reference to oxygen-nitrogen mixtures are limited (Danner and Wenzel 1969, Torii *et al.* 1973, Ruthven 1976, Nolan *et al.* 1981, and Sorial *et al.* 1983).

For the proper design and modelling of adsorption processes a reliable predictive technique of estimating mixture equilibria from the pure component isotherm data is required. A number of techniques have been published in the literature (Cook and Basmadjian 1965, Myers and Prausnitz 1965, Ruthven *et al.* 1973, and Suwanayuen and Danner 1980). The lack of a comparative analysis of their merits due to limited reported experimental data makes it difficult to choose between one method and another.

In the present work experimental adsorption equilibria data at 278.15, 293.15 and 303.15 K and at 1.7 and 4.4 bar for oxygen-nitrogen gas mixtures on 4-A molecular sieve pellets are presented together with the corresponding pure component data. The experimental binary data are analysed against reported prediction models.

Experimental

Apparatus

The apparatus was of the volumetric type. The total quantity of gas admitted to the system and the amount remaining in the gas phase after equilibrium had been established was determined by appropriate P-V-T measurements and analysis by a gas analyser. The adsorbed phase composition and amount adsorbed were determined by the difference between the admitted and remaining gases. Details of the apparatus and experimental procedure were described in an earlier publication (Sorial *et al.* 1983). A schematic sketch of the apparatus is outlined in Fig. 1.

Materials

The adsorbent used in the study was molecular sieve type 4A supplied by Laporte Chemicals Ltd. (U.K.). It was of the form of 3-5 mm diameter pellets containing 20% by weight of inert binder and 80% Na A synthetic zeolite. The oxygen and nitrogen gases used were BOC (U.K.) commercial grade. The purity of nitrogen as reported by the manufacturer was 99.9% minimum and that of oxygen was 99.5%.

Results

Pure Gas Adsorption

Pure gas adsorption isotherms of oxygen and nitrogen on 4A molecular sieve pellets were determined at three temperatures 278.15, 293.15 and 303.15 K with pressures up to 8 bar. The experimental equilibria data are represented graphically in Fig. 2 and 3. Tables of data are available (Sorial 1982).

Binary Gas Adsorption

Adsorption equilibria data of oxygen-nitrogen mixtures on molecular sieve type 4A were determined at three temperatures 278.15, 293.15 and 303.15 K and two pressures 1.7 and 4.4 bar. The experimental results are presented graphically in Fig. 4 and 5 as a plot of the total amount adsorbed per unit mass of adsorbent *versus* the adsorbed phase composition together with a plot of the adsorbed phase

