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CALCULATION OF EQUILIBRIUM CONSTANT FOR DIMERIZATION OF HEAVY WATER MOLECULES IN SATURATED VAPOR

The magnitude and the temperature dependence of the equilibrium constant of dimerization of heavy water molecules in saturated vapor in terms of the second virial coefficient of the equation of state have been determined. An expression is found for the equilibrium dimerization constant of water vapor molecules, which contains terms involving the monomer–monomer, monomer–dimer, and dimer–dimer interaction. The obtained results are compared with experimental data. The equilibrium constant of dimerization in heavy water vapor is shown to exceed that in light water vapor within the whole temperature interval.

Keywords: dimerization constant, heavy water.

1. Introduction

The unusual properties of water (H_2O) have been known since ancient times [1–3]. As a rule, they are explained by the existence of hydrogen bonds that arise between water molecules and result in the formation of molecular complexes, such as dimers, trimers, and so forth [4–6]. The discovery of heavy water (D_2O) and its further study showed that the substitution of hydrogen by deuterium results in substantial changes of properties in comparison with light water. For instance, the ternary point temperature for D_2O is by 3 K higher than the corresponding parameter for H_2O, whereas its critical temperature, on the contrary, is by 4 K lower. The volatility of heavy water is lower than that of light water. Heavy water is more hygroscopic. Even the 30% solution of heavy water in light one is toxic and leads to the death of live organisms. When studying the properties of the vapors of light and heavy waters, it is rather successful to apply the virial equation of state, which is usually confined to the second virial coefficient. The values of second virial coefficient found experimentally for light and heavy waters are different by a factor of 2÷3 in the whole temperature interval [8]. One should expect that this fact can considerably influence the value of equilibrium constant for the molecular dimerization in heavy water vapor.

Note that the differences between H_2O and D_2O manifest themselves not only in thermodynamic but also kinetic properties. In particular, the kinematic viscosity along the saturation curve of heavy water is about 25% higher than the kinematic viscosity of light water in the whole temperature interval [8]. This work aimed at calculating the dimerization degree in saturated D_2O vapor with the help of the second virial coefficient in the equation of state.

2. Determination of the Dimerization Constant for Molecules in Saturated Vapor

It is well known that the equilibrium properties of the dimerization process ($m + m \Leftrightarrow d$) are described by chemical thermodynamic methods. According to the latter, the chemical potentials of monomers, μ_m, and dimers, μ_d, satisfy the equality

$$\mu_d = 2\mu_m. \tag{1}$$

At the same time, they are functions of the corresponding concentrations. Therefore, Eq. (1) is actually an equation for the indicated concentrations. The molar concentrations of water monomers and water molecules united in dimers are defined as

$$c_m = n_m/n_0, \quad c_d = 2n_d/n_0, \tag{2}$$

respectively, where

$$n_0 = n_m + 2n_d = \frac{N_w}{V} \tag{3}$$

is the initial density of water monomers in non-dimerized vapor. According to the concentration definitions for monomers and dimers (2), the condition of their normalization looks like

$$c_m + c_d = 1. \tag{4}$$

It was shown in work [9] that, at small deviations of saturated vapor from the ideality, the concentration of dimers is determined as follows:

$$c_d \approx \zeta + ..., \tag{5}$$

where $\zeta = 2n_0 T K_p(T)$, and $K_p(T)$ is the dimerization constant. In the general case, the chemical potentials of components in a mixture of monomers and dimers contain additional contributions associated with the interaction between particles, which look like

$$\mu_i = \mu_i^{(\mathrm{id})} + \mu_i^{(\mathrm{ex})}, \tag{6}$$

where $i = m, d$. If the dimerization constant and, accordingly, $\zeta = 2n_0 T K_P(T)$ are unknown, the combination of Eq. (1) with the equation of state

$$P = n_0 T(1 + n_0 B_{\exp}(T) + ...) \tag{7}$$

allows one to obtain an explicit expression for $K_p(T)$. In work [9], a relation between the second virial coefficient $B_{\exp}(T)$ in the equation of state, the dimerization constant $K_p(T)$, and the parameters of the intermolecular interaction in partially dimerized water vapor was established. In the linear approximation in the concentration c_d, we have

