DEPENDENCE OF THE EQUILIBRIUM CONSTANT IN ISOTOPIC EXCHANGE ON THE BOND ENERGY OF MOLECULES AND THE MASSES OF ATOMS

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Abstract

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DEPENDENCE OF THE EQUILIBRIUM CONSTANT IN ISOTOPIC EXCHANGE ON THE BOND ENERGY OF MOLECULES AND THE MASSES OF ATOMS

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The equilibrium constant and the separation factor in isotopic exchange can at present be calculated theoretically with sufficient accuracy, proceeding from the vibrational frequencies of isotopic molecules ($^{1-4}$). In order to predict the character of changes in the equilibrium constant as a function of the properties of the exchanging molecules, it is necessary to express the frequencies and equilibrium constants through these properties of the molecules. The way to solve the problem lies in establishing a connection between the ratio of the sums over states (or β-factors), which characterize isotopic exchange, and the force constants of the potential energy of the molecules k_e, which are determined by the structure of these molecules (^{5}).

It was found (^{5}) that at sufficiently high temperatures (or at low frequencies), when $u < 2$, and at low temperatures ($u > 5$)

$$\beta^n\Big|_{u<2} = 1 + \frac{1}{96\pi^2}\left(\frac{h}{kT}\right)^2\left(\frac{1}{\mu} - \frac{1}{\mu^*}\right)k_e, \tag{1}$$

where

$$\beta^n\Big|_{u>5} = ae^{b\sqrt{k_e}}, \tag{2}$$

$$a = \sqrt{\frac{\mu}{\mu^*}} \quad \text{and} \quad b = -\frac{1}{4\pi}\frac{h}{kT}\left(\sqrt{\frac{1}{\mu^*}} - \sqrt{\frac{1}{\mu}}\right),$$

$u = hc\omega_e/kT$; ω_e is the vibrational frequency of the molecule; h is Planck' s constant; k is Boltzmann's constant; c is the speed of light; T is the temperature (°K); n is the number of substituted isotope atoms in the molecule; μ is the reduced mass; $\mu = mm_0/(m+m_0)$, where m and m_0 are the masses, respectively, of the isotopic and second atoms; the asterisk refers to the heavy isotope. Since (6)

$$k_e = 4\pi^2 c^2 c_1^2 (z_1 z_2)^{1/2} r_e^{-2c_2}, \tag{3}$$

where r_e is the equilibrium internuclear distance; z_1 and z_2 are the numbers of electrons in the outer shells of the two atoms, $c_1 = (2.065 \div 2.976) \cdot 10^3$ and $c_2 = 0.92 \div 1.23$ are constants, relations (1) and (2) give the connection of the β-factor with the structure of the outer electron shell of the molecule and with the equilibrium internuclear distance, and explain the periodic regularity of the β-factors as a function of the atomic number of the nonisotopic element (5).

It is of interest to establish the dependence of the β-factors on the bond energies of molecules. Qualitatively this dependence can be established with the aid of the well-known Morse formula (7), which is often used to describe the potential curve. From the Morse formula it follows that

$$k_e = 2D_e \varepsilon^2, \tag{4}$$

where D_e is the dissociation energy, and ε is a constant for the given molecule. Thus, the force constant is proportional to the bond energy. But from this it follows that the β-factor will vary in accord with the bond energy, since, as was shown earlier (5), the β-factor varies in accord with the force constant. Thus, the greater the bond energy (with the nonisotopic atom), the higher the β-factor, i.e., the more strongly the difference between the isotopes is manifested.

For quantitative calculations it is expedient to use the empirical relation (8)

$$k_e = c_3 D_0 / r_e, \tag{5}$$

where c_3 is a constant for the given series of similar molecules.

From relations (3) and (5) it follows that the internuclear distance is approximately inversely proportional to the bond energy:

$$r_e = \left[4\pi^2 c^2 c_1^2 (z_1 z_2)^{1/2} / c_3 D_0\right]^{\frac{1}{2c_2-1}} \sim D_0^{\frac{1}{2c_2-1}} \approx 1/D_0, \tag{6}$$

where $\sim$ is the sign of proportionality.

