at the Meeting of the Reactor Materials Subcommittee of the Japan Society for the Promotion of the Science, in Tokyo, on Feb. 14, 1961.)

(Received November 6, 1961)

—REFERENCE—

- (1) I. V. BUDAEV, A. N. VOLSKY : *A/Conf.*, 15/P/2195, (1958).
- (2) Y. SHIBATA : "Mukikagaku-Zensho (*Handbook of Inorganic Chemistry*)", XII-1, 221, (1953), Maruzen, Tokyo.
- (3) M. BENEDICT, T. H. PIGFORD : "Nuclear Chemical Engineering", 275, (1957), McGraw-Hill Book Co. Inc., New York.
- (4) L. L. QUILL : "The Chemistry and Metallurgy of Miscellaneous Materials-Thermodynamics", (National Nuclear Energy Series, Div. W, Vol.19B), 193, (1950), McGraw-Hill Book Co. Inc., New York.
- (5) A. GLASSNER : "The Thermodynamic Properties of the Oxides, Fluorides and Chlorides to 2500°K", ANL-5750, (1957).
- (6) L. BREWER, L. A. BROMLEY, P. W. GILLES, N. L. LOFGREN ; J. J. KATZ, E. RABINOWITCH, ed. : "Chemistry of Uranium", TID-5290, 219 (1958).
- (7) D. BRADLEY : *AERE-CE/R-2215*, (1954).

研究論文

200. Notes on Isotopic Exchange Reactions, (I)

Stepwise separating process

同位体交換反応に関するノート, (I)

段階的分離過程

By Kenji ISHIDA*,
Junichi SHIMOKAWA* and Yutaka YAMAMOTO*

It is difficult to experimentally determine the separation factor for the isotopic exchange reaction with a small equilibrium constant, even if the equilibrium constant can theoretically be evaluated. As a method to determine the separation factor of such an isotopic exchange reaction, the stepwise separating process, which also may be regarded as a simple cascade, has been investigated.

Most studies of the isotopic separation processes by means of exchange reaction, in both theories and experiments, have been made about light elements. According to the statistical thermodynamic theory of isotopic exchange equilibrium⁽¹⁾⁽²⁾, the possibility of isotopic separation is due to a quantum-mechanical effect. The chemical separation of isotopes takes advantage of the differences between the molecular energies of lighter and heavier isotopic molecules in the isotopic substitution and is substantially different from the physical separations such as gaseous diffusion and cent-

rifuge, where the difference between the masses of two isotopic molecules can directly be used. The chemical separation can only indirectly use it. For example, the ideal separation factor for the gaseous diffusion of uranium hexafluoride is 1.0043, but in the ideal isotopic exchange reaction $^{235}\text{UF}_6 + ^{238}\text{U} \rightleftharpoons ^{238}\text{UF}_6 + ^{235}\text{U}^{(3)}$, the equilibrium constant, which is equivalent to the separation factor, is 1.0019 according to the theoretical calcu-

* 石田健二, 下川純一, 山本 寛。Japan Atomic Energy Res. Inst. (日本原子力研究所)

lation. Generally speaking, the chemical separation factor is smaller compared with the physical one.

In the chemical separation of isotopes of a light element it is relatively easy to experimentally determine the single stage separation factor of the exchange equilibrium. But in the isotopic exchange reaction of a heavier element, for example, in such a case as the exchange reaction between uranyl and uranous ions, the equilibrium constant, which is equal to the separation factor and is experimentally and theoretically known to be about 1.001⁽³⁾⁽⁴⁾, is so small that it is difficult to obtain it by the single stage of exchange equilibrium. As a method to experimentally determine the separation factor of such cases, however, the stepwise enriching or depleting process such that the isotopic exchange equilibria are iterated many times is considered to be useful. Of course this method is tedious and impractical.

