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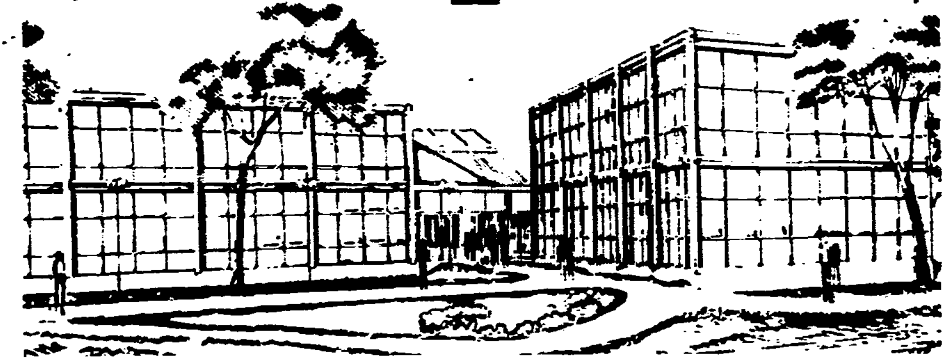

KINETICS OF β-PARTICLE-INDUCED EXCHANGE BETWEEN H_2, D_2, AND T_2 at 298 K

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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 298 K, we could not completely remove the mass discrimination inherent in our method. We estimate the accuracy of our room-temperature 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 at 298 K. The equivalent time interval in the exchange $D_2 + T_2 = 2DT$ is 3.5 to 7 h at the same temperature. This measured isotope effect of the factor two can be used to predict the rates of DT exchange from 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 (D-T) because the $D + T = \alpha + n$ reaction has the largest fusion cross section and ignites at the lowest temperature. Inertial-confinement fusion will require solid, hollow-sphere targets of this mixture. Magnetic-confinement fusion may also require the injection of solid D-T pellets in the fueling process. The cleanup of the spent D-T fusion fuel using isotope-separation processes is a common problem to both fusion efforts. The solution of these fueling and cleanup problems will require the compilation and measurement of many physical and chemical properties of the hydrogen isotopes. Therefore, we have begun an extensive program to characterize the physical and chemical properties of D-T mixtures, especially, but not exclusively, at cryogenic temperatures. Our program consists of: literature reviews, 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 few data on species containing tritium.

The chemical equilibrium constant gives the equilibrium composition of isotopic mixtures at various temperatures; the kinetic rate constant specifies 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

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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 report the kinetics of β-particle catalyzed H_2-T_2 and D_2-T_2 reactions at room temperature. This work is important to the fusion program because most fuel cleanup systems for fusion reactors use room-temperature equilibration units in their isotope separation plants. Rapid room-temperature kinetics would simplify the choice of catalyst for these units and might make it possible for a less expensive catalyst to be used.

EXCHANGE REACTIONS

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

$$H_2 + D_2 = 2HD \ , \quad (1)$$

$$H_2 + T_2 = 2HT \ , \quad (2)$$

$$D_2 + T_2 = 2DT \ . \quad (3)$$

These reactions take place 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 (2) and (3). Three additional exchange reactions can be written that relate the pure isotopic species H_2, D_2, and T_2 to the mixed isotopic species HD, HT, and DT:

$$H_2 + DT = HD + HT, \quad (4)$$

$$D_2 + HT = HD + DT, \quad (5)$$

$$T_2 + HD = HT + DT. \quad (6)$$

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

$$K_1 = P_{HD}^2/P_{H_2}P_{D_2} \ , \quad (7)$$

$$K_2 = P_{HT}^2/P_{H_2}P_{T_2} \ , \quad (8)$$

$$K_3 = P_{DT}^2/P_{D_2}P_{T_2} \ , \quad (9)$$

$$K_4 = P_{HD}\ P_{HT}/P_{H_2}\ P_{DT} \ , \quad (10)$$

$$K_5 = P_{HD}\ P_{DT}/P_{D_2}\ P_{HT} \quad (11)$$

$$K_6 = P_{HT}\ P_{DT}/P_{T_2}\ P_{HD} \ . \quad (12)$$

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 through K_6.(1) All of the calculations agree with those of Jones,(2) who found that $K_1 = 3.26$, $K_2 = 2.58$, $K_3 = 3.82$, $K_4 = 1.48$, $K_5 = 2.20$, and $K_6 = 1.74$ at 300 K.

