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KINETICS OF THE RADIATION-INDUCED EXCHANGE REACTIONS OF H_2, D_2, AND T_2, A REVIEW

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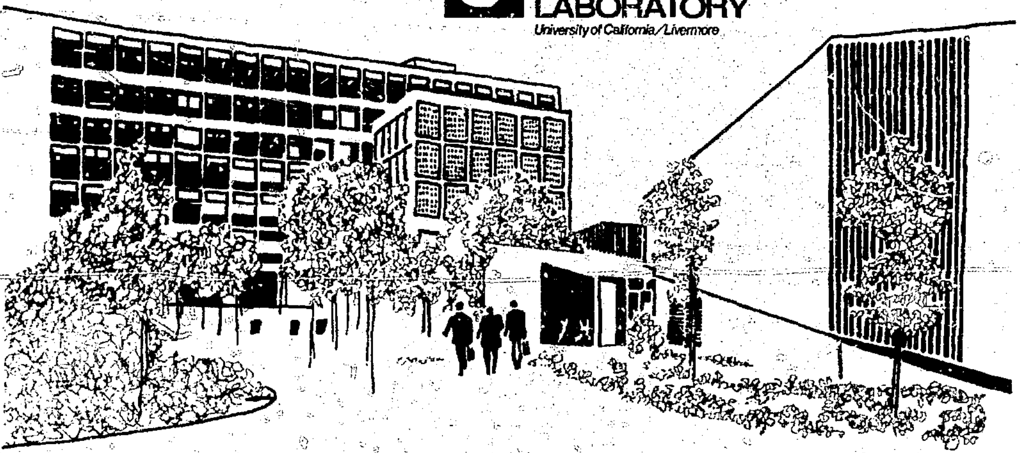

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Contents

KINETICS OF THE RADIATION-INDUCED EXCHANGE OF H_2, D_2, AND T_2, A REVIEW

Abstract

Mixtures of H_2-T_2 or D_2-T_2 will exchange to produce HT or DT due to catalysis by the tritium β particle. The kinetics of the reaction $D_2 + T_2 = 2DT$ may play an important role in designing liquid or solid targets of D_2-DT-T_2 for implosion fusion, and distillation schemes for tritium cleanup systems in fusion reactors. Accordingly, we have critically reviewed the literature for information on the kinetics and mechanism of radiation-induced self-exchange reactions among the hydrogens. We found data for the reaction $H_2 + T_2 = 2HT$ in the gas phase and developed a scheme based on these data to predict the halftime to equilibrium for any gaseous $H_2 + T_2$ mixture at ambient temperature with an accuracy of ±10%. The overall order of the $H_2 + T_2 = 2HT$ reaction is 1.6 based on an initial rate treatment of the data. The most probable mechanism for radiation-induced self-exchange reaction is an ion-molecule chain mechanism.

Introduction

The thermochemical and kinetic properties of the isotopic mixture D_2-DT-T_2 (hereafter referred to as DT) are of interest to hydrogen fusion programs since this mixture fuses at the lowest temperature. Targets of liquid or solid DT will be needed for fusion schemes involving implosion. And, in addition to gaseous DT to fuel the magnetic confinement reactors, tritium recovery systems will require the cryogenic distillation of DT mixtures.

Unfortunately, few data exist on tritium-containing molecules of hydrogen at temperatures near the triple point. To characterize the physical and chemical properties of DT at temperatures near the triple point, we have embarked on an extensive program. This program consists of survey reviews of the literature, theoretical modeling and calculations, and experiments to measure the various physical and chemical properties of the isotopic hydrogen molecules H_2, HD, D_2, HT, DT, and T_2.

This review focuses on the kinetics and mechanism of radiation-induced self-exchange reactions among the hydrogens. Of particular interest is the β-catalyzed exchange of D_2 and T_2 to produce DT. Mixtures of H_2-T_2 and D_2-T_2 will not remain isotopically pure for long since the β from the tritium catalyzes the exchange reactions, producing HT or DT. The β-catalysis likewise prevents the study of pure HT and DT since the mixed species disproportionates to H_2 and T_2 or D_2 and T_2. Therefore, whenever D_2 and T_2 or H_2 and T_2 are combined, a mixture of the three isotopes will be found.

