Isotopic Partition Function Ratios Involving H_2, H_2O, H_2S, H_2Se, and NH_3*

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(Z. Naturforsch. **28a**, S. 129–136, received 5 December 1972)

Alfred Klemm zum 60. Geburtstag gewidmet

Ideal gas phase isotopic partition function ratios involving both deuterium and tritium substitution for hydrogen and also heavy atom substitution in H_2, H_2O, H_2S, H_2Se, and NH_3 have been calculated at a number of temperatures. The results have been least squares fitted to a five term series in powers of $(300/T)$. Various correction factors to the harmonic approximation were considered in the calculation of the partition function ratios. It is demonstrated that the tabulated ratios can be used to calculate equilibrium constants for isotopic exchange reactions.

Introduction

Isotope effects on chemical equilibria can be expressed in terms of ratios of isotopic partition function ratios. Thus K for the equilibrium

$$NH_3 + D_2O = NHD_2 + H_2O \quad (1)$$

can be expressed as

$$K_1 = (Q_{NHD_2}/Q_{NH_3})/(Q_{D_2O}/Q_{H_2O}) \,. \quad (2)$$

Here Q refers to partition function of the relevant species. Conventionally the partition function ratios are usually taken as heavy molecule divided by light molecule. Alternatively, the equilibrium constant can be expressed in terms of the reduced partition function ratio $(s_2/s_1)f$ of BIGELEISEN and MAYER[1],

$$(s_2/s_1)\,f_{2/1} = (s_2/s_1)\,(Q_2/Q_1) \prod_j^N \left(\frac{m_{1j}}{m_{2j}}\right)^{3/2}, \quad (3)$$

where the product is over the N atoms of the molecule and m refers to the mass of the appropriate atom (in practice the product need only extend over isotopically substituted atoms). It is easy to calculate f from the corresponding partition function ratio. A knowledge of isotopic partition function ratios and their dependence on temperature enables one also to calculate isotope effects on thermodynamic properties other than equilibrium constants.

Precise ideal gas phase partition function ratios involving both deuterium and tritium substitution for hydrogen and also heavy atom substitution (e.g., N^{15} for N^{14}) in hydrogen, water, hydrogen sulfide, hydrogen selenide, and ammonia have been calculated here in the temperature range 220–600°K. The calculation of these partition function ratios was carried out within the framework of the Born-Oppenheimer approximation (i.e., molecular potential function is independent of isotopic substitution), on the basis of molecular potential functions (including equilibrium geometry) for the electronic ground states which have been deduced by other workers from spectroscopic studies. An alternative method is to use spectroscopic data directly in order to evaluate the sum over states, Q. However, spectroscopic data are not available for some of the isotopic molecules and quantities such as the anharmonic correction G_0 (see below) cannot usually be determined directly by spectroscopy anyhow. Moreover, it is often very difficult to determine small isotope effects on spectroscopic data directly with great accuracy. Thus the calculation of the isotope effect consistently from the potential function does appear to be the preferable procedure.

The common practice is to list the partition function ratios at various temperatures, usually equally spaced[2]. The value of a partition function ratio at an intermediate temperature can then be obtained by interpolation. The obvious way to eliminate the often cumbersome tables is to find the equation of the curve that connects the values of the partition function ratio at the various temperatures. The method of the least squares may serve the purpose. A discussion of this method can be found in standard texts on numerical analysis[3].

Calculation of the Partition Function Ratios

The harmonic approximation[1] leads to a first estimate of the partition function ratio. Calculations within the harmonic approximation have been discussed in great detail; they require a knowledge of atomic masses, equilibrium molecular geometry, and harmonic vibrational frequencies (which may be calculated from the harmonic force field). Aside from the Born-Oppenheimer

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* Work supported by the U.S. Atomic Energy Commission under Contract No. AT (04-3)-34, Project Agreement No. 188.

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approximation which underlies almost all isotope effect calculations and the assumption that it is not necessary to sum over excited electronic states (a good assumption for the molecules and the temperatures considered here), the assumptions made in the harmonic approximation include:

1. The vibrational degrees of freedom can be described as harmonic oscillators.
2. The rotor is a rigid classical rotor and there is no rotational-vibrational interaction.
3. The translational motion of the center of mass is classical.

