reason for the higher enthalpy of vaporization of barium bromide and this compound might well be the subject of further study.

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Excess Enthalpy, Volume, and Gibbs Free Energy of Cyclopentane-Tetrachloroethylene Mixtures at 25° C

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Molar excess enthalpies and volumes of the system cyclopentane-tetrachloroethylene at 25° C were determined by direct calorimetric and dilatometric measurements. Excess Gibbs free energies (also at 25° C) were obtained from a study of the vapor-liquid equilibrium in a circulation still. The values of the excess thermodynamic properties are compared with the results of a previous similar investigation of the system cyclopentane–carbon tetrachloride.

THE RESULTS of an investigation of the interactions of carbon tetrachloride and tetrachloroethylene with the polar material pyridine were published recently by Fried, Franceschetti, and Schneier (*9*), who studied vapor-liquid equilibria in the systems pyridine-carbon tetrachloride and pyridine-tetrachloroethylene. Assuming that the factors affecting the nonideal behavior of these systems are separable into nonspecific and specific (polar-double bond) contributions, it appears that the polar-double bond interaction contributes about 182 J mole^{-1} to the excess Gibbs free energy of an equimolar mixture of pyridine and tetrachloroethylene at 50° C.

In a previous investigation (*3*) we reported values of the excess enthalpy, volume, and Gibbs free energy of the system cyclopentane–carbon tetrachloride at 25° C. The present study was undertaken to provide similar information for the system cyclopentane-tetrachloroethylene and to make possible a comparison of the interaction of the carbon tetrachloride and tetrachloroethylene molecules with the nonpolar (and approximately spherical) cyclopentane molecule. Such a comparison should be helpful in assessing the validity of the assumption that the difference between the excess free energies of the two pyridine systems of Fried *et al.* (*9*) can be attributed to a specific polar–double bond interaction.

EXPERIMENTAL

The methods used in our laboratory for studying the excess thermodynamic properties of binary mixtures have been described (*2, 16, 18*). Reference can be made to these earlier publications for details of the apparatus and techniques. The outlines given below are intended only to indicate the nature of the various measurements and any changes which have been made for the present investigation.

Calorimetric Measurements. The dilution calorimeter described by Murakami and Benson (*16*) was used for determining the molar excess enthalpies. In this calorimeter, successive portions of one component contained over mercury can be added to a weighed amount (about 0.8 mole) of the other component in the absence of any vapor space. In the present application the cooling effect of the mixing process was compensated by Joule heating, and the amount of electrical energy needed to maintain a set value of the temperature (nominally 25.00° ± 0.01° C) in the mixing vessel was determined. During a dilution, temperature variations as large as ±0.003° C sometimes occurred for short periods of time, but usually there was close compensation between positive and negative deviations. In general, the temperature in the vessel was restored after each dilution to within ±0.0003° C of the set value. The errors of the enthalpy values for the present system are estimated to be less than ±1 J mole^{-1}.

Volumetric Measurements. A successive dilution technique (*18*) was also used in measuring the volumes of mixing. At the start of an experiment the mixing chamber of the

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Table I. Physical Constants Characterizing Component Liquids

Property	Cyclopentane		Tetrachloroethylene	
	Measured	Literature	Measured	Literature
Vapor pressure at 25° C, torr	317.50	317.46 (*1*)	18.40[a]	18.47 (*5*) 18.40[b] (*10*)
Density at 25° C, g cm^{-3}	0.74034	0.74045 (*24*)	1.61432	1.61446 (*5*)
Refractive index (n_D) at 20° C	1.40638	1.40646 (*24*)	1.50576	1.50534 (*5*)

[a] Calculated from Antoine form representing experimental results in Table III. [b] Assumes Antoine coefficients of Fried *et al.* (*10*) valid at 25° C.

dilatometer contained about 50 cm^3 of one component; the change in volume after each dilution was obtained from the change in level of the mercury in a capillary tube (nominal i.d. 0.5 mm) attached to the chamber. All measurements were made with the dilatometer immersed in a water thermostat operating at 25.00° ± 0.01° C and controlled to ±0.001° C. The positions of the mercury meniscus in the capillary and of a fiducial line on the tube were read to ±0.05 mm with a cathetometer. The excess volumes measured for cyclopentane-tetrachloroethylene are small and their determination is subject to relatively large errors; the uncertainty of the result for an equimolar mixture is estimated to be of the order of ±0.0005 cm^3 mole^{-1}.

