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A Correlation for the Second Interaction Virial Coefficients and Enhancement Factors for Moist Air*

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Experimental measurements of the enhancement factors for mixtures of water vapor and CO_2-free air have been made at −20, −10, and +70 °C. The results, coupled with previous experimental enhancement data, have been used to calculate the second interaction virial coefficients, B_{aw}, for water vapor air mixtures from −50 to +90 °C. Within this temperature range, an error analysis shows that the uncertainties in B_{aw} are between 6 and 10 percent. The calculated B_{aw} values are used in deriving enhancement factors at 10 °C intervals for $-50 < t < 90$ °C, at varying pressure intervals from 0.25 to 100 bar. The associated uncertainties are shown as a function of pressure and temperature. The enhancement factors are extrapolated to −80 °C.

Key words: Enhancement factor; equation of state; interaction virial coefficients; moist air; saturated air; second virial coefficients; virial coefficients.

1. Introduction

The objective of this paper is to take limited experimental data on the saturated water vapor content of CO_2-free air and develop a sound basis for predicting this saturated content over wide ranges of temperature and pressure. The approach is through the virial equation of state, and follows the methods outlined previously by Hyland and Wexler [1, 2],[1] where they reported experimental results for the range $30 \leq t \leq 50$ °C. In this paper the experimental range is extended to include $-20 \leq t \leq 70$ °C, and the results used to obtain both the second interaction virial coefficients, B_{aw}, for air-water vapor mixtures, and enhancement factors, defined below, over the temperature range $-50 \leq t \leq 90$ °C.

The experiments require the saturation of CO_2-free air at known conditions of pressure and temperature. The water vapor is then separated from the air, and the mole fractions of each component determined. The enhancement factor for the particular pressure and temperature of saturation may be expressed by

$$f = \frac{x_w P}{e_s} = \frac{(1-x_a)P}{e_s} \tag{1}$$

where f = the enhancement factor.

x_a, x_w = the mole fractions of air and water vapor in the saturated mixture.

P = total pressure above the surface of the condensed phase (water or ice).

e_s = the pure phase saturation vapor pressure of water substance at the temperature of saturation.

$x_w P$ = the effective water vapor pressure at the given pressure and temperature of saturation.

The determination of an empirical relationship for f as a function of pressure and temperature is impractical because of the large number of experiments involved. We therefore chose to use the theoretical equation of [2], given as eq (A–4) in the appendix to this paper. This equation yields enhancement factors, providing all required virial coefficients are known with sufficient accuracy. This was the case for all virial coefficients within our range of interest except B_{aw}. Our approach was to perform a limited number of enhancement factor measurements, and, by inverting eq (A–4) into a quadratic for B_{aw}, to calculate B_{aw} at each experimental point. The values obtained at each temperature were averaged, and the temperature dependence of the averages estimated by least-squares fitting them with the Lennard-Jones (12–6) potential function, resulting in the values found in table 4 of this paper. All of the information necessary for using eq (A–4) was then in hand, and the enhancement factors given in table 8 were obtained.

2. Experimental Method and Results at −20, −10, and +70 °C

Commercially supplied, compressed air, with impurity characteristics as described in [1], is passed

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[1] Figures in brackets indicate literature references at the end of this paper.

through a unit which lowers the CO_2 content to a level near 2 ppm. The air is then saturated by passage over the surface of either water or ice. Pressure and temperature within the saturator are monitored. The water vapor is subsequently removed from the air stream, and the mass of water vapor and associated dry air determined. One obtains the water vapor mole fraction from the mass ratio, and the pure phase saturation vapor pressure from the saturator temperature. Combining these with the saturator pressure in eq (1) determines the enhancement factor at the saturator P, T condition.

Several such experiments are done along an isotherm. Since B_{aw} is a function of temperature only, each experiment should yield the same value, providing a check on whether or not the apparatus is performing properly, and whether the equation relating B_{aw} to f (the inverse of eq (A–4) in this paper) is valid at the given conditions.

The details of the methods for experiments above 0 °C, including our new point at +70 °C, are found in [1, 2]. The 70 °C data and results are in table 2 of this paper.

The saturating apparatus of [1, 2] is unsuitable for use at temperatures below 0 °C. Instead, for our points at −20 and −10 °C, the low-frost point generator of Greenspan [3] was used. Air samples were prepared by first evacuating containers, then back-filling them through a CO_2-removal unit in series with a coil immersed in a bath at roughly −78 °C. The air pressure during filling increased monotonically from about 1 to 125 bar. The process provided containers of dry, low-CO_2 content (2–5 ppm) air. In the course of an experiment, the air mass passing through the saturator was found by weighing the air containers before and after the experiment on a modified, higher-capacity version of a balance described by Russell in [4]. The water mass was determined with the usual gravimetric drying train [5].

The experimental results at −10 and −20 °C are given in table 2, while table 3 summarizes the results obtained previously at 30, 40, and 50 °C.

All experimental results are referred to the International Practical Temperature Scale of 1948 (6). In table 4, above −20 °C, it makes no difference whether the given temperatures are considered to be on IPTS–48 or IPTS–68 (7). At −20, −30, and −40 °C, B_{aw} becomes more negative by 0.01 cm³/mol, and at −50 °C, 0.02 cm³/mol, if one considers the given values to be on the 1948 scale and converts to the 1968 scale. In table 8, to the number of reported places, the temperatures can be considered to represent either temperature scale.

