

EQUILIBRIUM THERMODYNAMIC STATE OF WATER VAPOR AND THE COLLISIONAL INTERACTION OF MOLECULES

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We consider all kinds of double and triple collisional interactions of molecules in a gas. Relation of the coefficients of the virial equation of state to dimer and trimer equilibrium constants is analyzed. The “excluded volume” for water vapor is estimated quantitatively. The volume is interpreted as an effective volume which is characterized by the range of molecular repulsive forces and is related to the collisional interaction of free monomers. Empirical data on water vapor in thermodynamic equilibrium are used for determination of the second and third virial coefficients, which serve for estimating the upper limits of the dimer and trimer equilibrium constants of water in the temperature range 273–1273 K.

1. INTRODUCTION

The history of studying the interaction of molecules is very long (see, e.g., [1]). Its ancient Greek origins can be traced, in particular, in the book by Titus Lucretius Carus “On the nature of things” [2]. I. Newton (1643–1727) proposed a hypothesis of the electromagnetic nature of the interaction between atoms. R. J. Bošković (1711–1787), a Croatian scientist, first introduced the law of interaction between the “particles of matter,” according to which any pair of point particles is subject to an oscillating force between them, which indefinitely increases as the particles approach each other and transforms to a Newtonian force of attraction at large distances. Bošković’s law of interaction is actually the first model potential used to explain the physical properties of matter. The forces acting between neutral atoms and molecules are called van der Waals forces, which is directly related to the derivation of the van der Waals equation of state (J. D. van der Waals, 1837–1923). This equation allows for both the attraction between gas molecules and the finiteness of their volume, which, in accordance with modern concept, implies the emergence of significant forces of intermolecular repulsion in a highly compressed gas.

A consistent theory of intermolecular forces started to develop after the creation of quantum mechanics. Approximate solution of the Schrödinger equation (E. Schrödinger, 1887–1961) for the motion of electrons in the field of fixed nuclei makes it possible to find the dependence of the energy of the system on the distance between nuclei in the form of a characteristic curve whose asymptotes are the horizontal and vertical positive semiaxes and the minimum corresponds to the equilibrium internuclear distance, i. e., the balance between repulsive and attractive forces. This energy is called the potential energy for the nuclear motion, or simply the potential. The interaction potential of two molecules is obtained in a similar way, but this requires averaging of the interaction over all kinds of the molecule orientation in space, and on the horizontal axis is the distance between the centers of mass of the molecules.

An analytical expression for the intermolecular interaction potential, which allowed one both to explain the experimental data on the viscosity and the data pertaining to the equation of state of some gases, was proposed by Jones (D. E. Lennard-Jones, 1894–1954) considered the father of modern quantum

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chemistry. He assumed that both the repulsive and attractive parts of the interaction potential are inverse power functions of the intermolecular distance [3].

Originally, the formation of dimers has not been associated with the pairwise collisional interactions of monomers for the kinetic energy of two colliding molecules under normal conditions is always greater than the “zero” energy corresponding to the total energy of the monomers making up a dimer, after its intermolecular bond dissociation. It was noted that a third body taking the excess energy in a collision is necessary for the dimer formation.

Paper [4], which analyzes the collisions of structureless monomers, is crucial for the modern understanding of the pairwise molecular interaction. In that paper, it was pointed out for the first time that short-lived metastable or quasibound binary molecules resulting from collisions should be taken into account. The ideas in this work were later generalized to the collisional interaction between nonpolar and polar and between polar and polar molecules, as well as interaction with the ions [5]. Subsequently, these ideas were developed by Vigasin (see, e.g., [6] and references therein). The most recent work, which gives an overview of the state of the art on the nature of the pairwise molecular interaction in a rarefied gas, is paper [7].

In the present work, we have ordered extensive material known to date on the intermolecular interaction in gases as applied to the formation of small molecular complexes in water vapor. We aim at determining the relation of the coefficients of the virial equation of state of a gas to parameters characterizing the number of binary and ternary molecules, i.e., dimers and trimers formed in a monomolecular gas under equilibrium conditions as a result of the collisional interaction. Note that for the dimers, an analytical expression for such a relation was first obtained in [4], and for the trimers, to the best of our knowledge, the relation was not established. In our paper, we present a detailed derivation of these relations. A new practical result of this work is also estimation of the upper limit of the number of ternary molecules in equilibrium water vapor over a wide range of temperatures. This estimation, as is shown in what follows, can be made by using empirical data on the state of water vapor [8]. The necessity for such an estimation is due, in particular, to the need for a quantitative description of the water vapor spectra measured at temperatures above critical and pressures of up to hundreds of atmospheres (see, e.g., [9] and references therein). The contribution of small water clusters, i.e., dimers, trimers, etc., in such spectra is large enough, and extracted quantitative information makes it possible to extrapolate the studied characteristics to standard conditions. Hence, the analysis of such spectra contributes to the understanding of the role of water clusters in the atmospheric absorption and, ultimately, facilitates the solution of the Earth’s energy balance problem.

2. PAIRWISE INTERACTIONS OF MOLECULES

The result of a collision between two molecules in a gas is fully determined by their relative speed of approach v , impact parameter b , i.e., minimum approach of the molecules to each other in the case of maintaining a rectilinear motion, and interaction potential $U(r)$, where r is the distance between the molecules. The trajectories of the molecules in the coordinate system bound with one of them in the cases of repulsive and attractive potentials are shown in Fig. 1. In reality, the interaction potential is always repulsive for short impact distances and is always attractive for long impact distances.

It can rigorously be shown (see, e.g., [10]) that if the distance between the colliding structureless molecules is studied as a function of time, then its kinematics is the same as that of a material point with the mass $\mu = m_1 m_2 / (m_1 + m_2)$ and the kinetic energy $K = \mu v^2 / 2$, where m_1 and m_2 are the masses of the colliding molecules, if such a point moves in the field of the effective potential $U_{\text{eff}}(r, L) = U(r) + L/r^2$, where $L = Kb^2$. Given that the angular momentum of the colliding molecules is $M = \mu v b$ and the moment of inertia is $I = \mu r^2$, we have $L/r^2 = M^2/(2I)$, which corresponds to the rotational energy of the interacting pair relative to the axis through the center of mass of the molecules.

A typical family of the effective-potential curves corresponding to different values of L is shown in Fig. 2. The presence of a minimum and a maximum on the potential curves for small values of L means that the colliding molecular pair may be inside the potential well. In terms of the magnitude of the total

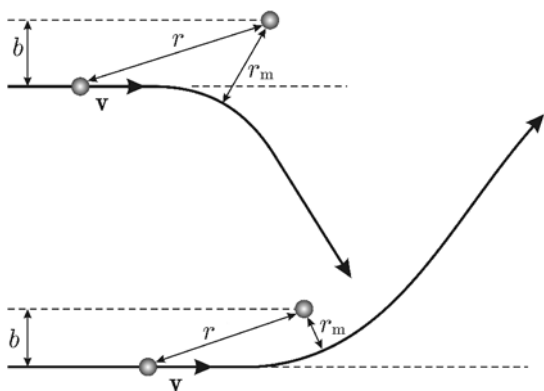


Fig. 1. Trajectories of the colliding molecules for the repulsive (upper curve) and attractive (lower curve) interaction potentials. The distance of the minimum approach of the molecules is denoted as r_m . This figure is adapted from [1].

In a collision with the third molecule, the metastable complex can impart its excess kinetic energy to it and pass to a bound state, which is apparently the only mechanism for the appearance of bound dimers.

For large values of L , the effective potential has neither a minimum, nor a maximum. In this case, the energy of the molecules is too great for the formation of a complex, and their collision resembles the collision of elastic spheres.

