

above the orifice during efflux from bins in ambient air surroundings. The density-difference term in eq 3 appears to be substantiated for cases in which the particles are lighter, as well as heavier, than their surrounding fluid medium.

Significance and Implications

The fact that the gravity flow of gases, liquids, and solids can all be represented by a common dimensionless equation is obviously of considerable interest. It also illustrates the inadequacy of the simple Francis weir equation in application to liquids other than water and to systems wherein the surrounding medium is of comparable density.

Of perhaps greater significance is the implication that the viscosity of liquids and hence also of bulk solids is manifested in the angular term in eq 3, 9, and 15. The experiments reported in Figures 3b and c were carried out with rather large particles, in which case the viscosity of the mass was essentially that of only one phase. The same experiments carried out with very fine powders yielded in some instances complete blockage of the orifices and hence no flow. It could be argued that those examples were not cases of high viscosity but perhaps cases of high surface

tension and small interparticle dimensions. The significance of viscosity or surface tension is an obvious subject for further investigation, using such pure fluids as methyl alcohol and mercury as well as their mixtures with a variety of powders. Identification of the controlling property is of importance not only in resolving the relationships for the flow of slurries but in understanding the problems associated with the efflux of non-free-flowing powders. In any event the experiments reported here support the presented derivations of the common equations.

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Vapor Pressures of Heavy Liquid Hydrocarbons by a Group-Contribution Method

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A group-contribution method gives parameters for a vapor-pressure equation based on a kinetic theory of fluids. All parameters are obtained from molecular structure only. Good representation is obtained for vapor-pressure data for 67 hydrocarbon liquids in the region 10-1500 mmHg. This group-contribution method is useful for estimation of vapor-pressures and enthalpies of vaporization for those heavy hydrocarbons where no experimental data are available.

An abundance of experimental vapor-pressure data is in the literature for low-molecular-weight hydrocarbons. However, with the exception of normal paraffins, reliable vapor pressures are scarce for compounds which have normal boiling points over 200 °C. For rational process design, especially for alternative energy processes, it is important to have good estimates for thermodynamic properties of heavy hydrocarbons. Since it is rarely feasible economically to determine experimentally all necessary data, correlations are often used to extend limited experimental information. However, for many high-molecular-weight hydrocarbons, no experimental data at all are available. Therefore it is desirable, when possible, to estimate physical properties from theoretically based correlations. This work presents a group-contribution method for determining parameters in a vapor-pressure equation.

Many vapor-pressure equations have been proposed. Most are either empirical or integrations of the Clapeyron equation coupled with simplifying assumptions. In almost all cases these equations take a form where the pressure is an exponential function of the temperature and of the

adjustable parameters; this exponential dependence requires accurate prediction of parameter values. Since common vapor-pressure equations contain at least three, and often more, adjustable parameters with no clear physical significance, it is not possible to determine unambiguous values of these parameters by group contribution.

Many equations use critical data to develop a corresponding-states relation. Such relations are suitable for most light compounds, but not for heavy hydrocarbons which are thermally unstable in the critical region. Critical data for heavy hydrocarbons are usually not known.

Several authors have correlated vapor pressures for homologous series, but such correlations are limited to specific compounds. While such correlations are sometimes more accurate, a group-contribution method, based on carbon types, is more general because it can be used for a wide variety of hydrocarbons. Not only can one estimate the vapor pressure of a homologous series, but in addition, it is possible to estimate the effect of substituting various branches and side chains onto an unbranched parent molecule.

Table I. Group Contributions to Vapor-Pressure Parameters s and E_0/R

carbon type	s_i	ϵ_{0i}/R , K	vapor pressure data used to obtain group parameters
aliphatic $-\text{CH}_3$	2.359	1162.7	normal paraffins $\text{C}_5\text{--C}_{40}$
aliphatic $-\text{CH}_2$	0.479	674.0	normal paraffins $\text{C}_5\text{--C}_{40}$
aliphatic $-\text{C}-\text{H}$	-2.189	-372.9	branched paraffins $\sim \text{C}_{10}$
aliphatic $-\text{C}-$	-4.318	-1127.1	branched paraffins $\sim \text{C}_{10}$
aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}-\text{H} \end{array}$	1.175	939.5	benzene
aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}-\text{R} \end{array}$	-0.520	583.0	substituted aromatics
condensed aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Ar} \end{array}$ cond	-0.774	432.5	naphthalene, anthracene, chrysene
condensed aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Ar} \end{array}$ cond cond	0.321	623.5	pyrene
naphthenic $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C} \end{array}$	1.188	928.0	cyclohexane
naphthenic $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \end{array}$	-1.936	-431.0	substituted cyclohexanes

Whenever a few reliable vapor-pressure data are at hand, they should be used for cautious interpolation and extrapolation. The correlation given here is to be used only when no reliable vapor-pressure data at all are available.

