Table II. Heats of Solution of Trioxane in Different Solvents

solvent	10^2-(slope)	ΔH_{sol},[a] kJ/mol	$\Delta H_{sol} - \Delta H_{fusion}$ kJ/mol
dichloromethane	7.3	14.0	−0.2
chloroform	7.1	13.6	−0.6
acetone	7.7	14.8	+0.6
benzene	11.8	22.7	+8.5
toluene	13.4	25.8	+11.6
carbon tetrachloride	24.0	46.1	+31.9
methanol	24.0	46.1	+31.9

[a] Heat of solution.

In ideal solution, the solubility of trioxane would be given by (*7*)

$$\log x = (\Delta H/2.303R)(1/T - 1/T_0) \tag{1}$$

where x = mole fraction of trioxane in solution; ΔH = 14.2 kJ/mol, the heat of fusion of trioxane (*8*); T_0 = 334 K, the melting point of trioxane; and R = 8.3144 J/(mol K), the gas constant.

Substituting these values

$$\log x = -742/T + 2.22 \tag{2}$$

The straight line representing eq 2 is shown as curve 1 in Figure 1. It appears that none of these solvents forms a perfectly ideal solution with trioxane. However, dichloromethane, chloroform, and acetone behave almost as ideal solvents; the deviations are negligible. In these three solvents, the heats of solution and the heat of fusion of trioxane would differ very slightly.

In higher normal paraffins like *n*-cetane, trioxane is almost insoluble; in lower paraffins like *n*-hexane, it is sparingly soluble. It is a little more soluble in cycloparaffins (e.g., cyclohexane), whereas the solubility is appreciable in methanol and carbon tetrachloride. Among the studied solvents the solubility increases in the following order: *n*-cetane, *n*-hexane, cyclohexane, water, methanol, carbon tetrachloride, toluene, benzene, acetone, chloroform, and dichloromethane.

Trioxane is highly soluble in the aromatic hydrocarbons benzene and toluene; this is probably due to the similarity of the cyclic structures. The deviations of solubilities from the ideal solution curve 1 show that there are large solute–solvent interactions with these solvents. The slopes of curves 2 and 3 are slightly lower than that of curve 1, while the slopes of curves 4–12 are higher than that of curve 1. The heats of solution in the latter cases would, therefore, be higher than the heat of fusion. These are shown in Table II. This extra heat might possibly be consumed in interaction reactions of an endothermic nature.

It may be mentioned here that the closeness of the solubility parameters indicates the ease of solubility, so it can be inferred that such data for trioxane (11.39) and carbon tetrachloride (8.60) are far more apart than methylene chloride (9.86) and chloroform (9.30). This probably is the reason that carbon tetrachloride is not an ideal solvent.

Literature Cited

(1) Walker, J. F. "Formaldehyde", 3rd ed.; Reinhold: New York, 1964.
(2) Lyobomilow, V. I.; Cherkasskaya, E. L. *J. Appl. Chem. USSR* (*Engl. Transl.*) **1966**, *39*, 683.
(3) Sharan, K. M.; Swarup, J.; Sagu, M. L.; Rawat, D. S. *Chem. Era* **1978**, *14*, 397.
(4) Fischer, K. *Angew. Chem.* **1935**, *48*, 394.
(5) Tanenbaun, M., Bricker, C. E. *Anal. Chem.* **1951**, *23*, 354.
(6) SMA-4 (Celanese method) given in a guide book on formaldehyde by Celanese Chemical Co., New York.
(7) Bares, Jiri; Cerny, Cestmir; Fried, Vojtech; Pick, Jiri. "Collection of Problems in Physical Chemistry"; Pergamon Press: Elmsford, NY, 1961; p 247.
(8) Berling, A. A.; Volfson, S. A.; Olenik, E. F.; Yenikolopyan, N. S. *Polym. Sci. USSR* (*Engl. Transl.*) **1970**, *12*, 506.

Received for review July 30, 1981. Revised manuscript received May 28, 1982. Accepted July 31, 1982.

