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Excess and Unlike Interaction Second Virial Coefficients and Excess Enthalpy of Mixing of (Carbon Monoxide + Pentane)

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The excess second virial coefficient of the mixture carbon monoxide + pentane has been determined at 299.5, 313.15, 328.15, and 343.15 K using the pressure change on mixing method. Unlike interaction second virial coefficients were derived and compared with the predictions of the Tsonopoulos correlation. The excess enthalpy of mixing was also estimated.

Introduction

The PVT behavior of (carbon monoxide + pentane) does not appear to have been studied previously. A recent paper (*1*) reported results for mixtures of carbon monoxide and isomers of butane, and this work is an extension of that study.

Carbon monoxide and pentane are minor components of natural gas and are included in the compilation of second and third virial coefficients of the Groupe de Recherches Gazieres (GERG) (*2*). Unlike interaction second virial coefficients were not covered, however, largely due to the low concentrations expected in treated natural gas. GERG has produced such a significant set of coherent data that its extension outside the parameters of the natural gas industry is valuable.

In this study unlike interaction second virial coefficients have been obtained from measurement of the pressure change Δp upon mixing of two pure gases at equal pressure.

The well established relation

$$\epsilon = 2RT\Delta p/[p^2(1 + \Delta p/p)] \qquad (1)$$

is employed, and since the excess second virial coefficient ϵ is related to virial coefficients by

$$\epsilon = B_{12} - (B_{11} + B_{22})/2 \qquad (2)$$

the unlike interaction second virial coefficient B_{12} can be obtained if the pure values B_{11} and B_{22} are known.

ϵ values and $d\epsilon/dT$ may be used to estimate the excess enthalpy of the mixture H^E.

The truncated pressure series virial equation for a binary mixture is

$$\begin{aligned} V_m &= RT/p + B_m \\ &= RT/p + y_1B_{11} + y_2B_{22} + 2y_1y_2\epsilon \qquad (3) \end{aligned}$$

And so

$$\begin{aligned} V^E &= V_m - y_1V_1 - y_2V_2 \\ &= 2y_1y_2\epsilon \qquad (4) \end{aligned}$$

$$dH^E = V^E dp + TdS^E \qquad (5)$$

$$\begin{aligned} (\partial H^E/\partial p)_T &= V^E + T(\partial S^E/\partial p)_T \\ &= V^E - T(\partial V^E/\partial T)_P \qquad (6) \end{aligned}$$

and since ϵ is not a function of pressure

$$H^E = 2y_1y_2p[\epsilon - T(d\epsilon/dT)] \qquad (7)$$

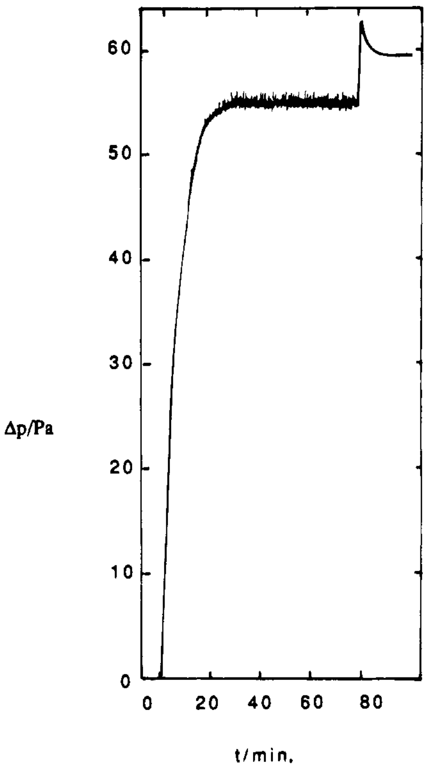

Figure 1. Rise of Δp with time showing completion of the mixing process.

Experimental Section

The apparatus (*3, 1*) has been described previously and was unchanged for this work. Equal volumes (approximately 3×10^{-3} m^3) of the two gases are mixed. This results in numbers of moles of each component being so close to equal that the term y_1y_2 may be taken as 0.25. Reversing the loading order of the gases has been shown to have no discernible effect on the ϵ value determined.