Substituting (6) into (3), we find that, within one subgroup of the periodic system, when $z_1 z_2 = \text{const}$, the force constant is approximately proportional to the square of the bond energy:

$$k_e = c_1' (z_1 z_2)^{-\frac{c_4-1}{2}} D_0^{c_4} \sim\approx D_0^2 / \sqrt{z_1 z_2}, \tag{7}$$

where $c_1' = (4\pi^2 c^2 c_1^2)^{1-c_4} c_3^{c_4}$, $c_4 = 2c_2/(2c_2 - 1) = 1.68 \div 2.2 \approx 2$. Substituting into (1) and (2), we obtain (for $u \ll 2$ and for $u \gg 5$):

$$\beta^n\big|_{u<2} - 1 = \frac{c_1'}{96\pi^2}\left(\frac{h}{kT}\right)^2 (z_1 z_2)^{-(c_4-1)/2} D_0^{c_4}\left(\frac{1}{\mu} - \frac{1}{\mu^*}\right) \sim D_0^{c_4} \approx D_0^2; \qquad (8)$$

$$\beta^n\big|_{u>5} = \sqrt{\mu/\mu^*}\,\exp\left[b\sqrt{c_1'}(z_1 z_2)^{-(c_4-1)/4} D_0^{c_4/2}\right] \sim \exp c' D_0^{c_4/2} \approx \exp c' D_0. \qquad (9)$$

Relations (8) and (9) express the desired dependence of the β-factors on the bond energy of the isotope with the nonisotopic atom. If we had used relation (4), we would have found a weaker dependence ($\beta^n - 1 \sim D$ and $\beta^n \sim e^{c''\sqrt{D}}$); the result obtained here (equations (8)–(9)) is due to allowance for the decrease in the internuclear distance with increasing bond energy (equations (6)–(7)).

For checking dependences (7)–(9), graphs were constructed (see Fig. 1) in the coordinates $\lg(\beta^n - 1)$— $\lg D_0$ for the molecules NaNa, NaK, NaRb, NaCs ($u < 2$) and

$$\frac{\lg \beta^n \sqrt{\mu^*/\mu}}{\sqrt{1/\mu} - \sqrt{1/\mu^*}} - \lg D_0$$

($u > 5$) for the hydrides HF, HCl, HBr, HJ. The β-factors of the isotopic exchange of potassium and sodium were calculated by the Bigeleisen–Mayer method (1), and for the hydrides they were taken from (9). As can be seen from Fig. 1, dependences (8)–(9) are satisfactorily fulfilled; for the series shown the values of c_3 are respectively 1.68 and 2.19; in the latter series the exception is the HF molecule, $c_3 = 1.68$.

Fig. 1. Dependence of $\lg(\beta^n - 1)$ and

$$\lg \frac{\lg \beta^n \sqrt{\mu^*/\mu}}{\sqrt{1/\mu} - \sqrt{1/\mu^*}}$$

on the dissociation energy of molecules.
1–$Na^{22-24}Na$, $Na^{22-24}K$, $Na^{22-24}Rb$, $Na^{22-24}Cs$; 2–$H^{1-2}F$, $H^{1-2}Cl$, $H^{1-2}Br$, $H^{1-2}J$

On the basis of the relations obtained, recommendations can be made for selecting pairs of substances in isotopic exchange. The separation coefficient in isotopic exchange is equal to the ratio of two β-factors. From the relation between the β-factor and the bond energy it can be concluded that the isotope separation coefficient will be greatest if isotopic exchange occurs between two compounds of the isotopic element with the greatest difference in bond energy.

Fig. 2

Figure 1: Fig. 2

When the exchange occurs between compounds located in two different phases, it is expedient to have a strong bond in one phase and a weak one in the other. By applying strong complex-forming agents in both phases, one may obtain the opposite effect instead of improved separation.

The indicated regularity is confirmed by numerous calculated and experimental data not only for diatomic but also for polyatomic molecules. For example, for deuterium-protium exchange in the molecules H_2O, H_2S, and H_2Se the values of the β-factors at 20° are respectively 11.62, 5.46, and 4.42 ([9]). The dissociation energies of the first hydrogen atom in the same compounds are respectively 116, 90, and 66 kcal/mole * ([10]), i.e., for polyatomic molecules as well there is a sympathetic dependence of the β-factors on the bond energies for a series of similar compounds. The quantitative relation between the β-factors and the dissociation energies in this case is more complicated, but the qualitative picture is the same **.

The dependence of the β-factors on the mass of the element being separated at small u follows from the following relation, which is obtained by substituting (3) into (1)

$$\beta^n\big|_{u<2} = 1 + \frac{1}{24}\left(\frac{hc}{kT}\right)^2 \tilde{c}_1^2 (z_1 z_2)^{1/2} r_e^{-2c_2} \frac{\Delta m}{\bar{m}^2}, \tag{10}$$

where $\Delta m = m^* - m,\ \bar{m} = \sqrt{m^* m}$.

If the internuclear distance does not depend on the atomic masses, then from (10) it follows that for a series of similar compounds M_{iE} the quantity $(\beta^n - 1)$ is inversely proportional to the square of the mass of the isotopic element (M_i are isotopic elements of one and the same subgroup, E is the second atom, identical for all i molecules).

