m = integral saturation limit defined by $m \leq v/\beta$
p_A, p_B = partial pressure of component A or B
q_o = limiting heat of sorption
v = volume of cavity of 5A sieve (776Å^3)
X_A, X_B = mole fraction of A (or B) in adsorbed phase
Y_A, Y_B = mole fraction of A (or B) in vapor phase
β = effective molecular volume of sorbate (Å^3/molecule)

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Correlation of Liquid Heat Capacities with a Four-Parameter Corresponding States Method

A four-parameter corresponding states method with the critical temperature, the critical pressure, the radius of gyration, and a fourth parameter developed from the Frost-Kalkwarf vapor pressure equation has been applied to the correlation of liquid heat capacities. An equation has been developed to predict the temperature dependence of the saturated liquid heat capacities of both normal and polar fluids over the liquid range from a reduced temperature of 0.35 to 0.96. The accuracy of the predictions obtained is superior to that of the presently available generalized correlation for polar liquids. The new correlation may be easily adopted for computer use.

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SCOPE

Liquid heat capacity is an important property in design calculations. Although experimental data are available for many compounds, frequently these data are restricted to a small temperature region, and in numerous other cases no data can be found. Therefore one must often rely on some predictive method to estimate the liquid heat capacity. Furthermore, in many computer applications generalized analytical methods of predicting physical properties are needed, since it is not practical to store specific data for all properties of all the compounds that may be of interest.

Although a number of methods have been published for the estimation of liquid heat capacities, most of them are not general enough in terms of the compounds to which they apply, or are not in an analytical form, or have a limited temperature range. In fact only one other truly generalized correlation that is applicable to polar compounds has been found. The purpose of the work described in this paper was to provide a completely generalized correlation for heat capacity covering as wide a liquid range as possible.

The most valuable generalized methods of predicting properties are based on the theorem of corresponding states. In its simplest, two-parameter form, this approach is applicable only to small, unassociated molecules. In order for polar molecules to be incorporated into this type of approach, four parameters are generally required. Passut and Danner (1974) have published a new four-parameter corresponding states method. This generalized approach has been applied to vapor pressure prediction (Passut and Danner, 1974) and to second virial coefficients (Passut, 1973). In this paper the heat capacity of polar and nonpolar liquids have been so correlated.

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CONCLUSIONS AND SIGNIFICANCE

The four-parameter corresponding states method of Passut and Danner (1974) has been successfully applied to the prediction of liquid heat capacities of nonpolar and associated compounds. From Equation (16) the molal heat capacity can be predicted from the critical temperature, the radius of gyration, and the association factor. The latter parameter can be calculated from the normal boiling point and the critical pressure [Equation (3)]. A tabulation of the four parameters for 250 compounds has been published (Passut and Danner, 1974).

The only other generalized correlation available for the heat capacity of polar liquids was published by Yuan and Stiel (1970). The present method gives better accuracy, covers a wider temperature range, and is more easily adopted for computer use than the Yuan and Stiel correlation.

The four-parameter corresponding states method involving the radius of gyration $\overline{R}$ and the association factor κ has now been successfully applied to predicting the vapor pressures, second virial coefficients, and liquid heat capacities of polar as well as of nonpolar compounds. This approach should also be useful in correlating other thermodynamic and physical properties.

THE FOUR-PARAMETER CORRESPONDING STATES CORRELATION

Passut and Danner (1974) have published a new four-parameter corresponding states correlation. This method uses the critical temperature, the critical pressure, the geometric mean radius of gyration, and a fourth parameter defined in terms of the vapor pressure behavior. Molecular size and shape effects are represented by the Thompson (1966) geometric mean radius of gyration defined for planer molecules as

$$\overline{R} = \sqrt{(AB)^{1/2}/MW} \tag{1}$$

and for three-dimensional molecules

$$\overline{R} = \sqrt{2\pi(ABC)^{1/3}/MW} \tag{2}$$

The fourth parameter or association factor is defined in terms of the deviation obtained by the Frost-Kalkwarf (1953) vapor pressure equation when an associated compound is compared to a normal paraffin hydrocarbon of the same radius of gyration at the normal boiling point. The association factor κ is calculated as follows:

$$\kappa = \frac{\ln Y - B_n(1-X) - C_n \ln X - 0.4218(YX^2-1)}{(1 - X + \ln X)} \tag{3}$$

$$X = \frac{T_c}{T_b} \tag{4}$$

$$Y = \frac{P_{\text{atm}}}{P_c} \tag{5}$$

$$B_n = 4.6773 + 1.8324\overline{R} - 0.03501\overline{R}^2 \tag{6}$$

$$C_n = 0.7751\, B_n - 2.6354 \tag{7}$$

Radii of gyration and association factors for 250 different compounds have been tabulated by Passut and Danner (1974). In this study the heat capacity of liquids is correlated in terms of the above parameters.

