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Direct Determination of Enthalpy of Mixing for the Binary Gaseous System Methane–Carbon Dioxide by an Isothermal Flow Calorimeter

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Enthalpies of mixing for the binary gaseous system methane–carbon dioxide were measured by an isothermal flow calorimeter at temperatures of 293.15, 305.15, and 313.15 K, with mole fractions of methane ranging from approximately 0.2 to 0.8. For the first two isotherms, the measurements were made at pressures of 0.507, 1.115, and 1.520 MPa (5, 11, and 15 atm, respectively). For the third isotherm, measurements were made at pressures of 0.507, 1.013, 1.520, 2.533, 3.546, and 4.600 MPa (5, 10, 15, 25, 35, and 45.4 atm, respectively). The experimental results were compared with those already available in the literature, as well as with predictions based upon the following equations of state: Benedict–Webb–Rubin (BWR), Redlich–Kwong, and the Redlich–Kwong equation with the modifications proposed by Jacoby and Robinson.

Introduction

Enthalpy data for pure compounds and mixtures are of fundamental importance in process design. They are also particularly important from a scientific point of view, owing to their utilization in verifying predictive methods for thermodynamic properties of mixtures. Such methods are based upon theories of molecular interaction.

It is necessary to determine data for the enthalpies of mixtures in the gaseous phase as functions of temperature, pressure, and mixture composition. The most direct method to obtain this network of data consists of the direct determination of heats of mixing, henceforth designated as excess enthalpies and denoted as H^E. The excess enthalpy of a mixture at constant temperature and pressure is defined as

$$H^E = \Delta H_m - \Delta H_m^{id} = [H_m - \sum_i x_i H_i]_{P,T} \qquad (1)$$

Since for an ideal solution the heat of mixing is zero, i.e., $\Delta H_m^{id} = 0$, the excess enthalpy of a mixture is numerically equal to the heat of mixing of the pure components, i.e., $H^E = \Delta H_m$.

Although many calorimetric determinations of enthalpies of mixing for liquids are reported in the literature, relatively few data for gas mixtures are available. The experimental difficulties involved in the determinations in the gas phase, as well as the high cost of the pure components, are the reasons for this scarcity of data. The investigations of excess enthalpies in the gas phase are summarized as follows. The first determinations by Beenakker et al. (*1–4*) comprised the following systems: CH_4–H_2, CH_4–Ar, H_2–N_2, H_2–Ar, Ar–N_2, He–CH_4, and He–Ar. Klein (*5*, *6*) studied the system CH_4–N_2. Hejmadi et al. (*7*, *8*) investigated the systems N_2–O_2, N_2–CO_2, and N_2–C_2H_6. Lee and Mather (*9*, *10*) studied the systems N_2–CO_2 and CH_4–CO_2, and Altunin et al. (*11*) the system N_2–CO_2. In our laboratories, Ba et al. (*12–14*) obtained data for the systems N_2–O_2, N_2–C_2H_4, and C_2H_4–CO_2. This paper presents data for the system CH_4–CO_2 at temperatures of 293.15, 305.15, and 313.15 K, with mole fractions of methane ranging from approximately 0.2 to 0.8. For the first two isotherms, the measurements were made at pressures of 0.507, 1.115, and 1.520 MPa (5, 11, and 15 atm, respectively). For the third isotherm, measurements were made at pressures of 0.507, 1.013, 1.520, 2.533, 3.546, and 4.600 MPa (5, 10, 15, 25, 35, and 45.4 atm, respectively).

Experimental Procedure

The experimental procedure, as well as a detailed description of the equipment utilized in this investigation, has been reported in previous articles (*7*, *12–14*). The two pure gases, CH_4 and CO_2, flow independently inside tubings of identical dimensions, arriving at the calorimeter at essentially the same temperature and pressure. The mixing of the two gases is accompanied by a temperature drop. To compensate for this temperature drop, a measured quantity of energy is supplied to the system by a Kepco Model SM-325-2A(M) power supply, with regulation to 0.01%. In this manner, the temperature difference between the two pure gases at the calorimeter inlet and the exit gas mixture is essentially brought to zero. The energy supplied is determined by measuring potential drops across standard calibrated resistors, utilizing a Leeds and Northrup K-5 potentiometer. Mole fractions of the gaseous constituents in the mixture were calculated from the measured values of individual flow rates.

Some improvements were performed with respect to the equipment described in the previous articles, including a forced-draft system for the calorimeter assembly and a disposal system for safe elimination of the gas mixtures to the atmosphere. The methane and the carbon dioxide were supplied by Lynde Co. of Canada and Air Liquid of Canada, respectively. The methane has a certified purity of 99%, containing 0.1% CO_2, 0.2% O_2, 0.2% N_2, 0.3% C_2H_6, and 0.2% C_3H_8. The carbon dioxide has a certified purity of 99.8%, containing 100 ppm of CO, 50 ppm of H_2, 100 ppm of H_2O, and approximately 0.2% N_2. The effect of the impurities in the gases was evaluated by utilizing Hejmadi's methods (*7*, *8*) and found to be negligible.

