J. Chem. Eng. Data **1994**, *39*, 873–875

Cross Second Virial Coefficients for the Systems $N_2 + O_2$ and $H_2O + O_2$

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We have extracted cross virial coefficients between 188 and 480 K for the system nitrogen + oxygen from existing *PVT* data for air. These values agree with literature values within experimental error. We have also extracted cross virial coefficients for the system water + oxygen from cross virial coefficients of moist air. Our calculations cover the temperature range from 298 to 373 K, but no previous values exist with which to compare. These values, extracted from experimental *PVT* data, extend or provide cross virial coefficients at conditions for which no previous values have been reported for nitrogen + oxygen and for water + oxygen. The extraction process is the normal procedure for recovering virial coefficients from experimental data.

Introduction

The theoretical and practical importance of the virial equation of state (EOS) is well known and accepted. In the calculation of thermodynamic properties from this EOS, it is necessary to know cross and pure virial coefficients. These virial coefficients result from experiments or regressions of *PVT* data.

Oxygen, nitrogen, and water are common components of gas mixtures. To represent the thermodynamic behavior of these gases, it is often convenient to use the virial EOS. In this equation we require pure and binary properties to ascertain the behavior of multicomponent mixtures. Compilations of virial coefficients such as that of Dymond and Smith (*1*) contain this information. However, some systems contain little or no experimental information. This is the case for the nitrogen + oxygen system for which Martin *et al.* (*2*) and Gorski and Miller (*3*) have measured cross virial coefficients. For the water + oxygen system experimental measurements of virial coefficients do not exist. Measurements of *PVT* data for mixtures with polar components are scarce.

In this work we extract the cross virial coefficients of the nitrogen + oxygen system from air *PVT* data, and the cross virial coefficient of the oxygen + water system from cross virial coefficients of moist air. The procedure is to extract from the second virial coefficient of a multicomponent mixture an unknown cross virial coefficient knowing the rest of the virial coefficients. Our calculated values cover the ranges 180–480 K for nitrogen + oxygen and 298–373 K for oxygen + water.

Development

The truncated second virial EOS in its density form is

$$Z = 1 + B\varrho \tag{1}$$

where Z is the compressibility factor, B is the second virial coefficient, and ϱ is the molar density. For pure components, the virial coefficients are functions of temperature while for mixtures they are functions of temperature and composition. The composition dependence of the second virial coefficient, $B(x)$, is

$$B(x) = \sum_{i=1}^{c} x_i^{\,2} B_{ii} + 2\sum_{i=1}^{c-1} \sum_{j=i+1}^{c} x_i x_j B_{ij} \tag{2}$$

where c is the number of components in the mixture, x_i is the mole fraction of component i in the mixture, and B_{ij} is the second cross virial coefficient. Equation 2 illustrates that the second virial coefficient of a mixture depends upon the values of the cross and pure virial coefficients of the components. If for a mixture there exists an unknown cross virial coefficient, it can be back-calculated from B in eq 2:

$$B_{k1} = (B(x) - (\sum_{i=1}^{c} x_i^{\,2} B_{ii} + 2\sum_{i=1}^{c-1} \sum_{j=i+1}^{c} x_i x_j B_{ij}))/2x_k x_1 \tag{3}$$

where $j \neq 1$ if $i = k$. In this work, we use eq 3 together with air and moist air data to calculate cross virial coefficients of $N_2 + O_2$ and $H_2O + O_2$.

Air Composition

Dry air is a multicomponent mixture of nitrogen, oxygen, carbon dioxide, argon, and traces of other components. We neglect the trace elements as constituents and consider air to be a four-component mixture. The composition of air for the calculation of cross virial coefficients is

$$x(N_2) = 0.781\,02$$

$$x(O_2) = 0.209\,46$$

$$x(CO_2) = 0.000\,36$$

$$x(Ar) = 0.009\,16$$

as reported by Jones (*4*).

