Decomposition of Atmospheric Water Content into Cluster Contributions Based on Theoretical Association Equilibrium Constants

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Water vapor is treated as an equilibrium mixture of water clusters $(H_2O)_i$ using quantum-chemical evaluation of the equilibrium constants of water associations. The model is adapted to the conditions of atmospheric humidity, and a decomposition algorithm is suggested using the temperature and mass concentration of water as input information and used for a demonstration of evaluation of the water oligomer populations in the Earth's atmosphere. An upper limit of the populations is set up based on the water content in saturated aqueous vapor. It is proved that the cluster population in the saturated water vapor, as well as in the Earth's atmosphere for a typical temperature/humidity profile, increases with increasing temperatures.

KEY WORDS: clustering; Earth's atmosphere; equilibrium constant; humidity; water oligomer; water vapor.

1. INTRODUCTION

There is much observational evidence (e.g., Refs. 1–5) supported by theoretical studies (e.g., Refs. 6–10) that water vapor contains, in addition to monomeric units, some populations of water oligomers $(H_2O)_i(g)$. Recently, the oligomers have been recognized [1–5] to be important for understanding some properties of and processes in the Earth's atmosphere. In that connection there is a need for a reliable evaluation of the oligomer populations under atmospheric conditions, i.e., information still missing in

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the literature. Since it is still difficult to obtain comprehensive data of this type, this paper attempts to fill the gap using the available sophisticated quantum-chemical sources of information.

2. CLUSTER MODEL OF WATER VAPOR

Let us consider an equilibrium mixture of the gas-phase species H_2O, $(H_2O)_2,...,$ $(H_2O)_i,....$ The partial pressures p_i of the associates obey equilibrium conditions,

$$K_{p,i} = p_i p_1^{-i} \tag{1}$$

with $K_{p,i}$ denoting the equilibrium constants of the associations (especially, $K_{p,1} = 1$),

$$iH_2O(g) \rightleftharpoons (H_2O)_i(g) \tag{2}$$

interconnected with the changes in the standard Gibbs energy $\Delta G^0_{T,i}$ of associations (2) (the standard-state choice throughout the paper—an ideal gas at 1 atm $= 1013.25$ mb $= 101,325$ Pa pressure),

$$K_{p,i} = \exp[-\Delta G^0_{T,i}/(RT)] \tag{3}$$

where T and R stand for the absolute temperature and the gas constant, respectively. Although it is a rather formal approach, we can quite generally admit clusters of any dimensions. If the presence of components other than water is excluded, the total pressure P of the gas phase is simply related to the partial pressures of clusters, p_i:

$$P = \sum_{i=1}^{\infty} p_i \tag{4}$$

(Clearly enough, if a cluster cannot in fact exist under given conditions, this will manifest in the zero value of the related association equilibrium constant.) Introducing the mole fraction of the monomer in the equilibrium mixture, x_1, the following master equation can be obtained:

$$P = \sum_{i=1}^{\infty} K_{p,i}(x_1 P)^i \tag{5}$$

If the value x_1 is available, the population of any cluster can be evaluated, e.g., in terms of its mole fraction:

$$x_i = K_{p,i} x_1^i P^{i-1} \tag{6}$$

Alternatively (and typically in atmospheric observations), the conditions in the gas phase can be characterized by the water-vapor density (i.e., mass per volume), C. Within the cluster approach the overall water concentration C is straightforwardly related to individual cluster concentrations, c_i:

$$C = \sum_{i=1}^{\infty} c_i \qquad (7)$$

Applying the perfect-gas equation of state to each cluster group, Eq. (7) can be reset into the following form (M denoting the water molecular mass):

$$C = \frac{M}{RT} \sum_{i=1}^{\infty} i p_i = \frac{M}{RT} \sum_{i=1}^{\infty} i K_{p,i} (x_1 P)^i \qquad (8)$$

In principle, knowing the association equilibrium constants $K_{p,i}$, Eqs. (5) and (8) can numerically be solved with respect to the unknown x_1 (and P) with any prescribed precision.

