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THE CHEMICAL EQUILIBRIA RELATING THE ISOTOPIC HYDROGENS AT LOW TEMPERATURES

J. W. Pyper and P. C. Souers

December 1, 1976

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THE CHEMICAL EQUILIBRIA RELATING THE ISOTOPIC HYDROGENS AT LOW TEMPERATURES

Abstract

Hydrogen fusion will require a fuel mixture of liquefied or frozen D_2 and T_2 . The composition of this fuel mixture is described by the equilibrium constant K_{DT} . We discuss in detail the theory of isotopic exchange reactions as it applies to the hydrogen isotopes. A literature survey of the values of K_{HD} , K_{HT} , and K_{DT} found no values of K_{DT} for temperatures below 25 K and no values of K_{HD} and K_{HT} for temperatures below 50 K.

The existing data are critically evaluated, and simplified formulas for the three equilibrium constants in the temperature range 50-300 K are derived from them. Using harmonic approximation theory with the rotational correction, we have calculated the values of K_{HD} , K_{HT} , and K_{DT} in the temperature range 4.2-50 K. We find that $K_{DT} = 2.995 \exp(-10.82/T)$ in the temperature range 16.7 to 33.3 K to an accuracy of 1%. Tables, graphs, and equations of K_{HD} , K_{HT} , and K_{DT} are given for the temperature range 4.2 to 50 K.

Introduction

The recent U.S. energy shortage has stimulated renewed interest in producing power by controlled hydrogen fusion. This laboratory and others are pursuing vigorous programs with goals of producing hydrogen fusion through magnetic confinement, electron beams, or laser implosion. All the programs need 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 purpose of this report is to collect and evaluate all of the chemical equilibrium data and theory on the isotopic self-exchange reactions of the hydrogen isotopes in all three states of matter: gaseous, liquid, and solid. We also show how simplified theory can be accurately used to predict the values of the equilibrium constants in certain ranges of interest.

Unfortunately, we found that, while the equilibrium constants of most interest are those near the triple points (below 20 K) and especially those in the condensed state, almost all of the data available are for the gaseous reactions above 50 K. We therefore must focus our review on reactions in the gas phase, because of the lack of data on these equilibria in the condensed phases.

For completeness, we will also survey the data for all the hydrogen isotopes, even though the D-T equilibrium is our main interest.

The isotopic self-exchange reactions of hydrogen are defined in the gas phase as follows:

The equilibrium constants for these reactions are written in the usual way in terms of the measured partial pressures P_i of the gaseous species i :

$$K_{\text{HD}} = P_{\text{HD}}^2 / P_{\text{H}_2} \cdot P_{\text{D}_2}; \quad (4)$$

$$K_{\text{HT}} = P_{\text{HT}}^2 / P_{\text{H}_2} \cdot P_{\text{T}_2}; \quad (5)$$

$$K_{\text{DT}} = P_{\text{DT}}^2 / P_{\text{D}_2} \cdot P_{\text{T}_2}. \quad (6)$$

In all cases found in the literature, the partial pressures were determined with a mass spectrometric method.

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. From Raoult's Law,

$$P_{\text{DT}} = N_{\text{DT}}^c P_{\text{DT}}^o(c), \quad (7)$$

where N_{DT}^c signifies the mole fraction of DT in a condensed-phase (liquid, ℓ , or solid, s) mixture, and $P_{\text{DT}}^o(c)$ represents the vapor pressure of pure DT in the condensed phase. Similar expressions can be written for the other components. The gas-phase equilibrium constant can therefore be expressed as

$$K_{\text{DT}}(\text{g}) = \frac{P_{\text{DT}}^2}{P_{\text{D}_2} \cdot P_{\text{T}_2}} = \left(\frac{N_{\text{DT}}^{\ell 2}}{N_{\text{D}_2}^{\ell} \cdot N_{\text{T}_2}^{\ell}} \right) \left(\frac{[P_{\text{DT}}^o(\ell)]^2}{P_{\text{D}_2}^o(\ell) \cdot P_{\text{T}_2}^o(\ell)} \right) \quad (8)$$

when the species in the gas phase are in equilibrium with each other and with the species in the liquid phase. The liquid-phase equilibrium constant then can be calculated by rearranging Eq. (8):

$$K_{\text{DT}}(\ell) = \frac{N_{\text{DT}}^{\ell 2}}{N_{\text{D}_2}^{\ell} \cdot N_{\text{T}_2}^{\ell}} = K_{\text{DT}}(\text{g}) \left(\frac{P_{\text{D}_2}^o(\ell) \cdot P_{\text{T}_2}^o(\ell)}{[P_{\text{DT}}^o(\ell)]^2} \right). \quad (9)$$

By a similar derivation, we obtain for the case of the gaseous isotopic species in equilibrium with the solid isotopic species:

$$K_{DT}(s) = \frac{N_{DT}^s{}^2}{N_{D_2}^s \cdot N_{T_2}^s} = K_{DT}(g) \left(\frac{P_{D_2}^o(s) \cdot P_{T_2}^o(s)}{[P_{DT}^o(s)]^2} \right) \quad (10)$$

The relationships would of course be much more complex in the cases where all three phases are in equilibrium with each other. We have not yet derived the necessary equations for these cases. In the above expressions, we have assumed that we are in the low-pressure regime, in which case we can ignore fugacities and activities. At very low temperatures the vapors of the hydrogen isotopes are quite dense, so fugacities and activities will have to be considered in future experiments.

At most temperatures, the ratio of the vapor pressures of the pure species¹ are very close to one. Therefore, $K_{DT}(g) \simeq K_{DT}(l)$ and $K_{DT}(g) \simeq K_{DT}(s)$ in the appropriate two-phase regions. The same arguments apply to the other systems. This points out the utility of the gas-phase equilibrium constants in estimating the equilibrium constants for the condensed phases. The theory and data developed in the rest of this paper for $K_{HD}(g)$, $K_{HT}(g)$, and $K_{DT}(g)$ can thus generally be applied to equilibria in the condensed phases.

