

present study, both the pyrazine + CO<sub>2</sub> and + CHF<sub>3</sub> systems show type A phase behavior, in spite of large values of  $\Delta T$  (both larger than 20 K). These findings would reflect some characteristic interactions between unlike molecules such as the strong affinity between CO<sub>2</sub> and Lewis base.

### Conclusions

Pressure-temperature-gaseous phase composition relations of high-pressure phase boundaries are reported for eight binary mixtures, which are composed of pyrimidine or pyrazine as the heavy component and CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, or CHF<sub>3</sub> as the light component. The phase boundaries are determined by straightforward visual observation, and in order to determine the gaseous phase composition, a small amount of the phase (ca. 0.012 cm<sup>3</sup>) is injected into the SFC. The observed phase boundaries are the gas-liquid critical line (G=L), the three-phase equilibrium lines (S<sub>1</sub>-L<sub>1</sub>-L<sub>2</sub>, S<sub>1</sub>-L-G, L<sub>1</sub>-L<sub>2</sub>-G), the critical end points (S<sub>1</sub>-L=G, L<sub>1</sub>-L<sub>2</sub>=G), and the quadruple points (S<sub>1</sub>-S<sub>2</sub>-L-G, S<sub>1</sub>-L<sub>1</sub>-L<sub>2</sub>-G).

The pyrimidine + CO<sub>2</sub> and + CHF<sub>3</sub> systems and the pyrazine + CO<sub>2</sub> and + CHF<sub>3</sub> systems are identified to show type A phase behavior according to the arbitrarily defined classification of phase behavior (Figure 1). The pyrimidine + C<sub>2</sub>H<sub>6</sub> and + C<sub>2</sub>H<sub>4</sub> systems and the pyrazine + C<sub>2</sub>H<sub>6</sub> system are identified to display type E phase behavior. And the pyrazine + C<sub>2</sub>H<sub>4</sub> system is revealed to belong to type F behavior. Although the

$\Delta T$  values of both the pyrazine + CO<sub>2</sub> and + CHF<sub>3</sub> systems are large enough to show type F, both systems show type A.

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**Registry No.** CO<sub>2</sub>, 124-38-9; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>2</sub>H<sub>6</sub>, 74-84-0; CHF<sub>3</sub>, 75-46-7; pyrimidine, 289-95-2; pyrazine, 290-37-9.

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## Excess Second Virial Coefficients for Binary Mixtures of Carbon Dioxide with Methane, Ethane, and Propane

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**For the binary systems methane + carbon dioxide, ethane + carbon dioxide, and propane + carbon dioxide, measurements of the pressure change on mixing at 303.15, 313.15 and 323.15 K are reported as well as the excess second virial coefficients calculated therefrom. The correlations due to Tsonopoulos, Hayden and O'Connell, and the Groupe Européen de Recherches Gazières are compared with the results.**

### Introduction

Apart from the virial equation, virtually all equations of state have been developed for single-component systems and extended to mixtures by application of combining rules for the parameters. These rules are invariably arbitrary in nature despite attempts to relate them to fundamental theory. The virial equation has the great advantage that the equations describing mixture behavior are rigorously derived from statistical mechanics.

At high pressures the virial equation has often been rejected because the series may not converge rapidly. In recent years, however, it has been demonstrated that for certain gas mixtures of industrial importance (e.g. reticulated natural gas), an excellent fit to available data can be obtained with second and third virial coefficients only (1). Consequently, the excellent features of the equation may be taken advantage of.

This study represents part of a broader investigation into both second and third virial coefficients.

