ON CONDITIONS ENSURING THE HIGHEST DIFFERENCE 
IN THE ASSOCIATION DEGREES 
OF THE EQUILIBRIUM H AND D STEAMS: 
CLUSTERING AND ISOTOPE ENRICHMENT

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A search for conditions leading to the highest possible difference between equilibrium association (clustering) degree in the H and D steam has been carried out and related optimal steam pressures evaluated. The difference decreases with increasing temperature but still is a few per cent at moderate temperatures.

Introduction

Recently, thermodynamics of water association in the gas phase has been evaluated theoretically on the basis of ab initio SCF CI MCY-B water-water pair interaction potential and remarkable agreement between theoretical and observed equilibrium constants for dimerizations to \((\text{H}_2\text{O})_2(\text{g})\) and \((\text{D}_2\text{O})_2(\text{g})\) has been found, so that applicability of the theoretical data to prediction purposes has been proved. Moreover, the data on the dimerization thermodynamics have been combined with the available theoretical information on higher oligomer formation and a unified, refined set of equilibrium constants of association to \((\text{H}_2\text{O})_i(\text{g})\) and \((\text{D}_2\text{O})_i(\text{g})\) has been constructed, any order of association being included. It enabled to treat the H and D steam as an equilibrium mixture of clusters \((\text{H}_2\text{O})_i(\text{g})\) or \((\text{D}_2\text{O})_i(\text{g})\) \((i = 1, 2, 3, \ldots)\). It has been pointed out that significant differences can exist in populations of H and D clusters of the same order at some temperatures and pressures, this having a relation to the problem of isotope enrichment. The aim of the present article is to elucidate conditions leading to the highest differences possible.

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**The cluster model of steam**

Any gas-phase species can be considered (e.g.\(^{10-13}\)) as a mixture of its self-associates, for example for water or heavy water the following equilibria:

\[
i X_2 O(g) \rightleftharpoons (X_2 O)_i(g), \quad (i = 1, 2, \ldots; \quad X = H \text{ or } D)
\]  

are to be considered, described by the equilibrium constants \(K_{p,i}(X)\):

\[
K_{p,i}(X) = \frac{p_i}{p_1},
\]

where \(p_i\) denotes the partial pressure of the cluster \((X_2 O)_i\) in the equilibrium H or D steam. It has been proved\(^5,6\) that for small water oligomers \((i < 6)\) the equilibrium constants form a geometrical series described by its quotient \(z\):

\[
z = \frac{K_{p,i+1}}{K_{p,i}}, \quad (i > 1)
\]

this useful feature was applied throughout the whole series.\(^5,6\)

The total pressure \(P\) of an isotopically homogeneous steam (i.e., either H or D steam) is simply expressed as:

\[
P = \sum_{i=1}^{\infty} p_i,
\]

or, in terms of mole fraction \(x_1\) of the monomer:

\[
P = \sum_{i=1}^{\infty} K_{p,i} (x_1 P)^i.
\]

Equation (5) can be solved with respect to the variable \(x_1\) giving the mole fraction of monomers:

\[
x_1 = \left\{-\frac{1}{z} - P + \left[\frac{1}{z + P} + 4P(K_{p,2}/z - 1)/z\right]^{1/2}\right\}/\left[2P(K_{p,2}/z - 1)\right],
\]

and thus also the degree of the equilibrium association (clustering), \(a\):

\[
a = 1 - x_1.
\]