

THE PREDICTION OF ADSORPTION EQUILIBRIA FOR OXYGEN AND NITROGEN GAS MIXTURES ON 5A MOLECULAR SIEVES BY IDEAL ADSORBED SOLUTION THEORY(IAS^T)

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Abstract—Equilibria data for the adsorption of oxygen, nitrogen and their binary mixtures were determined on 5A molecular sieve beads. The single species isotherm data were approximated by the Freundlich type isotherm in a piecewise manner.

The binary equilibria were presented at the pressure of 1.5 atm abs. and the three temperatures: 273, 283 and 293 K. The binary data were examined for values predicted by the ideal adsorbed solution theory using the piecewise Freundlich isotherms obtained from the single species isotherm data.

Predicted equilibria data showed a good agreement with experimental values.

INTRODUCTION

The application of zeolite molecular sieve adsorbents in pressure swing adsorption(PSA) process, which is becoming popular for air separation[1,2], involves the adsorption of multicomponent mixtures. Therefore a reliable method of estimating mixture equilibria from pure component isotherm data is required for the design and optimization of such a process.

A number of techniques[3-11] have so far been suggested but the deficiency of a comparative analysis of their advantages makes it difficult to choose between one method and another. And available experimental data at temperatures and pressures of interest to PSA process are limited[12-14]. This is true in the adsorption involving binary gas mixtures of oxygen and nitrogen.

The recent paper has provided useful data for oxygen, nitrogen and their binary mixtures on 5A molecular sieve pellets[15]. Of the predictive methods which have been applied in that paper, the ideal adsorbed solution theory(IAS^T) is in good agreement with the experimental data.

In this work Freundlich adsorption isotherms of oxygen and nitrogen on 5A molecular sieve beads are determined at 273, 283 and 293 K in a piecewise manner. In the same manner those isotherms permit the calculation of spreading pressure which is the main trouble of the IAS^T. And experimental adsorption equilibria data at 273, 283 and 293 K and at 1.5 atm abs.

for oxygen-nitrogen gas mixtures are compared with the corresponding predictive data that are obtained by the IAS^T.

PREDICTION OF ADSORPTION EQUILIBRIA BY THE IAS^T

The IAS^T is based on an analogy to Raoult's law ($P_{y_i} = P_i^*(\Pi)x_i$): the partial pressure of an adsorbate is equal to the product of the adsorbed mole fraction and equilibrium pressure that would be exerted by the pure component at the same temperature and spreading pressure as the mixture.

The binary predictions obtained by this method are quite sensitive to the spreading pressure difference between two components. This difference is a strong function of the method used to extrapolate the pure component isotherms to zero pressure.

Analytical fitting of the isotherms to a nonlinear form with 4 regression parameters leads to satisfactory results [15]. But such fitting is not easy.

In the present case the single species isotherm is written as

$$n_i^* = (K_i)_m (P_i^*)^{-X_i + m} \quad \text{for } (P_i^*)_{m-1} \leq P_i^* < (P_i^*)_m \quad (1)$$

namely the single species isotherm data are approximated by the Freundlich expression in a piecewise manner.

The spreading pressure Π of i-component becomes

$$\pi(P_i^0) = \frac{RT}{A} \sum_{h=1}^m \int_{(P_i^0)_{h-1}}^{(P_i^0)_h} \frac{(K_i)_h (P_i^0)^{(X_i)_h}}{P_i^0} dP_i^0 \quad (2)$$

where $(P_i^0)_0 = 0$

When the number of segments m which depends on the data is taken two, Eq. (2) is written as

$$\pi(P_i^0) = \frac{RT}{A} \left[\int_0^{(P_i^0)_1} \frac{(K_i)_1 (P_i^0)^{(X_i)_1}}{P_i^0} dP_i^0 + \int_{(P_i^0)_1}^{(P_i^0)_2} \frac{(K_i)_2 (P_i^0)^{(X_i)_2}}{P_i^0} dP_i^0 \right] \quad (3)$$

From Eq. (3) the binary equilibrium pressures of i and j components can be expressed in terms of π ,

$$P_i^0(\pi) = (C_i \pi + D_i)^{Z_i} \quad (4)$$

$$P_j^0(\pi) = (C_j \pi + D_j)^{Z_j} \quad (5)$$

where C_i , C_j , D_i , D_j , Z_i and Z_j are the constants depending on the equilibrium pressure. These are listed in Table 1.

