The Relation between D/H and T/H Isotopic Fractionation in Some Reactions of Chemical Interest[1]

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Reduced partition functions for deuterium- and tritium-substituted H_2O, H_2S, H_2Se, NH_3, PH_3, AsH_3, CH_3OH, CH_3SH, HCCH, CH_3CCH, and $HCONH_2$ have been calculated over the temperature range 100 to 1000 °K. Isotopic fractionation factors for the exchange of these molecules with H_2O have also been computed, and a comparison with experiment is made. The correlation between tritium and deuterium isotope effects is discussed.

I. Introduction

Experimental requirements frequently dictate the use, in a tracer or isotope effect study, of a particular rare hydrogen isotope, either deuterium or tritium. It then may become necessary, for example, in correlating experimental results with those obtained by others, to compare the effect of tritium substitution with that of deuterium substitution. Furthermore, for practical reasons, equilibrium constants for deuterium-protium exchange have been measured in many chemical systems, whereas determinations of the analogous constants for tritium-protium exchange reactions are rare. These latter quantities will be of increasing interest as power production by nuclear fission or controlled thermonuclear reactions becomes more important, since large quantities of tritium are either produced or used in these processes.

Consider two isotope exchange reactions, one exchanging protium and deuterium, the other exchanging protium and tritium:

(I) $H_nX + H_{m-1}DY \rightleftharpoons H_{n-1}DX + H_mY, \quad K_{H/D},$

(II) $H_nX + H_{m-1}TY \rightleftharpoons H_{n-1}TX + H_mY, \quad K_{H/T}.$

The isotopic fractionation factor for each eqilibrium is defined experimentally in terms of isotopic composition of the XH_n and YH_m species by the relations:

$$\alpha_{H/D} = \frac{(D/H)_{XH_n}}{(D/H)_{YH_m}} = \frac{m}{n} K_{H/D} \qquad (1)$$

and

$$\alpha_{H/T} = \frac{(T/H)_{XH_n}}{(T/H)_{YH_m}} = \frac{m}{n} K_{H/T}\,. \qquad (2)$$

The use of α's rather than K's has the advantage that symmetry number factors, which are purely classical and do not lead to isotopic fractionation, are omitted. The theoretical basis for the evaluation of the above equilibrium constants was established by BIGELEISEN and MAYER[2], who show that

$$K_{H/D} = \frac{f(H_{n-1}\,DX/H_nX)}{f(H_{m-1}\,DY/H_mY)} = \frac{f_{DX}}{f_{DY}}\,. \qquad (3)$$

The f quantity is a "reduced partition function" defined by the expression

$$(s_2/s_1)f = \prod_i \left[\frac{u_{2i}}{u_{1i}}\right]\left[\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}\right]\left[\frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}}\right]. \qquad (4)$$

In this equation, $u_i = h\nu_i/kT$, where ν_i is a vibrational frequency, T is the absolute temperature, and the subscripts 1 and 2 refer to the light and heavy isotopes, respectively.

Similar expressions apply to the equilibrium constant $K_{H/T}$, and it is convenient to define a new quantity that correlates $K_{H/D}$ and $K_{H/T}$:

$$\boldsymbol{r} = \ln K_{H/T}/\ln K_{H/D} = \ln \alpha_{H/T}/\ln \alpha_{H/D}\,. \qquad (5)$$

SWAIN, STIVERS, REUWER, and SCHAAD[3] evaluated $\boldsymbol{r}$ by making the simplifying assumptions that only zero-point energy effects [the last term in Eq. (4)] are important, and that all hydrogen vibrational frequencies are lowered by factors of $2^{1/2}$ or $3^{1/2}$. In this way they found $\boldsymbol{r} = 1.442$. The inclusion of excitation terms [the middle term of Eq. (4)] in their model led to a temperature-dependent correction term

$$\ln t/\ln K_{H/D}, \qquad 0.905 \leqslant t \leqslant 1.173\,.$$

BIGELEISEN[4] has also discussed the possible range of $\boldsymbol{r}$ values, and has shown rigorously that the lower limit (at high temperatures) is 1.333. At low temperatures, the upper limit is given by the value 1.442 of the SWAIN approximation; this may be reduced by the frequency ratio term [first term in Eq. (4)].