The last approximation needs no correction for all but very light molecules at very low temperatures and need not be considered further here. Correction factors for the other two major approximations will be considered. The polyatomic molecule corrections will be considered first.

The major correction from anharmonicity to an individual partition function arises from the correction to the vibrational zero-point energy (the ground state energy of the non-rotating molecule). This correction has the form (at temperature T)

$$\mathrm{ANHC} = \exp\left(-\left[G_0 + \sum_{i \leq j} x_{ij}\, d_i\, d_j/4\right] hc/kT\right). \tag{4}$$

The quantity G_0, the importance of which has been discussed in great detail elsewhere[4-6], is the constant term in the expansion of the vibrational-rotational energy expression in powers of $(n_i + d_i/2)$ for a molecule in its rotational ground state. The anharmonicity constants are designated by x_{ij}, while n_i is the principal quantum number of the i^{th} vibrational mode with degeneracy d_i. The i and j summations here and in Eqs. (5) and (8) below are over the normal vibrational modes of the N-atomic molecule with each degenerate mode counted only once. In Eq. (10) below, however, the summation does extend over $3N$-6 vibrations with two terms in the summations for each degenerate mode as appropriate.

The correction to the partition function arising from anharmonicity of excited vibrational modes is included in the following term which is taken from the work of PENNINGTON and KOBE[7].

$$\mathrm{ANHEXC} = \prod_i \left(\frac{1 - \exp(-u_i)}{1 - \exp(-u_i')}\right)^{d_i} \times \left[1 - \sum_{i \leq j} f_{ij} + \sum_i (\exp d_i\, \delta_i\, \{u_i'\} - 1)^{-1}\right]. \tag{5}$$

Here

$u_i \;\; = \omega_i hc/kT$ and ω_i is the harmonic frequency,
$u_i' \;\; = \nu_i hc/kT$ and ν_i is the fundamental frequency,
$f_{ij} \;\, = d_i d_j x_{ij} (hc/kT)(\exp\{u_i'\} - 1)^{-1}(\exp\{u_j'\} - 1)^{-1}$,
$f_{ii} \;\, = d_i (d_i + 1)\, X_{ii}\, (hc/kT)(\exp\{u_i'\} - 1)^{-2}$,
$X_{ii} = x_{ii} + (g_{ii}/3)(d_i - 1)$; $d_i = 1, 2$; g_{ii} defined in Ref. 6. (6)

The term $\sum_i d_i \delta_i (\exp\{u_i'\} - 1)^{-1}$ is not a correction term for anharmonicity but accounts for vibrational-rotational interaction. The quantity δ_i is defined as

$$\delta_i = \tfrac{1}{2} \sum_{\alpha, \sigma} b_{i\sigma}^{(\alpha\alpha)} / B_0^{(\alpha\alpha)} \tag{7}$$

in which all quantitites have been defined by NIELSEN[8]. Summation over α refers here, as well as below, to summation over the three principal axis directions x, y, z.

The term in δ_i above corrects for the change of effective moments of inertia in vibrationally excited states. The correction to the partition function arising from the deviation of the effective moments of inertia for rotation in the ground vibrational state from the equilibrium moments of inertia is given by

$$\begin{aligned} \mathrm{EFMC} &= \prod_\alpha \left(B_e^{(\alpha\alpha)} / B_0^{(\alpha\alpha)}\right)^{1/2} \\ &= \prod_\alpha \left(1 - \tfrac{1}{2} \sum_{i, \sigma} d_i\, b_{i\sigma}^{(\alpha\alpha)} / B_e^{(\alpha\alpha)}\right)^{-1/2}. \end{aligned} \tag{8}$$

