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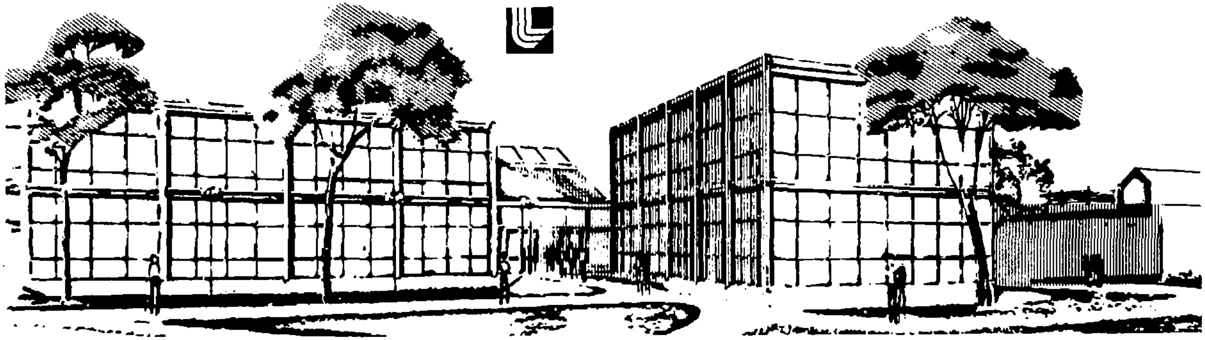

EQUILIBRIUM CONSTANTS FOR THE HYDROGEN ISOTOPIC SELF-EXCHANGE REACTIONS IN THE 4.2-50 K TEMPERATURE RANGE*

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ABSTRACT

Hydrogen fusion will require a mixture of liquefied or frozen D_2 and T_2. The equilibrium constant of the mixture describes the composition of this fuel. We have calculated the equilibrium constant, K_{DT}, for the reaction $D_2 + T_2 = 2DT$ in the 4.2-100 K temperature range. The results agree well with previous calculations at 25, 50, and 100 K. No calculations at temperatures below 25 K have been previously published. In the 16.7-33.3 K temperature range, which includes the triple point, K_{DT} can be represented by $K = 2.995 \exp[-10.82/T]$. The values of the analogous equilibrium constants for H_2-D_2 and H_2-T_2 are also given in the 4.2-50 K temperature range.

INTRODUCTION

Potential shortage of energy in the United States has stimulated interest in the production of power by controlled hydrogen fusion. All of the proposed methods (magnetic confinement, plasma focus, electron beam implosion, or laser implosion) require the fusion fuel that ignites at the lowest temperature — a mixture of the hydrogen isotopes D and T in the liquid or solid state. The values of the equilibrium constants are important to this effort since they describe the composition of the fuel in terms of the molecular species D_2, DT, and T_2.

The isotopic self-exchange reactions of hydrogen are defined as follows:

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

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

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

In the gas phase, the equilibrium constants are expressed in terms of the partial pressures, P_i, of the isotopic sp[illegible]

$$K_{HD} = P_{HD}^2 / P_{H_2} \cdot P_{D_2}, \qquad (4)$$

$$K_{HT} = P_{HT}^2 / P_{D_2} \cdot P_{T_2}, \qquad (5)$$

$$K_{DT} = P_{DT}^2 / P_{D_2} \cdot P_{T_2}. \qquad (6)$$

The equilibrium constants in the liquid and solid phases are expressed in terms of mole fractions N_i^P, where i is the isotopic species and P is the phase (liquid or solid). For example, K_{DT} in the liquid phase would be

$$K_{DT}(\ell) = \frac{\left(N^{\ell}_{DT}\right)^2}{N^{\ell}_{D_2} \cdot N^{\ell}_{T_2}} \quad , \tag{7}$$

and K_{DT} in the solid phase would be

$$K_{DT}(s) = \frac{\left(N^{s}_{DT}\right)^2}{N^{s}_{D_2} \cdot N^{s}_{T_2}} \quad , \tag{8}$$

