Excess molar volumes for CO$_2$-CH$_4$-N$_2$, mixtures

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Abstract: Vibrating-tube densimetry experiments are being performed to determine the excess molar volumes of single-phase CO$_2$-CH$_4$-N$_2$ 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) CO$_2$-CH$_4$, CO$_2$-N$_2$, CH$_4$-N$_2$, and CO$_2$-CH$_4$-N$_2$ mixtures at 100 bars, 50 °C; and (2) CO$_2$-CH$_4$ 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 CO$_2$-CH$_4$-N$_2$ mixtures that are in good agreement with our experimental data.

1 INTRODUCTION

H$_2$O, CO$_2$, CH$_4$, and N$_2$ 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 CO$_2$-CH$_4$-N$_2$ 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

\[ \rho - \rho_0 = K(\tau^2 - \tau_0^2), \]

where \( \rho \) is the density of an unknown gas; \( \rho_0 \) is the density of a known (standard) gas; \( K \) is a parameter that depends on the physical properties of the vibrating tube; \( \tau \) is the period of vibration for the unknown gas; and \( \tau_0 \) is the period of vibration for the known (standard) gas. \( K \) is evaluated using three standard gases (Ar, He, and N$_2$) 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 \( \rho \) and \( \tau^2 \) where the density of an unknown gas is measured relative to standard gases.

Figure 1. \( V_{\text{ex}} \) for CO$_2$-CH$_4$ mixtures at 1000 bars, 100 °C. Plot symbols and the \( V_{\text{ex}} \) curve illustrate, respectively, our experimental data and two-parameter Margules model.
Short term instrumental drift, although rarely observed, was checked for by repeated measurements on Ar during each run. Precisions achieved in experimentation were: P ± 0.1 bar, and T ± 0.01 °C. Conservative estimates of accuracy are: P ± 2.0 bar, T ± 0.2 °C. The precisions of τ, ρ, and V°mix derive from counting statistics and vary as a function of the density and composition of the gas mixture. The nominal uncertainty in V°mix is approximately ± 0.1 cm³/mole; however, the disposition of our data suggests that the actual uncertainty in V°mix 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°mix is calculated using the relation

$$V°mix = V - V°id = V - \sum_{i=1}^{n} X_i \mu_i.$$  \hspace{1cm} (2)

V°mix data for the binary systems were fit to an equation of the form

$$\frac{V°mix}{X_1X_2} = a + bX_2,$$ \hspace{1cm} (3)

which yields the W$_{V_i}$ and W$_{V_{ij}}$ parameters of the two-parameter Margules formulation according to the identities W$_{V_i} = a$ and W$_{V_{ij}} = b + W_{V_{ij}}$. Finally, V°mix for any binary composition can be calculated from the relation

$$V°mix = W_{V_i}X_1X_2 + W_{V_{ij}}X_iX_j.$$ \hspace{1cm} (4)

Our results for binary systems are summarized graphically in Figs. 1-4. Figure 1 shows that V°mix for CO$_2$-CH$_4$ mixtures is continuously positive and only slightly asymmetric at 100 °C and 1000 bars. Figure 2 illustrates the pressure dependence of W$_{V_{mix}}$ and W$_{V_{mix}}$ at 1-1000 bars, 100 °C. Values for these W$_{V_i}$s can be substituted into equation (4) to calculate V°mix for CO$_2$-CH$_4$ mixtures at 100 °C. Figures 3 and 4 show V°mix for CH$_4$-N$_2$ and CO$_2$-N$_2$ mixtures, respectively, at 50 °C and 1000 bars. V°mix for the CH$_4$-N$_2$ system is continuously positive, essentially symmetric, and smaller than the V°mix for the CO$_2$-CH$_4$ system (cf. Fig. 1). The CO$_2$-N$_2$ system, in contrast, exhibits a small V°mix that is mostly negative and strongly asymmetric. At 1000 bars, V°mix for the CO$_2$-CH$_4$ mixtures is unchanged between 50 °C (not illustrated) and 100 °C (Fig. 1). Despite the disparate

Figure 2. Margules parameters (W's) for CO$_2$ (circles) and CH$_4$ (squares) from 1 to 1000 bars at 100 °C. Plot symbols represent experimental data.

Figure 3. V°mix for CH$_4$-N$_2$ mixtures at 1000 bars, 50 °C. Plot symbols and the V°mix curve illustrate, respectively, our experimental data and two-parameter Margules model.

Figure 4. V°mix for CO$_2$-N$_2$ mixtures at 1000 bars, 50 °C. Plot symbols and the V°mix curve illustrate, respectively, our experimental data and two-parameter Margules model.
volumetric properties of the three binary systems, their $V^e_x$ 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 $V^e_x$ surface has been generated from these data (Fig. 5), and it has a complex topology with a region of negative $V^e_x$ 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 $V^e_x$ 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, 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 $V^e_x$ 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 $V^e_x$ that are in poor to fair agreement with our experimentally determined data, but calculated molar volumes differ from our experimentally
accurate than predictions from published equations of state (cf. Figs. 6 and 7).

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