Vapor-Liquid Equilibria. A still similar to that described by Boublik and Benson (*2*) was used to determine the vapor-liquid equilibria. The main modification was the replacement of the spiral tube around the thermometer well by a straight tube concentric with the well and providing an annular equilibrating space. A ridge was added to the surface of the well to guide the equilibrium liquid mixture in a spiral path as it flowed down the wall. A Beckmann thermometer calibrated against a standard platinum resistance thermometer was used to measure the equilibrium temperature. The equilibrium pressures were determined with a quartz spiral gage (Texas Instruments), calibrated with a water ebulliometer. The temperatures of the latter were measured with the standard platinum thermometer and the corresponding pressures of the water vapor were obtained from the tabulation of Bridgeman and Aldrich (*4*). The over-all precision of pressures measured with the gage calibrated in this way is estimated to be ±0.06 torr over the range 20 to 500 torr.

The still was filled at atmospheric pressure with about 120 cm^3 of mixture. After boiling had started, the pressure in the manostat was adjusted until a temperature of 25.000° ± 0.005° C was obtained in the still head. This value was maintained for 2 to 3 hours to ensure the establishment of equilibrium conditions. The boiling was then stopped abruptly by raising the pressure to atmospheric, and glass pipets were used to remove small samples (0.5 cm^3) of the equilibrium liquid and condensed vapor phases. The concentrations of these were determined by measuring their refractive indices at 20.000° ± 0.002° C. The variation of the refractive index with concentration was established from measurements on a series of mixtures of known composition. The precision of the analyses was about ±0.025 mole %.

Materials. The component liquids were purified by passing them through appropriate ¾-inch columns in an F&M preparative gas chromatograph. Cyclopentane (pure grade reagent from Phillips Petroleum Co.) was passed through a column packed with Chromosorb W (30/60 mesh) containing 20% squalane. A solid phase of Chromosorb P (60/80 mesh) loaded with 25% tricresyl phosphate was used for tetrachloroethylene (primary material from Eastman Organic Chemicals).

Densities, refractive indices, and vapor pressures (the latter determined ebulliometrically), characterizing the final products, are given in Table I along with values from the literature (*1, 5, 24*) for comparison. The discrepancies between the experimental and literature values of the density and refractive index for tetrachloroethylene may be due in part to the impurity content [0.22 mole % (*6*)] of the sample used for the determinations quoted by Dreisbach (*5*).

RESULTS

Experimental values of the molar excess enthalpy and of the molar excess volume, both at 25.00° C, are listed in Table II for various mole fractions of cyclopentane. These results are also presented graphically in Figures 1 and 2.

Vapor pressures of tetrachloroethylene reported recently (*8–10*) in general are somewhat lower than the older values represented by the Antoine coefficients given by Dreisbach (*5*). At 25° C the discrepancy is less than 0.1 torr but it increases to 1.7 torr at 70° C. In view of these differences, the vapor pressure of our sample of tetrachloroethylene was investigated in an ebulliometer at temperatures ranging approximately from 25° to 110° C. The results are summarized in Table III along with values of the coefficients corresponding to the least-squares fit of the data by an Antoine form of equation. Differences between the experimental results and smoothed values of the vapor pressure calculated from the Antoine representation are given in the last column of Table III. Our (smoothed) vapor pressures are compared with other values from the literature in Table IV. Our results at temperatures above 25° C fall between the two other sets of data.

