Third Virial Coefficient for Air-Water Vapor Mixtures*

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The third interaction virial coefficient C_{aww} for air-water vapor mixtures is estimated in the temperature range 0 to 100 °C, by means of an approximate method based on molecular association. The results are believed accurate to within a factor of two. The value of C_{aww} can be combined with previous estimates of the other interaction coefficient C_{aaw} and the values of the third virial coefficients of pure air and pure water vapor, to give a quantitative description of the equation of state of air-water vapor mixtures through the complete third virial coefficient. It is shown that the maximum total contribution from both C_{aww} and C_{aaw} to the compressibility factor is only of the order of parts in 10^4 up to 100 °C and 100 atmospheres total pressure. At -50 °C, it can be shown by extrapolation of C_{aww} that the contribution of the C_{aww} term to the compressibility factor is only on the order of parts in 10^{11}.

Key Words: Chemical association, Lennard-Jones potential parameters, virial coefficients, water vapor-air mixtures.

1. Introduction

The thermodynamic properties of air-water vapor mixtures near atmospheric pressure have been determined and tabulated by Goff and his co-workers [1–4].[1] Close correlation was found between the equation of state in the virial form and experimental observations; since the virial form has a sound theoretical basis, Goff was able to make accurate interpolations and extrapolations. In this work, Goff neglected terms involving the third interaction virial coefficients C_{aaw} and C_{aww}, which account respectively for interactions among two air molecules and one water molecule, and one air molecule and two water molecules. This neglect was dictated at least in part by necessity, since no information on C_{aaw} and C_{aww} was available at that time, but the good agreement between theory and experiment indicated that the neglect was probably justified. However, the effects of C_{aaw} and C_{aww} increase with increasing pressure, and it cannot be taken for granted that they can be neglected at high pressures, where interactions among three molecules become important. The situation was improved somewhat in 1963, when Mason and Monchick [5] presented theoretical estimates of C_{aaw}, believed accurate within a factor of two. Only C_{aww} then remained unknown in the treatment of the equation of state of moist air through the third virial coefficient.

The purpose of this paper is to present theoretical estimates of C_{aww}. Internal evidence in the calculations indicates that the results are reliable within a factor of two from 0 to 100 °C; even order of magnitude reliability would be valuable, however, because no other information whatever is available on C_{aww}. The results can be extrapolated down to -50 °C with no loss in overall accuracy in the equation of state, since the maximum water content of moist air is so small at low temperatures. The results can also be extrapolated above 100 °C, but the upper limit of usefulness is uncertain. At 100 °C and pressures up to 100 atm, however, the total contribution from both C_{aaw} and C_{aww} to the compressibility factor is only of the order of parts in 10^4, so considerable extrapolation is possible if only moderately accurate equation of state information is needed.

The rigorous calculation of C_{aww} is difficult because one of the pair interactions, ww, is qualitatively different from the other two, aw, inasmuch as a long-range dipole-dipole force is involved. However, if the dipole-dipole interaction is strong enough, a good approximation can be obtained by assuming that the two water molecules form a quasi-stable dimer, w_2, whose interaction with a single air molecule is relatively easy to calculate. This is the physical basis for the present theoretical estimates.

2. The Virial Equation of State

The virial equation of state through the third virial coefficient for a mixture is

$$\frac{PV}{RT} = 1 + \frac{B_{\text{mix}}}{V} + \frac{C_{\text{mix}}}{V^2} + \cdots \qquad (1)$$

which can also be written as a series in the pressure,

$$\frac{PV}{RT} = 1 + B_{\text{mix}} \frac{P}{RT} + (C_{\text{mix}} - B_{\text{mix}}^2)\left(\frac{P}{RT}\right)^2 + \ldots \qquad (2)$$

where

P = absolute pressure, atm,
V = molar volume of mixture, cm³/mol,
T = absolute temperature, °K,
R = gas constant, cm³-atm/mol-°K,
B_{mix} = second virial coefficient of the mixture, cm³/mol, and
C_{mix} = third virial coefficient of the mixture, (cm³/mol)².

