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THERMAL DIFFUSION FACTOR FOR HYDROGEN AND WATER MIXTURES

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ABSTRACT. The thermal diffusion factor for the system hydrogen and water-vapour, has been calculated from an equation which utilises only the experimental data on transport properties and their temperature derivatives and is independent of any particular form for the inter-molecular potential. The thermal diffusion factor has also been computed for other systems which emerge out of the different isotopic species of these two principal components. These values are of particular interest in interpreting the data obtained on the enrichment of hydrogen isotopes, in a thermal diffusion column, using the following chemical exchange reaction:

$$HD + H_2O \leftrightarrows HDO + H_2$$

INTRODUCTION

Considerable interest centres around the equilibrium and non-equilibrium properties of water and its mixtures with other gases. This is because of the presence of water vapour all around us in the atmosphere and design-engineers need all such data in connection with their problems involving heat transfer etc. References to such data are found in the work of Keenan and Keyes (1954), Hirschfelder, Curtiss and Bird (1954a), Powell (1958), and Liley (1958). In recent years, some success has been achieved in computing the properties of non-polar molecules from the theoretical results of statistical mechanics in conjunction with spherically symmetric intermolecular potentials. Unfortunately, the position for polar molecules is far from satisfactory. For such molecules, the complicated angle-dependent potentials make it very difficult, if not impossible, to calculate the various collision cross-sections. There is an additional interest in the thermal diffusion factor for the hydrogen and water system, for thermal diffusion coupled with chemical exchange has been tried by Pierce (1959) to enrich the hydrogen isotopes in a thermal diffusion column. The theoretical calculations of the thermal diffusion factor, in particular, are more complicated because of the following two reasons: Firstly, the infinite determinants which represent the thermal diffusion factor have been expanded into an infinite series by two different methods, viz., Chapman-Cowling (1952) and Kihara (1949), Mason (1957). Secondly, both these infinite series have in general rather poor convergence and consequently, to arrive at reliable results for actual systems elaborate numerical calculations have to be performed for the specific intermolecular potential. In this paper all these difficulties have been successfully surmounted and the values of the thermal diffusion factor for the various combinations of the stable isotopes of hydrogen with normal and heavy hydrogen water have been calculated in the temperature range 307°K to 350°K for both the ends of the concentration range.

FORMULAE FOR THE THERMAL DIFFUSION FACTOR

The general formula for the thermal diffusion factor, α_T, is given in the books of Chapman-Cowling (1952) and Hirschfelder, Curtiss and Bird (1954) as the ratio of infinite determinants. Various approximations are then obtained by expanding these infinite determinants according to the procedure of either Chapman-Cowling (1952) or Kihara (1949). Mason (1957) has studied in detail the convergence errors involved in α_T on various intermolecular potentials and for specific types of mixtures. Recently, Weissman, Saxená and Mason (1960) have shown that for a binary mixture, where the heavy component is in trace and the ratio of the molecular masses $\simeq 0.1$ or less, α_T, can be calculated within one to two percent by the following formula

$$[\alpha_T] = (6C_{12}^*-5)(-S_2/Q_2)(1+K), \qquad \ldots \quad (1)$$

where the subscript 2 represents the lighter component and for a mixture consisting of polar and nonpolar components (being designated by the subscripts p and n respectively) we have:

$$S_2 = -S_n = \frac{15M_p(M_p-M_n)}{2(M_p+M_n)^2} + \frac{4M_pM_nA^*_{p-n}}{(M_p+M_n)^2}$$

$$-\frac{M_n}{M_p}\left(\frac{2M_n}{M_n+M_p}\right)^{\frac{1}{2}}\left(\frac{\sigma^2_{n-n}\,\Omega_{n-n}{}^{(2,2*}}{\sigma^2_{p-n}\Omega_{p-n}{}^{(1,1)*}}\right), \qquad \ldots \quad (2)$$

$$Q_2 = Q_n = \frac{2}{M_p(M_p+M_n)}\left(\frac{2M_p}{M_p+M_n}\right)^{\frac{1}{2}}\left(\frac{\sigma^2_{n-n}\Omega_{n-n}{}^{(2,2)*}}{\sigma^2_{p-n}\Omega_{p-n}{}^{(1,1)*}}\right.$$

$$(3M_p{}^2+M_n{}^2+(8/5)M_pM_nA^*_{p-n}), \qquad \ldots \quad (3)$$

$$A^*_{p-n} = \Omega_{p-n}{}^{(2,2)*}/\Omega_{p-n}{}^{(1,1)*}, \qquad \ldots \quad (4)$$

$$C_{12}^* = C^*_{p-n} = \Omega_{p-n}{}^{(1,2)*}/\Omega_{p-n}{}^{(1,1)*}, \qquad \ldots \quad (5)$$

$$K = \frac{1}{42}(8E^*_{n-n}-7)^2+\frac{2}{21}\left(1-\frac{M_n}{M_p}\right)(8E^*_{n-n}-7)$$