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Analysis of Results

The three steps involved in the thermodynamic process taking place within the calorimeter are as follows: (1) The two pure gases A (CH_4) and B (CO_2) arrive independently at the respective inlet ports in the calorimeter at the temperatures and pressures denoted respectively as T_1, P_1 and T_2, P_2. The temperatures and pressures are nearly identical. (2) The two gases are thoroughly mixed within the calorimeter, this mixing process being accompanied by a temperature drop. (3) After the temperature drop is compensated by the addition of a measured quantity of energy, the gas mixture exits from the calorimeter at the outlet condition denoted as T_0 and P_0, for the temperature and pressure, respectively. These temperatures and pressures are nearly identical with the inlet values; thus, the calorimeter functions essentially in an isothermal and isobaric manner.

Application of the first law of thermodynamics for a flow process to the three-step thermodynamic process just described yields the following equation:

$$H_0^E = \Delta H_m = Q/F + x_A(H_{A,1} - H_{A,0}) + x_B(H_{B,2} - H_{B,0}) - \Delta E_k \quad (2)$$

In eq 2

$$H_{A,1} - H_{A,0} = \int_{T_0}^{T_1} C_{p,A}\, dT + \int_{P_0}^{P_1} \phi_A\, dP \quad (3)$$

$$H_{B,2} - H_{B,0} = \int_{T_0}^{T_2} C_{p,B}\, dT + \int_{P_0}^{P_2} \phi_B\, dP \quad (4)$$

where

$$\phi = (\partial H/\partial P)_T \quad (5)$$

$$C_p = (\partial H/\partial T)_P \quad (6)$$

$$\Delta E_k = E_{k,A,B,0} - (x_A E_{k,A,1} + x_B E_{k,B,2}) \quad (7)$$

Equations 3 and 4 refer to the so-called primary corrections to be applied to eq 2 in order to obtain H_0^E at the conditions P_0 and T_0 at the calorimeter outlet. Notice that for application of the primary corrections only thermodynamic properties of the pure gases A and B are required. In the case of our experiments for the system CH_4–CO_2, the pressure drops across the calorimeter, i.e., $\Delta P_1 = P_0 - P_1$ and $\Delta P_2 = P_0 - P_2$ are negligible. Also, the inlet pressures P_1 and P_2, as well as the inlet temperatures T_1 and T_2, were identical within the limits of precision of the respective measurements. Consequently, the mean values of the Joule–Thomson coefficients $\bar{\phi}_A$ and $\bar{\phi}_B$ can be utilized in the evaluation of the second integrals in eq 3 and 4.

This same reasoning is also valid for the first integrals in eq 3 and 4. In fact, for the experiments with the system CH_4–CO_2

$$T_1 = T_2 = T_i \pm 0.002 \text{ K}$$

$$T_1 - T_0 < 0.1 \text{ K}$$

Consequently mean values for the heat capacities, $\bar{C}_{p,A}$ and $\bar{C}_{p,B}$, can be utilized in the evaluation of the first integrals in eq 3 and 4. In this case, eq 3 and 4 become

$$H_{A,1} - H_{A,0} = \bar{C}_{p,A}(T_1 - T_0) + \bar{\phi}_A(P_1 - P_0) \quad (8)$$

$$H_{B,2} - H_{B,0} = \bar{C}_{p,B}(T_2 - T_0) + \bar{\phi}_B(P_2 - P_0) \quad (9)$$

Substitution of eq 7–9 into eq 2 leads to

$$H_0^E = Q/F + x_A\bar{C}_{p,A}(T_1 - T_0) + x_B\bar{C}_{p,B}(T_2 - T_0) + x_A\bar{\phi}_A(P_1 - P_0) + x_B\bar{\phi}_B(P_2 - P_0) + x_A E_{k,A,1} + x_B E_{k,A,2} - E_{k,A,B,0} \quad (10)$$

The value of H_0^E, obtained from eq 10, refers to the conditions at the calorimeter outlet, i.e., P_0 and T_0. Nevertheless, it is impossible to adjust the outlet pressures and temperatures to a unique set of values for a given experiment. In nearly all cases there is a small, but not necessarily negligible, difference between the measured temperatures and pressures and the nominal conditions (henceforth denoted as P_n and T_n), which serve as base values for graphical portrayal of the data. The following equation, which refers to the so-called secondary correction, is utilized to obtain H_n^E:

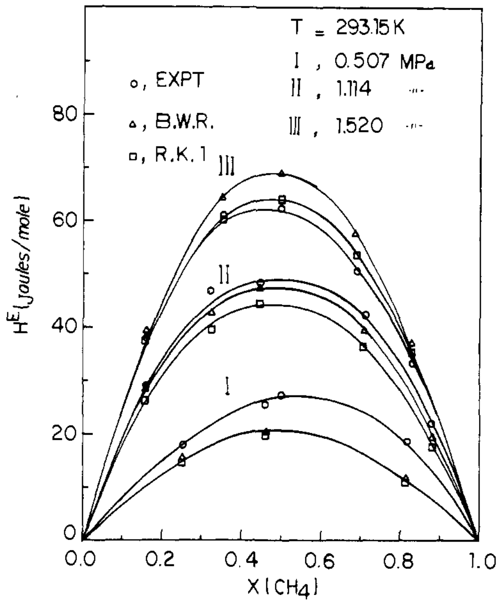

Figure 1. Enthalpy of mixing, H^E/(J mol^{-1}), of methane–carbon dioxide system at 293.15 K.

$$H_n^E = H_0^E + \int_{T_0}^{T_n} C_p^E\, dT + \int_{P_0}^{P_n} \phi^E\, dP \quad (11)$$

where

$$C_p^E = (\partial H^E/\partial T)_{P,x} \quad (12)$$

$$\phi^E = (\partial H^E/\partial P)_{T,x} \quad (13)$$

Notice that, contrarily to the case for the primary corrections, the application of secondary corrections requires knowledge of thermodynamic properties for the gas mixture. Since in the literature there are not available data to calculate C_p^E and ϕ^E for the CH_4–CO_2 mixtures, these values were determined from the equation obtained from the Benedict–Webb–Rubin equation of state for the pure components (*15*). The BWR constants for methane and carbon dioxide, as well as the mixing rules utilized to calculate C_p^E and ϕ^E for the CH_4–CO_2 mixtures, were those presented by Bishnoi and Robinson (*16*).