The pressure measuring instruments and procedures were unchanged from the previous studies. Temperatures were measured with an Automatic Systems Laboratory resistance bridge and platinum resistance thermometer with ±0.005 K claimed accuracy. The thermometers had been calibrated using IPTS-68, and the readings were converted to ITS-90 using standard tables.

The gases were mixed by circulating through the two vessels using a small reciprocating pump. A plot of the

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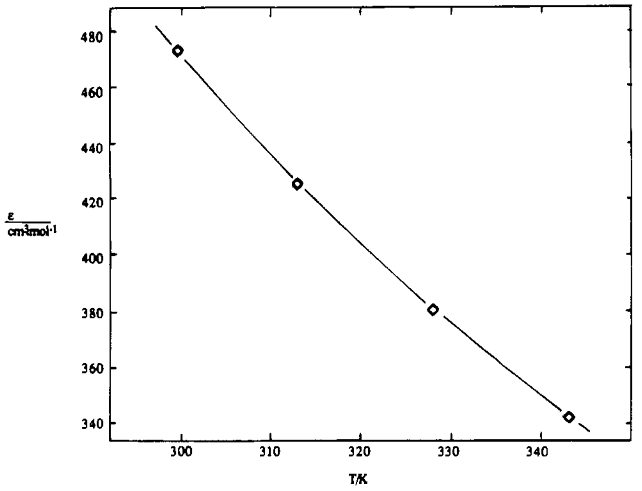

Figure 2. Excess second virial coefficients of ($CO + C_5H_{12}$): ◇, this work; —, curve fitted to results.

Table 1. (0.50 Carbon Monoxide + 0.50 Pentane) Experimental Results

T/K	p/kPa	Δp/Pa	ϵ/cm³·mol⁻¹
299.50	30.7137	89.85	473.0
299.50	30.8680	91.01	474.3
313.15	37.5488	115.18	424.1
313.15	37.4023	114.10	423.3
328.15	36.7118	93.92	379.3
328.16	37.7976	99.93	380.7
343.15	36.4223	79.09	339.5
343.15	36.5450	79.93	340.7

rise in pressure with time is shown in Figure 1. As can be seen the pressure rise is complete after 25 min, so circulation for 45 min or more should guarantee complete mixing.

The carbon monoxide gas was ultrahigh purity grade from Matheson Gas Products and was certified as having minimum CO concentration 99.8 mol % with N_2 the major impurity. The pentane was Aldrich Chemical Co. anhydrous Gold Label grade specified as greater than 99 mol % pentane and was used as supplied apart from degassing. It was degassed by freezing with liquid nitrogen, pumping to below 10^{-1} Pa, and then melting, with the process repeated at least six times.

The gauge that measured the pressure change of mixing had a full-scale range of 133 Pa, and to ensure this was not exceeded, total loading pressure was kept below 40 kPa. The saturation vapor pressure of pentane at the lowest temperature is 70.9 kPa. This means that the degree of saturation of the pentane gas is 56% or less, and so the effect of adsorption onto the glass walls of the vessels should be small.

Results and Discussion

The measured pressures and pressure change of mixing along with the excess second virial coefficient ϵ are presented in Table 1. ϵ has been plotted against temperature in Figure 2 and evidently decreases smoothly with temperature. The values of $d\epsilon/dT$ needed to determine H^E have been read from the plot, and the results obtained are listed in Table 2.

The uncertainty in the reported H^E values is estimated to be ±2 J·mol⁻¹.

To determine the unlike interaction second virial coefficient, pure component values must be obtained.

Measurements on pentane have been reported by a number of workers (*4*) and have been discussed (*5*) by An Xueqin et al. For this work we have fitted a smooth curve to the results of An Xueqin et al., McGlashan and Potter (*6*), and Hajjar et al. (*7*) and obtained the values listed in Table 2.