The AMP Equation

Extending a suggestion by Moelwyn-Hughes (1961), Abrams et al. (1974) presented an equation relating pressure P to absolute temperature T

$$\ln P = A + B/T + C \ln T + DT + ET^2 \quad (1)$$

where

$$A = \ln \left(\frac{R}{V_w} \right) + \left(s - \frac{1}{2} \right) \ln \left(\frac{E_0}{R} \right) - \ln [(s-1)!] + \ln \alpha \quad (2)$$

$$B = -E_0/R \quad (3)$$

$$C = \frac{3}{2} - s \quad (4)$$

$$D = \frac{(s-1)}{(E_0/R)} \quad (5)$$

$$E = \frac{(s-3)(s-1)}{2(E_0/R)^2} \quad (6)$$

Here V_w is the (hard-core) van der Waals volume; E_0 is the enthalpy of vaporization of the hypothetical liquid at $T = 0$; s is the number of equivalent oscillators per molecule and R is the gas constant (82.06 cm³·atm/g·mol K); E_0/R is in kelvins and the universal constant α is equal to 0.0966 when P is in atm and T is in kelvins.

Abrams et al. (1974) and Macknick et al. (1977) have shown that this equation gives reliable results for large molecules and that it is suitable for representing vapor-pressure data in the range 10^{-6} to 2 atm. While eq 1 has only three fundamental parameters (V_w , s , and E_0/R), the equation has a form similar to that of popular empirical equations with five adjustable parameters. The three fundamental parameters have physical significance; they reflect the size and shape, flexibility, and intermolecular

forces of the molecules. The small number of parameters and their physical significance facilitates correlation by a group-contribution method.

AMP Parameters from Group Contribution

As shown by Abrams et al. (1974) and by Macknick et al. (1977), parameters s , E_0/R , and V_w can be calculated from a nonlinear fit of experimental vapor-pressure data. In this work, when experimental data are not available, the parameters can be found from a group-contribution method

$$s = \sum_i \nu_i s_i \quad (7)$$

$$E_0/R = \sum_i \nu_i (\epsilon_{0i}/R) \quad (8)$$

$$V_w = \sum_i \nu_i v_{wi} \quad (9)$$

where s_i , ϵ_{0i} , and v_{wi} are contributions from a group containing carbon-type i ; ν_i is the number of carbon atoms of type i in a molecule. Table I gives contributions to s and E_0/R by carbon type. The (hard-core) van der Waals volume V_w is found from Bondi's (1968) group-contribution correlation.

Group parameters s_i and ϵ_{0i} were determined from experimental vapor-pressure data for 67 liquid hydrocarbons: 20 normal paraffins, 21 branched paraffins, 19 aromatics, and 7 naphthenics. The data were obtained from American Petroleum Institute Projects 42 and 44 (1966, Zwolinski, 1971). The Simplex (Nelder, 1965) regression routine was used to correlate the data. Table I gives the hydrocarbons used for evaluation of different group contributions. Whenever possible, the experimental data for data reduction were in the range 10–1500 mmHg. However, accurate experimental data for heavy hydrocarbons are sparse; for some compounds the only reliable experimental datum is the normal boiling point. Therefore, the group-contribution method given here is likely to be more accurate near normal-boiling-point temperatures.

Carbon-type analysis does not take into account differences in molecular fine structure. For example, the method given here does not distinguish between 1-

Table II. Comparison of Experimental and Predicted Vapor Pressures for Representative Liquids

compound	$t_{760}, ^\circ\text{C}$		$\Delta t_{760}, ^\circ\text{C}$	$t_{10}, ^\circ\text{C}$		$\Delta t_{10}, ^\circ\text{C}$
	exptl	calcd		exptl	calcd	
$n\text{-C}_{10}\text{H}_{22}$	174.2	173.9	-0.3	57.6	52.9	-4.7
$n\text{-C}_{20}\text{H}_{42}$	343.8	344.0	0.2	198.3	195.8	-2.5
$n\text{-C}_{40}\text{H}_{82}$	525.0	524.6	-0.4	353.0	360.6	7.6
3-ethyl-octane	122.3	130.7	8.4	12.5	8.1	-4.4
3,3-dimethyloctane	161.2	166.4	5.2	45.0	42.1	2.9
2,3-dimethyl-3-ethylhexane	163.7	164.7	1.0	45.0	36.3	-8.7
naphthalene	217.9	218.5	0.6	86.6	88.0	1.4
anthracene	341.2	340.2	-1.0	176.2	181.4	5.2
chrysene	448.0	448.5	0.5	-	-	-
2,6-dimethylantracene	370.0	369.3	-0.8	-	-	-
$n\text{-hexadecylbenzene}$	378.0	372.5	-5.5	227.0	224.0	-3.0
2-methyl-3-ethylnaphthalene	277.0	278.9	1.9	132.0	138.7	6.7
$n\text{-octylcyclohexane}$	263.6	262.7	-0.9	126.0	122.6	-3.4
$n\text{-hexadecylcyclohexane}$	379.0	379.7	0.7	224.0	223.7	-0.3