Results

The experimental results for the system methane–carbon dioxide are presented in Table I for the nominal temperatures T_n = 293.15 and 305.15 K at the nominal pressures P_n = 0.507, 1.115, and 1.520 MPa (5, 11, and 15 atm, respectively) and also for T_n = 313.15 K at the nominal pressures P_n = 0.507, 1.013, 1.520, 2.533, 3.546, and 4.600 MPa (5, 10, 15, 25, 35, and 45.4 atm, respectively).

Figures 1–3 present the same data in graphical form.

After application of the primary and secondary corrections, a series expansion of H^E as a function of the mole fraction of methane has been performed to verify the approximation, made in the analysis of results, to the effect that heat losses from the calorimeter are negligible. The equation utilized for the correlation of results is of the same form as that utilized by Hejmadi (*7*, *8*), i.e.

$$H^E/[x_A(1 - x_A)] = C + B(x_A - 0.5) + A(x_A - 0.5)^2 \quad (14)$$

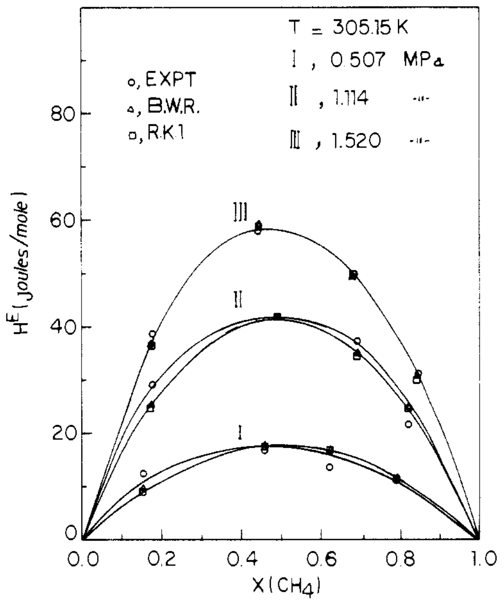

Figure 2. Enthalpy of mixing, H^E/(J mol^{-1}), of methane-carbon dioxide system at 305.15 K.

where A, B, and C are constants, which were determined by polynominal regression. The testing to the effect that heat losses from the calorimeter are negligible was based on the technique suggested by Montgomery and De Vries (*17*) which consists of preparing a plot of H^E vs. the inverse of flow rates. Ten experimental points, all in the vicinity of a mole fraction of 0.5 (ranging between 0.48 and 0.52), at 313.15 K and 1.013 MPa (10 atm), were normalized to x_A = 0.5. The plots of H^E vs. the inverse of flow rates indicate that, for variations of flow rates of ±40% from a base value (of the order of 5.153 mol s^{-1}), deviation of measured H^E's never exceeded 1.0%. This can be considered as a satisfactory test, since the maximum deviation is lower than the error in the experimental measurements. Table II presents the values for the constants in eq 14.

Accuracy of Experimental Results

There are two factors which affect the accuracy of the results: (1) inaccuracies in the instruments and experimental techniques and (2) errors introduced in the analysis of results. The technique utilized in the evaluation of errors is that described by Mickley, Sherwood, and Reid (*18*). The procedure involves adding weighed individual inaccuracies. The weighting factors are determined from a functional relation between the independent variables, e.g., accuracy of potentiometer, of standard resistors, etc. This method, as pointed out by the authors (*18*), actually overestimates the error in H_n^E, since it does not take into account the possibility of a partial cancellation of errors of opposite signs. In general, for a function G, whose value is a function of n independent variables g_i, the error in G is determined from the relationship

$$\frac{e(G)}{G} = \sum_{i=1}^{n} \left(\frac{1}{G}\frac{\partial G}{\partial g_i}\right)_{g_{j\neq i}} e(g_i) \qquad (15)$$

The readings of the potentiometer and the dead-weight gauge etc. can be listed as the independent variables for the function H_n^E.

The temperature and the pressure at the calorimeter outlet are known to ±0.05 °C and ±0.001 atm; the error for the ratio Q/F is estimated at 0.6% and the error in the value of the mole fractions varies between 0.003 and 0.005. Errors due to primary corrections depend on the accuracy of the experimental measurements of temperatures, pressures, heat capacities, and Joule-Thomson isothermal coefficients for the two pure components. For the case of the system methane-carbon dioxide, the relative error for the primary corrections was estimated to be between 0.5% and 1.5%. Relative errors due to the secondary corrections were also estimated. The inaccuracies are due to the estimates for $\bar{\phi}^E$ and $\bar{C}_p^E$ from the BWR equation of state. For the case of the system methane-carbon dioxide, the relative error in the secondary corrections was estimated to be between 0.5% and 1%. An appreciation of the order of magnitude for the primary correction can be obtained by calculating the average deviation $100[(H_0^E - Q/F)/(Q/F)]$. These deviations were 3.7%, 3.5%, and 2% at 293.15, 305.15, and 313.15 K, respectively, while those for the secondary corrections determined as $100[(H_0^E - H_n^E)/H_0^E]$ were 2.3%, 2.2%, and 1.3% at 293.15, 305.15, and 313.15 K, respectively.

