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Isotope Anomalies in Oxygen Isotope Exchange Equilibrium Systems

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SUMMARY. Equilibrium constants of the oxygen isotope exchange reactions between diatomic oxides were calculated in a wide temperature range on the basis of quantum statistical mechanics. Oxygen isotope separation factors were also calculated about the oxygen isotope exchange equilibrium systems which contained some of the above isotope exchange reactions. Many equilibrium constants and the separation factors showed anomalous mass effects. It can be concluded that some oxygen isotopic exchange equilibria cause the isotope anomalies.

1. INTRODUCTION

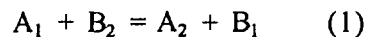
It has long been believed that any isotopic exchange equilibria can not produce the isotope anomalies, because isotope effects in isotopic exchange equilibria studied with different isotopes of the same element are a monotonic function of the isotopes' relative mass differences.

Recently, however, anomalous mass effects, which do not fit the above rule of the isotope effects have been found in some equilibrium systems(1 - 8).

The objective of the present work is to shed light on the isotope anomalies and the anomalous mass effects in the oxygen isotope equilibrium systems, according to the calculations of the equilibrium constants for oxygen isotopic exchange reactions between diatomic oxides, and the calculations of the oxygen isotope separation factors between two phases.

2. CALCULATION

An equilibrium constant(K) for an isotopic exchange reaction between diatomic species A and B,



can be written in terms of the reduced partition function ratios $\{(s_2/s_1)f\}$ for chemical species A and B,

$$K = (s_2/s_1)f[A_2/A_1] / (s_2/s_1)f[B_2/B_1] \quad (2)$$

where the subscripts 1 and 2 refer to the light and heavy isotopic species, respectively(9).

With the approximations that the vibrational motion is harmonic, that the rotational and translational motions are classical, and that there is no rotational-vibrational interaction, the reduced partition function can be presented by

$$(s_2/s_1)f = [u_2 \exp(-u_2/2) \{1 - \exp(-u_1)\}] / [u_1 \exp(-u_1/2) \{1 - \exp(-u_2)\}] \quad (3)$$

Here $u = h\nu/kT$, where ν refers to a normal mode vibrational frequency, h is Plank's constant, k Boltzmann's constant, and T the absolute temperature.

Equilibrium constants (K65, K67, K68, and K69) of $^{16}\text{O} - ^{15}\text{O}$, $^{16}\text{O} - ^{17}\text{O}$, $^{16}\text{O} - ^{18}\text{O}$, and $^{16}\text{O} - ^{19}\text{O}$ oxygen isotopic exchange reactions between diatomic oxides were calculated in a wide temperature range by the equations 2 and 3. The vibrational frequencies used in the calculations were determined on the basis of the force constants which were obtained from the frequencies observed.

An equilibrium constant of isotope exchange reaction is a function of temperature, force constants of the molecules contained in the reaction, and masses of atoms in the molecules, according to the equations 2 and 3. When the equilibrium constants of $^{16}\text{O} - ^{17}\text{O}$, $^{16}\text{O} - ^{18}\text{O}$, and $^{16}\text{O} - ^{19}\text{O}$ oxygen isotope exchange reactions between OH and the other diatomic oxide(MO) showed the anomalous mass effects, the force constants of MO were calculated as a function of atomic mass of M in the temperature range 50 - 2000 K by the Newton Raphson method.

Oxygen isotope separation factors $S6j$ ($j = 5, 7, 8, 9$) between the first phase and the second phase defined in the following equation.

$$S6j = \{(\text{Total amount of } ^{1j}\text{O in the second phase}) / (\text{Total amount of } ^{16}\text{O in the second phase})\} / \{(\text{Total amount of } ^{1j}\text{O in the first phase}) / (\text{Total amount of } ^{16}\text{O in the first phase})\}$$

$$^{16}\text{O in the first phase}) \quad ; j = 5, 7, 8, 9 \quad (4)$$

When CO and OH were in the first phase, SiO, AlO, FeO, and MgO were in the second phase, oxygen isotope separation factors(S65, S67, S68, and S69) between the two phases were calculated by the following equation 5, according to the theory of two phase distribution of isotopes(10).