$$[1-\tfrac{3}{4}(5-4B^*_{p-n})(6C^*_{p-n}-5)^{-1}], \qquad \ldots \quad (6)$$

$$B^*_{p-n} = [5\Omega_{p-n}{}^{(1,2)*} - 4\Omega_{p-n}{}^{(1,3)*}]/\Omega_{p-n}{}^{(1,1)*}. \qquad \ldots \quad (7)$$

$$E^*_{n-n} = \Omega_{n-n}{}^{(2,3)*}/\Omega_{n-n}{}^{(2,2)*} \qquad \ldots \quad (8)$$

where M represents the molecular mass, $\Omega^{(i,j)*}$ are the reduced Chapman-Cowling collision integrals and σ is the collision diameter. Here, we have arbitrarily chosen the subscript 2 for the nonpolar component, hydrogen, in order to be consistent with the convention of assigning the subscribpt 1 to the heavier component. In case, the lighter component is polar, correct values will be obtained, if the subscripts representing the molecular species are interchanged.

A straightforward calculation of α_T is not possible from these expressions, for the various collision cross-sections have not been evaluated for such an intermolecular potential which takes into account the polar nature of the molecules. The labour involved in the evaluation of these collision integrals is formidable and as yet this has not been accomplished. However, all these collision integrals (except A^*_{p-n}) can be replaced by the absolute values of the transport coefficients or their temperature derivatives. The required relations are:

$$(6C^*_{p-n} - 5) = 2\left[\,2 - \left(\frac{\partial \ln D_{p-n}}{\partial \ln T}\right)_{pr}\right], \qquad \ldots \quad (9)$$

$$(5 - 4B^*_{p-n}) = 5 - \tfrac{1}{3}\left[\,2\left(\frac{\partial \ln D_{p-n}}{\partial \ln T}\right)_{pr} - 1\,\right]$$

$$\left[\,9 - 2\left(\frac{\partial \ln D_{p-n}}{\partial \ln T}\right)_{pr}\right] - \frac{4}{3}\,\frac{d^2 \ln D_{p-n}}{d(\ln T)^2}, \qquad \ldots \quad (10)$$

$$(8E^*_{n-n} - 7) = 2\left[\,1 - \frac{\partial \ln \eta_{n-n}}{\partial \ln T} + \frac{\partial \ln f_n}{\partial \ln T}\right], \qquad \ldots \quad (11)$$

$$-S_n = \frac{15M_p(M_p - M_n)}{2(M_p + M_p)^2} + \frac{4M_pM_nA^*_{p-n}}{(M_p + M_n)^2} - \frac{5}{3}\,\frac{M_n{}^2}{(M_p + M_n)}\,\frac{pD_{p-n}f\eta,}{\eta_{n-n}RT}, \qquad \ldots \quad (12)$$

$$Q_n = \frac{10}{3}\,\frac{\mathrm{M}_n}{(M_n + M_p)}\left(\frac{pr\,D_{p-n}}{\eta_n\ {}_nRT}\right)_{i}\left((3M_p{}^2 + M_n{}^2 + \frac{8}{5}\,M_pM_nA^*_{p-n}\right), \ldots \quad (13)$$

$$f\eta = 1 + \frac{3}{196}\,(8E^*_{n-n} - 7). \qquad \ldots \quad (14)$$

In the above equations pr stands for the pressure. When the light component is in trace following Mason (1957) α_T can be calculated thus:

$$\alpha_T = \left[2 - \left(\frac{\partial \ln D_{p-n}}{\partial \ln T}\right)_{pr}\right]\left[\,1 - \mu_1\left(\frac{M_n}{M_p}\right)\right], \qquad \ldots \quad (15)$$

where

$$\mu_1 = \frac{(16A^*_{p-n}-10)-3(5-4B^*_{p-n})}{10+3(5-4B^*_{p-n})} \qquad \dots \quad (16)$$

Thus, if we know D_{p-n} and η_{n-n}as a function of temperature and A^*_{p-n} is assumed, α_T can be calculated. A_{p-n} is known to be fairly constant (1.10) over a long range of temperature, [Saxena, 1960] and does not vary much from the nature of the potential. Further, it is shown later that α_T is insensitive to the value of A_{p-n} and so an approximate guess will serve our present purpose. In this way the form of the intermolecular potential is completely removed from the expression for α_T in favour of measureable quantities and their temperature derivatives. The only limitations of these formulae are the basic assumptions involved in the derivation of the kinetic theory of gases. The one of special interest here, rigorously speaking, is that these formulae hold only for spherically symmetric molecules. This assumption is rather serious for the case of water which is polar, but as the transport properties are less sensitive to molecular orientations and as Krieger (1951) had some success for polar molecules with an angle-independent potential, we will continue to assume the applicability of central forces.