I. RELATION BETWEEN EQUILIBRIUM CONSTANT AND REACTING QUANTITY

We now consider the isotopic exchange equilibrium involving only one isotopic substitution ;

where I_1 and I_2 are the lighter and heavier isotope of an element I , respectively. In such cases the equilibrium constant is equivalent to the separation factor. In the isotopic exchange equilibrium involving more than two isotopic substitutions, however, the equilibrium constant corrected by the so-called symmetry number⁽⁵⁾ should be regarded as the separation factor. If the isotopic exchange reaction (1) is truly bimolecular, the equilibrium constant K is given by the relation

$$K = \frac{(a+x)(b'+x)}{(a'-x)(b-x)}, \quad (2)$$

where a' , b , a and b' denote the initial concentrations of reactants AI_1 , BI_2 , AI_2 and BI_1 , respectively, and x the reacting quantity at equilibrium. As already mentioned, since K is close to 1 and x is also very small compar-

ed with a' , b , a and b' , the equation

$$x = \frac{Ka'b-ab'}{K(a'+b)+(a+b')} \quad (3)$$

is derived from Eq. (2) on assuming that K is known. If we denote the total concentrations of AI and BI by α and β and further the mole fractions of AI_1 and BI_1 by ν_a and ν_b , respectively, we have the relations $a' = \alpha\nu_a$, $a = \alpha(1-\nu_a)$, $b' = \beta\nu_b$ and $b = \beta(1-\nu_b)$. We thus obtain, substituting these relations into Eq. (3),

$$x = \frac{\alpha\beta[K\nu_a(1-\nu_b)-(1-\nu_a)\nu_b]}{\alpha[1+(K-1)\nu_a]+\beta[K-(K-1)\nu_b]}. \quad (4)$$

In the isotopic exchange reaction under the condition $\nu_a = \nu_b (= \nu)$, this equation becomes

$$x = \frac{\alpha\beta(K-1)\nu(1-\nu)}{\alpha[1+(K-1)\nu]+\beta[K-(K-1)\nu]}, \quad (4')$$

which is the formula for the single stage of exchange equilibrium and is reduced to

$$x = \alpha \frac{K-1}{K+1} \nu(1-\nu)$$

if $\alpha = \beta$.

II. STEPWISE SEPARATING PROCESS

In order to determine the separation factor of the isotopic exchange equilibrium with very small K , we now return to the stepwise separating process and investigate the method constructing this process by using the Eq. (4').

Let us prepare a pair of compounds to be brought into exchange reaction from a given compound. If we denote the quantity of the starting material by L_s , the mole fraction of isotope I_1 by ν_s and the cut by θ_s at the s th stage in the separating process, we then have the following relations, with respect to the exchange reaction (1),

where $\theta < \theta_s < 1$ and x_s is the reacting quantity at equilibrium. According to Eq. (4'), we have

$$x_s = \frac{(K-1)L_s\nu_s(1-\nu_s)\theta_s(1-\theta_s)}{1+(K-1)\nu_s+(K-1)(1-2\nu_s)\theta_s}. \quad (5)$$

Differentiating this with respect to θ_s , we observe that Eq. (5) has a maximum value at

Fig. 1 Separation process of single stage

$$\theta_s = \frac{1 + (K-1)\nu_s}{(K-1)(1-2\nu_s)} \left(\sqrt{1 + \frac{(K-1)(1-2\nu_s)}{1 + (K-1)\nu_s}} - 1 \right).$$

Since $(K-1) \ll 1$ and $(K-1)\nu_s \ll 1$, the cut θ_s is given by the approximate equation

$$\theta_s \approx \frac{1}{2} \left\{ 1 - \frac{\varepsilon}{4} (1 - 2\nu_s) \right\}, \quad (6)$$

where $K-1=\varepsilon$. If we set $\varepsilon=2\delta$, we have $\theta_s \approx \{1 - \delta(1-2\nu_s)/2\}$ in agreement with the formula derived by Cohen⁽⁶⁾ on the theory of ideal cascade. In the isotopic exchange reaction with sufficient small K , therefore, we may set $\theta_s \approx 1/2$ with sufficiently good approximation. In other words, we would rather make AI react on BI at the same concentration⁽⁷⁾. We accordingly obtain the simpler equation

$$x_s = \frac{L_s \nu_s (1 - \nu_s)}{K + 1} \quad (7)$$

by putting $\theta_s = 1/2$ in Eq. (5). If we then introduce an abbreviation $\delta = (K-1)/(K+1)$ we finally have

$$x_s = \frac{L_s \nu_s (1 - \nu_s) \delta}{2}, \quad (7')$$

where $\delta \approx \varepsilon/2$ owing to $K+1 \approx 2$.