$$\begin{aligned} &\zeta = \zeta_0, \\ &\zeta_0 = \\ &= \frac{B_{\exp}(T) - v_0^{(m)} + a_{11}/T}{p_1(\frac{1}{2}v_0^{(d)} - \frac{3}{2}v_0^{(m)} - (a_{12} - 2a_{11})/T - 1/(2n_0))}, \end{aligned} \tag{8}$$

where

$$p_1 = 1 + 2n_0(v_0^{(m)} - (a_{11} - \frac{1}{2}a_{12})/T), \tag{9}$$

$v_0^{(m)}$ and $v_0^{(d)}$ are the excluded volumes of a monomer and a dimer, respectively; and a_{11} and a_{12} are the parameters of the van der Waals equation of state for a gas mixture, which describes the excess pressure induced by the monomer–monomer and monomer–dimer attraction forces, respectively. In the quadratic approximation in the concentration c_d, we obtain

$$\zeta = \zeta_0 + h\zeta_0^2 + ..., \tag{10}$$

where

$$\begin{aligned} &h = p_2 + 2p_1 \times \\ &\times \left(1 - \frac{3v_0^{(m)} - v_0^{(d)} - (7a_{11} - 4a_{12} + a_{22})/T}{4\left(-1/n_0 + v_0^{(d)} - 3v_0^{(m)} - (a_{12} - 2a_{11})\right)/T}\right), \\ &p_2 = 2n_0(0.25v_0^{(d)} + v_0^{(m)} - (a_{11} - a_{12} + 0.25a_{22})/T). \end{aligned}$$

The linear approximation in the concentration c_d contains the contributions that involve for only the monomer–monomer and monomer–dimer attraction (the parameters a_{11} and a_{12} of the equation of state in Eq. (8)). At the same time, the quadratic approximation also includes contributions which are a consequence of the dimer–dimer interaction (the parameter a_{22} in the equation of state). For the saturated vapor of light water, the account for those interactions is crucial [9].

3. Calculation of the Dimerization Constant

In order to determine the quantity $\zeta = 2n_0 T K_p(T)$ or, equivalently, $K_p(T)$, we need to know the experimental values of second virial coefficient $B_{\exp}(T)$, excluded volumes $v_0^{(i)}$ $(i = m, d)$, and gravitation constants a_{mn} $(m, n = 1, 2)$ in the van der Waals equation. The value of second virial coefficient for the saturated vapor of heavy water was calculated proceeding from the experimental data on the pressure, density, and temperature at the saturation curve [8]. The quantities $v_0^{(i)}$ $(i = m, d)$ and a_{mn} $(m, n = 1, 2)$ are connected with the behavior of intermolecular interaction potentials. Let us take into account that water monomers and dimers are permanently rotate in the gaseous state, so that the microscopic potentials determining the interaction between water molecules and dimers become effectively averaged [10–13]. A detailed discussion of the potential averaging over the monomer and dimer orientations can be found in works [14, 15].

For the averaged potentials of interaction between water monomers and dimers, let us take advantage of the Sutherland potential

$$U_{ij}(r_{12}) = \begin{cases} \infty, & r_{12} < \sigma_{ij}, \\ -\varepsilon_{ij}(\frac{\sigma_{ij}}{r_{12}})^6, & r_{12} > \sigma_{ij}, \end{cases} \quad (11)$$

where $i, j = m, d$. In this case, the quantities $v_0^{(m)}$ and a_{11} can be found, by using the known procedure [16]. As a result, they equal

$$v_0^{(m)} = \frac{16\pi}{3} r_m^3, \quad a_{11} = \varepsilon_m v_0^{(m)}.$$

In all further calculations, we suppose that the excluded volumes of monomers and dimers coincide with the four-fold volumes of hard spheres with the radii $r_m = 1.58$Å and $r_d = 2.98$Å, respectively. In addition, we adopt that the averaged values of interaction constant equal to those quoted in Table 1 (see work [14]). Those values are approximately four times larger than the constant of dispersion interaction [10–13], because the dipole moment of each water molecule is induced by both the fluctuations of the electron density at neighbor water molecules and changes in the orientations of the bare dipole moments of those molecules (see works [14, 15]).