Calculation

***$N_2 + O_2$* System.** When the air is considered as a four component system, the cross virial coefficient of $N_2 + O_2$ can be calculated from eq 3 because the other virial coefficients are known. Information about the virial coefficient and *PVT* behavior of air has existed since 1915, see Jacobsen *et al.* (*5*). To select a data set, it is necessary to check the accuracy and reputation of the measuring laboratory. We have selected the data of Michels *et al.* (*6*, *7*) between 188 and 348 K to obtain second and third virial coefficients using a curve-fitting procedure. The maximum percentage error is 0.03% in the compressibility factor. At

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Table 1. Parameters Used in Eq 4 for the Pure and Binary Pairs

system	a_0	a_1	a_2	a_3	a_4	a_5
$N_2 + N_2$	44.592	−121.997	−76.734			
$O_2 + O_2$	52.912	−269.933	316.639	−379.838		
$CO_2 + CO_2$	27.072		−1781.994	2263.415	−2788.171	
Ar + Ar	34.143	−131.806		−166.172		152.954
$N_2 + CO_2$				−2341.732	4657.601	−2924.031
$N_2 + O_2$	35.703	−105.347	−107.792			
N_2 + Ar	23.893			−2254.332	5139.745	−3419.537
$O_2 + CO_2$	−15.692					−5894.618
O_2 + Ar	40.183	−165.595				
CO_2 + Ar	35.148	−203.871				−1273.398
$CO_2 + H_2O$	79.586			−60654.111	327096.950	−504787.132
Ar + H_2O	−20.083				8187.263	−28353.059

Table 2. Cross Second Virial Coefficients for $N_2 + O_2$

T/K	B_{N_2,O_2}/(cm³·mol⁻¹)	T/K	B_{N_2,O_2}/(cm³·mol⁻¹)
188.15	−50.6 ± 1.7	370.00	−0.437 ± 0.8
203.15	−42.1 ± 1.7	380.00	0.717 ± 0.8
223.15	−33.3 ± 1.7	390.00	1.79 ± 0.8
248.15	−24.4 ± 1.7	400.00	4.61 ± 0.8
273.15	−17.2 ± 0.2	430.00	5.43 ± 0.8
298.15	−11.9 ± 0.2	440.00	6.20 ± 0.8
323.15	−7.58 ± 0.25	450.00	6.91 ± 0.8
348.15	−3.69 ± 0.25	460.00	7.58 ± 0.8
350.00	−3.00 ± 0.8	470.00	8.21 ± 0.8
360.00	−1.67 ± 0.8	480.00	8.80 ± 0.8

temperatures greater than 348 K, we use the formulation of Jacobsen *et al.* (*5*) to calculate the second virial coefficient.

Pure component virial coefficients of carbon dioxide, nitrogen, and oxygen appear in Dymond and Smith (*1*), Holste *et al.* (*8*), Duschek *et al.* (*9*), Duschek *et al.* (*10*), Gilgen *et al.* (*11*), and Wagner *et al.* (*12*). They have been fitted to polynomials of the form

$$B = \sum_{i=0}^{5} a_i (100/T)^i \tag{4}$$

The a_i coefficients appear in Table 1. The maximum absolute deviation between eq 4 and the experimental data is ±0.5 cm³·mol⁻¹.

The binary pairs in this mixture are $N_2 + CO_2$, N_2 + Ar, $O_2 + CO_2$, O_2 + Ar, CO_2 + Ar, and $N_2 + O_2$. Equation 4 also describes the temperature dependence of existing B_{ij} data within the estimated absolute experimental error. The maximum absolute error is ±7.5 cm³·mol⁻¹ for CO_2 + Ar. Because experimental B_{ij} values of $O_2 + CO_2$ and O_2 + Ar do not cover the whole temperature range, we use a combination rule to extrapolate the data:

$$B_{ij} = \frac{B_{ii} + B_{jj}}{2}(1 - k_{ij}) \tag{5}$$

with $k_{O_2,CO_2} = 0.417$ and $k_{O_2,Ar} = 0.040$.

Calculated cross virial coefficients for the system $N_2 + O_2$ are in Table 2. Figure 1 shows the agreement between the experimental data of Martin *et al.* (*2*) and Gorski and Miller (*3*) and the new values. The Tsonopoulos (*13*) correlation agrees with our values within a maximum deviation of ±1.65 cm³·mol⁻¹ when we use $k_{ij} = -0.016$. In Figure 1, the $B_{N_2O_2}$ values lie between the pure component values shown as solid and dashed lines. Up to 400 K they closely approximate an arithmetic mean combination rule. At higher temperatures, this combination rule does not hold, but calculated values from the rule are probably within an estimated experimental error.

