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Methods for Calculation of Engineering Parameters for Gas Separation

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16. Abstract

A group additivity method has been generated which makes it possible to estimate, from the structural formulas alone, the energy of vaporization and the molar volume at 25°C of many nonpolar organic liquids. From these two parameters and appropriate thermodynamic relations it is then possible to predict the vapor pressure of the liquid phase, and the solubility of various gases in nonpolar organic liquids. It is also possible to use the data to evaluate organic and some inorganic liquids for use in gas separation stages or liquids as heat exchange fluids in prospective thermochemical cycles for hydrogen production.

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ABSTRACT

A group additivity method has been generated which makes it possible to estimate, from the structural formulas alone, the energy of vaporization and the molar volume at 25°C of many nonpolar organic liquids. From these two parameters and appropriate thermodynamic relations it is then possible to predict the vapor pressure of the liquid phase, and the solubility of various gases in nonpolar organic liquids. It is also possible to use the data to evaluate organic and some inorganic liquids for use in gas separation stages or liquids as heat exchange fluids in prospective thermochemical cycles for hydrogen production.

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SECTION I

INTRODUCTION

For more than 50 years, a number of physical chemists have studied the nature of the solubility of gases in liquids and the processes of vaporization (Reference 1). In the following sections it will be shown how the thermodynamic relationships governing these phenomena, in conjunction with a group additivity system, make it possible to estimate the vapor pressure and solubility of a range of gases in nonpolar liquids. This opens the way with a minimum of information to make preliminary designs of gas separation or purification stages for new or existing thermochemical cycles. In the design or selection of liquids as possible heat exchange fluids, the boiling point, vapor pressure and degree of miscibility with sulfuric acid or other reagents can be estimated. Therefore it is possible to ascertain with sufficient accuracy the potential of a design application with very little or no physical properties data.

SECTION II

ESTIMATION OF THE ENERGY OF VAPORIZATION AND MOLAR VOLUME
BY THE GROUP ADDITIVITY METHOD

A number of group additivity methods already exist in the literature which assume that molecular properties can be partitioned among the individual functional groups and structural components of a molecule. Thus, simply by summing the group parameters, it is possible to estimate molecular properties from chemical structure alone. An extensive group additivity system for estimating both the energy of vaporization (ΔE_v^{298}) and molar volume (V) of organic liquids has been developed by Fedors (Reference 2). Based upon examination of a large amount of data on simple liquids, he assumed that:

$$\Delta E_v = \sum_i \Delta e_i \qquad\qquad [1]$$

$$V = \sum_i \Delta v_i \qquad\qquad [2]$$

where the Δe_i and the Δv_i are the atomic or group contributions to the energy of vaporization and molar volume at 25°C. The deviations between the experimentally measured values and those estimated by this method for a number of liquids were found to be less than 10 percent. The group contributions given by Fedors, although extensive, include only the parameters CF_3- and $-CF_2$- for fluorochemicals.

Our search of the literature uncovered adequate ΔH_v^{298} or vapor pressure/temperature data for only 19 perfluorochemicals, but extensive boiling point and density data were found. However, the following empirical relationship proposed by Hildebrand and Scott (Reference 3) relates the heat of vaporization of nonassociated liquids at 25°C to the boiling point (T_bK) at one atmosphere:

$$\Delta H_v^{298} = 0.020 T_b^2 + 23.7\ T_b - 2950 \qquad\qquad [3]$$

$$T_b {}^\circ K = \frac{-23.7 + [561.7 + 0.08(\Delta H_v + 2950)]^{\frac{1}{2}}}{0.04} \qquad [3a]$$

When Equation 3 was tested on the 19 perfluorochemicals for which $\Delta H_v{}^{298}$ was known, the calculated and experimental values were often in disagreement by several hundred calories. Subsequently, it became evident (Reference 4) that no fluorochemical data were included in calculating the constants in Equation 3. Using the data collected by us, the following relationship for perfluorochemicals ensues:

$$\Delta H_v{}^{298} = 0.0724 \, T_b{}^2 - 17.17 \, T_b + 5309 \qquad [4]$$

or in terms of the boiling point:

$$T_b {}^\circ K = \frac{17.17 + [294.9 - 0.2896 \, (5309 - \Delta H_v{}^{298})]^{\frac{1}{2}}}{0.1448} \qquad [5]$$

