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Abstract

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CALCULATION OF THE SINGLE-STAGE SEPARATION FACTOR FOR CERTAIN CHEMICAL EXCHANGE REACTIONS

(Presented by Academician A. N. Frumkin, 22 VI 1962)

The effectiveness of isotope separation by the method of chemical exchange is determined by the successful choice of the corresponding reaction. It is therefore very important to predict, at least approximately, the value of the single-stage separation factor. In this respect, the statistical calculation of the exchange constant of isotopic reactions is generally known; however, it cannot always be used for isotopic exchange of complex molecules. For the quantity sought it is always desirable to have such a functional dependence whose argument would be known in advance for all cases. Such an argument, with respect to the isotopic-exchange constant, may be the molecular weight. Consequently, the solution of the problem consists in finding the functional dependence of the single-stage separation factor on the isotope masses.

Let us consider a chemical exchange reaction of the type

$$\mathrm{A^*B} + \mathrm{AC} = \mathrm{A^*C} + \mathrm{AB}, \tag{1}$$

i.e., let us first consider the simplest case, when $K = \alpha$, the constant of the chemical exchange reaction is numerically equal to the single-stage separation factor, and the ratio of the symmetry numbers $\delta_1\delta_3/\delta_2\delta_4$ is equal to 1. The exchange constant of such a reaction, on the basis of statistical thermodynamics, may be written (^{1,2}) in the form

$$K = \frac{\left[\dfrac{I_{\mathrm{A^*C}}}{I_{\mathrm{AC}}}\left(\dfrac{M_{\mathrm{A^*C}}}{M_{\mathrm{AC}}}\right)^{3/2}\dfrac{1-e^{-u_{\mathrm{AC}}}}{1-e^{-u^*_{\mathrm{A}}\mathrm{C}}}e^{(u^*_{\mathrm{A}}\mathrm{C}-u_{\mathrm{AC}})/2}\right]}{\left[\dfrac{I_{\mathrm{A^*B}}}{I_{\mathrm{AB}}}\left(\dfrac{M_{\mathrm{A^*B}}}{M_{\mathrm{AB}}}\right)^{3/2}\dfrac{1-e^{-u_{\mathrm{AB}}}}{1-e^{-u^*_{\mathrm{A}}\mathrm{B}}}e^{(u^*_{\mathrm{A}}\mathrm{B}-u_{\mathrm{AB}})/2}\right]}, \tag{2}$$

where I is the moment of inertia of the molecule, M is the mass of the molecule, $u = hc\omega/kT$, and ω is the fundamental vibrational frequency.

Let us take the logarithm of expression (2) and consider each term separately:

$$\ln K = \ln \frac{I_{\mathrm{A^*C}}}{I_{\mathrm{AC}}} - \ln \frac{I_{\mathrm{A^*B}}}{I_{\mathrm{AB}}} + \frac{3}{2} \ln \frac{M_{\mathrm{A^*C}}}{M_{\mathrm{AC}}} - \frac{3}{2} \ln \frac{M_{\mathrm{A^*B}}}{M_{\mathrm{AB}}} - \frac{u_{\mathrm{A^*C}} - u_{\mathrm{AC}}}{2} + \frac{u_{\mathrm{A^*B}} - u_{\mathrm{AB}}}{2} + \ln \frac{1 - e^{-u_{\mathrm{AC}}}}{1 - e^{-u^*_{\mathrm{A}}\mathrm{C}}} - \ln \frac{1 - e^{-u_{\mathrm{AB}}}}{1 - e^{-u^*_{\mathrm{A}}\mathrm{B}}}. \tag{3}$$

1)

$$\ln \frac{M_{\mathrm{A^*C}}}{M_{\mathrm{AC}}} = \ln \left(1 + \frac{M_{\mathrm{A^*C}} - M_{\mathrm{AC}}}{M_{\mathrm{AC}}}\right) = \ln \left(1 + \frac{\Delta m}{M_{\mathrm{AC}}}\right).$$