DEVELOPMENT OF THE CORRELATION

An extensive literature search was made to locate liquid heat capacity data. From the total 2 279 data points collected, 1 805 data points for 91 polar and nonpolar compounds were useful. A detailed listing of the data sources and the reduced temperature ranges for the 91 compounds is given in the supplement to this paper.[*] Many of the original 2 279 points had to be eliminated because either the critical properties or the ideal gas heat capacity data were not available for the relevant compound.

Some of the literature data are for the heat capacity at constant pressure, and others are for the heat capacity under saturated conditions. These two properties are related by

$$C_P - C_{\text{sat}} = T\left(\frac{\delta V}{\delta T}\right)_P \left(\frac{\delta P}{\delta T}\right)_{\text{sat}} \tag{8}$$

At low temperatures $(\delta P/\delta T)_{\text{sat}}$ is negligible, and the two heat capacities may be equated. At high temperature, where the vapor pressure is large, however, the difference becomes significant. Most of the literature values are for the low temperature region; for high temperatures the data are generally reported as C_{sat}. Heat capacity at saturation is the property correlated in this work.

The liquid heat capacity may be described in terms of the P-V-T behavior by

$$C_P - C_P{}^o = -T\int_0^P \left(\frac{\delta^2 V}{\delta T^2}\right)_P dP \tag{9}$$

where $C_P{}^o$ is the heat capacity of the ideal gas. The combination of this equation with Equation (8) yields an analogous form in terms of the saturated liquid heat capacity:

$$C_{\text{sat}} - C_P{}^o = -T\int_0^P \left(\frac{\delta^2 V}{\delta T^2}\right) dP - T\left(\frac{\delta V}{\delta T}\right)_P \left(\frac{\delta P}{\delta T}\right)_{\text{sat}} \tag{10}$$

The form of these equations suggests that the property which one might best correlate is the heat capacity deviation from ideal gas behavior $C_{\text{sat}} - C_P{}^o$.

Since the four-parameter corresponding states method of Passut and Danner is based on the behavior of the normal paraffins, the following correlational approach was adopted:

$$C_{\text{sat}} - C_P{}^o = (C_{\text{sat}} - C_P{}^o)_n + (C_{\text{sat}} - C_P{}^o)_a \tag{11}$$

$$(C_{\text{sat}} - C_P{}^o)_n = f(T_r, \overline{R}) \tag{12}$$

$$(C_{\text{sat}} - C_P{}^o)_a = f(T_r, \kappa) \tag{13}$$

The $(C_{\text{sat}} - C_P{}^o)_n$ term is the correlation for normal paraffin hydrocarbons and is used to account for the gross size-shape effects. The $(C_{\text{sat}} - C_P{}^o)_a$ is the correction for association effects caused by polarity, weak hydrogen bonding, etc. The first task, therefore, was to correlate the heat capacity deviation for the normal paraffins. For the normal paraffin hydrocarbons, 414 reliable data points are available for the compounds methane through n-octadecane.

Supplementary material has been deposited as Document No. 02824 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N. Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