Let us consider the separation process shown in Fig. 2. The calculations for the enriching and depleting processes result in the followings.

1. Enriching process

Stage	Reacting quantity	Mole fraction of enriching side	Mole fraction of depleting side
initial	$x_0 = 0$	$\nu_0' = \nu_0$	$N_0'' = \nu_0$
1	$x_1 = \frac{a}{2} \nu_0 (1 - \nu_0) \delta$	$\nu_1' = \nu_0 + \frac{x_1}{a/2}$	$N_1'' = \nu_0 - \frac{x_1}{a/2}$
2	$x_2 = \frac{a}{2^2} \nu_1' (1 - \nu_1') \delta$	$\nu_2' = \nu_1' + \frac{x_2}{a/2^2}$	$N_2'' = \nu_1' - \frac{x_2}{a/2^2}$
...	...	...	...
s	$x_s = \frac{a}{2^s} \nu_{s-1}' (1 - \nu_{s-1}') \delta$	$\nu_s' = \nu_{s-1}' + \frac{x_s}{a/2^s}$	$N_s'' = \nu_{s-1}' - \frac{x_s}{a/2^s}$

Fig. 2 Stepwise separating process

a is the quantity of the starting material. ν_s' and N_s'' denote the mole fractions of the enriching and depleting sides at the s th stage, respectively.

(1) In the enriching side the equation

$$\nu_1' = \nu_0 [1 + (1 - \nu_0) \delta] \quad (8)$$

is derived from the relations of the first stage. The general equation is given by

$$\nu_s' = \nu_{s-1}' [1 + (1 - \nu_{s-1}') \delta]. \quad (9)$$

Substituting Eq. (8) into the relation $\nu_2' = \nu_1' [1 + (1 - \nu_1') \delta]$ for the second stage, we have

$$\nu_s' = \nu_0 [1 + (1 - \nu_0) \delta] (1 + (1 - \nu_0) \delta - \nu_0 (1 - \nu_0) \delta^2),$$

but since $\delta \gg \nu_0 \delta^2$, this becomes

$$\nu_s' \approx \nu_0 [1 + (1 - \nu_0) \delta]^s. \quad (10)$$

It is easily proved by the induction method that the general equation can be expressed in the form

$$\nu_s \approx \nu_0 [1 + (1 - \nu_0) \delta]^s. \quad (11)$$

We also find from Eq. (8)

$$\frac{\nu_1'}{1 - \nu_1'} = \frac{\nu_0}{1 - \nu_0} \frac{1 + (1 - \nu_0) \delta}{1 - \nu_0 \delta},$$

and so transforming this by using the abundance ratio $R = \nu / (1 - \nu)$, we have

$$\frac{R'}{R_0} \approx 1 + \delta. \quad (12)$$

We similarly obtain $R_2' / R_0 \approx (1 + \delta)^2$

from Eq. (10). The equation for the s th stage may also be derived by the induction method ;

$$\frac{R_s'}{R_0} \simeq (1+\delta)^s. \quad (13)^*$$

(2) In the depleting side the equation

$$N_1'' = \nu_0[1 - (1-\nu_0)\delta] \quad (14)$$

is derived from the relations of the first stage. Substituting Eq. (8) into the relation $N_2'' = \nu_1'[1 - (1-\nu_1')\delta]$ for the second stage, we have

