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MASTER

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ABSTRACT

We have constructed a quadrupole-mass filter system to measure the equilibrium constants and rates of reaction of the β-particle-induced exchanges between H_2, D_2, and T_2 at cryogenic temperatures. Even with careful calibration experiments at 25.4°C, we could not completely remove the mass discrimination inherent in our method. We estimate the accuracy of our mixture analyses to be ±2.2% in the D_2-DT-T_2 system, and ±9% in the H_2-HT-T_2 system. Preliminary kinetic experiments showed that the time to reach equilibrium in the exchange $H_2 + T_2 = 2HT$ is 7 to 14 h. The equivalent time interval in the exchange $D_2 + T_2 = 2DT$ is 3 to 7 h. This measured isotope effect of two can be used to predict the rates of the DT exchange from the HT rates in the literature.

INTRODUCTION

As part of the quest for new energy sources, research laboratories throughout the world are searching for the most practical method of harnessing nuclear fusion. All current fusion experiments require fuel mixtures of D_2, DT, and T_2, because the $D + T = \alpha + n$ reaction has the largest fusion cross section and ignites at the lowest temperature. Different physical and chemical properties may be necessary for each of the following processes: fabrication of liquid and solid targets or fuel pellets; isotope separation and spent fuel clean-up; and design of the gaseous fuel handling systems. Therefore, we have begun an extensive program to characterize the physical and chemical properties of DT mixtures, especially, but not exclusively, at cryogenic temperatures. Our program consists of reviewing the literature, theoretical modeling and calculations, and experiments that measure the chemical and physical properties of the isotopic hydrogens. The experiments are essential because there are very little data on T-containing species.

The chemical equilibrium constant gives the composition of the isotopic mixtures at various temperatures; the kinetics specify how rapidly equilibrium is achieved after mixing or how rapidly the composition of a mixture changes when the temperature is changed. In the future, we plan to measure the equilibrium and rate constants in the gas and liquid phases at cryogenic temperatures. We expect to use mass spectroscopy to study the species in the gas phase and infrared spectroscopy in the liquid phase. In this paper we evaluate the suitability of a quadrupole mass filter for studying the gaseous hydrogen isotopes at cryogenic temperatures. Part of this evaluation includes sensitivity calibration experiments at room temperatures. We also want to look at the β-particle catalyzed kinetics of H_2-T_2 and D_2-T_2 at room temperatures, especially the latter pair because there are practically no data on this exchange reaction.

EXCHANGE REACTIONS

The hydrogen isotopic molecules H_2, HD, HT, D_2, DT, and T_2 are related by the following self-exchange reactions:

$$H_2 + D_2 = 2HD, \tag{1}$$

$$H_2 + T_2 + 2HT, \tag{2}$$

$$D_2 + T_2 = 2DT. \tag{3}$$

These relationships hold in the gas, liquid, and solid phases. The rate of the reaction in Eq. (1) is very slow because there is no catalyst; the β-particle from the tritium readily catalyses reactions in Eqs. (2) and (3). Three additional exchange reactions can be written that relate the exchange between the pure isotopic species H_2, D_2, and T_2, and the mixed isotopic species HD, HT, and DT:

$$H_2 + DT = HD + HT, \tag{4}$$

$$D_2 + HT = HD + DT, \tag{5}$$

$$T_2 + HD = HT + DT. \tag{6}$$

The equilibrium constants in the gas phase are expressed in terms of the partial pressures P_i where i is the isotopic hydrogen specie:

$$K_1 = P_{HD}^2/P_{H_2} \cdot P_{D_2}, \tag{7}$$

$$K_2 = P_{HT}^2/P_{H_2} \cdot P_{T_2}, \tag{8}$$

$$K_3 = P_{DT}^2/P_{D_2} \cdot P_{T_2}, \tag{9}$$

$$K_4 = P_{HD} \cdot P_{HT}/P_{H_2} \cdot P_{DT}, \tag{10}$$

$$K_5 = P_{HD} \cdot P_{DT}/P_{D_2} \cdot P_{HT}, \tag{11}$$

$$K_6 = P_{HT} \cdot P_{DT}/P_{T_2} \cdot P_{HD}. \tag{12}$$

The equilibrium constants in the liquid and solid phases have the same form but are expressed in terms of mole fractions instead of partial pressures.

Several researchers have calculated the equilibrium constants $K_1 - K_6$ (see Ref. 1). All of the calculations agree with those of Jones[2] who also experimentally verified the values of the equilibrium constants.[3] At 300 K, Jones[2] found that $K_1 = 3.26$, $K_2 = 2.58$, $K_3 = 3.82$, $K_4 = 1.48$, $K_5 = 2.20$, and $K_6 = 1.74$.

The kinetics of the β-induced exchange between H_2 and T_2 have been studied by Dorfman and Mattraw[4,5] and by Jones[3,5]. In a paper on the mass spectroscopy of the hydrogen isotopes, Schott and Beau[6] indicate that it takes a month for a 94% H_2, 6% T_2 mixture to reach equilibrium. However, we found no published data on the kinetics of the β-induced exchange between D_2 and T_2.

MASS SPECTRUM OF THE HYDROGEN ISOTOPES

The mass spectrum of the hydrogen isotopes is complicated by several factors. If we use a conventional electron bombardment source with 70-eV electrons, the spectrum contains the fragment ions H^+, D^+, and T^+. The tritium decay produces helium-3 that appears at mass 3 as do T^+ and HD^+. The most difficult problem is that HT and D_2 appear at the same mass number. The ions appearing in the conventional mass spectrum are shown in Table 1. The mass spectrum can be simplified if we use electrons with energies lower than the appearance potentials (A.P) of ^3He and the fragement ions: [A.P. (^3He) ≅ 25 V, A.P. (H^+) ≅ 18 V]. As is shown in Table 1, we still have the

Table 1. Ions appearing in a conventional mass spectrum.

m/e	Ions, 70-eV electrons	Ions, 18-eV electrons
1	H^+	
2	H_2^+, D^+	H_2^+
3	HD^+, $^3HE^+$, T^+	HD^+
4	D_2^+, HT^+	D_2^+, HT^+
5	DT^+	DT^+
6	T_2^+	T_2^+

problem at m/e = 4 of the two competing ions D_2^+ and HT^+. The mass difference between these isotopic molecules is 4 mmu that requires a resolution of 920 for separation. Because the maximum resolution of our quadrupole mass filter is 600, we cannot separate D_2 and HT^+. Therefore, we cannot obtain independent values of the equilibrium constants K_2 and K_3 unless we provide an H_2-HT-T_2 system free of D_2 impurities, or a D_2-DT-T_2 system free of H_2 impurities. The former is possible but the latter is a difficult process. Thus, the equilibrium constants reported in this paper require previously measured values of K_3 and K_6 to separate the D_2^+ and HT^+ contributions to the mass four peak.

EXPERIMENTAL

Table 2 lists the gases we used in our experiments as well as their percentage purity. Most of the impurities were isotopic.

The gas inlet and mixing system is shown schematically in Fig. 1; Fig. 2 is a diagram of the prototype cryogenic cell and the quadrupole mass filter. The cell is identical to the one we plan to use at very low temperatures. The diameter of the pinhole leak is 2.5×10^{-6} m and the conductance is 3.92×10^{-6} l/s. The cell is connected to an expansion volume that maintains the pressure in the cell at a nearly constant value. (The pressure fluctuation was less than 0.1 Torr at 160 Torr for the sensitivity and mixture measurements, and about 1 Torr in 160 Torr for the kinetic measurements.) Note that this system was designed for cryogenic measurements in the 4-to-25-K range; it is not ideal for ambient temperature measurements because cell and connecting tube volumes are small, and could cause fractionation.

The calibration experiments measure sensitivity (S) as the intensity (I) divided by the pressure (P); we used the following procedure: a sample of the pure gas H_2, HD, D_2, or T_2 was admitted to the sample cell and 1/2-liter expansion volume. In our initial experiments we followed the sequence H_2, HD, D_2, and T_2, but a statistical analysis indicated that this procedure was biasing our results. Thus, for the last five calibration experiments we took the samples in random sequence, ignoring the first sample of the series because there appeared to be a warm-up effect. After the sample was added to the cell, the pressure increased gradually until it reached a maximum and then decreased very slightly. We waited 10 to 15 min after sample insertion to ensure that the pressure was stabilized. We then recorded five 1 1/2-min scans of the mass spectrum from masses 2 to 6. The H_2, HD, and D_2 samples were then pumped out for 10 min and the T_2 samples were gettered on the uranium trap. The gettering procedure lasted 30 to 45 min. The sequence was then repeated.

Table 2. Purity of gases.

Gas	Purity, %	Supplier
H_2	99.999	Matheson
HD	99	Stohler Isotope Chemical
D_2	99.4	Oak Ridge Laboratory
T_2	96.5	Savannah River Laboratory

The pressure selected for these calibration and mixture runs was 160 Torr or approximately the vapor pressure of T_2 at its triple point. We modified the power supply of the mass filter so that we could reduce the ionizing voltage of the electrons to 24 V. This is below the appearance potential of helium ions but slightly above the estimated appearance potentials of the fragment ions H^+, D^+, and T^+. However, at this voltage, fragment ions appeared to contribute very little to the spectrum and we needed the increased sensitivity brought about by increasing the ionizing voltage from 18 V (appearance potential of H^+) to 24 V. We used an electron multiplier for our detector because the faraday cup mode of the instrument was not sensitive enough.