Theory of Isotopic Exchange Reactions

GENERAL BIGEISEN-MAYER THEORY AND CORRECTIONS

To calculate the value of an equilibrium constant from theory, we need to know how the molecules are partitioned into the various energy states available to them. If we know this, then we can calculate the equilibrium constant from a simple relationship. The division of molecules in a system into the various energy states is given by the partition function, which is defined as²

$$Z = \sum_j g_j e^{-\epsilon_j/kT} \quad (11)$$

where T is the absolute temperature, k is Boltzman's constant, the ϵ_j 's are the allowed quantum mechanical energy levels for the molecule, and g_j is the statistical weight of the j th energy level. The terms in the summation of Z indicate how the molecules are partitioned among the various energy levels.

The equilibrium constant for the hydrogen isotopic exchange reaction of, for example, Eq. (6) is given by³:

$$K_{DT} = \frac{\left(\frac{z_{DT}^0}{N}\right)^2}{\left(\frac{z_{D_2}^0}{N}\right)\left(\frac{z_{T_2}^0}{N}\right)} e^{-\Delta\epsilon_0/kT}, \quad (12)$$

where z_i^0 is the partition function of an ideal gas i in its standard state, N is Avagadro's number, and $\Delta\epsilon_0$ is the energy difference between comparative chemical stabilities of different chemical systems (sometimes called the zero of energy difference). The N 's cancel in Eq. (12), and the exponential term is equal to one since $\Delta\epsilon_0 = 0$ for isotopic molecules. (According to the Born-Oppenheimer approximation,¹ the potential-energy curve for molecule formation is the same for isotopic molecules, therefore the zero of energy difference will be zero.)

In addition to the above simplifications, it is convenient to express K_{DT} in terms of heavy-over-light isotopic ratios of Z_i to take advantage of cancellations that occur. Hence

$$K_{DT} = \left(\frac{z_{DT}^0}{z_{D_2}^0}\right)\left(\frac{z_{T_2}^0}{z_{DT}^0}\right)^{-1}. \quad (13)$$

Notice that the heavier isotope always appears in the numerator of these ratios.

One of the implications of the Born-Oppenheimer approximation¹ is that one can separate each quantum mechanical energy level into a sum of translational (t), rotational (r), vibrational (v), and electronic (e) terms. That is

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e. \quad (14)$$

It follows that

$$Z = Z_t Z_r Z_v Z_e. \quad (15)$$

Since for Z_t , Z_r , and Z_v , the difference between energy levels is often less than kT (the hydrogen isotopes at low temperatures are the exception), these

partition functions can be integrated or summed⁴ to give the familiar closed-form equations for ideal gases. Equation (15) therefore becomes

$$Z^0(\text{diatomic molecule}) = \left\{ \frac{(2\pi MkT)^{3/2} V}{h^3} \right\} \left\{ \frac{8\pi^2 IkT}{\sigma h^2} \right\} \left\{ \frac{\exp\left(\frac{-h\nu}{2kT}\right)}{1 - \exp\left(\frac{-h\nu}{kT}\right)} \right\} Z_e, \quad (16)$$

where

M = the molecular mass;

h = Plank's constant;

V = the volume of the gas;

σ = the symmetry number;

I = the moment of inertia;

and ν = the vibrational frequency.

If we now use this form of the partition function, we can evaluate the ratio in Eq. (13). Taking the ratio $Z_{DT}^0/Z_{D_2}^0$ as an example, we obtain

$$\frac{Z_{DT}^0}{Z_{D_2}^0} = \left\{ \left(\frac{M_{DT}}{M_{D_2}} \right)^{3/2} \right\} \left\{ \frac{I_{DT}/\sigma_{DT}}{I_{D_2}/\sigma_{D_2}} \right\} \left\{ \frac{\exp\left(\frac{-h\nu_{DT}}{2kT}\right) \left[1 - \exp\left(\frac{-h\nu_{D_2}}{kT}\right) \right]}{\exp\left(\frac{-h\nu_{D_2}}{2kT}\right) \left[1 - \exp\left(\frac{-h\nu_{DT}}{kT}\right) \right]} \right\}. \quad (17)$$

The simplification is obvious: all the factors which are not a function of mass (including Z_e) cancel. A simpler and more useful ratio can be obtained if we multiply each side of Eq. (17) by $(m_D/m_T)^{3/2n}$ (where m_i is the mass of the atom being exchanged and n is the number being exchanged, in this case one) and multiply and divide the right side by u_{D_2}/u_{DT} , where $u_i = h\nu_i/kT$. Equation (17) then becomes

$$\left(\frac{m_D}{m_T} \right)^{3/2} \frac{Z_{DT}^0}{Z_{D_2}^0} = \left\{ \frac{\sigma_{D_2}}{\sigma_{DT}} \right\} \frac{u_{DT}}{u_{D_2}} \left\{ \frac{e^{-\frac{u_{DT}}{2}}}{e^{-\frac{u_{D_2}}{2}}} \right\} \left\{ \frac{(1 - e^{-u_{D_2}})}{(1 - e^{-u_{DT}})} \right\}, \quad (18)$$

since

$$\frac{I_{DT}}{I_{D_2}} \cdot \left(\frac{M_{DT}}{M_{D_2}} \right)^{3/2} \left(\frac{m_D}{m_T} \right)^{3/2} \cdot \frac{u_{D_2}}{u_{DT}} = 1 \quad (19)$$

from the Teller-Redlich product rule.⁵ Equation (18) is the Bigeleisen-Mayer⁶ f-function, and is a function only of the symmetry numbers and the vibrational frequencies, specifically the zero-order or harmonic vibrational frequencies. Since 1947, most calculations of isotopic equilibrium constants have been made through this formalism. Equation (18) is valid for all isotopic pairs of molecules except those whose rotations cannot be described by classical mechanics at the temperature of interest. The rotational energy-level spacings of isotopic hydrogen molecules are so much wider than kT , even at room temperature, that either a correction term⁶ must be applied to Eq. (18), or, at low temperatures, the rotational partition function must be evaluated by direct summation.⁷

In the above treatment, a number of approximations have been made, in addition to the Born-Oppenheimer approximation. For example, we have treated the rotating molecules as if they were rigid rotors, and the vibrations as if they could be described by simple harmonic motion. We also have assumed that there is no interaction between rotation and vibration. Therefore, if one wants to make a detailed comparison between theory and experiment, he must be able to calculate factors for various corrections. The most recent analysis of these corrections has been made by Wolfsberg and his co-workers over the past several years. In Ref. 7, they detail the calculations of the G_0 correction, the correction for anharmonic vibration, vibration-rotation interaction, and quantum mechanical rotation. They have also been investigating the possible breakdown of the Born-Oppenheimer approximation.⁸

Fortunately, in the special case of isotopic self-exchange reactions of hydrogen, the G_0 correction,⁹ the anharmonic vibration correction,⁹ and the correction for the Born-Oppenheimer approximation¹⁰ vanish. The only large correction to the equilibrium constants for these reactions is the correction for quantum mechanical rotation, which is discussed in a later section.

