Temperature dependence of isotopic fractionation factors

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Abstract—The temperature dependences of the partition function ratios of gaseous molecules at low and high temperatures, originally investigated by UREY (1947) and BIGELEISEN and MAYER (1947), are derived and clarified. For diatomic molecules at low temperatures, the logarithm of the partition function ratio becomes

$$\ln\left[\frac{Q_2}{Q_1}\right] \cong \frac{U_1 - U_2}{2} + \ln\left[\frac{\sigma_1 \nu_2}{\sigma_2 \nu_1}\right]$$

where U represent values of $h\nu/kT$, ν represent the molecular vibrational frequencies, and σ are the symmetry numbers. This expression is linear in $1/T$, as it is of the form $y = m/T + \text{const.}$, where m is proportional to the difference between the zero point energies of the ordinary (1) and isotopically substituted (2) molecules. At high temperatures the partition function ratio may be expanded in a power series; for example, for diatomic molecules:

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right] - \frac{U_2^2 - U_1^2}{24} + \frac{U_2^4 - U_1^4}{2880} - \frac{U_2^6 - U_1^6}{181440} + \cdots$$

The well-known $1/T^2$ dependence arises from the second term ($U^2/24$), which becomes increasingly important relative to the higher-order terms as temperature increases. Extension of these results to polyatomic molecules and to isotopic fractionation factors is straightforward.

INTRODUCTION

IT IS WELL KNOWN that the isotopic fractionation factor between two substances A and B, α_{AB}, is a function of absolute temperature (T) but generally not a function of pressure. Several useful introductory discussions (*e.g.*, O'NEIL, 1986; HOEFS, 1987) state that $\ln(\alpha_{AB})$ varies as $1/T$ at low temperatures and as $1/T^2$ at higher temperatures, ultimately approaching zero fractionation ($\alpha = 1$) at infinite temperature. Such discussions invariably refer to the seminal papers by UREY (1947) and BIGELEISEN and MAYER (1947) on isotopic fractionation, but when the latter are consulted for a detailed explanation of these functional dependences, one is apt to be left unsatisfied. UREY (1947), for example, merely states that his equations for the partition function ratios can be "easily expanded" at high temperatures to give his single term demonstrating the $U^2/24$ dependence. BIGELEISEN and MAYER (1947), on the other hand, make numerous approximations to represent the ratios in terms of their function "G," which they then graphically analyze to determine the temperature dependence.

The following derivations were undertaken in order that I might provide a more satisfactory explanation for the temperature dependences of isotopic fractionation factors for a class. Through a subsequent literature search I learned that many of these results had been previously published (BIGELEISEN, 1958; STERN *et al.*, 1968), albeit in papers that are little referenced by the geochemical community. For some years I have wondered why simplification of the partition function ratios (eqns. 3a,b, below) using the well-known approximation $e^U \approx 1 + U$, which would be expected to be very accurate at extremely high temperatures (small U), does not lead to the $U^2/24$ dependence derived by UREY. Similarly, one may immediately verify that this approximation does not reduce BIGELEISEN and MAYER's "G" function, represented by the sum $\frac{1}{2} - 1/U + 1/(e^U - 1)$, to its high temperature value of $U/12$. The proper derivation in either case requires that great care be taken to account for all product terms to sufficiently high order, which in turn requires that no less than *four* terms of the exponential expansion for e^U are used, together with sufficient terms in binomial expansions that are subsequently needed to invert the resulting denominators. Moreover, one would be very hard pressed to use such methods to calculate the succeeding term of a power series representing the partition function ratio, even though this term is of interest because it represents the bulk of the deviation of this ratio from the simple $U^2/24$ dependence. Also, the BIGELEISEN and MAYER approximation does not give the proper y-intercept for the $\ln K$ vs $1/T$ relation in the low temperature case.

In short, the above points number among several that to my knowledge have not been clearly discussed in the literature. It is hoped that the simple

derivations and discussions presented here will enlighten geochemists about the straightforward basis for the temperature dependence of isotopic fractionation factors for gaseous molecules, and remind them of some important but nearly forgotten papers.