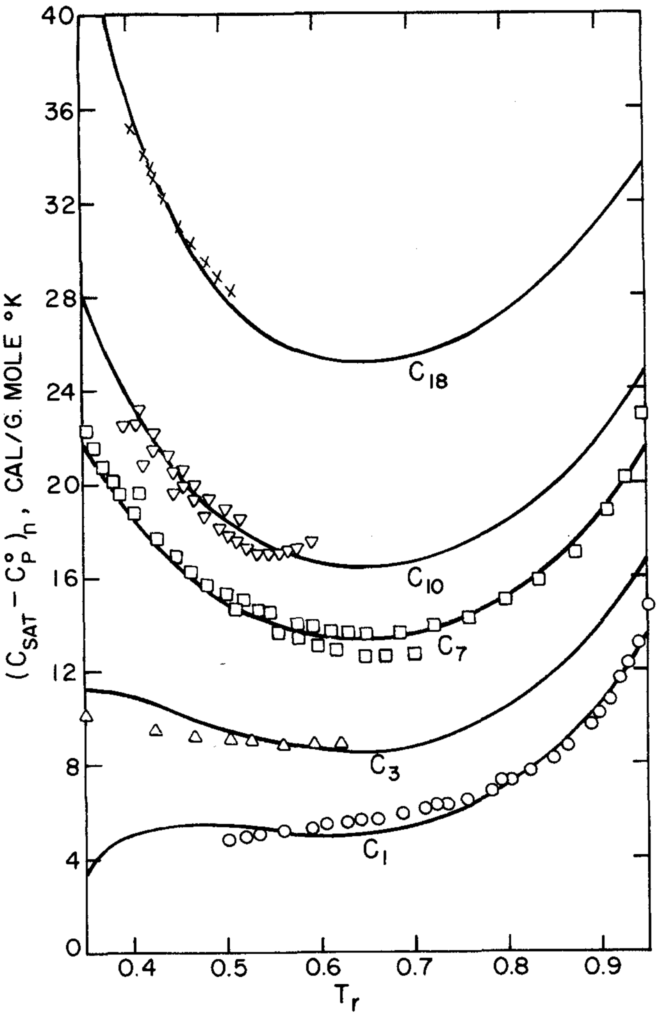

Fig. 1. Effect of reduced temperature on the molal heat capacity deviation for some normal paraffin liquids. Data points are experimental results; solid lines are predictions of Equation (14).

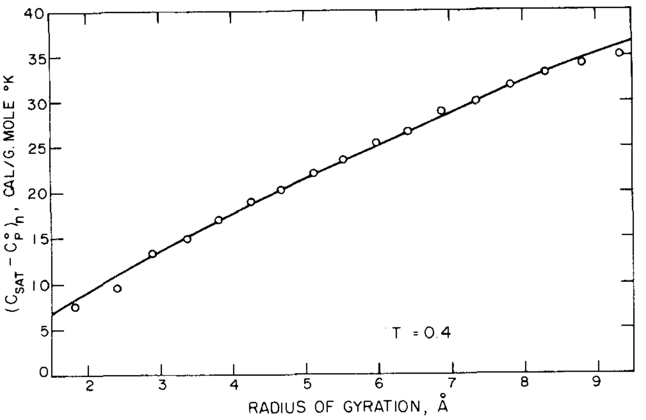

Fig. 2. Variation of the molal heat capacity deviation of normal paraffin liquids with radius of gyration. Data points are experimental results; solid line is prediction of Equation (14).

The experimental data points on Figure 1 show the relationship between the heat capacity deviation $(C_{sat} - C_P^o)_n$ and reduced temperature for several of the normal paraffins. Pronounced increases in the heat capacity are observed in both the low temperature region near the normal boiling point and in the high temperature region near the critical temperature. These curves suggest a mathematical form with high-order terms in reduced temperature to account for the high temperature region and high-order reciprocal terms for the low temperature region.

Table 1. Coefficients for Equations (14) to (16)

(Heat Capacities in cal/g. mole °K)

A_1	10.1273	B_1	0.31446
A_2	−15.3546	B_2	2.5346
A_3	3.2008	B_3	−2.0242
A_4	19.7302	B_4	−0.07055
A_5	−0.8949	B_5	0.07264
A_6	−0.01489		
A_7	0.2241		
A_8	−0.04342		

The experimental data points in Figure 2 show the relationship between the heat capacity deviation and the radius of gyration at a constant reduced temperature of 0.4 for the normal paraffins. The gently sloping line suggests an equation with low-order terms in radius of gyration. Since the heat capacity at saturation is being correlated, the system has only one degree of freedom, and no terms in reduced pressure are required.

A number of functional forms were examined to describe these curves. A statistical computer program was used to identify the significant terms (see Draper and Smith, 1966). In this method the correlational matrix containing all variables is inverted by using the Gauss-Jordon method of diagonal pivoting. The initial regression coefficients are calculated from this matrix after nonindependent variables have been eliminated. Variables are then deleted one at a time from the equation until only one remains. The variable chosen for deletion is the one that has, in absolute value, the smallest partial correlation coefficient with the dependent variable. From this analysis the final form of the equation was selected as follows:

$$(C_{sat} - C_P^o)_n = A_1 + T_r(A_2 + A_3\overline{R}) + T_r^5(A_4 + A_5\overline{R}) + A_6\overline{R}^2/T_r^2 + A_7\overline{R}/T_r^3 + A_8/T_r^5 \quad (14)$$

By using the numerical coefficients from Table 1, the heat capacity deviations for methane through *n*-octadecane were correlated with an overall average error of 1.0% and an average bias of 0.01% for the reduced temperature region between 0.35 and 0.96. (Detailed results for this are given in Table A.2 of the supplement.)* The predictions of Equation (14) are plotted as the solid lines on Figures 1 and 2.