Here again the notation is that of NIELSEN[8]. Another correction arising from vibrational-rotational interaction is the rotational stretching correction which has been described by WILSON[9]. It has the form

$$\mathrm{RSC} = 1 + \varrho T. \tag{9}$$

The quantity ϱ is defined[10] by:

$$\begin{aligned} \varrho = (k/4hc) \Bigg[3 \sum_\alpha \sum_{i=1}^{3N-6} \omega_i^{-2} \left(\frac{(a_i^{(\alpha\alpha)})^2}{I_{\alpha\alpha}^0}\right) (B_0^{(\alpha\alpha)}) \\ + \sum_{\alpha<\beta} \sum_{i=1}^{3N-6} \omega_i^{-2} \frac{(B_0^{(\alpha\alpha)}\, B_0^{(\beta\beta)})^{1/2}}{(I_{\alpha\alpha}^0\, I_{\beta\beta}^0)^{1/2}} (4 (a_i^{(\alpha\beta)})^2 + 2 a_i^{(\alpha\alpha)}\, a_i^{(\beta\beta)}) \Bigg]. \end{aligned} \tag{10}$$

All symbols have been defined by NIELSEN[8]. The summations over α and β are over the three principal axis directions.

Quantum mechanical rotation is taken into consideration by using the correction factor

$$\mathrm{QMRC} = \left(1 + \frac{\Theta_1}{T} + \frac{\Theta_2}{T^2}\right) \tag{11}$$

where[11]

$$\begin{aligned} \Theta_1 &= (hc/12k) \left[\sum_\alpha (2 B_0^{(\alpha\alpha)} - B_0^{(\alpha\alpha)}\, B_0^{(\beta\beta)} / B_0^{(\gamma\gamma)})\right], \\ \Theta_2 &= \frac{(hc/k)^2}{480} \Bigg[\sum_\alpha \{10 (B_0^{(\alpha\alpha)})^2 + 12 B_0^{(\alpha\alpha)}\, B_0^{(\beta\beta)} \\ &\quad - 12 ((B_0^{(\alpha\alpha)})^2\, B_0^{(\beta\beta)} + B_0^{(\alpha\alpha)} (B_0^{(\beta\beta)})^2) / B_0^{(\gamma\gamma)} \\ &\quad + 7 (B_0^{(\alpha\alpha)}\, B_0^{(\beta\beta)} / B_0^{(\alpha\alpha)})^2\}\Bigg]. \end{aligned} \tag{12}$$

The notation implies that, in the summation over all α ($\alpha = x, y, z$; $\alpha \neq \beta \neq \gamma$), the quantities α, β and γ are cyclic. The formula for QMRC has been derived by Stripp and Kirkwood[12].

The correction terms for the isotopic hydrogen molecules are very similar to those for the polyatomic molecules. G_0 for diatomic molecules has been discussed previously[4] and the correction term ANHC for diatomic molecules has the same form as that given. The term which correponds to ANHEXC in diatomic molecules has been extensively discussed in the literature[13] and follows from the term given. The term EFMC for diatomic molecules follows from that given before when it is recognized that there is only one rotational constant in diatomic molecules and that this constant must be raised to the first power. The RSC term at high temperature has the same form as Equation (9)[13]. At low temperatures, where the rotational partition function is obtained by direct summation, the RSC term is obtained by explicitly taking into account the energy term[14] in $[J(J+1)]^2$. Quantum mechanical rotation tends to be very important in hydrogen molecules at low temperature. Formulae which are analogous to Eq. (11) have been discussed in the literature[14]. At the lower temperatures here rotational partition functions were obtained by direct summation and summation was replaced by the formula analogous to Eq. (11) only at such temperatures at which the latter equation agreed with the summation to better than 0.01%. When carrying out the summation of rotational partition functions, one must consider the nuclear spin isomers of the isotopic hydrogen molecules (e.g. ortho and para hydrogen). However, even at the lowest temperatures in these calculations the difference between partition function ratios calculated with normal mixtures[2c] of spin isomers and equilibrium mixtures (which are tabulated here) is only of the order of 0.02%.