The virial coefficients of a mixture depend on both temperature and composition, but the composition dependence is simple. For a binary mixture of a and w, it is

$$B_{\text{mix}} = x_a^2 B_{aa} + 2x_a x_w B_{aw} + x_w^2 B_{ww} \qquad (3)$$

$$C_{\text{mix}} = x_a^3 C_{aaa} + 3x_a^2 x_w C_{aaw} + 3x_a x_w^2 C_{aww} + x_w^3 C_{www} \qquad (4)$$

where

x_a, x_w = mole fractions of air and water vapor, respectively,

B_{aa}, B_{ww} = second virial coefficients of pure air and pure water vapor, respectively,

B_{aw} = second interaction virial coefficient for one air molecule and one water molecule,

C_{aaa}, C_{www} = Third virial coefficients of pure air and pure water vapor, respectively, and

C_{aaw}, C_{aww} = third interaction virial coefficients for two air molecules and one water molecule and for one air molecule and two water molecules, respectively.

All the B_{ij} and C_{ijk} are functions of temperature only, and are independent of composition.

3. Association Treatment of Virial Coefficients

Our approximation is based on the treatment of the equation of state in terms of chemical association, as has been discussed, for example, by Woolley [6]. In this treatment, a single-component gas is considered to be an ideal mixture of molecular clusters consisting of monomers, dimers, trimers, etc. The actual non-ideal behavior of the gas is thus accounted for by the change in the total number of molecules due to the association—an ideal gas would consist only of monomers. This treatment leads to the following equation of state for one mole of a single-component gas:

$$\frac{PV}{RT} = 1 - K_2 P + (3K_2^2 - 2K_3)P^2 + \ldots \qquad (5)$$

where K_2 is the equilibrium constant for dimer formation, K_3 that for trimer formation, and so on.

At this point the results are completely rigorous, and in fact there is a one-to-one correspondence between the equilibrium constants and the Mayer cluster integrals of statistical-mechanical theory. Approximations enter only in the evaluation of the equilibrium constants, and the chemical association method is most useful in those cases where the interactions are strong enough that K_2, for instance, can be obtained by considering only those pairs of molecules which are bound together in their lowest energy state. If all states of binding are considered, then the ordinary virial equation of state is recovered, but couched in somewhat different language than usual.

For example, for pure water vapor, treated as a mixture of monomers, dimers, etc., comparison of eq (5) and the virial equation of state for water monomer shows that

$$B_{ww} = -K_2 RT, \quad C_{www} = (4K_2^2 - 2K_3)(RT)^2, \text{ etc.} \qquad (6)$$

According to the law of mass action,

$$K_2 = \frac{x_{w_2} V}{x_w^2 RT}, \qquad (7)$$

where x_{w_2} is the mole fraction of dimers and x_w the mole fraction of monomers. Combination of eqs (6) and (7) leads to

$$B_{ww} = -\frac{x_{w_2} V}{x_w^2} \text{ or } \frac{B_{ww}}{V} = -\frac{x_{w_2}}{x_w^2} \qquad (8)$$

and

$$\frac{PV}{RT} = 1 - \frac{x_{w_2}}{x_w^2} + \ldots \approx 1 - x_{w_2} + \ldots \qquad (9)$$

for $x_{w_2} \ll x_w$.

The treatment is easily extended to gas mixtures, and a hybrid description is even possible, in which strongly interacting components of the mixture are handled by the chemical association method, and weakly interacting components by the ordinary virial coefficient method. Such a hybrid description is appropriate for mixtures of air and water vapor. We will not, however, calculate B_{ww} from eq (6), but will take B_{ww} as an experimental quantity and use eq (8) to calculate the mole fraction of dimers, which will be needed in the estimation of C_{aww}.

Barua, et al. [7] have shown that for polar molecules a fairly good approximation to B and K_2 can be obtained by considering only those pairs of molecules which interact strongly enough to be bound together

in the lowest energy state—that is, by considering only dimers whose component molecules have their dipoles alined head-to-tail. The contributions from other dimer configurations can be ignored if the temperature is not too high. This study thus gives quantitative evidence for the validity of the concept of dimers of water molecules.

