

Excess molar volumes for CO₂-CH₄-N₂ mixtures

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Abstract: Vibrating-tube densimetry experiments are being performed to determine the excess molar volumes of single-phase CO₂-CH₄-N₂ gas mixtures at pressures as high as 3500 bars and temperatures up to 500 °C. In our initial experiments, we determined the P-V-T properties of: (1) CO₂-CH₄, CO₂-N₂, CH₄-N₂, and CO₂-CH₄-N₂ mixtures at 1000 bars, 50 °C; and (2) CO₂-CH₄ mixtures from 100 to 1000 bars at 100 °C. Excess molar volumes in the binary subsystems are very accurately represented by two-parameter Margules equations. Experimentally determined excess molar volumes are in fair to poor agreement with predictions from published equations of state. Geometric projection techniques based on binary system data yield calculated excess molar volumes for CO₂-CH₄-N₂ mixtures that are in good agreement with our experimental data.

1 INTRODUCTION

H₂O, CO₂, CH₄, and N₂ are key volatile constituents of the earth; therefore, thermochemical data on these gas species and their mixtures find application in geochemical modeling of crustal fluids in a wide variety of geologic environments. With the ultimate goal of developing new thermodynamic equations of state for gas-rich crustal fluids, we are currently collecting P-V-T data on binary and ternary CO₂-CH₄-N₂ gas mixtures at 100-1000 bars and 50-400 °C. In this article we describe our initial results at 50 and 100 °C.

2 EXPERIMENTAL METHODS

P-V-T data are being collected using a vibrating-tube densimeter designed to measure the P-V-T properties of fluids at P-T conditions as high as 3500 bars and 500 °C. An isobaric, isothermal flow-through method was employed in all of our experiments. The fundamental equation for calculating densities of gases by vibrating-tube densimetry is

$$\rho - \rho_0 = K(\tau^2 - \tau_0^2), \quad (1)$$

where ρ is the density of an *unknown* gas; ρ_0 is the density of a *known* (standard) gas; K is a parameter that depends on the physical properties of the

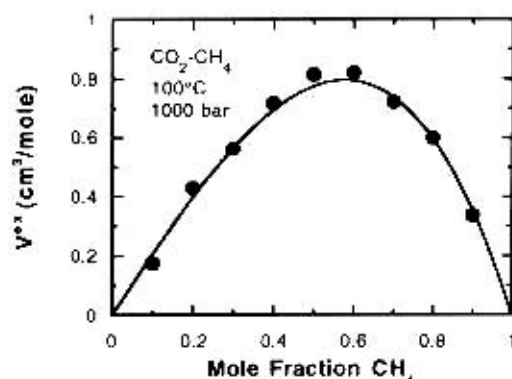


Figure 1. V^{ex} for CO₂-CH₄ mixtures at 1000 bars, 100 °C. Plot symbols and the V^{ex} curve illustrate, respectively, our experimental data and two-parameter Margules model.

vibrating tube; τ is the period of vibration for the *unknown* gas; and τ_0 is the period of vibration for the *known* (standard) gas. K is evaluated using three standard gases (Ar, He, and N₂) and has been found to be a constant at a given pressure and temperature (i.e., the vibrating tube behaves ideally). Therefore, equation (1) represents a *linear* relationship between ρ and τ^2 where the density of an unknown gas is measured relative to standard gases.

Short term instrumental drift, although rarely observed, was checked for by repeated measurements on Ar during each run. Precisions achieved in experimentation were: $P \pm 0.1$ bar, and $T \pm 0.01$ °C. Conservative estimates of accuracy are: $P \pm 2.0$ bar, $T \pm 0.2$ °C. The precisions of τ^2 , ρ , and V^{ex} derive from counting statistics and vary as a function of the density and composition of the gas mixture. The nominal uncertainty in V^{ex} is approximately ± 0.1 cm³/mole; however, the disposition of our data suggests that the actual uncertainty in V^{ex} may be considerably less than that.