ORTHO AND PARA FORMS OF THE HYDROGEN ISOTOPES

This section and the following one detail the necessary correction to K_i for quantum mechanical rotation. Neglect of the consideration of the ortho and para forms of the hydrogens can lead to incorrect values of the equilibrium constants, especially at cryogenic temperatures.

At low temperatures, the rotational partition function for the hydrogens cannot be expressed in a closed form but must be summed. The rotational partition function is given by⁴

$$Z_r = \sum (2J + 1) \exp \left[-J(J+1) \frac{hcB_e}{kT} \right] \quad (20)$$

where J is the rotational quantum number, c is the speed of light, and B_e is the rotational constant, different for each isotope. We define the rotational temperature θ_r as hcB_e/k , and $\rho_i = \theta_r/T$. At a particular temperature, Eq. (20) becomes

$$Z_r = \sum (2J + 1) \exp \left[-J(J + 1) \rho_i \right]. \quad (21)$$

From quantum mechanics we learn that for homonuclear diatomic molecules, the J values in Z_r must be either all odd or all even.⁴ If the nuclei are different, there is no restriction on the allowed J values. Table 1 gives the definitions of the ortho and para forms for the homonuclear diatomic hydrogens.

Table 1. Ortho and para hydrogen isotopes.

Molecule	Even J values allowed in Eq. (21)	Odd J values allowed in Eq. (21)
H_2	Para	Ortho
D_2	Ortho	Para
T_2	Para	Ortho

The even series takes the form:

$$Z_{r, \text{even}} = 1 + 5e^{-\theta_r/T} + 9e^{-20\theta_r/T} + \dots, \quad (22)$$

and the odd series takes the form:

$$Z_r(\text{odd}) = 3e^{-26_r/T} + 7e^{-126_r/T} + 11e^{-306_r/T} + \dots \quad (23)$$

The ortho forms in the presence of a conversion catalyst can be converted to the para forms and vice versa. Therefore an equilibrium can be established between the two forms. The calculations in this paper have taken into consideration the various rotational states of the isotopes and assume an equilibrium mixture of the ortho and para forms. For equilibrium D_2 , $Z_r = 2/3 Z_r(\text{even}) + 1/3 Z_r(\text{odd})$, and for equilibrium H_2 and T_2 , $Z_r = 1/4 Z_r(\text{even}) + 3/4 Z_r(\text{odd})$.^{11,12}

ROTATIONAL CORRECTIONS TO THE EQUILIBRIUM CONSTANT

According to Bigeleisen,¹¹ the f function defined as Eq. (7) in Ref. 6 is equal to:

$$f = \frac{Z_{QM} / Z_C}{Z'_C / Z'_C} \quad (24)$$

where QM and C denote the quantum mechanical and classical partition functions, respectively, and the prime designates the lighter molecule. Breaking the total partition function down into the translational (t), rotational (r), and vibrational (v) parts, we obtain

$$f = \frac{Z_{QM}(t) / Z'_C(t)}{Z_C(t) / Z'_C(t)} \cdot \frac{Z_{QM}(r) / Z'_C(r)}{Z_C(r) / Z'_C(r)} \cdot \frac{Z_{QM}(v) / Z'_C(v)}{Z_C(v) / Z'_C(v)} \quad (25)$$

The first ratio (translational) in Eq. (25) is always unity. The third ratio (vibrational) is the usual formulation for f given by Eq. (18). The second ratio (rotational) is unity, except in the case of the hydrogen isotopes, which we study here. Therefore, to accurately calculate K_{DT} (and analogously K_{HD} and K_{HT}) we must account for this ratio by multiplying Eq. (13) by the rotational correction $K_{DT}(\text{rot})$ as given in:

$$K_{DT}(\text{rot}) = \frac{\left(\frac{1}{3} \sum_{j=0,2,4,\dots} (2j+1) e^{-j(j+1)\theta_{D_2}} \right)^2}{\left(\frac{1}{3} \sum_{j=0,2,4,\dots} (2j+1) e^{-j(j+1)\theta_{D_2}} + \frac{1}{3} \sum_{j=1,3,5,\dots} (2j+1) e^{-j(j+1)\theta_{D_2}} \right) \left(\frac{1}{4} \sum_{j=0,2,4,\dots} (2j+1) e^{-j(j+1)\theta_{T_2}} + \frac{3}{4} \sum_{j=1,3,5,\dots} (2j+1) e^{-j(j+1)\theta_{T_2}} \right)} \cdot \frac{\left(\frac{1}{\theta_{DT}} \right)^2}{\left(\frac{1}{\theta_{D_2}} \right) \left(\frac{1}{\theta_{T_2}} \right)} \quad (26)$$

where $1/\rho_1$ is the classical rotational partition function. Note that the symmetry-number factor is completely contained in the numerator. Therefore when applying this correction, the symmetry-number ratios should be divided out of the uncorrected K_{DT} .