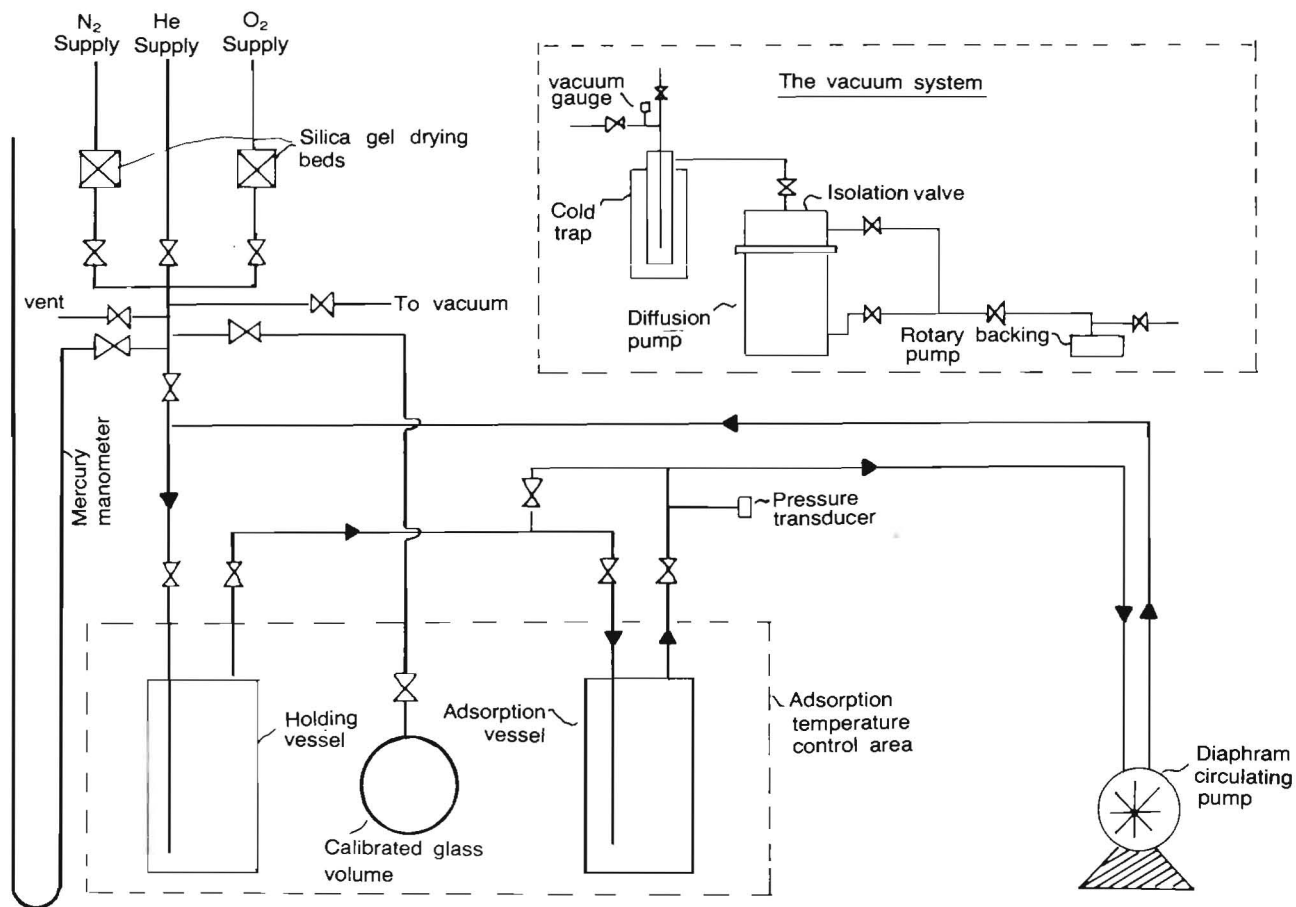


Fig. 1. Schematic sketch of the experimental apparatus

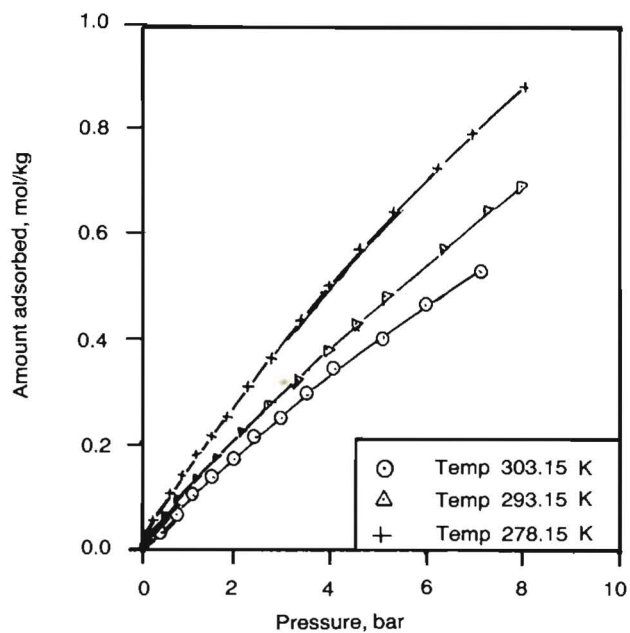


Fig. 2. Adsorption isotherms of oxygen on Laporte 4A molecular sieve pellets at 278.15, 293.15 and 303.15 K.