The kinetics of the DT equilibration reaction is vital since the method of preparing inertial targets for fusion with known isotopic concentrations will depend on how rapidly this β-catalyzed equilibration takes place. The rate of this isotopic exchange will also affect the design of cryogenic distillation columns for the tritium recovery systems necessary for fusion reactors.

A literature search failed to turn up any data on the radiation-induced exchange of D_2 and T_2. We did find some gas-phase studies on the radiation-induced exchange of H_2 and T_2, but no data for the liquid and solid phases. Since there are a number of studies on the radiation-induced exchange between H_2 and D_2, our review includes material on this exchange reaction.

We are beginning experimental studies of the $H_2 + T_2$ and $D_2 + T_2$ exchange reactions near the triple point. Gas-phase studies will be made *in situ* using a specially adapted quadrupole mass filter, and liquid-phase studies will be done with infrared spectroscopy. The liquid-phase studies are already underway and members of the cryogenic tritium group[1] have recently measured the first-ever induced-infrared spectra of DT and T_2. We are also completing some room-temperature kinetic measurements of H_2-T_2 and D_2-T_2 systems reported elsewhere.[2]

Rate Equation and Treatment of Experimental Data

SELF-EXCHANGE REACTIONS AND RELATIONSHIP OF RATE CONSTANT TO EQUILIBRIUM CONSTANT

The following isotopic self-exchange reactions will be discussed in this review:

$$H_2 + D_2 \rightleftharpoons 2HD \qquad (1)$$

$$H_2 + T_2 \rightleftharpoons 2HT \qquad (2)$$

$$D_2 + T_2 \rightleftharpoons 2DT \qquad (3)$$

Since these reactions form equilibrium mixtures, with the mixed specie product as abundant as the reactants, the kinetics are complex and we do not expect to observe a simple first- or second-order reaction. These equilibrations have opposing forward and reverse reactions. If we assume simple second-order kinetics for each reversible step, the equilibrium constant is related to the rate expression in a straightforward manner. Using reaction (3) as an example,

$$D_2 + T_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2DT \; .$$

The rate of the forward reaction, R_f, is given by

$$R_f = k_f \, [D_2][T_2] \; , \tag{4}$$

where k_f is the rate constant for the forward reaction. The rate, R_r, of the reverse reaction is given by

$$R_r = k_r \, [DT]^2 \; , \tag{5}$$

where k_r is the rate constant for the reverse reaction. At equilibrium, the forward reaction rate is equal to the reverse reaction rate; therefore,

$$R_f = R_r = k_f[D_2][T_2] = k_r[DT]^2 \tag{6}$$

and

$$\frac{k_f}{k_r} = \frac{[DT]^2}{[D_2][T_2]} = K_{eq} \; . \tag{7}$$

The equilibrium constant is equal to the forward rate constant divided by the reverse rate constant. This is true for uncomplicated second-order kinetics. As we will see, however, the mechanism of these self-exchange reactions is a complex chain process and Eq. (7) does not strictly obtain.

RATE EXPRESSION AND REACTION ORDER

The thermally induced exchange of H_2 and D_2 [Eq. (1)] was studied by Farkas and Farkas shortly after the discovery of deuterium.[3] They applied a rate expression for the progress of reaction (1) which Dorfman and Mattraw[4] later used to treat the data for reaction (2). The rate expression

$$[HD]_\infty - [HD]_t = [HD]_\infty \, e^{-kt} \tag{8}$$

reduces to

$$1 - \frac{[HD]_t}{[HD]_\infty} = e^{-kt} \; , \tag{9}$$

where $[HD]_t$ and $[HD]_\infty$ denote the concentrations of HD at time t and at equilibrium respectively, and k is a constant.

Differentiating Eq. (8) with respect to time gives the reaction rate at any time t,

$$\frac{d[HT]_t}{dt} = k[HT]_\infty \, e^{-kt} \; , \tag{10}$$

and setting t = o gives the true initial rate,

$$\left(\frac{d[HT]}{dt}\right)_{t=o} = k[HT]_\infty \; . \qquad (11)$$

The halftime of the exchange is found by setting $[HD]_t/[HD]_\infty = 0.5$ and solving for $t_{1/2}$ in Eq. (9). Thus,

$$t_{1/2} = 0.693/k \; . \qquad (12)$$

This has the same form as the $t_{1/2}$ for a first-order reaction. However, k is not a conventional first-order rate constant since there is a different k for each set of initial pressures.