The pressure change of mixing method used here employs relation 1 where  $y$ ,  $P$ ,  $\Delta P$ , and  $T$  are respectively the mole fraction, the pressure, the pressure change, and the temperature. The method has the advantage over measuring the

$$\begin{aligned} RT\Delta P/[P^2(1 + \Delta P/P)2y(1 - y)] &= B_{12} - (B_{11} + B_{22})/2 \\ &= B_{12}^E \end{aligned} \quad (1)$$

second molar virial coefficient  $B_m$  of a mixture that it is possible to measure the second molar excess virial coefficient  $E_{12}^E$  with greater accuracy than the second molar virial coefficients  $B_{11}$  and  $B_{22}$  of the pure gases, so that determination of the unlike interaction second molar virial coefficient  $B_{12}$  to an accuracy comparable with that of  $B_{11}$  and  $B_{22}$  can be achieved.

### Experimental Apparatus and Procedure

The apparatus, which has been described previously (2), consists essentially of three equally sized glass vessels, immersed in an oil bath. The first vessel contains gas maintained as a reference pressure, the second and third, components 1 and 2 all, at equal pressure. The two components are mixed and the resultant change in pressure is measured relative to the reference pressure.

The only change to the apparatus was the addition of two gas drying trains fitted with mercury-filled pressure relief "bubblers" with access tubes of sufficient height for the "train" to be evacuated prior to filling with test gas.

Loading pressures of 98.7 kPa were applied unless a pressure change on mixing in excess of a full scale gauge reading (133 Pa) resulted, in which case the loading pressure was halved.

The mixing procedure as in previous work consisted of application of liquid nitrogen to a "cold finger" in one of the component vessels. Both components are thus transferred into one vessel where mixing occurs on removal of the liquid nitrogen with resulting expansion back into both vessels.

In the case of methane, the vapor pressure is still 0.24 kPa at liquid nitrogen temperature, and so it would be possible for up to 15% of the methane to remain in the vessel without the cold finger. Because of this potential problem, application and removal of the liquid nitrogen was repeated several times, to ensure complete mixing.

In previous studies the absolute pressure was measured by using nitrogen balanced against the pressure of the first loaded component. For this work, the second component was also employed to pressurize the mercury manometer used to determine the absolute pressure. This considerably facilitated the performance of the experiment.

### Materials

All gases used were supplied by New Zealand Industrial Gases Ltd., and all were analyzed for impurities by gas chromatography. All gases were found to be better than 99 mol % pure with the only significant impurities being nitrogen in the carbon dioxide, carbon dioxide in methane, propane in ethane, and butane in propane.

An analysis of the effect on an impurity on the results of this experimental procedure (see Appendix I) gives the following expression:

$$RT\Delta P/[P^2(1 + \Delta P/P)2y_1y_2] = B_{12}^E + y_6[B_{11} - B_{22} + 2B_{26} - 2B_{16}] \quad (2)$$

where gas 1 contains impurity 6.

For the three binary systems studied, substituting  $B_{ij}$  and  $y$  values for the worst case situation in the above equation reveals maximum errors in  $B_{12}$  from this source of  $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$ . For the systems studied, therefore, corrections to take account of impurities were not applied since the overall experimental uncertainty is greater than  $1 \text{ cm}^3 \text{ mol}^{-1}$ .

### Pure Component Second Virial Coefficient Values

**Carbon Dioxide.** Holste and co-workers (3) conducted a comprehensive study and review of PVT behavior of carbon dioxide. They found that the equation for second virial coefficient  $B$

$$B = b_0 + b_1/T + b_2/T^2 \quad (3)$$

$$B_0 = 23.02991 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_1 = -2.455297 \times 10^3 \text{ K cm}^3 \text{ mol}^{-1}$$

$$B_2 = -1.226275 \times 10^7 \text{ K}^2 \text{ cm}^3 \text{ mol}^{-1}$$

fitted the available data well over the temperature range 280–320 K. We have used this equation to provide  $B$  for carbon dioxide in this work.