3. EVALUATIONS OF THE ASSOCIATION EQUILIBRIUM CONSTANTS $K_{p,i}$

The situation in theoretical evaluations of the dimerization equilibrium constant $K_{p,2}$ is quite satisfactory. Namely, the MCY-B modification [11] of the powerful MCY water–water pair interaction potential [12] has recently been proved [13, 14] to yield so far the best agreement with the available, fragmentary, observed data. The theoretical $K_{p,2}$ values [13] were evaluated in terms of the rigid-rotor and harmonic-oscillator partition functions based on molecular constants derived exclusively from the MCY-B potential. Particularly, it has turned out that the MCY-B temperature dependence of the standard Gibbs energy of water dimerization practically coincides with an optimum-fit curve constructed within the observed points. Thus, the MCY-B $K_{p,2}$ values represent a reliable data set applicable, moreover, in a wide temperature interval.

However, for higher water clusters the MCY-B $K_{p,i}$ equilibrium constants are not available yet. Thus, for the purposes of this paper their values were deduced from the EPEN potential data [15] for small oligomers ($2 < i < 6$, i.e., trimers to pentamers). Namely, it has been shown [14] recently that the EPEN $\Delta G^0_{T,i}$ terms [15] for the oligomers are a linear function of the number i of water molecules in cluster, or in other words the value of the increment δG^0_T when passing from the $\Delta G^0_{T,i}$ to the $\Delta G^0_{T,i+1}$ term is practically constant (equidistant Gibbs energy levels).

Moreover, the temperature dependence of the increment δG_T^0 itself is again linear. Supposing that both these linear relations found are valid generally, the value of $\Delta G_{T,i}^0$ can simply be extrapolated for any i at any temperature. In order to increase the reliability of such a prediction, the beginning of the extrapolating scale in this paper is adjusted not at the EPEN $K_{p,2}$ value [15] but at the more precise MCY-B value [13], while still keeping the value of the δG_T^0 increment and its temperature dependence derived from the EPEN data. Clearly enough within the equidistant model of the $\Delta G_{T,i}^0$ level spacing, the ratio of subsequent equilibrium constants is essentially constant (it is not critically important that the value of parameter z itself will be changed with changing standard-state choice—a change in standard state cannot introduce any change in the composition of the cluster mixture):

$$z = \frac{K_{p,i+1}}{K_{p,i}}, \qquad (i > 1) \tag{9}$$

where

$$z = \exp[-\delta G_T^0/(RT)] \tag{10}$$

i.e., the $K_{p,i}$ $(i > 1)$ values form a geometrical series.

4. ALGORITHM FOR EVALUATION OF CLUSTER POPULATIONS

The simplifying presumption (9) not only enables generation of the $K_{p,i}$ values $(i > 2)$ but also allows infinite summations (5) and (8) to be expressed in a closed form, viz.,

$$P = Q + K_{p,2} Q^2/S \tag{11}$$

$$C = \frac{MQ}{RT} [1 + (K_{p,2} - z)(1 + S)Q]/S^2 \tag{12}$$

where

$$Q = x_1 P \tag{13}$$

$$S = 1 - zQ \tag{14}$$

In principle, Eqs. (11) and (12) can further be condensed into just one relation between C and P or x_1, but for their numerical solution an iterative approach is quite satisfactory: to vary x_1 over the interval $(0; 1)$,

for a chosen value of x_1 to evaluate the P term from (11), then C from (12) and, finally, to repeat the procedure with an improved x_1 guess as long as a required consistency with the input C value is reached.

5. NUMERICAL RESULTS AND DISCUSSION

The values of the MCY-B $K_{p,2}$ terms and of the derived $K_{p,i}$ equilibrium constants $(2 < i < 6)$ are presented in Table I. The temperature dependence of the z factor is noteworthy. While at e.g., 200 K (for the standard state chosen), the value of $K_{p,i}$ increases by one order of magnitude per each added monomer unit, at room temperature the same process is connected with a decrease of one order of magnitude. The applicability of the equidistant model of the $\Delta G^0_{T,i}$ level spacing is well established for small oligomers $(2 < i < 6)$ because the Gibbs energy property follows [14] directly from the available theoretical data. The problem of applicability of Eq. (9) to higher clusters is not critical in this paper because the pressure regions studied do not allow any significant populations of clusters with $i > 5$.