The order of the thermal reaction (1) is 3/2; this was found by plotting $1/t_{1/2}$ versus P_T, where P_T is total pressure. Investigators using shock tube techniques for the homogeneous reaction (1) have recently found overall orders from 1.04 to 1.4 for the forward reaction[5,6] and 1.4 for the reverse reaction,[7] essentially confirming the reaction order given by Farkas and Farkas. Lifshitz[6,8] has suggested the early work really occurred under heterogeneous rather than homogeneous conditions so many of their conclusions are suspect.

RADIATION-INDUCED KINETICS OF $H_2 + T_2 = 2HT$

In 1953, Mattraw and Dorfman published a study of the β-ray catalysis of reaction (2). They showed by linear plots of $\ell n(1 - [HT]t/[HT]_\infty)$ versus time that the β-ray catalyzed reaction could be treated by the kinetic equation Farkas and Farkas[3] developed for the homogeneous thermal equilibration of H_2 and D_2. Their data are summarized in Table 1. They also made calculations of the

Table 1. Kinetic data for $H_2 + T_2 = 2HT$.

Run	Total pressure (Torr)	Tritium pressure (Torr)	Mole fraction HT_∞	k (min^{-1} × 10^4)	Halftime (min)	$\left(\frac{d[HT]t}{dt}\right)_{t=o}$ (moles/litre • min × 10^2)
1	59.0	46.1	0.320	8.47	818	8.55
2	119.3	64.6	0.454	12.6	550	36.4
3	123.7	81.6	0.418	13.3	522	36.7
4	213.2	33.2	0.248	13.7	504	38.7
5	295.4	147.7	0.458	19.5	355	140.6
6	399.9	133.6	0.411	26.7	260	233.9

adsorption of radiation by the hydrogen isotopes and found the initial rate proportional to the total pressure and the adsorbed β intensity.

The G value (the number of molecules of a given product formed or reactant converted for each 100 eV of energy absorbed) for the formation of HT ranged from 220 to 450 HT molecules per 100 eV. In a subsequent study[9] on the radiation-induced (using the tritium β-ray) self exchange of H_2 and D_2, Mattraw and Dorfman obtained G values of 2×10^4 HD molecules/100 eV at only 27.6 Torr total pressure. They indicated impurities in the earlier experiments inhibited the lengths of the chain carriers.

PREDICTION OF HALFTIME AND INITIAL RATE

One important practical question is "If H_2 and T_2 are mixed at specified gas pressures, how long will the mixture take to equilibrate?" We have developed an empirical method of treating the data of Ref. 4 so this estimation can be made. We can also treat the data of Ref. 4 so the initial order of the forward reaction can be calculated.

If the initial rate $(d[HT]/dt)_{t=o} = R_o$ or the constant k, which is proportional to the initial rate, are plotted versus the total pressure times the tritium pressure to the 1/2 power, we can obtain a reasonable linear correlation (see Figs. 1 and 2). The least-squares fitted equation in Fig. 1 is $R_o = (-18.064 \times 10^{-7}$ moles litre^{-1} min$^{-1}) + (5.06 \times 10^{-6}$ moles litre^{-1} min^{-1} Torr$^{-3/2}) \left(P_{T_2}^{1/2} P_T\right)$ with a coefficient of determination $r^2 = 0.975$. The least-squares fitted equation in Fig. 2 is $k = (8.364 \times 10^{-4}$ min$^{-1}) + (0.3699$ min^{-1} Torr$^{-3/2}) \left(P_{T_2}^{1/2} P_T\right)$ with a coefficient of determination of $r^2 = 0.953$. The halftime to equilibrium is obtained from k using Eq. (12). Therefore, one can, upon specifying the total pressure of the H_2-T_2 mixture and the T_2 pressure, estimate the initial rate and the halftime.