The kinetics of the β-induced exchange between H_2 and T_2 have been studied by Dorfman and Mattraw,(3,4) Jones,(4,5) and by Schott and Beau.(6) 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

Studying hydrogen isotopes by mass spectrometry is complicated by several factors. If we use a conventional electron bombardment source with 70-eV electrons, the fragment ions H^+, D^+, and T^+ interfere with some of the parent ions. Tritium decay produces ^3He, which appears at m/e = 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 in the source we use electrons with energies lower than the appearance potentials of ^3He and the fragment ions (for $^3He^+$ the appearance potential is about 25 V; for H^+, about 18 V); As shown in Table 1, we still have the problem at m/e = 4 of the two interfering ions D^+ and HT_2^+. The mass difference between these isotopic ions is

TABLE 1. Ions Appearing in a Conventional Mass Spectrum of an H-D-T Mixture

	Ions	
m/e	70-eV source electrons	18-eV source 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^+

four thousandths of a mass unit, requiring a resolution of 920 for separation. Because the maximum resolution of our quadrupole mass filter is only 600, we cannot separate D_2^+ and HT^+. Therefore, the rate 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 m/e = 4 peak.(7)

MEASUREMENTS

Apparatus and Procedure

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

The gas inlet and mixing system we used is shown schematically in Fig. 1 along with diagrams of the prototype cell and the quadrupole mass filter. While the measurements we report here were made at room temperature, we plan to use an identical cell for measurements at cryogenic temperatures. The diameter of the pinhole leak from the cell is 2.5 µm. The cell is connected to an expansion volume that maintains the pressure in the cell at a nearly constant value. (The pressure fluctuation was 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 room-temperature measurements because cell and connecting-tube volumes are small and could cause fractionation.

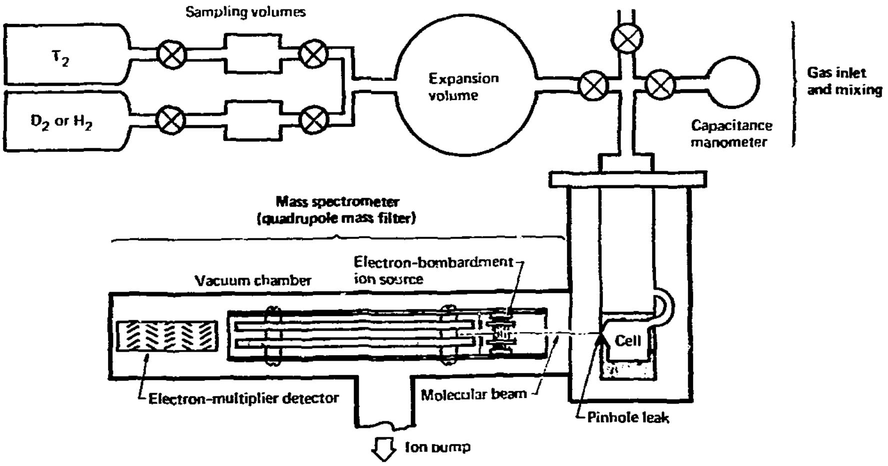

FIGURE 1. Gas mixing system, prototype cell, and quadrupole mass filter. The cell is designed for cryogenic use but was used for room-temperature measurements in the work reported here.