Following BIGELEISEN[4], we write

$$\varrho_x \equiv \frac{\ln f_{TX}}{\ln f_{DX}}, \qquad (6)$$

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Table I. Relative Tritium-Deuterium Isotope Effects for H_2X Molecules

			Isotopic fractionation with respect to H_2O				
			$\alpha_{H/D}$		$\alpha_{H/T}$		
Molecule	T, °K	ϱ	calc.	expt.	calc.	expt.	r
H_2O	100	1.415					
	200	1.410					
	298.16	1.404					
	500	1.392					
	1000	1.364					
H_2S	100	1.417	11.557		31.552		1.410
	200	1.408	3.4318		5.7113		1.413
	298.16	1.399	2.2956	2.19	3.2412	(3.03)[a]	1.415
	500	1.380	1.6341		2.0009		1.412
	1000	1.353	1.2396		1.3454		1.381
H_2Se	100	1.419	21.454		74.856		1.408
	200	1.409	4.7002		8.8818		1.411
	298.16	1.398	2.8383	2.62	4.3702	(3.90)	1.414
	500	1.376	1.8480		2.3775		1.410
	1000	1.350	1.3020		1.4387		1.378

[a] Parentheses indicate that $\alpha_{H/T}$ was calculated from $\alpha_{H/T}$, expt. $= (\alpha_{H/D}, \text{expt.})^r$.

with ϱ_y defined as the corresponding ratio for the H_mY species. Then

$$r = \frac{\varrho_x \ln f_{DX} - \varrho_y \ln f_{DY}}{\ln f_{DX} - \ln f_{DY}} = \varrho_x + \frac{(\varrho_x - \varrho_y) \ln f_{DY}}{\ln \alpha_{H/D}}. \quad (7)$$

BIGELEISEN calculated ϱ for several small molecules and found that it had the range 1.33–1.44. This led him to conclude that the second term in Eq. (7) was $\leqslant 0.11$, and hence the allowable range in r would be 1.33 to 1.55. However, this neglects the case where $\alpha_{H/D}$ is close to unity, and the denominator of the second term in Eq. (7) will be a very small positive or negative quantity. The second term then becomes large, and no limit on r can be established. In fact, it is evident from Eq. (5) that r will approach zero when $\alpha_{H/T}$ approaches unity, and r will approach $+\infty$ or $-\infty$ when $\alpha_{H/D}$ approaches unity.

Subsequently, STERN and VOGEL[5] computed relative tritium-deuterium *kinetic* isotope effects for a large number of model reactants and activated complexes, and found that anomalous values of r (or its analog in terms of rate constants) were not rare. They also evaluated r for many equilibria, but do not report the results in detail.

With this background of interest in the correlation of deuterium and tritium isotope effects, it appears worthwhile to examine values of r for several chemical systems of interest from the standpoint of isotopic enrichment.

II. Method of Calculation

Vibrational frequencies and values of f were calculated using the SHACHTSCHNEIDER and SNYDER[6] computer program as modified by Professor MAX WOLFSBERG. No corrections for anharmonicity were made, as the necessary vibrational constants are not known for all of the molecular species considered. WOLFSBERG and co-workers[7] have discussed the possible errors introduced by this approximation; the neglect of anharmonicity corrections for both molecular species in an exchange reaction appears to be a better approximation than to include them for only one species. An attempt was made to use the best available vibrational force fields of the valence force type, including interaction terms. However, because r is a "second-order" ratio, in terms of partition functions, the sensitivity to force constant changes should be slight.

The actual molecular geometries, internal coordinates, and force constants used in these calculations are given in the Appendix.

III. Results

A) H_2X Molecules

Table I contains values of ϱ for H_2O, H_2S, and H_2Se, together with values of $\alpha_{H/D}$, $\alpha_{H/T}$, and r for isotopic exchange with H_2O. There are several pertinent comparisons with experiment.