For a description only through the third virial coefficient, we can consider the three-molecule interactions either as trimer formation, or else as the nonideal interaction between a dimer and a monomer. Our model of a mixture of air and water vapor through the third virial coefficient will be that of a mixture of three species—air monomers, water monomers, and water dimers. All of these species interact with one another except for two water monomers, whose interaction is already taken into account by the existence of the water dimers. The equation of state of this ternary mixture is

$$\frac{PV}{RT} = 1 + (x_a'^2 B_{aa} + 2x_a' x_w' B_{aw} + x_w'^2 B_{ww}) \frac{1}{V}$$

$$+ (2x_a' x_{w_2} B_{aw_2} + 2x_w' x_{w_2} B_{ww_2}) \frac{1}{V}$$

$$+ (x_a'^3 C_{aaa} + 3x_a'^2 x_w' C_{aaw}) \left(\frac{1}{V}\right)^2 + \ldots \quad (10)$$

in which we have written B_{ww} explicitly rather than use eq (8), since we will take B_{ww} as an experimental quantity. Other interactions, such as those involving $B_{w_2 w_2}$ or C_{aaw_2}, contribute to the fourth virial coefficient and are neglected. The mole fractions have been written with primes to indicate that they are not the same as those appearing in eqs (3) and (4).

The degree of dimerization is on the order of parts per thousand of the total number of water molecules. We therefore make the approximation that the x_a' and x_w' of eq (10) are equal to the x_a and x_w of eqs (3) and (4). By comparison of these equations, we see that

$$C_{\text{mix}} = (2x_a x_{w_2} B_{aw_2} + 2x_w x_{w_2} B_{ww_2}) V$$

$$+ (x_a^3 C_{aaa} + 3x_a^2 x_w C_{aaw}). \quad (11)$$

Solving eq (8) for x_{w_2} and substituting into the first term on the right, we find

$$3x_a x_w^2 C_{aww} + x_w^3 C_{www} = -2x_a x_w^2 B_{aw_2} B_{ww} - 2x_w^3 B_{ww_2} B_{ww} \quad (12)$$

and therefore

$$C_{aww} = -\frac{2}{3} B_{aw_2} B_{ww} \quad (13)$$

$$C_{www} = -2B_{ww_2} B_{ww}. \quad (14)$$

The quantity sought, C_{aww}, has therefore been related to a product of second virial coefficients, one of which (B_{ww}) is known experimentally, and the other of which (B_{aw_2}) remains to be calculated. In addition, if C_{www} is known experimentally, we can use eq (14) as a check on the internal consistency of our above calculations or as a source of information on the dimer properties (through B_{ww_2}).

4. Calculation of B_{ww_2}

We can now calculate values of B_{ww_2} from eq (14), and compare with values obtained by methods described in this section. This affords a check on our procedures to this point.

It must be emphasized that we are not trying to derive values for B_{ww_2} as an end in itself—rather, we wish to determine the ranges within which the molecular potential parameters for the dimer-monomer interaction lie. This is important, for these parameters will be used to obtain, in order, the molecular potential parameters associated with the air-dimer interaction, B_{aw_2} itself, and finally C_{aww} from eq (13).

The values of B_{ww} and C_{www} are listed in table 1, as taken from the correlations of Goff [4] and Keyes [8]. The respective values of B_{ww} warrant using the average value in all calculations. The respective C_{www} values, however, should be considered individually. Goff [4] assigns a tolerance of ± 120 percent at 60 °C and of ± 30 percent at 90 °C to his values of C_{www}, with the tolerances taken as twice the probable error. This points out the large uncertainty in this quantity, particularly when we have used Goff's relations to extrapolate his values below 60 °C.

TABLE 1. *Experimental values of the second and third virial coefficients of water vapor; extrapolated values in parentheses*

Temp.	$-B_{ww}$ cm³/mol			$-C_{www}$ liter²/mol²	
	Goff [4]	Keyes [8]	Ave.	Goff [4]	Keyes [8]
°C					
0	(1832)	1854	1843	(64.3)	93.8
10	1510	1520	1515	(34.7)	49.3
20	1260	1266	1263	(19.7)	27.6
30	1074	1070	1072	(11.7)	16.2
40	924	917	920	(7.18)	9.87
50	803	794	798	(4.51)	6.26
60	705	695	700	3.01	4.06
70	625	613	619	2.03	2.76
80	558	546	552	1.39	1.92
90	501	489	495	0.98	1.37
100	(453)	441	447	(.70)	0.99

Two sets of B_{ww_2} values are calculated from eq (14), one set from Goff's C_{www}, the other from Keyes' C_{www}. The results are given in table 2.