In order to find $v_0^{(d)}$ and a_{22}, the rotation of dimers has to be taken into consideration. Therefore, the dimer radius should be taken equal to the monomer diameter: $r_d = \sigma_{mm}$. The average polarizability of a rotating dimer $\alpha_d \approx 2\alpha_m$. Therefore, $\varepsilon_d \approx 4\varepsilon_m$. Then

$$v_0^{(d)} = \frac{16\pi}{3} r_d^3 \Rightarrow 8v_0^{(m)}, \quad a_{22} = \varepsilon_d v_0^{(d)} \Rightarrow 32\varepsilon_m v_0^{(m)}.$$

Making allowance for dimer rotations, the interaction between a dimer and a monomer is described by the parameters $r_{dm} = 3r_m$ and $\varepsilon_{dm} = 2\varepsilon_{mm}$, which brings us to the formula

$$a_{12} \approx \frac{27}{4} v_0^{(m)} \varepsilon_{mm}.$$

The results of calculations are presented in Table 2.

4. Discussion of the Obtained Results and Conclusions

The analysis of the data quoted in Table 2 and work [9] demonstrates that the difference between the dimerization constants of heavy and light water vapors is rather substantial. Depending on the temperature, they differ from each other by a factor of 2 to 3. From the principal viewpoint, this is a result of the difference between the character of thermal excitations in heavy and light water dimers. Concerning the corresponding parameters of dimer ground states, they are close to one another. At the same time, the rotational quanta of heavy and light water dimers $Q_i = \hbar^2/2I_i$, where $\hbar$ is Planck's constant, and I_i

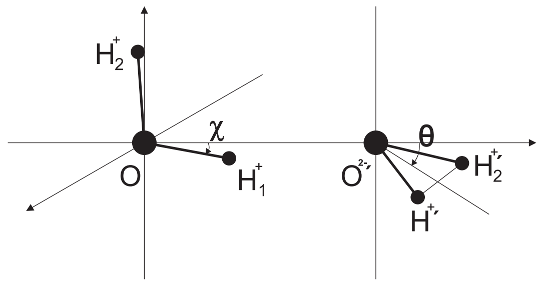

Fig. 1. Equilibrium configuration of a water dimer

Table 1. **Averaged constant of interaction between water molecules, ε_m (k_B is the Boltzmann constant, T_c is the critical temperature)**

T	300 K	400 K	500 K	600 K
ε_m/K_BT_c	3.08	3.05	2.70	1.78

Table 2. **Dimerization degree and the dimerization constant in the saturated vapor of heavy water**

T, K	c_d (D_2O)	$K_p(T)$ (D_2O)
300	0.005	0.1580
325	0.016	0.1279
350	0.034	0.0858
375	0.064	0.0593
400	0.102	0.0387
425	0.149	0.0257
450	0.202	0.0166
475	0.251	0.0104
500	0.295	0.0063
525	0.343	0.0038
550	0.373	0.0022
575	0.439	0.0014
600	0.552	0.0009
625	0.886	0.0008

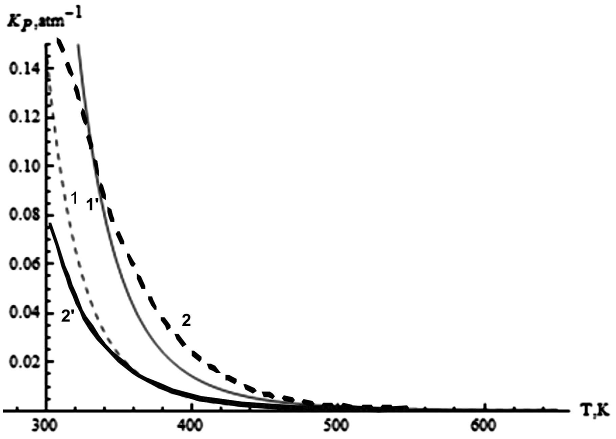

Fig. 2. Temperature dependences of the dimerization constant for the saturated vapors of heavy (*1*) and light (*1′*) waters according to the results of work [19] and for heavy (*2*) and light (*2′*) waters according to the calculations by formula (10)

Table 3. **Rotational quanta of dimers (in cm^{-1} units) for various intermolecular interaction potentials**