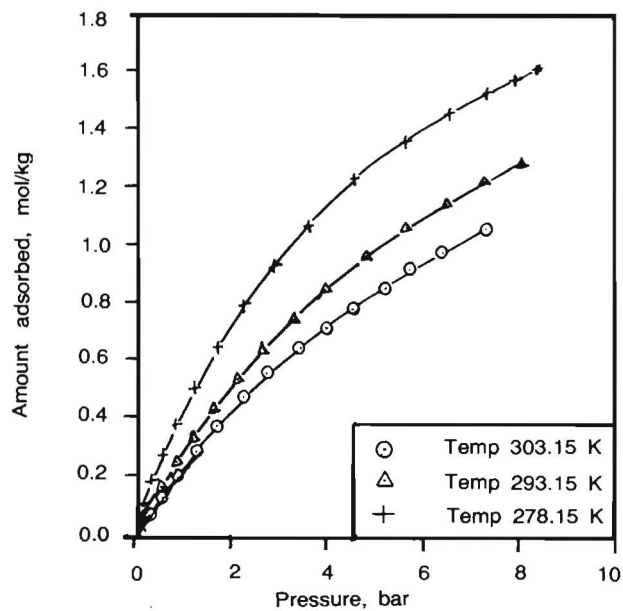


Fig. 3. Adsorption isotherms of nitrogen on Laporte 4A molecular sieve pellets at 278.15, 293.15 and 303.15 K.

composition *versus* the gas phase composition. Tables of binary equilibria data are also available (Sorral 1982). From Fig. 4 and 5 it can be seen that the separation factor ($y_{O_2} X_{N_2} / y_{N_2} X_{O_2}$) is very much less sensitive to temperature change or pressure change than is the total amount adsorbed and the total amount adsorbed is a strong function of the adsorbed phase composition.

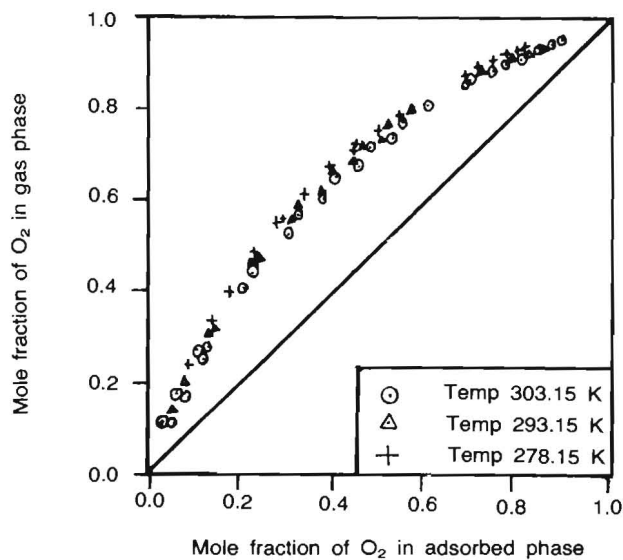
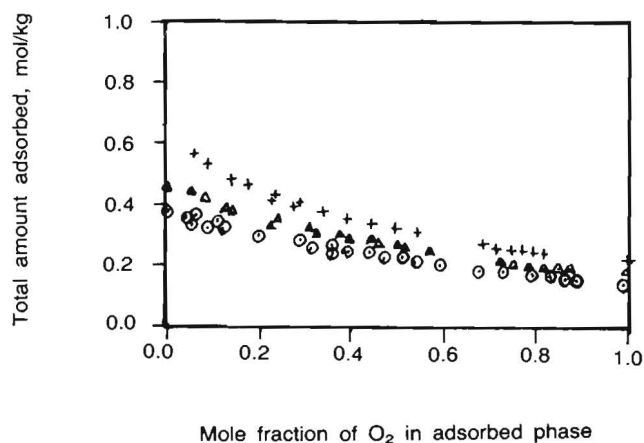


Fig. 4. Binary adsorption equilibria data of O₂/N₂ on Laporte 4A molecular sieve pellets at 303.15, 293.15 and 278.15 K (pressure = 1.7 bar).