with analogous expressions for the other equilibrium constants. The equilibrium constants in the liquid and solid phases can be calculated from the gas-phase equilibrium constant if one knows the vapor pressures of the pure, condensed species. For example, it is readily shown[1] by using Raoult's Law that

$$K_{DT}\ (\ell) = K_{DT}(g) \left(\frac{P^{o}_{D_2}(\ell) \cdot P^{o}_{T_2}(\ell)}{\left[P^{o}_{DT}(\ell)\right]^{2}} \right) \tag{9}$$

and that

$$K_{DT}(s) = K_{DT}(g) \left(\frac{P^{o}_{D_2}(s) \cdot P^{o}_{T_2}(s)}{\left[P^{o}_{DT}(s)\right]^{2}} \right) \tag{10}$$

(again, with analogous expression for the other equilibrium constants), where $P^{o}_{2}(j)$ is the vapor pressure of the pure isotopic species i in the liquid (ℓ) or solid (s) phase, j. At most temperatures, the ratio of the vapor pressures of the pure species in both the solid and liquid are very close to one.[2] Therefore, $K_{DT}(g) = K_{DT}(\ell)$ and $K_{DT}(g) \approx K_{DT}(s)$. Accordingly, the gas-phase equilibrium constants, which can be calculated from theory, can be used to estimate the equilibrium constants for the condensed phase.

We have made an extensive search of the literature[1] and found that no data on the equilibrium constants exist in either condensed phase. We did find values of the gas-phase equilibrium constants at temperatures for K_{HD} and K_{HT} above 50 K, and for K_{DT} above 25 K. For the hydrogen fusion programs, the temperature region of most interest is that near the triple points (the estimated triple point of DT is 19.7) and below. We therefore have calculated K_{HD}, K_{HT}, and K_{DT} using the Bigeleisen-Mayer theory[3] in the 4.2-50 K temperature range.

THEORY

For most isotopic exchange reactions, Bigeleisen and Mayer[3] showed that the equilibrium constants are a function of the vibrational frequencies only at constant temperature. The present situation, isotopes of hydrogen at low temperature, is an exception. In this case, the rotational partition functions must be determined by direct summation[4] and the proportion of the even and odd rotational states for the various hydrogens must be taken into account. To illustrate this method, we will show how K_{DT} was calculated. Equations for K_{HD} and K_{HT} are formulated in an analogous fashion. The vibrational part of K_{DT} is given[3] by

$$K_{DT}(\mathrm{vib}) = \frac{\left(\frac{u_{DT}}{u_{D_2}}\right)\left(\frac{e^{-u_{DT}/2}}{e^{-u_{D_2}/2}}\right)\left(\frac{1-e^{-u_{D_2}}}{1-e^{-u_{DT}}}\right)}{\left(\frac{u_{T_2}}{u_{DT}}\right)\left(\frac{e^{-u_{T_2}/2}}{e^{-u_{DT}/2}}\right)\left(\frac{1-e^{-u_{DT}}}{1-e^{-u_{T_2}}}\right)} , \tag{11}$$

where $u_i = hc\omega_e/kT$. The constants are defined as follows: h = Planck's constant, c = speed of light, ω_e is the harmonic vibrational frequency (different for each isotopic hydrogen molecule), k = Boltzmann's constant, and T = absolute temperature.

The frequencies for the various hydrogen isotopic molecules were obtained in the following manner: The ω_e value[5] for hydrogen is 4395.24 cm^{-1}. The isotopically independent force constant, k_e, is then calculated from the hydrogen ω_e value by solving for k_e in equation (12),

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu_i}}, \tag{12}$$

in which μ_i is the reduced mass of the isotopic molecule. Subsequently all of the ω_e values can be generated by using k_e and Eq. (12). Table 1 gives the results of these calculations. This procedure is more accurate than using ω_e values from various sources or using ω_e values that are not isotopically independent.[6]