Other estimates may be obtained from assumptions about the intermolecular forces. We represent the interaction between two molecules as the sum of a spherically symmetric Lennard-Jones (12–6) interaction and the interaction between point dipoles embedded in the center of each molecule. The potential

energy $\varphi_{ij}(r)$ between molecules i and j a distance r apart is thus

$$\varphi_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

$$-\frac{\mu_i\mu_j}{r^3}(2\cos\theta_i\cos\theta_j - \sin\theta_i\sin\theta_j\cos\phi) \quad (15)$$

where μ_i and μ_j are the dipole moments, θ_i and θ_j are the angles between the dipole axes and the line of centers of the molecules, ϕ is the azimuth angle of the axes, and ϵ_{ij} and σ_{ij} are adjustable constants. If either dipole moment is zero, eq (15) reduces to the Lennard-Jones (12–6) potential, for which ϵ_{ij} is the depth of the potential well and $\varphi(\sigma_{ij}) = 0$. Equation (15) is usually called the Stockmayer potential [9].

TABLE 2. *Experimental and calculated values of the water monomer-dimer second virial coefficient*

Temp.	$-B_{ww_2}$, liter/mol					
	Exptl., eq (14) (Keyes' C_{www})	(Goff's C_{www})	Calc. eq (18)	Calc. eq (19)	Calc. eq (21a)	Calc. eq (21b)
°C						
0	25.4	17.4	21.53	11.91	3.39	5.08
10	16.3	11.5	17.52	9.84	2.66	3.99
20	11.0	7.80	12.96	8.20	2.25	3.15
30	7.56	5.46	10.44	6.72	1.89	2.56
40	5.36	3.90	8.21	6.13	1.62	2.20
50	3.92	2.8	6.61	4.84	1.37	1.82
60	2.90	2.1.	5.58	4.22	1.21	1.55
70	2.23	1.64	4.27	3.67	1.09	1.36
80	1.74	1.26	3.65	3.16	0.96	1.18
90	1.38	0.99	3.10	2.73	.86	1.06
100	1.11	.79	2.63	2.46	.79	0.95

The values of ϵ_{ij} and σ_{ij} must be determined from some experimentally measured property. For pure air, which has no dipole moment, the values used by Mason and Monchick [5] and by Chaddock [10] are $\sigma_{aa} = 3.522$ Å and $\epsilon_{aa}/k = 99.2$ °K, where k is Boltzmann's constant. For pure water vapor, Rowlinson [11] gives $\sigma_{ww} = 2.65$ Å and $\epsilon_{ww}/k = 380$ °K from analysis of B_{ww}, and Monchick and Mason [12] give $\sigma_{ww} = 2.71$ Å and $\epsilon_{ww}/k = 506$ °K from analysis of viscosity data. Tabulations of virial coefficients for the Stockmayer potential are given in terms of a reduced dipole parameter, defined as

$$t_{ij}^* = \frac{\mu_i\mu_j}{\sqrt{8}\,\epsilon_{ij}\sigma_{ij}^3}. \quad (16)$$

The value of t_{ww}^* is 1.2 according to Rowlinson and 0.85 according to Monchick and Mason, with the dipole moment of water taken as $\mu_w = 1.83 \times 10^{-18}$ esu.

Stogryn and Hirschfelder [13] have shown how to estimate ϵ_{ij} and σ_{ij} for dimer-monomer interactions from those for monomer-monomer interactions, according to simple geometrical arguments. The results have been elaborated by Barua and Das Gupta [13] on the basis of the pressure dependence of the viscosity of superheated steam. They recommend the values

$$\epsilon_{ww_2} = 1.32\epsilon_{ww}, \ \sigma_{ww_2} = 1.16\sigma_{ww}. \quad (17)$$

Since we assume that the dimer consists of two monomers with their dipoles in a head-to-tail configuration, the dipole moment of the dimer is twice that of the monomer, $\mu_{w_2} = 3.66 \times 10^{-18}$ esu.

Once ϵ, σ, and t^* are known, it is straightforward to calculate B_{ww_2} from published numerical tables [9, 11] for the Stockmayer potential.

The Rowlinson [11] parameters for water vapor, based on virial coefficient data, are considered first, since so far only virial coefficient data have been used in this presentation.