TABLE 2. Purity of Gases

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

[a] Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

The pressure selected for the kinetic measurements was 160 Torr, 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 $^3He^+$, but still 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 more sensitivity than would result from an ionizing voltage of 18 V (appearance potential of H^+). We used an electron multiplier for our detector because the spectrometer was not sensitive enough with a Faraday-cup detector.

We began the kinetic experiments by first admitting the gas sample that was to have the lower partial pressure into the expansion volume. We then added the higher-pressure component, noted the time of mixing, and opened the valve to the cell so that the gases flowed into the quadrupole mass filter through the pinhole leak. Throughout the experiment, we followed and recorded the peak heights on a chart recorder. In general, the intensity of the peaks either increased or decreased smoothly with time, although there were a few anomalies. The peaks that belonged to a particular species were connected by a smooth curve and we measured the intensities from the curves at 10-min intervals. We converted these intensities to partial pressures by using sensitivities that were measured on the same day as the kinetic run. We did not attempt to follow the reactions to equilibrium. Instead, we estimated the pressures at equilibrium by extrapolating the kinetic curves.

Sensitivity Calibration

We calibrated this prototype mass spectrometer by using the gases listed in Table 2 to measure the spectrometer sensitivities, $S_i = I_i/P_i$, where I is the intensity of the peak resulting from species i, i being H_2^+, HD^+, D_2^+, or T_2^+. We also compared composition measurements of isotopic mixtures with those obtained using a magnetic sector mass spectrometer. The details of these experiments are given in Ref. 7. Our results showed that the quadrupole mass filter did not respond equally to all masses. We estimate the accuracy of our mixture analyses in the D_2-DT-T_2 system to be ±2.2% and in the H_2-HT-T_2 system to be ±9%. The latter is larger because of an apparent isotopic mass effect on sensitivity.

KINETICS

In our literature search,(4) we found no general treatment that would allow us to predict the time required for our mixtures to reach equilibrium. In Ref. 3, the kinetic analysis of 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. 2. By inspection, after intensities are converted to partial pressures, we derive the following expression for the product curve (xy represents the product — DT in this case):

$$P_\infty(xy) - P_t(xy) = e^{-k_{xy}t} . \qquad (13)$$

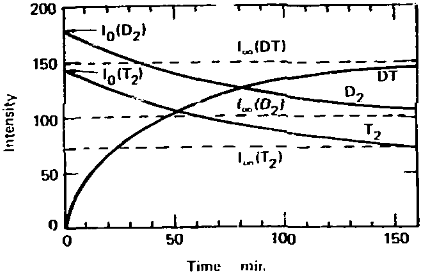

FIGURE 2. Plot of mass-spectrometer intensity vs time for mixtures that were originally 1% H, 55% D, and 44% T.

This equation can be rearranged to yield

$$Q \equiv 1 - \frac{P_t(xy)}{P_\infty(xy)} = e^{-k_{xy}t} . \qquad (14)$$

If we plot ln Q vs t, the slope of the resulting straight line will yield k_{xy}, which is kind of a rate constant but is different for each initial concentration of x_2 and y_2. The inverse of k_{xy} is τ_{xy}, which 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 ln Q to decrease by a factor of 1/e. If ln Q decreases by 1/e six times, the equilibration will be 99.8% complete. Therefore we take 6τ as the time for equilibration.

The expression that defines the kinetics of the reactants can be derived similarly by inspection (x_2 can represent H_2, D_2, or T_2):

$$P_t(x_2) = \left[P_0(x_2) - P_\infty(x_2)\right] \times \exp\left(-k_{x_2}t\right) + P_\infty(x_2) . \qquad (15)$$

This expression can be rearranged to yield

$$Q' \equiv \frac{P_t(x_2) - P_\infty(x_2)}{P_0(x_2) - P_\infty(x_2)} = \exp(-k_{x_2}t) . \qquad (16)$$

