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Anomalous Mass Effects in Isotopic Exchange Equilibria

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Abstract: We have carried out a systematic analytical and computational study of the crossover behavior in the isotopic exchange equilibria between dihydrogen and the hydrogen halides. The reactions have been studied for the isotopomers H, D, T, and ^{4}H. The crossover temperatures are related to the H–H and H–X force constants and the masses of the exchanging and nonexchanging hydrogen atoms. When the mass of the hydrogen atom in HX increases, the crossover temperature increases. When the mass of the nonexchanging hydrogen atom in dihydrogen increases, the crossover temperature decreases. Both of these effects are shown to be enthalpy controlled. The change in the crossover temperatures of the reactions $H_2 + 2^*HX$ with $m_{^*H}$ is shown to be entropy controlled. Graphical methods are presented which relate the range of force constants in HX molecules to the existence of a crossover in an isotopic exchange with dihydrogen. It is shown that not all isotopomers give the crossover in a given exchange reaction. Exchange reactions which show the crossover for H–D and H–T exchange do not necessarily show the crossover for T–D exchange or mass independent isotope fractionation. Conversely it is shown that some reactions show T–D crossover or mass independent isotope fractionation, without H–D and H–T crossovers. Such reactions have large mass independent isotope fractionation separation factors. The results obtained are illustrative of the type of behavior found in equilibrium and kinetic systems when isotopic substitution in one of the molecular species leads to a large change in the fraction of the total vibrational kinetic energy associated with the exchanging isotopomer.

Introduction

When isotope effects in a chemical system are studied with different isotopes of the same element, the effects are a monotonic function of their relative mass differences. This generalization follows rigorously from the theory of equilibrium[1,2] processes and for rate processes,[3] both within the first quantum approximation. It is in accord with experimental data with a few exceptions. A small number of cases have now been found which do not conform to the above generalization.

Clayton et al.[4] have found $^{17}O/^{16}O$ and $^{18}O/^{16}O$ abundance ratios in carbonaceous meteorites which show a mass independent fractionation compared with other meteoritic and terrestrial materials. Thiemens et al. have found a number of mass independent isotope effects involving the isotopes of oxygen in atom–molecule and radical–radical reactions. The reactions studied by Thiemens proceed through excited states. A recent example is the reaction of photochemically generated oxygen atoms with carbon monoxide to produce carbon dioxide.[5] Valentini et al.[6] have found a mass independent oxygen isotope fractionation in the photolysis of ozone to produce oxygen. While interesting per se and possibly an explanation of Clayton's findings, these anomalous mass effects[7] are not associated with either equilibrium processes nor rate processes within the framework of transition state theory.[8]

Anomalous mass effects have now been found in equilibrium systems. Fujii et al.[9] have found the $^{238}U/^{235}U$ separation factor, 1.3×10^{-3} at 300 K, in the U(IV)–U(VI) exchange reaction is 0.2×10^{-3}, 17%, larger than a linear interpolation between the $^{238}U/^{234}U$ and the $^{238}U/^{236}U$ separation factors in experiments in which all three separation factors were measured concurrently. Dujardin et al.[10] found the $^{238}U/^{235}U$ separation factor, 2.3×10^{-3} at 300 K, in the U(III)–U(IV) exchange reaction to be almost twice the $^{238}U/^{236}U$ separation factor. These anomalous effects are associated with nuclear interactions in ^{235}U in the chemical species U(III) and U(IV) and are discussed elsewhere.[11]

Numerical computations to date of isotope effects in equilibrium and rate processes, within the framework of transition state theory, for systems with arbitrary large quantum effects show no anomalous mass effects other than for systems which show the crossover.[12-14] The crossover temperature is that temperature at which the logarithm of an isotope enrichment factor changes sign.

In a systematic study of isotopic hydrogen exchange reactions as a function of temperature between polyatomic molecules, which do not show the crossover and in which the exchanging hydrogen atom is bonded to an atom with mass greater than ten times that of a proton, Weston[13] found that the ratios, *r*, of the logarithms of the T/H fractionation factors to the logarithms of the corresponding D/H fractionation factors fell in the narrow range of 1.33–1.44. This was well within the range of an earlier prediction of 1.33–1.55 for the range at 300 K.[15] Weston found small maxima in *r* in the temperature range 200–500 K. These maxima

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Table I. Vibrational Frequencies

molecule	ω_e (cm^{-1})	a_{ii} (mdyne Å^{-1})	ref
H_2	4395.52	5.74	*a*
HF	4138.78	9.66	*a*
HCl	2991.21	5.16	*a*
HBr	2650.10	4.12	*a*
HI	2309.66	3.14	*a*
HAt	1840.13	2.00	*b*

[a] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley & Sons, Inc.: New York, NY, 1978; p 106. [b] Lippincott, E. R.; Dayhoff, M. O. *Spectrochim. Acta* **1960**, *16*, 807.

are associated with the Boltzmann excitation of bending modes.

The crossover temperature in an isotopic exchange reaction is mass dependent. For simple systems the crossover temperature increases with the mass of the isotopomer. In these systems the deuterium–protium isotope effect is larger than the tritium–protium isotope effect in the neighborhood of the tritium–protium crossover temperature. In the short temperature interval between the tritium–protium and the deuterium–protium crossover temperatures the ratio *r*, e.g., $\ln (K_H/K_T)/\ln (K_H/K_D)$, goes from zero to minus infinity. In order to enlarge our understanding of equilibrium isotope effects we have carried out an analysis of the mass dependence of systems which show the crossover. Some of the unusual mass effects which we have found in systems which show the crossover are also exhibited by systems which do not show the crossover for the H–D or H–T fractionation factors. The results are applicable to the quantum factors of isotope effects in rate processes within the formulation of transition-state theory. The classical term in the isotopic rate equation from the crossing of the barrier does not lead to anomalous mass effects.[3,12] Although rate processes which proceed with extensive tunneling are mass dependent, they do not show any anomalous mass effects.

In this paper we report the results of the analyses of numerical computations of isotope exchange equilibria of the hydrogen isotopes H, D, and T and the unstable isotope ^{4}H, mass 4.02, between dihydrogen and the hydrogen halides. These are simple systems which illustrate the inherent properties associated with anomalous mass effects. The calculations suggest that anomalous kinetic mass effects in the absence of tunneling are to be expected in rate processes in which dihydrogen is a reactant in the rate limiting step. They are relevant to the current interest in kinetic and equilibrium isotope effects in reactions between dihydrogen and transition-metal complexes. The calculations serve as prototype models for the understanding of anomalous mass effects in the reactions of polyatomic molecules, not restricted to the isotopes of hydrogen. Since the calculations are of an illustrative nature, they are carried out in the usual approximations of harmonic oscillators and rigid rotors. The latter and the translations are treated classically. The molecular parameters used in the calculations are given in Table I.

General Theory

The logarithm of the symmetry corrected equilibrium constant, $\ln K/\pi\sigma$, or the logarithm of the isotope fractionation factor, $\ln \alpha$, for the exchange reaction

$$A'Y + AX = A'X + AY$$

is the difference in the logarithms of the reduced partition function ratios

$$\ln K/\pi\sigma = \ln (s/s')f\ (AY) - \ln (s/s')f\ (AX) \qquad (1)$$

The terms in eq 1 have their usual definition.[1,16] The logarithm of the reduced partition function ratio, $\ln (s/s')f$, of any compound is a positive monotonic function of the mass of the isotopic substituent. In the high temperature approximation

$$\ln (s/s')f = (1/24)(\hbar/kT)^2(\mu'_i - \mu_i)a_{ii} + O(\hbar/kT)^4 + \ldots \qquad (2)$$

$$\ln (s/s')f = (1/24)(\hbar/kT)^2\Sigma(g'_{ij} - g_{ij})f_{ij} + O(\hbar/kT)^4 + \ldots \qquad (3)$$

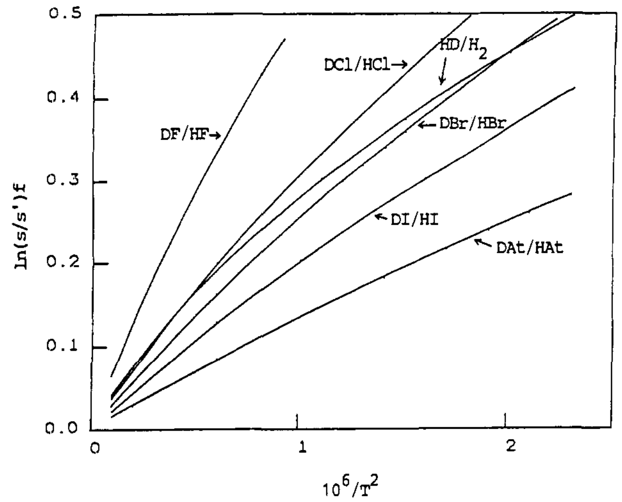

Figure 1. Plot of $\ln (s/s')f$ (DX/HX), X = F, Cl, Br, I, and At, and (HD/H_2) as a function of $1/T^2$.