Table II. Experimental Values of Molar Excess Enthalpy and Molar Excess Volume of Cyclopentane(1)-Tetrachloroethylene(2) Mixtures at 25° C

x_1	H^E, J Mole^{-1}	x_1	H^E, J Mole^{-1}	x_1	V^E, Cm^3 Mole^{-1}
0.0306	26.9	0.5412	234.3	0.0138	0.0010
0.0446	39.8	0.5445	234.5	0.0298	0.0017
0.0737	63.6	0.5673	232.6	0.0626	0.0033
0.0947	80.3	0.5862	229.5	0.1090	0.0037
0.1321	106.7	0.5873	229.5	0.1632	0.0041
0.1586	124.8	0.6215	223.5	0.2332	0.0030
0.2082	153.6	0.6322	220.8	0.3036	0.0013
0.2252	163.1	0.6363	219.9	0.3709	−0.0030
0.2859	190.5	0.6814	207.1	0.4238	−0.0054
0.2915	193.5	0.6845	205.8	0.5141	−0.0077
0.3476	212.3	0.7417	183.4	0.5566	−0.0083
0.3566	214.5	0.7425	183.2	0.6065	−0.0090
0.3951	223.8	0.8025	152.1	0.6663	−0.0094
0.4152	228.3	0.8102	148.2	0.7271	−0.0097
0.4298	229.5	0.8596	116.1	0.7887	−0.0084
0.4466	231.9	0.8913	94.2	0.8441	−0.0068
0.4645	234.5	0.9058	82.3	0.8968	−0.0050
0.4938	235.2	0.9536	43.1	0.9441	−0.0029
0.5009	235.9	0.9564	40.3	0.9714	−0.0016
0.5142	236.0				

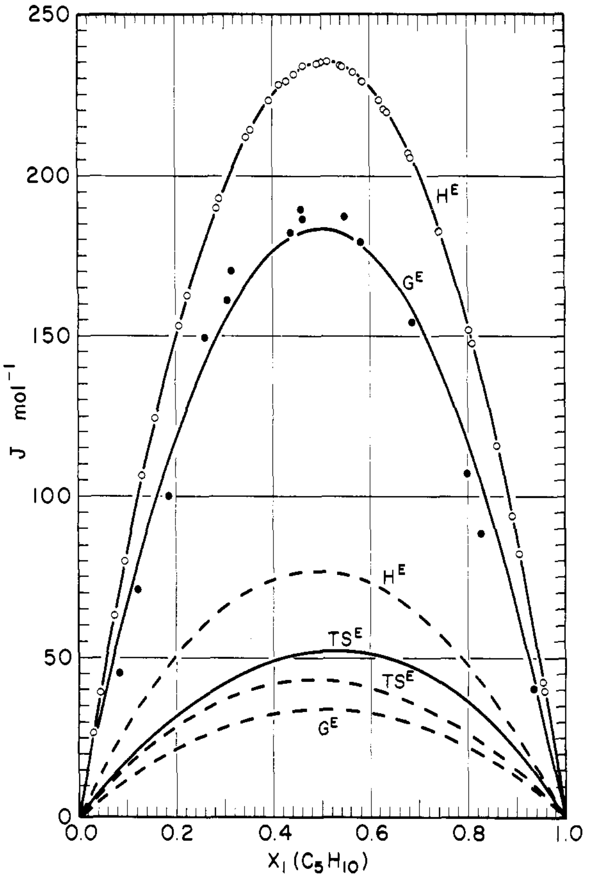

Figure 1. Molar excess enthalpies, Gibbs free energies, and entropies at 25° C

System $C_5H_{10} - C_2Cl_4$. Experimental results H^E, ○; G^E, ●.
— H^E and G^E least squares representations by Equation 4, TS^E obtained fram $H^E - G^E$
System $C_5H_{10} - CCl_4$. --- Smoothed values from (3)