$$S6j = \{X_{\text{SiO}}/K6j(\text{SiO}) + X_{\text{AlO}}/K6j(\text{AlO}) + X_{\text{FeO}}/K6j(\text{FeO}) + X_{\text{MgO}}/K6j(\text{MgO})\} / \{X_{\text{OH}} + X_{\text{CO}}/K6j(\text{CO})\} \quad j = 5, 7, 8, 9 \quad (5)$$

X_{MO} ; Mole fraction of MO in each phase

$K6j(\text{MO})$; $K6j$ between OH and MO

3. RESULTS AND DISCUSSION

Many equilibrium constants calculated showed the anomalous mass effects. For example, the equilibrium constants for the oxygen isotope exchange reactions between OH and the diatomic oxides(MO) showed the anomalous mass effects, and had the cross over temperatures and the mass independent fractionation(MIF) temperatures, when M was Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Cr, Mn, Fe, Co, Ir, Ni, Pt, Cu, Ag, Zn, Al, Ga, In, Ge, Sn, Pb, As, Sb, Bi, Se, Te, F, Cl, Br, I, La, Ce, Pr, Eu, Tb, Lu, Th, and U(47 elements). The force constants of these forty seven diatomic oxides were smaller than that of OH. The cross over temperature is that temperature at which the logarithm of an equilibrium constant changes sign. The MIF temperature is that temperature at which

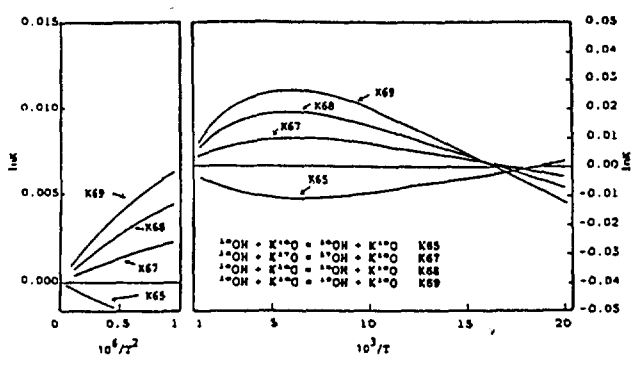
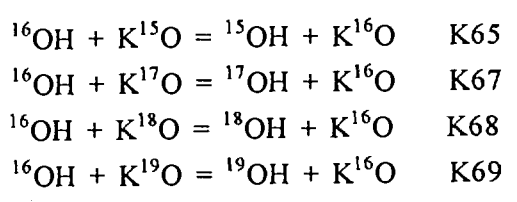


Figure 1 $\ln K$ for the Oxygen Isotope Exchange Equilibria $^{16}\text{OH} + \text{K}^*\text{O} = ^*\text{OH} + \text{K}^{16}\text{O}$ vs. $10^6/T^2$ (left), $10^3/T$ (right). $^*\text{O} = ^{15}\text{O}, ^{17}\text{O}, ^{18}\text{O}, ^{19}\text{O}$

an equilibrium constant is equal to the other one.

Figure 1 shows the temperature dependence of equilibrium constants for the oxygen isotope exchange reactions between OH and KO. The reactions are



For the reactions, there are the cross over and MIF temperatures and three maxima and one minimum of the equilibrium constants. The cross over temperature increases with the mass of the isotopomer ; $\ln K_{67}=0$ at 57.8K and $\ln K_{68}=0$ at 59.3K. The curves for $\ln K_{67}$, $\ln K_{68}$, and $\ln K_{69}$ cross one another above the cross over temperatures. The value of $\ln K_{67}$ is equal to that of $\ln K_{68}$ at 60.9K. Below this temperature $\ln K_{67}$ is larger than $\ln K_{68}$. The value of logarithm of equilibrium constant at the maximum increases with the mass difference between the isotopes in the exchange reaction.