3. Data Reduction

We first derive values of B_{aw} from enhancement data. The necessary equations have been discussed in refs. [1, 2]. However, the derivation of eq (12) of [2] is incorrect as presented, and the proper derivation is outlined in the appendix to this paper. Also summarized in the appendix are equations in which no changes have been made. Presented here are equations and constants which differ from those used in [1, 2]. These differences are associated with the wider temperature ranges considered. Also, the molecular weight of air containing 2–5 ppm CO_2 was recalculated, based on the proposal by Harrison [8] that the sum of the CO_2 and oxygen volume percentage is constant at 20.979. The molecular weight ratio of water to air becomes 0.622062, differing slightly from the value used in [1, 2].

3.1. Specific Volume of Hexagonal Ice I

The specific volume of hexagonal ice I, used in the calculation of B_{aw} from experimental enhancement data at temperatures below 0 °C, was formulated by first considering the specific volume data of Ginnings and Corruccini [9], along with a correlation of data on the linear expansion of ice from Jukob and Erk [10], Powell [11], Butkovich [12], Dantl [13], and LaPlaca and Post [14], resulting in

$$V_{P_a,T} = 1.074351 - 0.867004 \cdot 10^{-4}\, T + 0.656565 \cdot 10^{-6}\, T^2 - 0.430316 \cdot 10^{-9}\, T^3 \qquad (2)$$

where $V_{P_a,T}$ is the specific volume of ice at one standard atmosphere and at absolute temperature T.

Equation (2) is used in our correlation of Leadbetter's values [15] of the adiabatic compressibility of hexagonal ice I, to yield

$$V_{P,T} = V_{P_a,T}\,[1 - (8.875 + 0.0165T)(P - 1.01325) \cdot 10^{-6}] \qquad (3)$$

where the pressure unit is bars.[2]

3.2. Expressions for B_{aa}, C_{aaa}, and C_{aaw}

Equations (4), (5), and (6), below, were obtained by fitting, using the method of least squares, a wider range of data of Sengers et al. [16], Hilsenrath et al. [17], and Mason and Monchick [18] than was done in [2]. Polynomial equations were used for the fits. The data fitted here covers the nominal temperature range from −50 to +110 °C. The standard deviations of the fits do not, of course, reflect the overall uncertainties in the parameters.

$$B_{aa}(t) = -13.5110 + 0.24311t - 0.10846 \cdot 10^{-2}t^2 + 0.42504 \cdot 10^{-5}t^3 - 0.81851 \cdot 10^{-8}t^4 \text{ cm}^3/\text{mol}; \quad \sigma_{\text{fit}} = 0.023 \qquad (4)$$

$$C_{aaa}(t) = 1314.2 - 0.89988t - 0.30474 \cdot 10^{-2}t^2 + 0.42015 \cdot 10^{-4}t^3 - 0.40869 \cdot 10^{-6}t^4 + 0.43810 \cdot 10^{-8}t^5 - 0.20677 \cdot 10^{-8}t^6 \text{cm}^6/\text{mol}^2; \quad \sigma_{\text{fit}} = 0.157 \qquad (5)$$

$$C_{aaw}(t) = 860.82 - 2.4454t + 0.94106 \cdot 10^{-2}t^2 + 0.14909 \cdot 10^{-4}t^3 - 0.59389 \cdot 10^{-6}t^4 + 0.30265 \cdot 10^{-8}t^5 \text{ cm}^6/\text{mol}^2; \quad \sigma_{\text{fit}} = 0.353 \qquad (6)$$

The temperature, t, is degrees Celsius.

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[2] 1 bar = 10^5 pascals.

3.3. Expressions for the Henry's Law "Constants"

The correlation of the Henry's "constant", k, for air, from 0 to 100 °C, is based in part on the "constants" for nitrogen, as was done for the 0 to 50 °C range of [2].

For atmospheric nitrogen, correlations were obtained from the data of [19, 20, 21], and, for nitrogen at pressures of 50 and 100 atmospheres, from the data of [22] as reported in Dorsey [21], and from [23].

The 50- and 100-atmosphere air curves were obtained by requiring the same percentage differences between the 1- and 50-atmosphere curves and the 50- and 100-atmosphere curves as the corresponding differences for nitrogen.

The results, using bars as the pressure units, were fitted to the polynomial

$$10^6\,k=\sum_{i=0}^{n} C_i t^i \qquad (7)$$

where $n=4$ or 5, yielding the coefficients in table 1. The units of k are mole fraction/bar.

There seems to be no high pressure data for solubility of air in ice. At all temperatures less than 0 °C, the Henry's "constant" for water at 0 °C and 1 bar is used. The resulting systematic error estimate, given as 10 percent in [2], has been increased to 20 percent, introducing a maximum uncertainty on the order of 0.2 percent into the calculated value of B_{aw}.