O_2 + H_2O System. Having calculated the pseudoexperimental values of the $N_2 + O_2$ system, the cross virial coefficient of $O_2 + H_2O$ can be calculated if virial coefficients for the system air + water exist. Experimental cross virial coefficients for this system have been published by Hyland (*14*) and Hyland and Wexler (*15*). They obtained the virial coefficients from enhancement data between 253 and 343 K which they consider to be better than ±3.0 cm³·mol⁻¹. In their derivations, they considered air to be CO_2-free; the CO_2 contribution is small for practical situations because its mole fraction is small in air.

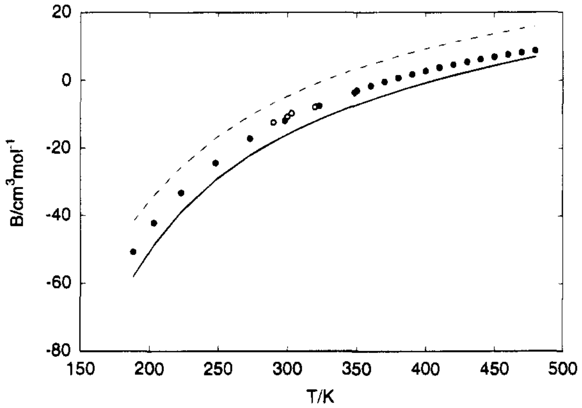

Figure 1. Virial coefficients for the $N_2 + O_2$ system. Solid circles are current calculations, open circles are from Dymond and Smith (*1*), the solid line is pure O_2, and the dashed line is pure N_2.

In this system the new binary pairs are $N_2 + H_2O$, $CO_2 + H_2O$, Ar + H_2O, and $O_2 + H_2O$. Experimental values for these systems of polar + nonpolar components are scarce, and they do not follow closely a combination rule with which to extrapolate. Our calculation procedure is limited to the lowest temperature range of one of the systems. In this case the temperature range is from 298 to 373.15 K in the $N_2 + H_2O$ system. Experimental values come from Dymond and Smith (*1*) and Patel *et al.* (*16*). Again, we use eq 3 to represent the B_{ij} values of the binary pairs with the exception of the system $N_2 + H_2O$ which requires further explanation.

For the $N_2 + H_2O$ system experimental values come from Rigby and Prausnitz (*17*) who derive B_{ij} from measurements of the solubility of water in compressed N_2. In our calculation, we have considered the mixture virial in both expanded and lumped forms:

$$B = \sum_{i=1}^{5}\sum_{j=1}^{5} x_i x_j B_{ij} = x_{air}^2 B_{air} + 2x_{air}x_{water}B_{air,water} + x_{water}^2 B_{water} \tag{6}$$

The virial coefficients for pure water cancel between the expanded and lumped forms which results in

$$\sum_{i=1}^{4} x_i^2 B_{ii} + 2\sum_{i=1}^{4}\sum_{j=i+1}^{5} x_i x_j B_{ij} = x_{air}^2 B_{air} + 2x_{air}x_{water}B_{air,water} \tag{7}$$

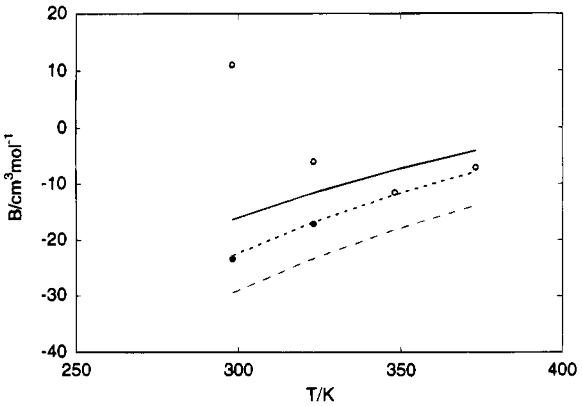

Figure 2. Comparison of current values (zero deviation line) with those calculated from McGlashan and Potter (*18*), dotted line; Lennard-Jones calculation, solid line; and O'Connell and Prausnitz (*20*), dashed line.