To obtain the total equilibrium constant,[7] we must multiply $K_{DT}(\mathrm{vib})$ by the rotational part of the equilibrium constant, $K_{DT}(\mathrm{rot})$:

$$K_{DT} = K_{DT}(\mathrm{vib}) \cdot K_{DT}(\mathrm{rot}). \tag{13}$$

This rotational part is given by

$$K_{DT}(\mathrm{rot}) = \frac{\dfrac{\left(\sum\limits_{J=0,1,2,\ldots}(2J+1)e^{-J(J+1)\sigma_{DT}}\right)^2}{\left(\frac{2}{3}\sum\limits_{J=0,2,4,\ldots}(2J+1)e^{-J(J+1)\sigma_{D_2}} + \frac{1}{3}\sum\limits_{J=1,3,5\ldots}(2J+1)e^{-J(J+1)\sigma_{D_2}}\right)\left(\frac{1}{4}\sum\limits_{J=0,2,4\ldots}(2J+1)e^{-J(J+1)\sigma_{T_2}} + \frac{3}{4}\sum\limits_{J=1,3,5\ldots}(2J+1)e^{-J(J+1)\sigma_{T_2}}\right)}}{\dfrac{\left(\frac{1}{\sigma_{DT}}\right)^2}{\left(\frac{1}{\sigma_{D_2}}\right)\left(\frac{1}{\sigma_{T_2}}\right)}}, \tag{14}$$

where $\rho_i = \frac{hc\,B_e}{kt}$; Be = the rotational constant, different for each isotope.

The constant B_e for the isotopic hydrogen molecules is proporational to μ^{-1}.[8] The B_e values for the isotopic hydrogen molecules were obtained in the same manner as the ω_e values; the hydrogen value[9] of $B_e = 60.864$ cm^{-1} was used to determine the proporationality constant, k, and then the B_e values were found from $B_e = k\mu^{-1}$. Table 2 gives the results.

Note that the summations of rotational energy states are weighted in Eq. (14) so as to give the equilibrium constant for equilibrium hydrogen; i.e., for D_2 2/3 ortho and 1/3 para and for T_2 1/4 para and 3/4 ortho.

RESULTS AND DISCUSSION

Using the data and the formulas discussed in the previous section, we calculated K_{HD}, K_{HT}, and K_{DT} as functions of temperature. The results are given in Table 3. These equilibrium constants have been previously calculated at higher temperatures by Jones.[10] Therefore, where possible, we compared our calculations with his. The agreement is good (within 1%). To be more accurate, we would have to include many more correction terms and calculations. We feel that the present accuracy is sufficient. Max Wolfsberg and his co-workers[11] are planning a more extensive calculation that will include all significant corrections.

A semilog plot of the values of K_{HD}, K_{HT}, and K_{DT} versus 1/T is shown in Fig. 1. Note that the plot of K_{DT} versus 1/T consists of two linear portions connected by an s-shaped region. This transition region occurs because the rotational correction becomes important at that point. The curves for K_{HD} and K_{HT} will show the same behavior at higher temperatures. Because the s-shaped curve occurs in the region of the triple point, we have blown it up in Fig. 2. As we see, in the temperature range from 16.7 to

33.3 K, the curve can be approximated by a straight line. The equation of this line from a least squares fit is

$$K_{DT} = 2.995 \exp \left[- \frac{10.82}{T} \right]. \qquad (15)$$

We can check the accuracy of this equation by comparing the original points calculated from theory to the fitted points. Table 4 shows this comparison. We see that the fitted equation gives results that are as accurate as the calculations themselves.

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WTW/sc/ta

Table 1. Reduced masses and vibrational frequencies for the hydrogen isotopic molecules.

Molecule	μ_i	ω_e(calculated)
H_2	0.5041	4395.24
HD	0.6719	3807.05
HT	0.7556	3590.00
D_2	1.0074	3109.14
DT	1.208	2839.27
T_2	1.5085	2540.78

Table 2. Reduced masses and rotational constants for the isotopic hydrogen molecules.