Qualitative features of the collisional interaction of polyatomic molecules are the same. Account for the anisotropy, which arises in the collisions of polyatomic molecules, results in that quasibound pair states can be formed, due, e. g., to the degrees of freedom of monomers in the dimer. In this case, excess kinetic energy of a pair passes, for example, to the internal rotation of monomers in the dimer around the axis along the bond between the monomers or to their other degrees of freedom.

Thus, all possible pairwise interacting molecules in a gas can be divided into three groups: (i) free molecules, (ii) metastable quasibound dimers, and (iii) bound dimers.

Consider the equation of state of a gas in virial form:

$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \quad (1)$$

Here, p , R , and V_m are, respectively, the pressure, universal gas constant, which is sometimes called molar, and the molar volume, and B and C are, respectively, the second and third virial coefficients, which are

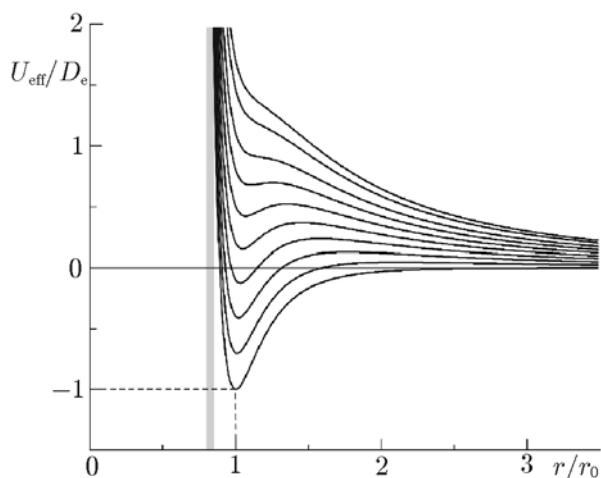


Fig. 2. A family of curves describing the effective potentials of intramolecular interaction, which correspond to the 6–12 Lennard-Jones potential for different values of the angular momentum of the interacting pair. The energy is normalized to the depth D_e of the potential well and the distance is normalized to the equilibrium intermolecular distance r_0 . The normalized angular momentum $L/(D_e r_0^2)$ is varied from 0 to 2.7. The range of intermolecular distances r/r_0 between 0.8 and 0.85 is shown gray.

functions of the temperature T . The term pV_m is stipulated by the forces acting on the walls of the gas-containing vessel, the term RT arises due to the kinetic energy of the molecules, and all other terms are related to the interaction between the gas molecules. In the case of an ideal gas, where the molecules can be represented as infinitesimal material points and their collisions are instantaneous and absolutely elastic, the right-hand side of the equation has only unity left. Collisional interaction of molecules, as was shown above on the example of pairwise interactions, is not instantaneous and not elastic. It is exactly the mechanism that makes the actual gases different from the ideal ones.

In order to show the role of the dimer formation, we consider the latter process as a reversible reaction of association of two monomers:



For such a reaction, according to the law of mass action (C.M. Guldberg, 1836–1902 and P. Waage, 1833–1900), the rate of the dimer formation is a product of the probability α that each interacting molecule hits the same point in space, the probability β of the dimer formation, and number densities $[M] = n_m$ of the interacting molecules:

$$V_1 = \alpha[M]\alpha[M]\beta = \alpha^2\beta n_m^2, \quad (3)$$

while the rate of the dimer decay reaction is a product of the decay probability δ and the dimer number density $[D] = n_d$:

$$V_2 = \delta[D] = \delta n_d. \quad (4)$$

Under equilibrium conditions, these rates are identical. The ratio n_d/n_m^2 , which is obtained from Eqs. (3) and (4) for $V_1 = V_2$ as

$$\frac{n_d}{n_m^2} = \frac{\alpha^2\beta}{\delta} = K_2^c, \quad (5)$$

is constant at a given temperature. This quantity is called the equilibrium constant of the reaction. If the interacting molecules can be regarded as an ideal gas, then at a constant temperature, their number densities are directly proportional to their partial pressures. Therefore, the equilibrium constant can be defined in terms of partial pressures of the initial and final products of the reaction:

$$\frac{p_d}{p_m^2} = K_2^p = K_2. \quad (6)$$

Such a definition of the equilibrium constant is more common, but less rigorous since the reaction of association (2) is caused by the collisions of molecules, whose number is proportional to the number of molecules per unit volume, i.e., number density rather than pressure, which is secondary.

In order to reveal the relation between the equilibrium constant and the second virial coefficient of the equation of state, we assume, following the ideas of Fowler (R. H. Fowler, 1889–1944) [11], that the difference of the gas from the ideal one is entirely due to the dimer formation. In terms of the intermolecular interactions, this means that at this stage of analysis, it is assumed that the attractive forces between molecules are present and the repulsive forces are neglected, i.e., that the interaction potential is only attractive. This approximation means that the gas which under nonequilibrium initial conditions comprised only monomers is regarded as a mixture of ideal monomers and dimers easily converting to each other under in equilibrium conditions. This mixture satisfies the equation of state

$$pV = (\nu_m + \nu_d) RT, \quad (7)$$

where V is the volume of the mixture, and ν_m and ν_d are the numbers of moles of the monomers and dimers, respectively, which formed under equilibrium conditions from ν moles of the initial gas. Using the definition of the amount of matter as the ratio of the mass m of the matter to the molar mass M , we obtain the

following relation for this mixture:

$$\nu = \frac{m}{M} = \frac{m_m + m_d}{M} = \frac{\nu_m M_m + \nu_d M_d}{M} = \frac{\nu_m M_m + \nu_d 2M_m}{M_m} = \nu_m + 2\nu_d. \quad (8)$$

Using definition (6) and taking into account that in this approximation,

$$\frac{p_m}{\nu_m} = \frac{p_d}{\nu_d} = \frac{RT}{V}, \quad (9)$$

we obtain

$$\nu_d = K_2 RT \frac{\nu_m^2}{V}. \quad (10)$$

For one mole of the initial gas when $\nu = 1$ and $V = V_m$, from Eqs. (8) and (10) we obtain a quadratic equation for ν_m :

$$2K_2 \frac{RT}{V_m} \nu_m^2 + \nu_m - 1 = 0, \quad (11)$$

which has only one positive root

$$\nu_m = \frac{V_m}{4K_2 RT} \left(\sqrt{1 + \frac{8K_2 RT}{V_m}} - 1 \right). \quad (12)$$

Transforming the equation of state (7) to the form

$$\frac{pV_m}{RT} = \frac{\nu_m + 1}{2}, \quad (13)$$

substituting Eq. (12), and expanding the right-hand side of the resulting expression in powers of $1/V_m$, we obtain

$$\frac{pV_m}{RT} = 1 - K_2 RT \frac{1}{V_m} + 4(K_2 RT)^2 \frac{1}{V_m^2} + \dots \quad (14)$$

It follows from a comparison of Eqs. (1) and (14) that for such a gas,

$$B(T) = -K_2 RT. \quad (15)$$

Account for the repulsive forces in the intermolecular interactions is directly related to the concept of the so-called excluded volume b_0 introduced by van der Waals. In this concept, the role of the repulsion, i. e., the presence of the repulsive part of the interaction potential, reduces to that the molecule precludes the penetration of other molecules into the volume it occupies. Then the equation of state of our hypothetic gas with allowance for the repulsion in Eq. (7) will go over to the formula

$$p(V_m - b_0) = (\nu_m + \nu_d) RT, \quad (16)$$

which, as in the previous case, can be transformed to the form

$$\frac{pV_m}{RT} = \frac{\nu_m + 1}{2} \left(1 - \frac{b_0}{V_m} \right)^{-1} = 1 + (b_0 - K_2 RT) \frac{1}{V_m} + (4K_2^2 R^2 T^2 - K_2 RT b_0 + b_0^2) \frac{1}{V_m^2} + \dots \quad (17)$$

Hence,

$$B(T) = b_0 - K_2 RT. \quad (18)$$

Using the methods of statistical mechanics (see, e. g., [4, 12]), it can be shown rigorously that the equilibrium constant K_2 can be represented as the sum of the components corresponding to the metastable

and bound dimers, i. e.,

$$K_2 = K_m + K_b, \quad (19)$$

and that the second virial coefficient of Eq. (1) corresponds to all pairwise interactions of the molecules and can therefore be divided into three parts,

$$B(T) = B_f(T) + B_m(T) + B_b(T), \quad (20)$$

where the coefficient B_f is responsible for the collisions of free molecules, B_b allows for the presence of bound pairs of molecules, or dimers, in a gas in equilibrium state, and the coefficient B_m allows for the presence of metastable dimers. Substituting Eq. (19) into Eq. (18) and comparing the resulting equality with Eq. (20), we obtain

$$B_b(T) = -K_b(T)RT, \quad B_m(T) = -K_m(T)RT, \quad B_f(T) = b_0. \quad (21)$$

Thus, it is seen that the excluded volume is directly related to the pairwise interaction of free molecules [4]. It is interesting to note that in [4] it is stated without proof that at low temperatures, the coefficient $B_f(T)$ and, therefore, b_0 become negative, which led the authors of [4] to the conclusion about the limitation of the concept of excluded volume.