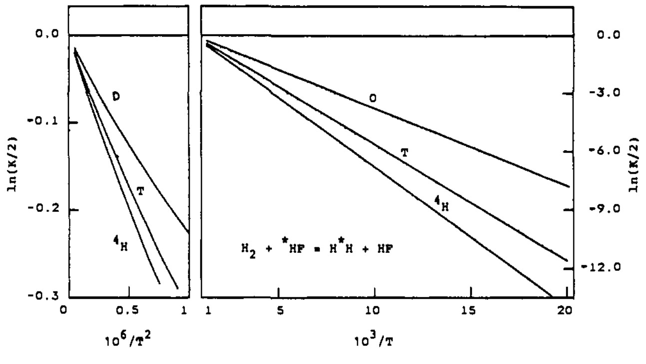

Figure 2. Plot of $\ln (K/2)$ for the exchange equilibria H_2 + *HF = H*H + HF vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ^{4}H.

where the prime designates the light isotope, μ'_i and μ_i are reciprocal atomic masses, a_{ii} is an abbreviation for the three-dimensional Cartesian force constant, and g_{ij} and f_{ij} are the Wilson **G** and **F** matrix elements, respectively. Curves for $\ln (s/s')f$ for D/H substitution in the hydrogen halides and the dihydrogen molecule are shown in Figure 1. They are typical of the high temperature behavior of the logarithm of the reduced partition function ratio. At temperatures above 2000 K, the order of the $\ln (s/s')f$ values is (DF/HF) > (HD/H_2) > (DCl/HCl) > (DBr/HBr) > (DI/HI) > DAt/HAt) in accord with eq 2 and the force constants given in Table I.

In the high temperature approximation

$$\ln (K/\pi\sigma) = (1/24)(\hbar/kT)^2(\mu'_i - \mu_i)\Sigma(f_{ij}(AY) - f_{ij}(AX)) + \ldots \qquad (4)$$

In this approximation the functional form of the logarithm of the exchange equilibrium constant with respect to mass dependence, temperature, and molecular forces is just the same as that for the logarithm of the reduced partition function ratio. In this approximation there are no anomalous mass effects at any temperature.

If the curves in Figure 1 for the hydrogen halides are extrapolated to low temperatures, they lead to equilibrium constants for isotopic exchange of the hydrogen halides between one another which follow the qualitative predictions from eq 4

$$\ln K/\pi\sigma \approx (\mu_H - \mu_D)(a_{HX_1} - a_{HX_2}) + \ldots \qquad (5)$$

We have studied the mass dependence as a function of temperature of exchange reactions between dihydrogen and diatomic molecules whose force constants are larger than that of H_2 and whose **G** matrix elements are smaller than H_2. These systems do not show the crossover nor anomalous mass effects. An example is the exchange reaction between H_2 and *HF, cf. Figure 2. The

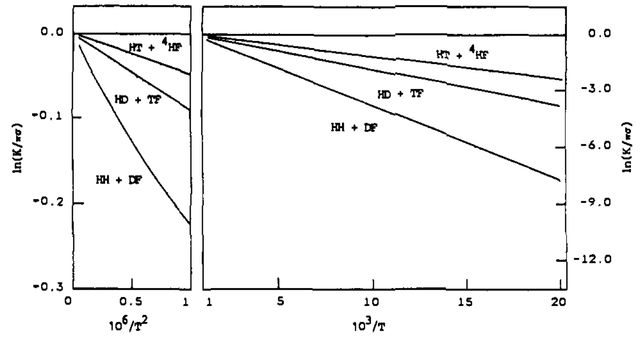

Figure 3. Plot of ln ($K/\pi\sigma$) for the exchange equilibria HH + DF = HD + HF, HD + TF = HT + DF and HT + ^{4}HF = H^{4}H + TF as a function of $1/T^2$ (left), $1/T$ (right).

heavy isotope, *H, concentrates in the HF molecule in preference to H_2 at all temperatures. Since both the force constant and the isotopic frequency shift are both larger in HF than in H_2, ln (s/s')f (*HF/HF) is larger than ln (s/s')f (H*H/H_2) at all temperatures. In this case the logarithm of the exchange equilibrium constant retains all the salient features of the dependence of ln (s/s')f (*HF/HF) on mass and temperature.

In Figure 3 we illustrate the temperature dependence of the sequential isotope exchange equilibria when dihydrogen is equilibrated with a diatomic molecule whose force constant is larger than that of H_2, e.g., HF. The reactions are[17]

$$\mathrm{HH + DF = HD + HF} \qquad K_{\mathrm{H,HD}}$$

$$\mathrm{HD + TF = HT + DF} \qquad K_{\mathrm{H,DT}}$$

$$\mathrm{HT + {}^4HF = H^4H + TF} \qquad K_{\mathrm{H,T^4H}}$$

For these sequential reactions the isotope effects are normal in all respects. At high temperatures the values of ln $K_{\mathrm{H,HD}}$, ln $K_{\mathrm{H,DT}}$, and ln $K_{\mathrm{H,T^4H}}$ are in the ratio 6:2:1, in accord with the differences in the reciprocal of the atomic masses of the exchanging atoms.

The curve of ln (s/s')f vs 1/T^2 for dihydrogen (HD/H_2) in Figure 1 shows much larger curvature than those of the hydrogen halides. This stems from the $(\hbar/kT)^4$ term in the power series expansion of ln (s/s')f[16]

$$O(\hbar/kT)^4 = -(1/2880)(\hbar/kT)^4[(\mu'^2_i - \mu^2_i)a^2_{ii} + 2(\mu'_i - \mu_i)\mu_j a^2_{ij}] \quad (6)$$

μ_j is the reciprocal mass of the atom in the molecule which does not undergo isotopic substitution. For the hydrogen halides μ_j is $1/m_X$; for dihydrogen in the above reactions μ_j is $1/m_H \cong 1$. In the case of the hydrogen halides more than 90% of the vibrational kinetic energy is in the motion of the hydrogen atom irrespective of the isotopomer. In contrast, in the dihydrogen molecule, H_2, each hydrogen atom has one-half the vibrational kinetic energy; this fraction is significantly altered by isotopic substitution.[18]

When the heavy isotope of hydrogen concentrates in a molecular species in which most of the vibrational kinetic energy of the molecule is carried by an isotopic exchange between the hydrogen halides, the isotope chemistry is particularly simple. It is convenient to define the reduced partition function ratio of an uncoupled oscillator, $c(u_{io})$, whose logarithm is

$$\ln c(u_{io}) = \tfrac{1}{2}\ln(g_{ii}/g'_{ii}) + (\hbar/2kT)f^{1/2}_{ii}\delta g^{1/2}_{ii} + \ln[(1-e^{-u'_{io}})/(1-e^{-u_{io}})] \quad (7)$$

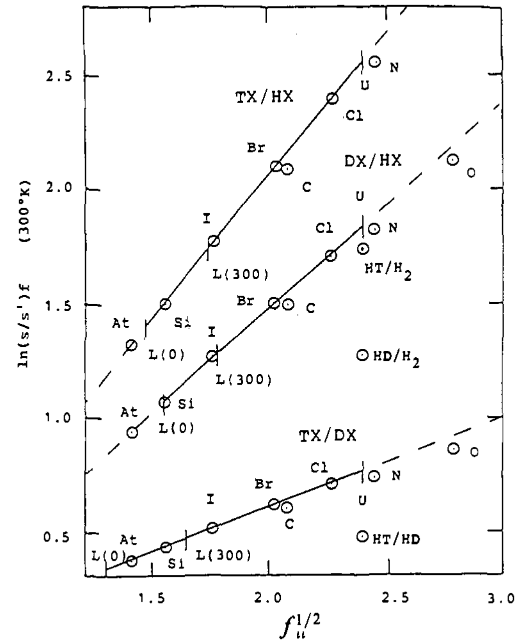

Figure 4. Plot of ln (s/s')f (TX/HX), (DX/HX), and (TX/DX) at 300 K vs $f^{1/2}_{ii}$ (f_{ii} is the H–X stretching force constant in mdyne Å^{-1}).

It is the exact value of the reduced partition function ratio, (s/s')f, of a diatomic molecule. It neglects contributions of off-diagonal **F** and **G** matrix elements to the exact eigenvalues of a polyatomic molecule. The latter are small in the isotope chemistry of hydrogen.[19] The contribution of a stretching motion, ln $c(u_{io})$, to ln (s/s')f for a large number of isotopic hydrogen molecules at 300 K is a linear function of the square root of the stretching force constant.[20] The value of ln $c(u_{io})$ at and below 300 K for the stretching motion of the H–X bond can be written in the form

$$\ln c(u_{io}) \cong mM + Z(m)f^{1/2}_{ii}/T \quad (8)$$

mM and $Z(m)$ are, respectively

$$mM = \tfrac{1}{2}\ln\frac{m_H}{m_{*H}} \times \frac{m_{*H} + m_X}{m_H + m_X} \quad (9)$$

$$Z(m) = (\hbar/2kT)[(\mu_H + \mu_X)^{1/2} - (\mu_{*H} + \mu_X)^{1/2}] \quad (10)$$

When $\mu_X \ll \mu_H, \mu_{*H}$ there are the further approximations

$$mM \cong \tfrac{1}{2}\ln\frac{m_H}{m_{*H}} \quad (9a)$$

$$Z(m) \cong (\hbar/2kT)[(\mu_H)^{1/2} - (\mu_{*H})^{1/2}] \quad (10a)$$

Within the approximations of eqs 9a and 10a, all values of ln $c(u_{io})$ for the stretching motions of H–X bonds lie on a straight line. Stretching motions per se of molecules whose values of ln $c(u_{io})$ lie on a single line do not lead to abnormal isotope effects in either the high temperature or low temperature approximations.