BASIC EQUATIONS

A generalized equation may be written to express isotopic exchange between two substances A and B, where the subscripts 1 and 2 indicate that the molecules, respectively, only contain either the light or the heavy isotope:

$$aA_1 + bB_2 = aA_2 + bB_1. \qquad (1)$$

The equilibrium constant K for such reactions may be written in terms of the simplified partition functions (Q's) of UREY (1947), where each Q represents the equilibrium constant between the compound of interest and its separated atoms, i.e.

$$K = \left(\frac{Q_{2A}}{Q_{1A}}\right)^a \Big/ \left(\frac{Q_{2B}}{Q_{1B}}\right)^b. \qquad (2)$$

Here

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \frac{U_2}{U_1} \frac{e^{-U_2/2}}{1 - e^{-U_2}} \frac{1 - e^{-U_1}}{e^{-U_1/2}} \qquad (3a)$$

for diatomic molecules, and

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_{i=1}^{3n-6} \frac{U_{2i}}{U_{1i}} \frac{e^{-U_{2i}/2}}{1 - e^{-U_{2i}}} \frac{1 - e^{-U_{1i}}}{e^{-U_{1i}/2}} \qquad (3b)$$

for nonlinear polyatomic molecules. The expression for linear polyatomic molecules is the same as the latter, except that there are only $3n - 5$ vibrational modes instead of $3n - 6$. In the above, the σ denote the symmetry numbers, that is, the number of indistinguishable ways of orienting the molecule in space (e.g., $\sigma = 12$ for the tetrahedral molecule CH_4). In addition, the U_i represent the quantities $h\nu_i/kT$, where h is Planck's constant, k is Boltzmann's constant, T is temperature in Kelvins, and the ν_i are the vibrational frequencies of the molecules.

The equilibrium constant (K) is related to the isotopic fractionation factor (α) by the expression (e.g., FERRONSKY and POLYAKOV, 1982)

$$\alpha = \left(\frac{K}{K_\infty}\right)^{1/ab} \qquad (4a)$$

where the product ab is equal to the number of atoms exchanged in the isotopic exchange reaction. Here K_∞ represents the limiting equilibrium constant at very high temperature, which is related only

to the stoichiometric coefficients of the exchange equation and to the symmetry numbers of the molecules:

$$K_\infty = \frac{(\sigma_{1A}/\sigma_{2A})^a}{(\sigma_{1B}/\sigma_{2B})^b}. \qquad (4b)$$

Note that the symmetry numbers cancel in the expression for α (Eqn. 4a), because the same factors are present in the expressions for both K and K_∞. Isotopic fractionation is a purely quantum mechanical effect and does not depend on classical factors such as symmetry numbers (BIGELEISEN and MAYER, 1947; STERN et al., 1968).

The above equations, and the assumptions upon which they are based, have been extensively discussed in the literature, so no additional description will be given here. For present purposes these equations will be taken as given, and attention will be confined to examination of their functional behavior in the cases where the U_i are either large (low temperature and/or high frequency) or small (high temperature and/or low frequency). These conditions are referred to below simply as the "low-temperature" and "high-temperature" cases, respectively.

LOW-TEMPERATURE CASE

At low temperatures (large U), it is evident that the $(1 - e^{-U})$ factors all approach unity. Accordingly, the basic equations (3a,b) for the simplified partition function ratios reduce to

$$\frac{Q_2}{Q_1} \cong \frac{\sigma_1}{\sigma_2} \frac{U_2}{U_1} e^{(U_1 - U_2)/2} \qquad (5a)$$

for diatomic molecules and to

$$\frac{Q_2}{Q_1} \cong \frac{\sigma_1}{\sigma_2} \prod_{i=1}^{3n-6} \frac{U_{2i}}{U_{1i}} e^{(U_{1i} - U_{2i})/2} \qquad (5b)$$

for nonlinear polyatomic molecules. The logarithm of these ratios may then be written as

$$\ln \left[\frac{Q_2}{Q_1}\right] \cong \frac{U_1 - U_2}{2} + \ln \left[\frac{\sigma_1 \nu_2}{\sigma_2 \nu_1}\right] \qquad (6a)$$

for diatomic gases and

$$\ln \left[\frac{Q_2}{Q_1}\right] \cong \sum_{i=1}^{3n-6} \frac{U_{1i} - U_{2i}}{2} + \sum_{i=1}^{3n-6} \left[\ln \frac{\sigma_1 \nu_{2i}}{\sigma_2 \nu_{1i}}\right] \qquad (6b)$$

for nonlinear polyatomic molecules, respectively. This equation is similar to one given, but not derived or justified, by STERN et al. (1968). Note that Eqns. (6a,b) are linear in $1/T$, being of the form $y = m/T + $ const., where the slope m is the difference between the zero point energies ($h\nu_i/2$) of the or-

dinary and isotopically substituted molecules divided by Boltzmann's constant. The identical slope is predicted by the $G\Delta U$ formulation of BIGELEISEN and MAYER (1947), although it does not predict the correct y-intercept in the low-temperature case. The dependence of $\ln (Q_2/Q_1)$ on the zero-point energy difference arises because, at low temperatures, the lowest possible vibrational energy states are populated by the molecules.