TABLE 1. *Coefficients to equation (7)*

i	Pressure, bars		
	1	50	100
0	23.5199	21.6663	19.7652
1	−0.60277	−0.54460	−0.47424
2	$.11518\cdot10^{1}$	$.93580\cdot10^{-2}$	$.81569\cdot10^{-2}$
3	$-.12556\cdot10^{-3}$	$-.75473\cdot10^{-4}$	$.67051\cdot10^{-4}$
4	$.74217\cdot10^{-6}$	$.24146\cdot10^{-6}$	$.22157\cdot10^{-6}$
5	$.17765\cdot10^{-8}$	—	—

3.4. Saturation Vapor Pressure Over Ice

The expression for the saturation vapor pressure of ice is that given by Goff, in [24]. At −10 and −20 °C, the estimated systematic uncertainty is 0.1 percent in the predicted vapor pressure.

Goff's equation is

$$\begin{aligned}\log_{10}(e_i)=&-9.096936\,[273.16/(T-1)]\\ &-3.56654\,\log_{10}(273.16/T)\\ &+0.876817\,(1-T/273.16)+0.786118\end{aligned} \qquad (8)$$

where e_i = saturation vapor pressure of pure ice, millibar
T = absolute temperature, kelvins.

This equation does not give the identical value of e_s at the triple point as that of water used above 0 °C (see [25], but the difference, 1×10^{-4} mbar, is negligible in the context of this paper.

3.5. Theoretical Smoothing Function for B_{aw}

In order to obtain an equation for the interpolation and extrapolation of B_{aw} versus t, the Lennard-Jones (12–6) potential was fitted to the mean, experimentally based values of B_{aw} found in tables 2 and 3, yielding the calculated values of table 4. The potential parameters are $b_0=51.994$ cm³/mol, and $\epsilon/k=143.513$ K. The data are not randomly distributed about the predicted curve; however, within the error limits assigned in section 5.2, this is not significant.

The analysis of Hanley and Klein [26] shows that, given a LJ (12–6) fit to data within the region where the reduced temperature T^* is between approximately 2.0 and 10.0, any two- or three-parameter function can be fitted equally well to the data. Furthermore, in this situation, extrapolation much beyond the experimental

TABLE 2. *Summary of experimental conditions and results*

Saturation temp. °C	Saturation vap. press. mb	Total press. bar	Mole fraction water vapor	Enhancement factor [a]	Interaction virial coeff. cm³/mol	Normalized [b] inter. vir. coefficient cm³/mol
t	e_s	P	x_w	f	B_{aw}	B_{aw}
70.0067	311.7533	24.0502	0.013640	1.0523	−16.59	−16.61
70.0007	311.6726	29.5089	.011258	1.0659	−18.25	−18.25
69.9952	311.5984	32.8965	.010172	1.0739	−17.84	−17.83
69.9991	311.6510	34.9783	.0096093	1.0785	−18.18	−18.18
					Mean =	−17.72
					std. dev. of mean =	0.38
−10.0043	2.595475	19.9975	.00014031	1.0857	−40.47	−40.46
−10.0000	2.596456	29.0621	.00010028	1.1268	−41.17	−41.17
					Mean =	−40.82
					std. dev. of mean =	0.35
−20.0125	1.03023	19.9953	.000056020	1.0873	−43.29	−43.29

[a] $f=x_wP/e_s$.

[b] By noting the slope of B_{aw} versus t, one adjusts the values of the previous column to correspond to exactly 70, −10, or −20 °C.

region, particularly toward lower temperatures, may be hazardous.

For our experiments, $1.76 < T^* < 2.40$, with two of the six points being below $T^*=2.0$. We verified that (9–6) and (24–6) potential fits produced, to well within experimental accuracies, the same results as the (12–6) fit from at least −50 to +90 °C, then dropped them from further consideration. The extrapolations probably could be extended upwards by another 20 or 30 °C with little change in the accuracy. However, because of the potential hazards of extrapolating downwards, we feel that assigning errors below −50 °C would be meaningless.

TABLE 3. *Mean values and uncertainties of the experimental NBS virial coefficients at 30, 40, and 50 °C* [2]

t	$\bar{B}_{aw}^{(a)}$	$\bar{\sigma}$ [b]	Systematic error	$3\bar{\sigma}$ + syst.
°C	cm³/mol	*Percent*	*Percent*	*Percent*
30	−29.2	0.6	4	5.8
40	−26.3	.7	4	6.1
50	−23.6	1.4	6	10.2

[a] From [2].
[b] $\bar{\sigma}$ = standard deviation of the mean value of $\bar{B}_{aw}$.

TABLE 4. *Results of fits to* B_{aw} [a]

t °C	B_{aw}, from LJ(12–6) cm³/mol	B_{aw}, from eq (9) cm³/mol
−50	−58.0	−58.0
−40	−53.0	−52.9
−30	−48.4	−48.4
−20	−44.2	−44.2
−10	−40.4	−40.5
0	−37.0	−37.0
+10	−33.8	−33.8
20	−30.9	−30.9
30	−28.2	−28.2
40	−25.7	−25.6
50	−23.3	−23.3
60	−21.2	−21.2
70	−19.2	−19.2
80	−17.3	−17.3
90	−15.5	−15.5

[a] From LJ (12–6) fit to data of tables 2 and 3, b_0 = 51.9941 cm³/mol and ϵ/k = 143.513 K.