Equations 9a and 10a do not hold for the isotopic dihydrogen molecules. As a result the isotope chemistry of dihydrogen, which has been largely neglected, exhibits a number of very interesting features in exchange equilibria with molecules with stretching force constants smaller than that of dihydrogen. When the fraction of the kinetic energy in a molecule associated with a particular atom is significantly altered by isotopic substitution, we may anticipate some unusual features in the isotope chemistry of that molecular species for reactions in which the heavy isotope concentrates in that molecular species. The isotope chemistry of dihydrogen is illustrative of the general class of reactions of the isotope chemistry of an element whose fraction of the total internal

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(17) We use the following notation to define the reactants in an isotope exchange equilibrium: the subscript to the left of the comma is a nonexchanging atom, the subscript immediately following the comma is the exchanging isotope in the dihydrogen molecule, and the last subscript is the isotope in the "HX" molecule.

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Table II. Minimum Force Constants, as a Function of Temperature, of Diatomic Molecules that Have Crossovers in Isotopic Exchange Reactions with Dihydrogen[a]

isotopic exchange reaction	f_{ll} (mdyne Å^{-1}) 0 (K)	50 (K)	100 (K)	300 (K)
Type 1 Reactions				
$H_2 + DX = HD + HX$	2.403	2.517	2.632	3.119
$H_2 + TX = HT + HX$	2.164	2.295	2.426	2.990
$HD + TX = HT + DX$	1.674	1.830	1.992	2.708
Type 2 Reactions				
$DH + DX = D_2 + HX$	3.377	3.474	3.569	3.960
$DH + TX = DT + HX$	3.124	3.239	3.353	3.828
$D_2 + TX = DT + DX$	2.588	2.739	2.890	3.538
Type 3 Reactions				
$DH + DX = D_2 + HX$	3.377	3.474	3.569	3.960
$TH + TX = T_2 + HX$	3.671	3.771	3.867	4.211
$DH + DX + T_2 = TH + TX + D_2$	4.383	4.487	4.588	5.003
Type 4 Reactions				
$H_2 + 2DX = D_2 + 2HX$	2.868	2.976	3.083	3.527
$H_2 + 2TX = T_2 + 2HX$	2.868	2.987	3.105	3.553
$D_2 + 2TX = T_2 + 2DX$	2.868	3.012	3.157	3.767

[a] The maximum HX force constant for all reactions is 5.736 (mdyne Å^{-1}), which is also the H_2 force constant.

kinetic energy is significantly altered by isotopic substitution.

In Figure 4 we plot $\ln (s/s')f$ for some diatomic hydrides at 300 K as a function, $f_{ll}^{1/2}$, of the force constant of the H–X bond. Separate plots are given for T/H, D/H, and T/D substitution. The straight lines are drawn in accord with eqs 8–10 with $m_X = \infty$. These lines give excellent representations of all the $\ln (s/s')f$ values except those of the first row hydrides. The values of the first row hydrides fall below their respective lines since the infinite mass approximation is not quite valid for these light atoms. Of particular interest are the values for the isotopic dihydrogen molecules. They lie significantly below their respective lines. This is a consequence of the relatively small zero point energy difference between the isotopomers as a result of the small mass of the hydrogen atom, H, to which the isotopomers are bound in the H*H molecules. HX molecules with force constants larger than H_2, e.g., NH, have values of $\ln (s/s')f$ larger than the appropriate dihydrogen isotopic pair at all temperatures. This class of molecules does not show the crossover at any temperature. HX molecules with values of $f_{ll}^{1/2}$ smaller than that of dihydrogen may show the crossover. The vertical lines L(300) give the minimum values of the force constants, calculated from eqs 8, 9, 9a, 10, and 10a and the exact values of $\ln (s/s')f$ (H^*H/H_2), which will show the crossover at or above 300 K. An HX molecule with a value of $\ln (s/s')f$ which falls within the triangle U-H^*H/H_2-($H^{**}H/H^*H$)-L(300) will show the crossover at or above 300 K with the respective dihydrogen molecule. Since the slopes of the solid lines and the values of $\ln (s/s')f$ for the isotopic dihydrogen molecules depend on temperature, the area of each respective triangle will be temperature dependent. The vertical lines L(0) give the minimum force constants for a crossover above 0 K.

The minimum force constant for a crossover of HX with dihydrogen depends on the mass of *H. Thus the H–T and D–T exchanges between "H_2" and "HI" show the crossover above 300 K. The H–D exchange crossover between "H_2" and "HI" is below 300 K. An interesting case is the exchange of the D and T isotopomers between dihydrogen and hydrogen astatide. Neither the H–T nor H–D exchanges show the crossover at any temperature. Their respective values of $\ln (s/s')f$ are smaller than the L(0) values for the respective isotopomers, which are the minimum values for a crossover at or above 0 K. On the other hand, the $\ln (s/s')f$ (TAt/DAt) is larger than L(0) for T–D exchange. T–D exchange of hydrogen astatide with dihydrogen will show a crossover between 0 and 300 K. The T–D crossover is the temperature for an exact mass independent fractionation for the T–H and D–H exchanges, respectively. In Table II we list the minimum force constants, as a function of temperature, of diatomic hydrides that have H–D, H–T, and D–T crossovers with dihydrogen. Figure 4 refers to the type 1 reaction in Table II.

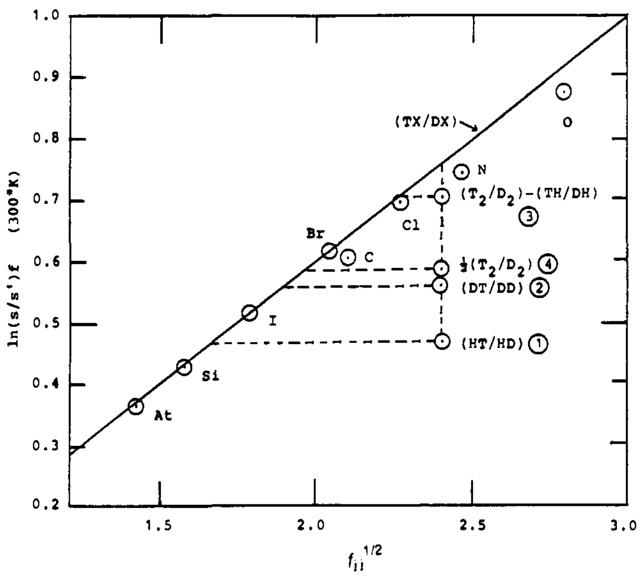

Figure 5. Plot of $\ln (s/s')f$ (TX/DX) at 300 K vs $f_{ll}^{1/2}$. Also $\ln (s/s')f$ values for (HT/HD), (DT/DD), $^1/_2 \ln (s/s')f$ (T_2/D_2), and [$\ln (s/s')f$ (T_2/D_2) − $\ln (s/s')f$ (TH/DH)].

$$HH + {}^*HX = H^*H + HX \qquad \text{type 1}$$

Other isotopic variants of the type 1 reaction with a given HX molecule result from isotopic substitution of the nonexchanging hydrogen atom in the dihydrogen molecule. Because of the failure of the first order rules of isotope chemistry for dihydrogen, these isotopomers of dihydrogen will exhibit different behavior from the type 1 reactions. We have studied the following additional reaction types:

$$YH + {}^*HX = Y^*H + HX \qquad \text{type2}$$

$$Y = D, T, {}^4H; Y \neq {}^*H$$

$${}^*HH + {}^*HX = {}^*H_2 + HX \qquad \text{type 3}$$

$$H_2 + 2{}^*HX = {}^*H_2 + 2HX \qquad \text{type 4}$$

$${}^*H = D, T, {}^4H$$

The T–D mass independent fractionation factors for these reactions correspond to the crossovers for the following exchange reactions:

$$HD + TX = HT + DX \qquad \text{type 1 MIIE}$$

$$DD + TX = DT + DX \qquad \text{type 2 MIIE}$$

$$DH + DX + T_2 = TH + TX + D_2 \qquad \text{type 3 MIIE}$$

$$D_2 + 2TX = T_2 + 2DX \qquad \text{type 4 MIIE}$$

In Figure 5 we plot $\ln (s/s')f$ (TX/DX) and the values of $\ln (s/s')f$ (HT/HD), $\ln (s/s')f$ (DT/DD), [$\ln (s/s')f$ (T_2/D_2) − $\ln (s/s')f$ (TH/DH)] and $^1/_2 \ln (s/s')f$ (T_2/D_2) all at 300 °K. Those HX molecules with $\ln (s/s')f$ (TX/DX) values that lie within each of the triangles formed by a segment of the solid line, the dotted vertical line, and the individual dotted horizontal lines will show the T–D crossover with the respective dihydrogen isotopomer at or above 300 K. Each of the reduced partition function ratios in Figure 5 corresponds to one T–D exchange. The T–D crossover is the MIIE for T–D in the respective type 1, 2, 3, or 4 reaction. Thus HI shows the T–D crossover only for the type 1 reaction at or above 300 K. None of the hydrogen halides show the T–D crossover for type 3 reactions at or above 300 K. There is a large spread in the T/D reduced partition function ratios between $\ln (s/s')f$ (HT/HD) = 0.462 and [$\ln (s/s')f$ (T_2/D_2) − $\ln (s/s')f$ (TH/DH)] = 0.699. In the first quantum approximation these