HIGH-TEMPERATURE SERIES

Considering that the Q_2/Q_1 ratios (Eqns. 3a,b) have so many product terms that are exponential in nature, and that the equilibrium constants and isotopic fractionation factors depend on quotients of these factors raised to stoichiometric powers, it is surprising that in their original papers neither UREY (1947) nor BIGELEISEN and MAYER (1947) took the logarithm of the basic equations before attempting to expand them in series. Equations (3a,b) directly become

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right] + \ln\left[\frac{U_2}{U_1}\right]$$
$$+ \frac{U_1 - U_2}{2} + \ln\left[\frac{1 - e^{-U_1}}{1 - e^{-U_2}}\right] \quad (7a)$$

for diatomic molecules and

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right] + \ln\prod_{i=1}^{3n-6}\left[\frac{U_{2i}}{U_{1i}}\right]$$
$$+ \sum_{i=1}^{3n-6}\frac{U_{1i} - U_{2i}}{2} + \ln\prod_{i=1}^{3n-6}\left[\frac{1 - e^{-U_{1i}}}{1 - e^{-U_{2i}}}\right] \quad (7b)$$

for nonlinear polyatomic molecules.

Equations (7a,b) can be simplified if the $\ln[1 - e^{-U_i}]$ terms are expanded in a series. This can be accomplished by first expanding e^{-U_i} in the well-known exponential series and factoring out U_i, e.g.

$$\ln[1 - e^{-U_1}]$$
$$= \ln\left[U_1\left\{1 - \frac{U_1}{2} + \frac{U_1^2}{6} - \frac{U_1^3}{24} + \ldots\right\}\right] \quad (8a)$$

or:

$$\ln[1 - e^{-U_1}] = \ln[U_1]$$
$$+ \ln\left[1 - \frac{U_1}{2} + \frac{U_1^2}{6} - \frac{U_1^3}{24} + \ldots\right]. \quad (8b)$$

Now, expanding the right-hand term in a Taylor (Maclaurin) series about $U_i = 0$ gives for high temperatures

$$\ln[1 - e^{-U_1}] = \ln[U_1] - \frac{U_1}{2} + \frac{U_1^2}{24}$$
$$- \frac{U_1^4}{2880} + \frac{U_1^6}{181440} - \frac{U_1^8}{9676800} + \ldots \quad (8c)$$

The computations become extremely laborious beyond the first few terms, and in practice this series was generated by the computer program "Mathematica" (WOLFRAM, 1988). Equation (8c) implies that

$$\ln\left[\frac{1 - e^{-U_1}}{1 - e^{-U_2}}\right] = \ln\left[\frac{U_1}{U_2}\right] - \left(\frac{U_1 - U_2}{2}\right)$$
$$+ \left(\frac{U_1^2 - U_2^2}{24}\right) - \left(\frac{U_1^4 - U_2^4}{2880}\right)$$
$$+ \left(\frac{U_1^6 - U_2^6}{181440}\right) - \left(\frac{U_1^8 - U_2^8}{9676800}\right) + \ldots \quad (8d)$$

Now using expansion (8d), Eqn. (7a) for diatomic gases becomes

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right] + \ln\left[\frac{U_2}{U_1}\right] + \frac{U_1 - U_2}{2}$$
$$+ \left\{\ln\left[\frac{U_1}{U_2}\right] - \frac{U_1 - U_2}{2} + \frac{U_1^2 - U_2^2}{24} - \frac{U_1^4 - U_2^4}{2880}\right.$$
$$\left. + \frac{U_1^6 - U_2^6}{181440} - \frac{U_1^8 - U_2^8}{9676800} + \ldots\right\}. \quad (9)$$

Cancellation of like terms gives, for diatomic gases,

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right] + \frac{U_1^2 - U_2^2}{24} - \frac{U_1^4 - U_2^4}{2880}$$
$$+ \frac{U_1^6 - U_2^6}{181440} - \frac{U_1^8 - U_2^8}{9676800} + \ldots \quad (10a)$$