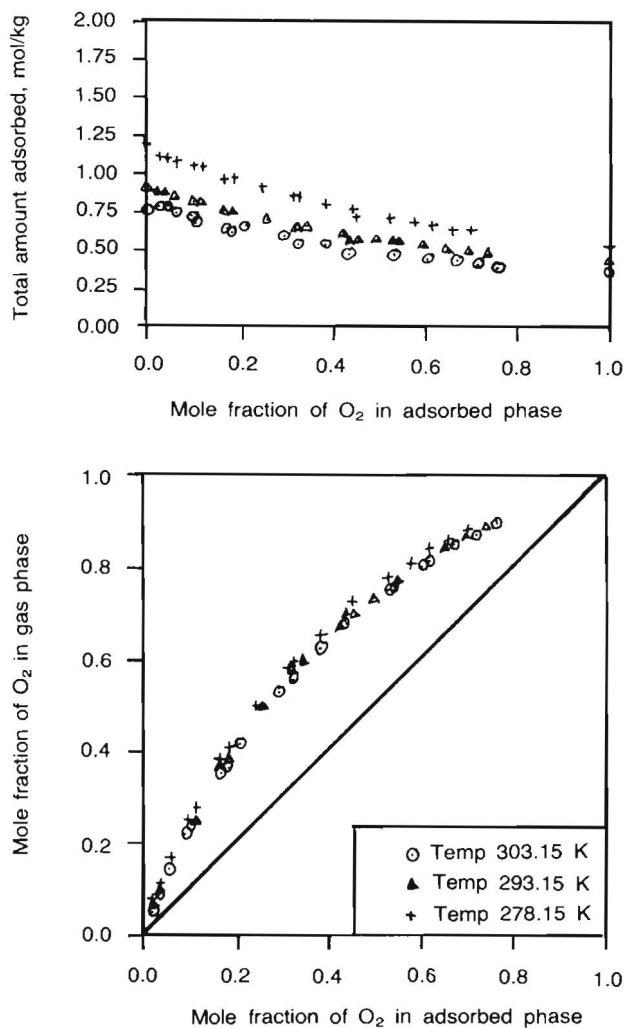


Fig. 5. Binary adsorption equilibria data of O_2/N_2 on Laporte 4A molecular sieve pellets at 303.15, 293.15 and 278.15 K (pressure = 4.4 bar).

Prediction of Binary Adsorption Equilibria

The prediction theories used for evaluating the data collected in this work were the semi-empirical model of Cook and Basmadjian (1965), the ideal adsorbed solution theory (IAST) by Myers and Prausnitz (1965), the statistical thermodynamic model of Ruthven *et al.* (1973) and the vacancy solution model by Suwanayuen and Danner (1980). A brief description of the method of application

of these models to this work is given by Sorial (1982) and Sorial *et al.* (1983). The regression parameters obtained from the pure component isotherms for the statistical thermodynamics model and the vacancy solution model are represented in Tables 1 and 2 respectively. For the Cook and Basmadjian model and the ideal adsorbed solution theory (IAST) the pure component isotherms were fitted to a rational equation of the form:

$$P = \left[\frac{A_1 n}{A_2 - n} \right] \exp \left[\frac{n}{A_3 - n} - A_4 n \right] \quad (1)$$

where A_1 , A_2 , A_3 and A_4 are regression parameters. The regression parameters of Equation (1) obtained from the pure component isotherms are represented in Table 3.

Table 1. Regression parameters for the statistical thermodynamic model*

Gas	$K = A_1 e^{A_2/T}$ molecule/cavity bar		$\beta = A_3 e^{A_4/T}$ A_3 /molecule		m molecules	Sum of squares of relative residual
	A_1	A_2	A_3	A_4		
O ₂	0.00118	1555.857	38.947	-38.3075	22	0.0093
N ₂	0.00011	2584.061	13.8418	453.834	11	0.016

* As applied to the adsorption of oxygen and nitrogen on Laporte 4A molecular sieve pellets at 278.15, 293.15 and 303.15 K

+ cavity volume = 776A³

1 mol/kg = 2.22 molecule-cavity

Amount of anhydrous adsorbent in pellet = 80%

Table 2. Regression parameters for the vacancy solution model*

Gas	n_m mol/kg	Temperature K	b mol/kg bar	A_{13}	A_{31}	Sum of squares of relative residual
O ₂	7.385	278.15	0.142	14.219	0.048	0.0029
		293.15	0.103	0.176	3.216	0.00034
		303.15	0.086	0.084	4.391	0.00016
N ₂	4.371	278.15	0.527	34.71	0.025	0.0022
		293.15	0.301	0.129	3.484	0.001
		303.15	0.237	0.142	3.391	0.0005