3. TRIPLE INTERACTIONS

It is well known that the role of triple interactions in common gases under standard conditions is even less significant than that of the binary interactions. This can be demonstrated by comparing the curves corresponding to the virial equation of state (1) shortened to one, two, and the first three virial terms. These curves, corresponding, e. g., to the gas phase of water vapor at room temperature, coincide with each other with graphical accuracy. The relative difference in the slopes between the first and the second and between the second and the third curves is only about 10^{-4} and $3 \cdot 10^{-9}$, respectively. The difference between the curves becomes noticeable only at very high pressures, which are attainable for water vapor at high temperatures near and above the critical temperature. It is worth mentioning the well-known fact that the virial equation of state truncated after the term with the third virial coefficient describes the available experimental data within their uncertainties for pressures of up to about 20 atm [8].

By analogy with the dimer, the trimer is formed by a collisional interaction of three monomers. The process occurs step by step in a few collisions. At first, a metastable dimer should be formed. After the transition to a bound state, this dimer can attach another monomer due to van der Waals forces to form a metastable trimer. Attachment of the third monomer to the dimer, while it is in a metastable state, is also theoretically possible, but is much less likely.

Despite the fact that the reaction of the formation of a trimer from monomers proceeds in two stages via the formation of a dimer, the equilibrium constant of a trimer, by analogy with the constant of a dimer, can be defined as

$$K_3^c = \frac{n_t}{n_m^3}, \text{ or } K_3^p = \frac{p_t}{p_m^3} = K_3. \quad (22)$$

The equilibrium constant of trimers, as well as that of dimers, is a function of temperature.

To obtain the relation of K_3 to the third virial coefficient, we perform calculations, which are similar to Eqs. (16)–(18), for a mixture of ideal monomers, dimers, and trimers (see Appendix 1). It follows that

$$C(T) = b_0^2 - b_0 K_2 RT + 4K_2^2 (RT)^2 - 2K_3 (RT)^2. \quad (23)$$

The coincidence of the first three terms on the right-hand side of Eq. (23) with the coefficient of $1/V^2$ in Eq. (17) confirms that this part of the third virial coefficient and, therefore, of the triple interactions in a gas is due to the interaction of only monomers and dimers. By analogy with the pairwise interactions, all kinds of triple interactions are divided in accordance with the terms of Eq. (23) into a triple collisional interaction of free monomers, collisional interaction of a free monomer with a free dimer, interaction of

two dimers (presumably, this includes the dimer–dimer collisions resulting in the formation of a trimer and a monomer), and, finally, the formation of trimers. It should be noted that in a gas in thermodynamic equilibrium, the trimers, as well as the dimers, can be both in bound and metastable states.

4. EXCLUDED VOLUME

The excluded volume for water vapor can be estimated by constants of the van der Waals equation of state. The relation of b_0 to critical pressure p_c and critical temperature T_c at which there is no distinction between the liquid and gaseous phases, is well known (see, e. g., [13]):

$$b_0 = \frac{RT_c}{8p_c}. \quad (24)$$

The values of the critical parameters for water vapor are known (see, e. g., [8]): $T_c = 647.096$ K and $p_c = 22.0640$ MPa. Substituting them into Eq. (24) yields a constant value $b_0 = 30.481$ cm³/mol for all temperatures.

The authors of [14] come to the conclusion that the excluded volume in the Van der Waals equation should be regarded not as a volume occupied by the molecules themselves, but as a volume determined by the effective range of the attractive forces or, in other words, as an interaction volume b_a of the molecules, which depends, in particular, on their dipole moments. Using the experimental data on the state of water vapor, the authors of [14] found that the interaction volume is 38.5 cm³/mol. This quantity, as the most reliable, is used both in work [15], whose results of experimentally determining the dimer equilibrium constant are considered the most reliable at present, and in [16], where the dimer equilibrium constant is calculated by the modern methods of quantum chemistry. However, the identity of the term “interaction volume,” which was introduced by the authors of [14], and the volume relating to the concept of an “interaction cross section” $\sigma = \pi b_e^2$, where b_e is the effective radius of the molecule interaction cross section, which is widely used in spectroscopy, is often the reason of a misunderstanding.

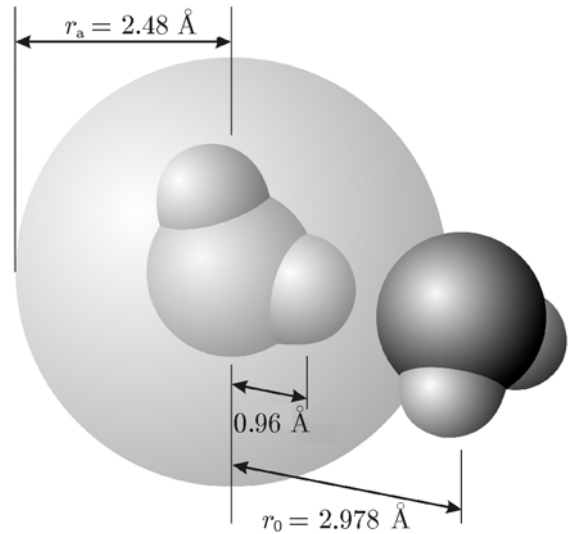
Spectroscopic measurements show (see, e. g., [17]) that for the polar molecules, the sphere volume determined by the radius b_e , may exceed b_a severalfold. Nevertheless, in the modern book describing collisional effects in the molecular spectra [18] it is suggested that to extend the applicability range of conventional profiles of the collisionally broadened lines, the excluded-volume effect should be taken into account by the method of the gas concentration correction in the form

$$\tilde{n} = n \left[1 + \left(\frac{5}{12} \pi b_e^3 \right) n \right]. \quad (25)$$

The numerical coefficient of the sphere volume in Eq. (25) shows that only part of the collisional interaction volume, which is about 1/3 of the total volume, is significant for the correction of the gas concentration. In Appendix 2, it is demonstrated that, e. g., for the water vapor molecules at room temperature and atmospheric pressure, only 1/120 of their total volume is significant for the observed gas-kinetic properties.

The reason for such a confusion is apparently not only the poorly used term, but also the fact that the authors of [14] characterize the gas-kinetic interaction volume by the effective range of attractive forces, although it would be more pertinent in this case to talk about the range of repulsive forces. Attractive forces for the polar molecules are determined by the dipole field, which decreases with distance from the molecule as $1/r^3$. Even at large distances, these forces are sufficiently effective to change the rotational state of a molecule or the phase of its rotation by more than π due to the collisional interaction. This becomes clear when the average translational kinetic energy of a gas molecule, which is known to be equal to $3kT/2$, is compared with the energy required to change the molecule rotational state in a collision. It is known (see [19] and references therein) that in a collisional interaction the selection rules that are valid for the electric dipole transitions are predominantly observed when the polar molecules pass from one state to another.