By the definition which a total adsorbed mole fraction $(x_i + x_j)$ is equal to unity

$$f(\pi) = x_i + x_j - 1 = \frac{Py_i}{P_i^0(\pi)} + \frac{Py_j}{P_j^0(\pi)} - 1 = 0 \quad (6)$$

Once π is calculated, x_i and x_j can be calculated from Eq. (4), (5) and (6).

The calculation of π (Eq. 6) is made using the Newton's iterative method;

$$f'(\pi) = -\frac{C_i Z_i P y_i}{(C_i \pi + D_i)^{Z_i + 1}} - \frac{C_j Z_j P y_j}{(C_j \pi + D_j)^{Z_j + 1}} \quad (7)$$

Table 1. Constants depending on the equilibrium pressure.

Equi. press., P^0	Constants	
	$0 < P^0 \leq (P^0)_1$	$(P^0)_1 < P^0 \leq (P^0)_2$
C_i	$\frac{B(X_i)_1}{(K_i)_1}$	$\frac{B(X_i)_2}{(K_i)_2}$
C_j	$\frac{B(X_j)_1}{(K_j)_1}$	$\frac{B(X_j)_2}{(K_j)_2}$
D_i	0	$1 - \frac{(X_i)_2 (K_i)_1}{(X_i)_1 (K_i)_2}$
D_j	0	$1 - \frac{(X_j)_2 (K_j)_1}{(X_j)_1 (K_j)_2}$
Z_i	$\frac{1}{(X_i)_1}$	$\frac{1}{(X_i)_2}$
Z_j	$\frac{1}{(X_j)_1}$	$\frac{1}{(X_j)_2}$

$$\pi_n = \pi_{n-1} - \frac{f(\pi_{n-1})}{f'(\pi_{n-1})} \quad (8)$$

where the subscript n denotes the n -th iterative value.

Futhermore the total amount adsorbed is obtained by the following Eq. (9).

$$\frac{1}{n_t} = \frac{x_i}{n_t} + \frac{x_j}{n_t} = \frac{x_i}{n_t^0} + \frac{x_j}{n_j^0} \quad (9)$$

EXPERIMENTAL

1. Adsorbent

The adsorbent used in the study was Davison Molecular Sieve type 5A(MS-5A), in the form of 8-12 mesh beads. Regeneration consisted of heating the adsorbents in vacuum at 573 K for 6 hrs.

Porosity and solid density of the adsorbent measured by Helium Pycnometer were 0.51 and 2.38 g/cm³ respectively.

2. Apparatus

The apparatus was of the volumetric type (Fig. 1). The volumes of the various parts of the dead space were determined by expanding helium gas from the unknown volume into an accurately measured stainless steel vessel.

The adsorption and holding column were made of stainless steel (double pipe of i.d. = 36.6 mm, o.d. = 70.0 mm and length = 500 mm) and maintained at a constant

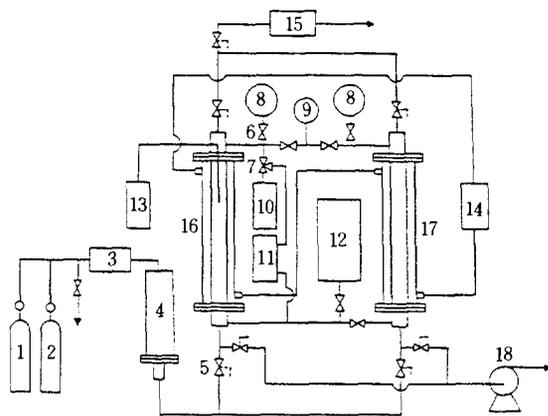


Fig. 1. Experimental apparatus

1. Nitrogen cylinder
2. Oxygen cylinder
3. Flow controller
4. Dryer (Silica gel)
5. Solenoid valve
6. Needle valve
7. 3-way valve
8. Pressure gauge
9. Vacuum gauge
10. Pressure transducer
11. Circulator (Gas)
12. Calibrated stainless steel volume
13. Digital thermometer
14. Circulator (Water)
15. Gas chromatograph
16. Adsorption column
17. Holding column
18. Vacuum pump

temperature by thermostatically controlled water bath. Standard 6 mm copper tubing was used throughout the piping system. Porous metal plates were placed at both ends of the bed to hold the adsorbents in their position, and copper-constantan thermocouple was inserted in the center of the bed.

