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# Corrections to Paper Entitled "Third Virial Coefficient for Air-Water Vapor Mixtures"

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This note points out errors in the values of the third virial coefficients for pure water vapor which appeared in a 1967 paper by Hyland and Mason. The errors arose while converting from the units of Goff and of Keyes to the desired units of (liter/mole)$^2$. The consequences of the errors are outlined, and it is shown that there is no effect on the primary results of the paper, namely, in the preferred values of the third interaction virial coefficient for air-water vapor mixtures, $C_{aww}$.

Key words: Chemical association; Lennard-Jones potential parameters; third interaction virial coefficients; virial coefficients; water vapor-air mixtures.

## 1. Introduction

In 1967 Hyland and Mason [1] [1] published a paper in which a third interaction virial coefficient for air-water vapor mixtures, $C_{aww}$, was derived. In that paper, a computational error was committed while converting the third virial coefficients for pure water, $C_{www}$, from the units of Goff [2] and Keyes [3] to the desired units of (liter/mole)$^2$. This note points out the consequences of that error.

## 2. Error Source, and Consequences

The incorrect values of $C_{www}$ appear in the last two columns of table 1 of [1]. The proper values would be obtained by subtracting the squares of the corresponding second virial coefficients. The revised version of table 1 is given below.

The errors were propagated into the first two columns of table 2 of [1], which gives values for $B_{ww_2}$, into equations (21a, b) and (24b, c), and finally into the $C_{aww}$ values of table 3 based on eqs (24b, c). The revised version of table 3 is given below. The appendix to this note indicates the changes necessary to correct the text, and points out that the $C_{aww}$ values which appear in table 3 (revised) are not significantly different from those given in table 3 of [1].

The viscosity-based values of $C_{aww}$, which are the preferred values, and their stated uncertainties, are the same in both versions of table 3. Obviously results in reference [1] depending on the incorrect values of $C_{www}$ must be ignored.

TABLE 1. *(Revised) Experimental values of the second and third virial coefficients of water vapor; extropolated values in parentheses*

| Temp. | $-B_{ww}$ cm$^3$/mol | | | $-C_{www}$ liter$^2$/mol$^2$ | |
|---|---|---|---|---|---|
| | Goff [4] | Keyes [8] | Ave. | Goff [4] | Keyes [8] |
| °C | | | | | |
| 0 | (1834) | 1854 | 1844 | (61.1) | 90.4 |
| 10 | 1510 | 1520 | 1515 | (32.4) | 47.0 |
| 20 | 1265 | 1266 | 1266 | (18.1) | 26.0 |
| 30 | 1074 | 1070 | 1072 | (10.5) | 15.1 |
| 40 | 924 | 917 | 920 | (6.34) | 9.03 |
| 50 | 803 | 794 | 798 | (3.93) | 5.63 |
| 60 | 705 | 695 | 700 | 2.51 | 3.58 |
| 70 | 625 | 613 | 619 | 1.64 | 2.38 |
| 80 | 558 | 546 | 552 | 1.09 | 1.62 |
| 90 | 501 | 489 | 495 | 0.738 | 1.13 |
| 100 | (453) | 441 | 447 | .506 | 0.793 |

## 3. Appendix 1

In reference [1] the paragraph ending page 222, and the paragraph below eq (20b) could be rewritten by substituting the value $-0.89$ liter/mol for the $-1.11$ value, $-0.57$ liter/mol for the $-0.79$ value, and $-0.73$ liter/mol for the $-0.95$ value.

The paragraph containing eqs (21a, b) would be rewritten as follows:

Empirical curve fitting with $B_{ww2}$, matching at the adjusted limit of $-0.73$ liter/mol, leads to the parameters

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

$$t^* = 1.1,\ \sigma_{ww_2} = 3.45\ \text{Å},\ \frac{\epsilon_{ww_2}}{k} = 380\ \text{K}. \tag{21a}$$

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

| Temp. | $-C_{aww}$, litter$^2$/mol$^2$ | | | | | |
|---|---|---|---|---|---|---|
| | Virial | | | Viscosity* | Limits | |
| | Eq (24a) | Eq (24b) | Eq (24c) | Eq (24d) | Eq (25a) | Eq (25b) |
| °C | | | | | | |
| 0 | 0.152 | 0.137 | 0.123 | 0.203 | 0.062 | 0.549 |
| 10 | .117 | .105 | .094 | .156 | .047 | .424 |
| 20 | .092 | .082 | .074 | .123 | .037 | .332 |
| 30 | .073 | .064 | .058 | .098 | .029 | .266 |
| 40 | .058 | .052 | .047 | .080 | .024 | .216 |
| 50 | .048 | .042 | .038 | .065 | .019 | .178 |
| 60 | .040 | .034 | .031 | .054 | .016 | .148 |
| 70 | .034 | .028 | .026 | .046 | .013 | .123 |
| 80 | .028 | .024 | .021 | .039 | .011 | .105 |
| 90 | .024 | .020 | .018 | .033 | .009 | .090 |
| 100 | .021 | .017 | .015 | .028 | .008 | .077 |

*Best estimates.

Within the limits specified by eqs (20a, b), the parameters cannot be adjusted to force the fit through the Goff-based value of $-0.57$ liter/mol at 100 °C. By adjusting the parameters as far as possible, we obtain

$$t^* = 0.98,\ \sigma_{ww_2} = 3.58\ \text{A}^\circ,\ \frac{\epsilon_{ww_2}}{k} = 380\ K, \tag{21b}$$

which leads to a value of $B_{ww_2}$ of $-0.62$ liter/mol at 100 °C.

The reader can obtain the relationships corresponding to eqs (24b, and 24c) of [1] leading to the $C_{aww}$ values appearing in columns 3 and 4 of table 3 (revised). The magnitudes are roughly 13 percent greater than the corresponding values appearing in table 3 of [1], and, in any event, are not the preferred values.

## 4. References


[1]. Hyland, R. W., and Mason, E. A., Third Virial Coefficient for Air-Water Vapor Mixtures, J. Res. Nat. Bur. Stand. (U.S.), **71A** (Phys. and Chem), No. 3, 219–224 (May–June 1967).

[2]. Goff, J. A., Standardization of Thermodynamic Properties of Moist Air, Heating, Piping and Air Conditioning (Journal Section), **21**, 118 (1949).

[3]. Keyes, F. G., The Thermodynamic Properties of Water Substance from 0° to 150 °C, J. Chem. Phys. **15**, 602 (1947).


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