The next step was to determine the correction term for associated compounds $(C_{sat} - C_P^o)_a$. The experimental data points in Figure 3 show the association correction

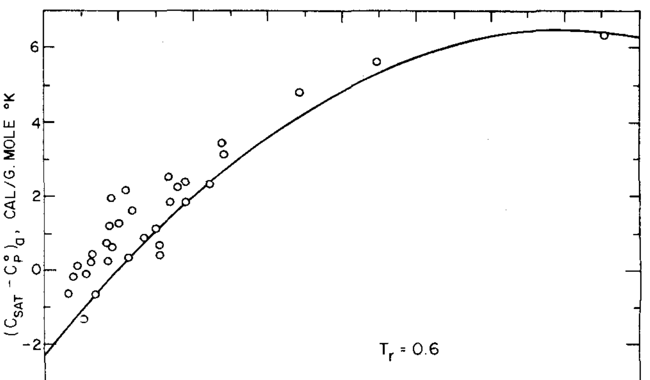

Fig. 3. Association correction for molal heat capacity deviation. Data points are experimental results; solid line is prediction of Equation (15).

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* See footnote on page 760.

TABLE 2. COMPARISON OF EQUATION

Reduced temperature ranges:
Nonpolar compounds: 0.40 to 0.96
Polar compounds: 0.44 to 0.94