In most cases it would be easier to use a polynomial representation of B_{aw} versus t, rather than to interpolate tables of Lennard-Jones values. Accordingly, the values predicted from the Lennard-Jones fit (column 2 of table 4), using the method of least squares, were fitted to a polynomial function of Celsius temperature, resulting in the equation

$$\begin{aligned}-B_{aw} = {} & 36.98928 - 0.331705t + 0.139035 \cdot 10^{-2}t^2 \\ & - 0.574154 \cdot 10^{-5}t^3 + 0.326513 \cdot 10^{-7}t^4 \\ & - 0.142805 \cdot 10^{-9}t^5 \text{ cm}^3/\text{mol}, \end{aligned} \tag{9}$$

valid for $-50 < t < 90$ °C. The values predicted by eq (9) are given in the final column of table 4.

The maximum difference between the rounded values of eq (9) and the Lennard-Jones values, is seen to be 0.1 cm³/mol. Equation (9) supercedes eq (37) of [2].

4. Uncertainties in B_{aw}

In this section are presented, first, a discussion of the uncertainties in the experimentally-based values of B_{aw}, and second, a discussion of the uncertainties in the predicted values.

4.1. Uncertainties in the Experimentally Derived Values

a. Contribution from Measured Quantities

At 70 °C, the systematic uncertainties from the measured quantities may all be placed into the measured enhancement factor, as was done in [2]. The systematic uncertainty in the measured enhancement factor is 0.07 percent just as it was for the 30, 40, and 50 °C values of [1]. This includes all but inconsequential effects from pressure, temperature (and through it, the saturation vapor pressure), and mole fraction of water vapor (as determined from the measured mixed ratio), and contributes an estimated 2 percent systematic uncertainty to B_{aw}.

The standard deviation of the mean value is used as the measurement of the random uncertainty of the 70 °C value of B_{aw}. As seen in table 2, this amounts to 2 percent. The first of the tabulated 70 °C results appears low relative to the others; if it were dropped from consideration, the standard deviation of the mean would decrease to 0.7 percent. However, there seems to be no valid reason for rejecting the point. (Note that, in table 7, the overall uncertainty would become 7 percent instead of 12 percent.)

The remaining discussion in this section applies to the −10 and −20 °C experiments. The standard deviations for the pressure and temperature measurements are the standard deviations of the means obtained during the experiments, while the standard deviations of the mixing ratios are based on the standard deviations of the weighings of the water absorption tubes and of the air containers.

The systematic uncertainty in the temperature measurements is the sum of estimated systematic uncertainties in the instrumentation, in the ice point resistance of the resistance thermometer, and in the resistance versus temperature curves used to represent the thermometer calibration data, plus an allowance of 0.005 °C for the possible deviation of the measured temperature from the temperature of saturation.

The systematic pressure uncertainty is primarily the sum of estimated systematic uncertainties in the curve used to represent the calibration of the manometer, in the manometer zero reading, plus small contributions from other corrections associated with the manometer.

The assigned systematic errors in the mixing ratio account for the possibility of water passing unabsorbed through the U-tubes [5], plus small contributions from the bouyancy corrections applied to the air containers during weighing and the effects of different starting and finishing pressures in the high-pressure lines.

Table 5 summarizes the experimental error sources and magnitudes, and the errors they induce in B_{aw}, for the experiments at −10 and −20 °C.

b. Contributions from Calculated Quantities

The error contributions from the various calculated quantities were obtained by changing the quantity by the amount of its estimated error, recalculating B_{aw}, and comparing with the originally calculated value.

Sengers et al. [16] estimate the 3σ error in B_{aa} to be 1.2 cm^3/mol. Uncertainties in B_{ww}, C_{aaa}, and C_{www}, were estimated by comparing available data, as described in [2], or, in the cases of C_{aaw} and C_{aww}, arbitrarily selected to indicate possible error magnitudes. The intent was to be conservative, but that cannot be guaranteed. The estimated uncertainties associated with the various virial coefficients are summarized in table 6, along with the systematic errors they induce in B_{aw}. Table 6 similarly lists the effects of the uncertainties in the Henry's and gas constants, and in the saturation vapor pressure. Below 0 °C, we indicate separately the error arising from use of eq (8). Above 0 °C, the 60 ppm error associated with the vapor pressure equation [25] was lumped into the experimental vapor pressure error. The final column of table 6 combines all contributions by quadrature, that is, the square root of the sums of the squares. This is

TABLE 5. *Experimental errors at −10 and -20 °C*

Nominal run conditions		Parameter	Estimated systematic errors			3σ-Random errors		
			Parameter uncertainty	Induced B_{aw} error		Parameter uncertainty	Induced B_{aw} error	
t(°C)	P(bar)			cm^3/mol	Percent		cm^3/mol	Percent
−10	20	t	0.017 °C	0.81	2.00	0.0003 °C	0.01	0.03
		P	.0172 bar	.43	1.06	.00041 bar	.10	.25
		r[a]	.07%	.38	.94	.11%	.59	1.46
				$\sum = 1.62$	4.00		Quad[b] = 0.60	1.48
−10	30	t	0.017 °C	0.55	1.33	0.0003 °C	0.03	0.07
		P	.0159 bar	.18	.44	.0062 bar	.07	.17
		r	.09%	.30	.72	.10%	.43	1.04
				$\sum = 1.03$	2.49		Quad = 0.44	1.06
−20	20	t	0.017 °C	0.82	1.89	0.0015 °C	0.07	0.1
		P	.0172 bar	.41	.95	.0041 bar	.10	.23
		r	.14%	.72	1.66	.10%	.51	1.18
				$\sum = 1.95$	4.50		Quad = 0.52	1.21

[a] r = Mass water/mass air, g/g

[b] Combined by quadratures, i.e., the square root of the sum of the squares.