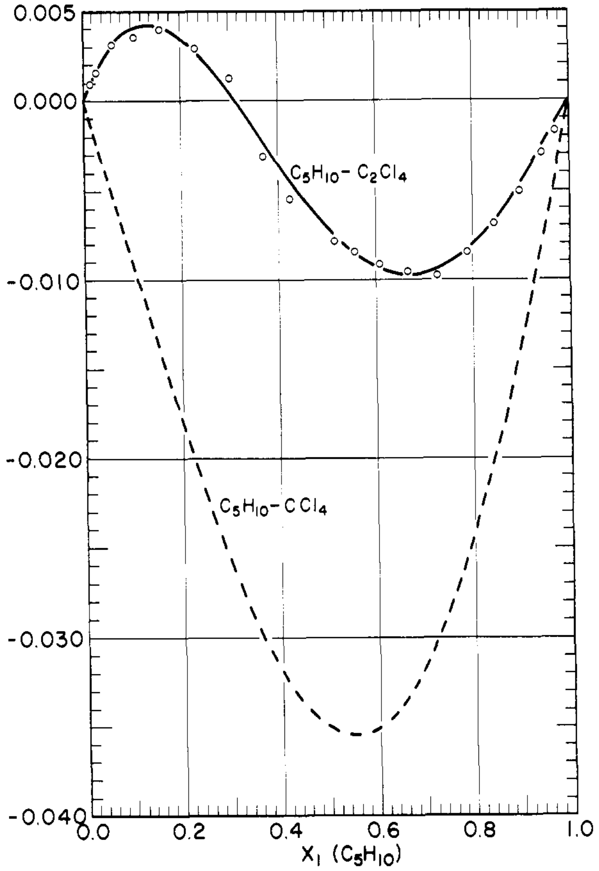

Figure 2. Molar excess volumes at 25° C.

System $C_5H_{10} - C_2Cl_4$. Experimental results V^E, ○
— Least squares representation by Equation 4
System $C_5H_{10} - CCl_4$. --- Smoothed values from (3)

Table V summarizes the results of the vapor-liquid equilibrium studies at 25.00° C. In the first three columns, the compositions of the equilibrium liquid and vapor phases and the total pressure are listed. The last column contains values of the molar excess Gibbs free energy

$$G^E = RT\,(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \tag{1}$$

where the activity coefficients were evaluated from the vapor-liquid equilibrium results, using the equations

$$\ln\gamma_i = \ln(y_i p/x_i p_i^\circ) + (B_{ii} - V_i^\circ)(p - p_i^\circ)/RT + (1 - y_i)^2 p\delta/RT \tag{2}$$

and

$$\delta = 2B_{12} - B_{11} - B_{22} \tag{3}$$

Values of the properties of the pure components at 25° C, used in the calculations of G^E, are collected in Table VI. The resulting excess free energies are plotted in Figure 1.

The area test (*22*) was used to check the consistency of the vapor-liquid equilibrium results. The absolute values of the integral $\int \ln(\gamma_1/\gamma_2)dx_1$ over the ranges for which the integrand is positive and negative are equal within 4.5%. A statistical analysis shows that the error in the value of G^E is due primarily to contributions from the errors in the values of y_i, p, and p_i°. Using the values $\sigma_x = \sigma_y = 0.00025$ and $\sigma_p = \sigma_{p^\circ} = 0.06$ for the standard errors of the concentrations and pressures, the standard error of G^E for an equimolar solution is estimated to be about 7 J mole^{-1}—i.e., about 3.5%—however, near the ends of the mole fraction range the error in G^E may amount to as much as 30%.