To test the accuracy of the halftime predictions, we took the predicted k values from the curve for experiments 1-6 of Ref. 4, calculated the halftimes, and compared them to the measured values. The results are shown in Table 2. As is seen, one can expect to predict the halftime of the $H_2 + T_2 = 2HT$ exchange to an accuracy of the order of ±10%.

$H_2 + T_2 = 2HT$ INITIAL REACTION ORDER

The initial order of the reaction can be calculated from the data in Table 1 using the following treatment. The initial rate is given by an equation of the form

$$\left(\frac{d[HT]}{dt}\right)_{t=o} = R_o = k_o[H_2]^a[T_2]^b \quad . \quad (13)$$

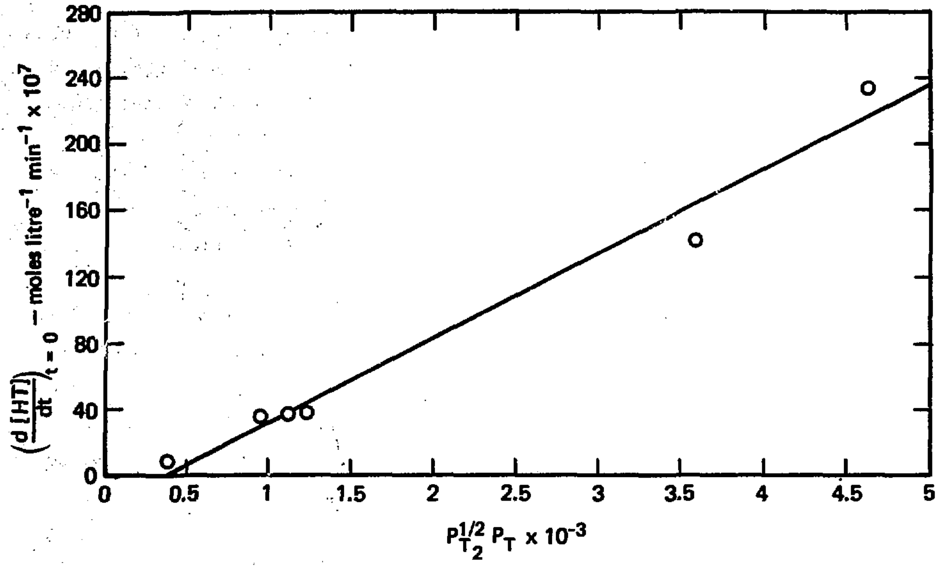

Fig. 1. Plot of initial rate vs $P_{T_2}^{1/2}P_T$.

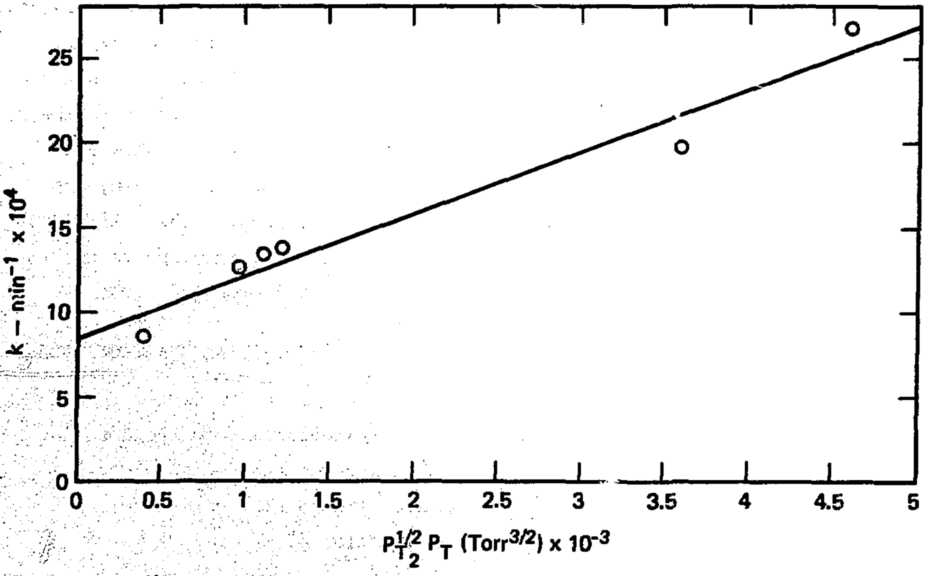

Fig. 2. Plot of k vs $P_{T_2}^{1/2}P_T$.