The equilibrium constant for the exchange

(III) $HD(g) + H_2O(g) \rightleftharpoons H_2(g) + HDO(g)$

has been determined[8,9]; its value is 3.41 or 3.54 at 25 °C. The data in Table I can be combined with ϱ for HD calculated from the vibrational frequencies given by HERZBERG[10]; this leads to a calculated value of 3.85, which is about 10% high. However, from the preceding experimental equilibrium constant and that[11] for

(IV) $HT(g) + H_2O(g) \rightleftharpoons H_2(g) + HTO(g)$, $K = 6.26$

one calculates $r = 1.472$, compared with a theoretical value of 1.448. This excellent agreement confirms the

Table II. Relative Tritium-Deuterium Isotope Effects for H_3X Molecules

			Isotopic fractionation with respect to H_2O				
			$\alpha_{H/D}$		$\alpha_{H/T}$		
Molecule	T, °K	ϱ	calc.	expt.	calc.	expt.	r
NH_3	100	1.408	0.77156		0.73920		1.165
	200	1.402	0.93455		0.93840		0.939
	298.16	1.396	0.99307	(0.971) [a]	1.0110	(0.980) [a]	−1.570
	500	1.383	1.0328		1.0575		1.732
	1000	1.359	1.0341		1.0498		1.449
PH_3	100	1.407	9.9782		27.182		1.436
	200	1.398	3.4131		5.8307		1.436
	298.16	1.389	2.3797	2.28	3.4701	(3.26) [b]	1.435
	500	1.370	1.7216		2.1674		1.424
	1000	1.347	1.2791		1.4055		1.383
AsH_3	100	1.406	16.261		54.610		1.434
	200	1.395	4.3840		8.3521		1.436
	298.16	1.384	2.8141	2.64	4.4134	(4.03) [b]	1.435
	500	1.365	1.8887		2.4703		1.422
	1000	1.343	1.3225		1.4715		1.382

[a] Not directly measured. See text. [b] From $\alpha_{H/T}$, expt. $= (\alpha_{H/D}$, expt.$)^r$.

contention that small errors in $\alpha_{H/D}$ or $\alpha_{H/T}$ will be further reduced in the ratio r.

The equilibrium

(V) $HDS(g) + H_2O(l) \rightleftharpoons H_2S(g) + HDO(l)$

is of great practical importance in the large-scale production of heavy water. The constant K_V can be converted to that for the entirely gas-phase reaction

(VI) $HDS(g) + H_2O(g) \rightleftharpoons H_2S(g) + HDO(g)$

by multiplication with the ratio of H_2O and HDO vapor pressures (1.074 at 25°)[12], corresponding to the equilibrium

(VII) $H_2O(l) + HDO(g) \rightleftharpoons H_2O(g) + HDO(l)$.

Experimental values[13] for K_{VI} at 25°C are 2.18, 2.20, 2.19, and 2.10, which may be compared with 2.30 in Table I. Using the experimental value of $\alpha_{H/D}$ (gas phase) and the calculated r, one obtains $\alpha_{H/T}$ (gas phase) $= 3.032$. The ratio of H_2O and HTO vapor pressures[14] (1.094 at 25°C) permits one to calculate $\alpha_{H/T}$ (liquid water) $= 3.333$.

For the equilibrium

(VIII) $HDSe(g) + H_2O(g) \rightleftharpoons H_2Se(g) + HDO(g)$,

the equilibrium constant is 2.62[13] at 25°C. compared with the value of 2.84 from Table I. Predicted values of $\alpha_{H/T}$ are 3.90 (gas phase) and 4.27 (liquid water).

B) H_3X Molecules

Calculated values of ϱ for NH_3, PH_3, and AsH_3 are given in Table II, together with fractionation factors for exchange with HDO and HTO.

The equilibrium constant at 25°C for the reaction

(IX) $HD(g) + NH_3(g) \rightleftharpoons H_2(g) + NH_2D(g)$

can be calculated from experimental values of PERLMAN, BIGELEISEN, and ELLIOTT[15] to be 5.36. Combining this with the equiblibrium constant for reaction (II), one obtains an expermental value of 0.971 for $\alpha_{H/D}$, compared with a value of 0.993 from Table II.

GUTMAN and WOLFSBERG[16], combining experimental and theoretical information, have given an expression for the equilibrium constant for the reaction

(X) $HT(g) + NH_3(g) \rightleftharpoons H_2(g) + NH_2T(g)$,

from which $\alpha_{H/T} = 0.980$ at 25°. From this and the experimental $\alpha_{H/D}$, one obtains $r = 0.700$ at this temperature, whereas the value in Table II is -1.5703. This is an example of the case where α is very close to unity, the second term in Eq. (7) becomes important, and r has a pole near 25°C.

The isotope exchange reaction

(XI) $H_2O(g) + PH_2D(g) \rightleftharpoons HDO(g) + PH_3(g)$

has been studied by BIGELEISEN and WESTON[17], and at 25°C, $\alpha_{H/D}$ is 2.28, compared with the calculated value of 2.38. From the experimental value and r, one predicts $\alpha_{H/T}$ (gas phase) $= 3.26$ and $\alpha_{H/T}$ (liquid water) $= 3.57$.