The procedure for analyzing the H_2-D_2 mixtures was similar to the above. The isotopic gases were mixed and then passed through a tube 3.2×10^{-3} m in diameter and 0.91 m long. The tube contained platinum in the form of sponge. This treatment was enough to equilibrate the mixtures. After 10 min, we took five 2-min scans and then analyzed the last scan, which was representative of the others. The mixture was pumped out and the procedure repeated.

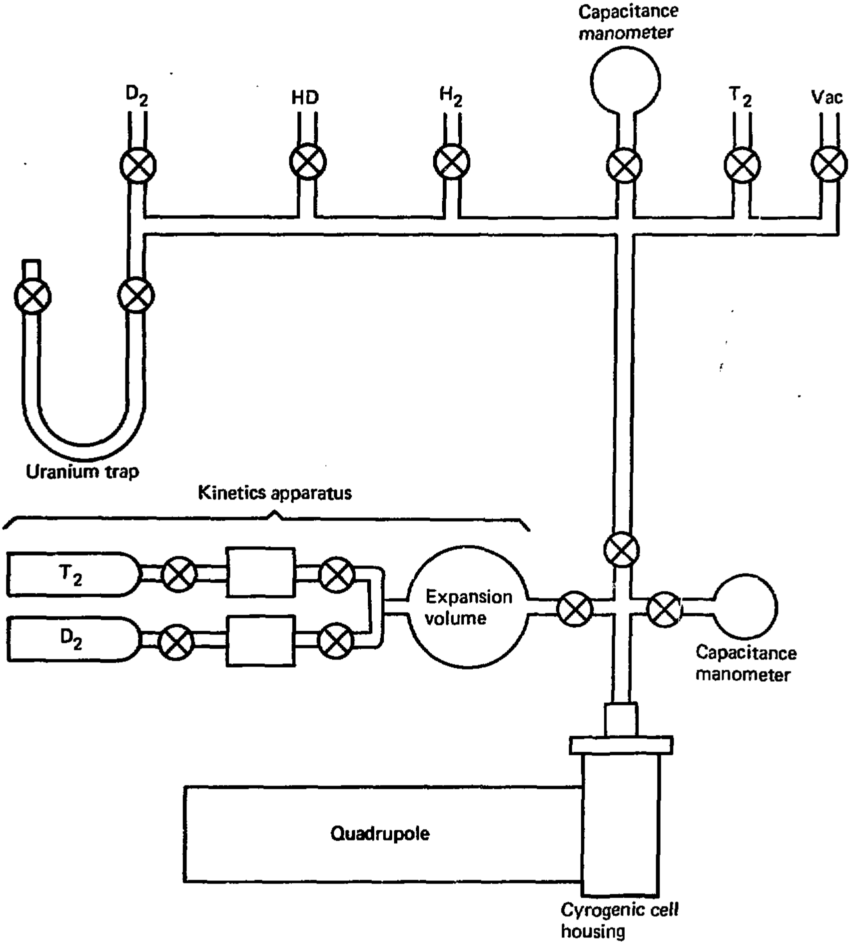

Fig. 1. Gas inlet and mixing system.

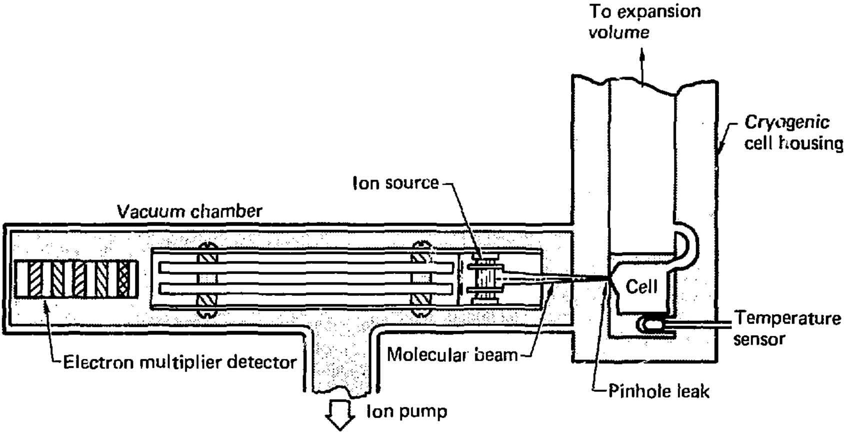

Fig. 2. Prototype cryogenic cell and quadrupole mass filter.

We prepared the H_2-T_2 and D_2-T_2 mixtures by degassing some T_2 from the uranium trap and adding enough H_2 or D_2 to obtain the desired composition at a total pressure of 760 Torr. Before analysis, we allowed the mixtures to equilibrate for 18 to 20 h. We knew this time period was long enough because we could not detect any difference between the β-catalyzed samples and those passed through the Pt-catalysis tube. The analytical procedure was similar to that used for H_2-D_2 mixtures except that we gettered the unused sample on the uranium trap. We monitored the temperature of the room during some of the mixture and kinetic experiments and found it to be 25.4 ± 0.4°C.

We began the kinetic experiments by first admitting the gas sample at the lower partial pressure into the expansion volume. We then added the other component which was at a higher pressure, noted the time of mixing, and opened the valve to the cryogenic cell so that the gases flowed into the quadrupole mass filter through the leak. Throughout the experiment, we followed and recorded the peak heights on a chart recorder. In general, the peaks increased or decreased with time in a smooth fashion, although there were a few anomalies. The peaks that belonged to a particular species were connected by a smooth curve and we picked the intensities off the curves at 10-min intervals. We converted these intensities to partial pressures using sensitivites that are measured in a sensitivity run on the same day of the kinetic run. Finally, we treated these partial pressures using methods that we will discuss later. We did not attempt to follow the reaction to equilibrium; we estimated the pressures at equilibrium by extrapolating the kinetic curves.

SENSITIVITIES OF H_2, HD, D_2, AND T_2

We did not expect the sensitivities of the isotopic hydrogens to be equal because so many phenomena associated with our quadrupole mass filter system are functions of the molecular mass. For example, we have identified three sources of mass discrimination; there may be others. According to the work of Ploch and Walcher,[7] the gain of electron multipliers is proportional to the inverse of the square root of the molecular mass. Gas conductance through an orifice[8] as well as the pumping speeds of diffusion[9] and ion pumps[10] are likewise inversely proportional to the square root of the molecular mass. The mass spectrometric sensitivites are proportional to the gain of the multiplier and the conductance through an orifice, but inversely proportional to the pumping speed. We do not know the weighting factors of these, and perhaps other, unidentified phenomena. Therefore, we have not been able to derive *a priori* a function that relates the sensitivities to the mass.

Sensitivity measurement is theoretically straightforward: a known pressure of the pure isotopic gas is placed in the expansion chamber and the intensity of the appropriate isotope peak is recorded; the intensity divided by the pressure of the pure gas sample equals the sensitivity. Each of the gases used for calibration contain isotopic impurities. There are also small amounts of residual gases from the previous sample present in the vacuum system. The contributions of these gaseous impurities must be subtracted from the total pressure of the sample to give the partial pressure of the gas used for calibration. The partial pressure of the impurity gases is obtained by dividing the intensities of the impurities by the appropriate sensitivity. Because these impurity sensitivities are not known *a priori* this correction calculation has to be repeated several times until a constant value for the sensitivity is obtained.

We measured the sensitivities of H_2, HD, D_2, and T_2 in a series of nine experiments. As mentioned previously, the last five experiments are expected to be more accurate than the first four. Figure 3 illustrates the type of results we obtained. It is obvious that sensitivites of these hydrogen isotopes differ greatly. The time dependence appears to be linear and nearly flat. All of the data obtained are given in Table 3.

We performed an extensive statistical analysis of the data and found [11] that the data fit an exponential function of the mass. In addition, the average slope with respect to time showed a slight positive bias. We also tried a multiplicative model $S(m,t) = am^b(1+t)^{c \cdot t}$ but it did not fit the data as well. The errors were found to be independent, homogeneous, and normally distributed. The exponential equation

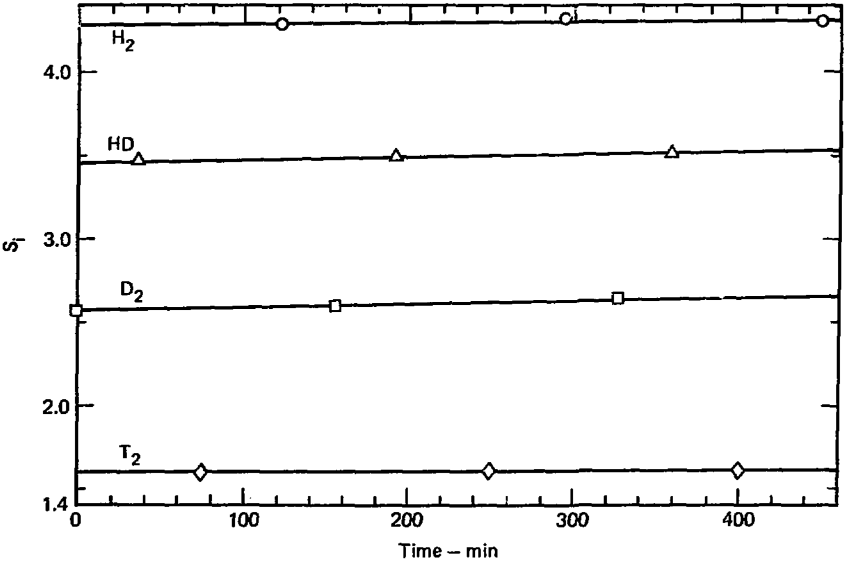

Fig. 3. Plot of S_i vs time, i = H_2, HD, D_2 or T_2.