QUALITATIVE IMPLICATIONS OF THE THEORY

If classical mechanics is employed to evaluate the partition function ratio for isotopic molecules, one obtains^{1,6} those ratios as

$$\frac{z_{DT}^o}{z_{D_2}^o} = \frac{\sigma_{D_2}}{\sigma_{DT}} \left(\frac{m_T}{m_D} \right)^{3/2} \quad \text{and} \quad \frac{z_{T_2}^o}{z_{DT}^o} = \frac{\sigma_{DT}}{\sigma_{T_2}} \left(\frac{m_T}{m_D} \right)^{3/2}. \quad (27)$$

Therefore, Eq. (13) becomes

$$K_{DT} = \frac{\sigma_{D_2}}{\sigma_{DT}} \left(\frac{m_T}{m_D} \right)^{3/2} \bigg/ \frac{\sigma_{DT}}{\sigma_{T_2}} \left(\frac{m_T}{m_D} \right)^{3/2} = \frac{\sigma_{D_2} \sigma_{T_2}}{(\sigma_{DT})^2} = \frac{(2)(2)}{1} = 4. \quad (28)$$

Similar equations can be written for the other self-exchange reactions. We would obtain this same value if we assume a random distribution of the deuterium and tritium atoms among the hydrogenic molecules; i.e., there is just one way to form D_2 and T_2 from their atoms, but there are two ways to form DT . Therefore K_{DT} would be

$$K_{DT} = \frac{(2)^2}{(1)(1)} = 4. \quad (29)$$

The fact that deviations from this value of K_{DT} are observed in these reactions (except at high temperatures) indicates that classical mechanics is inadequate to describe these systems. The quantum mechanical treatment shows that the quantum effect basically resides in the molecular vibrations. In particular, the zero-point energy term — the $\exp[h\nu_1/2kT]$ term in Eq. (18) — makes the largest contribution to the equilibrium constant,¹ especially at low temperatures.

Figure 1 shows the potential energy as a function of interatomic distance between the two atoms of a diatomic molecule. When the atoms are far apart, they are independent of each other. As they are brought together, they are attracted to one another and so form a bond, which is represented by an energy

level of the potential well. The term r_e is the equilibrium bond length of the diatomic molecule. If the atoms are pushed together to distances less than r_e , the potential rises sharply because of the repulsion energy.

According to quantum theory, the vibrating molecule cannot assume just any energy on the continuous curve shown in Fig. 1. It is restricted to discrete energy levels, the lowest of these being the zero-point energy, $E_0^0(i)$ where i indicates the isotopic form of the molecule. The zero-point energy, which is the vibrational energy contained by the molecule at absolute zero, is given by the expression

$$E_0^0 = \frac{1}{2} h\nu. \quad (30)$$

The vibrational frequency, ν , equals $1/2\pi(k/\mu)^{1/2}$, where k is the force constant and μ is the reduced mass $m_A m_B / (m_A + m_B)$ — A and B are hydrogen atoms. The force constant is related to the curvature of the potential well in Fig. 1, and is the same for all isotopic species within the Born-Oppenheimer approximation.

Since E_0^0 depends on ν , which in turn is an inverse function of mass, the zero-point energies for the isotopic hydrogen species will differ from each other. Tritium, with the smallest value of $1/\sqrt{\mu}$, will have the lowest zero-point energy. These levels are illustrated in Fig. 1. E_H , E_D , and

Fig. 1 Curve relating potential energy and interatomic distance. E_0^0 is the zero-point energy of the denoted molecule; E is the dissociation energy. The equilibrium bond length is labeled r_e .

E_T represent the energies necessary to dissociate the molecules H_2 , D_2 , and T_2 . Since more energy is required to dissociate the tritium molecules, they are the most stable of the isotopic hydrogens.

The reduced masses¹³ and the zero-point energies (calculated from Ref. 12) of hydrogen's isotonic molecules are given in Table 2. In Fig. 2, a plot of E_0^0 vs $1/\sqrt{\mu}$ shows a linear relationship, expected from theory. The function $1/\sqrt{\mu}$ would be a good function to correlate properties that are dependent on frequency of vibration.

Table 2. Reduced mass and zero-point energy.

Isotopic molecule	Reduced mass μ	$1/\sqrt{\mu}$	E_0^0 , KJ/mole
H ₂	0.5041	1.408	25.930
HD	0.6719	1.220	22.544
HT	0.7556	1.150	21.314
D ₂	1.0074	0.996	18.458
DT	1.208*	0.910	16.901
T ₂	1.5085	0.814	15.140

* Omitted from Herzberg (Ref. 13).

The rule of the geometric mean¹⁴ states that the value of the equilibrium constant should nearly equal the classically calculated value, for isotopic self-exchange reactions. The rule is exact at high temperature, as shown by Bigeleisen¹⁴ from the theory. One way of rationalizing this rule is to realize that even though there is an isotopic effect on both ratios of partition

functions in the expression for the equilibrium constant (see Eq. (13)), the two effects are in opposing directions and nearly cancel when the product is taken.

Wolfsberg¹ has discussed the high- and low-temperature limits of isotopic equilibrium constants as a function of temperature. At low temperatures, the $(1 - e^{-u_i})$ terms in Eq. (18) equal one, so the equilibrium constant as given by Eq. (13) has the form

$$K_{DT} = Ae^{B/t} \quad (31)$$

Fig. 2 Plot of E_0^0 vs $1/\sqrt{\mu}$.

where A reflects the products of frequencies and symmetry numbers, and B is the appropriate zero-point energy difference. For the isotopic exchange reactions of hydrogen, A should be close to the classical value of four, and the exponential term therefore contains the isotope effect. At absolute zero, the value⁵ of K_{DT} is zero. This is because the zero-point energy sum for the pure species is less than twice the zero-point energy of the mixed species.

Fig. 3. Form of $\ln K_{DT}$ vs $1/T$ from Eqs. (31) and (32).

At high temperatures, the equilibrium constant will have the form¹

$$K_{DT} = 4 + \frac{C}{T^2} \quad (32)$$

where C is a constant and must be negative. The high-temperature limit is the classical value of four. Using Eqs. (31) and (32) for the extreme cases, we can predict the form of $\ln K_{DT}$ vs $1/T$. This plot is shown in Fig. 3.