	No. of data points	*Tr* range	Yuan and Stiel			Equation (16)		
			Avg. % dev.*	Max. dev.	*Tr* at Max. dev.	Avg. % dev.*	Max. dev.	*Tr* at Max. dev.
Normal fluids								
N-alkanes								
Methane	61	0.50-0.96	2.3	−5.7	0.40	2.7	−10.1	0.96
Ethane	41	0.40-0.96	2.7	−7.3	0.96	2.4	4.5	0.91
Propane	7	0.42-0.62	0.6	2.9	0.96	2.0	5.6	0.42
n-butane	13	0.40-0.62	0.7	1.2	0.47	1.5	−2.2	0.46
n-pentane	35	0.41-0.64	0.7	−2.3	0.41	0.4	2.0	0.61
n-hexane	32	0.41-0.72	0.6	−2.5	0.41	0.3	1.5	0.58
n-heptane	69	0.40-0.94	0.7	−2.3	0.40	0.7	−2.0	0.94
n-octane	34	0.40-0.64	1.0	2.4	0.52	0.6	1.4	0.48
n-nonane	24	0.41-0.53	1.2	2.2	0.48	0.5	1.1	0.46
n-decane	36	0.41-0.59	1.3	2.9	0.41	0.6	2.6	0.41
n-undecane	10	0.41-0.46	0.9	1.7	0.47	0.2	−0.4	0.41
n-dodecane	10	0.41-0.48	0.8	1.8	0.45	0.4	1.0	0.45
n-tridecane	5	0.40-0.45	0.9	1.3	0.44	0.2	−0.4	0.40
n-tetradecane	4	0.41-0.44	1.4	1.7	0.44	0.1	−0.2	0.44
n-pentadecane	4	0.40-0.44	0.8	1.2	0.44	0.1	−0.2	0.40
n-hexadecane	6	0.40-0.44	0.7	1.0	0.43	0.2	−0.4	0.42
n-heptadecane	11	0.41-0.52	0.8	1.0	0.44	0.3	−0.5	0.41
n-octadecane	12	0.40-0.51	0.1	−0.3	0.45	0.3	0.7	0.41
Compound class average	414		1.2			1.0		
Isomeric paraffins								
2-methylpropane	18	0.40-0.93	2.6	−7.1	0.93	2.7	−7.0	0.93
2-methylbutane	69	0.40-0.65	1.7	−3.9	0.40	2.2	−3.1	0.57
2,2-dimethylpropane	7	0.59-0.64	1.5	−3.9	0.64	3.8	−6.2	0.64
2-methylpentane	3	0.41-0.45	5.0	−5.9	0.41	3.8	−3.8	0.45
3-methylpentane	14	0.41-0.65	1.6	1.8	0.55	0.6	2.3	0.41
2,2-dimethylbutane	22	0.40-0.61	2.1	−4.2	0.40	2.1	−3.2	0.57
2,3-dimethylbutane	42	0.40-0.61	1.2	−2.7	0.40	1.4	−2.4	0.58
2-methylhexane	16	0.41-0.55	2.0	2.6	0.52	1.2	2.8	0.41
2,2,3-trimethylbutane	12	0.47-0.60	0.4	1.6	0.55	0.8	−1.6	0.58
2-methylheptane	18	0.40-0.66	1.8	2.3	0.51	0.9	1.9	0.40
Compound class average	221		1.7			1.8		
Olefins, diolefins, alkynes								
Propene	14	0.42-0.61	6.0	−9.2	0.42	6.6	−7.5	0.42
1-butene	7	0.42-0.60	4.5	−7.0	0.42	4.6	−4.8	0.48
cis-2-butene	31	0.41-0.84	7.5	−13.1	0.41	8.2	−11.7	0.41
trans-2-butene	16	0.41-0.63	0.7	2.5	0.41	0.7	1.3	0.63
2-methylpropene	6	0.43-0.59	1.7	−2.5	0.43	1.5	−2.5	0.59
1-pentene	10	0.42-0.63	0.5	−1.0	0.42	2.0	2.2	0.63
cis-2-pentene	11	0.41-0.62	4.1	−7.5	0.41	4.7	−5.4	0.41
trans-2-pentene	11	0.41-0.63	1.6	−2.2	0.41	2.1	−3.1	0.61
2-methyl-1-butene	11	0.40-0.63	1.2	−3.7	0.40	1.5	−1.8	0.58
2-methyl-2-butene	19	0.41-0.64	1.4	2.6	0.61	0.6	1.8	0.61
1-hexene	11	0.42-0.62	0.4	0.7	0.48	0.9	−1.6	0.50
1-heptene	15	0.41-0.56	2.4	3.1	0.43	1.5	2.9	0.40
1-octene	9	0.41-0.55	1.4	1.7	0.44	0.7	1.7	0.41
1-decene	12	0.41-0.59	2.2	3.2	0.42	1.2	2.7	0.41
1-undecene	6	0.41-0.49	2.2	2.4	0.42	1.2	2.0	0.41
1-dodecene	5	0.41-0.47	2.0	2.2	0.43	1.0	1.6	0.41
1-hexadecene	2	0.42-0.43	1.7	1.7	0.43	0.6	0.7	0.42
1,2-butadiene	12	0.41-0.65	12.4	16.0	0.41	0.9	1.6	0.65
2,3-pentadiene	12	0.41-0.62	23.2	−31.1	0.41	3.2	−3.6	0.59
1-butyne	8	0.40-0.58	22.6	−27.2	0.40	15.1	−18.7	0.58
Compound class average	228		5.2			3.3		
Cyclohexanes								
Cyclohexane	9	0.50-0.54	2.8	−4.0	0.51	4.0	−5.1	0.53
Methylcyclohexane	11	0.41-0.51	2.4	−5.4	0.40	1.1	−1.5	0.50
1,1-dimethylcyclohexane	7	0.41-0.51	3.8	−5.9	0.41	2.8	−3.6	0.51
1,cis-2-dimethylcyclohexane	6	0.42-0.49	2.9	−4.5	0.42	1.6	−2.0	0.49
1,trans-2-dimethylcyclohexane	6	0.41-0.50	1.0	−2.5	0.41	0.6	1.2	0.41