Simple Method for the Calculation of Heat Capacities of Liquid Mixtures

Amyn S. Teja

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

A simple method based on the corresponding state principle is proposed for the calculation of the heat capacities of liquid mixtures. The method requires a knowledge of the heat capacities of two pure liquids as a function of temperature. For the 16 binary liquid mixtures studied in this work, average absolute deviations (AADs) between experimental and calculated heat capacities were found to be 3.03% when only the pure-component heat capacities were used in the calculations and 1.44% when binary data at a single temperature were used. The method is simple to use and can easily be generalized to multicomponent mixtures.

The heat capacity of liquids and liquid mixtures is important in many heat-transfer calculations (appearing, for example, in the Prandtl number and in enthalpy expressions). Although there are a number of heat capacities in common use, the heat capacity at constant pressure C_p is of greatest interest in heat-transfer work. The heat capacity of the saturated liquid C_{sat} is also of interest, but the difference between C_p and C_{sat} is usually negligible.

There are a number of estimation methods for the heat capacities of pure liquids (*1*). However, very few specific correlations have been suggested for mixtures. Normally, the use of an arithmetic mole or weight fraction average of the pure-component values is recommended (*1*) although this neglects any contribution due to the temperature variation of the enthalpy of mixing. Thus

$$C_{p\,m} = w_1 C_{p\,1} + w_2 C_{p\,2} \tag{1}$$

or

$$C_{p\,m} = x_1 C_{p\,1} + x_2 C_{p\,2} \tag{2}$$

Recently, Jamieson and Cartwright (*2*) assessed the effective-

0021-9568/83/1728-0083$01.50/0

ness of eq 1 and 2 using data for both aqueous and nonaqueous mixtures and concluded that, although the equations were moderately successful in predicting heat capacities of liquid mixtures, improvements were required to meet the higher-accuracy needs of industry. They therefore proposed the following equations for nonaqueous mixtures

$$C_{p\mathrm{m}} = (w_1C_{p1} + w_2C_{p2})(1 + \alpha + \beta) \tag{3}$$

where

$$\alpha = (0.00141|\Delta H_1 - \Delta H_2|^{0.88} - 0.08)w_1w_2 \tag{4}$$

$$\beta = (5 \times 10^{-5})|\Delta H_1 - \Delta H_2| \sin (360w_2) \tag{5}$$

and for aqueous mixtures, they proposed

$$C_{p\mathrm{m}} = (w_1C_{p1} + w_2C_{p2})(1 + Dw_1w_2) \tag{6}$$

where ΔH is the enthalpy of vaporization at the boiling point and D is a constant which was optimized for each system.

Jamieson and Cartwright (*2*) found that for 215 nonaqueous mixtures and a total of 1083 data points, eq 1 gave a maximum error of 12.5%, whereas the use of eq 3 reduced this maximum to 9.1%, with 95% of values lying within ±5%. For 52 aqueous systems and a total of 503 points, eq 1 gave a maximum error of 16.9%, whereas the use of eq 6 reduced this maximum to 10.2%, with 95% of values lying within ±7%.

We have recently proposed a generalized corresponding state principle (GCSP) for the thermodynamic (*3*) and transport (*4*, *5*) properties of liquids and liquid mixtures. The applications of the method to heat capacities at constant pressure are shown below. It is also shown that, under certain assumptions, the GCSP reduces to a simple mole fraction average of the heat capacities of the pure components at the *same reduced temperature*.

Generalized Corresponding State Principle for Heat Capacities

A generalized corresponding state principle (GCSP) for thermodynamic and transport properties has recently been proposed (*3*–*5*). According to the GSCP, a reduced property X of any pure fluid (with critical constants T_c, P_c, V_c, molecular weight M, and acentric factor ω) can be obtained from the known properties of two reference fluids (denoted by superscripts r1 and r2) at the same reduced temperature and pressure as follows:

$$X = X^{(\mathrm{r}1)} + \frac{\omega - \omega^{(\mathrm{r}1)}}{\omega^{(\mathrm{r}2)} - \omega^{(\mathrm{r}1)}}\{X^{(2)} - X^{(\mathrm{r}1)}\} \tag{7}$$