Also similarly, if we plot ln Q' vs t, the slope is k_{x_2}, and $\tau_{x_2} = 1/k_{x_2}$. It can be shown that $\tau_{x_2} = \tau_{xy} = \tau_{y_2}$.(7) Therefore, any of the reactant or product curves are a measure of the characteristic time and should all give the same value for it. Because of the stoichiometry of the reaction, products and reactants appearing or disappearing are related by the following equation:

$$-\frac{dP_t(x_2)}{dt} = -\frac{dP_t(y_2)}{dt} = \frac{1}{2}\frac{dP_t(xy)}{dt} . \qquad (17)$$

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

We performed three kinetic experiments using three mixtures that were initially approximately 27, 55, and 73% D_2. An example of the kinetic curves obtained at an initial concentration of 55% D is shown in Fig. 2. The slopes of all three sets of curves at four different times are given in Table 3. Note that in the 55 and 73% D_2 experiments, the slope of the product (DT) curves do not maintain their 2:1 ratio to the slopes of the reactant curves; however, they do in the 27% D_2 experiment. Note also that the total pressure as measured by the quadrupole mass filter 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 D-T. This undoubtedly explains some of the errors we observed in determining the characteristic times of these three mixtures.

We have plotted the ln Q or ln Q' against time for each of the species in each mixture (Figs. 3-5). The $P_\infty(i)$ for each species was not measured; instead, it was estimated from the kinetic curve. In some cases, we found that we obtained a better straight line fit if we adjusted the $P_\infty(i)$ by a small amount (a few percent). Note that the data for all of the species in each mixture fit straight lines on the semilog plots reasonably well. Note also that the slopes

TABLE 3. Slopes of the Kinetic Curves (such as in Fig. 2) for the Reaction $D_2 + T_2 = 2\ DT$ and Total Pressures of Each Isotopic Species at Various Times

		Slope, Torr/min				Total pressures, Torr			
		minutes after mixing				minutes after mixing			
Mixture	Species	20	50	100	150	20	50	100	150
27% D_2	D_2	-1.125	-0.485	-0.100	-0.025	114	114	114	114
	DT	+2.225	+0.835	+0.200	+0.085				
	T_2	-0.925	-0.425	-0.100	-0.015				
55% D_2	D_2	-0.825	-0.500	-0.300	-0.175	140	140	136	131
	DT	+1.6750	+0.950	+0.360	+0.100				
	T_2	-0.815	-0.500	-0.275	-0.150				
73% D_2	D_2	-0.875	-0.500	-0.325	-0.290	182	180	175	170
	DT	+1.825	+0.675	+0.260	+0.165				
	T_2	-1.000	-0.415	-0.250	-0.125				

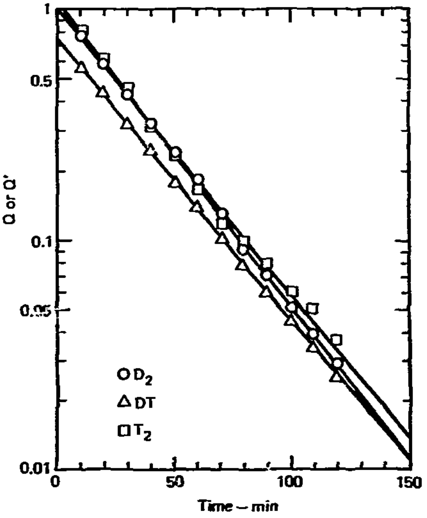

FIGURE 3. Plot of ln Q or ln Q' vs time for a D-T mixture that was initially 27% D.