Fig. 2. Dependence of $\lg(\beta^n - 1)$ on the logarithm of the mass of the isotopic atom. In all the series shown, the isotopic element is written first in the formula. β-factors were calculated for an isotope mass difference $\Delta m = 2$.
1 –LiLi, KLi, RbLi, CsLi, $\Delta = 0.22$;
2 –LiCl, NaCl, KCl, RbCl, CsCl, $\Delta = 0.14$;
3 –MgCl, CaCl, SrCl, BaCl, $\Delta = 0.10$;
4 –BCl, AlCl, GaCl, InCl, TlCl, $\Delta = 0.10$;
5 –CCl, SiCl, GeCl, SnCl, PbCl, $\Delta = 0.15$;
6 –O_2, SO, SeO, TeO, $\Delta = 0.14$;
7 –FCl, Cl_2, BrCl, ICl, $\Delta = 0.14$;
8 –ClO_3^-, BrO_3^-, IO_3^-, $\Delta = 0.16$.

Figure 2 presents the dependence of $\lg(\beta^n - 1)$ on the logarithm of the mass of the isotopic element for diatomic halides of the first, fourth, and seventh groups of the periodic system, as well as for interhalogen molecules of the first group and oxides of the fifth group. The values of the vibrational frequencies are taken from work (6) (except KF, KCl—from (11); LiCl—from (12); for FCl the frequency was calculated from the value of the force constant (8)).

From Fig. 2 it is evident that the dependences of $\lg(\beta^n - 1)$ on $\lg \bar{m}$ for all groups are linear and the slopes of the straight lines are very close to one another. The averaged tangent of the angle of inclination is -2.15. The deviation from the quadratic dependence can be explained by the fact that the internuclear distance also depends on the mass of the isotopic element; this gives an additional dependence of $\lg(\beta^n - 1)$ on the mass to the power $\Delta = 0.15$. It is interesting to note that the regularity found proved valid also in the region $u > 2$ (straight lines 4-7), although the analytical expression in this case is more complicated.

In Fig. 2 data are also plotted for polyatomic compounds

* For H_2Se the mean bond energy is given, which in absolute magnitude is close to the dissociation energy.
** An analogous sympathetic relation is apparently also observed for complexes with organic addends.

ClO_3^-, BrO_3^-, JO_3^-. The regularity is also well obeyed in this case.

From the linear dependence of $\lg(\beta^n - 1)$ on the logarithm of the mass of the isotopic atom there follows the relation

$$\frac{\beta_1^n - 1}{\beta_2^n - 1} = \left(\frac{m_2}{m_1}\right)^{2+\Delta}, \tag{11}$$

where the subscripts 1 and 2 refer, respectively, to two different isotopic elements (and molecules). Relation (12) makes it possible, starting from the β-factors of two molecules, to calculate the β-factors for a series of similar molecules M_{iR}, where M_i are elements of one and the same group of the periodic system, and R is a second atom (or a group of atoms symmetrically arranged around the central isotopic atom M_i). For an approximate calculation it is necessary to know only one β-factor, since, as indicated above, the slopes of all the straight lines are approximately the same and $\Delta = 0.15$.

Fig. 3. Dependence of $\lg(\beta^n - 1)$ on the logarithm of the mass of the second (nonisotopic) atom. In all the series presented, the isotopic element is written first in the formula. The β-factors were calculated for an isotope mass difference $\Delta m = 2$, except for hydrogen isotopes, where $\Delta m = 1$. The values of the β-factors of the hydrides are taken from Ref. (9).
1 –KF, KCl, KBr, KJ; 2 –LiLi, LiK, LiRb, LiCs; 3 –LiF, LiCl, LiBr, LiJ; 4 –HLi, HNa, HK, HRb, HCs; 5 –HMg, HCa, HSr. The values of δ are respectively 0.27; 0.30; 0.38; 0.31; 0.25.

In conclusion we shall make a remark about the dependence of the separation coefficient on the mass of the second (nonisotopic) atom m_0. Theoretical considerations lead to the conclusion that in the region of small quantum effects ($u < 2$) the β-factors do not depend on m_0 (13). As is seen from relation (10), this would be true if the internuclear distance r_e did not depend on m_0. Since, however, r_e increases with increasing m_0, it may be expected that, with increasing mass of the second atom m_0, the β-factor will decrease. Figure 3 shows that this indeed occurs, although the dependence is comparatively weak: $\beta^n - 1 \sim m_0^{-\delta}$, where $\delta = 0.25$–0.40. This effect also explains the decrease in the β-factors of hydrides with increasing atomic number of the element bonded to hydrogen (within one group of the periodic system).

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