Molecule	μ	μ^{-1}	B_e
H_2	0.5041	1.9837	60.86
HD	0.6719	1.4883	45.66
HT	0.7556	1.3235	40.61
D_2	1.0074	0.9927	30.46
DT	1.208	0.8278	25.40
T_2	1.5085	0.6629	20.34

Table 3. Values of K_{HD}, K_{HT} and K_{DT} as functions of temperature.

Temperature (K)T	K_{HD}	K_{HT}	K_{DT}
4.2	4.90×10^{-8}	1.74×10^{-17}	0.0472
5.0			0.104
7.0			0.336
10.0	2.67×10^{-3}	5.70×10^{-7}	0.795
12.5			1.14
13.3			1.24
14.3			1.36
15.4			1.45
16.7			1.56
18.2			1.66
20.0	0.137	2.60×10^{-3}	1.75
22.2			1.84
25.0			1.93 (1.95)[a]
28.6			2.04
30.0	0.500	3.38×10^{-2}	2.07
33.3			2.18
40.0	0.942	0.118	2.33
50.0	1.34 (1.33)[a]	0.244 (0.242)[a]	2.57 (2.60)[a]
66.7			2.89
100.0			3.29 (3.32)[a]

[a] Values in parentheses are those given by Jones, Ref. 10.

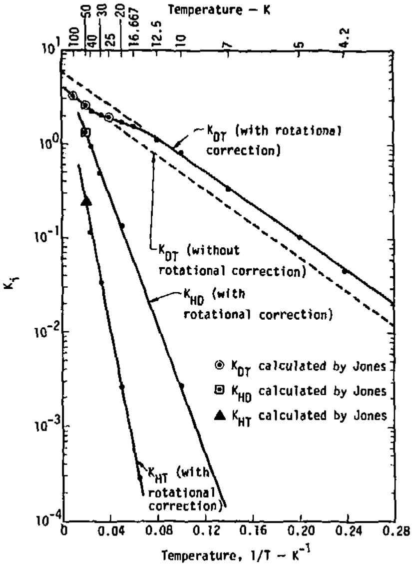
Table 4. Comparison of calculated and fitted points for K_{DT} in the temperature range from 16.7 to 33.3 K.

Temperature (K)	K_{DT}(calc)	K_{DT}(fit)
16.7	1.56	1.57
18.2	1.66	1.65
20.0	1.75	1.74
22.2	1.84	1.84
25.0	1.93	1.94
28.6	2.04	2.05
30.0	2.07	2.09
33.3	2.18	2.16

Figure Captions

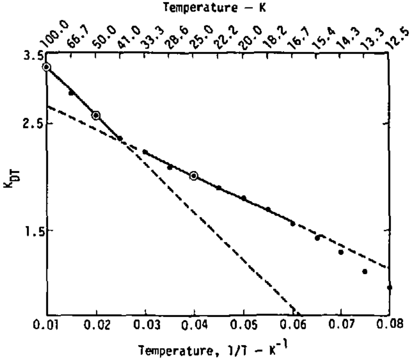
Fig. 1. Semilog plot of K_{HD}, K_{HT}, and K_{DT} as a function of 1/T.

Fig. 2. Semilog plot of K_{DT} versus 1/T in the temperature range from 12.5 to 100 K.



Temperature — K
100
50
40
30
25
20
16.667
12.5
10
7
5
4.2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
K_i
K_{DT} (with rotational correction)
K_{DT} (without rotational correction)
K_{HD} (with rotational correction)
K_{HT} (with rotational correction)
◉ K_{DT} calculated by Jones
⊡ K_{HD} calculated by Jones
▲ K_{HT} calculated by Jones
0
0.04
0.08
0.12
0.16
0.20
0.24
0.28
Temperature, 1/T – K^{-1}

Pyper - Fig. 1


Temperature — K
100.0
66.7
50.0
41.0
33.3
28.6
25.0
22.2
20.0
18.2
16.7
15.4
14.3
13.3
12.5
3.5
2.5
1.5
K_{DT}
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Temperature, 1/T – K^{-1}

Pyper – Fig. 2