			Yuan & Stiel			Equation (16)		
	No. of data Points	*Tr* range	Avg. % dev.*	Max. dev.	*Tr* at Max. dev.	Avg. % dev.*	Max. dev.	*Tr* at Max. dev.
1,cis-3-dimethylcyclohexane	7	0.41-0.50	3.5	−5.7	0.41	1.0	−1.7	0.50
1,trans-3-dimethylcyclohexane	7	0.40-0.50	7.6	−10.6	0.40	2.6	−3.4	0.50
1,cis-4-dimethylcyclohexane	6	0.42-0.51	3.8	−5.7	0.42	2.6	−3.2	0.51
1,trans-4-dimethylcyclohexane	7	0.41-0.51	2.8	−5.3	0.41	1.8	−2.2	0.51
Compound class average	66		3.4			2.0		
Benzenes								
Benzene	18	0.50-0.60	5.6	−6.7	0.52	6.6	−7.3	0.51
Methylbenzene	32	0.40-0.62	1.1	−5.3	0.53	1.5	−6.1	0.53
Ethylbenzene	17	0.41-0.49	1.4	3.2	0.49	1.3	2.6	0.41
1,2-dimethylbenzene	7	0.42-0.50	7.9	9.5	0.42	6.1	8.4	0.42
1,3-dimethylbenzene	11	0.41-0.49	2.2	3.2	0.48	1.2	2.3	0.41
1,4-dimethylbenzene	10	0.47-0.58	2.4	5.2	0.49	1.9	3.6	0.49
Isopropylbenzene	13	0.48-0.58	2.0	4.1	0.48	1.3	2.7	0.48
1,2,3-trimethylbenzene	4	0.41-0.45	7.8	8.6	0.41	4.9	6.0	0.41
1,2,4-trimethylbenzene	20	0.41-0.58	7.0	10.2	0.45	4.6	7.4	0.45
1,3,5-trimethylbenzene	16	0.46-0.59	5.8	11.6	0.46	4.5	9.8	0.46
Compound class average	148		3.4			3.1		
Miscellaneous								
Nitrogen	14	0.63-0.93	2.9	−4.7	0.82	6.5	5.7	0.93
Carbon dioxide	7	0.72-0.92	3.2	4.9	0.72	12.2	12.3	0.85
Compound class average	21		3.0			8.4		
Average for all normal fluids	1098		2.6			2.1		
Polar fluids								
Alcohols								
Methanol	27	0.46-0.75	14.8	21.4	0.48	16.8	26.9	0.63
Ethanol	34	0.46-0.74	3.1	−8.7	0.67	5.7	9.6	0.74
Propan-1-ol	32	0.45-0.67	4.4	7.5	0.46	3.1	5.1	0.47
Propan-2-ol	20	0.53-0.93	15.4	−21.8	0.59	7.0	−12.5	0.69
Butan-1-ol	8	0.45-0.52	30.9	−35.1	0.45	2.5	5.1	0.45
Butan-2-ol	42	0.44-0.64	5.2	−7.3	0.56	8.0	−18.1	0.64
Compound class average	163		8.7			7.7		
Ketones								
Propan-2-one	6	0.45-0.58	3.1	−3.7	0.54	0.6	1.6	0.58
Butan-2-one	17	0.45-0.60	7.9	−9.9	0.45	1.2	−2.1	0.45
Pentan-2-one	30	0.45-0.65	3.1	−3.4	0.45	2.3	−3.3	0.45
Pentan-3-one	20	0.44-0.57	14.7	32.8	0.57	2.4	−2.9	0.44
3-methylbutan-2-one	18	0.45-0.59	13.5	−19.3	0.45	2.0	−3.2	0.52
Compound class average	91		8.6			1.9		
Halogenated compounds								
Carbon tetrachloride	6	0.46-0.55	2.5	2.9	0.46	3.0	−5.0	0.55
Chloroform	8	0.45-0.56	12.5	14.6	0.46	1.7	−3.7	0.57
Ethyl chloride	15	0.45-0.62	6.4	−10.8	0.45	2.5	−3.4	0.45
Methyl chloride	9	0.46-0.60	13.0	−20.3	0.46	6.9	−9.9	0.46
Hydrogen chloride	4	0.46-0.58	47.9	−70.6	0.47	6.6	−11.9	0.47
Methyl iodide	8	0.46-0.57	4.1	−9.7	0.46	10.3	−13.2	0.46
Compound class average	50		11.1			4.8		
Miscellaneous								
Diethylether	41	0.44-0.64	4.5	−5.5	0.61	4.4	−5.2	0.55
Ethanethiol	13	0.45-0.63	6.6	7.5	0.51	2.7	−4.4	0.45
Ammonia	14	0.48-0.79	3.0	9.8	0.48	5.9	12.1	0.79
Dimethyl sulfide	7	0.46-0.57	6.5	7.0	0.51	3.5	−3.7	0.45
Sulfur dioxide	15	0.47-0.75	11.0	15.0	0.47	6.3	−10.1	0.47
Compound class average	90		5.9			4.7		
Average for all polar fluids	394		8.3			5.3		
Average for all fluids	1492		4.1			3.0		

* Avg. % dev. $= \frac{1}{n} \Sigma \left| \frac{(Cp)_{\text{calc}} - (Cp)_{\text{exp}}}{(Cp)_{\text{exp}}} (100) \right|$