Table 3. Sensitivity at given times and masses.

Exponential number	Mass	Cycle 1 Si	Cycle 1 Time, min	Cycle 2 Si	Cycle 2 Time, min	Cycle 3 Si	Cycle 3 Time, min
1	2.016	3.97	0	4.18	153	4.22	300
1	3.022	3.12	31	3.34	184	3.40	331
1	4.029	2.58	61	2.70	216	2.70	363
1	6.031	1.56	94	1.64	249	1.64	397
2	2.016	4.44	0	4.60	173	4.57	341
2	3.022	3.63	31	3.70	210	3.66	374
2	4.029	2.85	68	2.85	243	2.81	409
2	6.031	1.71	102	1.71	283		
3	2.016	3.86	0	4.05	231	4.045	396
3	3.022	3.10	42	3.18	264	3.23	428
3	4.029	2.43	73	2.49	296	2.47	461
3	6.031	1.43	142	1.48	331		
4	2.016	4.17	0	4.39	169	4.415	340
4	3.022	3.44	36	3.47	204	3.545	374
4	4.029	2.69	69	2.72	240	2.72	413
4	6.031	1.66	108	1.66	279	1.645	452
5	2.016	4.70	128	4.76	292	4.92	460
5	3.022	3.76	34	3.89	198	3.85	357
5	4.029	2.88	0	2.88	164	2.91	324
5	6.031	1.76	74	1.80	236	1.78	396
6	2.016	4.49	113	4.58	253	4.51	405
6	3.022	3.58	81	3.59	222	3.66	370
6	4.029	2.72	48	2.73	191	2.79	339
6	6.031	1.63	0	1.66	149	1.70	287
7	2.016	4.38	88	4.43	259	4.46	430
7	3.022	3.56	0	3.55	162	3.58	323
7	4.029	2.63	119	2.67	292	2.72	463
7	6.031	1.64	35	1.66	196	1.65	360
8	2.016	4.27	123	4.31	295	4.28	449
8	3.022	3.47	36	3.48	192	3.51	360
8	4.029	2.58	0	2.58	156	2.63	327
8	6.031	1.59	75	1.59	248	1.60	401
9	2.016	4.11	37	4.23	203	4.16	391
9	3.022	3.31	0	3.43	172	3.36	359
9	4.029	2.55	141	2.54	326		
9	6.031	1.51	76	1.57	235	1.54	431

(Fig. 4) is

$$S_i = 7.21\, e^{-0.246\, m} \qquad (13)$$

where i denotes the hydrogen isotopic molecule. The percentage error (2σ) of S_i is ±3.8%.

If we assume that the mass dependence is the same for the unmeasured HT and DT, we can compute a relative value for the sensitivities of all the hydrogen isotopes using Eq. (13). These are given in Table 4.

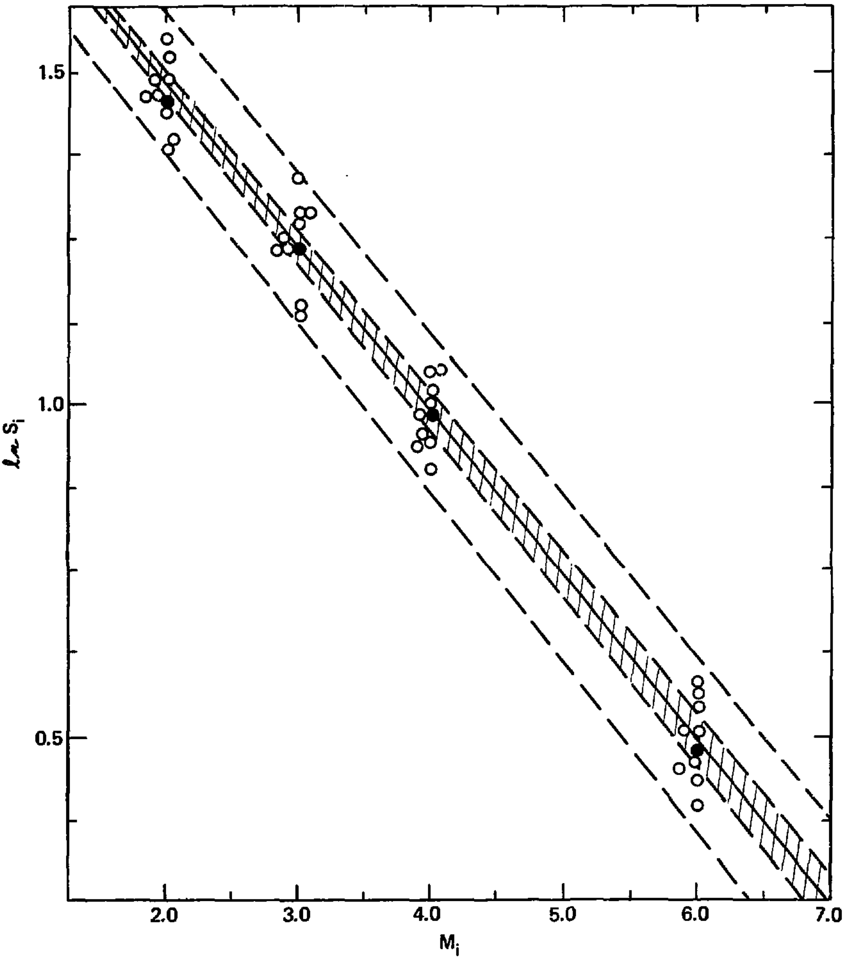

Fig. 4. Plot of ℓn S_i vs M_i where i = H_2, HD, D_2 or T_2. The line was fitted by a least squares technique. The cross hatched area represents the 95% confidence region for the predicted line. The dashed lines contain the 95% confidence region for a single observation at a specified mass. The open circles denote the individual experimental values. The shift from the integer mass values merely denote multiple values. The solid circles represent the overall average at each mass.

Table 4. Relative sensitivity values from Eq. (13).

Isotopic molecule	Mass	Relative sensitivity
H_2	2.016	4.39
HD	3.022	3.43
HT	4.024	2.68
D_2	4.029	2.68
DT	5.030	2.10
T_2	6.031	1.64

ANALYSIS OF HYDROGEN ISOTOPE MIXTURES

We have an independent method of checking our sensitivity calibration results. In our tritium facility, we have a 90°-sector magnetic mass spectrometer that analyzes the hydrogen isotope mixtures. It is equipped with a short-focal-length electron bombardment ion source and is designed to have very little mass discrimination. We made several mixtures of the hydrogen isotopes, allowed them to equilibrate by β-radiation or by passing them over a platinum catalyst, and then measured the relative percentages using both the quadrupole mass filter and the sector instrument. A comparison of the results from these two methods constitutes a check on the effectiveness of the calibration procedure.

The analysis of these mixtures is complicated by two factors. First, the mass four peak in tritium mixtures contains both D_2 and HT that must separate using previously measured equilibrium constants. Second, Mehrhoff and Humphries[12] used a propagation-of-errors analysis and found that, for the most accurate measurements of D_2-DT-T_2 mixtures, two different schemes should be used to correct the mass four peak. For T-rich mixtures, K_3 should be used to correct the data; for D rich mixtures, K_6 is necessary. The details of these mixture calculations are given in Appendix A.

Table 5 compares the composition of H_2-HD-D_2 mixtures as measured with both the quadrupole and sector instruments. The mixtures were equilibrated by passing them over platinum sponges at ambient temperatures. The percentage difference between them is calculated by the following relationship: % difference = [(% quad-% sector)/% sector]100. The differences vary from less than 1 to more than 6%. If we treat percentage difference values as standard deviations, we estimate our accuracy as ±4%. The quadrupole mass filter gives a higher value of the equilibrium constant than does the sector instrument, which agrees with the established value of K_1 = 3.26. Note that there still appears to be some residual mass discrimination because the percentage difference for the lowest mass H_2 is always negative, while the highest mass positive D_2 with the value for HD is nearly always intermediate (see Fig. 5).

The same general trend is found in the composition of the D_2-DT-T_2 mixtures shown in Table 6. The percentage differences tend to be smaller (usually less than 4%) but there is a trend to greater negative values of the percentage difference with increasing mass. Note that boxes have been placed in Fig. 6 to indicate the best set of data from the Mehrhoff-Humphries criterion[12] discussed earlier. Our data appear to be consistent with their results.

Most of the D_2-DT-T_2 samples were equilibrated by β-particle catalysis but some were also passed through the catalyst tube. We saw no difference in the results. Note that there are large differences between the quadrupole and sector results for the impurity species H_2, HD, and HT. We feel that these differences are real; also, we do not expect to accurately measure the impurity species. Note that the value of the equilibrium constant as measured with the quadrupole and the K_6 correction tends to be lower than the sector value that agrees better with

Table 5. Composition of H_2-HD-D_2 mixtures at 25.4 ± 0.4°C, using the relative sensitivities from Table 3. Errors are 1σ.