Equations (16) and (17) lead to

$$t_{ww_2}^* = 1.2, \ \sigma_{ww_2} = 3.07 \text{ Å}, \ \epsilon_{ww_2}/k = 501 \text{ °K}. \quad (18)$$

The values of B_{ww_2} obtained from these parameters are found in table 2. The agreement between the values of $-B_{aw_2}$ calculated from eqs (14) and (18) is generally good, although the latter are somewhat higher except at 0 °C. The implication is that the assumptions made to derive our model are at least as reasonable an approximation of the true physical situation as those used in the derivation of the Stogryn and Hirschfelder [13] model.

If the viscosity-derived parameters of Mason and Monchick [5] for water vapor are used with eqs (16) and (17), we find

$$t_{ww_2}^* = 0.83, \ \sigma_{ww_2} = 3.14 \text{ Å}, \ \epsilon_{ww_2}/k = 668 \text{ °K}. \quad (19)$$

The values of B_{ww_2} derived from these parameters are also given in table 2. The curve of this set of B_{ww_2} values versus T is flatter at the low temperature end than the three curves obtained above from virial coefficient data, but the agreement still is not unreasonable.

Since the values of B_{ww_2} derived from eq (14) do agree fairly well with those derived from other sources, we now seek, by curve fitting, improved Stockmayer potential parameters which will describe the values from eq (14). These will be needed in the calculation of C_{aww}.

The curve-fitting should be done so as to produce preferentially better agreement at high temperatures than at low temperatures for two reasons. First, the experimental values of C_{www} are less uncertain at high temperatures. Second, and more important, is the fact that the low-temperature values of B_{ww_2} are dominated more by $t_{ww_2}^*$ than are the high-temperature values, but the parameter $t_{ww_2}^*$ is of no interest for the present purposes, since it does not contribute at all to the determination of C_{aww}. In other words, we want the derived values of ϵ_{ww_2} and σ_{ww_2} to represent the spherical (12–6) part of the potential, not the dipole part, as there is no dipole contribution to B_{aw_2}.

Therefore, we require that the B_{ww_2} values obtained by fitting should lie between -0.79 liter/mol and -1.11 liter/mole at 100 °C, that is, between the values predicted respectively by using Goff's and Keyes' C_{www} in eq (14). At the same time the slopes of the curves in the 100 °C region must be almost the same to prevent any gross divergences at higher temperatures.

The limiting ranges of σ_{ww_2} and ϵ_{ww_2} are set arbitrarily, but not unreasonably, in the following manner. The lower limits are taken to be the corresponding values for pure water vapor given by Rowlinson [11]. This is equivalent to setting the coefficients of σ_{ww} and ϵ_{wv} in eq (17) equal to 1, a change of 13.8 percent in the former and 24.2 percent in the latter. The upper limits are set by raising the coefficients by the same percentages, and using the σ_{ww} and ϵ_{ww} parameters of Mason and Monchick [5] in eq (17). The limits on $t_{ww_2}^*$ are found by using the limiting values of ϵ_{ww_2} and σ_{ww_2} in eq (16).

This procedure leads to

$$\sigma_{ww_2} \geqslant (\sigma_{ww})_{\text{Rowlinson}} = 2.65 \text{ Å},$$

$$\epsilon_{ww_2}/k \geqslant (\epsilon_{ww}/k)_{\text{Rowlinson}} = 380 \text{ °K}, \qquad (20a)$$

$$t_{ww_2}^* \leqslant 2.4$$

$$\sigma_{ww_2} \leqslant 1.32(\sigma_{ww})_{\text{M. and M.}} = 3.58 \text{ Å},$$

$$\epsilon_{ww_2}/k \leqslant 1.64\,(\epsilon_{ww}/k)_{\text{M. and M.}} = 830 \text{ °K},$$

$$t_{ww_2}^* \geqslant 0.45. \qquad (20b)$$

Within these ranges, the predicted curves are slightly flatter in the 100 °C region than those predicted by eq (14). This means that a curve which predicts -1.11 liter/mole at 100 °C will diverge immediately from higher temperature B_{ww_2} values derived from Keyes' C_{www}. In order to prevent this immediate divergence, we changed the lower permissible B_{ww} limit at 100 °C from -1.11 liter/mol to -0.95 liter/mol, that is, midway between the limits set by eq (14).