The corresponding exchange reaction of arsine

(XII) $H_2O(g) + AsH_2D(g) \rightleftharpoons HDO(g) + AsH_3(g)$

has been investigated by ZELTMAN and GERHOLD[18]. They obtain $\alpha_{H/D} = 2.64$ at 25°C, compared with the value of 2.81 in Table II. From this value and r, one predicts $\alpha_{H/T}$ (gas phase) $= 4.03$ and $\alpha_{H/T}$ (liquid water) $= 4.41$.

Table III. Relative Tritium-Deuterium Isotope Effects for CH_3XH Molecules

			Isotopic fractionation with respect to H_2O				
			$\alpha_{H/D}$		$\alpha_{H/T}$		
Molecule	T, °K	ϱ	calc.	expt.	calc.	expt.	$\boldsymbol{r}$
CH_3OH	100	1.418	0.63821		0.51426		1.481
	200	1.410	0.90820		0.87352		1.404
	298.16	1.402	0.99498		0.99927		0.145
	353.16	1.398	1.0168	0.99	1.0304	(0.98)[a]	1.795
	500	1.388	1.0383		1.0593		1.532
	1000	1.361	1.0302		1.0430		1.415
CH_3SH	100	1.419	9.1759		22.408		1.403
	200	1.407	3.4025		5.6682		1.417
	298.16	1.396	2.3786	2.38[b]	3.4251	(3.42)[a]	1.421
	500	1.376	1.7042		2.1270		1.416
	1000	1.350	1.2670		1.3864		1.381

Bold-face letters indicate the exchanging atom.

[a] From $\alpha_{H/T}$, expt. = $(\alpha_{H/D}$, expt.$)^{r}$. [b] This value is for C_2H_5SH.

C) Methanol and Methanethiol

These molecules were investigated as additional examples of molecules containing the biologically important -O-H and -S-H groups. The results are compiled in Table III.

As one would anticipate, the isotopic fractionation between water and methanol is predicted to be very small, with $\alpha_{H/D} = 0.995$ at 25°C. Some early experimental work[19] was done on this equilibrium at 80°C, with both components in the liquid phase:

$$\text{(XIII)} \quad CH_3OD(l) + H_2O(l) \rightleftharpoons CH_3OH(l) + HDO(l)\,.$$

The value of 1.039 obtained for $\alpha_{H/D}$ can be converted to the quantity appropriate to the gas phase reaction, using P_{H_2O}/P_{HDO} and P_{CH_3OH}/P_{CH_3OD}[20]. This gives $\alpha_{H/D} = 0.987$, compared with 1.017 in Table III. The predicted value of $\alpha_{H/T}$ is 0.976 for the gas phase, and about 1.03 for the liquid phase, depending on the value of P_{CH_3OH}/P_{CH_3OT}.

This is another example of a system whith α close to unity at a particular temperature, and the value of $\boldsymbol{r}$ is seen to go through a pole at that point.

There is no experimental value for the isotopic fractionation between water and methanethiol. However, the exchange of ethanethiol was investigated by HOBDEN, et al.[21]:

$$\text{(XIV)} \quad C_2H_5SD(l) + H_2O(l) \rightleftharpoons C_2H_5SH(l) + HDO(l).$$

They also measured relative vapor pressure of the two isotopic mercaptans, and from their data one obtains $\alpha_{H/D}$ (gas phase) = 2.38 (25°C) in exact agreement with the value calculated for methanethiol. This agreement is undoubtedly fortuitous; however, α does not appear sensitive to molecular structure. Thus, for *n*-butanethiol, *sec*-butanethiol, *sec*-pentanethiol, and *n*-hexanethiol, values of 2.20, 2.46, 2.14, and 2.37 have been measured (all at 20°)[22]. All of these are close to the value for H_2S, as one would expect if the S-H vibration makes the major contribution to α. The predicted fractionation factor for tritium exchange (gas phase) is just the value of Table III (3.42), since there is exact agreement between experiment and calculation for $\alpha_{H/D}$.