where X is a property such as compressibility, reduced viscosity, or reduced thermal conductivity. We may write an analogous expression for the dimensionless residual heat capacity as follows:

$$\left(\frac{C_p - C_p{}^*}{R}\right) = \left(\frac{C_p - C_p{}^*}{R}\right)^{(\mathrm{r}1)} + \frac{\omega - \omega^{(\mathrm{r}1)}}{\omega^{(\mathrm{r}2)} - \omega^{(\mathrm{r}1)}}\left[\left(\frac{C_p - C_p{}^*}{R}\right)^{(\mathrm{r}2)} - \left(\frac{C_p - C_p{}^*}{R}\right)^{(\mathrm{r}1)}\right] \tag{8}$$

The two reference fluids r1 and r2 are chosen so that they are similar to the pure fluid of interest or, in the case of mixtures, to the key components of interest. If r1 is a simple fluid of zero acentric factor, then eq 8 reduces to the equation proposed by Lee and Kesler (*6*). Equation 8 states that, given the residual heat capacities of two reference fluids as functions of T_R and P_R (or V_R), we may predict the residual heat capacities of any (similar) fluid of interest as a function of T_R and P_R (or V_R).

Equation 8 may be extended to mixtures using, for example, a one-fluid model to replace T_c, V_c, M, and ω of a pure fluid by the pseudocritical properties T_cm, V_cm, M_m, and ω_m of a hypothetical equivalent substance as follows:

$$T_\mathrm{cm}V_\mathrm{cm} = \sum_i\sum_j x_ix_jT_{\mathrm{c}ij}V_{\mathrm{c}ij} \tag{9}$$

$$V_\mathrm{cm} = \sum_i\sum_j x_ix_jV_{\mathrm{c}ij} \tag{10}$$

$$M_\mathrm{m} = \sum_i x_i M_i \tag{11}$$

$$\omega_\mathrm{m} = \sum x_i\omega_i \tag{12}$$

There is some theoretical justification (*7*) for using the van der Waals one-fluid model (eq 9 and 10) for mixtures of nonpolar molecules which do not differ greatly in their sizes. Equation 11, on the other hand, arises naturally from a mass balance. However, eq 12 is completely arbitrary—its only justification being the success with which it has been applied in our previous studies.

The one-fluid model can be used to obtain the properties of mixtures provided values can be assigned to the cross-parameters $T_{\mathrm{c}ij}$ and $V_{\mathrm{c}ij}$ when $i \neq j$. Various mixing rules have been tried in this study including a geometric mean rule for $T_{\mathrm{c}ij}$ and an arithmetic mean rule for $V_{\mathrm{c}ij}$. However, there was little improvement over the mixing rules used in our previous studies, viz.

$$T_{\mathrm{c}ij}V_{\mathrm{c}ij} = \xi_{ij}(T_{\mathrm{c}ii}V_{\mathrm{c}ii}T_{\mathrm{c}jj}V_{\mathrm{c}jj})^{1/2} \tag{13}$$

$$V_{\mathrm{c}ij} = \tfrac{1}{8}(V_{\mathrm{c}ii}{}^{1/3} + V_{\mathrm{c}jj}{}^{1/3})^3 \tag{14}$$

and results for these rules are reported below. In eq 13, ξ_{ij} is a binary interaction coefficient which must be calculated from experimental data. An advantage of using appropriate reference fluids is that a single value of the binary interaction coefficient is often sufficient to characterize each binary mixture. Its value reflects, in part, our inability to represent intermolecular forces by means of eq 9–14.