$(C_{sat} - C_P{}^o)_{actual} - (C_{sat} - C_P{}^o)_n$ required at one reduced temperature. The scatter in these points reflects experimental errors as well as inaccuracies in isolating the polar effects for the various kinds of molecules. There is, however, a clear trend to this association effect with the association factor, a trend which suggests a mathematical form with low-order terms in the association factor. By using the same method as for the normal paraffin equation, a number of functional forms were tested for describing the correction term. The final form selected was

$$(C_{sat} - C_P{}^o)_a = \kappa(B_1 + B_2 T_r{}^2 + B_3 T_r{}^5) + \kappa^2(B_4 + B_5 T_r{}^2) \quad (15)$$

The numerical constants are listed in Table 1. The line shown on Figure 3 is a plot of the above equation. This line is not expected to be a best fit line for the data shown in Figure 3 since Equation (15) applies to all reduced temperatures between 0.35 and 0.96 rather than to just the reduced temperature of 0.6. Combination of Equations (11), (14), and (15) then gives the final result:

$$(C_{sat} - C_P{}^o) = A_1 + T_r(A_2 + A_3\overline{R}) + T_r{}^5(A_4 + A_5\overline{R}) + A_6\overline{R}^2/T_r{}^2 + A_7\overline{R}/T_r{}^3 + A_8/T_r{}^5 + \kappa(B_1 + B_2T_r{}^2 + B_3T_r{}^5) + \kappa^2(B_4 + B_5T_r{}^2) \quad (16)$$

This equation was evaluated with 1 805 data points for 91 compounds by using all available data in the reduced temperature range from 0.35 to 0.96. The average overall error was 3.17% with an average bias of −0.77%. A detailed summary of these results is given in Table A.2 of the supplement to this paper.* Results for a slightly smaller reduced temperature range (selected for comparison with another method) are given in Table 2. Examination of these tables reveals that there are no experimental data available for larger molecules ($\overline{R} > 3.0$) at high reduced temperatures ($T_r > 0.7$). Thus no estimate of the accuracy of the method can be made for this region.

COMPARISON WITH METHOD OF YUAN AND STIEL

A search of the literature uncovered only one other truly generalized method for predicting the heat capacity of both polar and nonpolar liquids. A correlation based on the four-parameter corresponding states approach of Halm and Stiel (1967) has been published by Yuan and Stiel (1970). These authors have developed an equation for nonpolar molecules of the form

$$(C_{sat} - C_P{}^o) = \Delta C_{sat}^{(0)} + \omega \Delta C_{sat}^{(1)} \quad (17)$$

Equations for $\Delta C_{sat}^{(0)}$ and $\Delta C_{sat}^{(1)}$ were developed at constant reduced temperature by a regression analysis of the data for 21 nonpolar compounds.

For polar compounds the correction term, χ, is used to account for effects which are not correlated by the acentric factor:

$$(C_{sat} - C_P{}^o) = \Delta C_{sat}^{(0)} + \omega\Delta C_{sat}^{(1)} + \chi\Delta C_{sat}^{(2)} + \chi^2\Delta C_{sat}^{(3)} + \omega^2\Delta C_{sat}^{(4)} + \omega\chi\Delta C_{sat}^{(5)} \quad (18)$$

In this case a cross product term of the third and fourth parameters is required. Values for the $\Delta C_{sat}^{(i)}$ terms were determined for a reduced temperature range of 0.44 to 0.94.

The third and fourth parameters of Yuan and Stiel are defined in terms of the vapor pressure at reduced temperatures of 0.7 and 0.6. Passut (1973) has determined values of these parameters by fitting the Frost-Kalkwarf vapor pressure equation to the available data for each compound. These are the values that have been used in this analysis. In some cases these values differ from those reported by Yuan and Stiel.

The Yuan and Stiel correlation and Equation (16) were compared for the data set applicable to Yuan and Stiel, consisting of 1 492 data points. Critical temperatures, radii of gyration, and association factors were taken from Passut and Danner (1974). Ideal gas heat capacities were calculated by using the coefficients of Passut and Danner (1972) or Thinh et al. (1971). The comparison is shown for each compound in Table 2. For the entire data set, the proposed method gave an average error of 3.0% compared to 4.1% for the method of Yuan and Stiel. For the normal fluids, Equation (16) yielded an average error of 2.1% compared to 2.5% for Yuan and Stiel. For the polar fluids the proposed method was 3% better on the average (5.3 vs. 8.3%).