Survey of the Literature for K_{HD} , K_{HT} , and K_{DT}

The first reference to deuterium in the literature is by Urey *et al.*¹⁵ in 1932, and the first reference to tritium is by Lozier *et al.*¹⁶ in 1934. We have surveyed the literature from these early papers through the July-December 1975 Chemical Abstracts Indices for references to the isotopic exchange equilibrium constants. The primary modern references found are a series of both theoretical calculations and experimental results by Jones.^{17,18,19} In addition to papers that explicitly report the values of equilibrium constants, there are papers that report free energy functions, from which the equilibrium constants can be calculated (see Ref. 12 for an example). We have not included these in our compilation of the data, especially since the theoretical calculations from many sources agree with one another.

THE EQUILIBRIUM CONSTANT K_{HD}

The experimental data found for K_{HD} are given in Table 3. In addition, all of the values of K_{HD} reported in Jones' theoretical paper¹⁸ are included in this table. Most of the points at low temperatures (large values of $1/T$) fall on a straight line (see Fig. 4). We have fitted the points on the line between $T = 50$ and $T = 300$ with a straight line by the method of least squares. The equation for the line is:

$$\ln K_{HD} = \frac{-53.22}{T} + 1.348; \text{ or } K_{HD} = 3.850 e^{-53.22/T} \quad (33)$$

In Table 4, the values of K_{HD} we estimated using Eq. (33) are compared with the experimental and accurately calculated values at those temperatures.

Since, as shown in Table 4, the error in using Eq. (33) is small, it can be used to estimate the equilibrium constant in the temperature interval specified with an accuracy of a few percent. Note that the pre-exponential

Fig. 4 Plot of $\ln K_{HD}$ vs $1/T$.

Table 3. Comparison of the various experimental (ex) and theoretical (th) values of K_{HD} .

Temperature, K	Rittenberg, et al. ²⁰ (1931)		Gould, et al. ²¹ (1934)		Urey ⁵ (1947)	Jones ¹⁸ (1949)	Thompson & Schaeffer ²² (1955)	Jones ¹⁹ (1967)	Bron, et al. ⁷ (1973)	Bron & Paul ²³ (1974)
	K_{ex}	K_{th}	K_{ex}	K_{th}	K_{th}	K_{th}	K_{ex}	K_{ex}	K_{th}	K_{th}
50						1.33				
76.7								1.93		
83			2.3	2.2						
100						2.26				
195			2.88	2.92						
200						2.90			2.899	2.898
273			3.18	3.19	3.18					
293							3.23 ±0.07			
298.1	3.28	3.28			3.25	3.26				
299								3.27		
300						3.26			3.264	3.264
383			3.53	3.46						
400					3.48	3.48				
500					3.62	3.62				
600					3.72	3.72			3.721	3.720
670	3.78	3.73								
700						3.78				
741	3.75	3.82								
800						3.83				
900						3.87				
1000						3.90				
1250						3.94				
1500						3.96				
2000						3.97				
2500						3.97				

Table 4. Comparison of estimated and calculated values of K_{HD} ($T = 50$ to $T = 300$ K).

T, K	Estimated K_{HD} from Eq. (33)	Calculated K_{HD} (from Table 3)	% Error
50	1.33	1.33	0.0
76.7	1.92	1.93*	-0.5
100.0	2.26	2.26	0.0
200.0	2.95	2.90	+1.7
293.0	3.21	3.23*	-0.6
300.0	3.22	3.26	-1.2

* Experimental values.

term is nearly the classical value of four. Also, remember that the constant in the exponential represents the zero-point energy change for the equilibrium reaction.

The very earliest data by Urey, *et al.*,²⁰ which was published in 1934, agrees well with recent theory^{7,18,23} and experiment.²⁰ This is in marked contrast to other isotopic systems, in which recent experiments and theory have changed the values of the equilibrium constants (see Wolfsberg's discussion of the equilibrium constant for water in Ref. 1). On the other hand, the 1934 data by Gould, *et al.*,²¹ has two points (at 83 K and 273 K) that are not on the line in Fig. 4, which makes these data suspect.

The theoretical calculations of K_{HD} by Jones were made by direct summation over rotational and vibrational states rather than by the method of Bigeleisen and Mayer.⁶ The value of K_{HD} from the work of Thompson and Schaeffer²² is interesting, since they used catalysis by α particles and 2-MeV electrons as well as chemical catalysts. They showed that the value of the thermodynamic equilibrium constant was the same no matter what phenomenon was used to bring about this equilibration. The experimental work of Jones in 1967¹⁹ nicely confirmed his earlier theoretical calculations.

In 1973, Wolfsberg and co-workers⁷ recalculated the partition function ratios for the isotopic hydrogens, making a real effort to include all of the relevant corrections to the simple theory. As Table 3 shows, the earlier calculations of Jones agree very well with the very precise calculations of Wolfsberg. Bron and Paul²³ report a recent calculation of the partition

function ratios obtained by a direct summation method, which also agrees well with Wolfsberg, *et al.*⁷

Note that the temperature dependence of $\ln K$, as shown in Fig. 3, is as predicted by Eqs. 31 and 32. At high temperatures, K_{HD} approaches the classical limit of four. The maximum value of $K_{HD} \approx 3.98$ at $T = 2000$ K, and subsequent decline of K_{HD} at higher temperatures predicted by Murphy²⁴ is contrary to modern theory and is therefore probably incorrect.

THE EQUILIBRIUM CONSTANT K_{HT}

The values for K_{HT} that we found in the literature are given in Table 5. In addition, all of the experimental points, plus the theoretical points calculated by Jones¹⁷ are plotted as $\ln K_{HT}$ vs $1/T$ in Fig. 5. As is seen, the points in the temperature range from 50-300 K fall on a straight line with one exception. The points in this temperature range have been fitted with a

Fig. 5 Plot of $\ln K_{HT}$ vs $1/T$.

Table 5. Comparison of the various experimental (ex) and theoretical (th) values of K_{HT} .