Similarly, Eqn. (7b), for polyatomic molecules, becomes

$$\ln\left[\frac{Q_2}{Q_1}\right] = \ln\left[\frac{\sigma_1}{\sigma_2}\right]$$
$$+ \sum_{i=1}^{3n-6}\left\{\frac{U_{1i}^2 - U_{2i}^2}{24} - \frac{U_{1i}^4 - U_{2i}^4}{2880}\right.$$
$$\left. + \frac{U_{1i}^6 - U_{2i}^6}{181440} - \frac{U_{1i}^8 - U_{2i}^8}{9676800} + \ldots\right\}. \quad (10b)$$

The $U^2/24$ dependence of $\ln[Q_2/Q_1]$ is evident from the second term of the series in Eqns. (10a,b) because the higher order terms become insignificant in comparison. Note that, as $T \to \infty$, Eqns. (10a,b) reduce to

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}. \qquad (11)$$

The latter result, which along with Eqn. (2) leads directly to the classical value given by Eqn. (4b), can also be obtained by applying l'Hopital's rule to Eqn. (3a), again as $T \rightarrow \infty$.

In terms of illustrating the high-temperature variation of the fundamental Eqns. (3a,b), these Taylor series representations have several advantages. First, the higher order terms are explicit in Eqns. (10a,b). Also, the expansion of $\ln \{ Q_2/Q_1 \}$ in series, rather than of Q_2/Q_1, is advantageous because the equilibrium constant and the isotopic fractionation factors depend on quotients of the Q ratios raised to various powers. This dependence can in the logarithmic representation be exactly taken into account by simple addition of like terms. In contrast, to derive K or α from the approximations given by UREY (1947) or BIGELEISEN and MAYER (1947), one must apply the rather poor approximation $\ln (1 + x) \approx x$ to the Q_2/Q_1 ratio for each molecule. It is therefore unfortunate that BIGELEISEN (1958), who long ago derived Eqn. (10) by a somewhat different method, published his result in a proceedings volume that is not available in most libraries. BIGELEISEN (1958) was also able to show that the numerical coefficients of the series (Eqns. (10a,b) are related to the Bernoulli numbers B_n (see GRADSHTEYN and RYZHIK, 1980, pp. xxix and 1079–1080). In the present notation, the coefficients are given by $B_n/\{ n(n!) \}$, where n is the exponent of U for the term of interest.

TEMPERATURE DEPENDENCE OF ISOTOPIC FRACTIONATION FACTORS

It is straightforward to relate Eqns. (6a,b) and (10a,b) to the logarithm of the fractionation factors for isotopic exchange reactions, because Eqn. (4a) may be written as

$$\ln \alpha = \frac{1}{b} \ln \left[\frac{\sigma_2 Q_2}{\sigma_1 Q_1} \right]_A - \frac{1}{a} \ln \left[\frac{\sigma_2 Q_2}{\sigma_1 Q_1} \right]_B. \qquad (12)$$

Making appropriate substitutions (from Eqn. 6a) for the Q_2/Q_1 ratios of the diatomic molecules A and B at low temperatures gives an expression that is linear in $1/T$:

$$\ln \alpha \cong \frac{a(U_{1A} - U_{2A}) - b(U_{1B} - U_{2B})}{2ab}$$
$$+ \ln \left[\left(\frac{\nu_{2A}}{\nu_{1A}} \right)^{1/b} \left(\frac{\nu_{1B}}{\nu_{2B}} \right)^{1/a} \right]. \qquad (13)$$

Proceeding similarly (i.e., by combining Eqns. 10a

and 12, but ignoring high-order terms) for reactions involving diatomic molecules at elevated temperatures gives an expression linear in $1/T^2$ with an intercept of zero:

$$\ln \alpha \cong \frac{a(U_{1A}^2 - U_{2A}^2) - b(U_{1B}^2 - U_{2B}^2)}{24ab}. \qquad (14)$$

In addition to representing these well-known temperature proportionalities, Eqns. (13) and (14) explicitly indicate the theoretical values for the slopes and y-intercepts of the fractionation lines in the low- and high-temperature cases. These two equations apply only to isotopic exchange between diatomic molecules; equations for exchange reactions involving polyatomic molecules are similar in form but contain sum and product terms. A linear, zero intercept relation between $\ln \alpha$ and $1/T^2$ also appears to have useful application to the empirical description of oxygen isotopic equilibria among nonhydrous silicates or oxides, in effect because the values of U are generally small for these substances at geologically relevant temperatures (BOTTINGA and JAVOY, 1975).