Fig. 3. Relative position of two water molecules for the equilibrium structure of the $(\text{H}_2\text{O})_2$ dimer [22]. The indicated distance 0.96 \AA between the centers of the oxygen and hydrogen atoms corresponds to the equilibrium structure of H_2O . A sphere of radius r_a centered at the center of the oxygen atom belonging to the donor molecule of a dimer corresponds to the excluded volume $b_a = 38.5 \text{ cm}^3/\text{mol}$. For comparison, the sphere radius corresponding to the collisional interaction cross section determined spectroscopically (see Appendix 2) amounts to 12.2 \AA for 296 K.



Hence, the energy required to change the rotational state of the molecule in a collision can be estimated by the frequency of the rotational spectral line and is equivalent to the energy of the radiation quantum absorbed by the molecule in the corresponding transition. For water vapor at a room temperature of 296 K, the average frequency of the rotational line with allowance for the statistical weight of the molecule states is approximately 7.2 THz or 240 cm^{-1} (according to calculations using the data from HITRAN [20] and Eq. (A2.4) of Appendix 2, in which, instead of the line width, its frequency is used). The average translational kinetic energy of the molecules for the same temperature corresponds to approximately 308 cm^{-1} . Thus, even a part of the translational energy of the disturbing molecule, which will be transferred to a collision partner in the dipole–dipole interaction at a considerable distance, is sufficient for the disturbed molecule to change its rotational state, which manifests itself as the broadening of the corresponding spectral line. Repulsive forces associated with the overlap of the electron orbitals of the interacting molecules are very short-range. For example, for the 6–12 Lennard-Jones potential, which is a widely known approximation frequently used to describe the interaction of nonpolar spherical molecules (see, e. g., [21]), the repulsive force decreases as $1/r^{12}$. However, it is exactly the forces that determine the distance of minimum approach of the colliding molecules [4] and, hence, the excluded volume which should be interpreted as the effective volume of intermolecular interaction due to the repulsive forces. It is exactly the forces that could stipulate the nonlinear gas-kinetic properties of gases, even in such a hypothetical case where the molecules do not have the attractive part of the interaction potential.

The radius determining this effective volume can be estimated from the equilibrium intermolecular distance in the dimers, which corresponds to the balance of attractive and repulsive forces at zero temperature. At present, this parameter is known with good accuracy for many molecules from spectroscopic experiments with low-temperature molecular beams. Thus, for the water dimer, whose equilibrium structure is shown in Fig. 3, the distance $r_0 = 2.978 \text{ \AA}$ [22]. Obviously, this value is an upper limit for the radius of the sphere of efficient gas-kinetic interaction. The distance of minimum approach of the monomers is somewhat less than the equilibrium value. This parameter in a dimer depends on its internal energy, and in a collision of free molecules it is determined by their total kinetic energy. For example, for the 6–12 Lennard-Jones potential, the distance of minimum approach is between 80 and 85% of the equilibrium distance (see Fig. 2). This implies that the effective radius of the sphere of the water molecule interaction at high temperatures can be estimated as $2.38\text{--}2.53 \text{ \AA}$, and the specific volume of the interaction sphere amounts to $34\text{--}41 \text{ cm}^3/\text{mol}$, which demonstrates very good agreement with the above-mentioned values 30.5 and $38.5 \text{ cm}^3/\text{mol}$ obtained, respectively, from the van der Waals equation by substitution of known experimental values of the critical parameters and by analysis of the results of the gas-kinetic experiments [14].

At low temperatures, the distance of minimum approach almost coincides with the equilibrium internuclear distance of a dimer and the corresponding excluded volume is $67 \text{ cm}^3/\text{mol}$. It follows from an

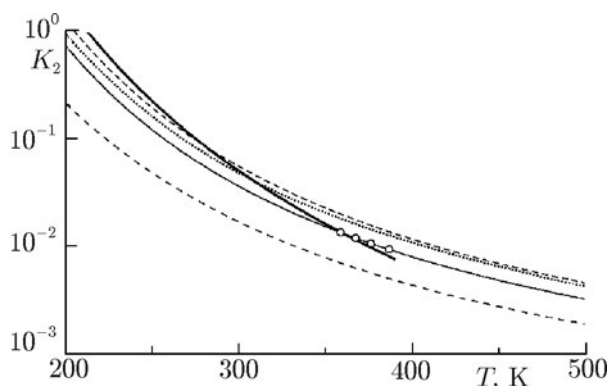


Fig. 4. Equilibrium constant K_2 of the dimer in water vapor, which was determined in the previous papers. The data from [15] are given by circles (experiment), a solid thin line (extrapolation by Eq. (11) from [15] on the assumption that variations in the enthalpy ΔH_2 and the entropy ΔS_2 during the dimer formation are temperature independent), and dashed lines, the distance between which corresponds to one standard deviation of found values of K_2 . The value determined by the second virial coefficient from [23] without allowance for the excluded volume is shown by a dotted line. The result of calculation by the methods of quantum chemistry [16] is shown by a solid bold line.

analysis of the curves in Fig. 2 that the distance of minimum approach at high temperatures is almost constant, which is due to a very rapid increase in the repulsive forces as the molecules approach each other. Thus, with increasing temperature, the excluded volume will first vary abruptly, probably exponentially, from about 67 to 37 cm³/mol and then will decrease very slowly, remaining almost unchanged.

An experimental estimate of b_0 can be obtained using Eq. (18) if the coefficients B and K_2 are determined independently. The most complete compilation of known data on the coefficient $B(T)$ for water vapor can be found in [23]. In the temperature range from 350 to 800 K, the uncertainty B , according to the estimates in [23], is about 2%. Outside this range, the uncertainty increases: it reaches 10% as the temperature increases up to 1200 K and amounts to 5% as the temperature decreases down to 300 K. Extrapolation to the lower temperatures guarantees the correct qualitative rather than quantitative behavior. The quantity $K_2(T)$ for water vapor is much poorer known. The measurements of $K_2(T)$ by the thermal conductivity of water vapor [15], performed at four temperatures ranging from 358 to 386 K, and calculations by the methods of quantum chemistry for the temperature range 190–390 K [16] are generally adopted as the most reliable source of information. These data are well consistent with each other (see Fig. 4). Both the experimental and calculated curves in the temperature range of the experiment lie below the curve which corresponds in this figure to the equilibrium constant determined by the second virial coefficient (see Eq. (18)) without allowance for b_0 . Allowance for b_0 makes this difference still greater. This means that the quantity b_0 determined in such a way will have the negative values.

To explain this result, we analyze the uncertainty of $K_2(T)$. The authors of both [15] and [16] do not make any estimation. However, the uncertainty of the experimental values of K_2 can be expressed through variations in the enthalpy ΔH_2 and the entropy ΔS_2 during the dimer formation (and their uncertainties analyzed in detail in [15]), which are analytically related to the constant K_2 (see Eq. (11) in [15]). Such an estimate shows that the uncertainty of the values of K_2 measured in [15] is 75–100%. This means that within the measurement error, the data of [15] are in good agreement with the values of $K_2(T)$ obtained from the second virial coefficient.

A somewhat underestimated value of $K_2(T)$ obtained in [16] in the temperature range of the experiment [15] can be explained by the fact that the metastable state of the dimer were not taken into account in the calculations. In fact, the authors of [15] calculated the value of $K_b(T)$. However, the number of metastable states can be significant, especially in the upper part of the temperature range considered [7, 29], and these contribute to the second virial coefficient [4]. The principle of measurement of K_2 in [15] automatically takes into account the contribution of not only bound, but also part of the metastable states. Only the metastable states of the dimer whose lifetimes are less than the time between collisions do not contribute to the thermal conductivity. However, they contribute to the second virial coefficient. This also explains the slightly underestimated values of K_2 obtained in the experiment [15].