Table 2. Measured and predicted halftime values.

Experiment	k estimated ($min^{-1} \times 10^4$)	$t^{1/2}$ estimated (min)	$t^{1/2}$ measured (min)	% error[a]
1	9.8	707	818	-13.6
2	11.9	582	550	+5.8
3	12.4	558	522	+6.9
4	12.9	537	504	+6.5
5	21.6	321	355	-9.6
6	24.2	286	360	-10.0

[a] 8.7% av ± 10.0% relative standard deviation.

Taking the natural logarithm, we obtain

$$\ln R_o = \ln k_o + a \ln[H_2] + b \ln[T_2] \ . \quad (14)$$

Since we know the initial rates and concentrations of $[H_2]$ and $[T_2]$ for the six experiments in Ref. 4, we can use these data to solve for k_o, a, and b. The number of possible combinations of these 6 data sets each taken 3 at a time is 20 ($C = {}_6P_3/{}_3P_3 = \frac{6\times5\times4}{3\times2\times1} = 20$).

We have solved the 20 combinations of simultaneous equations for the values of $\ln k_o$ a, and b. The results are given in Table 3. The averages were obtained without the data from combinations 2,3,4 and 1,3,5 which were checked and then eliminated on statistical grounds.

The value of $k_o = 4.45 \times 10^{-9}$ min^{-1} $moles^{-0.6}$ $litre^{+0.6}$. The initial order of the reaction with respect to H_2 is 0.77 and 0.86 with respect to T_2. The overall initial order is 0.77 + 0.86 = 1.63. This is similar to the results obtained for the homogeneous thermal reaction $H_2 + D_2 = 2HD$ which give overall initial orders from 1.04 to 1.5 [see discussion following Eq. (12)].

Jones[10] gives initial rate data for reaction (2) at 76.7 K. We have applied our $P_{T_2}^{1/2}P_T$ correlation to his data, which were taken over a large pressure range (~156 to 2400 Torr). The results are shown in Fig. 3 where we have plotted $\ln P_{T_2}^{1/2}P_T$ versus R_o to accommodate the three-orders-of-magnitude change in $P_{T_2}^{1/2}P_T$. Surprisingly, the data fall into three groups. Group 1, approximately a 50-50 H_2-T_2 mix, has the fastest initial rates. Group 2 has an initial T_2 of approximately 90%, and Group 3

Table 3. Results of solving simultaneous equations for $\ell n\ k_o$, a, and b.

Combination of data from experiments 1-6 of Ref. 4	$\ell n\ k_o$	a	b
1,2,3	-19.45	0.79	0.90
2,3,4	-13.73	0.14	0.16
3,4,5	-18.99	0.62	0.94
4,5,6	-21.49	1.07	1.00
1,3,4	-19.91	0.71	1.08
1,4,5	-19.37	0.69	0.95
1,5,6	-17.95	0.96	0.40
1,2,4	-20.41	0.72	1.20
1,2,5	-18.41	0.87	0.58
1,2,6	-19.05	0.82	0.78
1,3,5	-76.61	-9.83	22.94
1,3,6	-19.72	0.74	1.01
1,4,6	-19.99	0.71	1.10
2,3,5	-18.59	0.70	0.79
2,3,6	-17.43	0.56	0.64
2,4,6	-19.91	0.68	1.12
2,5,6	-18.31	0.97	0.46
3,4,5	-20.02	0.72	1.09
2,4,5	-19.83	0.67	1.11
3,5,6	-17.28	0.93	0.29
Averages[a]	-19.23	0.77	0.86

[a] Omitting data from 2,3,4 and 1,3,5.