TABLE 6. *Systematic uncertainties in B_{aw} from calculated parameters*

Temp.	Press.	Source of error								Quadrature
		B_{aa}	B_{ww}	C_{aaa}	C_{www}	C_{aaw}	C_{aww}	Other	e_s	
		Estimated error in source, percent								
		([a])	6	15	46	50	50	([b])	—	
°C	bar	Estimated error in B_{aw}, percent								
70	24.1	3.26	1.54	0.44	0.36	1.27	2.25	0.14	—	4.47
		Estimated error in source, percent								
		([a])	100	20	100	150	150	([b])	0.1	
		Estimated error in B_{aw}, percent								
−10	20.0	1.34	0.31	0.41	0.00	3.11	0.19	0.16	1.34	3.69
−10	29.1	1.42	.43	.29	.00	2.22	.18	.16	0.88	2.84
−20	20.0	1.32	.20	.29	.00	2.22	.09	.16	1.19	2.87

[a] Estimated 3σ error is 1.2 cm^3/mol.

[b] Quadrature of errors contributed by Henry's law, gas constant, and ignoring the correction to the law of ideal solutions.

justified on the basis that it is unlikely that all errors will contribute, in the same sign sense, to the uncertainty in B_{aw}.

Table 7 summarizes the systematic and random errors in the experimentally derived values of B_{aw}. The estimated contributions from the experimental and calculated parameter systematic sources are shown separately, then combined into a total systematic uncertainty in column 6. The estimated overall uncertainty at 70 °C is 12 percent. At −10 °C, both a calculated and observed estimate of the experimental random errors are available, leading to two estimates of the total error which are in good agreement. The larger estimate is 7 percent. At −20 °C, the total uncertainty is 6 percent.

4.2. Uncertainties in the Predicted Values of B_{aw}

The maximum error bands placed on the predicted values of table 4 reflect the maximum estimated uncertainties in the experimental quantities. For $-50 \leqslant t < 0$ °C, error bands of ±10 percent have been assigned. This is larger than the 7 percent estimate given in table 7, but since the errors associated with various other virial coefficients are only crude estimates in this region it is felt that the additional 3 percent on the error band is warranted. For $0 \leqslant t < 45$ °C, a 6 percent error band is assigned, commensurate with the estimated uncertainties of table 3. Above 45 °C, the error band is again increased to 10 percent. All experimental points lie within the error band of the predicted values, and vice versa. If either or both experimental end points (−20 or 70 °C) are omitted, the resultant LJ (12–6) fit still lies within the assigned bands over the entire range of interest.

5. Enhancement Factors

The enhancement factor is defined by eq (1).

To obtain the enhancement factor at a given (P, T) condition, one replaces the f in eq (A–4) of the appendix by eq (1), solves by iteration for x_a, then converts back to f through eq (1).

Table 8 gives the results of such calculations. The

TABLE 7. *Summary of errors in experimentally derived values of* B_{aw}

Temp.	Error source				
°C	Experimental random, $3\bar{\sigma}$[a]	Experimental systematic	Calc. parameters systematic	Quadrature of systematics	Overall quad. syst. $+3\bar{\sigma}$
	Error in B_{aw}, percent				
70	6.42	2.38	4.47	5.06	11.5
−10[b]	1.26	3.24	3.26	4.59	5.9
−10[c]	2.57	3.24	3.26	4.59	7.2
−20	1.21	4.49	2.87	5.33	6.5

[a] $\bar{\sigma}$ = Standard deviation of mean value.

[b] Based on means of the calculated uncertainties at 20 and 29 bar, tables 5 and 6.

[c] Random from the observed $\bar{\sigma}$ of table 2.

TABLE 8. *Predicted enhancement factors*

Total pressure bars	t °C							
	−80[a]	−70	−60	−50	−40	−30	−20	−10
0.25	1.0020	1.0018	1.0016	1.0014	1.0013	1.0012	1.0012	1.0012
.50	1.0041	1.0036	1.0032	1.0029	1.0026	1.0024	1.0022	1.0022
1.00	1.0082	1.0072	1.0064	1.0058	1.0052	1.0047	1.0044	1.0041
1.50	1.0123	1.0109	1.0097	1.0086	1.0078	1.0071	1.0065	1.0060
2.00	1.0165	1.0145	1.0129	1.0116	1.0104	1.0094	1.0086	1.0080
2.50	1.0207	1.0182	1.0162	1.0145	1.0130	1.0118	1.0108	1.0099
3.00	1.0249	1.0219	1.0195	1.0174	1.0156	1.0141	1.0129	1.0119
3.50	1.0291	1.0256	1.0228	1.0203	1.0183	1.0165	1.0150	1.0138
4.00	1.0334	1.0294	1.0261	1.0233	1.0209	1.0189	1.0172	1.0158
4.50	1.0377	1.0332	1.0294	1.0262	1.0236	1.0213	1.0194	1.0177
5.00	1.0420	1.0369	1.0327	1.0292	1.0262	1.0237	1.0215	1.0197
10.00	1.0865	1.0758	1.0669	1.0595	1.0533	1.0480	1.0435	1.0396
20.00	1.184	1.160	1.140	1.124	1.110	1.099	1.089	1.080
30.00	1.293	1.252	1.220	1.193	1.171	1.153	1.138	1.124
40.00	1.417	1.356	1.307	1.269	1.237	1.211	1.189	1.170
50.00	1.556	1.470	1.403	1.350	1.307	1.272	1.243	1.218
60.00	1.71	1.60	1.51	1.44	1.38	1.337	1.300	1.268
70.00	1.89	1.74	1.62	1.53	1.46	1.41	1.360	1.321
80.00	2.10	1.90	1.75	1.64	1.55	1.48	1.42	1.377
90.00	2.33	2.08	1.89	1.75	1.64	1.56	1.49	1.44
100.00	2.59	2.27	2.05	1.88	1.75	1.64	1.56	1.50