D) Acetylenes

The acetylenic hydrogen atom is sufficiently acidic to undergo base-catalyzed exchange with water. PYPER and LONG[23] have studied the reaction

$$\text{(XV)} \quad C_2HD(g) + H_2O(g) \rightleftharpoons C_2H_2(g) + HDO(g)$$

and they obtain $\alpha_{H/D} = 1.46$ at 25°C. The calculated value (Table IV) is about 10% high. For the corresponding tritium exchange, one predicts from the experimental $\alpha_{H/D}$ that $\alpha_{H/T}$ (gas phase) = 1.71 and $\alpha_{H/T}$ (liquid water) = 1.88.

MAHADEVAN and MONSE[24] have measured the equilibrium constant for the reaction:

$$\text{(XVI)} \quad H_3CCCD(g) + H_2O(g) \rightleftharpoons H_3CCH(g) + HDO(g)$$

and they obtain $\alpha = 1.19$ at 25°C, significantly lower than the experimental value for acetylene. By comparison, the value in Table IV is close to that calculated for acetylene, which is what one would anticipate. This discrepancy should be reinvestigated experimentally.

Table IV also contains calculated values of $\boldsymbol{r}$ and α for the hypothetical exchange of hydrogen in the methyl group of methylacetylene with water. Since there is an "inversion" of $\alpha_{H/D}$ between 100 and 200°K, i.e., a point at which it changes from less than unity to greather than unity, there is a corresponding anamoly in $\boldsymbol{r}$.

E) Formamide

This molecule was investigated as another example of a molecule containing an -N-H group, and as a

Table IV. Relative Tritium-Deuterium Isotope Effects for Acetylenes

			Isotopic fractionation with respect to H_2O				
			$\alpha_{H/D}$		$\alpha_{H/T}$		
Molecule	T, °K	ϱ	calc.	expt.	calc.	expt.	r
HCCH	100	1.415	2.5713		3.8025		1.414
	200	1.407	1.8653		2.4335		1.426
	298.16	1.400	1.6037	1.46	1.9654	(1.71)[a]	1.424
	500	1.385	1.3532		1.5343		1.415
	1000	1.358	1.1445		1.2052		1.383
H_3CCH	100	1.417	2.0595		2.7290		1.390
	200	1.409	1.6952		2.1122		1.417
	298.16	1.402	1.5057	1.19	1.7853	(1.28)[a]	1.416
	500	1.387	1.2969		1.4428		1.410
	1000	1.360	1.1207		1.1704		1.381
H_3CCH	100	1.410	0.86440		0.85251		1.095
	200	1.399	1.1008		1.1933		1.840
	298.16	1.390	1.1740		1.2956		1.614
	500	1.375	1.1907		1.3009		1.507
	1000	1.352	1.1176		1.1696		1.409

Bold-face letters indicate the exchanging atom.

[a] From $\alpha_{H/T}$, expt. = ($\alpha_{H/D}$, expt.)^r .

Table V. Relative Tritium-Deuterium Isotope Effects for Formamide (Planar Vibrations Only)

			Isotopic fractionation with respect to H_2O				
			$\alpha_{H/D}$		$\alpha_{H/T}$		
Molecule	T, °K	ϱ	calc.	expt.	calc.	expt.	r
$HCONH_2$	100	1.421	1.1727		1.1878		1.080
	200	1.411	1.1858		1.2671		1.389
	298.16	1.400	1.1820	(1.02)[a]	1.2760	(1.03)[b]	1.458
	500	1.383	1.1566		1.2381		1.468
	1000	1.356	1.0910		1.1304		1.407

Bold-face letters indicate exchanging atom

[a] For H_3CCONH_2. [b] From $\alpha_{H/T}$, expt. = ($\alpha_{H/D}$, expt.)^r .

possible model for the peptide group in proteins. Unfortunately, the force constant set was not very good, since it was derived from a Urey-Bradley force field. Also, out-of-plane vibrations were not included because force constants were not available. To avoid the calculation of frequencies for both cis- and trans-monosubstituted formamides, the values of f were calculated for $HCOND_2$ or $HCONT_2$. The rule of the geometric mean[25] indicates that the square root of these quantities will be a very good approximation to the exact values of $(s_2/s_1)\,f$ for HCONHD and HCONHT.