* As applied to the adsorption of oxygen and nitrogen on Laporte 4A molecular sieve pellets at 278.15, 293.15 and 303.15 K

Table 3. Regression parameters for equation (1)*

Gas	Temperature K	A ₁	A ₂	A ₃	A ₄	Sum of squares of relative residual
O ₂	278.15	19.013	2.665	102.255	0.1909	0.003
	293.15	34.55	3.577	5.117	0.2841	0.0004
	303.15	18.206	1.597	2.204	1.058	0.0004
N ₂	278.15	5.27	2.768	5.52 × 10 ⁷	-0.082	0.0018
	293.15	7.529	2.412	5.207 × 10 ⁶	0.051	0.0003
	303.15	8.848	2.181	2.073 × 10 ⁵	0.118	0.0003

* As applied to the adsorption of oxygen and nitrogen on Laporte 4A molecular sieve pellets at 278.15, 293.15 and 303.15 K

The relative residuals shown in Tables 2 and 3 are defined as the difference between the experimental and the predicted pressures divided by the experimental pressures whereas for Table 1 it is defined as the difference between the experimental and the predicted amount adsorbed divided by the experimental amount adsorbed.

The predicted results obtained by the four models at 293.15 K at pressures of 1.7 and 4.4 bar are shown in Fig. 6 and 7 by the respective lines. For the other temperatures studied similar trend was obtained (Sorial 1982).

Discussion of Results

Similar to our earlier reported work (Sorial *et al.* 1983), the predictions obtained by the statistical thermodynamic model, Cook and Basmadjian model and IAST were approximately the same and the predicted values were in good agreement with the experimental values (see Fig. 6 and 7).

The predictions obtained by the vacancy solution model were more reliable than the predictions obtained in our earlier work on 5A molecular sieve pellets (Sorial *et al.* 1983). They were in fair agreement with the experimental data. The deviations encountered by this model were again at oxygen concentrations in the adsorbed phase less than 50% for the 4.4 bar pressure study but were not as significant as those obtained on the 5A molecular sieve pellets. The effect of including the adsorbate-adsorbate interactions, A₁₂ and A₂₁, as suggested by Suwanayuen and Danner (1980), offered no significant improvement of the model.