A detailed knowledge of the force fields and geometries of the molecules is necessary for the calculations undertaken here. Within the framework of the Born-Oppenheimer approximation, these force fields in valence coordinates and geometries were taken independent of isotopic substitution. The force fields were taken to contain up to quartic terms in the displacement from equilibrium. For H_2O, H_2S, and H_2Se these parameters were obtained from the work of Kuchitsu and Morino[15]. While in some cases, these authors derived slightly different parameters for the H_2X and the D_2X species studied by them, the H_2X parameters were chosen here where appropriate. Kuchitsu and Morino did not derive quartic potential constants for H_2Se directly. In the present calculation all quartic potential constants in H_2Se except the diagonal stretching one were set equal to zero and the non-zero one was derived from the quadratic stretching constant by the Kuchitsu-Morino a_4 method. For the ammonia molecule the "fit" force field of Morino, Kuchitsu, and Yamamoto[16] was used. This force field and the corresponding geometry have been described in detail[6]. The inversion problem has been ignored as it was previously[6]. For molecular hydrogen, the values of ω_e, $\omega_e x_e$, B_e and α_e (harmonic frequency, anharmonic constant, rotational constant, rotation-vibration constant) for H_2 were taken from the work of Herzberg and Howe[17] and the corresponding quantities for the other isotopic molecules were calculated from the theoretical mass relationships for these quantities[18]. This procedure for these species can be easily shown to be equivalent to calculating the necessary parameters from a given force field and equilibrium geometry.

The conversion of force constants in internal valence displacement coordinates into force constants in dimensionless normal coordinates was accomplished by use of the method of Pariseau, Suzuki, and Overend[19]. Details of the calculations of ANHC and explicit expressions have been given and discussed before[4-6]. The calculations were carried out to second order accuracy. The quantities ω_i, x_{ij}, G_0, ν_i, $b_{i\sigma}^{(\alpha\alpha)}$, $B_0^{(\alpha\alpha)}$, $a_i^{(\alpha\alpha)}$, etc. were all directly calculated. The atomic masses, as well as the fundamental constants necessary, were taken from standard compilations[20].

For the polyatomic molecules the partition function ratios were calculated at 20 temperatures between 220 and 600°K (steps of 20°). For hydrogen, the partition function ratios were calculated at 20° increments between 200 and 700°K. Symmetry numbers were ignored in the calculations (i.e. $(s_2/s_1)(Q_2/Q_1)$ was evaluated). From these data the coefficients in the equation

$$Y = \ln(s_A Q_A / s_B Q_B) = \sum_{n=0}^{4} a_n (300/T)^n \tag{13}$$

were determined by use of the method of least squares[3]. The partition function ratios were recomputed with the resulting a_n values and compared with the original "exact" values. The maximum error in the recomputed Q_A/Q_B in any of the calculations was 0.1%. Maximum errors tend to occur near the end-points of the temperature range. The error could be reduced by increasing the number of terms in the expansion; however more terms would tend to defeat the purpose of the method and uncertainties in the various parameters used here certainly do not warrant an attempt to attain greater accuracy (see below). It is important to emphasize that no theoretical significance should be attached to the coefficients a_n. They are just the coefficients in Eq. (13) as obtained by the method of least squares.

It is appropriate at this point to comment on the accuracy of the partition function ratios to which the a_n expressions, Eq. (13), have been least squares fitted. The possibility of errors arises from various factors: failure of the Born-Oppenheimer approximation, inadequacy of the molecular potential functions used, and errors made in the calculations of the various corrections to the harmonic approximation.

Very little work has been done on the effect of failure of the Born-Oppenheimer approximation on isotope effects on chemical equilibria. Such failure would lead to another correction factor which has been ignored here. Some preliminary work by KLEINMAN and WOLFSBERG[21] suggests that the Born-Oppenheimer correction factors in their effect on computed equilibrium constants may well be more important than a number of correction factors considered. Comparison of very exact experiments with ratios of partition function ratios, calculated as here without consideration of Born-Oppenheimer failure, may give much insight into the Born-Oppenheimer correction.

The molecular potential functions used here are believed to be reasonably good approximations to the actual potential functions. No attempt has been made to assess systematically the effect of possible errors in the potential functions on the partition function ratios. It is conceivable that such effect may not be negligible. Even fairly small changes in harmonic force fields may change harmonic approximation partition function ratios by several percent.

Next to be considered is the possibility of errors in the various correction factors to the harmonic approximation. The x_{ij}'s and other parameters which depend on anharmonicity were calculated by a theory which is correct to second order. No numerical exploration has been carried out of the effect of higher order anharmonicity terms on isotope effects; it is hoped that such effects are negligible. The correction terms which are included in ANHEXC are calculated to first approximation. The correction terms RSC and QRMC are also approximations (except for the diatomic molecules where QRMC is rigorously calculated at low temperatures). It is guessed that the uncertainties in ANHEXC, RSC, and QMRC and the neglect of other factors (e.g., Fermi-Dennison resonances) may introduce errors of the order of some hundredths of a percent into the calculation of the ratios.