Equation 4 is based on least-squares computer curve fit for the 19 liquid perfluorochemicals whose $\Delta H_v{}^{298}$ and boiling point values were found in the literature or calculated from vapor pressure/temperature data. The perfluorinated compounds include eleven straight and branched alkanes, one dimethyl cyclobutane ring, one cyclopentane, two cyclohexanes, decalin, a methyl decalin and two tertiary amines. Figure 2-1 is a plot of Equations 3 and 4. As can be seen, perfluorochemicals have higher heats of vaporization than hydrocarbons of the same boiling point. This is especially true of those with boiling points below 300°K, after which perfluorochemicals parallel non-fluorinated liquids fairly closely.
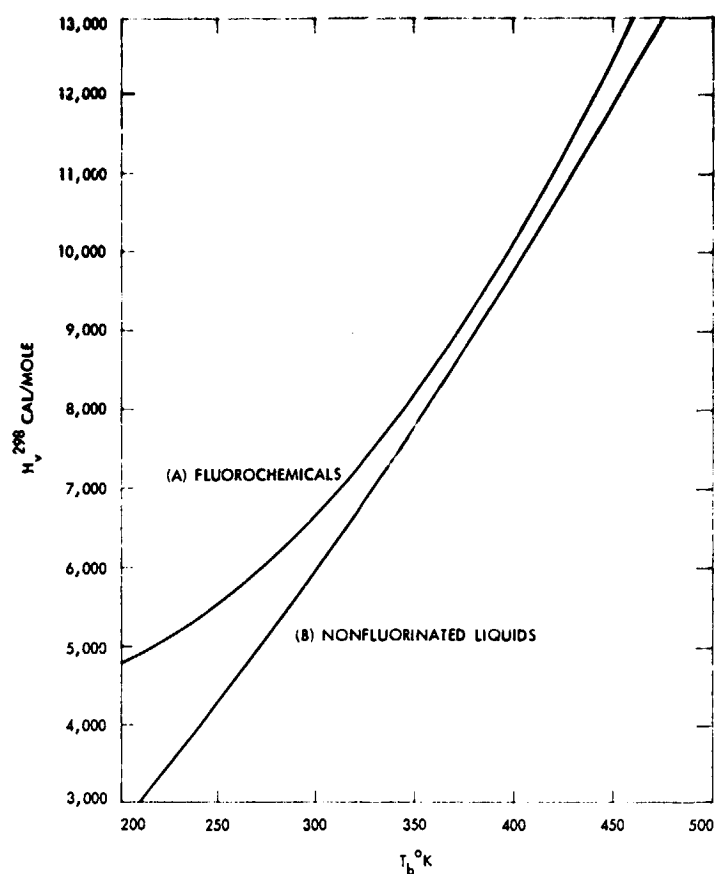
Figure 2-1. Relationship Between ΔH_v^{298} and T_b

With the assumption that Equation 4 is a good first approximation to estimating ΔH_v^{298} for perfluorochemicals, we calculated ΔH_v^{298} for a large number of such compounds from their literature boiling points. For example, by taking the boiling points for perfluorobutane and perfluoropentane, one can calculate their individual ΔH_v^{298} which can be used to calculate ΔE_v^{298} from:

$$\Delta E_v^{298} = \Delta H_v^{298} - RT \qquad [6]$$

The difference between the two ΔE_v^{298} values is an estimate of the group contribution of a $-CF_2-$ to the energy of vaporization. By using the boiling points for straight chain fluorocarbons from C_3-C_{13}, 10 values for Δe_i of a $-CF_2-$ were calculated, which were then averaged. Also, from the density data the molar volumes were calculated from:

$$V = \frac{MW}{D}.$$

MW = molecular weight; D = density   [7]

The Δv_i for $-CF_2-$ was calculated in a similar way. Table 2-1 contains a list of fluorochemical group additivity values calculated in this work, as well as some hydrocarbon values published by Fedors (Reference 2).

By summing the individual group parameters, obtained by inspection of the structural formula of a compound, the energy of vaporization and molar volume can be estimated before it is used in an actual experiment. Also, by calculating ΔH_v^{298} from Equation 6 and using this value in Equation 5, a reasonable estimate of the boiling point may be made. Similarly, the density of the compound can be estimated from the molar volume by Equation 7.

The predicted and reported boiling points for a number of perfluorochemicals are presented in Table 2-2.
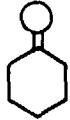
Table 2-1. Group Contributions to the Energy of Vaporization and Molar Volume at 25°C

Group	Δe_i^{298} cal/mole	Δv_i cm^3/mole
CF_3-	1933	54.8
$-CF_2-$	783	23.1
$-CFH-$	422	18.6
$-CF-$	-396	-15.0
$-C-$ (Perfluoro)	-1515	-38.3
$-N-$ (Perfluoro 3° Amine)	-914	-16.3
$-O-$ (Perfluoro Ether)	8	19.0
Ring: 5 atoms	2023	37.7
Ring: 6 atoms	2272	39.9
CH_3-	1125	33.5
$-CH_2-$	1180	16.1
$-CH-$	820	-1.0
$-HC=$	1030	13.5
$-C-$	350	-19.2
$-O-$	800	3.8

Values below the dashed line calculated by Fedors (Reference 2).