The only related isotope exchange equilibrium that has been studied experimentally is

(XVII)

$$H_3CCONHD(l) + H_2O(l) \rightleftharpoons H_3CCONH_2(l) + HDO(l).$$

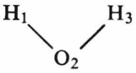
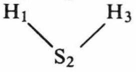
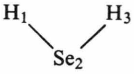
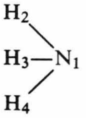
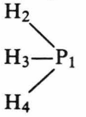
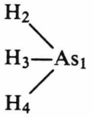
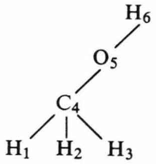
Brodskii[26] obtained a value of 1.02 for $\alpha_{H/D}$ at a temperature not specified but implied to be 25°C. Since the relative vapor pressures of the two isotopic forms of acetamide have not been measured, this is only approximately comparable with the calculated value of 1.18 given in Table V. Again this is an example of the case when $\alpha_{H/D}$ is close to unity and r is extremely variable.

IV. Discussion

Perhaps the most striking feature exhibited by the data in Tables I to V is the relative insensitivity of ϱ to molecular structure. This is shown again in Figure 1, where all the calculated values lie within the shaded region. This indicates that for any molecule, a value of f_{TX} accurate to 2 percent or better over the temperature range 100–1000°K can be calculated from the analogous value of f_{DX}, and a mean value of ϱ taken from Fig. 1. Since many more spectroscopic data are available for deuterium-labeled than for tritium-labeled molecules, this should be a useful approximation.

Figure 1 also shows that neither the high-temperature limiting value of ϱ nor the low-temperature limit (from the Swain approximation) are reached in the temperature range of 100 to 1000°K.

Appendix: Input Parameters for Calculations of Vibrational Frequencies

Chemical Species[a]	Equilibruim Parameters[b]	*Internal Coordinates*[c]		Force-constant Matrix[d]	Reference
		Number and type	Atoms		
Water 	R(O—H) = 0.9752 ∢ H—O—H = 104°31′	1,2 (stretch) 3 (bend)	1–2, 2–3 1–2–3	**1** = 8.454, **3** = 0.724, **1.2** = −0.101, **1.3** = 0.222	e
Hydrogen sulfide 	R(S—H) = 1.336 ∢ H—S—H = 92°12′	same		**1** = 4.284, **3** = 0.766, **1.2** = −0.012, **1.3** = 0.135	e
Hydrogen selenide 	R(Se—H) = 1.460 ∢ H—Se—H = 90°55′	same		**1** = 3.493, **3** = 0.697, **1.2** = −0.020, **1.3** = 0.080	e
Ammonia 	R(N—H) = 1.012 ∢ H—N—H = 106°40′	1–3 (stretch) 4–6 (bend)	1–2, 1–3, 1–4 2–1–3, 3–1–4, 4–1–2	**1** = 6.94020, **4** = 0.62042 **1.2** = 0.15970, **1.4** = 0.10303, **1.5** = 0.23640, **4.5** = −0.05752	f
Phosphine 	R(P—H) = 1.424 ∢ H—P—H = 93°50′	same		**1** = 3.32847, **4** = 0.73330, **1.2** = 0.05482, **1.4** = −0.07341, **1.5** = −0.00758, **4.5** = −0.02874	f
Arsine 	R(As—H) = 1.523 ∢H—As—H = 91°34′	same		**1** = 2.68937, **4** = 0.922251, **1.2** = 0.08280, **1.4** = 0.35655, **1.5** = −0.49674, **4.5** = −0.12596	f
Methanol 	R(C—H) = 1.093 R(C—O) = 1.434 R(O—H) = 0.937 ∢ H—C—H = 109°28′ ∢ H—C—O = 106°19′ ∢ C—O—H = 105°56′ 1, 4, 5, 6 cpolanar	1 (stretch) 2, 3 (stretch) 4 (stretch) 5 (stretch) 6, 7 (bend) 8 (bend) 9 (bend) 10, 11 (bend) 12 (bend) 13 (torsion) (one redundant)	1–4 2–4, 3–4 4–5 5–6 1–4–2, 1–4–3, 2–4–3 1–4–5 2–4–5, 3–4–5 4–5–6 1–4–5–6	**1** = 4.7537 **2** = 4.8908 **4** = 5.2658 **5** = 7.5312 **6** = 0.66427 **8** = 0.61254 **9** = 0.86251 **10** = 0.81078 **12** = 0.76017 **13** = 0.0267 **1.2** = −0.00596, **1.6** = 0.17806, **1.9** = 0.19854, **4.6** = −0.45723, **4.12** = 0.38012, **5.6** = −0.31517, **5.12** = −0.34885, **6.9** = 0.066642, **9.12** = 0.10465, **6.7, 6.8** = 0.08876, **6.12**, **8.12** = 0.00993, all others = 0	g