Table 3. Cross Second Virial Coefficients for $O_2 + H_2O$ and $N_2 + H_2O$

T/K	B_{O_2,H_2O}/ (cm^3·mol^{-1})	B_{N_2,H_2O}/ (cm^3·mol^{-1})	T/K	B_{O_2,H_2O}/ (cm^3·mol^{-1})	B_{N_2,H_2O}/ (cm^3·mol^{-1})
298.15	−23.4 ± 9	−31.0	348.15	−11.5 ± 2.5	−20.0
323.15	−17.2 ± 5	−25.0	373.15	−7.1 ± 2	−15.5

where dry air has four components and water is the fifth component. The cross virial coefficient of moist air from Hyland (*14*) is

$$B_{\text{air,water}}/(\text{cm}^3\cdot\text{mol}^{-1}) = 36.98928 - 0.331705(t/°\text{C}) + 0.139035 \times 10^{-2}(t/°\text{C})^2 - 0.574154 \times 10^{-5}(t/°\text{C})^3 + 0.326513 \times 10^{-7}(t/°\text{C})^4 - 0.142805 \times 10^{-9}(t/°\text{C})^5 \quad (8)$$

Equation 6 is the basis for the calculation of B_{O_2,H_2O} values. When using the values given by Rigby and Prausnitz (*17*) for the calculation, the calculated cross second virial coefficient at temperatures below 323.15 K lies above the virial coefficient of oxygen which is not likely. If we move the B_{N_2,H_2O} to less negative values, we calculate values that lie below the oxygen values. At 323.15, we have used the lower limit error band value for the second virial coefficient (at 298.15 K we need to use a value even lower than this limit). These *selected* values agree better with the Tsonopoulos (*13*) correlation. Table 3 contains cross virial coefficients for the $N_2 + H_2O$ and $O_2 + H_2O$ systems. We use $k_{ij} = 0.43$ to fit the high-temperature data of $O_2 + H_2O$ to the Tsonopoulos formula. The correlation agrees within ±1 cm^3·mol^{-1} over the lower temperature range as shown in Figure 2. If $k_{ij} = 0.40$, the Tsonopoulos (*13*) correlation underpredicts values at the higher temperatures.

Conclusions

We have extracted second cross virial coefficients for the systems $N_2 + O_2$ and $O_2 + H_2O$ from existing *PVT* data. The new values for $N_2 + O_2$ agree with previously reported values and cover a wider range of temperatures. This system follows a combination rule approximating the arithmetic mean. Figure 3 is a deviation plot for this mixture which compares the values presented in this paper (zero line) with the correlations of McGlashan and Potter (*18*), Lennard-Jones (*19*), and O'Connell and Prausnitz (*20*). We have used the geometric mean value for the critical temperature and the energy parameter. McGlashan and Potter do an excellent job of prediction followed by Lennard-Jones and then O'Connell and Prausnitz. The energy parameters we have used for Lennard-Jones are (nitrogen) $\epsilon = 95.448$, $\sigma = 3.703$ and (oxygen) $\epsilon = 118.385$, $\sigma = 3.482$.

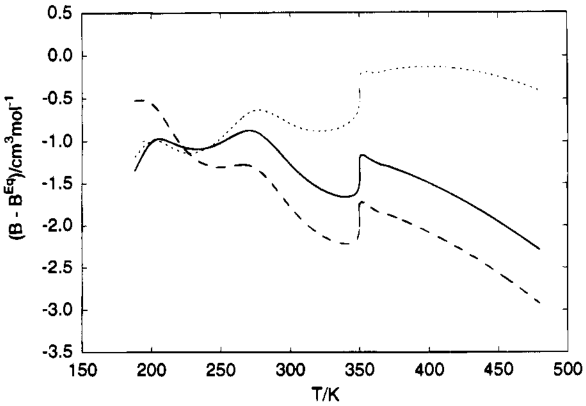

Figure 3. Virial coefficients for the $O_2 + H_2O$ system. Solid circles are current calculations, open circles are calculations without correcting B_{ij}, the solid line is pure O_2, the dashed line is the Tsonopoulos (*13*) correlation with $k_{ij} = 0.40$, and the dotted line is the Tsonopoulos (*13*) correlation with $k_{ij} = 0.43$.

For $O_2 + H_2O$ no previously reported values exist with which we can compare; however, the Tsonopoulos correlation agrees closely with our calculations using $k_{ij} = 0.43$. We have arbitrarily adjusted the data of Rigby and Prausnitz (*17*) to produce physically realistic values and included them in a table. Our calculations indicate that second cross virial coefficients can be extracted from multicomponent mixture data to provide values at previously unavailable conditions.

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Received for review April 12, 1994. Accepted July 25, 1994.® The authors acknowledge financial support from the Texas Engineering Experiment Station and Instituto Tecnologico de Celaya for this project.

® Abstract published in *Advance ACS Abstracts,* September 15, 1994.