$$\begin{aligned} N_2'' &= \nu_0(1 + (1-\nu_0)\delta)(1 - (1-\nu_0)\delta) \\ &\quad + \nu_0(1-\nu_0)\delta^2 \\ &\simeq \nu_0(1 + (1-\nu_0)\delta)(1 - (1-\nu_0)\delta) \\ &= \nu_0(1 - (1-\nu_0)^2\delta^2), \end{aligned}$$

but since $(1-\nu_0)^2\delta^2 \ll 1$, we obtain

$$N_2'' \simeq \nu_0. \quad (15)$$

The general equation is given by

$$N_s'' \simeq \nu_0[1 + (1-\nu_0)\delta]^{s-2}. \quad (16)$$

We thus obtain, as the equation corresponding to Eq. (13),

$$\frac{R_s''}{R_0} \simeq (1+\delta)^{s-2}. \quad (17)$$

By comparing Eq. (17) with (13), we deduce that the abundance ratio R'_{s-2} at the $(s-2)$ th stage in the enriching side is equal to the abundance ratio R_s'' at the s th stage in the depleting side. This is shown by the dotted lines in Fig. 2.

2. Depleting process

Stage	Reacting quantity	Mole fraction of depleting side	Mole fraction of enriching side
1	$y_1 = \frac{a}{2} \nu_0(1-\nu_0)\delta (=x_1)$	$\nu_1'' = \nu_0 - \frac{y_1}{a/2} (=N_1'')$	$N_1' = \nu_0 + \frac{y_1}{a/2} (= \nu_1')$
2	$y_2 = \frac{a}{2} \nu_1''(1-\nu_1'')\delta$	$\nu_2'' = \nu_1'' - \frac{y_2}{a/2^2}$	$N_2' = \nu_1'' + \frac{y_2}{a/2^2}$
...	...	...	...
s	$y_s = \frac{a}{2} \nu_s''(1-\nu_s'')\delta$	$\nu_s'' = \nu_{s-1}'' - \frac{y_s}{a/2^s}$	$N_s' = \nu_{s-1}'' + \frac{y_s}{a/2^s}$

ν_s'' and N_s' denote the mole fractions of the depleting and enriching sides at the s th stage, respectively.

(1) In the depleting side we have as the general equation

$$\nu_s'' = \nu_{s-1}''[1 - (1-\nu_{s-1}'')\delta]. \quad (18)$$

Substituting $\nu_1'' = \nu_0[1 - (1-\nu_0)\delta]$ of the first stage into $\nu_2'' = \nu_1''[1 - (1-\nu_1'')\delta]$ of the second stage, we obtain, by using $\delta \ll \nu_0\delta^2$,

$$\nu_2'' \simeq \nu_0[1 - (1-\nu_0)\delta]^2. \quad (19)$$

We thus have as the equation for any stage

$$\nu_s'' \simeq \nu_0[1 - (1-\nu_0)\delta]^s. \quad (20)$$

Since $\nu_1'' = N_1''$, $r_1''/R_0 \simeq (1+\delta)^{-1} \simeq R_1''/R_0$ is obtained by Eq. (17). And according to the induction method the general equation is given by

$$\frac{r_s''}{R_0} \simeq (1+\delta)^{-s}, \quad (21)$$

where $r_s'' = \nu_s''/(1-\nu_s'')$ denotes the abundance ratio at the s th stage.

(2) In the enriching side we also can

readily derive the similar formulae

$$N_s' \simeq \nu_0[1 - (1-\nu_0)\delta]^{s-2} \quad (22)$$

and

$$\frac{r_s'}{R_0} \simeq (1+\delta)^{-s+2}, \quad (23)$$

where $r_s' = N_s'/(1-N_s')$ denotes the abundance ratio at the s th stage in the enriching side. All the above results are summarized as follows ;

Enriching side	
enriching side	depleting side
$\nu_s \simeq \nu_0[1 + (1-\nu_0)\delta]^s$	$N_s'' \simeq \nu_0[1 + (1-\nu_0)\delta]^{s-2}$
$R_s' \simeq R_0(1+\delta)^s$	$R_s'' \simeq R_0(1+\delta)^{s-2}$

* We first assume that $\frac{R'_{s-1}}{R_0} \simeq (1+\delta)^{s-1}$ is concluded for the $(s-1)$ th stage. Substituting $\frac{R_s'}{R'_{s-1}} = \frac{1 + (1-\nu'_{s-1})\delta}{1-\nu'_{s-1}\delta} \simeq 1+\delta$ derived from Eq. (9) into $\frac{R_s'}{R_0} = \frac{R_s'}{R'_{s-1}}(1+\delta)^{s-1}$, we obtain $\frac{R_s'}{R_0} \simeq (1+\delta)^s$.