For the special case when the two pure components of a binary mixture are used as the reference fluids, use of eq 12 leads to the simplification

$$\left(\frac{C_{p\mathrm{m}} - C_{p\mathrm{m}}{}^*}{R}\right) = x_1\left(\frac{C_{p1} - C_{p1}{}^*}{R}\right) + x_2\left(\frac{C_{p2} - C_{p2}{}^*}{R}\right) \tag{15}$$

and, since $C_{p\mathrm{m}}{}^* = x_1C_{p1}{}^* + x_2C_{p2}{}^*$, we may write

$$C_{p\mathrm{m}} = x_1C_{p1} + x_2C_{p2} \tag{16}$$

The difference between eq 2 and eq 16 is that, by convention, eq 2 refers to heat capacities at the same temperature whereas the derivation of eq 16 requires that the heat capacities be evaluated at the reduced temperature and pressure of the mixture. Since pressure has little effect on the heat capacities of liquids, we may write eq 16 as

$$C_{p\mathrm{m}}[T_\mathrm{R}] = x_1C_{p1}[T_\mathrm{R}] + x_2C_{p2}[T_\mathrm{R}] \tag{17}$$

Predictions using eq 17 are shown below. It should be added that, in the general case, the heat capacities are functions of both T_R and P_R.

Reference-Fluid Calculations

The heat capacities of the pure-component reference fluids were correlated by means of the relationship

$$\ln (C_p/R) = A - B/T_\mathrm{R} \tag{18}$$

where A and B are constants and pressure effects have been neglected. The choice of the reference equation is arbitrary. Other, more accurate and/or more complex expressions could equally have been used (a four-constant polynomial in T_R was

Table I. Constants of Eq 18 for the Reference Fluids for Each System

no.	system	A_1	B_1	A_2	B_2
1	$(CH_3)_2CO + CS_2$	3.1506	0.2438	2.5450	0.1616
2	$(CH_3)_2CO + CHCl_3$	3.1506	0.2438	2.9470	0.1830
3	$C_6H_6 + CCl_4$	3.6107	0.4400	3.2316	0.2637
4	C_6H_6 + c-C_6H_{12}	4.4651	1.1085	4.6450	1.0824
5	$C_6H_6 + CH_2ClCH_2Cl$	3.3498	0.2985	3.1038	0.1906
6	$C_6H_6 + C_6H_5CH_3$	3.6760	0.4770	3.5225	0.3094
7	$CCl_4 + CHCl_3$	3.0826	0.1826	3.1808	0.3008
8	c-C_6H_{12} + C_2H_5OH	3.7769	0.4568	4.0193	0.8259
9	*n*-C_7H_{14} + C_2H_5OH	3.8983	0.3336	3.9368	0.7733
10	c-$C_6H_{11}CH_3$ + C_2H_5OH	3.5910	0.2553	3.2197	0.3583
11	$C_6H_5CH_3 + C_2H_5OH$	3.6152	0.3425	4.2453	0.9565
12	*n*-C_7H_{14} + *i*-C_3H_7OH	3.5353	0.1375	3.6269	0.4278
13	*n*-C_5H_{12} + C_3H_8	3.6524	0.4241	4.5219	1.5152
14	$CH_3OH + H_2O$	2.8410	0.3315	2.1492	−0.0258
15	*n*-C_3H_7OH + H_2O	3.6893	0.4673	2.1473	−0.0268
16	$(CH_2OH)_2 + H_2O$	3.5212	0.2988	2.2178	0.0065

Table II. Summary of Results

system no.[a]	no. of data points	temp range, K	AAD, %		ξ_{opt}
			$\xi_{12} = 1.0$	$\xi_{12} = \xi_{opt}$	
1	18	293.2-313.2	2.17	0.45	0.781
2	24	293.2-323.2	2.48	0.58	0.737
3	25	293.2-333.2	0.98	0.85	0.958
4	9	453.2-473.2	0.42	0.05	1.019
5	36	293.2-343.2	0.57	0.56	1.007
6	35	293.2-333.2	0.78	0.62	0.976
7	20	293.2-323.2	0.66	0.46	1.046
8	30	303.2-343.2	5.06	2.63	0.803
9	36	293.2-343.2	3.53	2.09	0.836
10	35	223.2-303.2	2.38	1.43	0.886
11	37	303.2-346.2	8.14	2.27	0.711
12	35	205.4-304.7	3.10	1.64	0.839
13	18	294.2-327.2	3.06	0.79	0.911
14	9	275.7-313.2	5.75	3.73	0.625
15	9	275.7-313.2	9.73	6.33	0.413
16	9	293.2-351.5	1.35	1.25	0.920
	385		3.03	1.44	