There are only two variable parameters in the model—temperature T and density C. For the purposes of this paper, the temperature is always lower than the critical temperature of water and thus the density values should not exceed the density of the saturated water vapor [17, 18] (with the possible exception of undercooled vapor [18]). Then it is useful to know the behavior of the cluster model just at the saturated vapor conditions [i.e., in addition to establishing chemical equilibria (2), also conditions of physical equilibrium are to be fulfilled—either for liquid/vapor or for solid/vapor coexistence]. Figure 1 presents the course of water dimer

Table I. MCY-B Equilibrium Constants[a] $K_{p,2}$ and Derived
Equilibrium Constants[a] $K_{p,i}$ $(2 < i < 6)$

T (K)	$K_{p,2}$ (atm^{-1})	$K_{p,3}$ (atm^{-2})	$K_{p,4}$ (atm^{-3})	$K_{p,5}$ (atm^{-4})
200	1.509×10^0	9.968×10^1	6.586×10^3	4.352×10^5
250	2.016×10^{-1}	3.008×10^{-1}	4.487×10^{-1}	6.693×10^{-1}
273.15	1.032×10^{-1}	4.258×10^{-2}	1.757×10^{-2}	7.251×10^{-3}
298.15	5.674×10^{-2}	7.313×10^{-3}	9.425×10^{-4}	1.215×10^{-4}
350	2.207×10^{-2}	4.326×10^{-4}	8.477×10^{-6}	1.661×10^{-7}

[a] Instead of the application of the thermodynamically correct dimensionless standard quantities [16], the usual practice of dimensioned equilibrium constants is followed (the underlying standard-state choice—an ideal-gas phase at 1 atm = 101,325 Pa pressure).
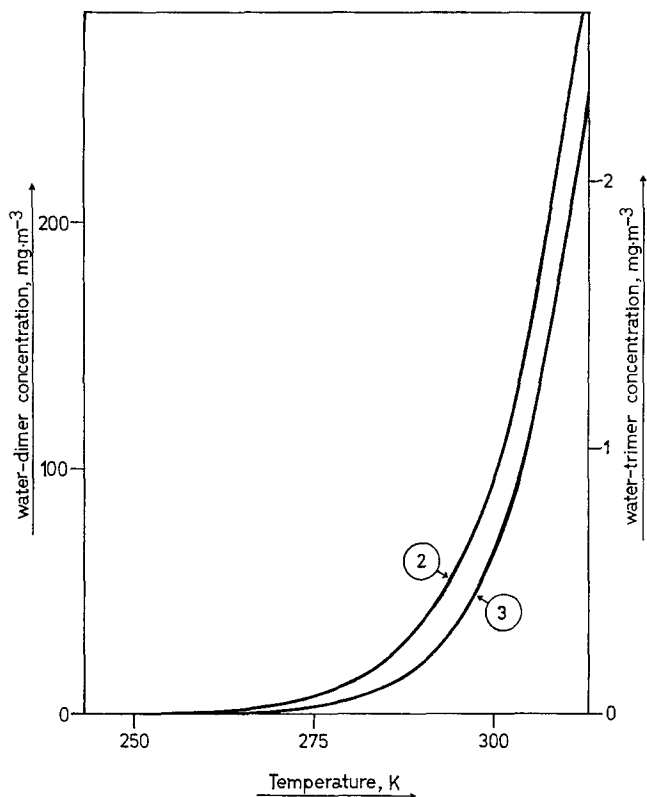
Fig. 1. Temperature dependence of the water dimer (2) and trimer (3) concentrations under conditions of the saturated [17] water vapor.

and trimer concentrations in the saturated vapor within the temperature region relevant for atmospheric conditions. The relatively fast increase in the oligomer populations with temperature is to be noted. Table II contains decomposition of the saturated water-vapor density for the first five members in the series $(H_2O)_i(g)$. In addition to the c_i terms, mole fractions, x_i, are considered, too. In both these scales the cluster populations ($1 < i < 6$) increase with increasing temperatures. This increase is in fact a result of competition between a decrease in the $K_{p,i}$ terms [Eq. (3)] and a nearly exponential increase [18] in the saturated steam pressure. Under the conditions surveyed in Table II only the concentration of dimer (and, of course, of monomer) exceeds a threshold of $1 \text{ mg} \cdot \text{m}^{-3}$. However, the dimer mole fraction exceeds, for example, the value of 0.1 and 1 % only at about 10 and 80°C, respectively.