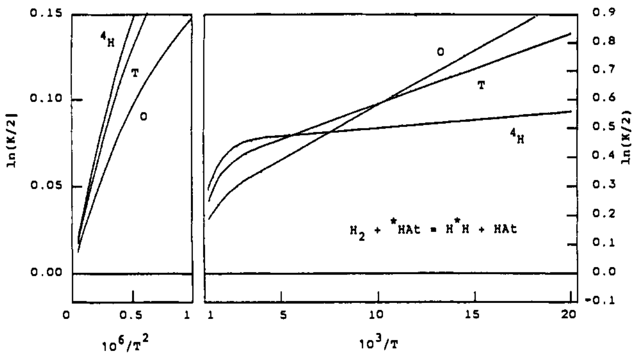

Figure 6. Plot of ln $(K/2)$ for the exchange equilibria $H_2 + {}^*HAt = H^*H + HAt$ vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ^{4}H.

quantities are equal. Figure 5 clearly demonstrates that the crossover behavior for exchange between an isotopomer of dihydrogen and a hydrogen halide depends on the mass of the nonexchanging hydrogen atom. Both crossover behavior and mass independent fractionation behavior are different for the types 1–4 reactions. These differences will also occur to a lesser extent in the isotope chemistry of other elements. The effects are maximal in reactions of dihydrogen because of the large H–H force constant and the small masses of all the hydrogen isotopomers.[16]

Mass Independent T–D Isotope Effects in the Absence of H–D and H–T Crossovers

Until now mass independent equilibrium isotope effects have been found only in systems which show crossovers for all the isotopomers of the element.[12–14] In this section we show that a mass independent T–D equilibrium isotope effect can occur when neither the H–D nor H–T exchange reactions show the crossover. In fact, systems that have mass independent equilibrium isotope effects without H–D or H–T crossovers have much larger fractionation factors at the mass independent fractionation temperature than do systems with the crossover. Consider the exchange reactions between dihydrogen and diatomic molecules such that

$$f_{\iota\iota}(H_2) > f_{\iota\iota}(HX) \text{ and } (\nu(H_2) - \nu(H^*H)) > (\nu(HX) - \nu(^*HX))$$

The reactions with the isotopic hydrogen astatide molecules meet these criteria and serve as good models. The exchange equilibrium constants as a function of temperature are shown in Figure 6. The relevant equilibrium parameters, calculated from the vibrational frequencies in Table I, for low and high temperatures of these exchange reactions are included in Table III. In all of the reactions shown in Figure 6 the heavy isotope concentrates in the molecular species dihydrogen at all temperatures. There are no cross overs. The high temperature behavior follows the first quantum condition:

$$\ln K_{H,H^4H} > \ln K_{H,HT} > \ln K_{H,HD'}$$

which is the order of the slopes of ln K vs $1/T^2$ at high temperatures. At low temperatures the sequence of equilibrium constants is the reverse of the high temperature behavior, i.e., $\ln K_{H,HD} > \ln K_{H,HT} > \ln K_{H,H^4H}$. In the low temperature limit

$$\ln K/\pi\sigma \rightarrow (\hbar/2kT)[(\nu_{H_2} - \nu_{H^*H}) - (\nu_{HAt} - \nu^*{}_{HAt})] \qquad (11)$$

$$\ln K/\pi\sigma \rightarrow (\hbar/2kT)[\delta g_{H_2}^{1/2} f_{H_2}^{1/2} - \delta g_{HAt}^{1/2} f_{HAt}^{1/2}] \qquad (11a)$$

As a consequence of the fact that H and *H vibrate against an almost infinite mass in HAt and *HAt, respectively, the value for $\delta g_{\iota\iota}^{1/2} = (g'^{1/2}_{\iota\iota} - g_{\iota\iota}^{1/2})$ is larger for hydrogen astatide than for dihydrogen. For HAt it is $(1 - \mu_{^*H}^{1/2})$; for dihydrogen it is $[\sqrt{2} - (1 + \mu_{^*H})^{1/2}]$. The difference between $\delta g_{\iota\iota}^{1/2}(HAt)$ and $\delta g_{\iota\iota}^{1/2}(H_2)$ increases with the mass of *H. The zero point energy differences $(\hbar/2)[(\nu_{H_2} - \nu_{H^*H}) - (\nu_{HAt} - \nu^*{}_{HAt})]$ decrease from 38.16 K when *H = D to 5.29 K when H = ^{4}H. Thus the low temperature slopes and values of ln K in the exchange reactions between dihydrogen and hydrogen astatide are in the order $\ln K_{H,HD} > \ln K_{H,HT} > \ln K_{H,H^4H}$. Therefore, there are crossing points between each of the isotopic exchange reactions among one another. In the temperature range 100–200 K there are regions in which two of the isotopomers, e.g., D, T, ^{4}H, have almost the same fractionation factors.

Table III. Equilibrium Parameters in the Exchange Reactions

$$H_2 + {}^*HX = H^*H + HX \qquad (1)$$

$$DH + {}^*HX = D^*H + HX \qquad (2)$$

$$^*HH + {}^*HX = {}^*H_2 + HX \qquad (3)$$

$$\ln (K/\Pi\sigma) = A + B/T \qquad (T < 300 \text{ K})$$

$$\ln (K/\Pi\sigma) = D/T^2\ [D(1) = D(2) = D(3)] \qquad (T > 2000 \text{ K})$$

*H	$A(1)$	$B(1)$	$A(2)$	$B(2)$	$A(3)$	$B(3)$	$10^{-6} \times D$
				X = F			
D	0.1779	−395.6	0.1192	−316.9	0.1192	−316.9	−0.2846
T	0.2978	−592.5	0.2070	−475.5	0.1545	−417.2	−0.3794
^{4}H	0.3869	−716.8	0.2757	−577.3	0.1646	−461.0	−0.4270
				X = Cl			
D	0.1887	−185.2	0.1299	−106.5	0.1299	−106.5	+0.0415
T	0.3185	−294.2	0.2276	−177.5	0.1752	−119.0	+0.0553
^{4}H	0.4168	−368.7	0.3056	−229.2	0.1945	−112.9	+0.0622
				X = Br			
D	0.1962	−126.1	0.1375	−47.41	0.1375	−47.41	+0.1175
T	0.3333	−211.2	0.2424	−94.45	0.1900	−35.90	+0.1566
^{4}H	0.4385	−272.5	0.3273	−133.1	0.2162	−16.78	+0.1762
				X = I			
D	0.1985	−58.30	0.1398	+20.41	0.1398	+20.41	+0.1882
T	0.3379	−114.1	0.2470	+2.63	0.1946	+61.18	+0.2508
^{4}H	0.4454	−158.3	0.3341	−18.85	0.2231	+97.42	+0.2823
				X = At			
D	0.2001	+38.16	0.1413	+116.9	0.1413	+116.9	+0.2711
T	0.3409	+24.54	0.2501	+141.3	0.1976	+199.8	+0.3612
^{4}H	0.4500	+5.29	0.3341	+144.8	0.2277	+261.0	+0.4065

Exchange reactions for which

$$\sum(\delta\nu_\iota^2 > \delta\nu_j^2);\ \sum(\delta\nu_\iota > \delta\nu_j);\ \delta g_{\iota\iota}^{1/2} < \delta g_{jj}^{1/2} \qquad (12)$$

may give rise to crossing points in the equilibrium constants between reactions involving different isotopomers of the same element. In this case there is a temperature range in which the isotope effect is almost mass independent. Individually, these isotope exchange reactions show normal temperature dependencies.

Inasmuch as the T–D mass independent isotope effect occurs without any H–D or H–T cross over, it will be large and comparable to normal isotope effects. In the present case ln α (MIIE) ≈ 0.5. This is a factor of 2 larger than the mass independent isotope effects of systems that have H–D and H–T crossovers, even after correction of those systems for the higher MIIE temperature.

Systems with the Crossover: General Considerations

In the exchange reaction of the isotopes A and A′ between the compounds AY and AX one crossover may occur for each molecular vibration for which[21]

$$\delta\nu_\iota^2(AY) > \delta\nu_\iota^2(AX); \qquad \delta\nu_\iota(AY) < \delta\nu_\iota(AX) \qquad (13)$$

The criterion for a minimum of one crossover in the exchange reaction is

$$\sum\delta\nu_\iota^2(AY) > \sum\delta\nu_\iota^2(AX); \qquad \sum\delta\nu_\iota(AY) < \sum\delta\nu_\iota(AX) \qquad (14)$$

The inequality (14) follows from eq 4 and the generalization of eqs 11 and 11a to the polyatomic molecule. If the molecular parameters B and D in Table III for the exchange reactions

$HH + {}^*HX = H^*H + HX$ type 1

$DH + {}^*HX = D^*H + HX$ type 2

$^*HH + {}^*HX = {}^*H_2 + HX$ type 3

are of opposite sign, the exchange reaction will show a crossover. When they are of the same sign, cf. reactions of dihydrogen with

Table IV. Temperatures of the Maxima in the Equilibrium Constants for the Isotopic Exchange Reactions