3 THEORY AND DATA

Excess molar volumes were calculated using measured and ideal molar volumes for the mixtures, the latter being derived from the molar volumes of the end member gases measured during the same experiment. V^{ex} is calculated using the relation

$$V^{ex} = V - V^{id} = V - \sum_{i=1}^n X_i v_i \quad (2)$$

V^{ex} data for the binary systems were fit to an equation of the form

$$\frac{V^{ex}}{X_1 X_2} = a + b X_2 \quad (3)$$

which yields the W_{V_1} and W_{V_2} parameters of the two-parameter Margules formulation according to the

identities $W_{V_1} = a$ and $W_{V_2} = b + W_{V_1}$. Finally, V^{ex} for any binary composition can be calculated from the relation

$$V^{ex} = W_{V_1} X_1 X_2^2 + W_{V_2} X_1^2 X_2 \quad (4)$$

Our results for binary systems are summarized graphically in Figs. 1-4. Figure 1 shows that V^{ex} for CO₂-CH₄ mixtures is continuously positive and only slightly asymmetric at 100 °C and 1000 bars. Figure 2 illustrates the pressure dependence of $W_{V_{CO_2}}$ and $W_{V_{CH_4}}$ at 1-1000 bars, 100 °C. Values for these W_{V_i} 's can be substituted into equation (4) to calculate V^{ex} for CO₂-CH₄ mixtures at 100 °C. Figures 3 and 4 show V^{ex} for CH₄-N₂ and CO₂-N₂ mixtures, respectively, at 50 °C and 1000 bars. V^{ex} for the CH₄-N₂ system is continuously positive, essentially symmetric, and smaller than the V^{ex} for the CO₂-CH₄ system (cf. Fig. 1). The CO₂-N₂ system, in contrast, exhibits a small V^{ex} that is mostly negative and strongly asymmetric. At 1000 bars, V^{ex} for the CO₂-CH₄ mixtures is unchanged between 50 °C (not illustrated) and 100 °C (Fig. 1). Despite the disparate

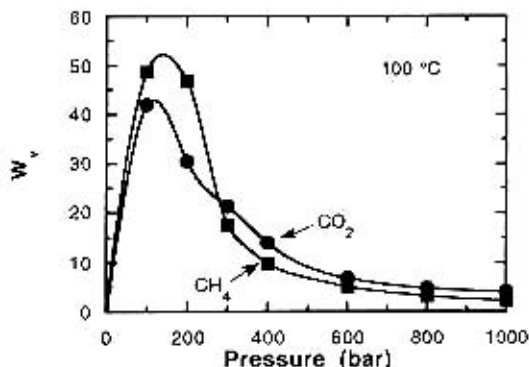


Figure 2. Margules parameters (W_{V_i} 's) for CO₂ (circles) and CH₄ (squares) from 1 to 1000 bars at 100 °C. Plot symbols represent experimental data.

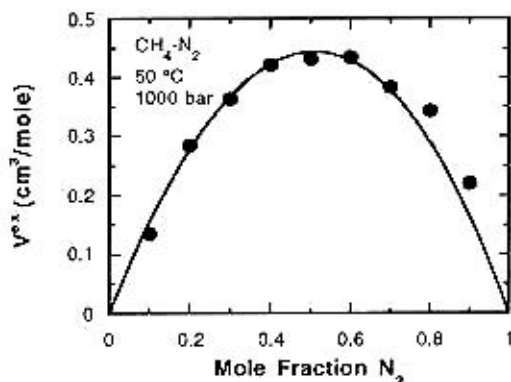


Figure 3. V^{ex} for CH₄-N₂ mixtures at 1000 bars, 50 °C. Plot symbols and the V^{ex} curve illustrate, respectively, our experimental data and two-parameter Margules model.