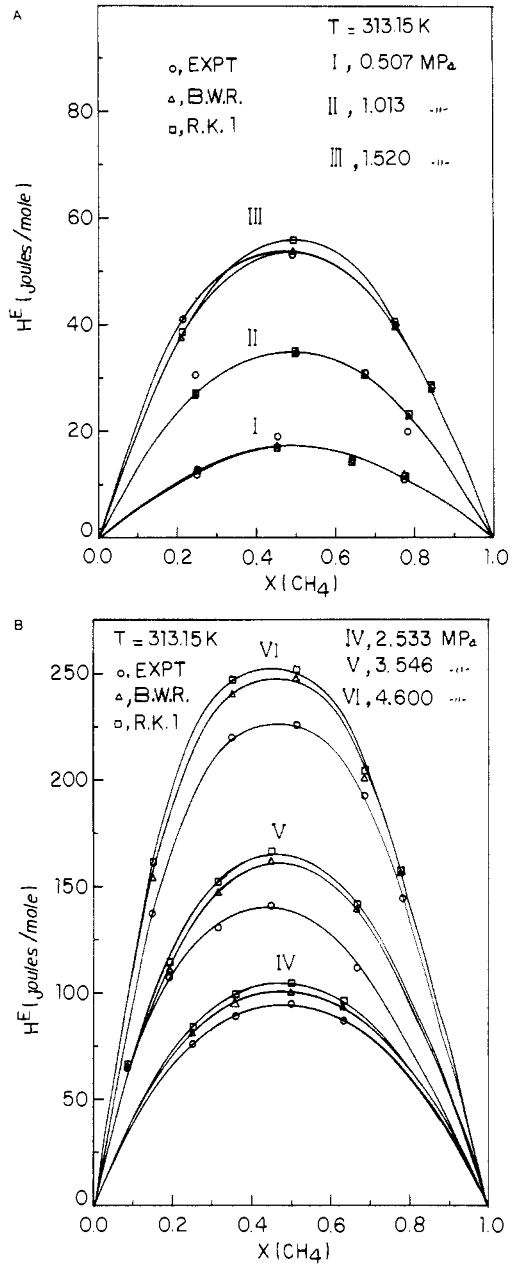

Figure 3. Enthalpy of mixing, H^E/(J mol^{-1}), of methane-carbon dioxide system at 313.15 K.

Comparison with Literature Results

The only results available in the literature for the system methane-carbon dioxide are those reported by Lee and Mather

(*10*), which cover a range of temperatures and pressures of 283.15–353.15 K and 1.013–101.3 MPa.

For the temperature of 315.15 K and the pressure of 1.013 MPa, which correspond to data encompassing the same region covered by these authors, their reported values of the excess enthalpies obtained by extrapolation are 24.5, 34.0, 28.5, and 19.83 J mol^{-1} for 0.248, 0.500, 0.679, and 0.784 mole fractions, respectively, whereas our values for the same mole fractions are 27.5, 34.4, 31.88, and 21 J mol^{-1}. A comparison between these two sets of figures shows an average deviation of less than 7%, which, as will be shown later, is less than the average deviation of the Redlich–Kwong and BWR equations. This agreement is considered satisfactory.

Comparison of Experimental Data with Predictions from Equations of State

The excess enthalpies H_n^E for the system methane–carbon dioxide were compared with predicted values calculated from the following equations of state: Redlich–Kwong (*19*), henceforth referred to as RK1; Redlich–Kwong with Jacoby–Robinson modifications (*20*), henceforth referred to as RK2; and Benedict–Webb–Rubin (*15*).

The RK1 equation was applied to calculate the excess enthalpies H_n^E in conjunction with the modified mixing rules proposed by Chueh and Prausnitz (*21*). The network of equations for these calculations is as follows:

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \tag{16}$$

$$a = x_1^2 a_{11} + x_2^2 a_{22} + 2x_1 x_2 a_{12} \tag{17}$$

$$b = x_1 b_1 + x_2 b_2 \tag{18}$$

$$a_{11} = \Omega_{a1} R^2 T_{C1}^{2.5}/P_{C1} \tag{19}$$

$$a_{22} = \Omega_{a2} R^2 T_{C2}^{2.5}/P_{C2} \tag{20}$$

$$a_{12} = (\Omega_{a1} + \Omega_{a2}) R^2 T_{C12}^{2.5}/(2P_{C12}) \tag{21}$$

$$b_1 = \Omega_{b1} R T_{C1}/P_{C1} \tag{22}$$

$$b_2 = \Omega_{b2} R T_{C2}/P_{C2} \tag{23}$$

$$T_{C12} = (T_{C1} T_{C2})^{1/2}(1 - k_{12}) \tag{24}$$

$$P_{C12} = Z_{C12} R T_{C12}/V_{C12} \tag{25}$$

$$Z_{C12} = 0.291 - 0.08(\omega_1 + \omega_2)/2 \tag{26}$$

$$V_{C12}^{1/3} = \tfrac{1}{2}(V_{C1}^{1/3} + V_{C2}^{1/3}) \tag{27}$$

The enthalpies of the pure components, CH$_4$ and CO$_2$, were calculated from the following equation, which is derived from basic thermodynamic relationships and the Redlich–Kwong equation of state:

$$(H - H^*)_0 = \frac{b}{V - b} RT - \frac{a}{T^{1/2}(V + b)} - \frac{3}{2}\frac{a}{bT^{1/2}} \ln \frac{V + b}{V} \tag{28}$$