It should also be mentioned that according to the estimates presented above, the contribution of b_0 to K_2 for 360–370 K is fairly small and amounts to about 10%.

These arguments show that b_0 cannot be estimated in such a way because of the insufficient accuracy with which the value of $K_2(T)$ is known at present.

On the basis of this analysis we have decided to use hereafter the value $b_0 = b_a = 38.5 \text{ cm}^3/\text{mol}$, which was obtained in [14] and corresponds to the above estimates, for all the temperatures. The radius corresponding to such an effective excluded volume is $r_a = 2.48 \text{ \AA}$. The sphere corresponding to this radius is shown in Fig. 3 for comparison with the conventional form of the monomer and dimer water molecules.

5. EQUILIBRIUM CONSTANTS OF DIMERS AND TRIMERS

If the separation of molecules into bound and metastable states is neglected, then the following relation between the equilibrium constant of dimers and the second virial coefficient can be found from Eq. (18):

$$K_2(T) = \frac{b_0 - B(T)}{RT}, \quad (26)$$

and the equilibrium constant of trimers can be found from Eq. (23):

$$K_3(T) = -\frac{C(T) - b_0^2 + b_0 K_2 RT - 4K_2^2 (RT)^2}{2(RT)^2}. \quad (27)$$

It was mentioned in the preceding section that the quantity $B(T)$ for water vapor at temperatures exceeding room temperature is fairly well known [23]. Such a compilation for $C(T)$, to the best of our knowledge, was not performed. However, the values of $B(T)$ and $C(T)$ can be determined by the data on the parameter pV/T of the gas state as follows.

With allowance for the fact that the molar concentration ρ_m is related to the molar volume by $\rho_m = 1/V_m$, Eq. (1) can be written as

$$\frac{p}{\rho_m RT} = 1 + B(T)\rho_m + C(T)\rho_m^2 + \dots \quad (28)$$

Then the coefficients $B(T)$ and $C(T)$ can be found via the first- and second-order partial derivatives, respectively, of the left-hand side of Eq. (28) with respect to the molar concentration:

$$B(T) = \lim_{\rho_m \rightarrow 0} \left[\frac{d}{d\rho_m} \left(\frac{p}{\rho_m RT} \right) \right], \quad C(T) = \frac{1}{2} \lim_{\rho_m \rightarrow 0} \left[\frac{d^2}{d\rho_m^2} \left(\frac{p}{\rho_m RT} \right) \right]. \quad (29)$$

The most complete compilation of known thermodynamic characteristics of water vapor was made in [8]. The data obtained in this compilation are currently the standard reference data. In numerical form, they can be extracted from the common-access database NIST Chemistry Webbook [24] for the temperature range 273–1275 K and pressures from 0 to 1000 MPa, i. e., about 9869 atm. The declared relative uncertainty of the data is less than 0.1%. For each given temperature, the code of the database [24] makes it possible to calculate the positions of up to two hundreds of points (p, ρ_m) with up to 12 significant digits. This is quite sufficient for the approximation of these points by a polynomial of the sixth to eighth order and for single-valued calculation of B and C by Eqs. (29) using the standard computation codes. A 10-K temperature step turned out to be sufficient for the approximation of the temperature dependencies $B(T)$ and $C(T)$ over

TABLE 1. Coefficients of approximating function (30) for $B(T)$ and $C(T)$.

	$B(T), \text{ cm}^3/\text{mol}$	$C(T), \text{ cm}^6/\text{mol}^2$
s	6	9
a_0	$-7.804242 \cdot 10^6$	$-5.2331832 \cdot 10^{11}$
a_1	$8.345651 \cdot 10^4$	$4.0791610 \cdot 10^9$
a_2	$-4.212794 \cdot 10^2$	$-1.7322727 \cdot 10^7$
a_3	$1.242946 \cdot 10^0$	$4.6636033 \cdot 10^4$
a_4	$-2.409822 \cdot 10^{-3}$	$-8.3911426 \cdot 10^1$
a_5	$3.017768 \cdot 10^{-6}$	$1.0171702 \cdot 10^{-1}$
a_6	$2.518957 \cdot 10^{-9}$	$-8.0946594 \cdot 10^{-5}$
a_7	$1.350628 \cdot 10^{-12}$	$4.1124096 \cdot 10^{-8}$
a_8	$-4.134191 \cdot 10^{-16}$	$-1.2609901 \cdot 10^{-11}$
a_9	$5.530774 \cdot 10^{-20}$	$1.9229771 \cdot 10^{-15}$

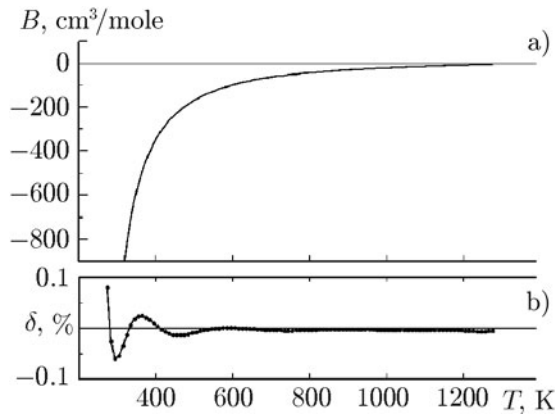


Fig. 5. The second virial coefficient of the equation of state of water vapor, which was obtained in this paper on the basis of [23, 24]: the temperature dependence (a) and the percentage difference δ of the obtained values from approximating function (30) with the coefficients from Table 1 (b).

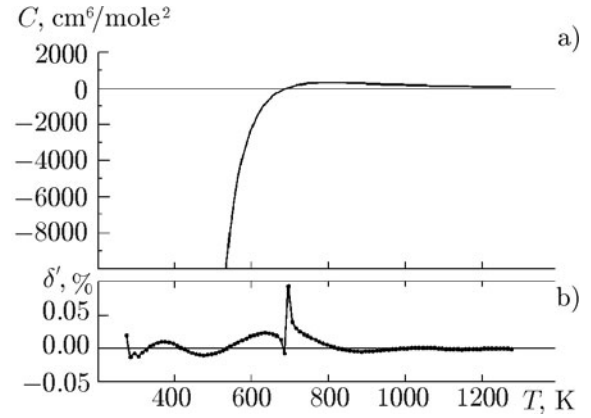


Fig. 6. The third virial coefficient of the equation of state of water vapor, which was obtained in this paper on the basis of [23, 24]: the temperature dependence (a) and the percentage difference δ' of the obtained values from approximating function (30) with the coefficients from Table 1 (b).

the entire above-mentioned range by a polynomial function of the form

$$F_1(T) = \left(\frac{100}{T}\right)^s \sum_{i=0}^9 a_i T^i, \quad (30)$$

where a_i are constant coefficients, $s = 6$ for $B(T)$, and $s = 9$ for $C(T)$. The use of such a function, unlike the approximating function employed in [23], makes it unnecessary to choose the initial values of the varied coefficients and yields a more accurate description of the data. The polynomial order and the number of significant digits in the coefficients were chosen such that the relative deviation of the function from the values of B and C found by the above-mentioned method did not exceed the relative accuracy 0.1% of the initial thermodynamic data. The coefficients found by fitting the function (30) to the values of B and C are presented in Table 1.

The temperature dependence of the second virial coefficient obtained in such a way is shown in Fig. 5. In its lower part, the dots show the percentage difference of the B values calculated by Eq. (30) from the corresponding values determined from thermodynamic data. Similar dependencies for $C(T)$ are presented in Fig. 6.

The presented dependencies $B(T)$ and $C(T)$ are in good agreement with similar curves shown in Figs. 7.19 and 7.20 of [8], which confirms that the found values of B and C are correct. Note that the approximating function determined in our paper gives qualitatively correct dependencies with extrapolation both to much lower and higher temperatures, up to about 1800 K for $B(T)$ and up to about 1400 K for $C(T)$.