**Methane.** In a recent study Kleinrahn and co-workers (4) present new high-precision data on the compression factor of methane and a detailed review of previous work. The equation proposed for the second virial coefficient of methane in the temperature range 273.15–323.15 K is

$$B_{22}/(\text{cm}^3 \text{ mol}^{-1}) = 16.0428(0.376136/T_r^{0.25} - 0.708823/T_r^{1.25}) \quad (4)$$

where  $T_r = T/(273.15 \text{ K})$ . Equation 4 has a claimed uncer-

Table I. Second Molar Virial Coefficients  $B_{ii}$  of Pure Components at Temperatures  $T$

component	$B_{ii}/(\text{cm}^3 \text{ mol}^{-1})$		
	303.15 K	313.15 K	323.15 K
carbon dioxide	-118.2	-109.3	-101.9
methane	-40.9	-37.4	-34.3
ethane	-179.3	-167.3	-156.5
propane	-377.3	-351.8	-329.5

Table II. Initial Pressure  $P$ , Pressure Change  $\Delta P$ , and Calculated Excess Molar Virial Coefficients  $B_{12}^E$  and Molar Unlike Interaction Second Virial Coefficients  $B_{12}$  at Temperatures  $T$

$T/\text{K}$	$P/\text{Pa}$	$\Delta P/\text{Pa}$	$B_{12}^E/(\text{cm}^3 \text{ mol}^{-1})$	$B_{12}/(\text{cm}^3 \text{ mol}^{-1})$
Methane + Carbon Dioxide				
303.38	89 537	21.79	13.73	-65.8
303.33	51 563	8.01	15.18	-64.4
313.34	97 766	28.18	15.36	-58.0
313.30	77 962	14.18	12.15	-61.2
323.15	38 523	3.43	12.40	-55.7
Ethane + Carbon Dioxide				
303.49	86 594	37.37	25.14	-123.6
313.24	51 904	13.27	25.64	-112.7
313.25	95 042	39.02	22.49	-115.8
323.16	98 806	35.21	21.96	-107.2
323.15	79 860	27.06	22.79	-106.4
Propane + Carbon Dioxide				
303.26	58 189	53.02	78.90	-168.9
303.33	52 443	43.42	79.56	-168.2
313.24	51 963	35.66	68.75	-161.8
313.07	51 694	37.40	72.81	-157.8
313.28	51 409	36.32	71.54	-159.0
313.25	50 811	33.53	67.60	-162.9
323.18	68 689	55.72	63.41	-152.2
323.15	82 547	81.15	63.93	-151.8

tainty of  $0.15 \text{ cm}^3 \text{ mol}^{-1}$ . We have used this equation to generate the  $B_{22}$  values required (Table I).

**Ethane.** Ethane behavior has been reviewed by Holste and co-workers (3) who confirmed that the reasonably comprehensive data for this system are fitted, apparently within experimental uncertainty, by the equation developed by Goodwin and co-workers (5). This equation has been used to generate second virial coefficients for pure ethane in this work (Table I).

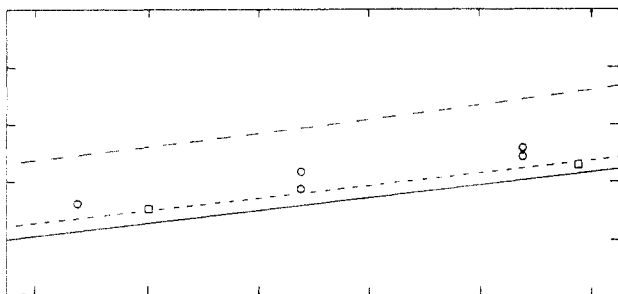
**Propane.** This system has been the subject of several studies, and the available data were reviewed by Goodwin (6) and by Thomas and Harrison (7). Additional work by Barber and co-workers (19) is in good agreement with earlier work, particularly that of McGlashan and Potter (8). The fitting equations developed by Goodwin and by McGlashan and Potter appear to represent the data within experimental error, and we have used the Goodwin equation to generate the propane  $B$  values required here (Table I).