Mixture	Isotopic molecule	Mole percentage Quadrupole	 Sector	Difference
	H_2	7.10 ± 0.05	7.57 ± 0.14	−6.2%
4 runs	HD	37.01 ± 0.03	36.92 ± 0.37	+0.2%
26.0% D	D_2	55.89 ± 0.03	55.49 ± 0.55	+0.7%
74.0%				
	K_1	3.45 ± 0.03	3.24 ± 0.03	+6.3%
	H_2	26.25 ± 0.06	27.64 ± 0.28	−5.0%
4 runs	HD	47.78 ± 0.09	47.62 ± 0.48	+0.3%
51.5% H	D_2	25.96 ± 0.12	24.72 ± 0.25	+5.0%
48.5%				
	K_1	3.35 ± 0.02	3.32 ± 0.03	+0.9%
	H_2	55.29 ± 0.02	56.78 ± 0.57	−2.6%
4 runs	HD	37.47 ± 0.03	36.12 ± 0.36	+3.7%
74.8% H	D_2	7.24 ± 0.05	7.09 ± 0.14	+2.1%
25.2% D				
	K_1	3.51 ± 0.02	3.24 ± 0.03	+8.3%

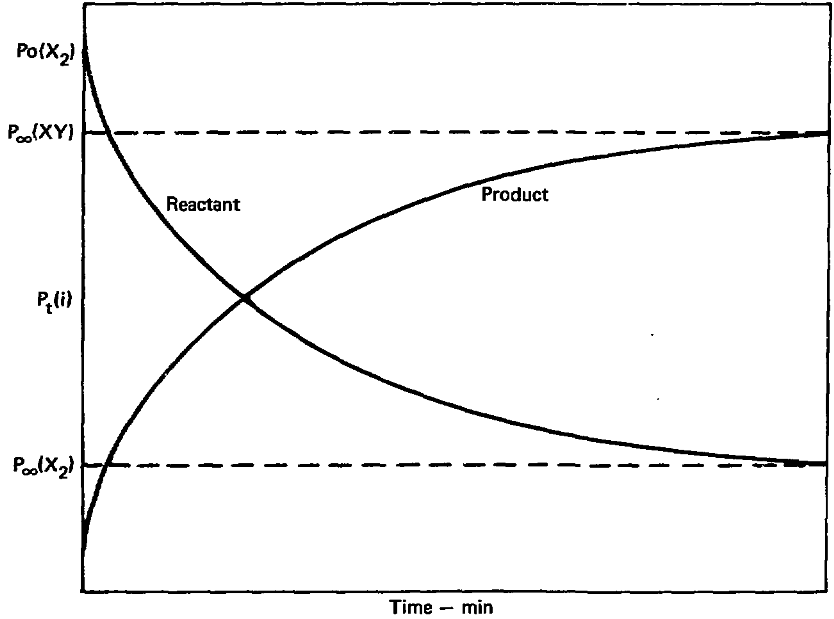

Fig. 5. Plots of $P_t(x_2)$ [x_2 = H_2, D_2, or T_2] for reactants and $P_t(xy)$ for products [xy = HD, HT, or DT] vs time. The symbol ∞ denotes the time at equilibrium.

Table 6. Composition of D_2-DT-T_2 mixtures at 25.4 ± 0.4° C, using the relative sensitivities from Table 3. Errors are 1σ.

Mixture	Isotopic molecule	Quadrupole, K_3 correction	Percentage difference	Quadrupole, K_6 correction	Percentage difference	Sector
	H_2	0.19 ± 0.01		0.19 ± 0.01		
5 runs	HD	0.77 ± 0.06		0.77 ± 0.06		0.18 ± 0.01
0.2% H	HT	1.61 ± 0.12		2.34 ± 0.19		0.63 ± 0.03
21.8% D	D_2	4.99 ± 0.02	+0.6%	4.26 ± 0.16	-14.1%	4.96 ± 0.05
78.0%	DT	33.51 ± 0.05	-1.3%	33.51 ± 0.05	-1.3%	33.94 ± 0.34
	T_2	58.93 ± 0.15	-2.2%	58.93 ± 0.15	-2.2%	60.25 ± 0.60
	K_3	3.82		4.48 ± 0.16	+16.1%	3.86 ± 0.04
3 runs	H_2	0.21 ± 0.02		0.21 ± 0.01		
0.3% H	HD	1.07 ± 0.02		1.07 ± 0.02		0.32 ± 0.02
48.6% D	HT	1.31 ± 0.05		0.97 ± 0.02		0.32 ± 0.02
50.6%	D_2	24.18 ± 0.03	-0.1%	24.52 ± 0.04	+1.3%	24.21 ± 0.24
	DT	48.14 ± 0.02	-1.7%	48.14 ± 0.02	-1.7%	48.95 ± 0.49
	T_2	25.09 ± 0.02	-4.2%	25.09 ± 0.02	-4.2%	26.19 ± 0.26
	K_3	3.82		3.77 ± 0.01	-0.3%	3.78 ± 0.04
6 runs	H_2	0.22 ± 0.01		0.22 ± 0.01		
0.3% H	HD	1.09 ± 0.02		1.09 ± 0.02		0.35 ± 0.02
52.6% D	HT	1.47 ± 0.07		0.88 ± 0.02		0.32 ± 0.02
47.9% T	D_2	26.99 ± 0.06	-2.1%	27.58 ± 0.03	+0.1%	27.56 ± 0.28
	DT	47.95 ± 0.03	-2.0%	47.95 ± 0.03	-2.0%	48.95 ± 0.49
	T_2	22.29 ± 0.02	-2.3%	22.29 ± 0.02	-2.3%	22.82 ± 0.23
	K_3	3.82		3.74 ± 0.01	-1.8%	3.81 ± 0.04
	H_2	0.26 ± 0.01		0.26 ± 0.01		
5 runs	HD	1.30 ± 0.03		1.30 ± 0.03		0.47 ± 0.02
0.3% H	HT	2.18 ± 0.29		0.45 ± 0.01		0.14 ± 0.01
72.1% D	D_2	50.47 ± 0.37	-3.4%	52.20 ± 0.11	0.0%	52.22 ± 0.52
27.5% T	DT	38.22 ± 0.07	-3.0%	38.22 ± 0.07	-3.0%	39.42 ± 0.39
	T_2	7.57 ± 0.07	-2.3%	7.57 ± 0.07	-2.3%	7.75 ± 0.14
	K_3	3.82		3.69 ± 0.02	-2.3%	3.84 ± 0.04

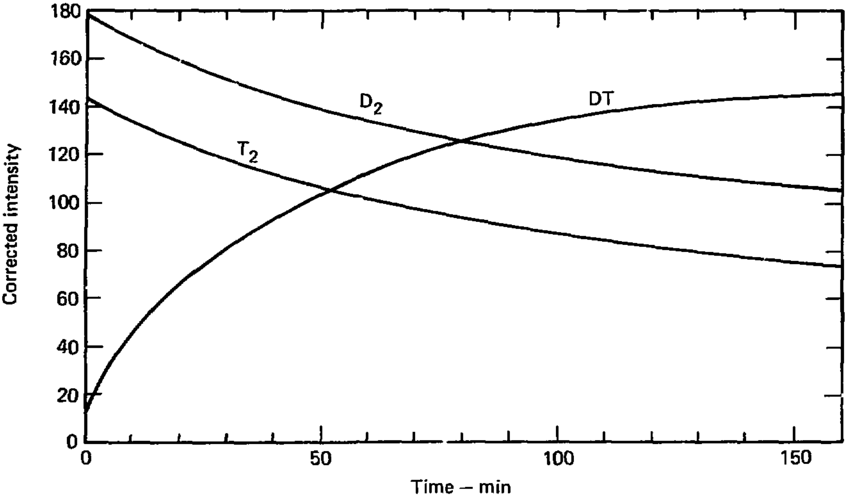

Fig. 6. Plot of corrected intensity vs time for 1% H, 55% D, 44% T mixture.

the established value of $K_3 = 3.82$. The quadrupole results that use the K_3 correction are, of course, not independent of K_3.

Because we found that the sensitivities varied from day to day, we wondered if we could improve our accuracy by running mixture analyses and calibration experiments on the same day. Accordingly, in conjunction with our kinetic runs, we analyzed six more mixtures. The three D_2-DT-T_2 results are shown in Table 7, and the H_2-HT-T_2 results are shown in Table 8. The errors in the D_2-DT-T_2 mixtures appear to have magnitudes comparable to those in Table 6. The mass discrimination trend is opposite, however, as the percentage difference increases to larger positive values with mass. The mass discrimination trends in the H_2-HT-T_2 results go both directions and in some cases the percentage difference values are as high as 19%. The established value of K_2 is 2.58. The sector values are somewhat higher and in two cases the quadrupole values are considerably higher. Again, if we treat the percentage differences as standard deviations, we estimate an accuracy for the quadrupole mixture measurements for H_2-HT-T_2 mixtures as ±9%, and ±2.2% for D_2-DT-T_2 mixtures.

Table 7. Composition of D_2-DT-T_2 mixtures at 25.4 ± 0.4°C. Sensitivity measured the same day of the mixture analysis.

Mixture	Isotopic molecule	Quadrupole, K_3 correction	Percentage difference	Quadrupole, K_6 correction	Percentage difference	Sector
	H_2	0.19		0.19		
3% H	HD	0.89		0.89		1.21
28% D	HT	2.41		2.04		4.10
70% T	D_2	7.64	0.0%	8.00	+4.7%	7.64
	DT	38.38	+2.9%	38.38	+2.9%	37.71
	T_2	50.49	+2.4%	50.49	+2.4%	49.31
	K_3	3.82	+1.3%	3.65	-3.2%	3.77
	H_2	0.18		0.18		0.95
	HD	1.35		1.35		0.04
1% H	HT	0.88		0.99		0.82
55% D	D_2	29.51	-2.5%	29.40	-2.9%	30.27
44% T	DT	47.80	-0.1%	47.80	-0.1%	47.84
	T_2	20.27	+1.1%	20.27	+1.1%	20.05
	K_3	3.82	+1.3%	3.83	+1.6	3.77
	H_2	0.19		0.19		
1% H	HD	1.59		1.59		1.29
73% D	HT	2.07		0.55		0.46
26% T	D_2	50.17	-5.5%	51.69	-2.6%	53.09
	DT	38.32	+2.3%	38.32	+2.3%	37.94
	T_2	7.66	+6.5%	7.66	+6.5%	7.19
	K_3	3.82		3.71		3.77

Table 8. Composition of H_2-HT-T_2 mixtures at 25.4 ± 0.4° C. Sensitivity measured the same day as the mixture analysis.