3. Pure gas adsorption

The adsorption column had been filled with about 0.373 kg of regenerated MS-5A with helium gas flowing through the column.

After the circulating system which consisted of the holding column and the interconnecting tube had been evacuated together with the adsorption column, a quantity of adsorbate was admitted into the circulating system from gas cylinder supplier via silica gel dryer. The charged adsorbate was then expanded into the adsorption column and reached equilibrium state. The pressures were measured before and after sharing experiment by a pressure transducer.

Similarly successive charges of the adsorbate were expanded from the dosing volume (circulating system) into the adsorption column and successive measurements of pressure were carried out.

This procedure was repeated until the final equilibrium pressure was up to 8 atm abs. at each temperature; 273, 283 and 293 K.

4. Binary gas adsorption

The binary gas adsorption isotherm were determined by using the constant volume method.

After the whole system (adsorption column and circulating system) had been evacuated, the circulating system admitted a certain amount of one of pure gases. It was then expanded to the adsorption column and pressurized with a certain amount of the other gas which was controlled by the flow controller.

When the whole system was pressurized the gas mixture was circulated around the system by the circulating pump until equilibrium was reached which was indicated by the constancy of the total pressure. Then the whole system was sealed off. The holding column was isolated from the system and its gas analysed using the gas chromatograph.

The system was evacuated and the circulating system admitted the same second gas and the same procedure repeated again.

RESULTS AND DISCUSSION

1. Pure gas adsorption

The amount of pure gas adsorbed was determined by performing a material balance on the number of moles present in the gas and adsorbed phase before and after the addition of a new dose of gas to the adsorption column using the appropriate P-V-T measurements.

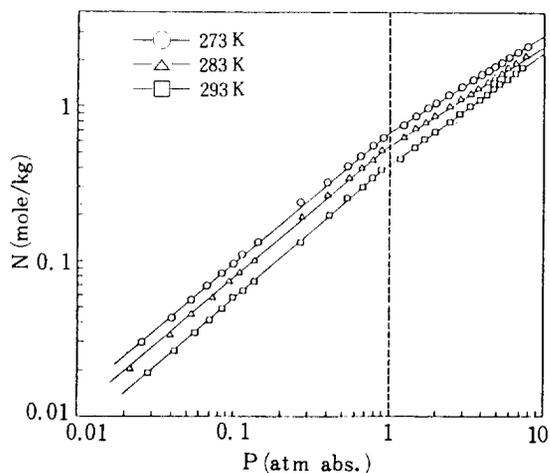


Fig. 2. Freundlich plot of adsorption equilibria data for nitrogen on MS-5A at 273, 283 and 293 K.

The experimental equilibria data for both gases are approximated by the piecewise Freundlich isotherms ($n_i = K_i P_i^{X_i}$) in Fig. 2 and 3, and the parameters K and X are given in Table 2. With the result of each approximation, the standard deviation is about 0.015-0.04 in all cases. In those isotherms, the pressure of component i and j in segment 1, $(P^0)_i$, is chosen to 1 atm abs. and that in segment 2 is above 1 atm abs.

On the basis of Freundlich isotherms (Fig. 2 and 3), it is apparent that nitrogen exhibits higher intercept K_i than oxygen at each temperature. And for nitrogen the slope X_i is higher in segment 1 than that in segment 2 while for oxygen the opposite is true. These results may be due to the adsorptive capacity of each gas; the quanti-

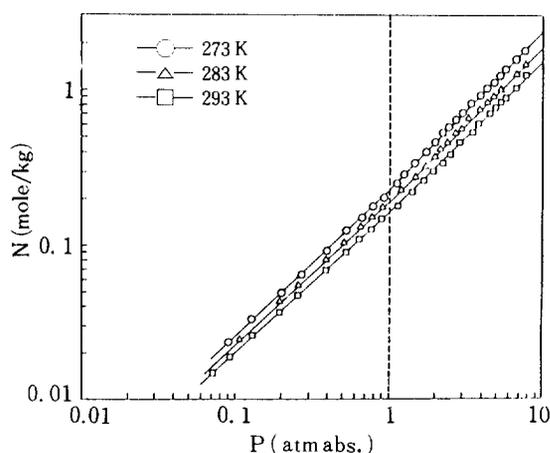


Fig. 3. Freundlich plot of adsorption equilibria data for oxygen on MS-5A at 273, 283 and 293 K.

