THE MECHANISM OF THE ISOTOPIC EXCHANGE REACTIONS.

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The total energy of a molecule can be expressed by $E_e + E_v + E_r$, where E_v and E_r represent the vibrational and rotational energies, respectively, and E_e is the electronic energy, which is, of course, of a greater order of magnitude than E_v and E_r ($E_e \gg E_v \gg E_r$). Consequently there will be three different possible manifestations of the isotopic effect.

The electronic isotopic effect, which has not been worked out even for the simplest of diatomic molecules, must be very small (Jeppesen,(1) Beutler and Mie, and Johnston(2) have observed rather unexpected isotopic effect, i.e. 135 cm.$^{-1}$ in H_2 and 20 cm.$^{-1}$ in OH). For all present purposes, this will be possibly ignored. The vibrational isotopic effect, which is much larger, has been much more important in the isotopic exchange reactions.(3) The rotational isotopic effect is small compared with the vibrational effect.

The apparent energy differences of isotope molecules can be interpreted as the difference of the zero point energies, assuming that the total energies of isotopic molecules are the same. For present purposes it will be sufficient only to consider the difference of the zero point vibrational energies.

The energy of vibration will be expressed in the usual way as

$$E_v = h_c \omega_e \left(v + \frac{1}{2}\right) - x_e \omega_e \left(v + \frac{1}{2}\right)^2 + \dots ,$$

where ω_c is the frequency of vibration and is expressed by

$$\omega_e = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} .$$

K is the so-called restoring force, i.e. the force acting upon the nuclei when their distance is increased by one unit from its equilibrium value. μ is the reduced mass expressed by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, where m_1 and m_2 are the masses of both nuclei. K corresponds to the binding force between two nuclei.

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(1) *Phys. Rev.*, **45** (1934), 480.

(2) *Naturwissenschaften*, **21** (1933), 495.

(3) Urey and Rittenberg, *J. Chem. Physics*, **1** (1933), 137; Rittenberg, Bleakney, and Urey, *J. Chem. Physics*, **2** (1934), 48; L. Farkas and A. Farkas, *Trans. Faraday Soc.*, **30** (1934), 1071.

If it is assumed that the distances between two nuclei are the same,⁽⁴⁾ the binding force, that depends only upon the charges of the constituent nuclei and electrons, is the same in both kinds of molecules. While the reduced mass of the molecule of the heavier isotope is larger than that of the lighter one, the vibration frequency ω_e and consequently the zero point energy of vibration will be smaller in the former. If ω_{eI} is the wave number of the vibrational band of the heavier molecular isotope I, then the corresponding band for the molecular isotope II will be displaced by an amount which can be calculated from

$$\frac{\omega_{eI}}{\omega_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

The quantity $\frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}$ is usually denoted ρ .

For instance, the molecule HCl^{37}, vibrating by reason of its increased mass a little slower than HCl^{35}, would have its vibrational band displaced towards smaller frequencies. And conversely in the isotopic molecules $Cl^{35}M$ $Cl^{37}M$, when M is substituted by a heavier element, the vibration frequencies of chlorine atom and consequently the frequency differences of two molecular isotopes must increase. These isotopic effect has been actually observed in diatomic spectra.⁽⁵⁾ The differences of the zero point energies of vibration of $Cl^{35}M_1$–$Cl^{37}M_1$ and $Cl^{35}M_2$–$Cl^{37}M_2$ are not the same, and when $M_2 > M_1$, the difference is larger for the latter. This effect has been pointed out heretofore. Let us call this effect "effect A".

The author has investigated the equilibrium of the exchange reactions between heavy water and various hydrogen compounds⁽⁶⁾ and found that the equilibrium constants depend upon the polarities of molecules. For instance, in the reaction between hydrogen ion and water $(=OH^+) + (-OD) = (=OD^+) + (-OH)$, the equilibrium constant is 1.60; on the other hand the equilibrium constant of the reaction between hydroxyl ion and water $(OH^-) + (-OD) = (OD^-) + (-OH)$ is 0.42. In these cases the isotopic effect due to "effect A" can not be considered. In general, the larger the zero point energy differences between molecular isotopes, the greater the equilibrium constant.

Bernal and Tamm⁽⁷⁾ considered following isotopic effect. They said, "the marked differences between the physical properties of H_2O and D_2O and

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(4) Anderson and Yost, *J. Chem. Physics*, **3** (1935), 242; van Cleave and Mass, *Can. J. Research*, **12** (1935), 57; Amdur, *J. Am. Chem. Soc.*, **57** (1935), 588.

(5) Aston, "Mass Spectra and Isotopes," p. 209.

(6) *Tech. Repts Kyushu Imp. Univ.*, **10** (1935), 272.

(7) *Nature*, **135** (1935), 229.

of all polar compounds of H and D can not be due to intramolecular differences, which are far too small, but must be connected with differences of effective intermolecular forces. It is possible to account for these differences in a quantitative way by taking into consideration the differences in the frequency of angular vibration or libration of a molecule in the field of its neighbours ".

These considerations are very interesting in connection with the author's experimental results. But according to the author's opinion it is not absolutely necessary to assume the isotopic effect of the so-called angular vibration or libration of polar compounds. It is very natural to consider that the fundamental vibration of $=OH^+$, $-OH$, and OH^- are not the same and therefore the frequency differences of vibration or zero point energy differences of OH^+-OD^+, $(-OH)-(-OD)$, or OH^--OD^- are also not the same. From these results it is possible to say that the isotopic effect will be greatest in the positively changed molecular ions. These results must be based upon the differences of the deformation of atoms or the differences of electronic binding forces in the different states of polarisation. This theory can also be applied to neutral molecules.

The equilibrium constant of the reaction $H_2O + HD = HDO + H_2$ is about 3 at 20°C.(8) In this case hydrogen atom of water is positively polarised. According to the author's theory the zero point energy difference between $-OH$ and $-OD$ will exceed the difference between HH and HD by reason of the electropositiveness of hydrogen atom of hydroxyl bond. The author has investigated the isotopic shift of oxygen by sulphuric acid(9) and observed that O^{18} in H_2O^{18} can be removed by the flow of air. In this case oxygen atom of water is negatively polarised. The zero point energy difference between $O^{16}O^{16}$ and $O^{16}O^{18}$ will exceed that of $O^{16}H$ and $O^{18}H$ by reason of the electronegativeness of oxygen atom of hydroxyl bond. These isotopic effects due to polarisation of atom will probably play the most important rôle in the isotopic exchange reactions. Let us call this " effect B ". According to effect B it is concluded that the element is rich in heavier isotope when it is in the more positively polarised state. Various methods of separation of isotopes by the application of effects A and B will be considered.

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(8) Bonhoeffer and Rummel, *Naturwissenschaften*, **22** (1934), 45; A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), A, **144** (1934), 467; *Trans. Faraday Soc.*, **30** (1934), 1071.

(9) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), 25.