Temperature,	Urey ⁵ (1947)	Jones ¹⁷ (1948)	Mattrau et al. ²⁵ (1952)	Jones ¹⁹ (1967)	Bron, et al. ⁷ (1973)	Bron & Paul ²⁴ (1974)
K	K_{th}	K_{th}	K_{ex}	K_{ex} K_{th}	K_{th}	K_{th}
50		0.242				
76.7				0.69 ±0.02	0.63 ±0.02	
100		0.947				
192				1.92 ±0.014	1.915	
200		1.948			1.947	1.946
273.1	2.42					
298.1	2.56	2.57	2.87* ±0.06			
299				2.58 ±0.014	2.575	2.573
300		2.58				
400	2.97	2.99				
500	3.24	3.26				
600	3.44	3.45			3.442	3.442
700		3.59				
800		3.68				
900		3.76				
1000		3.81				
1250		3.90				
1500		3.94				
2000		3.98				
2500		3.99				

* This number has been discredited in the literature.

straight line by the method of least squares. The equation for the line is:

$$\ln K_{HT} = - \frac{140.86}{T} + 1.385; \text{ or } K_{HT} = 3.995 e^{-140.86/T} . \quad (34)$$

In Table 6 the values of K_{HT} estimated from Eq. (34) are compared with the experimental and accurately calculated values as a function of temperature.

Table 6. Comparison of estimated and calculated values of K_{HT} (50-300 K).

T, K	Estimated K_{HT} (from Eq. (34))	Calculated K_{HT} (from Table 5)	% Error
50	0.239	0.242	-1.2
76.7	0.64	0.63	0.0
100	0.977	0.947	+3.2
192	1.92	1.92	0.0
200	1.98	1.95	+1.5
300	2.50	2.58	-2.7

The largest errors obtained from using Eq. 34 are on the order of 3%. Therefore, Eq. (34) can be used to estimate K_{HT} with an error of 3% or less. Note again that the pre-exponential term of K_{HT} is approximately the classical value of four, that the constant in the exponential is proportional to the zero-point energy change for the equilibrium reaction, and that the shape of the curve formed by the points in Fig. 5 is as predicted by Eq. (31).

The earliest theoretical calculation of K_{HT} by Urey⁵ in 1947 and those of Jones¹⁷ in 1948 agree very well with the most recent calculations,^{7,23} which include latest possible spectroscopic data and corrections. The theory also agrees very well with the experimental data of Jones.¹⁹ The experimental data of Mattraw, *et al.*,²⁵ do not agree with the theory. These workers equilibrated the hydrogen-tritium mixtures using the β ray from the tritium. The work of Jones¹⁹ suggests that it may have been impurities in the gaseous mixture that caused the discrepancy. Thompson and Schaeffer²² showed that there was no difference in K_{HT} when the mixtures were equilibrated by radiation fields or chemical catalysts. In view of their findings, we believe that the K_{HT} reported by Mattraw, *et al.*,²⁵ is erroneous.

THE EQUILIBRIUM CONSTANT K_{DT}

The values of K_{DT} from the literature are shown in Table 7. Also, the values of K_{DT} calculated from spectroscopic data by Jones¹⁸ and his experimental measurements of K_{DT} ¹⁹ are plotted in Fig. 6. It should be noted that Jones calculated a point at 25 K for this reaction only. It does not fit on the linear plot of $\ln K_{DT}$ vs $1/T$. This deviation from linearity is due to the rotational correction becoming significant, as shown in the next section.

We have fitted the points in the temperature range 50-300 K with a straight line, using the least squares method. The equation for the line is:

$$\ln K_{DT} = -\frac{22.72}{T} + 1.421; \text{ or } K_{DT} = 4.141 e^{-22.72/T} . \quad (35)$$

Fig. 6 Plot of $\ln K_{DT}$ vs $1/T$.

Table 7. Comparison of the various experimental (ex) and theoretical (th) values of K_{DT} .

Temperature, K	Urey ⁵ (1947)	Jones ¹⁸ (1949)	Jones ¹⁹ (1967)		Bron <u>et al.</u> ⁷ (1973)	Bron & Paul ²³ (1974)
	K_{th}	K_{th}	K_{ex}	K_{th}	K_{th}	K_{th}
25		1.95				
50		2.60				
76.7			3.12	3.11		
100		3.32				
150		3.57				
192			3.64	3.67		
200		3.69			3.683	3.684
250		3.77				
273.1	3.79					
298.1	3.82	3.82				
299			3.82	3.82	3.811	3.811
300		3.82				
400	3.88	3.88				
500	3.92	3.93				
600	3.94	3.96			3.942	3.942
700		3.97				
800		3.98				
900		3.98				
1000		3.99				
1250		4.00				
1500		4.00				
2000		4.00				
2500		4.00				

The estimated values of K_{DT} , as calculated using Eq. (35) and as compared with the accurately calculated values, are given in Table 8 as a function of temperature. The maximum error from this procedure was about 1%, so Eq. (35) can be used to estimate K_{DT} within 1%. Note that the pre-exponential term is larger than the classical value of four. This, of course, is due to the fact that the linear relationship in Fig. 6 is above the high-temperature points. The constant in the exponential is proportional to the zero-point energy change for the equilibrium reaction.

Again, the earliest theoretical calculations of K_{DT} by Urey⁵ in 1947 and Jones¹⁸ in 1949 agree very well with the latest^{7,23} calculations and also with the experimental data of Jones.¹⁹

Table 8. Comparison of estimated and calculated values of K_{DT} (50-300 K).

T, K	Estimated K_{DT} (from Eq. 35)	Calculated K_{DT} (from Table 7)	% Error
50	2.63	2.60	+1.1
76.7	3.08	3.12*	-1.3
100	3.30	3.32	-0.6
150	3.56	3.57	-0.2
192	3.68	3.64*	+1.1
200	3.70	3.69	+0.3
250	3.78	3.77	+0.3
300	3.84	3.82*	+0.5

*Experimental values.

Calculation of K_{HD} , K_{HT} , and K_{DT} at Temperatures Between 4.2 and 50 K

To compute the vibrational contribution to the equilibrium constant as given by Eq. (13), we have to obtain the vibrational frequency ω_e for each molecule. The ω_e value for hydrogen is 4395.24 cm^{-1} . We calculate the isotopically independent force constant k_e from the hydrogen ω_e value by solving for k_e in the following equation:

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k_e}{\mu_1}} \quad (36)$$

Next, we calculate the ω_e values for each molecule by using k_e and Eq. (36). The values of the reduced masses and the calculated vibrational frequencies are given in Table 9. This procedure is more accurate than using various published ω_e values or ω_e values that are not isotopically independent.²⁶

To compute the rotational correction from Eq. (26), it is necessary to compute the B_e values (Eq. (20)) for each isotopic molecule. The constant B_e is proportional to μ^{-1} .²³ Therefore the B_e values are computed in the same way as the μ values: the hydrogen value of $B_e = 60.864 \text{ cm}^{-1}$ (from Ref. 27) is used to determine the proportionality constant k , and the B_e values are found from $B_e = k\mu^{-1}$. The results are given in Table 10.