CALCULATION OF THE THERMAL DIFFUSION FACTOR

The diffusion coefficients have been experimentally measured for the hydrogen and water system by Winkelmann (1884, 1889), Schwertz and Brow (1951) and Crider (1956). The results of Winkelmann and Crider agree with each other but are systematically lower than those of Schwertz and Brow. The reason of this disparity probably lies in the effect of supercooling at the vapour-liquid interface (Le Blanc and Wuppermann, 1916) and in the difference in the solubility of hydrogen in water. Schwertz and Brow have avoided this difficulty and I feel their data is the most reliable one at the moment. This latter data can be represented by a linear plot of log D vs. log T in the entire temperature range (307.3—352.7°K), with the average standard deviation of 0.6% only. Consequently, we will treat $(\partial \ln D/\delta \ln T)_{pr}$ as constant in the formulae of the previous section and then to this approximation, $\partial^2 \ln D/\ (\ln T)^2$ can be neglected in this temperature range.

The data for the viscosity of hydrogen in this temperature range is given by Trautz and Binkele (1930), Trautz and Heberling (1931), Trautz and Husseini (1934), Johnston and McCloskey (1940) and Wobser and Nuller (1941). All this data can again be represented by a linear plot of log η *vs.* log T in this temperature range with an average deviation of 0.1% only. The value of the term, $\partial \ln f_n/\partial \ln T$, was found to be negligible in this temperature range [Saxena, 1956].

Table I lists the values of the thermal diffusion factor for the two limiting ends of the composition range and for the three temperatures at which the experimental diffusion data are available. In column 2 are tabulated the α_T values, calculated according to Eq. (1) in conjunction with Eq. (6) and from (9) to (14) while the column 4 values emerge out of the use of Eqns. (15), (16) and (10). These values, designated as first set, utilise the diffusion data of Schwertz and Brow (1951) The second set of α_T values listed in columns 3 and 5 of Table I have similarly been calculated, except that the diffusion data of Winkelmann (1884, 1889) has been used. In these calculations a constant value of 1.10 for A^* was used. However, these calculations are insensitive to the A^* value, in as much as a change of 20% in A^* changes $\alpha_T(X_1 = 0$, at 328.6°K) only by 0.2%. α_T values, calculated using the diffusion data of Schwartz and Brow, are always higher than those obtained using the data of Winkelman. The author feels that the first set of α_T values is more reliable

TABLE I

Thermal diffusion factor for H_2 H_2O system

Temp.°K	α_T calculated, $X_1 = 0$		α_T calculated, $X_2 = 0$	
	First set	Second set	First set	Second set
307.3	1.21	1.04	0.812	0.61
328.6	1.24	1.07	0.812	0.61
352.7	1.30	1.08	0.812	0.61

In Table II, are tabulated the diffusion coefficients and the thermal diffusion factors at 300°K and 350°K for the various systems, permuting out of the isotopes of hydrogen (H_2, HD and D_2) and heavy hydrogen substituted water (H_2O, HDO and D_2O). The diffusion coefficients have been calculated from the measured values for H_2-H_2O system, by applying the mass correction factor. α_T values are calculated in the same way as that of Table I. The η values also were generated from the experimental values available for hydrogen and by multiplying these with appropriate mass correction factors. The α_T values for those system, where the mass ratio is considerably more than 0.1 will be somewhat inaccurate because of the use of Eq.(6). However, even for the worst case of D_2-H_2O, K has only a value of 0.0145 and consequently the values given in Table II can be treated as fairly reliable. These values of α_T are very useful in assessing the data obtained in connection with the enrichment of hydrogen in a thermal diffusion column, using the following chemical exchange

$$HD+H_2O \rightleftarrows HDO+H_2.$$

TABLE II

Diffusion coefficients and thermal diffusion factors

System	D_{p-n} in cm²/sec.		α_T at 300°K		α_T at 350°K	
	300°K	350°K	$X_1 = 0$	$X_2 = 0$	$X_1 = 0$	$X_2 = 0$
H_2–H_2O	0.996	1.195	1.193	0.812	1.290	0.812
H_2–HDO	0.994	1.192	1.206	0.812	1.303	0.812
H_2–D_2O	0.991	1.189	1.217	0.813	1.316	0.813
HD–H_2O	0.834	1.000	1.078	0.807	1.167	0.807
HD–HDO	0.830	0.996	1.104	0.808	1.187	0.808
HD–D_2O	0.828	0.993	1.112	0.809	1.203	0.809
D_2–H_2O	0.739	0.886	0.970	0.803	1.052	0.803
D_2–HDO	0.735	0.882	0.993	0.803	1.076	0.803
D_2–D_2O	0.732	0.878	1.012	0.804	1.097	0.804

In fact, the present work was undertaken out of the need to interpret such results.

Unfortunately, at present there is no regorous procedure for calculating the transport properties of mixtures consisting of a polar and a non-polar component. Hirschfelder, Curtiss and Bird (1954b) have advanced an approximate procedure, which also has not been extensively tested so far. This approach is based on the concept that the effective potential between a polar and a non-polar molecule has the same form as that between two non-polar molecules. An attempt is being made to assess such semi-empirical approaches proceeded by a redetermination of the force constants for pure polar gases from the upto date data.

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