§7. Quantum Chemical Analysis of Thermodynamic Hydrogen Isotope Effects

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It has been well known that thermodynamic isotope effects in the equilibria are dependent on the relative mass difference of the isotopes. Anomalous mass effects which do not fit the above rule of the isotope effects, however, have been found theoretically in hydrogen isotope exchange equilibria between diatomic hydrides[1)-2)], and in oxygen isotope exchange equilibria between diatomic oxides[3)-4)].

The objective of the present work is to shed light on the thermodynamic isotope effects and the anomalous mass effects in hydrogen isotope exchange reactions between water and diatomic hydrides, according to the theoretical calculations of the equilibrium constants for the reactions.

The equilibrium constants of the reactions were calculated in the temperature range 50 - 2000K on a basis of quantum statistical mechanics within the framework of the harmonic oscillator-rigid rotor approximation. The vibrational frequencies used of isotopomers were calculated using the force constants which were obtained from the molecular spectroscopic data.

A large number of the calculated equilibrium constants showed the anomalous mass effects. For example, the equilibrium constants($Khd(F), Kht(F)$) for the H - D, H - T exchange reactions between water and hydrogen fluoride showed the anomalous mass effects, and had the mass independent fractionation (MIF) and the cross over temperatures. The MIF temperature is that temperature at which an equilibrium constant is equal to the other one. The temperature dependence of $\ln Khd(F)$, $\ln Kht(F)$, and the ratio ($\ln Kht(F)/\ln Khd(F)$) for the reactions is presented in Table 1.

Table 1 Temperature Dependence of $\ln Khd(F)$, $\ln Kht(F)$, and the Ratio for Hydrogen Isotope Exchange Reactions, $H_2O + {}^*HF = H^*HO + HF$, $^*H = D, T$.

T(K)	$\ln Khd(F)$	$\ln Kht(F)$	$\ln Kht(F)/\ln Khd(F)$
50.0	1.6880	2.2104	1.309
300.0	0.1744	0.2199	1.261
720.9	0.0175	0.0175	1.000
929.9	0.0028	0.0000	0.000
960.0	0.0016	-0.0013	-0.813
1007.8	0.0000	-0.0031	-∞
1050.0	-0.0011	-0.0043	3.909
1500.0	-0.0053	-0.0081	1.528

It is clear from Table 1 that the values of the ratio widely vary with temperature, although the value should hold constant at 1.333 according to what is called the normal mass effects for the quilibrium constant of isotopic exchange reaction. : (1) The ratio becomes unity at 720.9 K (MIF temperature), since the value of $\ln Khd(F)$ is equal to that of $\ln Kht(F)$, 0.0175 at the temperature. In this case, D and T are enriched in water by the same separation factor. (2) At 1007.8 K, the ratio becomes -∞, since $\ln Khd(F)$ is 0.0000 and $\ln Kht(F)$ -0.0031. Therefore, at the temperature T is enriched in hydrogen fluoride, and D is not enriched in both water and hydrogen fluoride.

The values of equilibrium constants,($Kht(Fe)$, $Kht(Ni)$, $Kht(H)$) for H - T exchange reactions, $H_2O + MT = HTO + MH$($M = Fe, Ni, H$) which showed the anomalous mass effects, are presented in Table 2. The magnitudes of these equilibrium constants are in the following sequence in the temperature range 278.1 - 323.1 K : $Kht(Fe) > Kht(Ni) > Kht(H)$. And then, all the values are larger than 1.000. Therefore, in cases of these reactions, T are enriched in water. The separation factor becomes largest at the reaction between water and iron hydride.

Table 2 Equilibrium Constants($Kht(Fe), Kht(Ni), Kht(H)$) of H-T Exchange Reactions, $H_2O + MT = HTO + MH$, $M = Fe, Ni, H$.

T(K)	Kht(Fe)	Kht(Ni)	Kht(H)
278.1	13.779	11.459	8.033
283.1	13.115	10.944	7.679
288.1	12.504	10.469	7.351
293.1	11.940	10.029	7.048
298.1	11.419	9.622	6.768
303.1	10.936	9.244	6.507
313.1	10.072	8.563	6.038
323.1	9.322	7.970	5.629

Since Clayton et al. discovered the oxygen isotope anomalies in carbonaceous chondrites in 1973, a number of the anomalies have been experimentally found in various chemical systems. And then it has been believed that the anomalies are not due to the isotope exchange equilibria known to be going on at present within the solar system. It, however, can be now concluded that the hydrogen isotopic exchange equilibria between water and diatomic hydrides which show the anomalous mass effects must be able to produce hydrogen isotope anomalies and anomalous hydrogen isotope separations.

References
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