$H_2 + {}^*HX = H^*H + HX$

*H	D	T	⁴H
	X = Cl		
T_{max}	2385.8	2388.3	2389.5
$\ln K_{max}$	0.0033	0.0044	0.0050
	X = Br		
T_{max}	1210.6	1219.4	1223.6
$\ln K_{max}$	0.0290	0.0390	0.0441
	X = I		
T_{max}	723.8	748.6	759.9
$\ln K_{max}$	0.0894	0.1198	0.1353

either hydrogen fluoride or hydrogen astatide, they will not show the crossover for H–*H exchange. In a given exchange reaction, e.g., DH + *HI, not all isotopomers will show the crossover in the reaction. For the above example, only ⁴HI shows the crossover with DH; DI and TI do not show the crossover with DH. The existence of a crossover depends, among other variables, on the mass of the nonexchanging atom in the chemical species with the smaller $\delta g_{ii}^{1/2}$ term. The dependence of the crossover temperature on the mass of exchanging isotopomer, A, and on the mass of the spectator atom, Y, in the defined reaction

$$A'Y + AX = A'X + AY$$

can be given in analytical form both in the zero point energy[22] and finite polynomial[23] approximations. For simplicity we will analyze the mass dependence of the crossover temperature within the zero point energy approximation. The crossover temperature is

$$T_{cr} = (\hbar c/2k) [\sum(\nu'_i - \nu_i)_{AX} - (\nu'_i - \nu_i)_{AY}]/\sum[\ln(\nu_i/\nu'_i)_{AY} - \ln(\nu_i/\nu'_i)_{AX}] \tag{15}$$

For the exchange between two diatomic molecules eq 15 becomes

$$T_{cr} = (\hbar c/k \ln[(M/M')_{AY}(M'/M)_{AX}])\{(f_{AY}/m_Y)^{1/2}[(M/m)^{1/2} - (M'/m')^{1/2}]_{AY} - (f_{AX}/m_X)^{1/2}[(M/m)^{1/2} - (M'/m')^{1/2}]_{AX}\} \tag{16}$$

In eq 16 M and M' are molecular weights and f is the force constant. Differentiation of eq 16 with respect to m_A leads to the result that the crossover temperature for reactions between diatomic molecules increases with m_A when X or Y is not an isotope of A. For a positive crossover temperature $f_{AY} > f_{AX}$ and $(\nu' - \nu)_{AX} > (\nu' - \nu)_{AY}$. Therefore $(\nu' - \nu)_{AX}$ increases faster with m_A than does $(\nu' - \nu)_{AY}$. In the AX molecule the atom A vibrates against a heavier atom than it does in the AY molecule. Differentiation of eq 16 with respect to m_Y leads to the result that the crossover temperature for reactions of diatomic molecules decreases with increase in the mass of the nonexchanging atom Y. This is the case of the sequence of exchange reactions of HH, DH, TH, and ⁴HH with *HX. As the mass of the nonexchanging hydrogen atom increases, the isotopic difference in zero point energies between any hydrogen halide and dihydrogen decreases. This lowers the crossover temperature.

Systems with a single crossover will show one maximum, above the crossover temperature, in a plot of $\ln(K/\pi\sigma)$ vs $1/T$ or $1/T^2$. The value of $\ln(K/\pi\sigma)$ at the maximum increases with the mass difference between the isotopes in the exchange reaction. Typical results are shown in Table IV for the type 1 reaction. At temperatures above the maximum the larger the mass difference, the larger the slope in a $1/T^2$ plot. This follows from eq 4. At temperatures below the maximum, the larger the mass difference the smaller the slope (or larger negative slope) in a plot of $\ln(K/\pi\sigma)$ vs $1/T$. This follows from eq 11. If the heavier of two isotopomers, e.g., T vs D in exchange with H, has a higher crossover temperature, which is the case for types 1 and 2 reactions between dihydrogen and the hydrogen halides, cf. Table V, then the curves for $\ln K_D$ and $\ln K_T$ will cross one another above the crossover temperature. At this crossing there will be a mass independent isotope effect, e.g., $\ln K_D \cong \ln K_T$. Below this temperature $\ln K_D$ is larger than $\ln K_T$. A typical result is shown for the exchange reaction between H_2 and *HI in Figure 7.

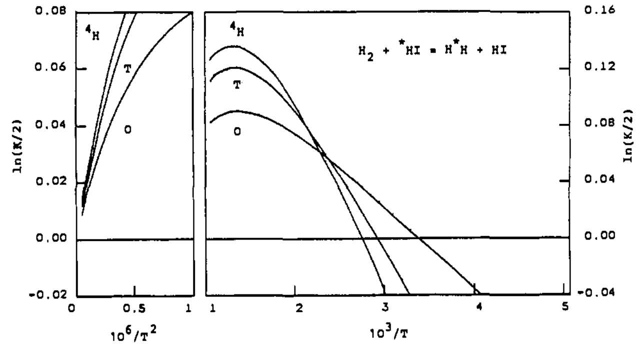

Figure 7. Plot of $\ln(K/2)$ for the exchange equilibria $H_2 + {}^*HI = H^*H + HI$ vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ⁴H.

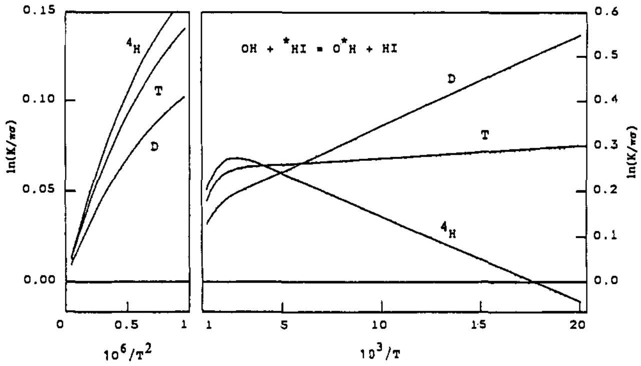

Figure 8. Plot of $\ln(K/\pi\sigma)$ for the exchange equilibria $DH + {}^*HI = D^*H + HI$ vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ⁴H.

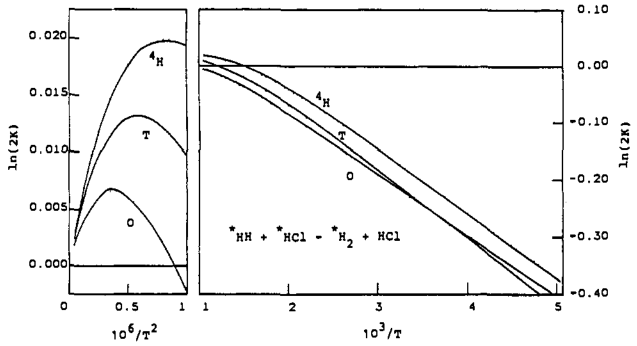

Figure 9. Plot of $\ln(2K)$ for the exchange equilibria ${}^*HH + {}^*HCl = {}^*H_2 + HCl$ vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ⁴H.

When the mass of the nonexchanging hydrogen atom in the dihydrogen molecule increases, the crossover temperature decreases. Not all isotopomers of a given hydrogen halide necessarily show the crossover in type 2 reactions. These systems, nevertheless, show mass independent isotope effects, cf. Figure 8.

In type 3 reactions the heavier of the two isotopes has the lower crossover temperature, cf. Table V. The decrease in the crossover temperature from the increase in the mass of the nonexchanging hydrogen atom in dihydrogen is larger than the increase associated

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Table V. Crossover Temperatures in the Exchange Reactions between Dihydrogen and Hydrogen Halides

A. $YH + {}^*HX = Y^*H + HX$
Types 1, 2, and 3

	*H =		
	D	T	^4H
	X = Cl		
Y = H	1600.8	1608.8	1612.9
Y = D	1060.0	1073.5	1080.2
Y = T	800.4	820.0	829.8
Y = ^{4}H	628.0	655.5	669.0
	X = Br		
Y = H	701.5	722.3	732.6
Y = D	345.8	395.3	418.6
Y = T	88.9	188.9	235.5
Y = ^{4}H			77.6
	X = I		
Y = H	294.1	341.1	363.4
Y = D			56.43
Y = T			
Y = ^{4}H			

B. $H_2 + 2{}^*HX = {}^*H_2 + 2HX$
Type 4

*H =		
D	T	^4H
	X = Cl	
1346.0	1251.4	1198.0
	X = Br	
537.7	490.9	461.8
	X = I	
112.0	99.4	91.1

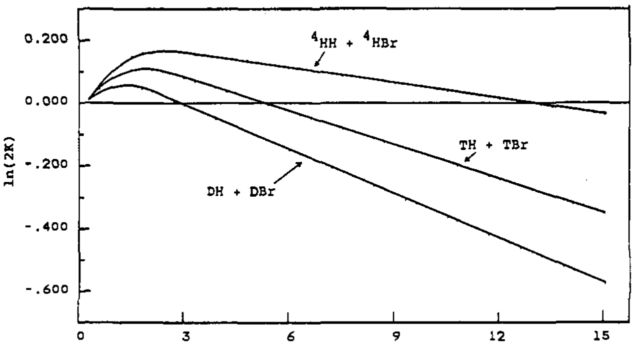

Figure 10. Plot of ln (2*K*) for the exchange equilibria $^*HH + {}^*HBr = {}^*H_2 + HBr$ vs $1/T$. *H = D, T, ^{4}H.

with the mass increase in the hydrogen halide. The curves of ln *K* vs $1/T$ cross one another below the crossover temperature of the heavier isotope, cf. Figure 9. The temperature at which ln K_D is larger than ln K_T is below the tritium crossover temperature. In type 3 reactions the slopes of the different isotopomers below the crossover temperature may increase or decrease with m_{*H} (cf. column B(3) of Table III). When the slope increases with m_{*H}, there is no mass independent isotope fractionation, cf. the reactions $^*HH + {}^*HBr = {}^*H_2 + HBr$, Figure 10.