	Isotopic molecule	Quadrupole	Sector	Percentage difference
	H_2	7.76	8.95	-13.3
27% H	HD	1.30	1.00	
2% D	HT	35.72	35.31	+1.2
71% T	D_2	0.04	0.03	
	DT	2.93	2.62	
	T_2	52.24	52.02	+0.4
	K_2	3.15	2.68	+17.5
	H_2	34.01	32.28	+5.4
55% H	HD	1.79	1.40	
1% D	HT	45.26	43.18	+4.8
44% T	D_2	0.02	0.01	
	DT	1.22	1.13	
	T_2	17.71	21.92	-19.2
	K_2	3.40	2.64	+28.8
	H_2	53.55	53.03	+1.0
72% H	HD	1.54	0.93	
1% D	HT	35.64	36.50	-2.4
28% T	D_2	0.01		
	DT	0.70	0.34	
	T_2	8.57	9.17	-6.5
	K_2	2.77	2.74	+1.1

ERROR ANALYSIS AND CONCLUSIONS

It is well-known that quadrupole mass filters show mass discrimination, especially when using an electron multiplier as a detector. However, in spite of this problem, we wanted to use the filter because its small size would enable us to observe the cold gaseous hydrogen species as they come out of the cryostatic cell. It should be emphasized that the vacuum system and cell were made for cryogenic measurements; if our primary interests were room temperature measurements, we would have designed a different gas inlet system to minimize possible fractionation effects. The errors in the D_2-DT-T_2 system are smaller than those found in the other systems, because the mass differences between isotopic species are smaller. Therefore, we feel that the quadrupole-mass-filter system is accurate enough to at least study the D_2-DT-T_2 kinetics at low temperatures.

Gas impurities may be one source of error. Jones[3] has pointed out that the hydrogen isotopic gases must be purified by passing them through a hot Pd thimble. If not, one obtains a steady state in the H_2-HT-T_2 system with a value of the steady-state coefficient Q (which has the form of the equilibrium constant) that is always larger than the thermodynamic equilibrium constant. We did not use a hot Pd thimble to purify our gases, which may explain our erroneous equilibrium-constant values. Note that even the values of K_2 for the sector instrument were high in the H_2-HT-T_2 system.

KINETICS

Now that we have calibrated the quadrupole mass filter system for mixture measurements, we would like to use this system to make some crude, room-temperature kinetic measurements, especially in the D_2-T_2 system where no data exist. We will also look at the H_2-T_2 system for completeness.

In our literature search for the review report[5] we did not find any general treatment that would allow us to predict the time-to-equilibrium for these reactions. The treatment used for the H_2-T_2 data was apparently derived from the appearance of the kinetic curves. Kinetic curves for products and reactants have the general shapes shown in Fig. 5. By inspection, we derive the following expression for the product curve:

$$P_\infty(xy) - P_t(xy) = e^{-k_{xy}t} P_\infty(xy) . \qquad (14)$$

This equation can be rearranged to

$$Q = 1 - \frac{P_t(xy)}{P_\infty(xy)} = e^{-k_{xy}t} . \qquad (15)$$

If we plot

$$\ell n \left[1 - \frac{P_t(xy)}{P_\infty(xy)} \right] \text{ vs } t ,$$

the slope of the resulting straight line will yield k_{xy} which is a kind of a rate constant but different for each initial concentration of x and y. The inverse of k_{xy} is τ_{xy} that we define as the characteristic time of the reaction and which has the dimensions of time (in our case, minutes). The characteristic time is the time for the function

$$\ell n \left[1 - \frac{P_t(xy)}{P_\infty(xy)} \right]$$

to decrease by a factor of 1/e. Within 6-1/e time periods, the equilibration will be 99.8% complete. Therefore 6τ will be taken as the time for equilibration.

The expression that defines the kinetics of the reactants can be derived in a similar manner by inspection:

$$P_t(x_2) = \left[P_0(x_2) - P_\infty(x_2) \right] e^{-k_{x_2}t} + P_\infty(x_2) . \qquad (16)$$

This expression can be rearranged to

$$Q' = \frac{P_t(x_2) - P_\infty(x_2)}{P_0(x_2) - P_\infty(x_2)} = e^{-k_{x_2}t} . \qquad (17)$$

Again, if we plot

$$\ell n \frac{P_t(x_2) - P_\infty(x_2)}{P_0(x_2) - P_\infty(x_2)} \text{ vs } t,$$

the slope is k_{x_2} and $\tau_{x_2} = 1/k_{x_2}$. It can be shown that $\tau_{x_2} = \tau_{xy}$ (see Appendix B). Therefore, any and all of the reactant or product curves are a measure of the characteristic time.

The instantaneous rates of the products and reactants are related by the following equation:

$$-\frac{dP_t(x_2)}{dt} = -\frac{dP_t(y_2)}{dt} = \frac{1}{2} \left| \frac{dP_t(xy)}{dt} \right| , \qquad (18)$$

where x and y are isotopes of hydrogen, because of the stoichiometry of the reaction.

Kinetics of The β-Particle-Catalyzed Equilibrium $D_2 + T_2 = 2DT$

We performed three kinetic experiments using mixtures that were initially approximately 27% D_2, 55% D_2, and 73% D_2. The kinetic curves obtained for the 55% D_2 mixture are shown in Fig. 6 as an example, the slopes of these curves at four different times are given in Table 9. Note that in the 55 and 73% D_2 experiments, the slopes of the product (DT) curve do not maintain their 2/1 ratio to the slopes in the reactant curve; however, they do in the 27% D_2 experiment. Note also that the total pressure as measured by the quadrupole mass filter also decreases with time for the 55 and 73% D_2 experiments. These observations imply either a general sag in sensitivity or a reduction, somehow, of the total amount of DT; this undoubtedly explains some of the errors we observed in determining the characteristic times of these three mixtures.

Table 9. Slopes of the kinetic curves for $D_2 + T_2 = 2\ DT$ at various times; total pressures of the isotopic species at various times.

	Slope, min				Total pressure, min (torr)			
Specie	20	50	100	150	20	50	100	150
27% D_2								
D_2	−1.125	−0.485	−0.100	−0.025				
DT	2.225	0.835	0.200	0.085	114	114	114	114
T_2	−0.925	−0.425	−0.100	−0.015				
55% D_2								
D_2	−0.825	−0.500	−0.300	−0.175				
DT	+1.6750	+0.950	+0.360	+0.100	140	140	136	131
T_2	−0.815	−0.500	−0.275	−0.150				
73% D_2								
D_2	−0.875	−0.500	−0.325	−0.290				
DT	1.825	0.675	0.260	0.165	182	180	175	170
T_2	−1.000	−0.415	−0.250	−0.125				

The $\ell n\ Q$ or $\ell n\ Q'$ for each of the species in each mixture was plotted vs time (see Figs. 7 through 9). The $P_\infty(i)$ for each species was only estimated from the kinetic curve because it was not measured. In some cases we found that we obtained a better straight line if we adjusted the $P_\infty(i)$ by a small amount (a few percent). In those cases, we have given the k_i and τ_i values for the adjusted lines. Note that all of the species in every mixture fit the straight lines on the semilog plots to a good approximation. Note also that the slopes of the lines agree only for D_2 and T_2 in the 55% D_2 experiment. The slopes in Fig. 7 are in better overall agreement than in the other two experiments. Recall that the total pressure did not sag for this experiment and that the slopes of the kinetic curves maintained their proper relationship. Because we do not know how to choose the slope that best represents the rate of the reaction for a particular mixture, we will report an average slope of the three species. The values of k, τ, and the time to equilibrium for these DT mixtures are given in Table 10.

In our analysis[5] of the $H_2 + T_2 = 2HT$ data from Ref. 4, we showed that the k values, and therefore the τ values, were roughly directly proportional to the total pressure and the tritium pressure to the 1/2 power. These admittedly rough and limited DT data do not show this correlation.

Kinetics of The β-Particle-Catalyzed Equilibrium $H_2 + T_2 = 2HT$

We performed three kinetic experiments using mixtures of H_2-T_2 that were initially approximately 27% H_2, 55% H_2, and 75% H_2. Table 11 shows the slopes and total pressures at specified times as measured with the quadrupole mass filter. The slopes in these experiments show the approximate 2/1, product/reactant ratio; they appear to be more consistent than the slopes in the DT experiments. The total pressure in the 27% H experiment remains constant, but increases somewhat in the other two. This increase could be explained by an upward drift in sensitivity. Again we see that this system is subject to errors that are hard to control.

In all cases, the $\ell n\ Q$ or $\ell n\ Q'$ was plotted vs time. The results for each mixture are shown in Figs. 10 through 12. We estimated the $P_\infty(i)$ for each species by the same procedure used for the DT experiments. *Again, the $\ell n\ Q$ or $\ell n\ Q'$ can always be approximated* by a straight line. None of the slopes are the same for any of the species in a particular experiment.