Table 2. Coefficients of Freundlich adsorption isotherm.

Temp., Adsorbate	273K		283K		293K		*278.15 K	
	N ₂	O ₂						
(K) ₁	0.64	0.22	0.5	0.19	0.38	0.15	0.47	0.16
(X) ₁	0.98	0.9	0.96	0.88	0.96	0.87	0.89	0.87
(K) ₂	0.68	0.19	0.58	0.16	0.42	0.14	0.47	0.16
(X) ₂	0.63	1.0	0.65	0.99	0.68	0.98	0.63	0.95

*Based on the data of G. A. Sorial et al. [15]

ty of nitrogen adsorbed is larger over the segment than oxygen, while that of oxygen adsorbed increases more sharply in segment 2 than nitrogen.

Though the adsorption data of G. A. Sorial et al. [15] have only a few points below 1 atm abs. and slightly different values to ours, the Freundlich plot of their data (Fig. 4) shows the similar changes of slope to ours.

2. Binary gas adsorption

The total quantity of each gas admitted to the system and the amount of each gas in the vapor remaining after

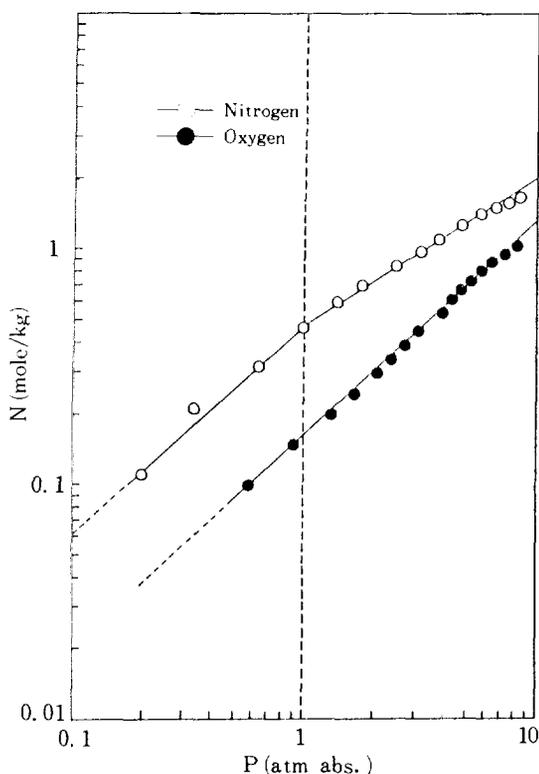


Fig. 4. Freundlich plot of adsorption data of G. A. Sorial et al. at 278.15 K.

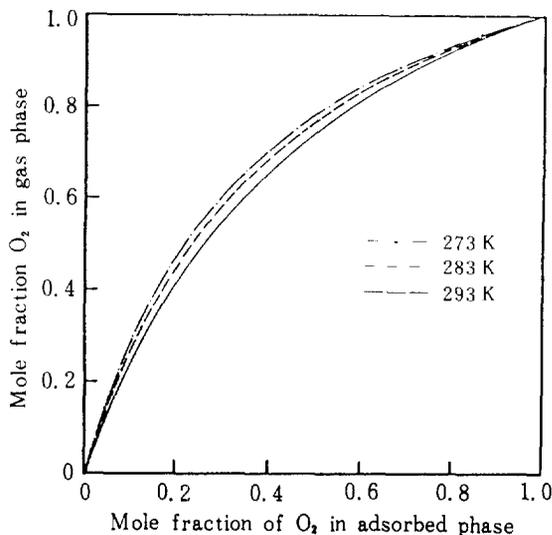


Fig. 5. Predicted phase diagram for oxygen-nitrogen mixtures on MS-5A by IAST at 273, 283 and 293 K(P = 1.5 atm abs.).

adsorption equilibrium was established were determined by appropriate P-V-T measurements and analysis by a gas chromatograph. The adsorbed phase compositions and the adsorption quantities were then determined by the difference between the quantities of admitted and remaining gases.