Overall, the authors feel that there is justification for thinking that the partition function ratios have significance to the order of a tenth of a percent for the given molecular potential functions which were employed. Although it is realized that the molecular potential functions introduce uncertainties into the calculations, the least squares fitting was carried out in such a way that a corresponding accuracy of 0.1 % would be obtained.

Results and Discussion

Calculations were carried out of the ratio Q_{AXY}/Q_{AH_2} with A = oxygen, sulfur, selenium and X, Y = hydro-

Table I. $\ln (s_{\mathrm{AXY}}\, Q_{\mathrm{AXY}}/s_{\mathrm{AH_2}}\, Q_{\mathrm{AH_2}}) = \sum_{n=0}^{4} a_n (300/T)^n$.

A	X	Y	a_0	a_1	a_2	a_3	a_4
O^{18}	H	D	0.71044	2.50500	0.60819	−0.36865	0.08405
	D	D	1.43499	4.92253	1.40737	−0.83593	0.18816
	H	T	1.17511	3.42311	1.06839	−0.65400	0.15042
	T	T	2.36903	6.72049	2.41707	−1.41904	0.31708
	D	T	1.89797	5.84214	1.87541	−1.10548	0.24732
O^{16}	H	D	0.71417	2.48942	0.61629	−0.37622	0.08636
	D	D	1.43595	4.92275	1.36924	−0.81114	0.18206
	H	T	1.17789	3.41487	1.05224	−0.64512	0.14859
	T	T	2.36921	6.72980	2.34075	−1.36953	0.30491
	D	T	1.90271	5.82673	1.85332	−1.09449	0.24524
S^{34}	H	D	0.82111	1.33205	1.08821	−0.64182	0.14384
	D	D	1.64698	2.63489	2.22952	−1.29103	0.28649
	H	T	1.36466	1.65628	1.86212	−1.09462	0.24449
	T	T	2.73288	3.28400	3.77355	−2.16182	0.47629
	D	T	2.18866	2.96614	2.99015	−1.72054	0.37986
S^{32}	H	D	0.82298	1.32375	1.10005	−0.65136	0.14654
	D	D	1.64449	2.64857	2.20030	−1.27062	0.28119
	H	T	1.36505	1.65575	1.85908	−1.09373	0.24447
	T	T	2.72849	3.30781	3.72446	−2.12820	0.46770
	D	T	2.19161	2.95396	3.00495	−1.73376	0.38377
Se*	H	D	0.86557	1.00061	1.24342	−0.72341	0.16081
	D	D	1.72856	2.00934	2.47065	−1.41105	0.31049
	H	T	1.43163	1.18836	2.05779	−1.18303	0.26009
	T	T	2.85929	2.38633	4.09440	−2.30569	0.50222
	D	T	2.29768	2.18068	3.31223	−1.88194	0.41260

gen, deuterium, tritium. The a_n values are listed in Table I. Calculations for water were carried out with oxygen masses corresponding to O^{18}, O^{16}, and O natural abundance. The a_n values obtained for O natural abundance reproduce both the O^{16} ratios and the O natural abundance ratios to within the above quoted error limit of 0.1% and these a_n values are reported as O^{16} in Table I. Likewise, calculations for hydrogen sulfide were carried out with sulfur masses corresponding to S^{34}, S^{32}, and S natural abundance. The a_n values obtained for S natural abundance reproduce the S^{32} ratios and the S natural abundance ratios to within the error limit of 0.1% and these a_n values are reported as S^{32} in Table I. For hydrogen selenide, selenium masses corresponding to Se^{80}, Se^{78} and Se natural abundance were employed. The Se natural abundance a_n values reproduce the Se^{80}, Se^{78} and Se natural abundance ratios to within the 0.1% error limit (except for T_2Se where the error is 0.12%) and these values are reported as Se* in Table I.