In Table 12 we list the values of the equilibrium and initial pressure plus the values of k, τ, and the time to equilibrium for these HT mixtures. Note

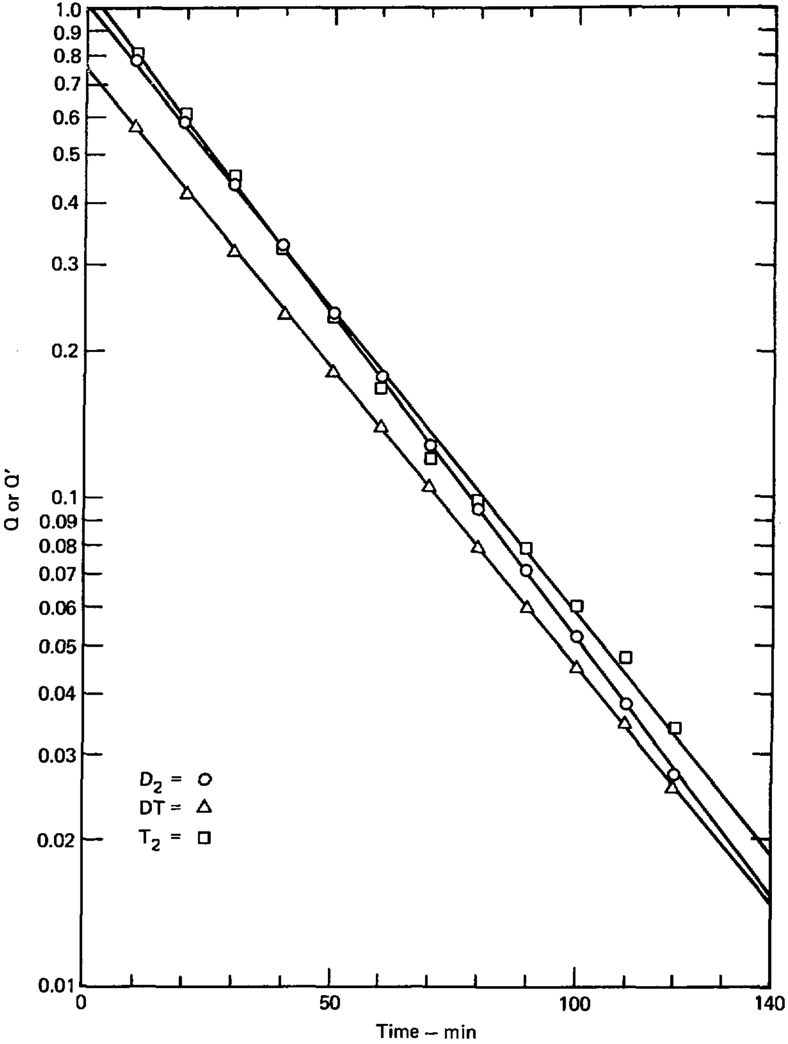

Fig. 7. Plot of *ℓn* Q or *ℓn* Q′ vs t for DT mixture No. 1 (27% D).

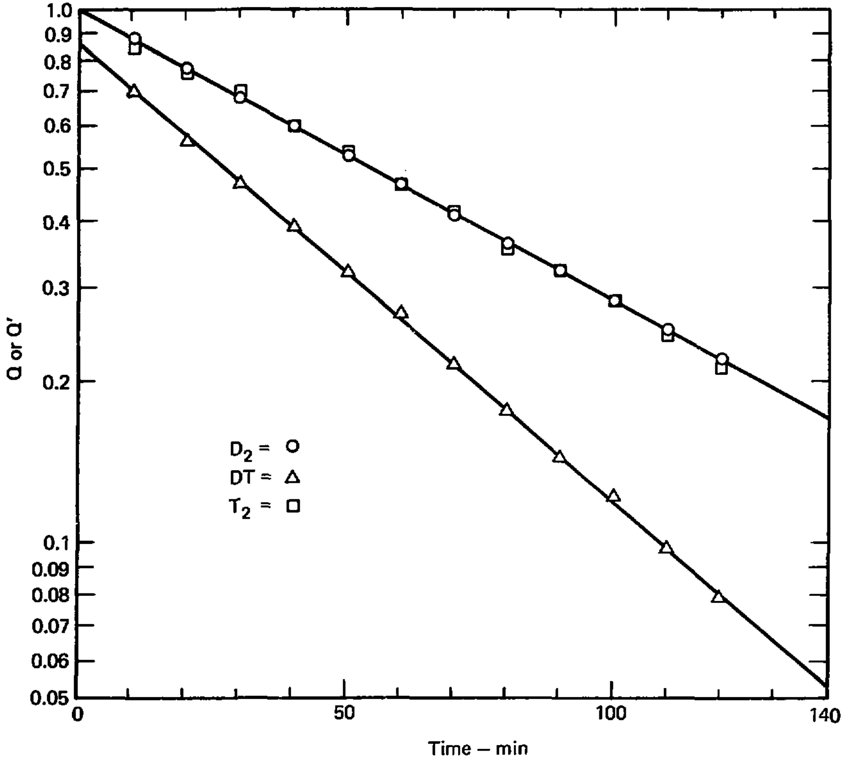

Fig. 8. Plot of $\ln Q$ or $\ln Q'$ vs t for DT mixture No. 2 (55% D).

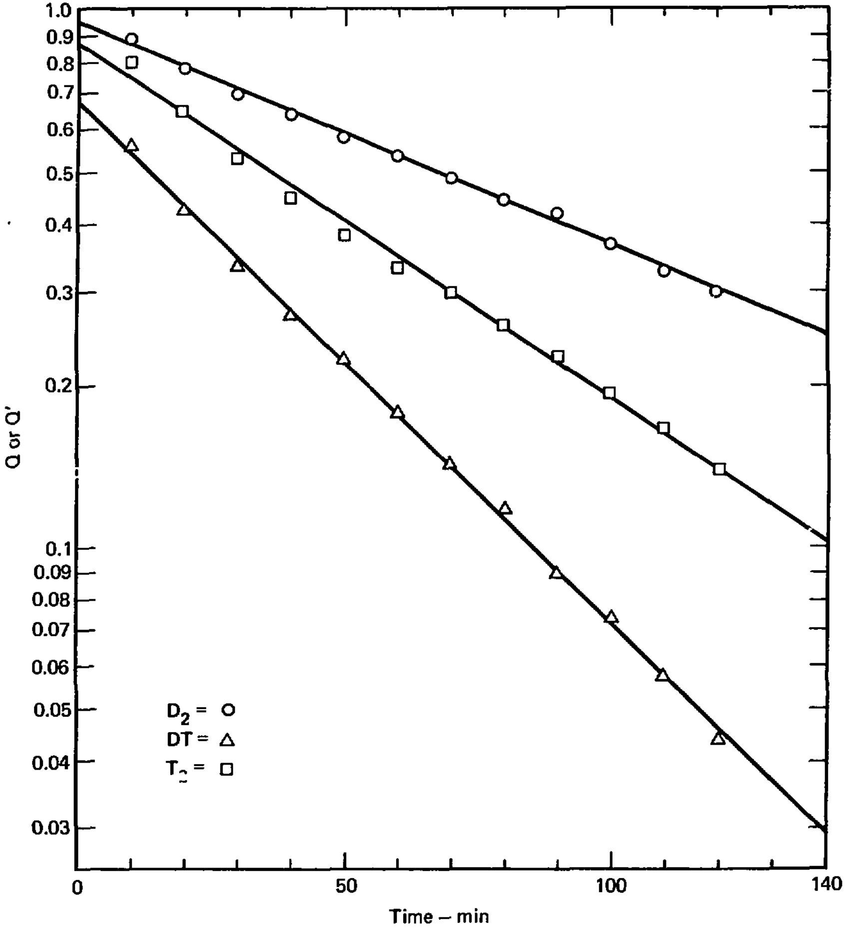

Fig. 9. Plot of *ℓn* Q or *ℓn* Q′ vs t for DT mixture No. 3 (73% D).

Table 10. Results of the kinetic analysis, $D_2 + T_2 = 2\ DT$ at 25.4 ± 0.4°C.

DT mixture number	Isotopic composition	Pressures, Torr					k_i, min^{-1}	k_i(ave), min^{-1}	τ(ave), min	Time to equilibrium, h
		$P_0(D_2)$	$P_\infty(D_2)$	$P_0(T_2)$	$P_\infty(T_2)$	$P_\infty(DT)$				
1	2.7% H						0.0304 (D_2)			
	27.1% D	28.4	11.8	72.8	59.5	43.5	0.0280 (DT)	0.0290	34.5	3.45
	70.2% T						0.0286 (T_2)	±0.0012		
2	0.9% H						0.0125 (D_2)			
	54.7% D	71.2	38.0	57.6	26.0	61.0	0.0197 (DT)	0.0149	67.1	6.72
	44.4% T						0.0125 (T_2)	±0.0042		
3	0.9% H						0.00965 (D_2)			
	72.7% D	125.0	88.0	41.2	12.0	60.0	0.0226 (DT)	0.0159	63.1	6.30
	26.4% T						0.0153 (T_2)	±0.0065		

Table 11. Characteristics of the kinetic curves $H_2 + T_2 = 2\ HT$ at 25.4 ± 0.4°C.