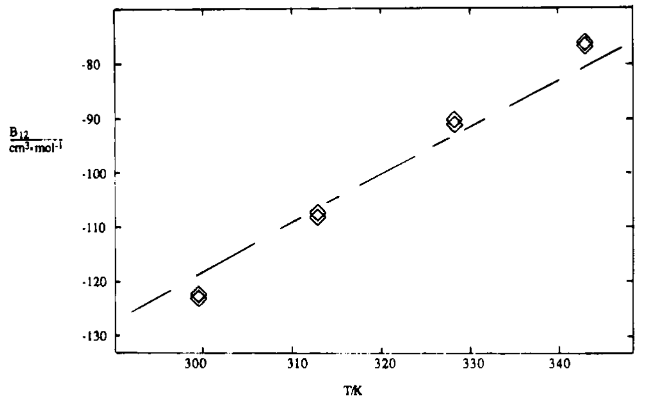

Figure 3. Unlike interaction second virial coefficient of ($CO + C_5H_{12}$): ◇, this work; —, Tsonopoulos equation (eq 9) with k_{12} = 0.075.

Table 2. (0.50 Carbon Monoxide + 0.50 Pentane) Second Virial Coefficients and Excess Enthalpy

T/K	B(CO)/ cm³·mol⁻¹	$B(C_5H_{12})$/ cm³·mol⁻¹	B_{12}/ cm³·mol⁻¹	$H^E(2py_1y_2)^{-1}$/ cm³·mol⁻¹	$H^E(p$ = 30 kPa)/ J·mol⁻¹
299.50	−8.2	−1185	−123.6	1710	25.7
299.50	−8.2	−1185	−122.3		
313.15	−5.4	−1058	−107.6	1485	22.3
313.15	−5.4	−1058	−108.4		
328.15	−2.6	−940	−92.0	1299	19.5
328.15	−2.6	−940	−90.6		
343.15	−0.1	−833	−77.0	1197	18.0
343.15	−0.1	−833	−75.8		

The second virial coefficient of carbon monoxide has been discussed previously (*1*), and for this work we have used the equation due to Goodwin (*8*):

$$B(\mathrm{CO})/\mathrm{cm^3\cdot mol^{-1}} = 55.956 - 201.6749/(T/\mathrm{K}) + 66.554 \times 10^4/(T/\mathrm{K})^2 - 109.7726 \times 10^6/(T/\mathrm{K})^3 \quad (8)$$

The values used are listed in Table 2 along with the unlike interaction second virial coefficient B_{12} derived using eq 2.

The B_{12} values obtained are plotted in Figure 3 and evidently exhibit a considerably greater uncertainty than does ϵ. The estimated uncertainties are δB(CO) = ±2 cm³·mol⁻¹, δB(pentane) = ±15 cm³·mol⁻¹, and $\delta\epsilon$ = ±1.5 cm³·mol⁻¹, and a simple combination of uncertainties means that ±10 cm³·mol⁻¹ is to be expected in B_{12}.

The Tsonopoulos modification (*9*) of the Pitzer and Curl equation (*10*)

$$Bp_c/RT_c = f^{(0)}(T_R) + \omega f^{(1)}(T_R) \quad (9)$$

often provides a good representation of B_{12}. Commonly used combining rules are

$$T_{c,ij} = (T_{c,i}T_{c,j})^{1/2}(1 - k_{ij}) \quad (10)$$

and

$$P_{c,ij} = \frac{4T_{c,ij}(p_{c,1}V_{c,1}/T_{c,1} + p_{c,2}V_{c,2}/T_{c,2})}{(V_{c,1}^{1/3} + V_{c,2}^{1/3})^3} \quad (11)$$

The factor k_{ij} can be employed as a fitting parameter, and in Figure 2 the Tsonopoulos equation using these combining rules with $k_{ij} = 0.075$ evidently provides a good representation of the experimental results. A number of correlations have been proposed for k_{ij} values of particular classes of binary mixtures, but CO-containing systems have not been widely studied.

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