[a] The system no. corresponds to that used in Table I.

also used but did not yield significantly better results). The choice of the reference substances is also arbitrary. However, the use of the simple relationship given by eq 17 requires that the two pure components be used as the reference substances for each binary mixture. Constants *A* and *B* for various reference substances are given in Table I and are applicable in the temperature range given in Table II. In the general case, the actual heat capacities of the reference fluids at the same reduced conditions may be used. The data were taken from the compilation of Jamieson and Cartwright (*2*).

It should be added that eq 8 does not require that the pure components be used as the reference substances. In fact, the expression may be used to predict the (unknown) heat capacities of the pure components given the (known) heat capacities of two (similar) fluids at the same reduced conditions.

Results

Sixteen binary systems and a total of 385 data points were examined using eq 17. Only those systems where a single investigator had measured the heat capacities at three or more different temperatures were selected for study. The systems included nonpolar mixtures, mixtures containing polar molecules, and aqueous mixtures. The results are shown in Table II. The experimental data used in the comparisons were taken from the compilation of Jamieson and Cartwright. Table II shows average absolute deviations between experimental and calculated heat capacities both with the binary interaction coefficient ξ_{12} set equal to 1.0 (i.e., using pure-component data only) and with the binary interaction coefficient optimized by using the binary mixture data at the lowest temperature. To a good approximation, ξ_{12} was found to be independent of temperature and composition. Thus, the use of the same value of ξ_{12} over a 100 °C range of temperature in some cases did not lead to any significant decrease in accuracy of the predictions. The average absolute deviation between calculation and experiment was found to be 3.03% with all $\xi_{12} = 1.0$. The average deviations could be reduced to 1.44% if a single binary interaction coefficient (independent of temperature and composition) was included in the calculations. As expected, the method works best for nonpolar mixtures and is least accurate for aqueous mixtures. The larger than average deviations for aqueous systems are in part due to the inadequacy of the reference-fluid equation (eq 18) for water and in part due to the fact that water is strongly associated in solution. Nevertheless, the method compares favorably with available methods for all systems. An additional advantage is that eq 17 can easily be generalized to multicomponent systems and requires, at most, only binary information at a single temperature for the prediction of heat capacities of multicomponent mixtures.

Glossary

A, B	reference-fluid-equation constants
C	heat capacity
D	constant in eq 6
H	enthalpy
M	molecular weight
R	gas constant
T	temperature
V	molar volume
w	weight fraction
x	mole fraction

Greek Letters

α, β	constants in eq 3
ω	acentric factor
ξ	binary interaction coefficient

Subscripts

c	critical value
i, j	component *i*, *j*
m	mixture value
p	constant pressure
R	reduced value, e.g., $T_R = T/T_c$

Literature Cited

(1) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977, Chapter 5.

(2) Jamieson, D. T.; Cartwright, G. "Properties of Binary Liquid Mixtures: Heat Capacity", NEL Report No. 648; National Engineering Laboratory: East Kilbride, U.K.; Jan 1978.

(3) Teja, A. S.; Sandler, S. I.; Patel, N. C. *Chem. Eng. J.* **1981**, *21*, 21-8.

(4) Teja, A. S.; Rice, P. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 77-81.

(5) Teja, A. S.; Rice, P. *Chem. Eng. Sci.* **1981**, *36*, 417-22.

(6) Lee, B. I.; Kesler, M. G. *AIChE J.* **1975**, *21*, 510-27.

(7) Leland, T. W.; Rowlinson, J. S.; Sather, G. A. *Trans. Faraday Soc.* **1968**, *64*, 1447-58.

Received for review February 16, 1982. Accepted August 26, 1982. Part of this work was carried out under grant no. CPE 8104201 from the National Science Foundation.