Since for most isotopic molecules $\Delta m \ll M_{\mathrm{AC}}$, then

$$\ln \frac{M_{\mathrm{A^*C}}}{M_{\mathrm{AC}}} = \frac{\Delta m}{M_{\mathrm{AC}}}.$$

2)

$$\ln \frac{I_{\mathrm{A^*C}}}{I_{\mathrm{AC}}} = \ln \left(1 + \frac{\Delta I}{I_{\mathrm{AC}}}\right).$$

If the geometrical difference is neglected

of isotopic molecules, one can write $\Delta I \approx r^2(\mu_{A*C} - \mu_{AC})$, where μ is the reduced mass of the molecule, and r is the equilibrium distance between the atoms in the molecule. For $\Delta\mu$ one can write:

$$\Delta\mu = \frac{(m + \Delta m)b}{(m + \Delta m) + b} - \frac{mb}{m + b},$$

where m is the mass of the isotopic atom, for example A; b is the mass of the other atom, for example B or C.

$$\Delta\mu \approx \frac{\Delta m b^2}{(m + b)^2} = \frac{\mu^2}{m^2} \Delta m$$

or

$$\ln \frac{I_{A*C}}{I_{AC}} = \ln \left(1 + \frac{\mu \Delta m}{m^2}\right) = \frac{\mu}{m^2} \Delta m.$$

3) $\ln \frac{1 - e^{-u_{AC}}}{1 - e^{-u_{A*C}}}$ for many isotopic molecules may be approximately taken to be equal to zero. In this case the constant of the isotope-exchange reaction can be written in the form

$$\ln K = \left[\left(\frac{3}{2}\frac{1}{M_{AC}} + \frac{\mu_{AC}}{m^2}\right) - \left(\frac{3}{2}\frac{1}{M_{AB}} + \frac{\mu_{AB}}{m^2}\right)\right]\Delta m + \frac{\Delta u_{AC} - \Delta u_{AB}}{2}. \quad (3')$$

For brevity let us denote

$$\left(\frac{3}{2}\frac{1}{M_{AC}} + \frac{\mu_{AC}}{m^2}\right) - \left(\frac{3}{2}\frac{1}{M_{AB}} + \frac{\mu_{AB}}{m^2}\right) = -\varepsilon_\lambda; \quad (4)$$

then

$$\ln K = \ln \alpha = \varepsilon = \left[-\varepsilon_\lambda + \frac{\Delta u_{AC} - \Delta u_{AB}}{2\Delta m}\right]\Delta m, \quad (5)$$

where $\varepsilon = \alpha - 1$.

It is known that with increasing T, $\varepsilon \to 0$; therefore let us denote by T_0 the temperature at which $\varepsilon = 0$. Then

$$0 = \left[-\varepsilon_\lambda + \left(\frac{\Delta u_{AC} - \Delta u_{AB}}{2\Delta m}\right)_{T_0}\right]\Delta m$$

or

$$\left(\frac{\Delta u_{AC} - \Delta u_{AB}}{2\Delta m}\right)_{T_0} = +\varepsilon_\lambda.$$

We rewrite equation (5) as follows:

$$\varepsilon = \left\{-\varepsilon_\lambda\left[1 - \frac{(\Delta u_{AC} - \Delta u_{AB})_T}{(\Delta u_{AC} - \Delta u_{AB})_{T_0}}\right]\right\}\Delta m. \quad (6)$$

It can be shown on the basis of the Teller–Redlich theorem (^{1,2}) that

$$\Delta u_{AC} = u_{AC}(\beta + \gamma) = \frac{\omega_{AC} hc}{kT}(\beta + \gamma),$$

where β and γ are certain constants depending only on the molecular weight of the molecules. Then equation (6) is rewritten in the form

$$\varepsilon = \left\{-\varepsilon_\lambda\left[1 - \frac{\frac{\omega_{AC} hc}{kT}(\beta + \gamma) - \frac{\omega_{AB} hc}{kT}(\beta' + \gamma')}{\frac{\omega_{AC} hc}{kT_0}(\beta + \gamma) - \frac{\omega_{AB} hc}{kT_0}(\beta' + \gamma')}\right]\right\}\Delta m = -\varepsilon_\lambda\left(1 - \frac{T_0}{T}\right)\Delta m.$$