The theoretical predicting data of binary adsorption equilibria are shown graphically in Fig. 5 and 6. From Fig. 5 and 6 it can be seen that the separation factor ($y_{O_2} x_{N_2} / y_{N_2} x_{O_2}$) is much less sensitive to temperature change than is the total amount adsorbed. The total quantity adsorbed is a strong function of the adsorbed phase composition, decreasing more sharply at high oxygen concentration.

A summary of the experimental results obtained is

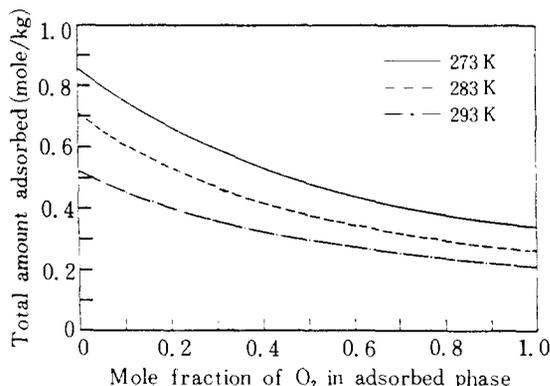


Fig. 6. Predicted total amount of adsorption for oxygen-nitrogen mixtures on MS-5A by IAST at 273, 283 and 293 K(P = 1.5 atm abs.).

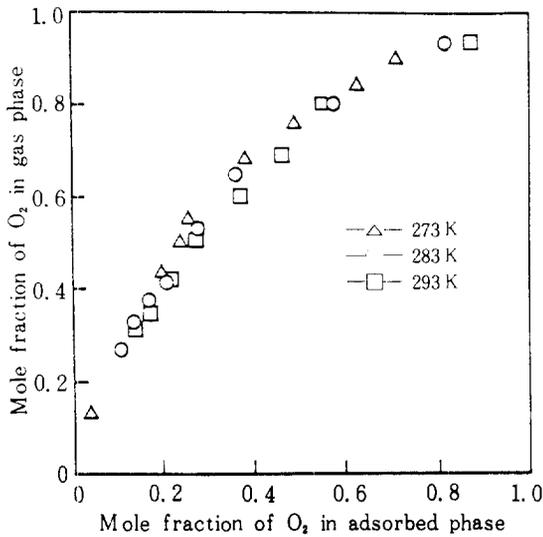


Fig. 7. Experimental results(adsorption phase) for the adsorption of oxygen-nitrogen mixtures on MS-5A at 273, 283 and 293 K(P=1.5 atm abs.).

given graphically in Fig. 7 and 8. The temperature dependency of the separation factor is not particularly strong (Fig. 7) but the total quantity adsorbed is a strong function of temperature (Fig. 8). These experimental results exhibit the same trend as would be predicted.

In order to see the success in using the piecewise Freundlich isotherm to predict binary adsorption equilibrium, predicted values are compared with the experimental results in Fig. 9 and 10. In those Figures method 1 and 2 are the adoption of piecewise isotherm and single isotherm (Freundlich isotherm in whole segment) to calculate the spreading pressure respectively.

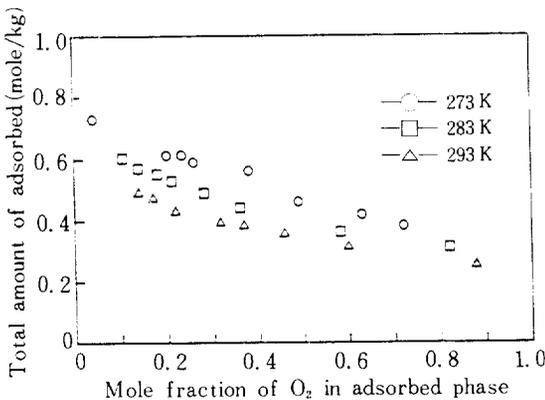


Fig. 8. Experimental results(total amount adsorbed) for the adsorption of oxygen-nitrogen mixtures on MS-5A at 273, 283 and 293 K(P=1.5 atm abs.).