This equation is written for the CH$_4$ and CO$_2$ (as pure gases) and the mixture CH$_4$–CO$_2$. The excess enthalpy, H_0^E, is then

$$H_0^E = H_{m,0} - (x_1 H_{1,0} + x_2 H_{2,0}) \tag{29}$$

The values for the dimensionless constants a_i and b_i, and the accentric factors ω_i utilized in our computations, were those of Chueh and Prausnitz (*22*). The interaction constant k_{12} in eq 24 was obtained by an iterative procedure leading to the best possible fit for the excess enthalpy data. We found that a single value of k_{12} equal to 0.1327 represents well our entire network of data whereas the corresponding value of k_{12} in the BWR equation was found to be 0.012 96. The values of all pertinent constants utilized in this computation are presented in Table III.

The RK2 equation was also applied to calculate the excess enthalpies H_n^E. The modifications proposed by Jacoby and Robinson (*20*) are as follows:

$$\frac{a}{R^2} = \alpha + \beta(T - 311) \tag{30}$$

$$\frac{b}{R} = \gamma + \delta(T - 311) \tag{31}$$

$$2a_{12} = K_{12} a_1 + (1 - K_{12}) a_2 \tag{32}$$

The values for constants α, β, γ, and δ are also presented in Table III. The value of the dimensionless constant K_{12}, obtained by an iterative procedure leading to the best possible fit for the excess enthalpy data, was equal to −0.2384. The value for this constant for the system CH$_4$–CO$_2$, obtained by Reamer et al. (*23*) is −0.5.

Finally, the BWR equation of state was also applied to predict the excess enthalpies H_n^E. The network of equations utilized in this computation is as follows:

enthalpy departure

$$(H - H_0) = \left(B_0 RT - 2A_0 - \frac{4C_0}{T^2}\right)\rho + (2bRT - 3a)\frac{\rho^2}{2} + \frac{6a\alpha\rho^5}{5} + \frac{C\rho^2}{T^2}\left[\frac{3(1 - e^{-\gamma\rho^2})}{\gamma\rho^2} - \frac{e^{-\gamma\rho^2}}{2} + \gamma\rho^2 e^{-\gamma\rho^2}\right] \tag{33}$$

Joule–Thomson isothermal coefficient

$$\phi = \left\{\left(B_0 RT - 2A_0 - \frac{4C_0}{T}\right) + (2bRT - 3a)\rho + 6a\alpha\rho^4 + \frac{e^{-\gamma\rho^2}}{T^2}(5c\rho + 5c\gamma\rho^3 - 2c\gamma^2\rho^5)\right\} \Big/ \left\{RT + 2\rho\left(B_0 RT - A_0 - \frac{C_0}{T^2}\right) + 3\rho^2(bRT - a) + 6a\alpha\rho^5 + \frac{e^{-\gamma e^2}}{T^2}(3c\rho^2 + 3c\gamma\rho^4 + 2c\gamma^2\rho^6)\right\} \tag{34}$$

heat capacity at constant pressure

$$(C_p - C_p^0) = -R + \frac{6C_0\rho}{T^3} - \frac{6c}{\gamma T^3} + ce^{-\gamma\rho^2}\left(\frac{6}{\gamma T^3} + \frac{3\rho^2}{T^3}\right) + \left[R\rho + B_0 R\rho^2 + bR\rho^3 + \frac{2C_0\rho^2}{T^3} - e^{-\gamma\rho^2}\left(\frac{2c\rho^3}{T^3} - \frac{2c\gamma\rho^5}{T^3}\right)\right]^2 \Big/ \left\{R\rho^2 + 2B_0 R\rho^3 - \frac{2A_0\rho^3}{T} - \frac{2C_0\rho^3}{T^3} + 3bR\rho^4 - \frac{3a\rho^4}{T} + \frac{6a\alpha\rho^7}{T} + \frac{e^{-\gamma\rho^2}}{T^3}(3c\rho^4 + 3c\gamma\rho^6 - 2c\gamma^2\rho^6)\right\} \tag{35}$$

In the calculation of the excess enthalpies from the BWR equation of state, the constants for the methane and carbon dioxide and the mixing rules were those presented by Bishnoi and Robinson (*16*). The BWR constants are presented in Table

Table I. Excess Enthalpies (H^E) for xCH_4 + $(1 - x)CO_2$ Where x Denotes Mole Fraction