Thus it follows that ε is a multiple of ε_λ, i.e.,

$$\ln \alpha = \varepsilon = -n\varepsilon_\lambda \Delta m. \tag{7}$$

For many reactions carried out at room temperature, a good approximation proved to be the value $n = -0.7$. This means, according to formula (7), that for $T > 500^\circ\text{K}$, $\varepsilon \approx 0$, which is indeed the case. Therefore, finally one may write

$$\ln \alpha = \varepsilon = 0.7\,\varepsilon_\lambda \Delta m. \tag{8}$$

The entire course of reasoning was carried out under the assumption that AB and AC are diatomic molecules. However, as the calculation showed, formula (8) is also applicable to polyatomic molecules, if such molecules are replaced by a model of a diatomic molecule whose reduced mass is calculated successively.

Table 1

Comparison of calculated and experimental values of α for some chemical-exchange reactions

Reaction	α by formula (8)	α, experimental	α, calculated from spectral data
In the gas phase			
$N^{15}O + N^{14}O_2 = N^{14}O + N^{15}O_2$	1,021	1,028 (4)	1,040 (5)
$N^{15}O + N^{14}OCl = N^{14}O + N^{15}OCl$	1,008	1,005 (3)	1,014 (5)
$C^{135}O_2 + HCl^{37} = HCl^{35} + Cl^{37}O_2$	1,021	–	1,027 (2)
$C^{13}O + C^{12}O_2 = C^{12}O + C^{13}O_2$	1,024	–	1,086 (6)
In interphase exchange			
$S^{34}O_2 + HS^{32}O_3^- = S^{32}O_2 + HS^{34}O_3^-$	1,014	1,012 (7)1,016–1,021 (8)	—

Reaction	α by formula (8)	α, experimental	α, calculated from spectral data
$S^{36}O_2 + HS^{32}O_3^- = S^{32}O_2 + HS^{36}O_3^-$	1,028	1,043 (8)	–
$C^{13}O_2 + HCl^{12}O_3^- = Cl^{12}O_2 + HC^{13}O_3^-$	1,026	1,014 (9)	–
$C^{12}O_3^- + C^{13}O_2 = C^{12}O_2 + C^{13}O_3^{2-}$	1,012	1,017 (10, 2)	1,012 (6)
$HC^{12}N + C^{13}N^- = HC^{13}N + C^{12}N^-$	1,027	1,026 (11)1,015 (12)1,013 (13)	1,030 (2)
$N^{15}O + HN^{14}O_3 = N^{14}O + HN^{15}O_3$	1,042	1,045–1,065 (14)	1,070 (5)
$Si^{28}F_4 + Si^{30}F_6^{2-} = Si^{30}F_4 + Si^{28}F_6^{2-}$	1,008	–	1,002 (15)
$Sn^{120}Cl_4 + Sn^{118}Cl_6^{2-} = Sn^{118}Cl_4 + Sn^{120}Cl_6^{2-}$	1,0006	–	1,00025 (15)
$(U^{235})^{4+} + (U^{238}O_2)^{2+} = (U^{238})^{4+} + (U^{235}O_2)^{2+}$	1,0013	1,0012 (16)	–
$B^{10}F_3 + B^{11}F_3(CH_3)_2O = B^{11}F_3 + B^{10}F_3(CH_3)_2O$	1,027	1,025 (17)	–
$B^{10}F_3 + B^{11}F_3(C_2H_5)_2O = B^{11}F_3 + B^{10}F_3(C_2H_5)_2O$	1,031	1,031 (18)	–