We have also studied the mass dependence of oxygen isotope exchange equilibria between OH and eleven diatomic oxides (BO, CO, NO, O₂, SiO, PO, SO, NbO, HfO, TaO, and WO) whose force constants were larger than that of OH. These equilibria showed no anomalous mass effects. The heavy oxygen isotope concentrated in the eleven diatomic oxides in preference to OH at all temperatures.

When the equilibrium constants of $^{16}\text{O} - ^{17}\text{O}$, $^{16}\text{O} - ^{18}\text{O}$, and $^{16}\text{O} - ^{19}\text{O}$ oxygen isotope exchange reactions between OH and the other diatomic oxide (MO) showed the anomalous mass effects, the force constants of M-O were calculated as a function of atomic mass of M and temperature. As the result we found the following. The M-O force constant depended on the atomic mass of M, particularly below mass 20. The force constant increased with decreasing the atomic mass of M. The cross over and MIF temperatures increased with the force constant.

We have studied the oxygen isotope separation factors(S65, S67, S68, and S69) between the first phase(OH and CO) and the second phase(SiO, AlO, FeO, and MgO) as a function of temperature and the mole fractions of OH and CO, the mole fractions of four oxides in the second phase being kept constant at 0.25, respectively. The results are given in Figure 2. For the separation factors, there are cross over temperatures, MIF temperatures, maxima, and minima, when the mole fraction of OH is 1.00, 0.60, or 0.50. The cross over temperature of a separation factor is that temperature at which the logarithm of a separation