### Results and Discussion

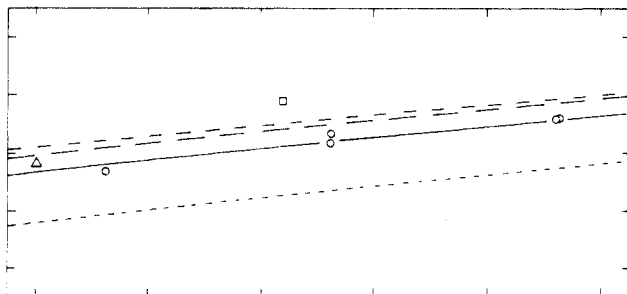
The primary data and the calculated second molar excess virial coefficients for the three systems at three temperatures are presented in Table II.

A simple error analysis of the procedure indicates that the dominant source of uncertainty is expected to be in the measure of  $\Delta P$  and that  $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$  in  $\epsilon_{12}$  should be attainable. Duplicate measurements however do not show this level of consistency, particularly for those runs at 313.15 K. Strenuous efforts were made to ensure complete mixing of the components, but independent evidence that this has been achieved is difficult to obtain. Duplicate measurements suggest that an uncertainty of  $\pm 3 \text{ cm}^3 \text{ mol}^{-1}$  is representative of the data.

The  $B_{12}^E$  values have been used to generate  $B_{12}$  values through use of eq 1 and the pure component second virial



**Figure 1.** Unlike interaction second molar virial coefficients  $B_{12}$  for carbon dioxide + methane as a function of temperature  $T$ . Lines: (—) Tsonopolous (13) and modified Hayden and O'Connell (17) correlation; (- -) GERG equation (1); (- · -) Hayden and O'Connell correlation (14). Points, experimental values: (□) Martin et al. (10); (○) this work.



**Figure 2.** Unlike interaction second molar virial coefficients for carbon dioxide + ethane as a function of temperature  $T$ . Lines: (—) Tsonopolous correlation (13); (- -) modified Hayden and O'Connell correlation (17); (- · -) GERG equation (1); (- · -) Hayden and O'Connell correlation (14). Points, experimental values: (□) Zaalishvili (11); (Δ) Holste et al. (3); (○) this work.

coefficient values listed in Table I. The results have been plotted in Figures 1–3 along with measurements reported in the literature.

For carbon dioxide + methane, results in the temperature range have been reported by Zaalishvili (9) and by Martin and co-workers (10). The results reported here lie between those of the above workers.

The carbon dioxide + ethane system has been studied by Zaalishvili (11) whose reported results are somewhat smaller in absolute magnitude. Holste and co-workers (3) have also studied this system at slightly lower temperatures, and as indicated in Figure 2, the results appear to be in excellent agreement.

Propane + carbon dioxide second virial coefficients in the temperature range have been reported by Gunn (12) whose values are consistent with but numerically slightly smaller in absolute magnitude than the values reported here.

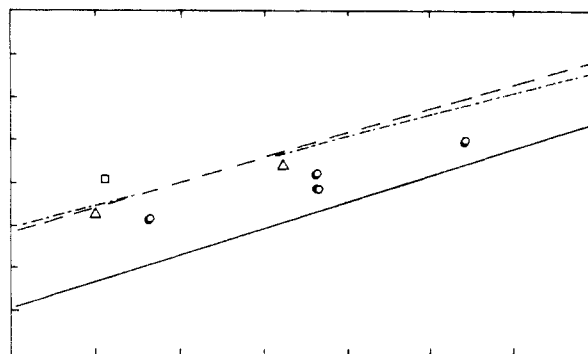
Given that the  $B_{12}$  values, whether obtained from  $B_{12}^E$  or second virial coefficients of mixtures, require introduction of pure component  $B_{ii}$  values, agreement with the small amount of existing data is excellent.

Also plotted on Figures 1–3 are correlations due to Tsonopolous (13) and Hayden and O'Connell (14) and the equation developed by the Groupe Européen de Recherches Gazières (GERG) (1, 15).