Table III. Experimental Values of Vapor Pressure of Tetrachloroethylene

Temp., °C	p°, Torr	Δp^a, Torr
27.887	21.52	-0.07
35.758	32.06	-0.04
41.702	42.67	-0.01
46.502	53.26	0.02
57.065	84.58	0.02
61.254	100.60	0.07
68.065	132.16	-0.01
74.529	169.07	0.05
81.957	221.68	-0.01
88.055	274.20	-0.05
94.568	341.02	-0.11
98.917	392.40	-0.01
104.269	464.10	0.04
107.692	515.25	0.05

Antoine form with coefficients $A = 7.05854$, $B = 1438.947$, $C = 223.368$ represents vapor pressure results with standard error of 0.05 torr. $^a\Delta p = p^\circ$ (Antoine) $- p^\circ$ (exptl).

Vapor-liquid equilibria were also determined at 35° and 45° C. Details of these are not presented, since the resulting values of G^E differed from those obtained at 25° C by less than the combined estimates of their errors.

Table IV. Comparison of Smoothed Values of Vapor Pressure of Tetrachloroethylene

Temp., °C	Vapor Pressure, Torr		
	Present research	(*5*)	(*8-10*)
25	18.40	18.47	18.40
50	62.34	62.63	61.91
60	95.61	96.09	94.88
70	142.44	143.14	141.38
100	406.13	407.73	405.08

Table V. Vapor-Liquid Equilibria of Cyclopentane(1)-Tetrachloroethylene(2) Mixtures at 25° C

x_1	y_1	p, Torr	G^E, J Mole^{-1}
0.0843	0.6607	49.85	46.0
0.1226	0.7432	63.49	71.6
0.1864	0.8218	85.40	100.6
0.2614	0.8697	108.85	150.0
0.3069	0.8906	122.76	162.0
0.3176	0.8951	126.56	171.2
0.4382	0.9302	161.16	183.3
0.4593	0.9336	165.94	190.5
0.4635	0.9348	167.28	187.1
0.5490	0.9504	190.96	188.2
0.5829	0.9560	200.43	179.8
0.6872	0.9700	228.93	155.0
0.8007	0.9826	260.32	108.0
0.8267	0.9854	267.58	88.9
0.9362	0.9947	298.45	41.2

Table VI. Properties of Pure Components at 25° C Used in Calculations of G^E

	Cyclopentane	Tetrachloroethylene
p_i°, torr	317.50[a]	18.40[a]
V_i°, cm^3 mole^{-1}	94.734[b]	102.727[b]
B_{ii}, cm^3 mole^{-1}	−1054[c]	−2566[d]
δ, cm^3 mole^{-1}	238[e]	

[a] Our smoothed value from Table I. [b] Calculated from experimental density in Table I. [c] Estimated by Hermsen and Prausnitz (*11*). [d] Calculated according to formula of Pitzer and Curl (*19*), using critical temperature from (*15*), and critical pressure estimated by Lydersen method (*23*). [e] Based on value of B_{12} estimated from formulas given by O'Connell and Prausnitz (*17*).

The method of least squares was used to fit the results for each of the excess properties with a Redlich-Kister type of equation

$$X^E = x_1(1 - x_1) \sum_{p=1}^{n} c_p(1 - 2x_1)^{p-1} \tag{4}$$

In the case of the excess enthalpies and volumes, the mole fractions were considered to be known accurately, and equal weights were assigned to the experimental excess quantities. In treating the vapor-liquid equilibrium results, the weights assigned to the primary experimental data (x_1, y_1, and p) were inversely proportional to the squares of their estimated errors. The number of coefficients used in Equation 4 was varied and in each case the minimum number needed to represent the results adequately was determined by examining the standard error of estimate

$$\sigma = \left[\sum (X^E_{\text{obsd}} - X^E_{\text{calcd}})^2 / (n_{\text{obsd}} - n) \right]^{1/2} \tag{5}$$

The resulting values of the coefficients are given in Table VII along with the standard error of estimate for each of the excess functions. Using these coefficients, the continuous curves for H^E, G^E, and V^E in Figures 1 and 2 were calculated from Equation 4.

The molar excess entropy is related to the excess enthalpy and excess free energy by the equation

$$TS^E = H^E - G^E \tag{6}$$

Using this, the curve for TS^E shown in Figure 1 was calculated from the smoothed values of H^E and G^E.