Table III. Comparison of Experimental and Predicted Enthalpies of Vaporization at the Normal Boiling Point for Representative Liquids

compound	ΔH^V , kcal/g-mol		
	exptl	calcd	% error
$n\text{-C}_{10}\text{H}_{22}$	10.12	9.59	-5.3
$n\text{-C}_{20}\text{H}_{42}$	15.28	15.14	-0.9
$n\text{-C}_{40}\text{H}_{82}$	25.00 ^a	23.10	7.6
3-ethyl-octane	10.11	9.22	-8.7
3,3-dimethyloctane	9.87	8.96	-9.2
2,3-dimethyl-3-ethylhexane	9.98	8.49	-15.0
naphthalene	10.85	10.96	1.0
anthracene	14.10	14.05	-0.4
$n\text{-hexadecylbenzene}$	17.01	16.60	-2.4
2-methyl-3-ethylnaphthalene	13.23 ^a	12.93	-2.2
$n\text{-octylcyclohexane}$	12.56	11.96	-4.8
$n\text{-hexadecylcyclohexane}$	16.55	16.14	-2.5

^a Because of a lack of experimental data, ΔH^V_{exp} was calculated from the slope of the vapor-pressure curve between T_{10} and T_{760} .

methylnaphthalene and 2-methylnaphthalene. However, the method does account for differences in gross molecular structure; a distinction is made, for example, between 1,2-dimethylnaphthalene and 1-ethylnaphthalene. Inability to account for fine structure usually produces an error of less than $\pm 7^\circ\text{C}$ at the normal boiling point. Predictions for highly branched compounds are less reliable than those for compounds whose molecules contain only simple substitutions on a nonbranched parent molecule.

Results

Tables II and III compare predicted and experimental boiling points and enthalpies of vaporization. In Table II, T_{10} and T_{760} are respectively the temperatures where the vapor pressures equal 10 and 760 mmHg; ΔT is the difference between calculated and experimental values.

Experimental enthalpies were obtained by differentiating the experimental vapor-pressure data using a form of the Clausius-Clapeyron equation valid at low pressures

$$\frac{d(\ln P)}{dT} = \frac{\Delta H^V}{RT^2} \quad (10)$$

Calculated enthalpies of vaporization were determined using eq 1 and 10 to give

$$\Delta H^V_{\text{calc}} = R[-B + CT + DT^2 + 2ET^3] \quad (11)$$

For 67 liquids, the average error in T_{760} is $\pm 2.1^\circ\text{C}$, and that for ΔH^V at the normal boiling point is $\pm 5.4\%$.

Equation 1 holds for a large range of pressures; gross errors are not expected even for temperatures well below

Table IV. Sample Calculation for Parameters in Eq 1: 1,2-Dimethylnaphthalene^a

carbon type	ν_i	s_i	ϵ_{oi}/R , K	v_{wi} , cm ³ /g-mol
aliphatic $-\text{CH}_3$	2	2.359	1162.7	13.67
aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}-\text{R} \end{array}$	2	-0.520	583.0	5.54
aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}-\text{H} \end{array}$	6	1.175	939.5	8.06
condensed aromatic $\begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}-\text{cond} \end{array}$	2	-0.774	432.5	4.74

^a $s = \sum \nu_i s_i = 9.18$; $E_o/R = \sum \nu_i (\epsilon_{oi}/R) = 9993.4 \text{ K}$; $V_w = \sum \nu_i v_{wi} = 96.26 \text{ cm}^3/\text{g-mol}$. van der Waals volumes obtained from Bondi (1968).

Table V. Sample Calculation for Parameters in Eq 1: 2-Methyl-5-ethylheptane^a

carbon type	ν_i	s_i	ϵ_{oi}/R , K	v_{wi} , cm ³ /g-mol
aliphatic $-\text{CH}_3$	4	2.359	1162.7	13.67
aliphatic $>\text{CH}_2$	4	0.479	674.0	10.23
aliphatic $\geq\text{CH}$	2	-2.189	-372.9	6.78

^a $s = \sum \nu_i s_i = 6.974$; $E_o/R = \sum \nu_i (\epsilon_{oi}/R) = 6601.0 \text{ K}$; $V_w = \sum \nu_i v_{wi} = 109.16 \text{ cm}^3/\text{g-mol}$. van der Waals volumes obtained from Bondi (1968).

the normal boiling point. For example, for eicosane ($n\text{-C}_{20}\text{H}_{42}$), Macknick and Prausnitz (1978) report that $T_{0.01} = 83.85^\circ\text{C}$; $T_{0.01}$ is the temperature where the vapor pressure is 10^{-2} mmHg. Using the group contributions given here, and recalling that they were determined from data in the range 10–1500 mmHg, the calculated $T_{0.01}$ is 79.60°C ; this error of 4.25°C is remarkably low, considering an extrapolation in pressure of a little more than three orders of magnitude.