					H_n^E, J mol^{-1}			
T_0, K	P_0, MPa	x	Q/F, J mol^{-1}	H_0^E, J mol^{-1}	expt	BWR	RK1	RK2
Nominal Conditions: T_n = 293.15 K; P_n = 0.507 MPa								
293.140	0.516	0.253	19.50	18.20	17.90	15.4	14.3	14.6
293.155	0.521	0.477	26.66	26.23	25.63	20.1	18.8	19.7
293.166	0.532	0.501	28.83	27.47	26.39	20.1	18.8	19.1
293.154	0.521	0.816	16.27	18.76	18.45	12.0	11.2	11.4
Nominal Conditions: T_n = 293.15 K; P_n = 1.114 MPa								
293.160	1.139	0.169	30.33	30.01	29.30	27.7	25.8	26.1
293.220	1.101	0.317	46.47	46.34	46.98	42.1	39.2	39.6
293.180	1.160	0.393	50.32	50.39	48.21	46.1	42.9	43.4
293.150	1.160	0.445	49.30	49.98	47.72	47.5	44.2	44.7
293.180	1.167	0.707	46.43	44.86	42.78	39.7	36.3	36.8
293.150	1.146	0.883	25.18	22.57	21.95	19.3	17.9	18.2
Nominal Conditions: T_n = 293.15 K; P_n = 1.520 MPa								
293.150	1.525	0.165	37.81	37.00	36.82	39.7	37.0	37.3
293.154	1.539	0.358	61.21	62.06	61.05	64.6	60.0	60.5
293.147	1.510	0.500	61.18	62.00	62.54	69.1	64.1	64.7
293.145	1.493	0.689	49.68	49.26	50.48	58.1	53.8	54.4
293.149	1.514	0.829	33.39	33.60	33.78	37.9	35.1	35.5
Nominal Conditions: T_n = 305.15 K; P_n = 0.507 MPa								
305.136	0.522	0.168	13.81	12.51	12.18	10.0	9.0	10.0
305.155	0.531	0.459	17.08	17.76	16.89	17.6	17.5	17.5
305.150	0.532	0.630	14.86	14.08	13.21	16.5	16.3	16.4
305.153	0.509	0.799	11.49	11.16	11.12	11.3	11.2	11.2
Nominal Conditions: T_n = 305.15 K; P_n = 1.114 MPa								
305.165	1.140	0.179	30.95	29.71	29.06	25.0	24.9	24.9
305.151	1.129	0.493	43.02	42.59	41.97	41.7	41.3	41.3
305.147	1.127	0.696	39.26	37.79	37.34	34.8	34.5	34.5
305.141	1.123	0.817	22.78	21.73	21.53	24.5	24.2	24.2
Nominal Conditions: T_n = 305.15 K; P_n = 1.520 MPa								
305.140	1.565	0.181	30.94	40.18	38.85	36.5	36.3	36.2
305.161	1.511	0.443	57.86	57.42	57.82	59.1	58.5	58.4
305.170	1.549	0.689	51.18	51.34	50.23	50.2	49.6	49.6
305.148	1.504	0.843	32.49	30.64	31.01	30.6	30.3	30.3
Nominal Conditions: T_n = 313.15 K; P_n = 0.507 MPa								
313.133	0.522	0.252	11.66	11.58	11.17	12.4	12.8	12.7
313.135	0.537	0.456	19.02	19.55	18.51	16.2	16.7	16.6
313.152	0.524	0.644	15.21	15.14	14.60	14.9	15.4	15.3
313.156	0.512	0.770	10.26	10.01	9.88	11.5	11.8	11.8
Nominal Conditions: T_n = 313.15 K; P_n = 1.013 MPa								
313.151	1.033	0.248	31.59	31.50	30.94	26.0	26.9	26.7
313.152	1.004	0.487	35.04	35.52	35.87	34.3	35.4	35.1
313.148	1.007	0.490	33.35	33.72	33.94	34.3	35.4	35.1
313.149	1.006	0.491	33.83	34.30	34.58	34.3	35.4	35.1
313.154	1.005	0.500	33.92	34.40	34.71	34.3	35.4	35.1
313.156	1.008	0.503	33.98	34.57	34.83	34.3	35.4	35.1
313.155	1.010	0.504	33.79	34.27	34.38	34.3	35.4	35.1
313.149	1.014	0.508	34.04	34.84	34.80	34.3	35.4	35.1
313.148	1.020	0.520	33.09	33.79	33.54	34.3	35.5	35.1
313.145	1.023	0.679	31.71	31.88	31.56	29.7	30.6	30.3
313.100	1.060	0.784	21.12	21.00	19.83	22.9	23.6	23.5
Nominal Conditions: T_n = 313.15 K; P_n = 1.520 MPa								
313.183	1.495	0.212	41.10	40.44	41.18	37.2	38.6	38.2
313.160	1.513	0.493	53.20	53.08	53.35	54.3	56.0	55.5
313.180	1.526	0.757	39.98	40.02	39.87	39.1	40.3	39.9
313.150	1.523	0.842	28.80	28.51	28.45	28.1	29.0	28.7
Nominal Conditions: T_n = 313.15 K; P_n = 2.533 MPa								
313.140	2.536	0.255	73.73	74.83	74.71	80.4	83.5	82.3
313.180	2.547	0.361	88.82	89.52	88.85	95.8	99.2	97.8
313.133	2.538	0.496	93.49	94.66	94.38	101.6	104.8	103.4
313.120	2.562	0.630	87.20	88.07	86.64	92.9	95.5	94.3
Nominal Conditions: T_n = 313.15 K; P_n = 3.546 MPa								
313.161	3.507	0.095	61.10	61.90	63.11	63.0	66.3	64.9
313.147	3.559	0.192	105.83	107.08	106.48	110.0	114.9	112.6
313.154	3.532	0.313	128.80	130.07	131.04	147.0	152.4	149.4
313.145	3.522	0.513	137.72	138.91	140.56	162.0	166.6	163.7
313.140	3.524	0.668	107.16	110.18	111.45	138.9	142.3	139.9