It needs to be pointed out, however, that Eqns. (13) and (14) cannot predict many of the complex behaviors that may be exhibited in gaseous equilibria, and which are accounted for by Eqns. (3a,b). For example, Eqn. (14) does not predict any crossovers, inflection points, or maxima or minima in fractionation equations. Equation (13) predicts a single crossover, albeit one that may lie outside its range of validity (see below). An interesting discussion and examples of such effects are given by STERN et al. (1968).

Equations of the form $\ln \alpha = C_1 + C_2/T + C_3/T^2$, where the C's are empirical constants, are commonly used to describe laboratory determinations of certain fractionation factors that, over temperature ranges of interest, do not appear to strictly follow either the $1/T$ and $1/T^2$ limiting dependences (e.g., MAJOUBE, 1971). JONES (1958) argues theoretically that equations of this form (with $C_1 = 0$) are useful in the description of the vapor pressure ratios of isotopic solids. In an attempt to establish the theoretical validity of this latter type of equation for isotopic equilibria among gaseous molecules, the partition function ratios (Eqn. 3) were expanded in terms of asymptotic series in powers of $1/T$. All terms in odd powers of $1/T$ cancelled, so that an expression of the above form was not obtained. The result in fact reaffirmed Eqns. (10a,b) by yet another independent method, but did not provide any additional justification for the type of power series mentioned above.

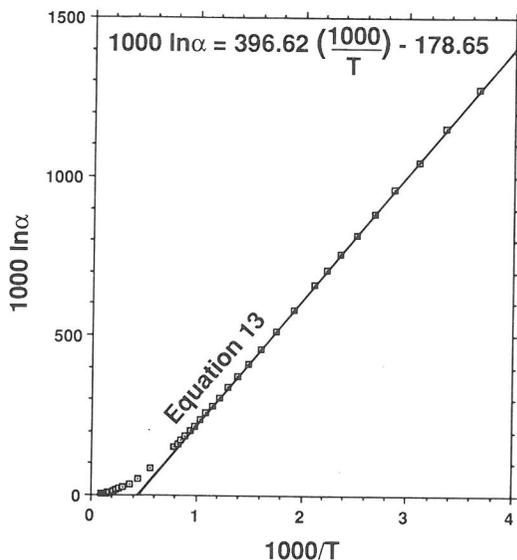$$1000 \ln\alpha = 396.62 \left(\frac{1000}{T}\right) - 178.65$$

Equation 13

FIG. 1. Graph showing the variation of $1000 \ln \alpha$ with inverse temperature, for deuterium exchange between hydrogen gas and hydrogen fluoride. The individual points (squares) were calculated by combining Eqns. (2, 3a, and 4), whereas the straight line represents the low-temperature correlation represented by the indicated formula, which was determined from Eqn. (13). As temperature increases, the deviation increases between this straight line and the calculated points, and a crossover would erroneously be predicted from the linear approximation at 2220 K (*i.e.*, $1000/T \approx 0.45$).

Of course, the range of Eqn. (14) can be extended by inclusion of additional terms, for example

$$\ln \alpha \cong \frac{a(U_{1A}^2 - U_{2A}^2) - b(U_{1B}^2 + U_{2B}^2)}{24ab}$$

$$+ \frac{a(U_{1A}^4 - U_{2A}^4) - b(U_{1B}^4 - U_{2B}^4)}{2880ab} + \dots \quad (15)$$

Unfortunately, convergence is lost before the $1/T$ dependence is reached.