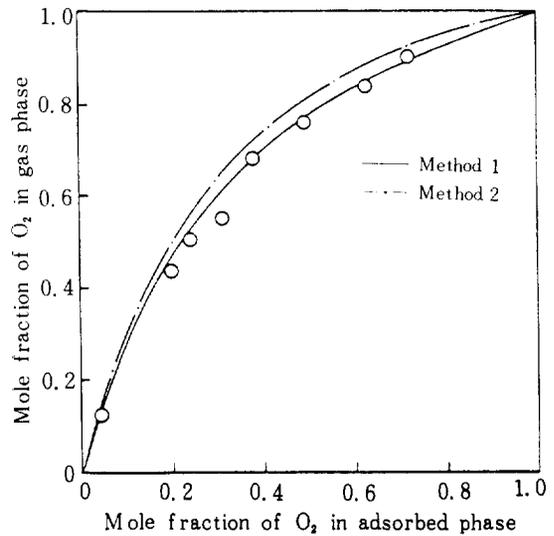


Fig. 9. Comparison of theoretical predictions with experimental data at 273 K(P=1.5 atm abs.).

From Fig. 9 it is seen that the predicted values by method 1 are in good agreement with the experimental values and the accurate prediction depends on the method of extrapolating the pure component isotherms to zero pressure.

The comparisons at 283 and 293 K are not shown, but they look quite similar to the case at 273 K.

Fig. 10 is based on the piecewise Freundlich plot of

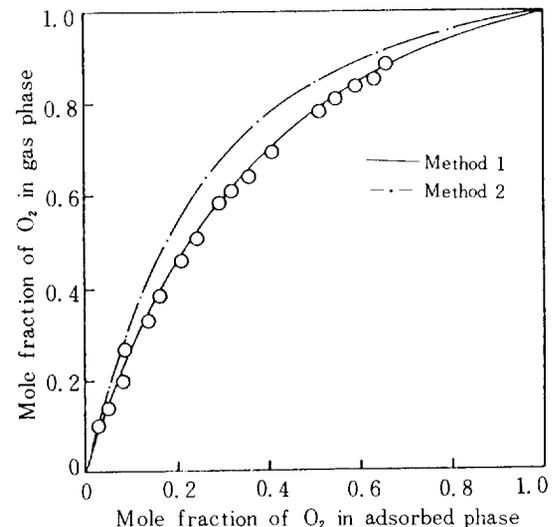


Fig. 10. Comparison of theoretical predictions with the experimental data of G. A. Sorial et al. at 278.15 K(P=1.7 bar).

the adsorption data of G. A. Sorial et al. (Fig. 4) and then method 1 shows a fairly good prediction.

CONCLUSION

Adsorption equilibrium data of nitrogen and oxygen were approximated by the Freundlich isotherm in a piecewise manner.

Predicted equilibrium data by the IAST using the piecewise Freundlich isotherm to calculate the spreading pressure showed a good agreement with experimental values.

NOMENCLATURE

- A : specific surface area of adsorbent, m^2/gr
 B : defined as A/RT
 C : constant depending on the equilibrium pressure
 D : constant depending on the equilibrium pressure
 K : coefficient in Freundlich isotherm, $mole/kg \cdot (atm \text{ abs.})^X$
 n^o : number of moles of pure component in adsorbed phase per unit mass of adsorbent, $mole/kg$
 n_t : total number of moles in adsorbed phase per unit mass of adsorbent, $mole/kg$
 P : total pressure, atm abs.
 P^o : pressure of pure component
 $P^o(\pi)$: equilibrium pressure for pure component corresponding to spreading pressure π
 R : gas constant
 T : absolute temperature
 X : coefficient in Freundlich isotherm
 x : mole fraction in adsorbed phase
 y : mole fraction in gas phase
 Z : constant depending on the equilibrium pressure
 π : spreading pressure, $joule/m^2$

Subscripts

- i : component
 j : component
 m : number of segments for the Freundlich isotherm
 n : iteration

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(Errata)

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Page	Equation	Correct form
p. 16	4	$K_i C_i x_i \rightarrow K_i C_i^{x_i}$
"	5, 6, 9, 10	$K_o C_o x_o \rightarrow K_o C_o^{x_o}$
"	7, 8, 11, 12	$K_N C_N x_N \rightarrow K_N C_N^{x_N}$