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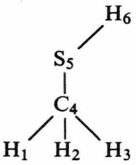
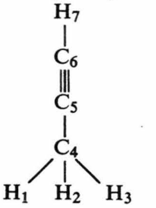
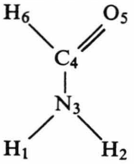
[a] The numbering of atoms corresponds to that used in describing internal coordinates. Atomic masses used are: $m_H = 1.00815$, $m_D = 2.01474$, $m_T = 3.01700$, $m_c = 12.01000$, $m_N = 14.00670$, $m_O = 16.00000$, $m_P = 30.97380$, $m_S = 32.06400$, $m_{As} = 74.92160$, $m_{Se} = 78.96400$.

[b] Bond lengths in Ä.

[c] Internal valence coordinates are: stretch 1–2 = change in 1–2 bond distance; bend 1–2–3 = change in angle between 1–2 and 2–3 bonds; torsion 1–2–3–4 = change in dihedral angle between 1–2–3 plane and 2–3–4 plane.

[d] Diagonal elements are indicated by a single number; e.g. **1** means $F_{1,1}$. Values are not repeated for elements that are identical because of symmetry (e.g. the two O—H stretching constants in H_2O). Off-diagonal elements are designated by two numbers; e.g. **1.2** means $F_{1,2}$. Units are as follows: stretch and stretch-stretch interaction, millidynes/Ä; bend, torsion, and bend-bend interaction, millidynes Ä/rad²; stretch-bend interaction, millidynes/rad.

Appendix: (continued)

Chemical Species[a]	Equilibrium Parameters[b]	*Internal Coordinates*[c] Number and type	Atoms	Force-constant Matrix[d]	Reference
Methanethiol	R(C—H) = 1.10	1–3 (stretch)	1–4, 2–4, 3–4	**1** = 4.663	h
	R(C—S) = 1.82	4 (stretch)	4–5	**4** = 3.213	
	R(S—H) = 1.33	5 (stretch)	5–6	**5** = 3.800	
	∢ H—C—H = 109°28′	6–8 (bend)	1–4–2, 2–4–3, 3–4–1	**6** = 0.536	
	∢ H═S—C = 109°28′	9–11 (bend)	1–4–5, 2–4–5, 3–4–5	**9** = 0.615	
	∢ C—S—H = 96°30′	12 (bend)	4–5–6	**12** = 0.814	
		13 (torsion)	1–4–5–6	**13** = 0.0345	
		(one redundant)		**1.1** = 0.026, **4.9** = 0.349,	
				4.12 = 0.322, **9.10** = −0.015,	
				9.12 = 0.184, all others = 0	
Acetylene	R(C—H) = 1.060	1 (stretch)	2–3	**1** = 15.72	i
	R(C≡C) = 1.207	2, 3 (stretch)	1–2, 3–4	**2** = 5.92	
		4–7 (bend)	1–2–3, 1–2–3	**3** = 0.24053	
			2–3–4, 2–3–4	**1.2** = −0.037, **4.5** = 0.8828	
Methylacetylene	R(C—H, methyl) = 1.093	1–3 (stretch)	1–4, 2–4	**1** = 4.9967, **4** = 16.312,	j
			3–4	**5** = 5.1266, **6** = 6.4415	
	R(C—C) = 1.462	4 (stretch)	5–6	**7** = 0.54168	
	R(C≡C) = 1.204	5 (stretch)	4–5	**10** = 0.67148	
	R(C—H) = 1.057	6 (stretch)	6–7	**13** = 0.30993, **15** = 0.21194	
	∢ H—C—H =	7–9 (bend)	1–4–2, 2–4–3	**4.5** = 0.47059	
			3–4–1	**5.7** = −0.28621,	
	∢ H—C—C = 109°28′	10–12 (bend)	1–4–5, 2–4–5, 3–4–5	**7.10** = 0.01513	
		13, 14 (bend)	4–5–6, 4–5–6	**13.15** = 0.05239	
		15, 16 (bend)	5–6–7, 5–6–7		
		(one redundant)			
Formamide	R(N—H) = 1.04	1, 2 (stretch)	1–3, 2–3	**1** = 5.8, **3** = 4.72	k
	R(C—N) = 1.30	3 (stretch)	3–4	**4** = 9.2, **5** = 4.5	
	R(C═O) = 1.225	4 (stretch)	4–5	**9** = 1.00, **10** = 0.99	
	R(C—H) = 1.07	5 (stretch)	4–6	**11** = 1.84	
	∢H—N—H =	6 (bend)	1–3–2	Force constants calculated in this work to fit frequencies of Ref. k	
	∢ H—N—C				
	= ∢ N—C—H =	7, 8 (bend)	1–3–4, 2–3–4		
	∢ H—C—O = 120°	9 (bend)	5–4–6		
	Assumed planar	10 (bend)	3–4–5		
		11 (bend)	3–4–6		
		in-plane coordinates only			
		(two redundant)			