Empirical curve fitting with B_{ww_2} matching at both -0.79 liter/mol and -0.95 liter/mol at 100 °C led respectively to these choices of parameters:

$$t_{ww_2}^* = 1.14, \ \sigma_{ww_2} = 3.41 \text{ Å}, \ \epsilon_{ww_2}/k = 380 \text{ °K} \qquad (21a)$$

$$t_{ww_2}^* = 1.25, \ \sigma_{ww_2} = 3.30 \text{ Å}, \ \epsilon_{ww_2}/k = 380 \text{ °K}. \qquad (21b)$$

The σ_{ww_2} values are not unreasonable. The fact that ϵ_{ww_2}/k is the same as the value for pure water vapor (lower limit) in both cases is perhaps annoying, but can be accepted in the present context without undue alarm.

The values of B^* versus T^* for the parameters were interpolated graphically between tabulated values of t^* [9], and these in turn were extrapolated graphically to the lowest temperatures. Therefore the derived parameters may not be the "best" ones in a least squares sense, but they are certainly close enough for our purposes.

The values of B_{ww_2} corresponding to eqs (21a) and (21b) are given in table 2, and clearly the agreement with the curves derived from eq (14) is poor except at the highest temperatures. The reason for the discrepancy is open to some speculation, but we remind the reader again that first, we demanded a fit at the high temperatures to have the σ and ϵ values be more representative of the spherical part of the potential, and second, we are seeking various estimates of σ_{ww_2} and ϵ_{ww_2} rather than attempting to derive B_{ww_2}.

Summarizing this section, we have obtained four sets of σ_{ww_2} and ϵ_{ww_2} parameters (t^* is of no further interest). Two were obtained through the method of Stogryn and Hirschfelder [13], using first experimental virial coefficient data and then experimental viscosity data, and two from curve-fitting, subject to several restraints, to the B_{ww_2} values derived with the methods of this paper. We also obtained what are thought to be reasonable outside limits on the values of σ_{ww_2} and ϵ_{ww_2}.

5. Calculation of C_{aww}

The various values of σ_{ww_2} and ϵ_{ww_2} derived in the previous section may now be used to obtain the parameters σ_{aw_2} and ϵ_{aw_2} for the air-dimer interaction, from which B_{aw_2} and finally C_{aww} may be obtained. The procedure is based on semi-empirical combining rules [9] for ϵ and σ,

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}, \ \sigma_{ij} = (1/2)(\sigma_{ii} + \sigma_{jj}). \qquad (22)$$

These rules work fairly well for both polar and nonpolar molecules [15]. Applying these rules twice, we obtain expressions for the desired parameters ϵ_{aw_2} and σ_{aw_2},

$$\epsilon_{aw_2} = \epsilon_{ww_2}(\epsilon_{aa}/\epsilon_{ww})^{1/2},$$

$$\sigma_{aw_2} = \sigma_{ww_2} + (1/2)(\sigma_{aa} - \sigma_{ww}). \qquad (23)$$

The values of σ_{aw_2} and ϵ_{aw_2} are derived from the four sets of ww_2 parameters obtained in the previous section. For the three associated with virial coefficient data [eqs (18), (21a), (21b)] we use in eq (23) Rowlinson's [11] values for ϵ_{ww} and σ_{ww}, while for the set associated with viscosity data [eq (19)] we use in eq (23) the Mason and Monchick [5] values. We find

$$\epsilon_{aw_2}/k = 256 \text{ °K} \qquad \sigma_{aw_2} = 3.51 \text{ Å [from eq (18)]} \qquad (24a)$$

$$\epsilon_{aw_2}/k = 194 \text{ °K} \qquad \sigma_{aw_2} = 3.85 \text{ Å [from eq (21a)]} \qquad (24b)$$

$$\epsilon_{aw_2}/k = 194 \text{ °K} \qquad \sigma_{aw_2} = 3.74 \text{ Å [from eq (21b)]} \qquad (24c)$$

$$\epsilon_{aw_2}/k = 296 \text{ °K} \qquad \sigma_{aw_2} = 3.55 \text{ Å [from eq (19)]} \qquad (24d)$$

The last set is of particular interest, since it is derived entirely from viscosity data. The viscosity is relatively insensitive to the dipole interaction [12], so the values of ϵ_{ww_2} and σ_{ww_2} from which eq (24d) is derived should be good representations of the spherical part of the potential.