Reaction	α by formula (8)	α, experimental	α, calculated from spectral data
$B^{10}F_3 + B^{11}F_3(C_4H_9)_2O = B^{11}F_3 + B^{10}F_3(C_4H_9)_2O$	1,033	1,027 (^{19})	–
$B^{10}F_3 + B^{11}F_3(C_2H_5)_3N = B^{11}F_3 + B^{10}F_3(C_2H_5)_3N$	1,031	1,023 (^{20})	–
$B^{10}F_3 + B^{11}F_3C_6H_5OH = B^{11}F_3 + B^{10}F_3C_6H_5OH$	1,031	1,027 (^{19})	–
$B^{10}F_3 + B^{11}F_3 \cdot H_2O = B^{11}F_3 + B^{10}F_3 \cdot H_2O$	1,024	1,025 (^{18})	–
$B^{10}F_3 + B^{11}F_3(Cu_3)_2S = B^{11}F_3 + B^{10}F_3(Cu_3)_2S$	1,030	1,036 (^{21})	–
$B^{10}F_3 + B^{11}F_3(C_2H_5)_2S = B^{11}F_3 + B^{10}F_3(C_2H_5)_2S$	1,031	1,040 (^{21})	–
$B^{10}F_3 + B^{11}F_3HCOOC_2H_5 = B^{11}F_3 + B^{10}F_3HCOOC_2H_5$	1,030	1,028 (^{22})	–
$B^{10}F_3 + B^{11}F_3C_6H_5OCH_3 = B^{11}F_3 + B^{10}F_3C_2H_5OCH_3$	1,032	1,032 (^{19})	–
$B^{10}F_3 + B^{11}F_3(C_4H_9)_2S = B^{11}F_3 + B^{10}F_3(C_4H_9)_2S$	1,031	1,033 (^{21})	–
$H_3B^{10}O_3 + C_6H_{13}B^{11}O_3 = H_3B^{11}O_3 + C_6H_{13}B^{10}O_3$	1,008	1,003 (^{23})	–

Reaction	α by formula (8)	α, experimental	α, calculated from spectral data
$H_2S^{32} + (HS^{34})^- = H_2S^{34} + (HS^{32})^-$	1,003	1,006 (24)	–
$N^{15}N_3 + (NH_4^{14} \cdot H_2O)^+ = N^{14}H_3 + (N^{15}H_4 \cdot H_2O)^+$	1,032	1,023 (25)	–
$Cl^{135}O_4^- + HCl^{137} = HCl^{135} + Cl^{137}O_4^-$	1,092	–	1,077 (26)

Table 1 gives the values of the single-stage separation coefficients calculated by formula (8) for gas reactions, which are compared with experimental values and with those obtained as a result of calculation from spectroscopic data.

Between the exchange constant in the gas phase and in solution there exists the relation

$$K_{\mathrm{p}} = K_{\mathrm{g}} \cdot \varphi, \tag{9}$$

where K_{r} is the exchange constant in solution, $K_{\mathrm{g.ph}}$ is the exchange constant in the gas phase, and φ is the ratio of the isotope distribution coefficients between the phases. Experience shows that for most isotopes $K_{\mathrm{g.ph}} - 1 \gg \varphi - 1$; therefore one may write $K_{\mathrm{g.ph}} \approx K_{\mathrm{r}}$. Consequently, the exchange constant in interphase exchange can also, to a first approximation, be calculated from equation (8). Examples of such calculations are given in Table 1.

Comparison of the calculated data with experimental data shows satisfactory agreement. It should be noted, however, that the calculation is limited as a result of the approximations used in deriving formula (8), namely:

1. The calculation is inapplicable if there is an appreciable geometrical difference between the two isotopic molecules; the formula is inapplicable to calculating exchange reactions of hydrogen isotopes.
2. The derivation is valid for $\Delta m/M \ll 1$; therefore formula (8) cannot be used to calculate the constant of the reaction $Li^7 + Li^6H = Li^7H + Li^6$, where $\Delta m/M = 1/7$.

3. For reactions for which the slope of the temperature dependence of E on T^{-1} is gentler than that allowed for in the derivation, larger discrepancies between the calculated α and the experimental α are possible.
4. The calculation is limited to the case $K \equiv \alpha$.

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