Using the above data, we calculated K_{HD} , K_{HT} , and K_{DT} , as products of Eqs. (13) and (24), at various temperatures. The results are given in Table 11. At higher temperatures, where comparison is possible, our values of the equilibrium constants are compared with the theoretical values of Jones.¹⁸ The agreement is good, within 1%.

A semi-log plot of the values of K_{HD} , K_{HT} , and K_{DT} versus $1/T$ is shown in Fig. 7. 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 at the temperatures where the rotational correction begins to become important. The curves for K_{HD} and K_{HT} will show the same behavior at higher temperatures.

Since the S-shaped curve occurs in the region of the triple point, which is the temperature range of interest, we have shown it more closely in Fig. 8. As is seen, in the temperature range 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

$$K_{DT} = 2.995e^{-10.82/T}. \quad (37)$$

We can check the accuracy of this equation by comparing the original points calculated from theory to the fitted points. This comparison is shown in Table 12. As is seen, the fitted equation gives results that are certainly as accurate as the calculations themselves.

Table 9. Reduced masses and vibrational frequencies for the hydrogen isotopic molecules.

Molecule	μ_i	ω_e (calculated), cm^{-1}
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 10. Reduced masses and rotational constants for the isotopic hydrogen molecules.

Molecule	μ	μ^{-1}	B_e , cm^{-1}
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

Fig. 7. Semi-log plot of K_{HD} , K_{HT} , and K_{DT} as a function of $1/T$.

Fig. 8. Semi-log plot of K_{DT} versus $1/T$ in the temperature range 12.5 to 100 K.

The semi-log plot of K_{DT} versus $1/T$ in Fig. 7 was also fitted with a least squares plot in the temperature range 4.2 to 12.5 K. The exponential equation of the resulting line is

$$K_{DT} = 5.924e^{-20.24/T}. \quad (38)$$

In Table 13, values of K_{DT} from Eq. (38) are compared with those originally calculated. The reproduction error is less than 3%.

Table 11. The values of K_{HD} , K_{HT} , and K_{DT} as a function of temperature. Values in parentheses are those of Jones.¹⁸

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)
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)	0.244 (0.242)	2.57 (2.60)
66.7			2.89
100.0			3.29 (3.32)

The semi-log plots for K_{HD} and K_{HT} in Fig. 7 were also fitted by the method of least squares with a straight line in the temperature range 4.2 to 50 K. The resulting equations for these equilibrium constants are

$$K_{HD} = 6.785e^{-78.70/T}, \quad (39)$$

and

$$K_{HT} = 10.22e^{-171.1/T}. \quad (40)$$

Table 12. Comparison of calculated and fitted points for K_{DT} in the temperature range 16.7 to 33.3 K.

T	Estimated K_{DT} (from Eq. 37)	Calculated K_{DT} (from Eqs. 13 and 24)	% Error
16.7	1.57	1.56	+ 0.5
18.2	1.65	1.66	- 0.6
20.0	1.74	1.75	- 0.6
22.2	1.84	1.84	0.0
25.0	1.94	1.93	+ 0.5
28.6	2.05	2.04	+ 0.5
30.0	2.09	2.07	+ 0.9
33.3	2.16	2.18	- 0.9

Table 13. Comparison of the calculated and fitted points for K_{DT} in the temperature range 4.2 to 12.5 K.

T	Estimated K_{DT} (from Eq. 38)	Calculated K_{DT} (from Eqs. 13 and 24)	% Error
4.2	0.0479	0.0472	+ 1.5
5.0	0.103	0.104	- 0.1
7.0	0.329	0.336	- 2.1
10.0	0.783	0.795	- 1.5
12.5	1.17	1.14	+ 2.6

Table 14. Comparison of the calculated and fitted points for K_{HD} and K_{HT} in the temperature range 4.2 to 50 K.

T	Estimated K_{HD} (from Eq. (39))	Calculated K_{HD} (from Eqs. (13) and (24))	% Error	Estimated K_{HT} (from Eq. (40))	Calculated K_{HT} (from Eqs. (13) and (24))	% Error
4.2	4.94×10^{-8}	4.90×10^{-8}	+ 0.8	2.06×10^{-17}	1.74×10^{-17}	+ 18.4
10.0	2.59×10^{-3}	2.67×10^{-3}	- 3.0	3.78×10^{-7}	5.70×10^{-7}	- 33.7
20.0	0.133	0.137	- 2.9	1.96×10^{-3}	2.60×10^{-3}	- 24.6
30.0	0.492	0.500	- 1.6	3.40×10^{-2}	3.38×10^{-2}	- 0.6
40.0	0.949	0.942	+ 0.7	0.142	0.118	+ 20.3
50.0	1.41	1.34	+ 5.2	0.333	0.244	+ 36.5

The values of these equilibrium constants range over many orders of magnitude, so Eqs. (39) and (40) are not as accurate as the equation for K_{DT} . This point is illustrated in Table 14.

Conclusions and Proposals for Future Work

A review of the literature from the early 1930's to December 1975 produced a number of theoretical and experimental values of the equilibrium constants for the isotopic self-exchange reactions of hydrogen. Generally, in the temperature range of 50 to 2500 K, these calculations are in good agreement with each other and with experiment at the prescribed temperatures. The few experimental data points that do not agree with theory and other experiments appear to be invalid. If the precise values of K_{HD} , K_{HT} , and K_{DT} are desired in the temperature range of 220 to 600 K, we suggest using the fitted equations of Bron, Chang, and Wolfsberg,⁷ or in the range 200 to 800 K the fitted equations of Bron and Paul.²⁴

We have used the partition function ratios from these two papers to derive expressions for the various equilibrium constants compared with earlier work in Tables 3, 4, and 7. So that others may use these equations, we report

in Appendix B the equations we derived from the partition function ratios of these two papers. We have fitted linear equations to the available data for K_{HD} , K_{HT} , and K_{DT} in the temperature range 50 to 300 K. These equations are more convenient to use if errors of the order of 1-3% are acceptable.