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[e] Force constants and geometry from K. KUCHITSU and Y. MORINO, Bull. Chem. Soc. Japan **38**, 814 (1965).

[f] Geometry from S. SUNDARAM, F. SUSZEK, and F. F. CLEVELAND, J. Chem. Phys. **32**, 251 (1960), Table I. Force constants from Table II of this paper.

[g] Geometry and force constants from M. MARGOTTIN-MACLOU, J. Phys. Rad. **21**, 634 (1960). Calculated frequencies differed from those in this reference by up to 10 cm^{-1}.

[h] Force constants and geometry from D. W. SCOTT and M. Z. EL-SABBAN, J. Mol. Spect. **30**, 317 (1969). Force constant **13** (as tabulated) is threefold the value they report. This reproduced their calculated torsional frequency.

[i] Geometry from J. OVEREND and H. W. THOMPSON, Proc. Roy. Soc. London **A232**, 291 (1955); ibid., **A234**, 306 (1956). Force constants from G. HERZBERG, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, New York 1945, p. 189.

[j] Force constants and geometry from A. G. MEISTER, J. Chem. Phys. **16**, 950 (1948). Force constant **13** was changed from MEISTER's value of 0.27175 to obtain his calculated frequencies.

[k] Force constants were adjusted to fit vibrational frequencies of I. SUZUKI, Bull. Chem. Soc. Japan **33**, 1359 (1960). Geometry from his paper.

The calculated values of α given in Tables I to V are in reasonably good agreement with experimental data, where the latter are available for comparison. While this work was not directed towards precise evaluation of fractionation factors, the agreement found here supports the reliability of the ϱ and r factors.

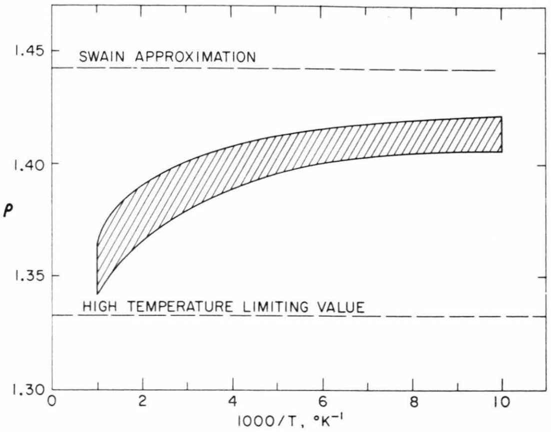

Fig. 1. Relative T/H and D/H reduced partition functions as a function of inverse temperature. All values of $\varrho (\equiv \ln f_{TX}/\ln f_{DX})$ from Tables I–V lie within the shaded area.

As one would expect from Eq. (7), values of r show a much wider range than do the individual ϱ factors. In reactions where isotopic fractionation is important (α or $\alpha^{-1} \geqslant 1.1$), r is within the range of 1.33 to 1.55 predicted by Bigeleisen[4]. When $\alpha_{H/D}$ is close to unity, there is no obvious way to predict r, which may even be negative. From a practical standpoint, the erratic behavior of r for small isotopic fractionation of deuterium is not particularly important because predicted values of $\alpha_{H/T}$ will also be close to unity in the cases considered here. However, Stern and Vogel[5] have found that this statement cannot be generalized, and that when either $\alpha_{H/D}$ or $\alpha_{H/T}$ exhibits an anomolous dependence on temperature, values of r will be outside the normal range even when $\alpha_{H/D}$ is large.

[1] This work performed under the auspices of the U.S. Atomic Energy Commission.
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