Table I (*Continued*)

T_0, K	P_0, MPa	x	Q/F, J mol^{-1}	H_0^E, J mol^{-1}	H_n^E, J mol^{-1} expt	BWR	RK1	RK2
Nominal Conditions: $T_n = 313.15$ K; $P_n = 4.600$ MPa								
313.145	4.602	0.158	135.82	137.67	137.5	153.8	161.6	157.1
313.150	4.599	0.351	218.54	219.87	220.0	240.0	248.0	241.9
313.147	4.584	0.514	223.95	225.39	226.88	247.5	253.1	247.4
313.131	4.601	0.686	192.78	193.25	193.13	201.8	205.2	201.0
313.152	4.553	0.782	140.50	142.40	145.0	155.4	157.7	154.5

Table II. Regression Coefficients for the Equation $H^E/[x_A(1 - x_A)] = C + B(x_A - 0.5) + A(x_A - 0.5)^2$

T, K	P_n, MPa	A, J mol^{-1}	B, J mol^{-1}	C, J mol^{-1}	$100\lvert(H_n^E{}_{\text{exptl}} - H_n^E{}_{\text{calcd}})/H_n^E{}_{\text{exptl}}\rvert_{\text{av}}$
293.15	0.507	−75	6.32	103.61	6.5
	1.114	167.22	24.51	198.36	2.2
	1.52	12.61	−50.72	252.19	2.5
305.15	0.507	182.31	−30.68	62.96	5.1
	1.114	−0.88	−64.02	176.88	5.5
	1.52	180.22	−30.06	234.18	0.9
313.15	0.507	242.71	−4.13	74.25	1.0
	1.013	86.82	−92.57	137.93	2.1
	1.52	192.25	−53.38	215.85	1.0
	2.533	58.57	−47.37	377.78	0.1
	3.546	516.87	−190.1	573.89	1.2

Table III. Constants Utilized in RK1 and RK2 Equations of State

	CH_4	CO_2	ref
Ω_a, dimensionless	0.4546	0.4184	*10*
Ω_b, dimensionless	0.0872	0.0794	*10*
T_C, K	190.6	304.2	*18*
P_C, MPa	4.60	7.38	*18*
V_C, cm^3 mol^{-1}	99.0	94.0	*18*
ω, dimensionless	0.013	0.225	*18*
α, K$^{2.5}$ MPa^{-1}	44.648	90.175	*22*
β, K$^{1.5}$ MPa^{-1}	−24.969	27.338	*22*
γ, K MPa^{-1}	3.375	3.316	*22*
$10^4\delta$, MPa^{-1}	0.00	0.691	*22*

Table IV. Constants for the BWR Equation (*15*)

	CH_4	CO_2
A_0, MPa dm^6 mol^{-2}	0.189 603 6	0.186 104 7
10^2B_0, dm^3 mol^{-1}	4.320 305	3.201 492 7
C_0, MPa dm^6 mol^{-2} K^2	23 811.516	17 836.04
10^3b, dm^6 mol^{-2}	3.978 738 2	6.253 007 8
a, MPa dm^9 mol^{-3}	0.007 011 487	0.024 525 569
$10^{-4}c$, MPa dm^9 mol^{-3} K^2	0.305 791 7	0.192 599 78
$10^5\alpha$, dm^9 mol^{-3}	9.683 576 5	4.878 406 6
$10^3\gamma$, dm^6 mol^{-2}	5.711 812 50	4.280 821 8

IV. The largest deviation between our results and those predicted by the BWR equation was 21% at 0.507 MPa (5 atm). In all other cases the deviation was below 10%. In general, the predictions from the BWR equation of state compare better with our experimental results than the prediction from either the RK1 or RK2 equation. Also, the results obtained from the two latter equations are approximately the same.

One of the interesting results of this comparison is the good fit obtained with the Redlich–Kwong equation either in the original-version RK1 or with the Jacoby–Robinson modification RK2. Indeed replacing the two-constants RK equation with the eight-constants BWR equation yields a rather small improvement in the average deviation. In both cases only one adjustable constant k_{ij} was utilized.

Glossary

a	constant in Redlich–Kwong equation, Pa K$^{1/2}$ cm^6 mol^{-1}
a_{11}, a_{22}, a_{12}	terms in Redlich–Kwong equation defined by eq 19–21, respectively
b	constant in Redlich–Kwong equation, cm^3 mol^{-1}
b_1, b_2	terms in Redlich–Kwong equation defined by eq 22 and 23, respectively
a, b, c, A_0, B_0, C_0	constants in BWR equation of state, eq 33, dimensions listed in Table IV
C_p	molar heat capacity at constant pressure, J mol^{-1} K^{-1}
E_k	kinetic energy, J mol^{-1}
F	flow rate, mol s^{-1}
H	molar enthalpy, J mol^{-1}
k_{12}	characteristic binary constant for RK1 equation, eq 24, dimensionless
K_{12}	characteristic binary constant for RK2 equation, eq 32, dimensionless
P	pressure, MPa
P_{C12}	term defined by eq 25, MPa
Q	heat supplied to gas system by the power supply, J s^{-1}
R	universal gas constant, J mol^{-1} K^{-1}
T	temperature, K
T_{C12}	term defined by eq 24, K
V	molar volume, cm^3 mol^{-1}
x	mole fraction, dimensionless
Z_{C12}	term defined by eq 26, dimensionless