See footnote at end of table.

TABLE 8.
Predicted enhancement factors—Continued

Total pressure bars	0 °C	
	Ice	Water
0.25	1.00132	1.00131
.50	1.00221	1.00217
1.00	1.0040	1.0039
1.50	1.0057	1.0056
2.00	1.0075	1.0074
2.50	1.0093	1.0091
3.00	1.0111	1.0108
3.50	1.0129	1.0126
4.00	1.0146	1.0144
4.50	1.0164	1.0161
5.00	1.0182	1.0179
10.00	1.0364	1.0356
20.00	1.074	1.072
30.00	1.113	1.111
40.00	1.154	1.151
50.00	1.197	1.193
60.00	1.242	1.237
70.00	1.289	1.282
80.00	1.338	1.330
90.00	1.389	1.381
100.00	1.44	1.43

TABLE 8. *Predicted enhancement factors*—Continued

Total pressure, bars	*t* °C								
	10	20	30	40	50	60	70	80	90
0.25	1.00148	1.00173	1.00202	1.00223	1.00211	1.00111			
.50	1.00229	1.00251	1.00284	1.00323	1.00358	1.00362	1.00288	1.00051	
1.00	1.00388	1.00400	1.00426	1.00467	1.00519	1.00571	1.00599	1.00564	1.00394
1.50	1.0055	1.00547	1.00564	1.00599	1.00651	1.00713	1.00772	1.00801	1.00754
2.00	1.0071	1.0069	1.00701	1.00728	1.00775	1.00839	1.00910	1.00968	1.00980
2.50	1.0087	1.0084	1.0084	1.0086	1.0090	1.00959	1.01034	1.01108	1.01154
3.00	1.0103	1.0099	1.0097	1.0098	1.0102	1.0108	1.01151	1.01234	1.01300
3.50	1.0119	1.0114	1.0111	1.0111	1.0114	1.0119	1.0125	1.01351	1.01432
4.00	1.0135	1.0128	1.0125	1.0124	1.0126	1.0130	1.0138	1.0146	1.01553
4.50	1.0151	1.0143	1.0138	1.0136	1.0138	1.0142	1.0149	1.0157	1.0167
5.00	1.0167	1.0158	1.0152	1.0149	1.0150	1.0153	1.0159	1.0168	1.0178
10.00	1.0330	1.0308	1.0290	1.0277	1.0269	1.0265	1.0266	1.0271	1.0280
20.00	1.066	1.0615	1.0573	1.0539	1.0512	1.0493	1.0480	1.0474	1.0474
30.00	1.101	1.093	1.087	1.081	1.076	1.073	1.0698	1.0680	1.0670
40.00	1.138	1.126	1.117	1.109	1.102	1.096	1.092	1.0890	1.0869
50.00	1.175	1.161	1.148	1.137	1.128	1.121	1.115	1.111	1.107
60.00	1.215	1.196	1.180	1.167	1.155	1.146	1.139	1.133	1.128
70.00	1.256	1.233	1.213	1.197	1.183	1.172	1.163	1.155	1.149
80.00	1.298	1.271	1.248	1.228	1.212	1.198	1.187	1.178	1.171
90.00	1.343	1.311	1.284	1.261	1.242	1.226	1.212	1.202	1.193
100.00	1.389	1.352	1.320	1.294	1.272	1.254	1.238	1.226	1.216

[a] Values below −50 °C are based on a questionable extrapolation of B_{aw}. They are given as a matter of interest, but no error bands can be assigned.

lowest tabulated pressures at 70, 80, and 90 °C are exceeded by the saturation vapor pressure, precluding the existence of a saturation equilibrium condition. The enhancement factors calculated under those conditions are meaningless in the context of this paper, and have been omitted.

In the error discussion to follow, no attempt was made to assign uncertainties below −50 °C, for reasons discussed in section 3.

However, as a matter of interest, table 8 has been extrapolated to −80 °C. The necessary B_{aw} extrapolation used the Lennard-Jones (12−6) relationship, not eq (9).

For those interested in interpolation, note that, at low pressures, the enhancement factors increase rapidly as the pressure increases from the value of the saturation vapor pressure. The slope then suddenly decreases, the curve becoming more linear. The location of the slope change along the pressure axis, no greater than about 3 bar for the temperatures considered here, is a function of temperature.