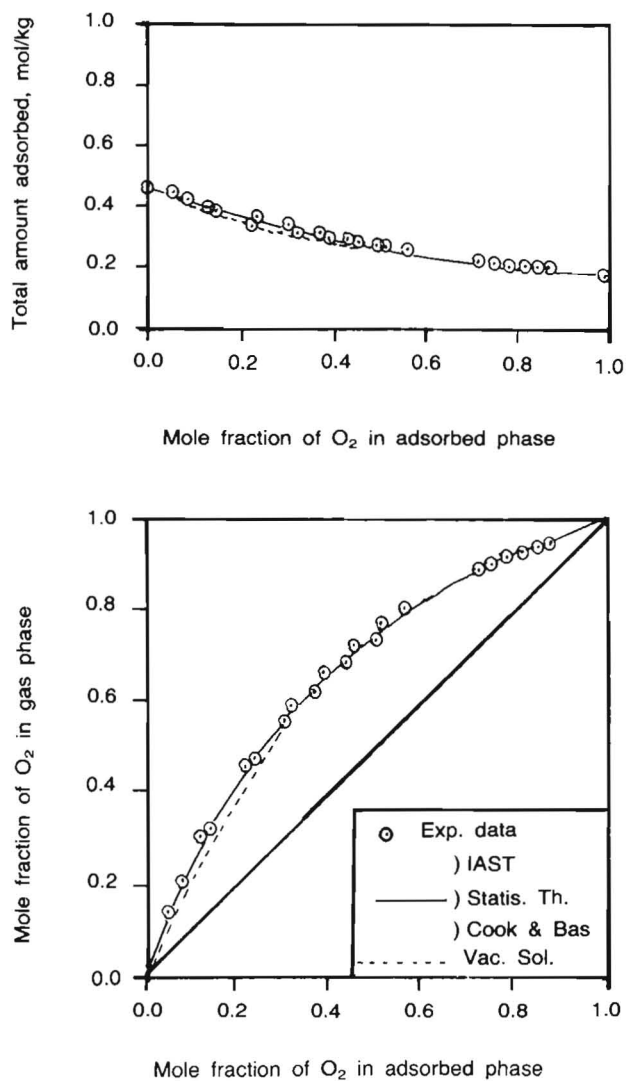


Fig. 6. Comparison of theoretical predictions of various models with experimental binary equilibria of O₂/N₂ on Laporte 4A molecular sieve pellets at 293.15 K (pressure = 1.7 bar)

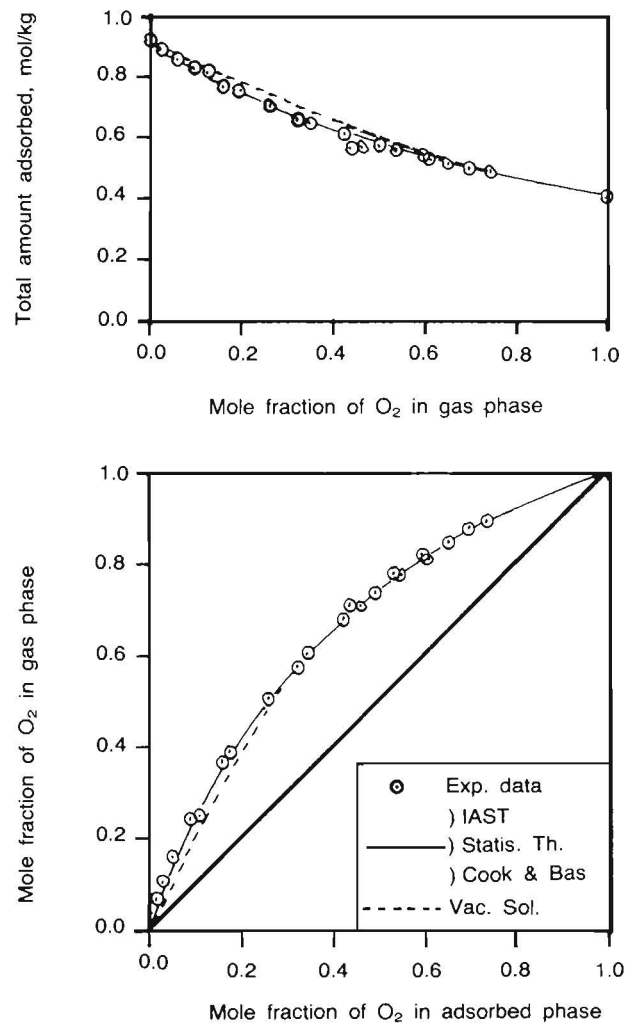


Fig. 7. Comparison of theoretical predictions of various models with experimental binary equilibria of O₂/N₂ on Laporte 4A molecular sieve pellets at 293.15 K (pressure = 4.4 bar)

Conclusions

Similar to our earlier reported work on 5A molecular sieve pellets (Sorial *et al.* 1983), the experimental data collected in this work showed that the effects of both temperature and pressure were very much less sensitive on the separation factor than the total amount adsorbed.

The statistical thermodynamic model, IAST and Cook and Basmadjian model predicted the binary experimental data with a good accuracy.

The predictions obtained by the vacancy solution model were not as good as the other three models and only fair agreement with the experimental data was achieved.

Nomenclature

A_{12} , A_{21}	Wilson's parameters for molecular interaction between 1 and 2 (vacancy solution model)
A_{13} , A_{31}	Wilson's parameters for surface interaction between 1 and 3 (vacancy solution model)
b	Henry's law constant in the vacancy solution model (mol/kg bar)
K	Henry's law constant in the statistical thermodynamic model (molecule/cavity bar)
n	amount adsorbed (mol/kg)
n_m	maximum number of moles on the adsorbed surface in vacancy solution model (mol/kg)
P	gas phase pressure (bar)
T	temperature of adsorption (K)
x	mole fraction in adsorbed phase
y	mole fraction in gas phase