EXAMPLE CALCULATION

For purposes of illustration, it is useful to compare the predictions of the high- and low-temperature approximations given above with the more exact values for the fractionation factors that, given the availability of computers, are easily calculated with Eqns. (3a,b). As an elementary example, consider the exchange of deuterium between hydrogen gas and hydrogen fluoride, represented by the exchange reaction

$$HD + HF = H_2 + DF. \quad (16)$$

$$1000 \ln\alpha = 284.68 \left(\frac{10^6}{T^2}\right)$$
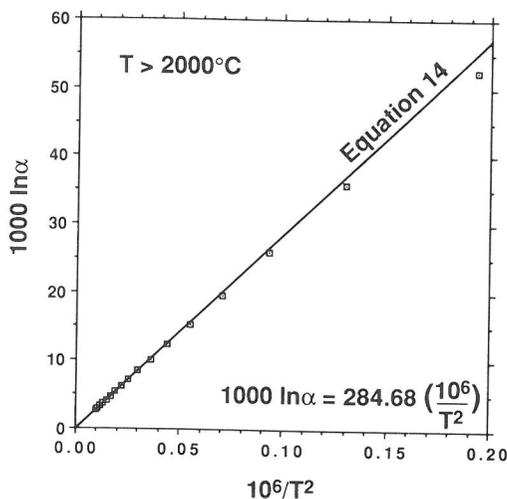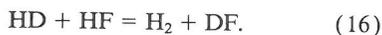
T > 2000°C

Equation 14

FIG. 2. Graph showing the variation of $1000 \ln \alpha$ with the square of the inverse temperature, for deuterium exchange between hydrogen gas and hydrogen fluoride. At extremely high temperatures, Eqn. (14), the straight line represented by the indicated formula, agrees very well with individual points (squares) calculated with Eqns. (2, 3a, and 4), but the agreement deteriorates below 3000 K. Note that the isotopic fractionation effect vanishes at extremely high temperatures, even though the equilibrium constant for the exchange reaction (Eqn. 16) approaches ½.

The number of atoms exchanged in the reaction (ab) equals 1 and the symmetry numbers (σ's) for the HD, HF, and DF molecules are all equal to unity, whereas that for H_2 is equal to 2. The equilibrium constant and the isotopic fractionation factor accordingly differ by the factor $K_\infty = 1/2$ (Eqn. 4a,b). RICHET *et al.* (1977) list the following values for the wavenumbers (cm^{-1}) of the pertinent diatomic molecules: $\omega_{DF} = 2998.192$; $\omega_{HF} = 4138.32$; $\omega_{HD} = 3812.293$; $\omega_{H_2} = 4401.118$. These values may be converted to frequencies (sec^{-1}) simply by multiplying by the speed of light. RICHET *et al.* (1977) also calculated that $K_{(0°C)} = 1.77141$ and $K_{(1000°C)} = 0.58021$ for the above reaction. These values compare well with the values of 1.78641 and 0.58164 that one can easily calculate with Eqns. (2) and (3a), given above. The small discrepancy arises from the inclusion of corrections for anharmonicity by RICHET *et al.* (1977); such corrections are in fact well known to be significant for hydrogen isotopes.

The smooth variation of $1000 \ln \alpha$ with temperature for these gases, as calculated with Eqns. (2, 3a, and 4), is shown by the individual points on Figs. 1 and 2. At temperatures below 1000 K, $\ln \alpha$ varies inversely with temperature, as expressed by the straight line (Eqn. 13) having a slope of 396.62

K and a y-intercept of -178.65. At progressively higher temperatures, the deviation increases between this line and the fractionations calculated with Eqns. (2, 3a, and 4). Were this straight line, representing the low-temperature behavior, extrapolated to high temperatures beyond its range of validity, a "crossover" (reversal in the sign of $\ln \alpha$) would erroneously be predicted at about 2220 K (Fig. 1).

At high temperatures (>3000 K), $\ln \alpha$ varies linearly with $1/T^2$ for these gases (Fig. 2). The numerical value for the slope (284.68 K^2) of the high-temperature correlation may be calculated from Eqn. (14), and it is evident that the y-intercept, representing the limiting fractionation at high temperature, is zero (*i.e.* $\alpha = 1$). Note on Fig. 2 that at progressively lower temperatures, the deviation increases between the points calculated with Eqns. (2, 3a, and 4) and the high-temperature line given by Eqn. (14).

CONCLUSIONS

For isotopic exchange reactions between gases at low and very high temperatures, the logarithms of the isotopic fractionation factors may be expressed as straightforward linear relations of inverse temperature or inverse temperature squared, respectively. The slopes and intercepts of these equations are explicitly related to the vibrational frequencies of the molecules and the stoichiometric coefficients of the exchange reaction, but (unlike K) are independent of the symmetry numbers. Extrapolation of these limiting equations beyond their range of applicability leads to erroneous predictions. No theoretical justification was found for the inclusion of both $1/T$ and $1/T^2$ terms in the same fractionation equation for isotopic equilibria among gaseous molecules.

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