In Table II, a_n values are given corresponding to partition function ratios of various deuterated and/or tritiated ammonias and NH_3. Calculations were carried out with nitrogen masses corresponding to N^{15}, N^{14}, and N natural abundance. The reported N^{14} a_n values reproduce both the N^{14} and N natural abundance ratios to within 0.1%.

In Table III, a_n values are given for (Q_{XY}/Q_{H_2}), where X, Y = H, D, T. No further comment is needed. A least squares series with fewer than five terms could probably have been used here.

Partition function ratios involving heavy atom isotope effects are listed in Table IV. In the least squares fitting procedure, the maximum error made by the fitting function here in reproducing the exact ratios is less than 0.001%. The basic errors in the calculated ratios are also expected to be one to two orders of magnitude less than for the hydrogen isotope effect ratios. These ratios may be used in the calculation of heavy atom isotope effects on equilibria when other such ratios are available. The ratios in Table IV serve as a link for establishing relationships among various isotopic molecules. If, for example, the ratio $(Q_{N^{15}HD_2}/Q_{N^{14}HD_2})$ needs to be known, it can be obtained by simple subtraction and addition:

$$R = \ln(Q_{N^{15}HD_2}/Q_{N^{14}HD_2}) = \ln(Q_{N^{15}HD_2}/Q_{N^{15}H_3}) + \ln(Q_{N^{15}H_3}/Q_{N^{14}H_3}) - \ln(Q_{N^{14}HD_2}/Q_{N^{14}H_3}). \quad (14)$$

Table II. $\ln(s_{AXYZ}\, Q_{AXYZ}/s_{AH_3}\, Q_{AH_3}) = \sum_{n=0}^{4} a_n (300/T)^n$.

A	X	Y	Z	a_0	a_1	a_2	a_3	a_4
N^{15}	D	D	D	2.18207	6.64855	3.51242	−1.99914	0,43776
	T	T	T	3.63513	8.87288	5.73204	−3.22237	0.69973
	H	H	D	0.73610	2.19393	1.16752	−0.69078	0.15566
	H	D	D	1.44008	4.50803	2.18517	−1.25223	0.27516
	H	H	T	1.19090	3.06744	1.68183	−0.98473	0.21982
	H	T	T	2.39460	6.05445	3.54707	−2.02681	0.44477
	D	D	T	2.66686	7.38990	4.24980	−2.41290	0.52749
	D	T	T	3.14191	8.17585	4.91260	−2.76349	0.59947
	H	D	T	1.91711	5.28253	2.86395	−1.64264	0.36135
N^{14}	D	D	D	2.17476	6.68916	3.41091	−1.92825	0.41926
	T	T	T	3.62831	8.91575	5.60951	−3.13968	0.67858
	H	H	D	0.71656	2.27699	1.02927	−0.59858	0.13292
	H	D	D	1.44355	4.49477	2.18778	−1.25737	0.27699
	H	H	T	1.19232	3.06437	1.67071	−0.97915	0.21874
	H	T	T	2.39638	6.05289	3.51747	−2.01040	0.44115
	D	D	T	2.66611	7.40038	4.19516	−2.37834	0.51901
	D	T	T	3.14679	8.16051	4.89747	−2.75978	0.59951
	H	D	T	1.92056	5.27137	2.85669	−1.64149	0.36164

Table III. $\ln(s_{XY}\, Q_{XY}/s_{H_2}\, Q_{H_2}) = \sum_{n=0}^{4} a_n (300/T)^n$.

X	Y	a_0	a_1	a_2	a_3	a_4
H	D	0.89156	1.36456	−0.00075	−0.00625	0.00658
H	T	1.44049	1.85581	0.02076	−0.02085	0.01015
D	D	1.74669	2.88780	0.16472	−0.12030	0.03493
D	T	2.26697	3.49816	0.18639	−0.12791	0.03531
T	T	2.78976	4.07518	0.37271	−0.24981	0.06440

By the appropriate addition or subtraction of the coefficients of equal powers of $(300/T)$, R is obtained as a power series.