We have calculated the values of K_{HD} , K_{HT} , and K_{DT} at various temperatures in the range 4.2 to 50 K using the Bigeleisen-Mayer theory including rotational correction. We feel that these calculations are accurate to 1%. Max Wolfsberg and his co-workers at the University of California at Irvine are planning to make detailed computer calculations of K_{HD} , K_{HT} , and K_{DT} incorporating all of the significant corrections in the temperature range 0 to 200 K, which will provide a check on our calculations. We are presently building a cryostat-quadrupole mass filter system to measure these equilibrium constants in the temperature range 4.2 to 25 K.

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Appendix A

Sample Calculation of K_{DT} at 25 K

Data for calculation

Molecule	ω_e, cm^{-1}	u_1	B_e, cm^{-1}	ρ
D_2	3109.14	178.96	30.46	1.753
DT	2839.27	163.43	25.40	1.462
T_2	2540.78	146.25	20.34	1.171

From Bigeleisen and Mayer:⁶

$$\frac{\sigma}{\sigma'} f = \frac{u_i}{u_i'} \exp\left(\frac{u_i' - u_i}{2}\right) \frac{(1 - e^{-u_i'})}{(1 - e^{-u_i})} \quad (\text{Prime signifies lighter molecule; } \sigma\text{'s are symmetry numbers.})$$

$$\begin{aligned} \frac{1}{2} f \frac{DT}{D_2} &= \frac{163.43}{178.96} \exp\left(\frac{178.96 - 163.43}{2}\right) \frac{(1 - e^{-178.96})}{(1 - e^{-163.43})} = 0.913 \cdot 2356.66 \frac{(1 - 0.000)}{(1 - 0.000)} \\ &= 2152, \quad f \frac{DT}{D_2} = 2(2152). \end{aligned}$$

$$\begin{aligned} \frac{2}{1} f \frac{T_2}{DT} &= \frac{146.25}{163.43} \exp\left(\frac{163.43 - 146.25}{2}\right) \frac{(1 - e^{-163.43})}{(1 - e^{-146.25})} = 0.895 \cdot 5377.61 \\ &= 4813, \quad f \frac{T_2}{DT} = 1/2(4813) \end{aligned}$$

$$K_{DT}(\text{uncorrected}) = f \frac{DT}{D_2} / f \frac{T_2}{DT} = 4 \frac{(2152)}{(4813)} = 4(0.447_1) = 1.78_9$$

$$\begin{aligned} Z_{QM}^{D_2}(r) &= 0.6667 \left[1 + 5e^{-6(1.753)} \right] + 0.3333 \left[3e^{-2(1.753)} + 7e^{-12(1.753)} \right] \\ &= 0.6968 \end{aligned}$$

$$Z_{QM}^{DT}(r) = 1 + 3e^{-2(1.462)} + 5e^{-6(1.462)} = 1.1693$$

$$Z_{QM}^T(r) = 0.25 \left[1 + 5e^{-6(1.171)} \right] + 0.75 \left[3e^{-2(1.171)} + 7e^{-12(1.171)} \right]$$

$$= 0.4674$$

$$K_{DT}(\text{rot}) = \frac{\frac{1.1693}{(0.6968)(0.4674)}}{\left(\frac{1}{1.462}\right)^2} = \frac{4.1452}{(0.9604)} = 4.316$$

$$\frac{\left(\frac{1}{1.753}\right)\left(\frac{1}{1.171}\right)}{\left(\frac{1}{1.462}\right)^2}$$

Since the symmetry-number factor is completely contained in the numerator of the equation for $K_{DT}(\text{rot})$, the factor is divided out of $K_{DT}(\text{uncorrected})$ in calculating $K_{DT}(\text{corrected})$:

$$K_{DT}(\text{corrected}) = \frac{K_{DT}(\text{uncorrected})}{\text{symmetry factor}} \cdot K_{DT}(\text{rot})$$

$$= (0.4471)(4.316) = 1.93 \text{ (Jones)}^{18} = 1.95).$$

Appendix B

Equations Expressing K_{HD} , K_{HT} , and K_{DT} as a Function of Temperature

Authors	Ref.	Equation	Valid temperature range	Value of τ
Bron, Chang, Wolfsberg	7	$\ln(K_{HD}/4) = 0.03643 - 0.15868(\tau)$ $- 0.16622(\tau^2) + 0.10780(\tau^3)$ $- 0.02177(\tau^4)$	220-600 K	300/T
Bron, Chang, Wolfsberg	7	$\ln(K_{HT}/4) = 0.09122 - 0.36356(\tau)$ $- 0.33119(\tau^2) + 0.20811(\tau^3)$ $- 0.04410(\tau^4)$	220-600 K	300/T
Bron, Chang, Wolfsberg	7	$\ln(K_{DT}/4) = - 0.00251 + 0.03334(\tau)$ $- 0.16465(\tau^2) + 0.11429(\tau^3)$ $- 0.02871(\tau^4)$	220-600 K	300/T
Bron, Paul	23	$\ln K_{HD} = 0.373949050 \ln \tau$ $- 0.036321650 \tau^{-1} + 1.6352125$ $- 0.366926193 \tau + 0.056262493 \tau^2$	200-800 K	T/500
Bron, Paul	23	$\ln K_{HT} = 0.41144563 \ln \tau$ $- 0.21968795 \tau^{-1} + 1.7435060$ $- 0.401679993 \tau + 0.057340145 \tau^2$	200-800 K	T/500
Bron, Paul	23	$\ln K_{DT} = - 0.006034320 \ln \tau$ $- 0.040822500 \tau^{-1} + 1.4047699$ $+ 0.004119873 \tau - 0.002737999 \tau^2$	200-800 K	T/500

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