Two more sets of aw_2 parameters should be derived—namely, those associated with the limiting cases of the ww_2 parameters [eqs (20a) and (20b)]. From these we obtain respectively

$$\epsilon_{aw_2}/k = 194 \text{ °K} \qquad \sigma_{aw_2} = 3.09 \text{ Å} \qquad (25a)$$

$$\epsilon_{aw_2}/k = 423 \text{ °K} \qquad \sigma_{aw_2} = 4.02 \text{ Å}. \qquad (25b)$$

From each of these six sets of parameters, we calculate first B_{aw_2} and then, using eq (13), C_{aww}. The results of the latter are given in table 3.

TABLE 3.—*Calculated value of the third interaction virial coefficient C_{aww} based on the parameters of eqs (24) and (25)*

Temp	$-C_{aww}$, liter²/mol²					
	Virial			Viscosity*	Limits	
	Eq (24a)	Eq (24b)	Eq (24c)	Eq (24d)	Eq (25a)	Eq (25b)
°C						
0	0.152	0.121	0.111	0.203	0.062	0.549
10	.117	.090	.083	.156	.047	.424
20	.092	.072	.066	.123	.037	.332
30	.073	.057	.052	.098	.029	.266
40	.058	.046	.042	.080	.024	.216
50	.048	.037	.034	.065	.019	.178
60	.040	.030	.028	.054	.016	.148
70	.034	.025	.023	.046	.013	.123
80	.028	.021	.019	.039	.011	.105
90	.024	.018	.016	.033	.009	.090
100	.021	.015	.014	.028	.008	.077

*Best estimates.

Those derived from experimental viscosity values [i.e., from eq (24)] are felt to be the most reliable. This is based on the relative independence of viscosity on the dipole interaction, and on the success of the dimer-monomer model in predicting the pressure dependence of the viscosity of steam [13, 14].

The viscosity-based values differ from the limiting values derived for eq (25a, b) by at most a factor of three, and from all other values by no more than a factor of two.

We are confident that the values are accurate to within a factor of four, and probably to within a factor of two.

6. Discussion

We are now in a position to estimate the contributions of C_{aaw} and C_{aww} to the compressibility factor of moist air; that is, to estimate the magnitudes of the terms $(3x_a^2 x_w C_{aaw}/V^2)$ and $(3x_a x_w^2 C_{aww}/V^2)$, as compared to unity. Since the maximum water vapor content of air increases rapidly with increasing temperature, the largest contribution of these terms comes at high temperatures, even though C_{aaw} and C_{aww} decrease in magnitude with increasing temperature. At 100 °C the partial pressure of water vapor can be taken as 1 atm, and the mole fractions as

$$x_a = P_a/(P_a+1), \; x_w = 1/(P_a+1) \qquad (26)$$

where P_a is the partial pressure of the air. These relations are only approximate for nonideal gases, but adequate here because in C_{mix} we are seeking only the highest-order deviation terms. Similarly, the molar volume of the mixture is

$$V = RT/(P_a+1). \qquad (27)$$

Taking $C_{aaw} = +696$ (cm³/mol)² [5] and $C_{aww} = -2.8 \times 10^4$ (cm³/mol)² (table 3), we find from eqs (26) and (27) that

$$3x_a^2 x_w C_{aaw}/V^2 = 2.23 \times 10^{-6} P_a^2/(P_a+1) \qquad (28a)$$

$$3x_a x_w^2 C_{aww}/V^2 = 0.90 \times 10^{-4} P_a/(P_a+1). \qquad (28b)$$

Thus even for $P_a = 100$ atm the contribution of these two terms is only of the order of parts in 10^4.

The present results are readily extendable to higher or lower temperatures by means of the aw_2 parameters of eq (24d) in conjunction with tabulated virial coefficients for the (12–6) potential [9]. There is no loss in overall accuracy in PV/RT by extrapolation to low temperatures. For example, a calculation similar to that performed above, based on a temperature of -50 °C ($P_w = 3.9 \times 10^{-5}$ atm) with $P_a = 100$ atm and $C_{aww} = -1 \times 10^6$ (cm³/mol)², indicates that the contribution of the C_{aww} term to the compressibility factor is on the order of parts in 10^{11}. There is loss in accuracy by extrapolation to high temperatures because of the increasing water vapor content; how much extrapolation is permissible depends on how much uncertainty in PV/RT is acceptable. It must also be remembered that the physical model of dimer formation becomes less accurate as the temperature increases.

6. References

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