In type 4 reactions

$$H_2 + 2{}^*HX = {}^*H_2 + 2HX \qquad \text{type 4}$$

crossovers are observed for all halides which show type 1 crossovers. In contrast with the type 1 reactions, the crossover temperatures of type 4 reactions decrease with m_{*H}, cf. Table V. The enthalpy change in a type 4 reaction increases with m_{*H}. This leads to an increase in the crossover temperature with m_{*H}. The entropy change, $\ln (\nu/\nu')_{H_2}/(\nu'/\nu)^2_{HX}$, increases with m_{*H} faster than the enthalpy change. Thus the crossover temperature decreases with m_{*H}. There are mass independent isotope effects below the crossover temperatures, cf. Figure 11.

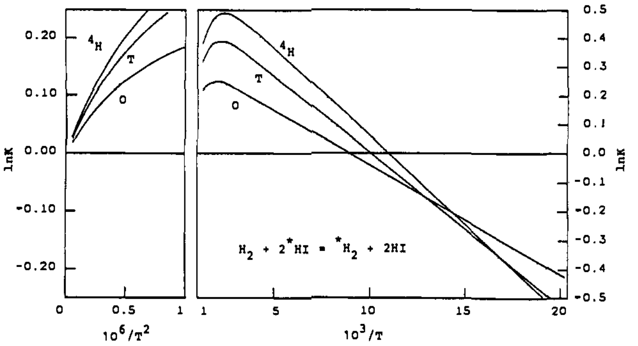

Figure 11. Plot of ln *K* for the exchange equilibria $H_2 + 2{}^*HI = {}^*H_2 + 2HI$ vs $1/T^2$ (left), $1/T$ (right). *H = D, T, ^{4}H.

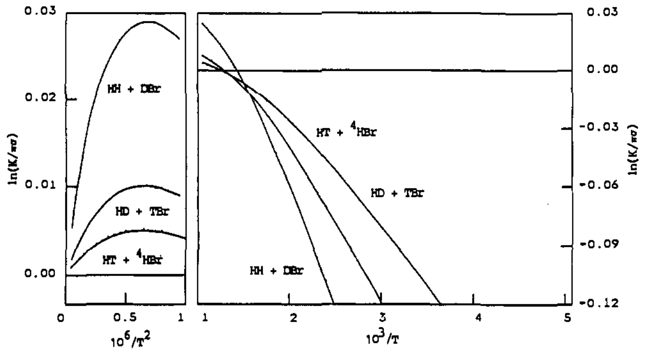

Figure 12. Plot of ln $(K/\pi\sigma)$ for the exchange equilibria $HH + DBr = HD + HBr$, $HD + TBr = HT + DBr$, and $HT + {}^4HBr = H^4H + TBr$ as a function of $1/T^2$ (left), $1/T$ (right).

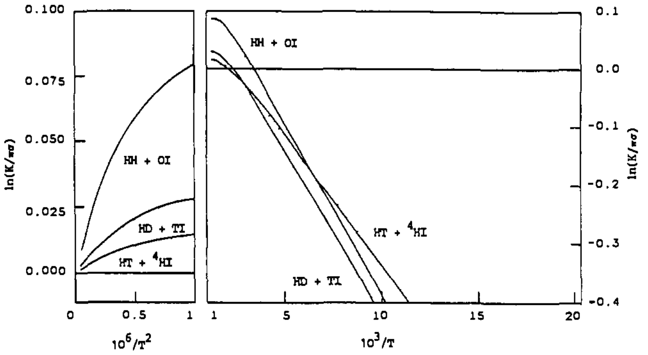

Figure 13. Plot of ln $(K/\pi\sigma)$ for the exchange equilibria $HH + DI = HD + HI$, $HD + TI = HT + DI$, and $HT + {}^4HI = H^4H + TI$ as a function of $1/T^2$ (left), $1/T$ (right).

We have studied the sequential or incremental mass effects in reactions of type 5 when the nonexchanging atom, Y, is H or D.

$$YH + DX = YD + HX \qquad \text{type 5.Y,HD}$$

$$YD + TX = YT + DX \qquad \text{type 5.Y,DT}$$

$$YT + {}^4HX = Y^4H + TX \qquad \text{type 5.Y,T}^4\text{H}$$

The sums $[\ln K_{5.Y,HD} + \ln K_{5.Y,DT}]$ and $[\ln K_{5.Y,DT} + \ln K_{5.Y,T^4H}]$ are the logarithms of the equilibrium constants for the YH–TX and YD–^{4}HHX exchange reactions, respectively. The relative equilibrium parameters for the type 5 reactions are given in Table VI. The crossover temperatures of these reactions increase in the sequence DX, TX, and ^{4}HX. Mass independent isotope effects for type 5 reactions, if any, occur at temperatures below the crossover temperatures, cf. Figures 12 and 13.

Type 1 Reactions

Type 1 reactions have crossovers for X = Cl, Br, and I for each of the isotopomers *H = D, T, and ^{4}H. In this class of reactions the enthalpy change increases faster with m_{*H} than does the entropy change. Thus the crossover temperature increases with m_{*H}. The entropy changes in this class of reactions are inde-

Table VI. Equilibrium Parameters in Some Sequential Isotope Exchange Equilibria between Dihydrogen and Hydrogen Halides

$$\mathrm{YH + DX = YD + HX} \qquad 5\mathrm{Y,HD}$$
$$\mathrm{YD + TX = YT + DX} \qquad 5\mathrm{Y,DT}$$
$$\mathrm{YT + {}^4HX = Y^4H + TX} \qquad 5\mathrm{Y,T^4H}$$
$$\mathrm{Y = H,\ X = Br,\ I,\ At;\ Y = D,\ X = I}$$
$$\ln K/\Pi\sigma = A + B/T \qquad (T < 300\ \mathrm{K})$$
$$\ln K/\Pi\sigma = D/T^2 \qquad (T > 2000\ \mathrm{K})$$

	5H,HD		5H,DT		5H,T⁴H	
	A	B	A	B	A	B
			Y = H, X = Br			
$\ln K/\Pi\sigma$	0.1962	−126.1	0.1370	−85.09	0.1053	−61.35
$\ln K/\Pi\sigma$ 10^{-4} D	11.75		3.910		1.963	
T @ $\ln K/\Pi\sigma = 0$	701.5		767.8		790.7	
			Y = H, X = I			
$\ln K/\Pi\sigma$	0.1985	−58.30	0.1393	−55.80	0.1075	−44.24
$\ln K/\Pi\sigma$ 10^{-4} D	18.82		6.263		3.144	
T @ $\ln K/\Pi\sigma = 0$	294.1		419.7		458.0	
			Y = H, X = At			
$\ln K/\Pi\sigma$	0.2001	+38.16	0.1408	−13.62	0.1090	−19.26
$\ln K/\Pi\sigma$ 10^{-4} D	27.11		9.022		4.528	
T @ $\ln K/\Pi\sigma = 0$			96.7		177.1	
	5D,HD		5D,DT		5D,T⁴H	
	A	B	A	B	A	B
			Y = D, X = I			
$\ln K/\Pi\sigma$	0.1398	+20.41	0.1072	−17.77	0.08714	−21.49
$\ln K/\Pi\sigma$ 10^{-4} D	18.82		6.263		3.144	
T @ $\ln K/\Pi\sigma = 0$			165.8		248.7	

pendent of the H–X force constant. The entropy change is a very slow function of $m_{*\mathrm{H}}$. Thus the overall zero point energy change, which increases with the H–X force constant, controls the change of the crossover temperature with the H–X force constant. For each hydrogen halide which shows the crossover, the crossover temperature increases with $m_{*\mathrm{H}}$ and with the force constant of the HX molecule. For each hydrogen halide which shows type 1 crossover, there are crossings of each ln K vs $1/T$ curve with the other two isotopomer curves. The mass independent isotope effects come at temperatures above the crossover temperature and below the maximum in a ln K vs $1/T^2$ plot. The mass independent isotope effect is a consequence of the fact that the zero point energy difference between HX and *HX increases faster with $m_{*\mathrm{H}}$ than does the zero point energy difference between $\mathrm{H_2}$ and H*H. Figure 7, apart from scale, is typical of type 1 reactions. The mass independent temperatures increase in the order T at which $\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,HT}} < T$ at which $\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,H^4H}} < T$ at which $\ln \alpha_{\mathrm{H,HT}} = \ln \alpha_{\mathrm{H,H^4H}}$, cf. Table VII.

The increase in the value of A(1), Table III, with the mass of the exchanging isotopomer, $m_{*\mathrm{H}}$, for each hydrogen halide is due to the larger ratio $\nu_{\mathrm{HX}}/\nu_{*\mathrm{HX}}$ compared with the ratio $\nu_{\mathrm{H_2}}/\nu_{\mathrm{H*H}}$. The increase in A(1) with the mass of the halogen, e.g., A(1)($\mathrm{H_2}$ + DBr) − A(1)($\mathrm{H_2}$ + DCl) = 0.0075, is due to the finite mass of the halogen compared with m_{H} and $m_{*\mathrm{H}}$.