The reduced partition function ratios $(s_2/s_1)f$ can be readily obtained from the partition function ratios, by Eq. (3), especially if one remembers that the partition function ratios calculated here are (s_2/s_1) (Q_2/Q_1) since symmetry numbers have been ignored. Thus

$$\ln (s_2/s_1) f = a_0' + \sum_{n=1}^{4} a_n \left(\frac{300}{T}\right)^n \qquad (15)$$

with

$$a_0' = a_0 + n \ln \left(\frac{m_1}{m_2}\right)^{3/2} = a_0 + n \varkappa (2/1) . \qquad (16)$$

Here, it is assumed that only one type of isotopic substitution has been carried out (e.g., D for H). n is the number of such substitutions and m_2 and m_1 refer to the isotopic atomic masses. $\varkappa$ values are listed in Table V. The extension of Eq. (16) to multiple substitutions is straightforward.

In Table VI the values of the various correction factors to the harmonic approximation for isotopic partition function ratios are shown for a few cases. It is seen that the major correction factor is ANHC except for the isotopic molecular hydrogens where QMRC is of the same magnitude as ANHC. The magnitude of the deviation of the ANHC and QMRC correction factors from unity decreases with increasing temperature. ANHC for multiple deuterium substitution tends to be equal to ANHC for single deuterium substitution raised to the power of the number of substitutions, i.e. $(\mathrm{ANHC})_{D_2O/H_2O} \simeq (\mathrm{ANHC})^2_{HDO/H_2O}$; this result has been discussed previously[5, 6]. The magnitude of the deviation of the correction factors from unity tends to be larger for tritium substitution than for deuterium substitution. The deviation from unity of the total correction factor, which is the product of the factors in Table VI, is sizable. It is also clear that, when appropriate ratios of partition function ratios are taken to obtain equilibrium constants, there will tend to be some cancellation of correction factors. Among the molecular species considered here, one would expect the largest deviations from unity in the correction factors to the equilibrium constants calculated in the harmonic approximation for tritium/hydrogen equilibria involving ammonia and molecular

Table IV. $10^3 \ln (s_{AH_i}\, Q_{AH_i}/s_{BH_i}\, Q_{BH_i})^* = \sum_{n=0}^{4} a_n (300/T)^n$.

A	B	a_0	a_1	a_2	a_3	a_4
O^{18}	O^{16}	169.4027	60.8745	14.6651	− 8.8831	2.0247
S^{34}	S^{32}	89.3298	9.9055	4.6587	− 2.6319	0.5680
Se^{80}	Se^{78}	37.9983	0.3409	2.8011	− 1.9077	0.4837
N^{15}	N^{14}	96.0419	54.1469	25.7176	−13.6000	2.8027

* $i = 2$ if A, B = O, S, Se and $i = 3$ if A, B = N.

Table V. $\varkappa(2/1)$ Values for Conversion to $(s_2/s_1)f$ — Eqs. (15, 16).

2/1	D/H	T/H	O^{18}/O^{16}	S^{34}/S^{32}	Se^{80}/Se^{78}
$\varkappa$	−1.03849	−1.64423	−0.1770818	−0.0908281	−0.0380015

Table VI. Corrections to Partition Function Ratios.

Ratios[a]	T (°K)	ANHC	ANHEXC	EFMC	RSC	QMRC
NH_2D/NH_3	220	0.882	1.000	0.998	1.000	0.997
NH_2D/NH_3	300	0.912	1.001	0.998	1.000	0.998
NH_2D/NH_3	600	0.955	1.002	0.998	1.000	0.999
ND_3/NH_3	300	0.760	1.005	0.997	1.000	0.995
NT_3/NH_3	300	0.694	1.007	0.995	1.000	0.994
HDO/H_2O	300	0.918	1.000	0.999	1.000	0.995
HDO/H_2O	600	0.958	1.000	0.999	0.999	0.997
D_2O/H_2O	300	0.843	1.000	0.998	1.000	0.993
HDS/H_2S	300	0.952	1.000	0.999	1.000	0.998
$HDSe/H_2Se$	300	0.967	1.000	0.999	1.000	0.998
HD/H_2	300	0.975	1.000	0.997	1.000	0.977
T_2/H_2	300	0.935	1.000	0.989	1.000	0.939
H_2O^{18}/H_2O^{16}	300	0.997	1.000	1.000	1.000	1.000

[a] N, O, S, Se below refer to N^{14}, O^{16}, S^{32}, Se^{78} respectively.

hydrogen. The last entry in Table VI shows the deviation of the correction factors from unity for heavy atom substitution is quite small.