Greek symbols

β	effective molecular volume of adsorbate ($A^3/\text{molecule}$) (statistical thermodynamic model)
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Subscripts

N_2	nitrogen component
O_2	oxygen component
1,2	adsorbates (vacancy solution model)
3	vacancy (vacancy solution model)

References

- Breck, D.W.** (1973) *Zeolite Molecular Sieves*, Wiley and Sons, New York, 259 p.
- Cook, W.H.** and **Basmadjian, D.** (1965) The Prediction of Binary Adsorption Equilibria from Pure Component Isotherms, *Can. J. Chem. Engng.* **43**: 78-83.
- Danner, R.P.** and **Wenzel, L.A.** (1969) Adsorption of Carbon Monoxide-Nitrogen, Carbon Monoxide-Oxygen, and Oxygen-Nitrogen Mixtures on Synthetic Zeolites, *A.I.Ch. E.J.* **15**: 515-520.

- Myers, A.L. and Prausnitz, J.M.** (1965) Thermodynamics of Mixed-Gas Adsorption, *A.I.Ch.E.J.* **11**: 121-127.
- Nolan, J.T., Mcheehan, T.W., and Danner, R.P.** (1981) Equilibrium Adsorption of Oxygen, Nitrogen, Carbon Monoxide, and Their Binary Mixtures on Molecular Sieve Type 10X, *J. Chem. Engng. Data* **26**: 112-115.
- Ruthven, D.M.** (1976) Sorption of Oxygen, Nitrogen, Carbon Monoxide, Methane, and Binary Mixtures of these Gases in 5A Molecular Sieve, *A.I.Ch.E.J.* **22**: 753-759.
- Ruthven, D.M., Loughlin, K.F., and Holborow, K.A.** (1973) Multicomponent Sorption Equilibrium in Molecular Sieves, *Chem. Engng. Sci.* **28**: 701-709.
- Sorial, G.A.** (1982) Binary Gas Adsorption on Molecular Sieves, *Ph.D. Thesis*, University of Bradford, 329 p.
- Sorial, G.A., Granville, W.H. and Dally, W.O.** (1983) Adsorption Equilibria for Oxygen and Nitrogen Gas Mixtures on 5A Molecular Sieves, *Chem. Engng. Sci.* **38**: 1517-1523.
- Suwanayuen, S. and Danner, R.P.** (1980) Vacancy Solution Theory of Adsorption from Gas Mixtures, *A.I.Ch.E.J.* **26**: 76-83.
- Torii, I., Hotta, M., Onodera, Y., and Asaka, H.** (1973) Adsorption of Nitrogen-Oxygen on Zeolite Tuff, *Trans. Chem. Soc. Japan* **2**: 225-232.

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توازن الامتزاز الثنائي على المنخل الجزئي ٤ أ

١ جورج عياد سوريال و ٢ هاري جرانتقل

١ قسم الكيمياء التطبيقية وتكنولوجيا الكيمياء - كلية العلوم والتكنولوجيا - جامعة الجزيرة

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٢ قسم الهندسة الكيميائية - المعهد الفني بويلز - ميد جلامورجن - بريطانيا

حددت حالة الاتزان الامتزازي الثنائي للأوكسيجين والنيروجين على حبة المنخل الجزئي ٤ أ تحت ضغط ١,٧ و ٤,٤ بار وفي درجة حرارة مطلقة ٢٧٨,١٥ و ٢٩٣,١٥ و ٣٠٣,١٥. خطوط درجة المتساوية حددت للعناصر النقية المتناظرة على نفس درجات الحرارة المطلقة وتحت ضغط يصل إلى ٨ بار. البيانات الناتجة من التجارب على النظام الثنائي وجد أنه يمكن التنبؤ بها بدرجة جيدة من الصحة باستعمال النماذج الآتية:

١ - نظرية الامتزاز المحلوي المثالي لمايرز و براونيز (١٩٦٥).

٢ - نظرية كوك و بازماجيان (١٩٦٥).

٣ - نظرية الديناميكا الحرارية الاحصائي لروثين (١٩٧٣) وكان هناك اتفاق

مناسب مع نموذج المحلول الخالي لسواناين و دانر (١٩٨٠).