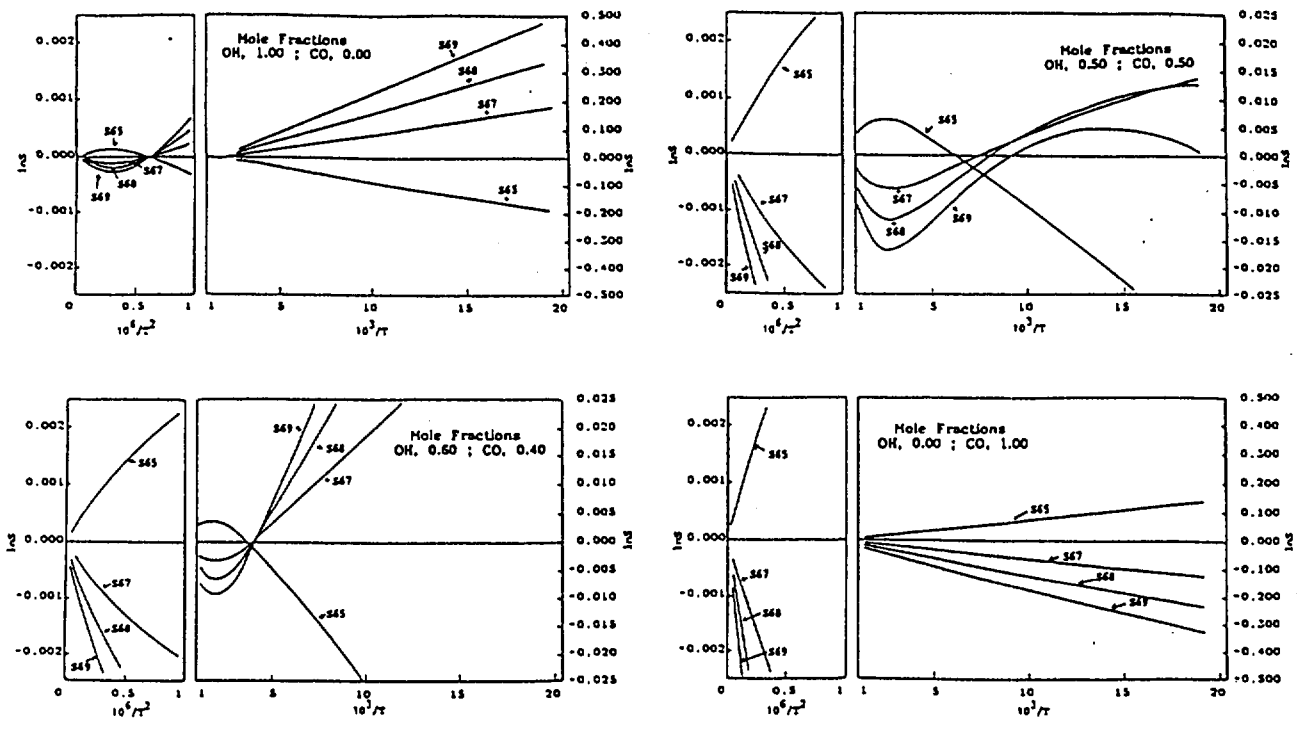


Figure 2 Logarithms of Oxygen Isotope Separation Factors between First Phase(OH and CO) and Second Phase(SiO, AlO,FeO, and MgO) vs. $10^6/T^2$ (left), $10^3/T$ (right).

The mole fractions of four oxides in the second phase were kept constant at 0.25.

factor changes sign. The MIF temperature of a separation factor is that temperature at which a separation factor is equal to the other one. The results are reasonable, because in the two phases there are the oxygen isotope exchange equilibria which have the anomalous mass effects. The temperature dependence of the separation factors widely varies with the mole fraction of OH.

In Figure 3 we plot $\ln S_{67}$ against $\ln S_{68}$ as the mole fraction of OH being 0.5, and then the values of $\ln S_{67}$, $\ln S_{68}$, and the ratios are given in Table 1. The value of $\ln S_{68}/\ln S_{67}$ should be 1.885 because the value of $\ln K_{68}/\ln K_{67}$ is 1.885, according to the high temperature approximation for the equilibrium constant of isotopic exchange reaction(II). However, the ratios obtained widely varies with temperature. For example, at

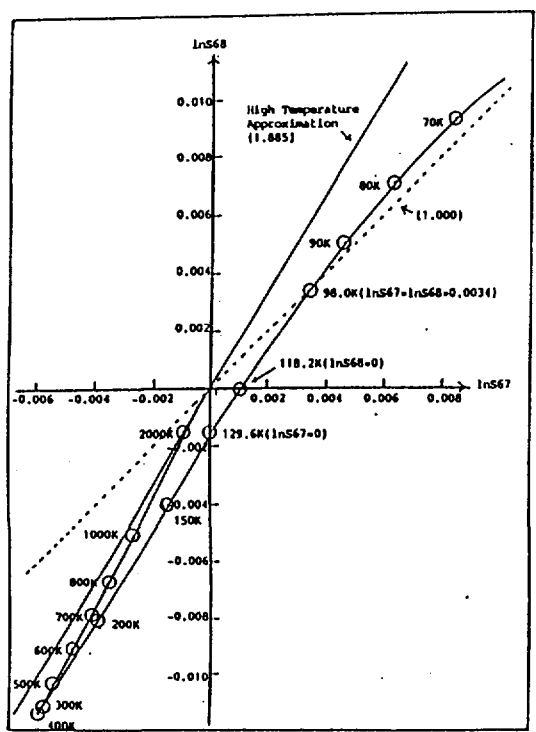


Figure 3 Plot of $\ln S_{67}$ vs. $\ln S_{68}$ for Oxygen Isotope Exchange Equilibrium System between First Phase(OH and CO) and Second Phase (SiO, AlO, FeO, and MgO) The mole fraction of OH was 0.5.

Table 1 Temperature Dependence of $\ln S_{67}$, $\ln S_{68}$, and the Ratio for Oxygen Isotope Exchange Equilibrium System between First Phase(OH and CO)and Second Phase(SiO, AlO, FeO, andMgO) The mole fraction of OH was 0.5.