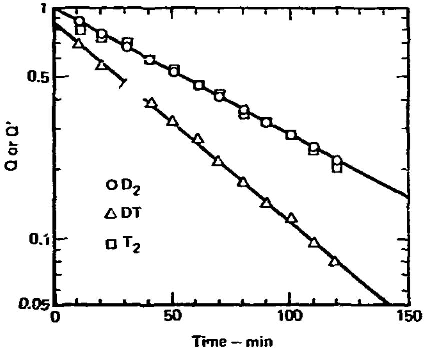

FIGURE 4. Plot of ln Q or ln Q' vs time for a D-T mixture that was initially 55% D.

of the lines agree only for D_2 and T_2 in the 55% D_2 experiment. The slopes of the 27% experiment (Fig. 3) agree better overall than those of the other two experiments. Recall that the total pressure did not sag for this experiment and that the slopes of the kinetic curves maintained the proper 2:1 relationship. Because we do not know how to choose which slope best represents the rate of the reaction for a particular mixture, we report an average slope of the three species. The values of k and τ and the time to equilibrium for these D-T mixtures are given in Table 4.

TABLE 4. Results of the Kinetic Analysis for the Reaction $D_2 + T_2 = 2\ DT$ at 296.4 ± 0.4 K

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

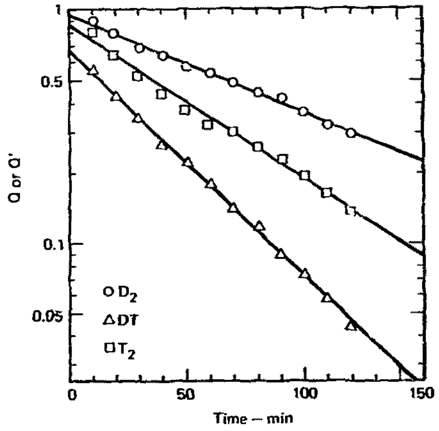

FIGURE 5. Plot of ln Q or ln Q' vs time for a D-T mixture that was initially 73% D.

In our analysis[4] of the $H_2 + T_2 = 2HT$ data from Ref. 3, we showed that the k values, and therefore the τ values, were roughly directly proportional to the total pressure and to the square root of the tritium pressure. The admittedly rough and limited D-T data reported here 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 and T_2 that were initially approximately 27, 55, and 75% H_2. Table 5 shows, for various times, the slopes and total pressures as measured with the quadrupole mass filter. The slopes in all these experiments show the approximate 2:1 product:reactant ratio. They appear to be more consistent than the slopes in the D-T experiments. The total pressure remains constant in the 27% H_2 experiment but increases somewhat in the other two. This increase could be explained by an upward drift in sensitivity, an error that is hard to control in this system.

In all cases, ln Q or ln Q' was plotted against time. The results for each mixture are shown in Figs. 6-8. We estimated the $P_\infty(i)$ for each species by the same procedure used for the D-T experiments. As in the D-T experiments, all the ln Q or ln Q' plots can be approximated by a straight line. In none of the H-T experiments did any two species have the same slope.

In Table 6 we list the values of the equilibrium and initial pressures plus the values of k and τ and the time to equilibrium for these H-T mixtures. Note that the characteristic times τ for the H-T reactions are about

TABLE 5. Characteristics of the Kinetic Curves for the Reaction $H_2 + T_2 = 2\ HT$ at 298.4 ± 0.4 K

		Slope, Torr/min				Total pressure, Torr			
		minutes after mixing				minutes after mixing			
Mixture	Species	25	50	100	150	25	50	100	150
27% H_2	H_2	-0.240	-0.180	-0.075	-0.040	188.6	189.4	189.1	189.4
	HT	+0.640	+0.370	+0.185	+0.100				
	T_2	-0.190	-0.185	-0.085	-0.060				
55% H_2	H_2	-0.520	-0.270	-0.225	-0.125	321.8	324.4	325.8	328.4
	HT	+0.900	+0.625	+0.450	+0.295				
	T_2	-0.350	-0.275	-0.215	-0.130				
75% H_2	H_2	-0.320	-0.200	-0.160	-0.105	357.4	361.7	373.2	374.5
	HT	+0.800	+0.650	+0.165	0.285				
	T_2	-0.425	-0.285	-0.170	-0.160				