Table II. Decomposition[a] of the Saturated Water-Vapor Density[b] into Contributions of Water Oligomers $(H_2O)_i(g)$

$T(K)$	C	$i=1$		$i=2$		$i=3$		$i=4$		$i=5$	
		c_1	x_1	c_2	x_2	c_3	x_3	c_4	x_4	c_5	x_5
253.15	1.074	1.074	99.98	5×10^{-4}	0.023	1×10^{-6}	3×10^{-5}	2×10^{-9}	5×10^{-8}	4×10^{-12}	8×10^{-11}
263.15	2.358	2.356	99.96	2×10^{-3}	0.038	5×10^{-6}	8×10^{-5}	1×10^{-8}	1×10^{-7}	3×10^{-11}	3×10^{-10}
273.15	4.847	4.841	99.94	6×10^{-3}	0.062	2×10^{-5}	2×10^{-4}	7×10^{-8}	4×10^{-7}	2×10^{-10}	1×10^{-9}
283.15	9.399	9.381	99.90	0.018	0.097	8×10^{-5}	3×10^{-4}	3×10^{-7}	9×10^{-7}	1×10^{-9}	3×10^{-9}
293.15	17.300	17.249	99.85	0.050	0.15	3×10^{-4}	5×10^{-4}	1×10^{-6}	2×10^{-6}	6×10^{-9}	7×10^{-9}

[a] Concentration terms, C and c_i, are given in $g \cdot m^{-3}$, mole fractions, x_i, as percentages.
[b] Temperature dependence of the standard water-vapor density taken from Ref. 17.

It has become common (see, e.g., Ref. 19) to record temperature and vapor density in various levels of the Earth's atmosphere using a radiosonde and to condense the observed data into temperature and density profiles. Figure 2 presents a typical example [19], following the conventional coding of height above the Earth's surface by the term of atmospheric pressure. The temperature and humidity profiles were employed in the decomposition treatment and the related height profile of the water dimer and trimer concentration was constructed (Fig. 2). Clearly enough, the highest density of water oligomers is to be typically expected in the lowest atmospheric layers. Nevertheless, in the atmospheric pressure region of 700–800 mb, the water dimer and trimer concentrations are to be
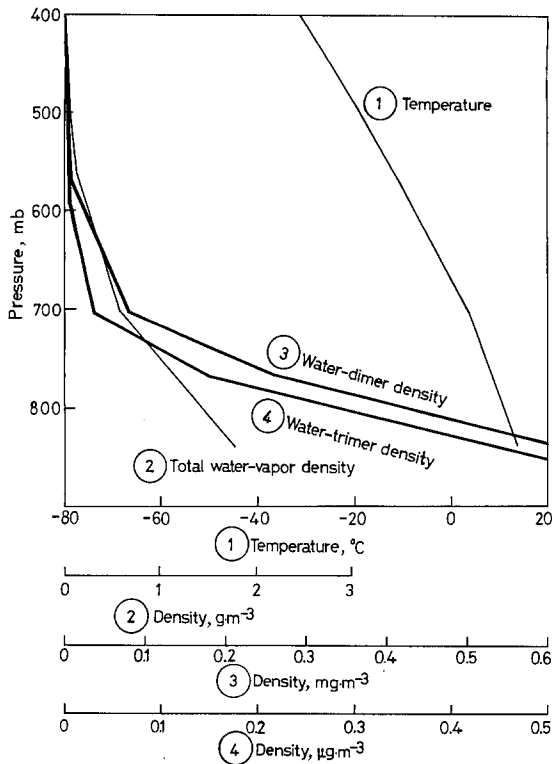

Fig. 2. Water dimer concentration profile derived from a temperature–humidity atmospheric profile from radiosonde observations [19]. The height above the Earth's surface is coded by the term of atmospheric pressure at the vertical axis in mb (1 mb = 100 Pa); the atmospheric pressure region considered corresponds approximatively to the heights between 1 and 7 km.

expected of the order of $0.1 \, \text{mg} \cdot \text{m}^{-3}$ and $0.1 \, \mu\text{g} \cdot \text{m}^{-3}$, respectively. It should be mentioned, finally, that an inversion in the temperature and/or density atmospheric profile can create a nonuniform cluster-density height profile.

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