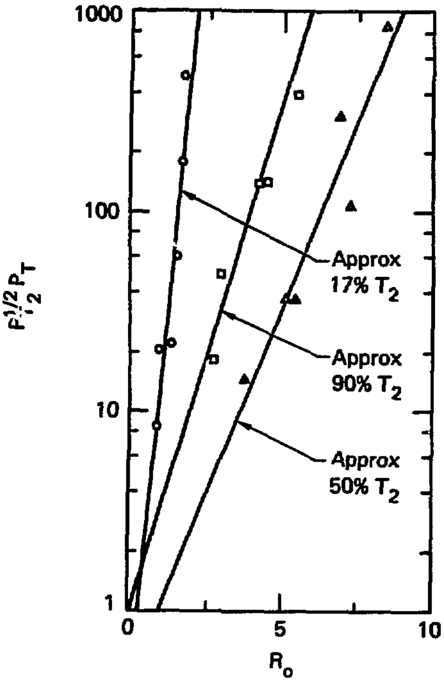

Fig. 3. Plot of $\ell n\ P_{T_2}^{1/2}P_T$ vs R_o.

with approximately 17% T_2 is the slowest. It is probable that each initial concentration of T_2 would have a separate line. Therefore, this scheme cannot be used to predict the halftimes for the $H_2 + T_2$ exchange from the data at 76.7 K. We do not know why the initial rate of the 50-50 mix is faster than those mixes with higher tritium concentrations.

Radiation-Induced Exchange Mechanism

Determining the mechanism of a chemical reaction is a complex and subtle quest. Reactions such as $H_2 + I_2 = 2HI$, which for years was given in text books as the classical bimolecular mechanism with a four-atom transition state, has recently been shown to be either a termolecular or atom-chain mechanism.[11] Ironically, the homogeneous thermal conversion in the hydrogen system represented by reaction (1), which was originally thought to have an *atom-molecule chain mechanism*,[3] now appears to have a molecular mechanism. Also in this case, the simple bimolecular mechanism has been ruled out.[8] It is, therefore, not surprising that the proposed mechanism for radiation-induced self exchange among the hydrogens has changed drastically through the years as more data become available.

The earliest data we could find in the literature on radiation-induced self exchange among the hydrogens was a study by Mund et al.[12] of reaction (1) induced by α particles. The change in resistance of a hot platinum wire was used to detect the progress of exchange. Mund et al. made a series of subsequent studies[13-16] of this particular reaction mechanism. They interpreted data in terms of an atom-molecule chain mechanism. Later works have shown an atom-molecule chain mechanism is relatively unimportant; therefore, we shall not discuss this early work further. The studies of reactions (1) and (2) induced by tritium β particles by Dorfman et al.[4,9] were also interpreted using the atom-molecule chain mechanism proposed by Mund.

Thompson and Schaeffer[17,18] showed the most probable mechanism of the radiation-induced self exchange of hydrogen isotopes was an ion-molecule chain mechanism with the H_3^+ ion as the charge carrier. Their evidence came from studies of inhibition of the rate of α-particle-induced $H_2 + D_2$ exchange by rare gases Kr and Xe, which have ionization potentials below hydrogen. These rare gases inhibit the chain mechanism by removing the H_3^+ carrier.

Thompson and Schaeffer's ion-molecule chain mechanism has been essentially confirmed by mass spectroscopic studies of the relevant ion-molecule reactions[19] and by studies of the inhibition of these reactions by application of electric fields.[20-22] However, a detailed review of these mechanistic studies is beyond the scope of this paper, especially since the evidence has been critically reviewed by A. R. Anderson.[23]

Jones,[10] has shown that this ion-molecule chain mechanism is the most probable one for reaction (2). By extension, we can reasonably assume it is also the most probable mechanism for reaction (3). The tritium mechanism given by Jones is shown below:

Ionization: $H_2 \rightarrow H_2^+ + e$

Initiation: $H_2^+ + H_2 \rightarrow H_3^+ + H$ (1)

Chain propagation: $H_3^+ + T_2 \rightarrow H_2T^+ + HT$ (2)

or

$H_3^+ + T_2 \rightarrow H_2 + HT_2^+$

Chain termination: $H_3^+ + (-) \rightarrow H_2 + H$

or $\rightarrow 3\,H$, (3)

where (-) denotes an electron, negative ion, or wall recombination.

Obviously, a similar mechanism could be written using T_3^+ as the chain carrier or, in the case of reaction (3), with D_3^+ as the chain carrier. In any case, the present evidence convinces us that the radiation-induced self exchange mechanism of the hydrogen isotopes is of the ion-molecule type given above.

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