6. Uncertainties in the Predicted Enhancement Ratios

In section 4, the contributions to the B_{aw} uncertainty from various calculated quantities (virial coefficients, saturation vapor pressure, etc.) were outlined. When the uncertainty in B_{aw} is considered as one computes the uncertainties in the predicted enhancement factors, the contributions from the remaining parameters are directly included, as part of the B_{aw} error. Therefore, the only quantity of concern in calculating the uncertainty in the predicted enhancement factors of table 8 is the interaction coefficient B_{aw}. For table generation, pressure and temperature are considered exact. At −50 °C and above the significant figures are given to the place which is affected by the maximum uncertainty (table 9) by no more than five units, plus one more place.

Table 9 outlines the estimated uncertainty in the predicted enhancement factors as a function of pressure and temperature. Linear interpolation of the errors, between adjacent tabulated pressure along the isotherm, allows error estimates to within 0.05 percent.

It is important to reemphasize that, below −50 °C, the error bands are considered unknown and, at present, unobtainable. Research at temperatures below −20 °C will be needed for further B_{aw} extrapolation and bracketing of the enhancement factors.

TABLE 9. *Estimated maximum percentage uncertainties in calculated* f [a]

P bar	Temperature, °C							
	90	70	50	30	+10	−10	−30	−50
1.00	0.001	0.01	0.01	0.01	0.03	0.04	0.05	0.06
2	.01	.02	.03	.03	.06	.07	.10	.13
3	.02	.03	.05	.04	.09	.11	.14	.19
4	.03	.05	.06	.05	.11	.15	.19	.25
5	.04	.06	.08	.07	.14	.18	.24	.32
10	.09	.13	.17	.13	.29	.37	.48	.64
20	.20	.26	.35	.27	.58	.75	.98	1.30
40	.41	.54	.70	.54	1.2	1.5	2.0	2.7
60	.62	.82	1.1	.82	1.8	2.3	3.1	4.2
80	.83	1.1	1.4	1.1	2.4	3.2	4.2	5.8
100	1.1	1.4	1.8	1.4	3.1	4.1	5.4	7.5

[a] No errors are assigned to values below −50 °C, nor should any attempt be made to do so.

7. Comparison With Other Work

Comparisons with other virial coefficient work may be found in [2].

The work of Goff [27] and Webster [28] are the two extensive experimentally based works with which we will compare our air-water vapor enhancement factors.

Table 10 compares selected high pressure data with Webster, while table 11 compares selected low pressure data with Goff. The disagreement with the former is within a factor of two of the NBS estimated maximum uncertainty except at −20 °C and 50 bar. However, the discrepancies will increase as the temperature decreases. The disagreement between NBS and Goff is within the NBS estimated uncertainty in all cases, ranging from 0.01 percent at 0.25 bar to 0.05 percent at 1 bar.

TABLE 10. *Comparison of* f*-values with Webster*

P bar		Temperature, °C		
		−20	0	+50
50	Webster	1.36	1.24	1.14
	NBS	1.243	1.193	1.128
	Difference, percent	9.4	3.9	1.1
100	Webster	1.75	1.50	1.28
	NBS	1.563	1.433	1.272
	Difference, percent	12.0	4.7	0.6

TABLE 11. *Comparison of* f*-values with Goff*

P bar		Temperature, °C				
		60	20	0	−20	−50
0.25	Goff	—	1.0018	1.0014	1.0013	1.0015
	NBS	1.0011	1.0017	1.0013	1.0012	1.0014
0.50	Goff	—	1.0027	1.0024	1.0024	1.0030
	NBS	1.0036	1.0025	1.0022	1.0022	1.0029
1.00	Goff	1.0060	1.0045	1.0044	1.0048	1.0060
	NBS	1.0057	1.0040	1.0040	1.0044	1.0058

8. Summary

New experimental enhancement factor data at −20, −10, and +70 °C, coupled with previously reported values at 30, 40, and 50 °C, have been used to obtain the air-water vapor interaction virial coefficient, B_{aw}, at those temperatures. The B_{aw} values have in turn been fitted by a Lennard-Jones (12–6) potential, to permit extrapolation and interpolation. An empirical equation for B_{aw} versus temperature is also given. Either equation predicts values considered uncertain by no more than 10 percent, for $-50 \leq t \leq 0$ °C and for $45 \leq t \leq 90$ °C. For $0 \leq t \leq 45$ °C, the uncertainty is 6 percent. Using these B_{aw} values, enhancement factors have been derived for air over ice from −50 to 0 °C, and for air over water from 0 to +90 °C, at 10 °C intervals, and at varying pressure intervals from 0.25 to 100 bar. The associated uncertainties vary according to condition, and are best seen in table 9. Extrapolations of the enhancement factor, to −80 °C for air over ice, are presented, but no uncertainties are assigned.

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9. Appendix

The derivation of eq (12) of [2], which refers only to the gas phase, begins with

$$\mu_i = \frac{\partial G_i}{\partial n_i}, \qquad \text{(A-1)}$$

where μ and n are the chemical potential and number of moles of water vapor, and G the Gibbs function, associated either with the mixture $(i=m)$ or pure water vapor $(i=w)$.