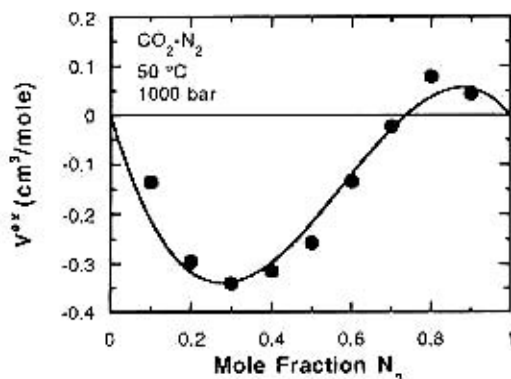


Figure 4. V^{ex} for CO₂-N₂ mixtures at 1000 bars, 50 °C. Plot symbols and the V^{ex} curve illustrate, respectively, our experimental data and two-parameter Margules model.

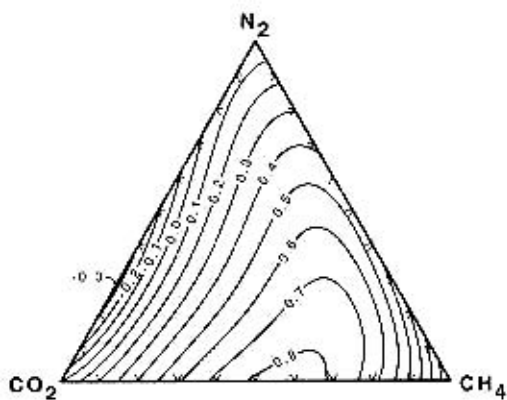


Figure 5. Experimentally determined V^{ex} for CO_2 - CH_4 - N_2 mixtures at 1000 bars, 50 °C. Contours indicate mixtures of constant excess volume (cm^3/mole).

volumetric properties of the three binary systems, their V^{ex} relations can be represented very accurately by two-parameter Margules equations.

We have also collected P-V-T data on CO_2 - CH_4 - N_2 mixtures at 50 °C and 1000 bars. A contoured V^{ex} surface has been generated from these data (Fig. 5), and it has a complex topology with a region of negative V^{ex} near the CO_2 - N_2 binary.

4 EQUATIONS OF STATE

We have compared our experimental data with excess volumes calculated from various equations of state, and representative results are illustrated in Fig. 6. There is generally poor agreement between excess volumes calculated from the Redlich-Kwong (RK) equation of state (Redlich and Kwong, 1949) and our experimentally determined values, and molar volumes calculated from this model differ from our data by as much as 4%. The modified Redlich-Kwong (MRK) equation of state developed by Holloway (1977) yields accurate calculated values of V^{ex} for gas mixtures with compositions illustrated in Fig. 6, but calculated excess volumes for other CO_2 - CH_4 - N_2 mixtures at 1000 bars, 50 °C are not nearly as accurate. Also, molar volumes calculated from the Holloway MRK equation differ from our experimentally determined values by as much as 6%.

We have also evaluated equations of state in two software packages that are commercially available from the National Institute of Standards and Technology (NIST): Supertrapp (Ely and Huber, 1990) and DDMIX (Ely, 1988). With Supertrapp,

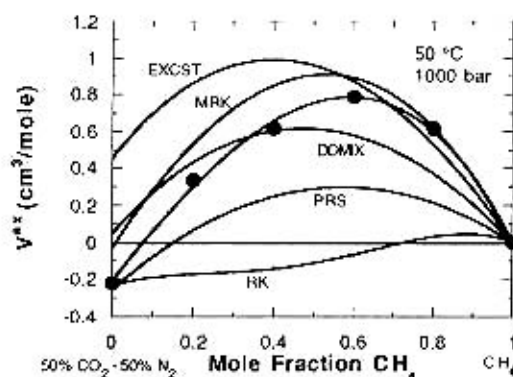


Figure 6. Calculated and experimentally determined excess volumes for CO_2 - CH_4 - N_2 mixtures at 1000 bars, 50 °C (see text for explanation). Filled circles represent experimental data along the $X_{\text{CO}_2} = X_{\text{N}_2}$ pseudobinary join.