The Tsonopolous correlation provides a reasonable prediction of the unlike interaction second virial coefficient for the three systems but is consistently too positive in all cases. In applying this correlation values of the unlike interaction critical temperatures  $T_{12}^c$  are required. This quantity is commonly obtained with the relation

$$T_{12}^c = (T_1^c T_2^c)^{1/2} (1 - k_{12}) \quad (5)$$

where  $T_1^c$ ,  $T_2^c$ , and  $k_{12}$  are the critical temperatures of 1 and 2 and the association parameter, respectively.



**Figure 3.** Unlike interaction second molar virial coefficients for carbon dioxide + propane as a function of temperature  $T$ . Lines: (—) Tsonopolous correlation (13); (- -) modified Hayden and O'Connell correlation (17); (- · -) GERG equation (1); (- · -) Hayden and O'Connell correlation (14). Points, experimental values: (Δ) Gunn (12); (□) Bougard and Jadot (20); (○) this work.

A value of  $k_{12}$  must therefore be obtained from another source, or  $k_{12}$  may be used as a fitting parameter. In this work we have used the  $k_{12}$  values reported by Chueh and Prausnitz (16), which are 0.05, 0.08, and 0.11 for  $\text{CO}_2 + \text{CH}_4$ ,  $\text{CO}_2 + \text{C}_2\text{H}_6$ , and  $\text{CO}_2 + \text{C}_3\text{H}_8$ , respectively. These values are quoted as being accurate to within  $\pm 0.02$ . Holste and co-workers (3) calculated  $k_{12}$  values from their measured cross virial coefficients for  $\text{CO}_2 + \text{C}_2\text{H}_6$  and obtained  $k_{12} = 0.088$  at 300 K. They found that  $k_{12}$  decreased with increasing temperature but would be within the range quoted of  $0.08 \pm 0.02$  over the span of temperature covered in this work.

The Hayden and O'Connell correlation though widely used does not predict the behavior of pure carbon dioxide at all well. However, particular modifications for application to  $\text{CO}_2$  have been imposed by Prausnitz and co-workers (17), and with this procedure, a good fit to the data is generated. For the systems studied here, the modified form of the equation applied to mixtures generates  $B_{12}$  values that are very similar to those predicted by the Tsonopolous equation. The unmodified equation provides no better a prediction of  $B_{12}$  than it did for  $B_{11}$  (carbon dioxide).

The values generated by the GERG equation are also plotted. The ethane + carbon dioxide results are in excellent agreement with experiment. For carbon dioxide mixtures with methane the GERG values appear too negative and with propane too positive.

The GERG equation (1, 15) parameters have been selected with the aim of fitting natural gas mixture compression factor behavior. Second and third virial coefficients only have been used in fitting available compression factor data. Small deviations from the limiting low-pressure second virial coefficients might therefore be expected for systems at lower reduced temperatures. The small deviation for the propane + carbon dioxide unlike interaction coefficient could arise for this reason. That the methane + carbon dioxide system is not well represented by the GERG equation however suggests that reevaluation of the coefficients would be worthwhile. An earlier study on carbon dioxide rich natural gas (18) also suggested that the GERG coefficients for this system could be improved.

#### Glossary

$B_m$	second molar virial coefficient of gas mixture, $\text{cm}^3 \text{mol}^{-1}$
$B_{11}$	second molar virial coefficient of pure $\text{CO}_2$ , $\text{cm}^3 \text{mol}^{-1}$
$B_{22}$	second molar virial coefficient of pure methane, $\text{cm}^3 \text{mol}^{-1}$
$B_{12}$	unlike interaction second virial coefficient, $\text{cm}^3 \text{mol}^{-1}$
$B_{12}^E$	excess second molar virial coefficient, $\text{cm}^3 \text{mol}^{-1}$
$b_0$ , etc	coefficients in eq 3

$P$	pressure, Pa
$P_m$	mixture pressure, Pa
$\Delta P$	pressure change on mixing, Pa
$R$	molar gas constant, $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$
$T$	thermodynamic temperature, K
$y$	mole fraction