Potential model	H_2O			D_2O		
	Ox	*Oy*	*Oz*	*Ox*	*Oy*	*Oz*
GSD	0.21	8.65	0.21	0.18	4.32	0.21
SPC	0.23	8.49	0.22	0.20	4.24	0.24
SPC/E	0.24	8.39	0.22	0.20	4.19	0.25
TIPS	0.24	9.42	0.22	0.20	4.71	0.25
TIP3P	0.24	9.44	0.22	0.20	4.72	0.25
SPCM	0.21	9.58	0.23	0.18	4.79	0.21

Table 4. **Frequencies (in cm^{-1} units) of vibrations in H_2O and D_2O dimers for the SPC and TIPS potentials [18]**

	SPC		TIPS	
	H_2O	D_2O	H_2O	D_2O
ω_1	70.51	49.86	73.71	52.12
ω_2	240.73	170.22	212.63	172.24
ω_3	246.00	219.58	243.59	201.72
ω_4	310.53	233.37	322.32	227.19

is the moment of inertia with respect to the i-th axis, are different. In the case of the dimer configuration depicted in Fig. 1, the rotational quanta of dimers for various potentials of intermolecular interaction are indicated in Table 3. The corresponding differences amount to 15–20% for rotations about the axes x and z and approximately 100% for rotations about the axis y [17].

The energies of vibrational excitations are also considerably different. The frequencies of small vibrations in H_2O and D_2O dimers are compared in Table 4.

In Fig. 2, the results of calculations of the dimerization constant for light and heavy water vapors carried out on the basis of the second virial coefficient in the equation of state are shown, as well as the results of direct calculations of the dimerization constant using the statistical physics methods by determining the internal partition functions of monomers and dimers [19]. It is evident that the dimerization constants determined on the basis of experimental values for the second virial coefficient correlate well with the results of theoretical calculations of the dimerization constants obtained in works [20–22]. One can see that the equilibrium constant of dimerization of heavy water molecules substantially depends on the effects of the interaction between monomers and dimers. It is owing to this interaction that the dimerization of molecules takes place. On the basis of the experimental values of second virial coefficient, we obtained the value of dimerization constant.

Attention should be paid to the fact that the temperature dependences of the dimerization constant for light and heavy waters, which were calculated using different methods, have an opposite relative arrangement. Moreover, at temperatures in a vicinity of the ternary point, a considerable discrepancy is observed between the values obtained for $K_p(T)$ by different methods. Unfortunately, we cannot explain now the origin of this difference, because the values of second virial coefficient in the temperature interval 300–459 K, which were used at calculations, are not quite reliable. It is so because 1) there is a discrepancy in the determination of experimental values for the parameters in the equation of state [8, 23], and 2) there is no possibility to verify the values of $B_{\exp}(T)$ with the help of experimental values obtained for the viscosity of heavy water vapor. In addition, in the case of the direct calculation of $K_p(T)$, the determination accuracy for vibrational frequencies is directly connected with the choice of intermolecular potentials. Unfortunately, it is difficult to specify, which of the potentials used in the literature is the most adequate. Moreover, intramolecular vibrational and rotational modes are considered independent in work [19]. However, at the large values of rotational quantum number, the dimer parameters considerably differ from their values in the ground state, which should be accompanied by changes in the vibrational and rotational modes. At temperatures higher than 400 K, the relative influence of indicated factors decreases, and the values of equilibrium dimerization constant for saturated vapors of light and heavy water molecules agree with the results of direct calculations carried out in work [19]. We intend to study those issues elsewhere in more detail.

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РОЗРАХУНОК КОНСТАНТИ
РІВНОВАГИ ДИМЕРІЗАЦІЇ МОЛЕКУЛ
НАСИЧЕНОЇ ПАРИ ВАЖКОЇ ВОДИ

Р е з ю м е

Робота присвячена визначенню величини та температурної залежності константи рівноваги димеризації молекул насиченої пари важкої води відповідно до другого віріального коефіцієнта рівняння стану. Знайдено вираз для константи рівноваги димеризації молекул водяної пари, який містить доданки, що враховують взаємодію мономер–мономер, мономер–димер і димер–димер. Проведено порівняння отриманих результатів з експериментальними даними. Показано, що у всій області температур константа рівноваги димеризації пари важкої води перевищує константу рівноваги димеризації молекул пари легкої води.