T(K)	$\ln S_{67}$	$\ln S_{68}$	$\ln S_{68}/\ln S_{67}$
50.0	0.0139	0.0127	0.914
60.0	0.0109	0.0114	1.046
80.0	0.0063	0.0071	1.127
98.0	0.0034	0.0034	1.000
118.2	0.0010	0.0000	0.000
129.6	0.0000	-0.0016	--
140.0	-0.0008	-0.0029	3.625
150.0	-0.0015	-0.0040	2.667
300.0	-0.0058	-0.0113	1.948
1000.0	-0.0027	-0.0051	1.889

98.0 K the value of $\ln S_{67}$ is equal to that of $\ln S_{68}$, 0.0034. As a result, both oxygen isotopes ^{17}O and ^{18}O are enriched in the second phase by the same separation factor. In the range below 98.0 K to 50 K the value of $\ln S_{67}$ is almost equal to that of $\ln S_{68}$. Therefore oxygen isotopes ^{17}O and ^{18}O are also enriched in the second phase by about the same separation factor in this range. At 129.6 K ^{18}O is enriched in the first phase, whereas ^{17}O is not enriched in both the first phase and the second phase, since the value of $\ln S_{68}$ is -0.0016 and the value of $\ln S_{67}$ is 0.0000. Therefore the oxygen isotope anomalies can occur in

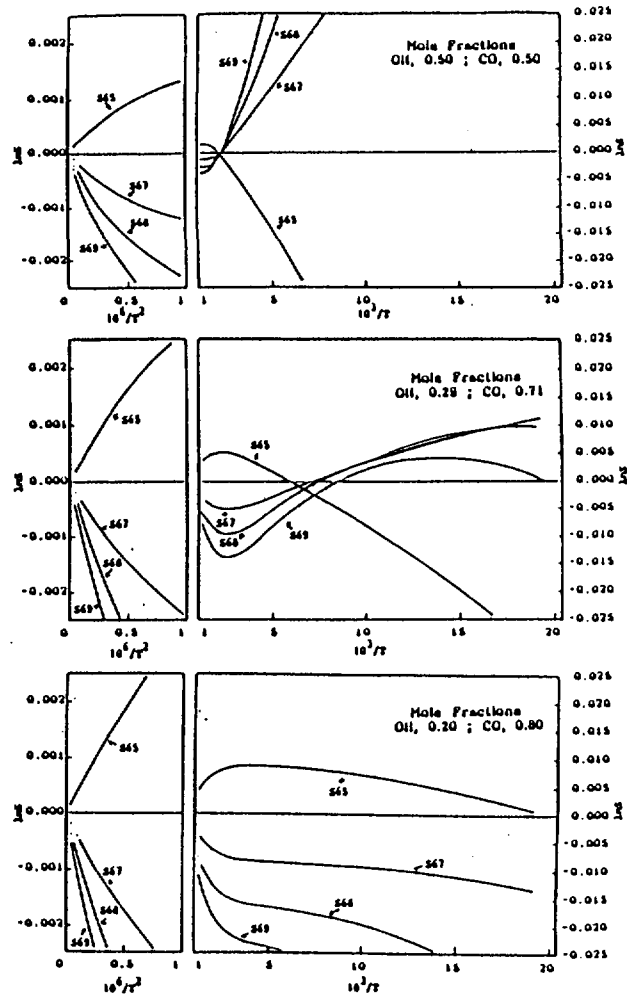


Figure 4 Logarithms of Oxygen Isotope Separation Factors between First Phase (OH and CO) and Second Phase(SiO) vs. $10^6/T^2$ (left), $10^3/T$ (right).

the two phases at these temperatures.

When only SiO was in the second phase, and OH and CO were in the first phase, we also studied the oxygen isotope separation factors between the two phases. The results are given in Figure 4. Although there is no oxygen isotopic exchange equilibrium with the anomalous mass effects in the two phases, the oxygen isotope separations have the cross over temperatures, the MIF temperatures, maxima, and minima, when the mole fraction of OH is 0.50 or 0.29.

Whether the oxygen isotopic exchange equilibria in two phases have the cross over temperatures, the MIF temperatures, maxima, and minima, or not, the oxygen isotope separation factors between the two phases show the anomalous mass effects on certain conditions. Therefore the exchange equilibria can produce the oxygen isotope anomalies under the conditions.

4. CONCLUSION

It can be concluded from the results obtained in the present work that some oxygen isotopic exchange equilibria cause the anomalous mass effects, the anomalous oxygen isotope separation factors, and then the oxygen isotope anomalies.

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