### Appendix I. Effect of Component Impurity on $B_{12}$

If we label the primary components 1 and 2, consider an impurity in 1 labeled 6, and use the truncated pressure series virial equation, we obtain the following.

$$V = (RT/P + B_{m1})(n_1 + n_6) \quad (\text{A1})$$

$$V = (RT/P + B_{22})n_2 \quad (\text{A2})$$

$$2V = (RT/P_m + B_m)(n_1 + n_2 + n_6) \quad (\text{A3})$$

Equating (A3) with (A1) + (A2) and dividing by  $(n_1 + n_2 + n_6)$ , we obtain

$$RT(1/P - 1/P_m) = B_m - (y_1 + y_6) B_{m1} - y_2 B_{22} \quad (\text{A4})$$

Substituting  $B_m = \sum_i \sum_j y_i y_j B_{ij}$ , we obtain

$$RT(1/P - 1/P_m) = y_1^2 B_{11} + y_2^2 B_{22} + y_6^2 B_{66} + 2y_1 y_2 B_{12} + 2y_1 y_6 B_{16} + 2y_2 y_6 B_{26} - y_1^2 B_{11}/(y_1 + y_6) - y_6^2 B_{66}/(y_1 + y_6) - 2y_1 y_6 B_{16}/(y_1 + y_6) - y_2 B_{22} \quad (\text{A5})$$

Since  $y_6$  is much smaller than  $y_1$ , the approximation  $1/(1 + y_6/y_1) \approx 1 - y_6/y_1$  is a good one, especially for the purposes of error estimation. With this substitution, collecting coefficients gives

$$RT(1/P - 1/P_m) = 2y_1 y_2 [B_{12} - 0.5(B_{11} + B_{22})] - B_{11} y_6 (y_1 - 1) - B_{22} y_6 y_2 + B_{16} y_6 (y_1 - 1 + y_6/y_1) + 2B_{26} y_6 y_2 + B_{66} y_6 (y_6 - y_6/y_1 + y_6^2/y_1^2) \quad (\text{A6})$$

This expression may be used to calculate  $B_{12} - 0.5(B_{11} + B_{22})$  or alternatively to assess possible uncertainties.

Now

$$B_{12}^E = B_{12} - 0.5(B_{11} + B_{22})$$

and

$$B_{12}^E(\text{apparent}) = RT(1/P - 1/P_m)/2y_1 y_2$$

To assess the likely magnitude of the error associated with ignoring the effect of the impurity, we may assume  $y_1 = y_2 = 0.5$  and ignore terms containing  $y_6^2$ . This gives

$$B_{12}^E(\text{apparent}) = B_{12}^E + y_6 [B_{11} - B_{22} + 2B_{26} - 2B_{16}]$$

The extension to the case of more than one impurity is straightforward.

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## Heat Capacities of the Water-Lithium Bromide-Lithium Iodide System

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The heat capacities of the water-lithium bromide-lithium iodide system (salt mole ratios 4:1) were measured in the range of temperatures from 283.15 to 343.15 K and in the range of absorbent concentrations from 15.4 to 66.6 wt %. An empirical formula for this system was obtained from the experimental data by the least-squares method. Maximum and average absolute deviations between the experimental data and the calculated values from this empirical formula were 0.95% and 0.33%, respectively. The heat capacity data obtained for this system were compared with the predicted values on the basis of the principle of a corresponding state proposed by Kamoshida et al.

### Introduction

The water-lithium bromide system (1) is being used as the working fluid in absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The water-lithium bromide-lithium iodide system (salt mole ratios 4:1) was proposed in order to improve the performance characteristics of the water-lithium bromide system.

The heat capacity data for working medium-absorbent systems are one of the most important basic properties for the research and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. This investigation was undertaken to obtain data on the heat capacities of lithium bromide-lithium iodide aqueous solutions in