% H		Slope, min				Total pressure (P_T), min (Torr)			
	Specie	25	50	100	150	25	50	100	150
27									
	H_2	−0.240	−0.180	−0.075	−0.040				
	HT	+0.640	+0.370	+0.185	+0.100	188.6	189.4	189.1	189.4
	T_2	−0.190	−0.185	−0.085	−0.060				
55									
	H_2	−0.520	−0.270	−0.225	−0.125				
	HT	+0.900	+0.625	+0.450	+0.295	321.8	324.4	325.8	328.4
	T_2	−0.350	−0.275	−0.215	−0.130				
75									
	H_2	−0.320	−0.200	−0.160	−0.105				
	HT	0.800	0.650	0.465	0.285	357.4	361.7	373.2	374.5
	T_2	−0.425	−0.285	−0.170	−0.160				

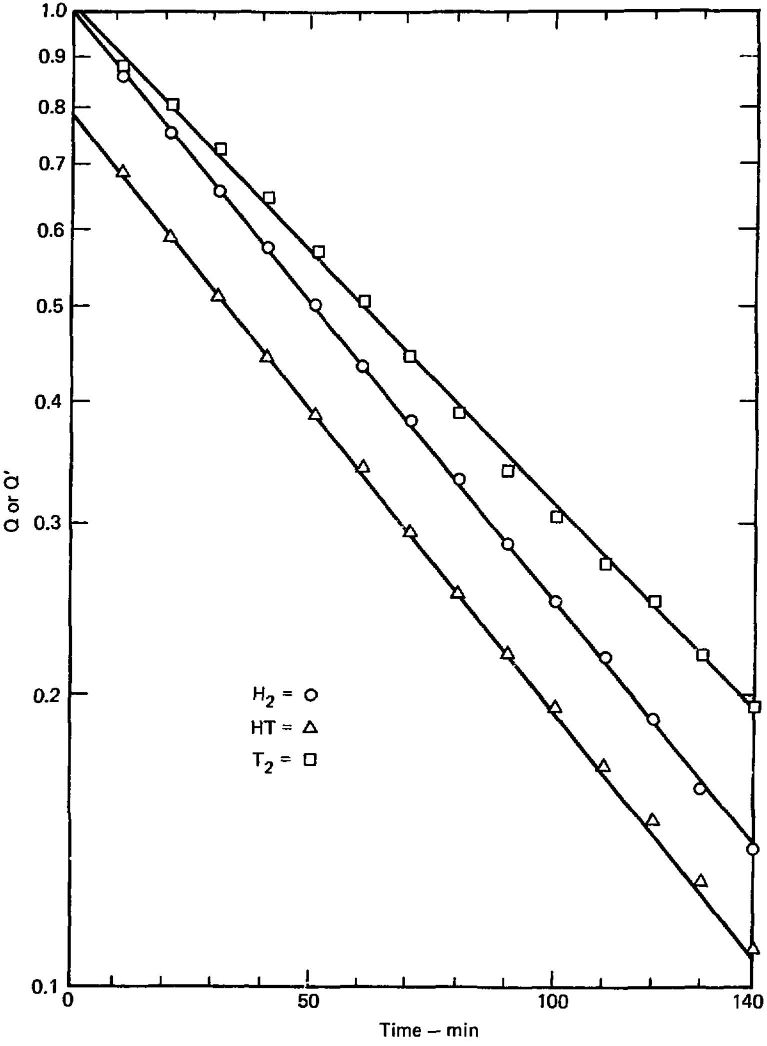

Fig. 10. Plot of ℓn Q or ℓn Q′ vs t for HT mixture No. 1 (27% H).

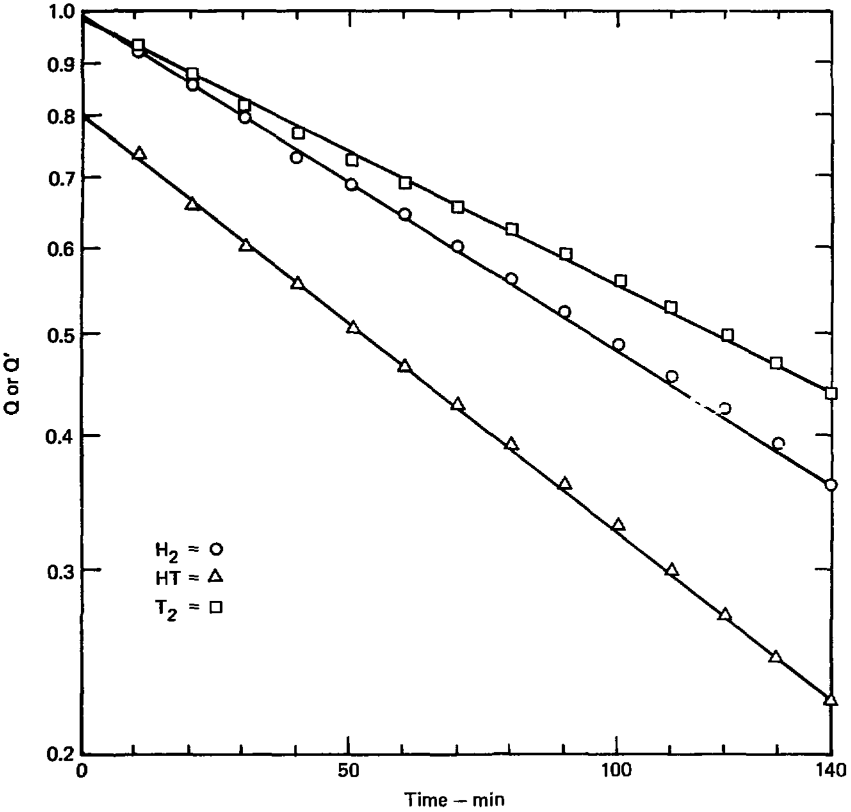

Fig. 11. Plot of *ℓn* Q or *ℓn* Q' vs t HT mixture No. 2 (55% H).

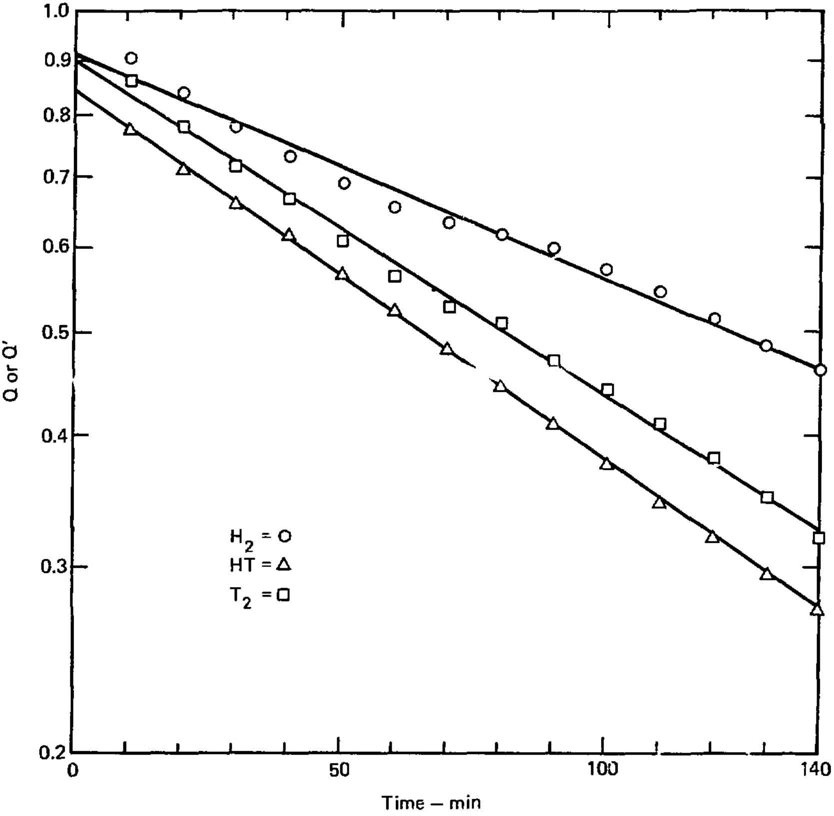

Fig. 12. Plot of *ln* Q or *ln* Q' vs t HT mixture No. 3 (71% H).

Table 12. Results of the kinetic analysis $H_2 + T_2 = 2\ HT$ at 25.4 ± 0.4°C.

HT mixture number	Isotopic composition	Pressures, Torr $P_0(H_2)$	$P_\infty(H_2)$	$P_0(T_2)$	$P_\infty(T_2)$	$P_\infty(HT)$	k_i, min^{-1}	k_i(ave), min^{-1}	τ(ave), min	Time to equilibrium, h
1	27% H						0.0143 (H_2)			
	2% D	21.2	8.0	65.0	52.5	33.5	0.0141 (HT)	0.0133	75.2	7.5
	71% T						0.0118 (T_2)	±0.0013		
2	55% H						0.0072 (H_2)			
	1% D	63.2	39.5	51.4	25.5	60.0	0.0090 (HT)	0.0073	137	13.7
	44% T						0.0057 (T_2)	±0.0017		
3	72% H						0.0049 (H_2)			
	1% D	99.3	77.0	36.1	12.0	59.0	0.0081 (HT)	0.0068	147	14.7
	28% T						0.0073 (T_2)	±0.0017		

that the characteristic times for the HT *reactions* are about twice as long as they were in the DT reactions. This isotope effect is shown in Table 13 where the ratio k_{DT}/k_{HT} is determined for mixtures of nearly identical T composition. The fact that this ratio is approximately two enables us to estimate the DT rates from the measured HT rates in the literature.[4,5]

Table 13. Comparison of k_{DT}/k_{HT} values.