Equation (A-2) evaluates the Gibbs function difference between the saturated equilibrium state at pressure P and a reference state at pressure P_o.

$$G_i\ (T, P, n_a, n_i) - G_i\ (T, P_o, n_a, n_i) = \int_{P_o}^{P} V_i dP \qquad \text{(A-2)}$$

where n_a is the number of moles of air and V_i the volume of the gas under consideration at temperature T. The volumes V_i are obtained from the appropriate virial equation of state. (Note, however, that the magnitudes of n_i differ in the expressions for V_m and V_w).

The right side of (A-2) is evaluated for the mixture between P_o and the saturated equilibrium pressure P, and for pure water vapor between P_o and the saturation vapor pressure e_s. Equation (A-1) yields the corresponding chemical potential differences. By subtracting the results of these operations and rearranging, one obtains the chemical potential difference $\Delta\mu$ of the water vapor between the equilibrium conditions at pressure P in the mixture and e_s in the pure phase.

Let P_o be low enough so that both the mixture and pure water vapor can be considered as ideal gases in the reference state. The term μ_m (T, P_o, n_a, n_m) appearing in the expression for $\Delta\mu$ can be written as

$$\mu_m(T, P_0, n_a, n_m) = \mu_m(T, P_0, 0, n_m) + RT \ln x_w \qquad \text{(A-3)}$$

where x_w is the mole fraction of water vapor. Then, since in the ideal gas limit $\mu_m(T, P_0, 0, n_m)$ cancels a similar term, $-\mu_w(T, P_0, 0, n_w)$, and since all nonideal contributions become negligible when the integrals of (A-2) are evaluated at $P=P_0$, one is left with eq (12) of [2], with the left side replaced by $\Delta\mu$. Two wrong signs appearing in eq (12) are corrected in eq (29a) of [2]. Equation (29a), reproduced here as eq (A-4), is used for the general calculation of the enhancement ratio, after substituting for f its definition, eq (1) of this paper. The procedure is one of iteration, to solve for the mole fraction of air, x_a. This same equation may be inverted into a quadratic form in B_{aw}, to permit evaluation of B_{aw} from experimental enhancement factor data, as was done in [2].

$$\begin{aligned}
RT\ \ln f = {} & g(T,P) + RT\ \ln\,(1 - kx_aP) + B_{aa}x_a^2P \\
& - B_{ww}(P - e_s - x_a^2P) + C_{aaa}\frac{x_a^3P^2}{RT} \\
& + C_{aaw}\frac{3x_a^2(1-2x_a)P^2}{2RT} - C_{aww}\frac{3x_a^2(1-x_a)P^2}{RT} \\
& - B_{aa}^2\frac{3x_a^4P^2}{2RT} - C_{www}\frac{(1+2x_a)(1-x_a)^2P^2 - e_s^2}{2RT} \\
& - B_{aa}B_{ww}\frac{x_a^2(1-3x_a)(1-x_a)P^2}{RT} \\
& - B_{ww}^2\frac{e_s^2 - (1+3x_a)(1-x_a)^3P^2}{2RT} \\
& + B_{aw}\left[-2x_a^2P - B_{aa}\frac{2x_a^3(2-3x_a)P^2}{RT}\right. \\
& \left. + B_{ww}\frac{6x_a^2(1-x_a)^2P^2}{RT}\right] \\
& - B_{aw}^2\frac{2x_a^2(1-x_a)(1-3x_a)P^2}{RT} \qquad \text{(A-4)}
\end{aligned}$$

where B_{aa}, B_{ww} = the second virial coefficients for air and water, cm^3/mol

B_{aw} = the second interaction virial coefficient for air-water vapor mixtures, cm^3/mol

C_{ijk} = third virial coefficients for air and water $(i=j=k)$, or third interaction virial coefficients (cm^3/mol)^2

R = universal gas constant, 83.1434 bar-cm^3/mol-K

T = absolute temperature, K

P = total pressure, bar

e_s = saturation vapor pressure of the pure condensed water phase, bar

x_a = mole fraction of air in the gas mixture

k = Henry's "constant," mol fraction/bar

$g(T, P)$ = the product of the specific volume of pure phase, at the given (T, P) condition, and the difference $(P - e_s)$.

one needs, in addition to other equations given in this paper, the following relationships, discussed in [2]:

$$B_{ww} = 33.97 - \frac{55306}{T} \times 10^{\frac{72000}{T^2}} \text{ cm}^3\text{/mol} \qquad \text{(A-5)}$$

$$C_{www} = 2.85558\,\frac{B_{ww}^3}{T} + B_{ww}^2 \text{ cm}^6\text{/mol}^2 \qquad \text{(A-6)}$$

$$\begin{aligned}
C_{aww} \times 10^{-6} = {} & -0.20263 + 0.52695 \cdot 10^{-2}t \\
& - 0.74761 \cdot 10^{-4}t^2 \\
& + 0.57576 \cdot 10^{-6}t^3 \\
& - 0.18065 \cdot 10^{-8}t^4 \text{ cm}^6\text{/mol}^2 \qquad \text{(A-7)}
\end{aligned}$$

t = degrees Celsius, $T = t + 273.16$

Equations (A–5) and (A–6) are modifications of Goff's equations [27], which are based on IPTS–48. Use of $T=t+273.15$ causes insignificant changes in the results of this paper (see sec. 2).

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