DISCUSSION

It is interesting to compare the results for the present system with those obtained previously for cyclopentane–carbon tetrachloride. Values calculated for the latter system at 25° C from equations given by Boublik *et al.* (*3*) are represented by the broken curves in Figures 1 and 2.

From Figure 1 it can be seen that the excess entropy of the two systems is nearly the same (within the experimental uncertainty). This is not unexpected from purely spatial considerations, since the volumes of the two halide molecules are almost equal (within 5%); also it has been suggested (*8*) on the basis of the nearly ideal behavior of the system carbon tetrachloride–tetrachloroethylene (*8, 21*) that tetrachloroethylene behaves like a spherical molecule, although in the strict sense it has only the symmetry of the point group D_{2h}. However, despite this similarity in the size and shape of the carbon tetrachloride and tetrachloroethylene molecules, the volume behavior of the two systems formed by mixing them with cyclopentane is different. Apparently the slightly smaller quasispherical carbon tetrachloride molecules can be packed more closely with cyclopentane than with tetrachloroethylene molecules. This interpretation seems preferable to one based on postulating a stronger interaction between cyclopentane and carbon tetrachloride molecules, than between cyclopentane and tetrachloroethylene molecules. Indeed such a postulation would lead to difficulties in interpreting the excess enthalpies and free energies.

It is clear from Figure 1 that the energetic behavior of tetrachloroethylene when mixed with cyclopentane is very different from that of carbon tetrachloride under similar conditions, since the values of the excess enthalpy and free energy for the present system are much larger than values for the system cyclopentane–carbon tetrachloride at corresponding concentrations, while the excess entropy (as noted above) is nearly the same for the two systems. If the free energies are considered to be made up of additive parts [as in the pyridine systems (*9*)], the interaction of the olefinic bond with the nonpolar cyclopentane molecule contributes about 150 J mole^{-1} in an equimolar mixture. This is not much smaller than the interaction with the polar pyridine molecule, 182 J mole^{-1} at 50° C. Presumably the value of the latter interaction would be somewhat larger at 25° C. Nevertheless the similarity of the results tends to cast some doubt on the separability of the excess free energy into contributions from specific and nonspecific interactions.

The molar excess energy at constant volume

$$U_V^E = H^E - T(\alpha/\beta)V^E \tag{7}$$

is generally related more directly to theories of mixtures than is H^E (the excess enthalpy at constant pressure). The

Table VII. Values of Coefficients c_p in Equation 4 Determined by Method of Least Squares

Function X^E	c_1	c_2	c_3	σ
H^E, J mole^{-1}	942.55	−23.87	12.39	0.34
V^E, cm^3 mole^{-1}	−0.02834	0.06050	0.03855	0.00045
G^E, J mole^{-1}	734.5			8.6

"experimental" values of U_V^E shown in Figure 3 at intervals of 0.05 in the mole fraction were computed from Equation 7 using values of α and β which were estimated for the mixtures from data for the pure components (given in Table VIII) assuming additivity on a volume fraction basis.

The U_V^E "results" for cyclopentane-tetrachloroethylene can be represented very well by the basic equation of the theory of regular solutions (*12*)

$$U_V^E = (x_1 V_1^\circ + x_2 V_2^\circ) A_{12} \phi_1 \phi_2 \tag{8}$$

where

$$\phi_i = x_i V_i^\circ / (x_1 V_1^\circ + x_2 V_2^\circ) \tag{9}$$

is the volume fraction of component i referred to the unmixed state. Using a value of A_{12} = 9.652 J cm^{-3} determined by the method of least squares, the standard error of estimate is σ_U = 0.41 J mole^{-1}. The results for cyclopentane–carbon tetrachloride cannot be fitted as well by Equation 8; however, a value of A_{12} = 3.666 J cm^{-3} provides a reasonably good approximation (σ_U = 1.04 J mole^{-1}). The continuous curves in Figure 3 were calculated from Equation 8 with these values of A_{12}.