Subscripts

A	denotes pure gas A (CH_4)
B	denotes pure gas B (CO_2)
A, B	denotes gas mixture (CH_4–CO_2)
C	denotes critical temperature or critical pressure: namely, P_{C1} and P_{C2}, critical pressures for gases 1 and 2, respectively; T_{C1} and T_{C2}, critical temperatures for gases 1 and 2, respectively
i	denotes component i
m	denotes mixture
n	denotes a nominal outlet condition, in conjunction with H_n^E, P_n, or T_n
P, T	denotes constant temperature and pressure
1	denotes inlet conditions (P_1, T_1) for gas 1
2	denotes inlet conditions (P_2, T_2) for gas 2
0	denotes outlet conditions (P_0, T_0) for gas mixture
E	denotes an excess thermodynamic property, namely, excess enthalpy, H^E
id	denotes ideal solution
‾	denotes mean values (for Joule–Thomson coefficient and for heat capacities at constant pressure, C_p)
*	denotes a hypothetical ideal gas state at temperature T and zero pressure

Greek Letters

α, γ	constants in BWR equations of state, eq 33, dimensions listed in Table IV
α, β, γ, δ	constants in RK2 equation of state (refer to eq 30–32), dimensions listed in Table III
ΔE_k	change of kinetic energy for gaseous system across calorimeter, J mol^{-1}
ΔH	enthalpy change, J mol^{-1}
ΔH_m	heat of mixing for a real solution, J mol^{-1}

ΔH_m^{id}	heat of mixing for an ideal solution ($\Delta H_m^{id} = 0$), J mol^{-1}
ρ	gas density, mol cm^{-3}
ϕ	isothermal Joule-Thomson coefficient, defined by eq 5, J mol^{-1} Pa^{-1}
Ω_a, Ω_b	constants in eq 19-21, dimensionless
ω	accentric factor, eq 26, dimensionless (ω_1 and ω_2 refer to accentric factors for CH_4 and CO_2, respectively)

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Investigation of Vapor Pressures and Heats of Vaporization of Condensed Aromatic Compounds at Elevated Temperatures

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A high-temperature static apparatus is used to investigate vapor pressures in the range 1-2780 mmHg over the temperature range 425-640 K for three aromatic compounds similar to those which are often found in coal liquids: fluorene, dibenzofuran, and dibenzothiophene. The experimental vapor pressure data of fluorene and its homomorphs cited above have been fitted to Chebyshev polynomials. The values of d*p*/d*T* calculated from the Chebyshev polynomials, the compressibility factors of saturated vapor and liquid estimated from three-parameter corresponding states correlation, and the acentric factors determined from their experimental vapor pressure data presented in this paper were used to evaluate the heats of vaporization of the aromatic compounds mentioned above from the Clapeyron equation.

Introduction

The purposes of this article are (I) to investigate the vapor pressures of some commercially important substances found in coal liquids, viz., fluorene, dibenzofuran, and dibenzothiophene, and (II) to determine the heats of vaporization of fluorene and the homomorphs mentioned above. The determination of vapor pressures of some oxygen- and sulfur-containing coal-derived liquids is an important consideration from not only the purely scientific standpoint but also a commercial standpoint. Hydrocarbon fractions derived from the liquefaction of coal are composed largely of hydrogen-deficient condensed-ring molecular systems. Since many of the pure compounds that are members of these systems are low vapor pressure solids at room temperature, the amount of reliable physical and thermodynamic data available for them, compared to that for alkane hydrocarbons (*1*), is sparse. Vapor pressure is an important physical property required in designing coal-liquid processing and separation plants. The idea of choosing these condensed aromatic compounds is that the thermodynamic properties are virtually unknown, especially at high temperatures. Moreover, it is interesting and valuable to study the properties of the coal-related compounds belonging to the same family or homomorphs (*2*) which will help to generate best correlations for better prediction of physical properties. No experimental vapor pressure values are reported in the literature for these compounds in the temperature range of the present investigation. However, Edwards and Prausnitz (*3*) report vapor pressure measurements in solid and liquid dibenzothiophene at fairly low temperatures. The experimental data of vapor pressures were fitted to Chebyshev polynomials and values of d*p*/d*T* were calculated. No literature measurements of heats of vaporization over the range of temperatures were found for these compounds. For design of coal-conversion processes these data are very much necessary. The following paper presents the calculated values of heats of vaporization from our experimental vapor pressure data over a range of temperature. The Clapeyron equation was used to calculate the heat of vaporization. The compressibility factors of saturated vapor and liquid needed for the above calculation were estimated from Pitzer's three-parameter corresponding states correlation using the acentric parameters obtained from this study.

Experimental Vapor Pressure Measurements

Materials. All compounds studied were purchased from Aldrich Chemical Co. with the following purities: fluorene, 98%; dibenzofuran, 98%; and dibenzothiophene, 95%. These substances were purified by 48 passes in a zone refiner to a purity of 99.99%. The purity was estimated by the freezing-point

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