NOTATION

$A_1 \ldots A_8$ = constants for Equations (14) and (16) as listed in Table 1
AB = product of the two principal moments of inertia
ABC = product of the three principal moments of inertia
$B_1 \ldots B_5$ = constants for Equations (15) and (16) as listed in Table 1
B_n, C_n = coefficients of the Frost-Kalkwarf equation for normal paraffins, see Equations (6) and (7)
C_P = molal heat capacity at constant pressure
$C_P{}^o$ = ideal gas molar heat capacity at constant pressure
C_{sat} = molar heat capacity at saturated conditions
MW = molecular weight
P_{atm} = standard atmospheric pressure
P_c = critical pressure
$\overline{R}$ = radius of gyration, Å
T = temperature
T_b = normal boiling point temperature
T_c = critical temperature
T_r = reduced temperature
V = molar volume
X = reciprocal of reduced boiling point temperature, see Equation (4)
Y = reduced pressure at standard atmospheric pressure
κ = association factor defined by Equation (3)
χ = polarity factor of Halm and Stiel (1967)
ω = acentric factor

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Particle Attrition in Shear Flow of Concentrated Slurries

A first order kinetic formulation of brittle particle attrition is suggested. Experimental data show that it applies to coal particle attrition in Couette flow. These data reveal that particles are reduced by loss of surface protuberances, which are much smaller than their mean diameter. It is also shown how changes of the size spectrum, due to shearing, can be predicted.

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SCOPE

Concentrated slurries made of ~1 to ~10^3 μ particles are currently studied in connection with long distance pipeline transportation of commodities such as coal and iron ore, usually with water or oil as the liquid carrier. Particle attrition can affect the slurry rheological properties and can present difficulties in the solid/liquid separation at the pipeline terminal.

Attrition is caused by particle-particle collisions and particle impingement on solid boundaries. A statistical description of this process, involving a distribution of particle sizes and associated kinematic properties, although very desirable, is almost impossible at present. A more direct and fruitful approach is to study attrition in a well-defined flow field and to relate observed changes of an initial particle size distribution to some characteristic bulk flow properties, for example, the shear rate. This approach requires an appropriate mathematical formulation of the attrition process.

The problem of particle attrition in slurry flow has not been adequately studied. Only a few exploratory studies on this subject have been published so far (for example, Worster and Denny, 1955; Bjorklund and Dygert, 1968). In the case of coal, for instance, there is essentially no published information about the rate at which small particles degrade in slurry flow, or about the size distribution of the resulting fragments. This lack of information is partly due to difficulties encountered in doing meaningful laboratory experiments, especially with settling suspensions.

The main objective of this study is to suggest a kinetic type of formulation of particle diminution in suspension flow which can serve as the framework for interpreting experimental data and for modeling particle attrition in slurry transportation and processing systems. Another objective is to develop techniques for accurate measurement of attrition and to demonstrate how changes of a wide particle size distribution (PSD) can be predicted (as a function of initial PSD, flow conditions, and time) on the basis of a few experimentally determined parameters.

CONCLUSIONS AND SIGNIFICANCE

Size diminution of brittle, irregular in shape, particles due to slurry flow is described as a rate process, similar to a first-order chemical reaction. This formulation involves two sets of parameters, that is, the coefficients k_i representing the rate of material loss of a particular size fraction, of mean diameter d_i, and the parameters $b_{i,j}$ describing the manner in which the attrition products from fraction i are distributed into various smaller size fractions j. At present, these parameters can only be determined experimentally. The above formulation is fairly general and can provide the basis for attrition studies in any slurry flow field. It is often used in grinding studies, as discussed in an excellent review paper by Austin (1971).

Experiments have been performed with bituminous coal particles of two very narrow size fractions (d = 210 to 250 μ and 150 to 210 μ) and one rather wide continuous distribution ($d \simeq 1$ to 300μ). The laminar Couette flow field, characterized by a nearly uniform shear rate, has been employed in these tests. The results have been interpreted in accordance with the previously described formulation, and the parameters k_i and $b_{i,j}$ have been estimated. It has been found that coal particle attrition generally proceeds rather slowly; for example, k is of order 10^{-4} hr^{-1} for $\dot{\gamma} \simeq 100$ s^{-1} and $d \simeq 200$ μ. Also, the measured distribution of attrition products (parameters $b_{i,j}$, Table 4) provides strong evidence that size diminution is caused by loss of particle surface protuberances (surface abrasion) and not by particle breakage into nearly equal parts.

As expected, the rate of size reduction (k_i) increases with particle diameter d_i and shear rate $\dot{\gamma}$. Equation (19), relating k_i to d_i and $\dot{\gamma}$, has been obtained on the basis of limited data only to demonstrate how the attrition formulation suggested here can be used to predict changes (with time of shearing) of a wide particle size distribution. Satisfactory agreement has been obtained between predicted and measured changes.