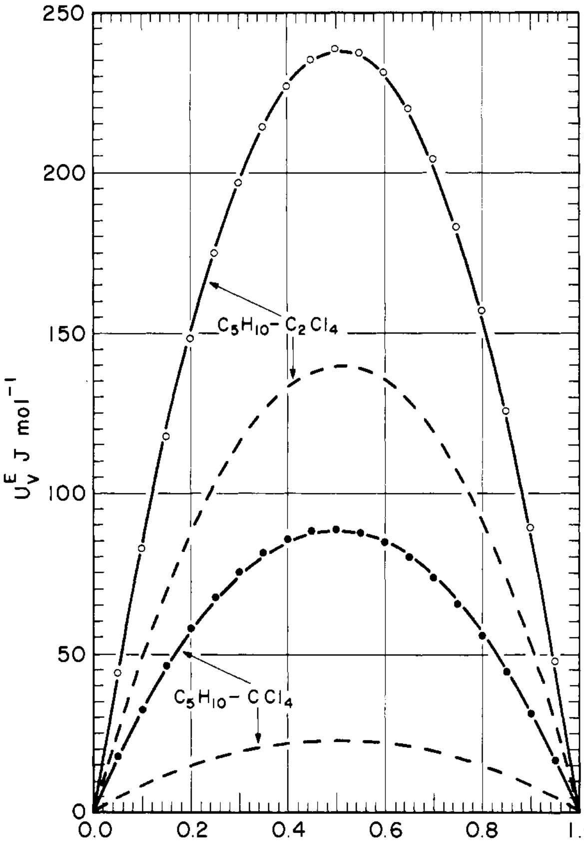

Figure 3. Molar excess energies at constant volume and 25° C

Points calculated from smoothed values of H^E and V^E

— Calculated from Equation 8 with A_{12} = 9.625 J cm^{-3} for C_5H_{10} – C_2Cl_4 and 3.666 J cm^{-3} for C_5H_{10} – CCl_4

--- Calculated from solubility parameters

Table VIII. Properties of Pure Components at 25° C Used in Calculations of U_V^E

	Cyclopentane	Tetrachloroethylene	Carbon Tetrachloride
$10^3\ \alpha$, deg^{-1}	1.325[a]	1.020[b]	1.212[a]
$10^6\ \beta$, atm^{-1}	135.1[a]	76.5[c]	109.1[a]
c_{ii}[d], J cm^{-3}	276.54	361.47	309.50
δ_i[d], J$^{1/2}$ cm$^{-3/2}$	16.630	19.012	17.593

[a] Taken from (*3*), source of value indicated there. [b] Estimated from densities given in (*5*). [c] Interpolation of data from (*13*). [d] Cohesive energy densities and solubility parameters estimated by method of Polák (*20*) which includes correction for imperfect behavior of vapor.

According to the theory of regular solutions, coefficient A_{12} has the form of an interchange energy and can be written as

$$A_{12} = c_{11} + c_{22} - 2c_{12} \tag{10}$$

where c_{ij} characterizes the interaction between a pair of molecules of species i and j. In particular, c_{ii} is the cohesive energy density of component i and can be evaluated from properties of the pure component (*12, 20*). If the Berthelot relation is assumed,

$$c_{12}^2 = c_{11}\, c_{22} \tag{11}$$

and

$$A_{12} = (\delta_1 - \delta_2)^2 \tag{12}$$

where

$$\delta_i = (c_{ii})^{1/2} \tag{13}$$

is the solubility parameter. Values of c_{ii} and δ_i for the present component liquids are given in Table VIII.

The solubility parameter theory leads to values of 5.679 and 0.928 J cm^{-3} for A_{12} in the tetrachloroethylene and carbon tetrachloride systems, respectively. Consequently the theory produces estimates of U_V^E which are much too small, as shown by the broken curves in Figure 3.