Depleting process	
depleting side	enriching side
$\nu_s'' \approx \nu_0[1 - (1 - \nu_0)\delta]^s$	$N_s' \approx \nu_0[1 - (1 - \nu_0)\delta]^{s-2}$
$r_s'' \approx R_0(1 + \delta)^{-s}$	$r_s' \approx R_0(1 + \delta)^{-s+2}$

The experiments by which can confirm the theory have been recorded by Woodard⁽¹⁴⁾. His results for the exchange reaction between uranous and uranyl ions are shown in Table 1, where the values ε 's are obtained by the equation $R_s'/r_s'' \approx (1 + \delta)^{2s} \approx (1 + \varepsilon)^s$ derived from $R_s' \approx R_0(1 + \delta)^s$ and $r_s'' \approx R_0(1 + \delta)^{-s}$.

The average of ε is 0.00109. We deduce,

Table 1 Data of $U^{+4}-UO_2^{+2}$ exchange reaction

stage	mole fraction of ^{235}U in enriching run	mole fraction of ^{235}U in depleting run	ε
1	0.7052	-	-
2	0.7052	0.7054	-
3	0.7058	0.7041	0.000809
4	0.7071	0.7032	0.00139
5	0.7072	0.7038	0.000972
6	0.7090	0.7029	0.00145
7	0.7063	0.7031	0.000653
8	0.7086	0.7027	0.00105
9	0.7096	0.7015	0.00129

accordingly, that the separation factor is about 1.001. The theory can also explain the experimental data for $U^{+4}-U(C_6H_5N_2O_2)_4$ exchange reaction⁽⁸⁾.

III. SUMMARY

For given equilibrium constant the isotopic

exchange reaction $AI_1 + BI_2 \rightleftharpoons AI_2 + BI_1$ has the maximum value of the reacting quantity at equilibrium when the concentration of reactant AI is equal to it of BI. In the chemical separation process by means of isotopic exchange reaction, that is to say, the cut must be 1/2. The stepwise separating process has been considered as an experimental procedure to determine the separation factor for the isotopic exchange reaction with very small equilibrium constant.

We would like to express our gratitude to each member of Isotope Separation Research Group of J.A.E.R.I. for their encouragement and helpful suggestions.

(Received November 27, 1961)

—REFERENCE—

- (1) J. BIGELEISEN, M. G. MAYER : *J. Chem., Phys.*, **15**, 261 (1947).
- (2) G. VOJTA : *Kernenergie*, **3**, 917 (1960).
- (3) C. A. HUTCHISON, G. M. MURPHY : *TID-5224*, (1952).
- (4) R. W. WOODARD : *Y-185*, (1948).
- (5) J. BIGELEISEN : "*Proceedings of the International Symposium on Isotope Separation*", p. 126, (1958), North-Holland.
- (6) K. COHEN : "*The Theory of Isotope Separation as Applied to the Large-Scale Production of ^{235}U* ", p.9 (1951), McGraw-Hill.
- (7) G. H. CLEWETT, W. B. SCHAAP : *Y-41*, (1947).
- (8) G. H. CLEWETT, De Wayne A. LEE : *US-Pat.* 2,835,687, (1952).

投 稿 歓 迎

研究論文・資料のほか、会員の自由投稿欄として、談話室(1頁1,600字程度)・寄書(約2~3頁)・討論(約1~2頁)が設けられています。
会員各位のご意見、ご希望などお気軽にご投稿願います。