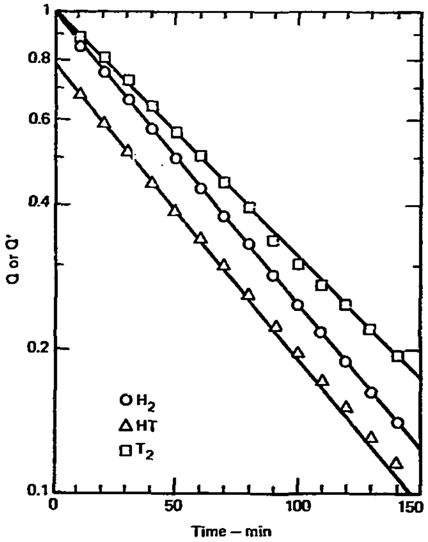

FIGURE 6. Plot of ln Q or ln Q' vs time for an H-T mixture that was initially 27% H.

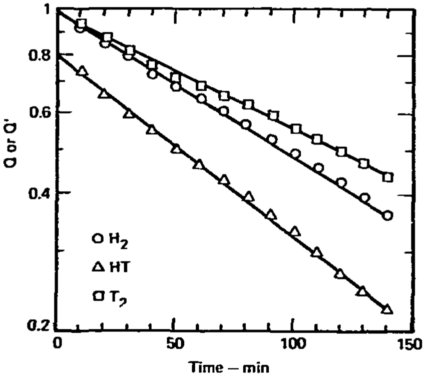

FIGURE 7. Plot of ln Q or ln Q' vs time for an H-T mixture that was initially 55% H.

twice as long as they were in the D-T reactions. This isotope effect is shown in Table 7, where the ratios k_{DT}/k_{HT} are listed for mixtures of nearly identical T composition. Because this ratio is approximately two, we can estimate the D-T rates at other compositions and total pressures from the measured H-T rates in the literature.(3,4)

TABLE 6. Results of the Kinetic Analysis for the Reaction $H_2 + T_2 = 2\ HT$ at 298.4 ± 0.4 K

Initial composition of mixture, %			Pressures, Torr					Slope (k), min^{-1}				τ(av), min	Time to equilibrium, h
H	D	T	$P_0(H_2)$	$P_\infty(H_2)$	$P_0(T_2)$	$P_\infty(T_2)$	$P_\infty(HT)$	H_2	HT	T_2	av		
2.7	2	71	21.2	8.0	65.0	52.5	33.5	0.0140	0.0141	0.0118	0.0133 ±0.0013	75.2	7.5
55	1	44	63.2	39.5	51.4	25.5	60.0	0.0072	0.0090	0.0057	0.0073 ±0.0017	137	13.7
72	1	26	99.3	77.9	36.1	12.0	59.0	0.0049	0.0081	0.0073	0.0068 ±0.0017	147	14.7

ACKNOWLEDGMENTS

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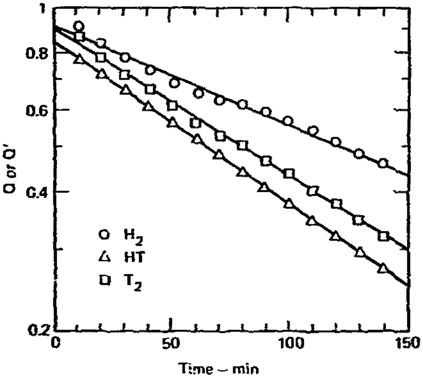

FIGURE 8. Plot of ln Q or ln Q' vs time for an H-T mixture that was initially 71% H.

TABLE 7. Isotope Effect on Rate Constants

Initial mixtures, %				
H-T		D-T		
H	T	D	T	k_{DT}/k_{HT}
27	71	27	70	2.2
55	44	55	44	2.0
72	28	73	26	2.3

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