Figure 7 shows the relative difference of our approximation of $B(T)$ from the results of [23]. The form of the curve exactly corresponds to the description of the uncertainty of the approximation in [23]. This indicates that the authors of [23] estimated the accuracy of their approximation in the same way. Hence, for the further calculations of the coefficients K_2 and K_3 by Eqs. (26) and (27), respectively, we used our data on $B(T)$, which are in much more exact agreement with the empirical data of [8, 24].

The results of calculation of the equilibrium constants of dimers and trimers by Eqs. (26) and (27) are presented in Fig. 8.

To obtain analytical expressions corresponding to the temperature dependencies of K_2 and K_3 , we employed the approximating function $F_2(T)$, which was similar to that used in [16] for the parameterization

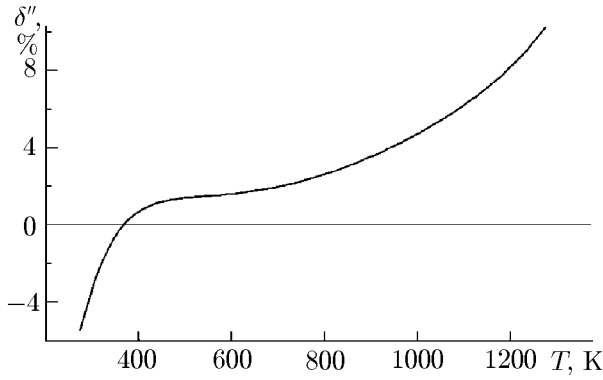


Fig. 7. Percentage difference δ'' of the approximation of $B(T)$ from the results of [23].

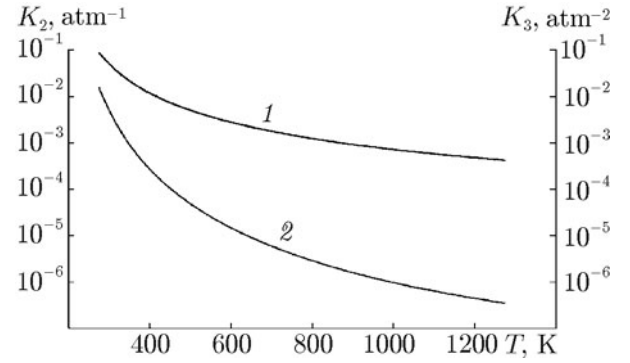


Fig. 8. Equilibrium constants of dimers (curve 1) and trimers (curve 2) in water vapor, which were obtained in this paper.

of K_2 :

$$F_2(T) = \exp \left[\left(\sum_{i=0}^5 c_i T^i \right) / T \right]. \quad (31)$$

The coefficients c_i determined as a result of approximation of the obtained dependencies $K_2(T)$ and $K_3(T)$ by function (31) are shown in Table 2. The order of the approximating polynomial for K_2 and K_3 and the number of significant digits in its coefficients were chosen as a tradeoff between the most exact correspondence to the obtained values and appropriate behavior of the function extrapolated to the higher and lower temperatures. For the coefficient K_2 in the temperature range 273–1275 K, the deviation of approximating function (31) from the obtained values did not exceed 0.8%. The deviation increases up to 10% when the function is extrapolated down to 200 K and up to 1500 K. For the coefficient K_3 in the range 273–1275 K, the deviation is no more than 1.7% and increases up to 10% when the function is extrapolated down to 207 K and up to 1440 K. It should be noted that in this case, the extrapolation results are compared with the values of K_2 and K_3 obtained from the values of B and C , which also result from an extrapolation of function (30).

TABLE 2. Coefficients of function (31) for the equilibrium constants of dimers and trimers in water vapor.

	$K_2(T), \text{atm}^{-1}$	$K_3(T), \text{atm}^{-2}$
c_0	$2.1833 \cdot 10^3$	$4.3410 \cdot 10^3$
c_1	$-1.2660 \cdot 10^1$	$-2.4395 \cdot 10^1$
c_2	$1.2122 \cdot 10^{-2}$	$2.3617 \cdot 10^{-2}$
c_3	$-1.6900 \cdot 10^{-5}$	$-3.3435 \cdot 10^{-5}$
c_4	$1.0485 \cdot 10^{-8}$	$2.1021 \cdot 10^{-8}$
c_5	$-2.4717 \cdot 10^{-12}$	$-4.9974 \cdot 10^{-12}$

6. DISCUSSION AND CONCLUSIONS

Many authors (see, e. g., [15, 25]) note that separation of water vapor into monomers, dimers, etc. is conditional. This is attributed to the fact that due to the presence of metastable states in a gas there is a variety of forms of molecules (binary, ternary, etc.) ranging from long-lived dimers, trimers, etc. which are rigidly bound by hydrogen bonds and have a well-defined spatial structure, to, for example, partial orbiting of one molecule around another in a collision. The latter can also be described by a very short-lived dimer. The division into stable and metastable states, as follows from a comparison of the total internal energy of a molecular complex with the dissociation energy of bonds between its constituent monomers [4], is clear only from the mathematical point of view. If a dimer or trimer is formed by polyatomic molecules, then the total internal energy of such a complex may significantly exceed its dissociation energy and be distributed over many vibrational and rotational degrees of freedom of its constituent monomers. The lifetime of the complex in a metastable state can be much larger than the average time between collisions. Hence, its both spectroscopic and thermodynamic properties will be exactly the same as those of a rigidly bound complex.

Naturally, as the temperature increases, the number of metastable states also increases and, therefore,

the boundaries between monomers and their complexes become less pronounced. Nevertheless, analysis of the water vapor spectra under equilibrium conditions at a temperature of 650 K and a pressure of 5 to 130 atm [9] shows that even with such extreme parameters, which are more typical of the steam engines than of the terrestrial conditions, can the contributions of the monomers, dimers, and trimers be singled out in the observed spectrum.

It is of interest to compare the values of the equilibrium constants obtained from the analysis of these high-temperature spectra with the calculations in this paper. The experimental values of K_2 and K_3 for a dimer and a trimer amount to $0.87 \cdot 10^{-3} \text{ atm}^{-1}$ and $2.2 \cdot 10^{-6} \text{ atm}^{-2}$, respectively, and the calculated values are $2.19 \cdot 10^{-3} \text{ atm}^{-1}$ and $9.06 \cdot 10^{-6} \text{ atm}^{-2}$, respectively. Recall that the equilibrium constants calculated in this paper are estimates of their upper limits since they include the total contribution of both bound and all metastable states of binary and ternary molecules. The constants obtained from the observed spectra take into account all bound states and only part of the metastable states. In accordance with this, the experimental values are about factors 2.5 and 4 less than the values calculated for the dimers and trimers, respectively, which may be considered a very good agreement.

It should be noted that under normal conditions, e. g., in the atmosphere at a temperature of 20.5°C and a relative humidity of 50%, the water complexes are very few. The partial pressure of water vapor is about 9 Torr. In this case, the partial pressure of dimers and trimers is, to our estimates, 5 mTorr and 11 μ Torr, respectively. Nevertheless, a comparative analysis of the dimer spectrum intensity and the observed absorption shows that it is exactly the water dimers that stipulate almost all the experimentally observed quadratic-humidity part of the continuum absorption of the atmosphere in the millimeter-wave range [26–28] and a significant part of this absorption in the infrared range [7]. It also follows from the estimates of dimer absorption line intensity that the resolved rotational spectrum of the water dimer under equilibrium thermodynamic conditions similar to atmospheric can be observed using the existing spectrometers [30].

In conclusion, we summarize the main results of this work.