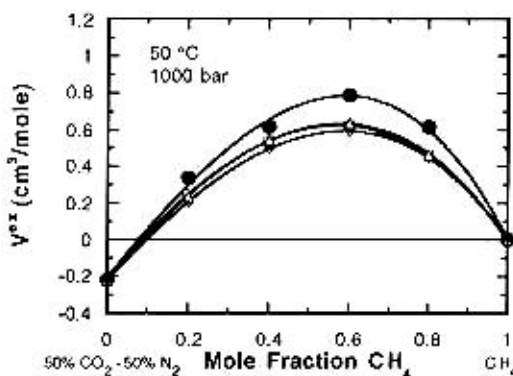


Figure 7. Experimentally determined (filled circles, this study) and calculated (different binary projection methods; diamonds - method of Hillert, triangles - methods of Colinet and Muggianu, squares - method of Kohler) excess volumes for CO_2 - CH_4 - N_2 mixtures at 1000 bars, 50 °C along the $X_{\text{CO}_2} = X_{\text{N}_2}$ pseudobinary join.

the volumetric properties of mixtures can be calculated using either a Peng-Robinson (PRS) model or the NIST extended corresponding states (EXCST) model. The PRS model yields calculated values for V^{ex} that are in poor to fair agreement with our experimental data; however, the molar volumes derived from this model differ from our experimentally determined values by as much as 10%. Likewise, the EXCST model yields calculated values for V^{ex} that are in poor to fair agreement with our experimentally determined data, but calculated molar volumes differ from our experimentally

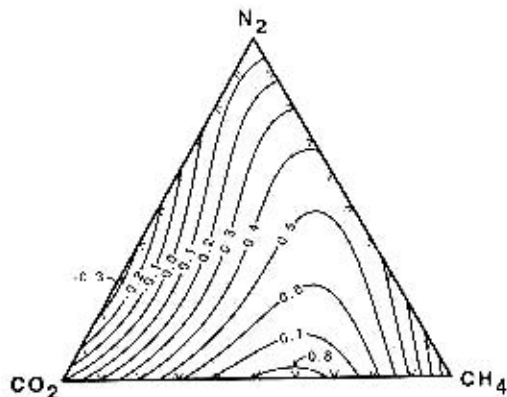


Figure 8. Excess volumes for CO₂-CH₄-N₂ mixtures at 1000 bars, 50 °C, calculated using the method of Muggianu (1975). Contours indicate mixtures of constant excess volume (cm³/mole).

determined values by less than 3%. Finally, DDMIX yields calculated values for V^{ex} that are in fair to good agreement with our experimental data, whereas molar volumes calculated from this model differ from our experimentally determined values by less than 1%.

5 GEOMETRIC PROJECTION METHODS

We have evaluated various empirical geometric methods for predicting the volumetric properties of a ternary system using the excess molar volumes of the binary subsystems (Kohler, 1960; Colinet, 1967 as referenced by Hillert, 1980; Hillert, 1980; Muggianu et al., 1975). Each of these methods estimates the ternary properties by projection from the binary subsystems, but they employ different projection vectors. The reader is referred to Hillert (1980, and references therein) for a review of these techniques. Geometric projection equations have the distinct advantage of reducing to a two-parameter equation along each binary sideline.

Figure 7 shows that the various projection methods yield similar results for our data. The methods of Colinet (1967) and Muggianu et al. (1975) yield essentially identical results. Figure 8 depicts the contoured V^{ex} surface of ternary CO₂-CH₄-N₂ mixtures calculated using the method of Muggianu et al. (1975). Comparison of these results with experimental data (cf. Figs. 5 and 8) indicates that this methodology is useful in predicting excess properties for ternary fluid mixtures. In fact, V^{ex} predicted by the Muggianu method can be more

accurate than predictions from published equations of state (cf. Figs. 6 and 7).

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