Composition	k_{DT}/k_{HT}
27% H – 71% T 27% D – 70% T	2.2
55% H – 44% T 55% D – 44% T	2.0
72% H – 28% T 73% D – 26% T	2.3

CONCLUSIONS

The quadrupole-mass filter system we built can measure equilibrium constants and the rates of the β-catalyzed hydrogen self-exchange reactions at cryogenic temperatures in the D_2-T_2 system. We used preliminary experiments to characterize the kinetics of reactions (2) and (3): the time to reach equilibrium for reaction (2) was 7 to 14 h and for reaction (3) was 3 to 7 h. The isotope effect at approximately 2 can predict the rates of reaction (3) from the reaction (2) data in the literature.

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APPENDIX A
MIXTURE CALCULATIONS

The analysis is complicated by the fact that we have both D_2 and HT appearing at mass position 4 (see Table 1). Let

$$I_2 = I_{H_2}, I_3 = I_{HD}, \quad I_4 = I_{D_2} + I_{HT}, I_5 = I_{DT}, \text{and } I_6 = I_{T_2},$$

where I_i is the intensity at the various mass positions. The percentage composition of H_2, HD, DT, and T_2 is straightforward. For example,

$$\% \ H_2 = \frac{P_{H_2}}{P_T} \times 100 = \frac{I_{H_2}/S_{H_2}}{P_T} \times 100 \ , \tag{A-1}$$

using our definition of sensitivity and noting that P_T is the total pressure. For percentages D_2 and HT, however, we must use the calculated values of two equilibrium constants to separate the contribution made by the two species.

At this point we digress and describe the relationship between the equilibrium constants and the sensitivities. Let us use K_1 for an example. If we assume there is no tritium in the system and therefore $I_4 = I_{D_2}$, K_1 is given by

$$K_1 = \frac{P^2_{HD}}{P_{H_2} \cdot P_{D_2}} = \frac{I^2_{HD}}{I_{H_2} \cdot I_{D_2}} \cdot \frac{S_{H_2} \cdot S_{D_2}}{S^2_{HD}} \ . \tag{A-2}$$

Because the sensitivity as a function of mass is an exponential, the ratio of the sensitivities in all the equilibrium constants is unity, and therefore

$$K_1 = \frac{I^2_{HD}}{I_{H_2} \cdot I_{D_2}} \ . \tag{A-3}$$

All of the equilibrium constants $K_1 - K_6$ can therefore be expressed in terms of the appropriate intensities.

The analysis of mixtures of H_2, HD, and D_2 is easy because we can assume there is very little T_2 present; therefore, $I_4 = I_{D_2}$. The analysis of H_2-HT-T_2 mixtures is more complicated because we need to use K_3 to calculate the amount of D_2 impurity present. Therefore,

$$\% \ HT = \frac{P_{HT}}{P_T} \times 100 = \frac{I_{HT}/S_{HT}}{P_T} \times 100 = \frac{I_{HT}}{S_{HT}P_T} \times 100 = \frac{I_4 - \dfrac{I^2_{DT}}{K_3 I_{T_2}}}{S_{HT}P_T} \times 100$$

$$\% \ HT = \frac{I_4 I_{T_2} K_3 - I^2_{DT}}{K_3 S_{HT} I_{T_2} P_T} \times 100 \ . \tag{A-4}$$

Again, if there is no D_2 present as an impurity, I_{DT} will equal zero and the computation is simplified.

The analysis of D_2-DT-T_2 mixtures is even more complex. First, there is always some H present in the mixture as an impurity and thus there will always be some HT. Second, as previously stated, Mehrhoff and Humphries [12] used a propagation of errors analysis to show that, for highest accuracy, K_3 should be used to calculate the D_2 composition where the percentage of tritium is high and K_6 should be used to calculate the HT impurity where the tritium percentage is low. Therefore, when the tritium percentage is high,

$$\% \, D_2 = \frac{P_{D_2}}{P_T} \times 100 = \frac{I_{D_2}/S_{D_2}}{P_T} \times 100 \, \frac{\dfrac{I_{DT}^2}{K_3 I_{T_2}}}{S_{D_2} P_T} \times 100 \, ,$$

$$\% \, D_2 = \frac{I_{DT}^2}{K_3 I_{T_2} S_{D_2} P_T} \times 100. \qquad (A\text{-}5)$$

It is apparent that we cannot measure an independent value of K_3 where the percentage of tritium is high because the P_{D_2} for calculating K_3 must itself be calculated using a previously determined value of K_3.

$$\% \, HT = \frac{P_{HT}}{P_T} \times 100 = \frac{I_{HT}/S_{HT}}{P_T} \times 100 = \frac{I_{HT}}{S_{HT} P_T} \times 100 = \frac{I_4 - I_{D_2}}{S_{HT} P_T} \times 100 = \frac{I_4 - \dfrac{I_{DT}^2}{K_3 I_{T_2}}}{S_{HT} P_T} \times 100 \, ,$$

$$\% \, H = \frac{I_4 K_3 I_{T_2} - I_{DT}^2}{K_3 I_{T_2} S_{HT} P_T} \times 100 \, . \qquad (A\text{-}6)$$

At low percentage T_2

$$\% \, D_2 = \frac{P_{D_2}}{P_T} \times 100 = \frac{I_{D_2}/S_{D_2}}{P_T} \times 100 = \frac{I_{D_2}}{S_{D_2} P_T} \times 100 = \frac{I_4 - I_{HT}}{S_{D_2} P_T} \times 100 = \frac{I_4 - \dfrac{K_6 I_{T_2} I_{HD}}{I_{DT}}}{S_{D_2} P_T} \times 100 \, ,$$

$$\% \, D_2 = \frac{I_4 I_{DT} - K_6 I_{T_2} I_{HD}}{I_{DT} S_{D_2} P_T} \times 100 \, , \qquad (A\text{-}7)$$

and

$$\% \text{ HT} = \frac{P_{HT}}{P_T} \times 100 = \frac{I_{HT}/S_{HT}}{P_T} \times 100 = \frac{I_{HT}}{S_{HT}P_T} \times 100 = \frac{\dfrac{K_6 I_{T_2} I_{HD}}{I_{DT}}}{S_{HT}P_T} \times 100 \ ,$$

$$\% \text{ HT} = \frac{K_6 I_{T_2} I_{HD}}{I_{DT} S_{HT} P_T} \times 100. \qquad \text{(A-8)}$$

When the tritium percentage is low, it is possible to determine a value of K_3 independent of K_3. It still depends, however, on a previously determined value of K_6.

APPENDIX B
PROOF THAT THE CHARACTERISTIC TIME FOR EACH SPECIES IN A EQUILIBRIUM EXCHANGE REACTION IS THE SAME

Let x and y be any two hydrogen isotopes. From Eq. (16), we can write the time derivative of $P_t(x_2)$ as

$$\frac{dP_t(x_2)}{dt} = -k_{x_2}\ [P_0(x_2) - P_\infty(x_2)]\ e^{-k_{x_2}t} \ . \tag{B-1}$$

At t = 0, the time derivative becomes

$$\frac{dP_0(x_2)}{dt} = -k_{x_2}\ [P_0(x_2) - P_\infty(x_2)] \ . \tag{B-2}$$

The equation for the time derivation of $P_t(y_2)$ is similar:

$$\frac{dP_0(y_2)}{dt} = -k_{y_2}\ [P_0(y_2) - P_\infty(y_2)] \ . \tag{B-3}$$

The time derivative for the mixed specie xy comes from differentiating Eq. (14):

$$\frac{-dP_t(xy)}{dt} = -k_{xy}\ e^{-k_{xy}t}\ P_\infty(xy) \ . \tag{B-4}$$

At zero time,

$$\frac{dP_0(xy)}{dt} = k_{xy}\ P_\infty(xy) \ . \tag{B-5}$$

We know from Eq. (18) that

$$\frac{dP_t(xy)}{dt} = -2\ \frac{dP_t(x_2)}{dt} = -2\ \frac{dP_t(y_2)}{dt} \ . \tag{B-6}$$

Therefore, at t = 0

$$k_{xy}\, P_\infty(xy) = -2\, k_{x_2}\, [P_0(x_2) - P_\infty(x_2)]$$

$$= -2\, k_{y_2}\, [P_0(y_2) - P_\infty(y_2)]. \tag{B-7}$$

If we rearrange the values, we have three equations, remembering that $r_2 = 1/k_i$:

$$\frac{k_{xy}}{k_{x_2}} = - \frac{2[P_0(x_2) - P_\infty(x_2)]}{P_\infty(xy)} = \frac{\tau_{x_2}}{\tau_{xy}} \, , \tag{B-8}$$

$$\frac{k_{xy}}{k_{y_2}} = - \frac{2[P_0(y_2) - P_\infty(y_2)]}{P_\infty(xy)} = \frac{\tau_{y_2}}{\tau_{xy}} \, , \tag{B-9}$$

$$\frac{k_{x_2}}{k_{y_2}} = \frac{P_0(y_2) - P_\infty(y_2)}{P_0(x_2) - P_\infty(x_2)} = \frac{\tau_{y_2}}{\tau_{x_2}} \; . \tag{B-10}$$

From the stoichiometry of Eq. (1), (2), and (3),

$-2[P_o(x_2) - P_\infty(x_2)] = -2[P_o(y_2) - P_\infty(y_2)] = P_\infty(xy)$.

Therefore, the ratios in Eq. B-8 through B-10 reduce to unity and $t_{x_2} = \tau_{y_2} = \tau_{xy}$.