Type 2 Reactions

We have studied the mass dependence of the crossover temperature as a function of the mass, m_{Y}, of the nonexchanging hydrogen atom in dihydrogen. The results are given in Table V. The reactions of DH typify all the type 2 reactions, and we shall discuss the characteristics of the type 2 reactions by specific reference to the reactions of DH. In common with the type 1 reactions, the crossover temperatures and the values of ln $K_{\max}$ and $T_{\max}$ increase with $m_{*\mathrm{H}}$ at constant m_{Y}. The crossover temperature increases with the force constant of the HX molecule. Although the type 2 reactions between DH + DI and DH + TI do not show the crossover, they do have mass independent isotope effects, cf. Table VII.

Table VII. Mass Independent Fractionation Temperatures for Dihydrogen–Hydrogen Halide Isotope Exchange Reactions

$$\mathrm{H_2 + {*HX} = H{*H} + HX} \qquad \text{type 1}$$

	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,HT}}$	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,H4_H}}$	$\ln \alpha_{\mathrm{H,HT}} = \ln \alpha_{\mathrm{H,H4_H}}$
		X = Cl	
T (K)	1630.7	1634.4	1641.7
ln α	0.00039	0.00043	0.00057
		X = Br	
T (K)	767.8	776.1	790.7
ln α	0.0099	0.0109	0.0140
		X = I	
T (K)	419.7	434.5	458.0
ln α	0.0564	0.0605	0.0748
		X = At	
T (K)	96.7	131.5	177.1
ln α	0.5948	0.4901	0.4793

$$\mathrm{DH + {*HX} = D{*H} + HX} \qquad \text{type 2}$$

	$\ln \alpha_{\mathrm{D,HD}} = \ln \alpha_{\mathrm{D,HT}}$	$\ln \alpha_{\mathrm{D,HD}} = \ln \alpha_{\mathrm{D,H4_H}}$	$\ln \alpha_{\mathrm{D,HT}} = \ln \alpha_{\mathrm{D,H4_H}}$
		X = Cl	
T (K)	1106.2	1112.0	1122.7
ln α	0.0015	0.0016	0.0021
		X = Br	
T (K)	474.2	489.4	513.2
ln α	0.0346	0.0372	0.0462
		X = I	
T (K)	165.8	202.3	248.7
ln α	0.2629	0.2407	0.2572

$$\mathrm{{*HH} + {*HX} = {*H_2} + HX} \qquad \text{type 3}$$

	$\ln \alpha_{\mathrm{D,HD}} = \ln \alpha_{\mathrm{T,HT}}$	$\ln \alpha_{\mathrm{D,HD}} = \ln \alpha4_{\mathrm{H,H4_H}}$
	X = Cl	
T (K)	274.5	99.1
ln α	−0.2582	−0.9455

$$\mathrm{H_2 + 2{*HX} = {*H_2} + 2HX} \qquad \text{type 4}$$

	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,HT}}$	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,H4_H}}$	$\ln \alpha_{\mathrm{H,HT}} = \ln \alpha_{\mathrm{H,H4_H}}$
		X = Cl	
T (K)	988.8	927.7	812.2
ln α	−0.0315	−0.0426	−0.0821
		X = Br	
T (K)	398.9	371.2	328.9
ln α	−0.1034	−0.1351	−0.2303
		X = I	
T (K)	77.4	69.8	58.8
ln α	−0.1511	−0.2048	−0.3670

$$\mathrm{H_2 + DX = HD + HX} \qquad \text{type 5}$$
$$\mathrm{HD + TX = HT + DX}$$
$$\mathrm{HT + {}^4HX = H^4H + TX}$$

	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,DT}}$	$\ln \alpha_{\mathrm{H,HD}} = \ln \alpha_{\mathrm{H,T4_H}}$	$\ln \alpha_{\mathrm{H,DT}} = \ln \alpha_{\mathrm{H,T4_H}}$
		X = Cl	
T (K)	1583.2	1591.0	1618.6
ln α	−0.00025	−0.00014	−0.00006
		X = Br	
T (K)	642.5	668.7	737.3
ln α	−0.0120	−0.0063	−0.0022
		X = I	
T (K)	42.0	154.5	348.6
ln α	−1.1887	−0.1788	−0.0235

At high temperature the symmetry corrected equilibrium constant for each type 2 reaction is equal to the corresponding symmetry corrected type 1 equilibrium constant.

There exists a general theorem to the effect that the zero point energy difference between successive members of a series of equivalent isotopic homologues, $\mathrm{A'_nX}$, $\mathrm{A'_{n-1}AX}$, ...$\mathrm{A'A_{n-1}X}$, $\mathrm{A_nX}$, increases with the number of atoms of the heavy isotope A in the molecule.[24,25] The difference in the zero point energy differences between (HD − D_2) and (H_2 − HD) is 78.7 K. Thus each low temperature enthalpy change in the type 2 reaction DH + DX, B(2) in Table III, is greater than B(1) for the corresponding HH + DX reaction. The corresponding entropy related difference between types 1 and 2 reactions, [A(1) − A(2)], is 0.05875. Changes in [B(2) − B(1)] and [A(1) − A(2)] in a similar direction are found for the reactions of DH with TX and ^{4}HX, respectively. The differences in [A(1) − A(2)] and [B(2) − B(1)], respectively, increase in the order *H = D < T < ^{4}H. The order of the sequence relates to the fact that the exchanging atom, *H, vibrates against a heavier mass in D*H than in H*H. As a consequence of the fact that each B(2) is larger than the corresponding B(1), not all reactions of a given hydrogen halide, for which all isotopomers show the crossover in type 1 reactions, show crossover for all isotopomers in type 2 reactions. An example is the DH + *HI reactions shown in Figure 8, which has a crossover only for *H = ^{4}H. It is interesting to note that B(2) for the DH + TI reaction is approximately zero. This is an example of a temperature "independent" equilibrium isotope effect. Other examples are to be found in exchange reactions between dihydrogen and the hydrogen halides, e.g., ^{4}HH + TBr.

The effect of replacing the nonexchanging H atom in H_2 by D has a larger effect on the enthalpy change than the entropy change of the corresponding reactions. As a result the following differences are found between corresponding type 2 and type 1 reactions: at low temperatures (1) ln $\alpha(2)$ > ln $\alpha(1)$, (2) $T_{cr}(1) > T_{cr}(2)$, and (3) the mass independent isotope effect temperatures and fractionation factors are in the order $T_{\mathrm{MIIE}}(1) > T_{\mathrm{MIIE}}(2)$ and ln $\alpha(2)_{\mathrm{MIIE}}$ > ln $\alpha(1)_{\mathrm{MIIE}}$.

Type 3 Reactions

The type 3 reactions are structurally different from types 1 and 2 reactions. The type 3 reactions involve an exchange of the isotopomers *H = D, T, and ^{4}H in HX with the same isotopomer as a nonexchanging atom in *HH. The first in the sequence of type 3 reactions is DH + DX, which is also the first of the type 2 reactions. The other type 3 reactions are TH + TX and ^{4}HH + ^{4}HX. A change in *H in HX is accompanied by a corresponding change in the nonexchanging atom, *H, in *HH. HCl and HBr show the crossover for the isotopomers D, T, and ^{4}H in type 3 reactions. The exchanging hydrogen atom in dihydrogen, H, vibrates against a heavier mass, D, T, and ^{4}H, in all type 3 reactions. The zero point energy difference between *HH and *H_2 is larger than that between HI and *HI for each isotopomer *H. The *HI type 3 reactions do not show crossovers nor anomalous mass effects.

In type 3 reactions the entropy term A(3), Table III, increases faster than the enthalpy term, B(3), with $m_{*\mathrm{H}}$, the mass of the nonexchanging atom in dihydrogen. As a result the crossover temperatures for type 3 reactions decrease with $m_{*\mathrm{H}}$. Although *HBr shows the crossover for all isotopomers in type 3 reactions, this set of type 3 reactions has no mass independent isotope effects, cf. Figure 10. This follows from the mass dependence of the crossover temperatures and the low and the high temperature enthalpy changes in type 3 reactions.

Not only is ln (s/s')f (*H_2/*HH) larger than ln (s/s')f (*HH/H_2) at low temperatures but also it is larger at all temperatures. Consider the high temperature approximation to ln (s/s')f through terms in $(\hbar/kT)^4$. The first quantum correction, terms in $(\hbar/kT)^2$, is the same for the logarithms of each reduced partition function ratio, ln (s/s')f (*H_2/*HH) and ln (s/s')f (^{8}HH/H_2). The first term in the second order quantum correction, $(\mu_\iota'^2 - \mu_\iota^2)a_{\iota\iota}^2$, is also the same for each of the logarithms of the respective reduced partition function ratios. The second term in the second order quantum correction, which is $-2(\mu'_\iota - \mu_\iota)a_{\iota\iota}^2/m_{*\mathrm{H}}$ for ln (s/s')f (*H_2/*HH), is smaller than the similar second order quantum correction, $-2(\mu'_\iota - \mu_\iota)a_{\iota\iota}^2/m_{\mathrm{H}}$, for ln (s/s')f (*HH/H_2). Since the slope of ln (s/s')f vs $1/T^2$ decreases monotonically with $1/T^2$, the slope of ln (s/s')f (*H_2/*HH), which is equal to that of (*HH/H_2) in the high temperature limit, increases monotonically with respect to the slope of ln (s/s')f (*HH/H_2) with increase in $1/T$ or $1/T^2$. Thus ln $(K_3/\pi\sigma)_{*\mathrm{H,H}*\mathrm{H}}$ is larger than ln $(K_1/\pi\sigma)_{\mathrm{H,H}*\mathrm{H}}$ at low temperature; the two respective equilibrium constants are equal to one another at high temperature.