Use of the formula due to Erdös (*7*) leads to values of U_V^E even smaller than those calculated from the solubility parameters. The difference between experimental and theoretical excess energies is decreased somewhat if values of c_{12} estimated by the method of Kohler (*14*) are used instead of those based on the Berthelot relation; however, the discrepancies which remain are still relatively large. To obtain values of A_{12} in agreement with the least-squares results, the interactions of cyclopentane with tetrachloroethylene and with carbon tetrachloride must be characterized by values of c_{12} = 314.18 and 291.19 J cm^{-3}, respectively.

ACKNOWLEDGMENT

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NOMENCLATURE

A, B, C = constants in Antoine vapor pressure equation
A_{12} = constant in regular solution theory (Equation 8)
B_{ii} = second virial coefficient of pure component i
B_{12} = cross virial coefficient
$c_1, c_2, \ldots c_p$ = coefficients in Redlich-Kister representation of G^E, H^E, and V^E by Equation 4
c_{ij} = interaction parameters
G^E = molar excess Gibbs free energy
H^E = molar excess enthalpy
n = number of coefficients in Equation 4
n_{obsd} = number of experimental points

p = total vapor pressure
p_i° = vapor pressure of pure component i
R = gas constant
S^E = molar excess entropy
T = absolute temperature
U_V^E = molar excess energy at constant volume
V^E = molar excess volume
V_i° = molar volume of pure component i
X^E = typical molar excess property
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase

Greek Letters

α = coefficient of thermal expansion
β = coefficient of isothermal compressibility
γ_i = activity coefficient of component i in liquid phase
δ = difference of virial coefficients, as defined in Equation 3
δ_i = solubility parameter of component i
ϕ_i = volume fraction of component i, referred to unmixed state
$\sigma, \sigma_x, \sigma_y, \sigma_p, \sigma_U$ = standard errors

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Measurements of Gaseous Diffusion Coefficients for Dilute and Moderately Dense Gases by Perturbation Chromatography

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THE DIFFUSION COEFFICIENT, $\mathscr{D}$, has various definitions dependent upon the theoretical assumptions—i.e., kinetic theory, Fick's laws, molecular transport, etc. However, at infinite dilution, the conditions of this study, all the definitions become equal (*35*). Extensive discussions are available in standard references (*12, 23, 37*).

The dispersion of a very small (infinite dilution) amount of solute injected into a steady-state stream of solvent flowing through a tube is comprised of two effects: the dispersion due to molecular diffusion and the dispersion induced by the velocity profile of the steady-state stream combined with any geometrical effects of the system. For the case of laminar flow of a Newtonian fluid in a circular tube of infinite length, the effective diffusion coefficient is defined (*3, 43*) as

$$\mathscr{D}_e = \mathscr{D} + (\bar{u}\, r_t)^2/(48\mathscr{D}) \qquad (1)$$

Diffusivity, $\mathscr{D}_e$, is a function of the variance. The variance, σ^2, defined in Equation 5, is a function of the distribution of the concentration of the injected solute down the tube from the injection point, as determined by the elapsed time and flow rate of the solvent.

There are two roots for $\mathscr{D}$ in Equation 1, only one of which satisfies the condition that the diffusivity is independent of the flow rate. Previous investigators (*18*) stated that up to the critical flow rate the larger (positive) root should be taken; however, careful examination of Figure 1 will show that this is not a satisfactory criterion, because the critical flow is not calculable without additional information. Subscripts 1 and 2 in Figure 1 refer to measurements at two different flow rates. Both roots for the diffusivity and the associated critical velocities are indicated. Either measurements at two different flow rates or a knowledge of the magnitude of $\mathscr{D}$ is required to determine the correct root.

PREVIOUS WORK

The second term of Equation 1 was first measured by Taylor (*43*) in a liquid system. Some gaseous diffusion