Since the derivation of eq 1 assumes ideal gas behavior, it is not applicable at temperatures near the critical region. For eicosane, Reid et al. (1977) report $T_c = 494^\circ\text{C}$ and $P_c = 11.0 \text{ atm}$. At the critical pressure, the group-contribution method estimates $T = 514^\circ\text{C}$, giving an error of 20°C .

Tables IV and V give sample group-contribution calculations for compounds which were not used in obtaining the group parameters. Figure 1 compares experimental and predicted vapor pressures. Agreement is about the

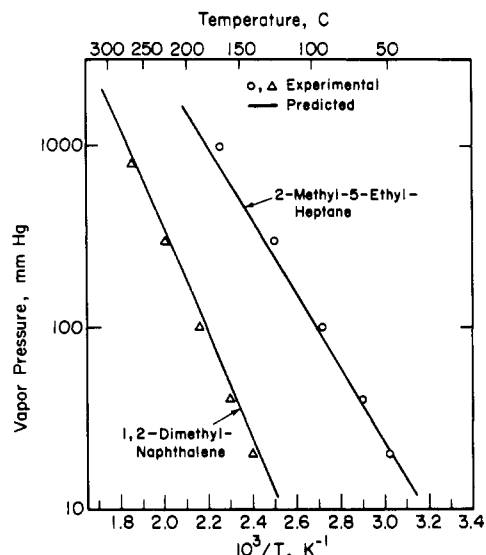


Figure 1. Comparison of experimental and predicted vapor pressures.

same as that indicated in Table II.

Conclusions

The semitheoretical correlation presented here can supply reliable estimates for vapor pressures and enthalpies of vaporization for heavy hydrocarbons. This correlation is especially useful for preliminary design considerations where it is not economically feasible to make experimental measurements.

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Nomenclature

A, B, C, D, E = AMP equation parameters, functions of E_0/R , V_w , and s

E_0 = AMP equation parameter: energy of vaporization of hypothetical liquid at $T = 0$, $\text{cm}^3 \text{ atm/g-mol}$
 ΔH^v = enthalpy of vaporization, kcal/g-mol
 P = vapor pressure, atm
 R = gas constant, $82.06 \text{ cm}^3 \text{ atm/g-mol K}$
 s = AMP equation parameter: number of equivalent harmonic oscillators per molecule
 s_i = contribution by group i to parameter s
 t = temperature, $^\circ\text{C}$
 T = temperature, K
 v_{wi} = contribution by group i to parameter V_w
 V_w = AMP equation parameter: (hard-core) van der Waals volume, $\text{cm}^3/\text{g-mol}$

Greek Letters

α = AMP equation universal constant equal to 0.0966 when P is in atm and T is in K
 ϵ_{0i} = contribution by group i to parameter E_0
 ν_i = number of i groups per molecule

Subscripts

0.01, 10, and 760 = at pressures of 10^{-2} , 10, and 760 mmHg, respectively
 c = at critical point

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Solubility and Partitioning. 3. The Solubility of Halobenzenes in Water

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The aqueous molar solubilities S_w of 26 mono- and multi-halogenated benzenes at $25 \pm 1^\circ\text{C}$ were determined. These values, along with values obtained from the literature for nine additional compounds, can be estimated by $\log S_w = -0.0095(\text{MP}) - 0.9874 \log(\text{PC}) + 0.7178$, where (MP) is the melting point in $^\circ\text{C}$ and (PC) is the estimated octanol-water partition coefficient for each halobenzene. The data were also found to be in agreement with $\log S_w = -0.0103(\text{MP}) - 0.04225(\text{TSA}) + 3.2970$, where (TSA) is the total molecular surface area of the halobenzene.

Introduction

In a previous publication (Yalkowsky and Valvani, 1979), it was shown that the solubility of 33 planar polycyclic hydrocarbons can be expressed as a function of their melting points (MP) and either their total molecular surface area (TSA) or their approximate octanol-water partition coefficient (PC). The latter parameter is easily calculated from f values which are group contributions to

$\log(\text{PC})$. The regression equations obtained for the hydrocarbons are

$$\log S_w = -0.0095(\text{MP}) - 0.0282(\text{TSA}) + 1.42 \quad (1)$$

and

$$\log S_w = -0.01(\text{MP}) - 0.88 \log(\text{PC}) - 0.012 \quad (2)$$

In both cases the correlation coefficient is greater than 0.9877 and the standard error is less than 0.271.