The *HCl type 3 reactions show mass independent isotope effects for (DH + DCl) with (TH + TCl) and (DH + DCl) with (^{4}HH + ^{4}HCl), cf. Table VII. The pair (TH + TCl) does not cross with (^{4}HH + ^{4}HCl). This can be seen from the enthalpy terms, B(3), in Table III. At all temperatures ln K(TH + TCl) is smaller than ln K(^{4}HH + ^{4}HCl). The mass independent isotope effect temperature for the pair (DH + DCl) with (TH + TCl) is higher than the crossing temperature of (DH + DCl) with (^{4}HH + ^{4}HCl) because the low temperature enthalpy difference between the first pair is twice that of the second pair, while the entropy difference between the second pair is but 40% larger than that of the second pair, cf. Table III.

Type 4 Reactions

The logarithm of the symmetry corrected type 4, H_2 + 2*HX, equilibrium constant, ln $K(4)/\pi\sigma$, is the sum of the logarithms of the corresponding types 1 and 3 symmetry corrected equilibrium constants. Thus, the type 4 reactions can be rationalized in terms of the properties of the types 1 and 3 reactions. Insofar as the latter two may differ, the type 4 reaction will more closely resemble the type 3 reaction, since the fractionation factors for the type 3 reactions are equal to or larger than the corresponding type 1 reactions. In particular, we call attention to the fact that the crossover temperatures of type 4 reactions decrease with the mass of the exchanging isotopomer in contrast to the type 1 reactions. As explained in the section General Considerations, the mass dependence of the crossover temperature of type 1 reactions is enthalpy controlled. In the type 4 reactions it is entropy controlled. The entropy effect is opposite in sign from the enthalpy effect, and thus we find the opposite behavior for the mass dependence of the crossover temperature between types 1 and 4 reactions.

The general features of the type 4 reactions are as follows: 1. The crossover temperature decreases with $m_{*\mathrm{H}}$. 2. The crossover temperatures of type 4 reactions lie between those of the corresponding types 1 and 3 reactions. 3. The order of ln $K(4)_{\max}$ is ^{4}H > T > D. 4. The order of T at ln $K(4)_{\max}$ is ^{4}H < T < D. 5. The absolute values of the slopes in plots of ln $K(4)$ vs $1/T$ at low temperature are in the order |^{4}H| > |T| > |D|. 6. The order of the low temperature equilibrium constants is ln K(^{4}H) < ln K(T) < ln K(D). 7. There are mass independent isotope effects for each isotopomer in each corresponding reaction that shows type 1 mass independent isotope effects. The temperature of the mass independent isotope effect decreases with $m_{*\mathrm{H}}$. Since type 3 mass independent crossing temperatures are lower than the corresponding type 1 temperatures, the mass independent crossing temperatures of type 4 reactions are lower than the corresponding type 1 temperatures.

Type 5 Reactions

The relative values of the logarithms of the symmetry corrected equilibrium constants for type 5 reactions at high temperatures are

$$\ln K_{5,\mathrm{HD}}:\ln K_{5,\mathrm{DT}}:\ln K_{5,\mathrm{T^4H}} = 6:2:1$$

as a consequence of the smaller differences in the reciprocal masses of the exchanging isotopomers with the increase in the mass of the exchanging isotopomer. The type 5 exchange reactions of hydrogen fluoride and hydrogen chloride do not present any new features. For the halogens Br and I crossovers are found for each isotopomer pair. The crossover temperatures increase with the mass of the exchanging isotopomers both for the 5H and 5D reactions, cf. Table VI. The low temperature behavior of the type 5 reactions are quite different for each of the hydrogen halides HBr, HI, and HAt. The different behavior from one halide to the next is related to the sequence of enthalpy rather than entropy changes in the reactions. The entropy changes, A in Table VI, are insensitive to the halogen for each Y. The enthalpy change is the difference in the zero point energy difference between (Y*H − Y**H) and (*HX − **HX), where $m_{*\mathrm{H}} - m_{**\mathrm{H}} = -1$. Thus it is just the difference in zero point energy between (*HX −

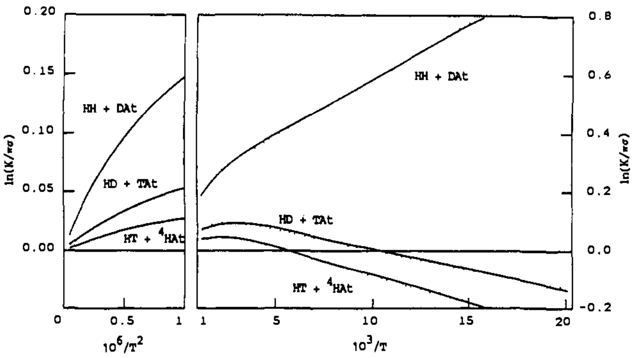

Figure 14. Plot of ln ($K/\pi\sigma$) for the exchange equilibria HH + DAt = HD + HAt, HD + TAt = HT + DAt, and HT + ^{4}HAt = H^{4}H + TAt as a function of $1/T^2$ (left), $1/T$ (right).

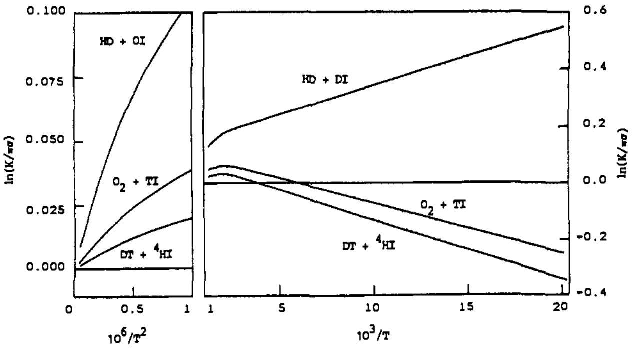

Figure 15. Plot of ln ($K/\pi\sigma$) for the exchange equilibria DH + DI = D_2 + HI, D_2 + TI = DT + DI, and DT + ^{4}HI = D^{4}H + TI as a function of $1/T^2$ (left), $1/T$ (right).

HX) for each *H that accounts for the different low temperature behavior of HBr, HI, and HAt in type 5 reactions, cf. Figures 12–14. For a given hydrogen halide the low temperature behavior for the different isotopomer reactions depends both on the entropy and enthalpy changes as a function of the isotopomer pair *H–H in dihydrogen and the hydrogen halide, cf. Table VI.

For the HBr type 5 exchange reaction there is a "single" mass independent isotope effect for the three exchange reactions in the neighborhood of 700 K. Below 642.5 K the order of the values of ln $K/\pi\sigma$ is HH + DBr < HD + TBr < HT + ^{4}HBr, just the inverse order of the high temperature behavior. Both are a consequence of the fact that the H–H force constant is larger than the H–Br force constant. In the sequence of reactions starting from HH + DBr to HT + ^{4}HBr both A and B in the equation

$$\ln K/\pi\sigma = A + B/T \tag{17}$$

change by a factor of 2.

For the HI type 5 reactions, Figure 13, the sequence of the low temperature values of ln $K/\pi\sigma$ is temperature dependent. In the region 42–154 K the sequence is HD + TI < HH + DI < HT + ^{4}HI. Note the slopes of the HD + TI and HH + DI curves differ by only 4%. The value of ln $K/\pi\sigma$ for the HH + DI reaction is larger than the that of the HD + TI reaction as a result of the larger entropy change in the former. The enthalpy change in the HT + ^{4}HI reaction differs significantly from the other two reactions. As a result the HT + ^{4}HI reaction shows a mass independent isotope effect with the HH + DI reaction at 154 K and with the HD + TI reaction at 350 K. Above 350 K the sequence of ln $K/\pi\sigma$ values is HT + ^{4}HI < HD + TI < HH + DI which is also the sequence in the high temperature limit.

The type 5 reactions with HAt, which do not show crossovers for any of the isotopomers in types 1, 2, and 3 reactions, show crossovers for the HD + TAt and HT + ^{4}HAt reactions, Figure 14. There are, however, no mass independent isotope effects. The HH + DAt reaction has the largest value of ln $K/\pi\sigma$ at all temperatures. The behavior is readily understood in tems of the entropy and enthalpy parameters for the reactions given in Table VI.

In Figure 15 we display the type 5 reactions for HI when the nonexchanging hydrogen atom in dihydrogen is D. The sequence of ln $K/\pi\sigma$ values at all temperatures is the same as the HAt reactions. The high temperature behavior of the DH and HH reactions are identical. The low temperature behavior is completely different from the HI reactions with dihydrogen in which the nonexchanging hydrogen atom is H, Figure 13.

Registry No. H_2, 1333-74-0; hydrogen chloride, 7647-01-0; deuterium, 7782-39-0; tritium, 10028-17-8; hydrogen isotope of mass 4, 12596-08-6; hydrogen fluoride, 7664-39-3; hydrogen bromide, 10035-10-6; hydrogen iodide, 10034-85-2; hydrogen astatide, 13464-71-6.