To show the utility of the ratios, the following reactions[22] are taken as examples:

$$NH_3 + D_2O = NHD_2 + H_2O \qquad K_1 \qquad (17)$$

$$H_2O + D_2O = 2HDO \qquad K_2 \qquad (18)$$

$$H_2O + HDS = HDO + H_2S \qquad K_3 \qquad (19)$$

$$NH_3 + HD = NH_2D + H_2 \qquad K_4 \qquad (20)$$

$$NH_3 + T_2 = NHT_2 + H_2. \qquad K_5 \qquad (21)$$

By the appropriate addition or subtraction of the coefficients of equal powers of $(300/T)$, each K is obtained as a power series. The results are shown in Tables VII and VIII. It can be seen that the power series method gives values very close to the "exact" values. The agreement between theory and experiment for K_2 and K_4 has been discussed before[5, 6]. It is to the be noted that exact calculation of K_2 here includes the consideration of correction factors not considered rigorously before. The agreement between theory and experiment for K_3 is very gratifying. Table VIII also compares the equilibrium constants calculated just from isotopic partition function ratios in the harmonic approximation with the "exact" values. It is seen that the effect of the correction factors to the harmonic approximation may be extremely small as in the K_2 calculation or it may be quite sizable as in K_5. It is certainly true that in many cases the correction factor to the harmonic approximation will be very close to unity. However, since the correction factor is not always close to unity, it cannot be ignored.

FRIEDMAN, HAAR, and BECKETT[1c] have emphasized that from a knowledge of isotopic partition function ratios and their temperature dependences the isotope effect on thermodynamic properties other than equilibrium constants can be calculated. This fact extends the utility of the listed ratios, especially since temperature derivatives can be obtained easily.

Summary

The partition function ratios of various isotopic species of H_2O, H_2S, H_2Se, NH_3, and H_2 have been calculated on the basis of given molecular potential energy functions and geometries. Various correction factors to the harmonic approximation have been included. The results have been listed by using the new way of expressing $\ln (Q_A/Q_B)$ as a power series in $(300/T)$ which is obtained by least squares fitting the ratios calculated at a large number of temperatures. The relative magnitudes of the deviations from unity of the correction factors to the harmonic approximation have been discussed. The major corrections arise from the anharmonicity correction of the vibrational zero-point energy except in molecular hydrogen where quantum rotation is also important. The application of the partition function ratios has been illustrated by the calculation of several equilibrium constants. There does tend to be some cancellation in the correction factors to the harmonic approximation partition function ratios when equilibrium constants are obtained. The isotopic partition function ratios may be used to calculate isotope effects on other thermodynamic properties.

Table VII. $\ln (sK_i)^a = \sum_{n=0}^{4} a_n (300/T)^n$.

	a_0	a_1	a_2	a_3	a_4
$\ln (K_1/3)$	0.00760	−0.42798	0.81854	−0.44623	0.09493
$\ln (K_2/4)$	−0.00761	0.05609	−0.13666	0.05870	−0.00934
$\ln (K_3)$	−0.10881	1.16567	−0.48376	0.27514	−0.06018
$\ln (2K_4/3)$	−0.17500	0.91243	1.03002	−0.59233	0.12634
$\ln (K_5/3)$	−0.39338	1.97771	3.14476	−1.76059	0.37675

[a] s is the appropriate symmetry number ratio. Where appropriate, N^{14} and O^{16} data from Tables I and II were used.

Table VIII. Equilibrium Constants of Deuterium Exchange Reactions.

	T(°K)	Harmonic Approx.	Power Series	"Exakt"[a]	Experiment
K_1	300	3.17	3.14	3.14	—
K_2	298	3.85	3.85	3.85	3.76[23]
K_3	300	2.28	2.20	2.20	2.17[24]
K_4	210	12.3	11.4	11.4	11.1[25]
K_5	220	518.9	440.6	440.4	—
K_5	300	95.2	85.1	85.1	—

[a] Calculated directly from the partition function ratios, including the correction factors, without conversion to power series.

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