We have analyzed the relation between the collisional interaction of molecules and the coefficients of the virial equation of state of a gas. We have derived analytical expressions relating the second and third virial coefficients to the equilibrium constants of dimers and trimers and the excluded volume interpreted as an effective volume which characterizes the range of repulsive molecular forces and is associated with the collisional interaction of free monomers. The results obtained in this paper are used to determine the parameters characterizing the collisional interaction of water vapor molecules. In particular, we have estimated the excluded volume and its temperature dependence and performed an empirical parameterization of the second and third virial coefficients in the temperature range of 273–1273 K. It is shown that the presented parameterization of the second virial coefficient offers a more than an order of magnitude higher precision of correspondence to the empirical thermodynamic data on the state of water vapor than its predecessor. Parameterization of the third virial coefficient has not been performed to date, as far as the authors are aware. Using the found virial coefficients and the value of the excluded volume, we parameterize temperature dependencies of the equilibrium constants of the water dimers and trimers, including the total contribution of bound and metastable states, which can be used as estimates both in the interpretation of experimental data and in various calculations.

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APPENDIX 1

DERIVATION OF THE ANALYTICAL RELATION BETWEEN COEFFICIENTS IN THE VIRIAL EQUATION OF STATE WITH THE EQUILIBRIUM CONSTANTS K_2 , K_3 , AND B_0

Assume that a gas in equilibrium is a mixture of ideal monomers, dimers, and trimers. Interaction of free molecules is taken into account by introducing the effective excluded volume b_0 . The equation of state of such a gas has the form

$$p(V - b_0) = (\nu_1 + \nu_2 + \nu_3) RT,$$

where the monomer, dimer, and trimer are denoted by the subscripts 1, 2, and 3, respectively.

The amount of substance in moles is given by the formula

$$\nu = \frac{m}{M} = \frac{m_1 + m_2 + m_3}{M} = \frac{\nu_1 M_1 + \nu_2 M_2 + \nu_3 M_3}{M} = \frac{\nu_1 M_1 + \nu_2 2M_1 + \nu_3 3M_1}{M_1} = \nu_1 + 2\nu_2 + 3\nu_3.$$

Passing to the molar concentrations, we obtain

$$n_1 = \frac{\nu_1}{V}, \quad n_2 = \frac{\nu_2}{V}, \quad n_3 = \frac{\nu_3}{V}, \quad n = n_1 + 2n_2 + 3n_3, \quad (\text{A1.1})$$

$$p \left(1 - \frac{b_0}{V} \right) = (n_1 + n_2 + n_3) RT. \quad (\text{A1.2})$$

We define the equilibrium constants as

$$K_2 = K_2^c = \frac{n_2}{n_1^2}, \quad K_3 = K_3^c = \frac{n_3}{n_1^3}.^1$$

Then from Eq. (A1.1) we have

$$n = n_1 + 2K_2 n_1^2 + 3K_3 n_1^3 = n(n_1), \quad (\text{A1.3})$$

and from Eq. (A1.2) we obtain

$$\frac{p}{RT} = \frac{n_1 + K_2 n_1^2 + K_3 n_1^3}{1 - b_0/V}. \quad (\text{A1.4})$$

For one mole of the initial gas of monomers when $V = V_m$ and $n = 1/V_m$, from Eqs. (A1.4) and (A1.3) we obtain that

$$\begin{aligned} \frac{pV_m}{RT} &= \frac{p}{RT} \frac{1}{n} = \frac{n_1 + K_2 n_1^2 + K_3 n_1^3}{(1 - b_0/V_m)(n_1 + 2K_2 n_1^2 + 3K_3 n_1^3)} = \frac{n_1 + K_2 n_1^2 + K_3 n_1^3}{(1 - b_0 n)(n_1 + 2K_2 n_1^2 + 3K_3 n_1^3)} \\ &= \frac{n_1 + K_2 n_1^2 + K_3 n_1^3}{[1 - b_0(n_1 + 2K_2 n_1^2 + 3K_3 n_1^3)](n_1 + 2K_2 n_1^2 + 3K_3 n_1^3)} = F(n_1). \end{aligned} \quad (\text{A1.5})$$

We can express the quantity n_1 through n in the third-order equation (A1.3), substitute this quantity into Eq. (A1.5), and expand the resulting relation in a power series of n , or can use the inverse function according to the evident equalities $n = f(n_1)$ and $n_1 = f^{-1}(n)$.

By definition of the Taylor series expansion,

$$F[n_1(n)] = F[n_1(n)] \Big|_{n=0} + \frac{dF}{dn} \Big|_{n=0} n + \frac{1}{2} \frac{d^2 F}{dn^2} \Big|_{n=0} n^2 + \dots$$

¹ Note that the notation of equilibrium constants, which is adopted to simplify the subsequent expressions, is different from that used in the text of this paper where they were defined through partial pressures. Obviously, in the approximation used, where vapor is considered a mixture of ideal monomers, dimers, and trimers, the constants defined via number densities and pressures are unambiguously related to each other by the formula $pV = \nu RT$, whence it follows that $n = p/(RT)$. Thus, $K_2^c = K_2^p RT$ and $K_3^c = K_3^p (RT)^2$.

According to the rules of taking derivatives of a complex function, we have

$$\frac{dF[n_1(n)]}{dn} = \frac{dF(n_1)}{dn_1} \frac{dn_1}{dn} = \frac{dF}{dn_1} \left(\frac{dn}{dn_1} \right)^{-1}, \quad (\text{A1.6})$$

$$\begin{aligned} \frac{d^2F[n_1(n)]}{dn^2} &= \frac{d}{dn} \left[\frac{dF}{dn_1} \left(\frac{dn}{dn_1} \right)^{-1} \right] = \frac{d^2F}{dn_1^2} \frac{dn_1}{dn} \left(\frac{dn}{dn_1} \right)^{-1} + \frac{dF}{dn_1} \frac{d}{dn} \left[\left(\frac{dn}{dn_1} \right)^{-1} \right] \\ &= \frac{d^2F}{dn_1^2} \left(\frac{dn}{dn_1} \right)^{-2} + \frac{dF}{dn_1} \frac{d}{dn_1} \left[\left(\frac{dn}{dn_1} \right)^{-1} \right] \frac{dn_1}{dn} \\ &= \frac{d^2F}{dn_1^2} \left(\frac{dn}{dn_1} \right)^{-2} + \frac{dF}{dn_1} \frac{d}{dn_1} \left[\left(\frac{dn}{dn_1} \right)^{-1} \right] \left(\frac{dn}{dn_1} \right)^{-1}. \end{aligned} \quad (\text{A1.7})$$

Thus, finding the coefficients of expansion of the function F in a power series of n reduces to taking partial derivatives of the functions $F(n_1)$ and $n(n_1)$ with respect to n_1 , which is not difficult:

$$\frac{dn}{dn_1} = 1 + 4K_2n_1 + 9K_3n_1^2, \quad (\text{A1.8})$$

$$\begin{aligned} \frac{dF}{dn_1} &= \frac{\frac{d}{dn_1}(n_1 + K_2n_1^2 + K_3n_1^3)}{(n_1 + 2K_2n_1^2 + 3K_3n_1^3) - b_0(n_1 + 2K_2n_1^2 + 3K_3n_1^3)^2} \\ &\quad - \left\{ \frac{d}{dn_1} [1 - b_0(n_1 + 2K_2n_1^2 + 3K_3n_1^3)] (n_1 + 2K_2n_1^2 + 3K_3n_1^3) \right\} \\ &\quad \times \frac{n_1 + K_2n_1^2 + K_3n_1^3}{[(n_1 + 2K_2n_1^2 + 3K_3n_1^3) - b_0(n_1 + 2K_2n_1^2 + 3K_3n_1^3)^2]^2} \\ &= \frac{n_1 + 2K_2n_1 + 3K_3n_1^2}{(n_1 + 2K_2n_1^2 + 3K_3n_1^3) - b_0(n_1 + 2K_2n_1^2 + 3K_3n_1^3)^2} \\ &\quad - [1 + 4K_2n_1 + 9K_3n_1^2 - 2b_0(1 + 4K_2n_1 + 9K_3n_1^2)(n_1 + 2K_2n_1^2 + 3K_3n_1^3)] \\ &\quad \times \frac{n_1 + K_2n_1^2 + K_3n_1^3}{[(n_1 + 2K_2n_1^2 + 3K_3n_1^3) - b_0(n_1 + 2K_2n_1^2 + 3K_3n_1^3)^2]^2}. \end{aligned} \quad (\text{A1.9})$$

The expression for the second virial coefficient $B = dF/dn|_{n=0}$ is obtained by substitution of Eqs. (A1.9) and (A1.8) into Eq. (A1.6) and tending n_1 to zero, since for $n \rightarrow 0$ the number density $n_1 \approx n$. As a result, we have an expression identical to that found in [4]:

$$B = b_0 - K_2.$$

In a similar way, we calculate d^2F/dn_1^2 , substitute the result together with Eqs. (A1.8) and (A1.9) into Eq. (A1.7), and tend n_1 to zero. As a result, we obtain the desired expression for the third virial coefficient:

$$C = \left. \frac{1}{2} \frac{d^2F}{dn^2} \right|_{n=0} = b_0^2 + 4K_2^2 - b_0K_2 - 2K_3.$$

APPENDIX 2

RELATION BETWEEN SPECTROSCOPIC AND GAS-KINETIC INTERACTION VOLUMES OF THE WATER VAPOR MOLECULES

Spectroscopic collisional interaction cross section can be determined fairly exactly by measurement of the spectral linewidth $\Delta\nu$ as [17]

$$\sigma = \pi b_e^2 = \frac{2\pi \Delta\nu}{nv}, \quad (\text{A2.1})$$

where n is the number density and v is the velocity of molecules. Expressing n through pressure, using the ideal-gas approximation, determining the velocity through the average thermal velocity known from the Maxwell distribution, and passing from the linewidth to the pressure-independent parameter $\gamma = \Delta\nu/p$ of the collisional broadening, we obtain

$$\sigma = \gamma \sqrt{\pi^3 m k T / 2}. \quad (\text{A2.2})$$

The volume in which the molecule interaction resulting in broadening of the spectral lines takes place is written as

$$\frac{4}{3}\pi b_e^3 = \gamma^{3/2} \frac{4}{3}\pi \left(\frac{k T m \pi}{2} \right)^{3/4}. \quad (\text{A2.3})$$

All information needed to determine this volume in the case of water vapor at room temperature can be found, for example, in the HITRAN spectroscopic database [20]. It should be borne in mind that the broadening of each spectral line is a result of time-averaged interaction between the molecules in quantum states corresponding to the lower and upper energy levels of the transition and all other gas molecules. The collisional broadening parameter in Eq. (A2.3), averaged over the entire ensemble of gas molecules, can be found as an average value of this parameter over all rotational lines of the ground vibrational state. This value is calculated with statistical weight equal to the population of the lower level corresponding to the rotational transition with allowance for the rotational degeneracy:

$$\gamma = \frac{\sum_i \gamma_i (2J_i + 1) \exp[-E_i^{\text{low}}/(kT)]}{\sum_i (2J_i + 1) \exp[-E_i^{\text{low}}/(kT)]}, \quad (\text{A2.4})$$

where J is the quantum number corresponding to the total angular momentum in the lower state and E^{low} is the energy of the lower level of the rotational transition. Neglect of excited vibrational states is justified by that these are virtually not populated at room temperature. The Boltzmann factor for the population of the lowest vibrational state of H_2O is only 0.0004.

Such an estimation for the spectroscopically defined volume of the collisional interaction of water-vapor molecules at 296 K under the atmospheric pressure yields about $4600 \text{ cm}^3/\text{mol}$, which is about a factor of 120 greater than the interaction volume $38.5 \text{ cm}^3/\text{mol}$ determined by the gas-kinetic methods in [14]. The corresponding radius of the collisional cross section is almost a factor of 5 greater.

REFERENCES

1. I. G. Kaplan, *Introduction to the Theory of Intermolecular Interactions* [in Russian], Nauka, Moscow (1982).
2. T. Lucretius Carus, *On the Nature of Things*, Penguin, London (1994), Book 2, verses 333–477.
3. J. E. Jones, *Proc. Roy. Soc. Lond. A*, **106**, 441 (1924).
4. D. E. Storgyn and J. O. Hirschfelder, *J. Chem. Phys.*, **31**, 1531 (1959).
5. J. M. Calo and J. H. Brown, *J. Chem. Phys.*, **61**, 3931 (1974).

6. A. A. Vigasin, in: C. Camy-Peyret and A. A. Vigasin, eds., *Weakly Interacting Molecular Pairs: Unconventional Absorbers of Radiation in the Atmosphere*, Kluwer, Dordrecht (2003), p. 111.
7. I. V. Ptashnik, K. P. Shine, and A. A. Vigasin, *J. Quantum Spectrosc. Rad. Transfer*, **112**, 1286 (2011).
8. W. Wagner and A. Pruss, *J. Phys. Chem. Ref. Data*, **31**, 387 (2002).
9. M. Yu. Tretyakov and D. S. Makarov, *J. Chem. Phys.*, **134**, 084306 (2011).
10. L. D. Landau and E. M. Lifshitz, *Mechanics*, Butterworth–Heinemann, Oxford (1976).
11. R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press, Cambridge (1939).
12. T. L. Hill, *Statistical Mechanics*, McGraw-Hill, New York (1956).
13. A. N. Matveev, *Molecular Physics* [in Russian], Vysshaya Shkola, Moscow (1981), Ch. 4.
14. J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).
15. L. A. Curtiss and D. J. Frurip, *J. Chem. Phys.*, **71**, 2703 (1979).
16. Y. Scribano, N. Goldman, R. J. Saykally, and C. Leforestier, *J. Phys. Chem. A*, **110**, 5411 (2006).
17. C. H. Tawnes and A. L. Schawlow, *Microwave Spectroscopy* McGraw-Hill, New York (1955), Ch. 13.
18. J.-M. Hartman, C. Boulet, and D. Robert, *Collisional Effects on Molecular Spectra*, Elsevier, Amsterdam (2008), p. 48.
19. P. W. Daly and T. Oka, *J. Chem. Phys.*, **53**, 3272 (1970).
20. L. S. Rothman, I. E. Gordon, A. Barbe, et al., *J. Quantum Spectrosc. Rad. Transfer*, **110**, 533 (2009). <http://www.cfa.harvard.edu/HITRAN>.
21. J. Buldyreva, N. Lavrentieva, and V. Starikov, *Collisional Line Broadening and Shifting of Atmospheric Gases*, Imperial College Press, London (2011), Ch. 2.
22. F. N. Keutsch, N. Goldman, H. A. Harker, et al., *Mol. Phys.*, **101**, 3477 (2003).
23. A. H. Harvey and E. W. Lemmon, *J. Phys. Chem. Ref. Data*, **33**, 369 (2004).
24. NIST Chemistry WebBook. <http://webbook.nist.gov/chemistry/fluid>.
25. M. A. Suhm, *Science*, **304**, 823 (2004).
26. Y. Scribano and C. Leforestier, *J. Chem. Phys.*, **126**, 234301 (2007).
27. A. F. Krupnov and M. Yu. Tretyakov, *Opt. Atmos. Okeana*, **22**, 107 (2009).
28. M. A. Koshelev, E. A. Serov, V. V. Parshin, and M. Yu. Tretyakov, *J. Quantum Spectrosc. Rad. Transfer*, **112**, 2704 (2011).
29. A. A. Vigasin, *Mol. Phys.*, **108**, 2309 (2010).
30. A. F. Krupnov, M. Yu. Tretyakov, and C. Leforestier, *J. Quantum Spectrosc. Rad. Transfer*, **110**, 427 (2009).