Table 2-2. Calculated Boiling Point and Vapor Pressure
for Some Nonpolar Liquids

Compound	Calc'd. ΔH_v 298 (1)*	Calc'd. B.P.°C 760 Torr (2)*	Lit. B.P.°C 760 Torr (4)*	Calc'd. V.P. mm/Hg 25°C (3)*	Lit. V.P. mm/Hg at T°C (4)*
n-C_6F_{14}	7,590	59	57	202	220/25
(F F bicyclic structure)	10,608	141	142	11.1	6.6/25
$CF_3CHF[OCF_2CF(CF_3)]_3F$	11,110	152	152	7.4	10./37.5
$CF_3CHF[OCF_2CF(CF_3)]_5F$	15,766	244	224	0.4	0.4/37.5
$(CF_3CF_2CF_2CF_2)_3N$	12,524	183	174	2.6	2.5/37.5
(cyclohexanone structure)	11,87C	179	155.8	1.6	2.7/25
n-C_9H_{20}	11,051	160	148.8	3.0	4.3/25
n-C_8H_{18}	9,860	130	123.0	14.0	7.7/25
(ring) $CH_2CH_2CH_2CH_2$	12,097	185	181.4	1.4	1.1/25
(ring) Br	10,839	154	152.3	3.5	4.2/25

*1. From Values in Table 2-1 or Reference 7
*2. Equation 3a, in terms of the boiling point is

$$T_B°K = \frac{-23.7 + [561.7 + 0.08(\Delta H_v + 2950)]^{\frac{1}{2}}}{0.04}$$

*3. From Equation 9
*4. References 7 and 8

SECTION III

ESTIMATION OF VAPOR PRESSURE

In the pr¹iminary design phase of a thermochemical cycle it is important to have data on the vapor pressure characteristics of the materials involved in the cycle. The liquids can be used for gas treatment and/or as heat exchange fluids.

From Hildebrand's general rule, Equation 6, that compounds have equal entropies of vaporization at equal molar volumes of their vapor, (Reference 5), the entropy of vaporization for nonpolar liquids can be predicted from a relationship developed by K. Sato (Reference 6).

$$\Delta S_v = \frac{\Delta H_v}{T} = \alpha R \left(\frac{P}{T}\right)^{\beta-1} \tag{8}$$

In terms of the vapor pressure (P in torr), Equation 8 becomes:

$$P = T \left(\frac{\Delta H_v}{\alpha R T}\right)^{\frac{1}{\beta-1}} \tag{9}$$

where T is the temperature in °K at which the vapor pressure is desired and R is the gas constant in cal mole^{-1} °K^{-1}. Thus, Equation 9 provides a useful way of estimating the vapor pressure of a nonpolar liquid from its heat of vaporization when the constants α and β are known. Sato originally calculated α and β from vapor pressure/temperature data for 10 nonpolar liquids containing hydrogen.

New values of α and β for perfluorochemicals have been calculated by the same procedure in this work. By plotting dP/dT vs. P/T from vapor pressure/ temperature data, a family of overlapping curves was generated. The deviations of the vapor from ideality were corrected by fitting the data for each substance to an equation of the form:

$$\frac{dP}{dT} = \alpha \left(\frac{P}{T}\right)^{\beta} \tag{10}$$

and then taking the average of the α and β values. Using these new constants, the vapor pressures of perfluorochemicals calculated from Equation

9 matches their literature vapor pressures much more closely than when Sato's original α and β values were used. Sato's constants and our values for perfluorochemicals are:

Nonpolar liquids:	$\alpha = 11.8822$	$\beta = 0.8810$
Perfluorochemicals:	$\alpha = 12.2497$	$\beta = 0.8846$

Thus, by estimating ΔE_v^{298} of a hydrocarbon or a perfluorohydrocarbon from the group additivity values given in Table 2-1, calculating its ΔH_v^{298} with Equation 6 and using Equation 9 with the α and β constants for hydrocarbons or perfluorohydrocarbon, the vapor pressure of the compound can be estimated before it is used in a cycle. Alternatively, if the boiling point of the compound is known, its ΔH_v^{298} can be estimated from Equation 4 and its vapor pressure predicted from Equation 9. Table 2-2 contains vapor pressure of some hydrocarbons and perfluorohydrocarbons calculated from Equation 9, and corresponding experimentally measured values. It is believed that the accuracy of the vapor pressure predicted by this method is sufficiently reliable to make decisions on the utility of new hydrocarbon or perfluorohydrocarbons as material components of a thermochemical cycle, or other chemicals in energy systems.

ESTIMATION OF GAS SOLUBILITIES IN NONPOLAR LIQUIDS

In selecting gas-carrying materials involved in thermochemical cycles it is desirable to have a method of making estimations of the solubility of gases in candidate liquids.

It is possible, using regular solution theory as developed by Hildebrand and others, to make useful predictions of the solubility of a number of gases in a wide range of solvents.

There are two equations based on regular solution theory that are frequently used to calculate gas solubilities (Reference 11). The first is:

$$-\log x_2 = -\log x_2^i + \frac{0.4343\bar{V}_2(\delta_1-\delta_2)^2}{RT} \qquad [11]$$

where the subscript 1 refers to the solvent and 2 refers to the solute. R is the gas constant (cal mole^{-1} °K^{-1}), T(°K) is the temperature at which the gas solubility is to be estimated, $\bar{V}_2$ is the partial molar volume of the gas in the solvent, δ is the solubility parameter defined as:

$$\delta = \left(\frac{\Delta H_v - RT}{v}\right)^{1/2} = \left(\frac{\Delta E_v}{V}\right)^{1/2} \qquad [12]$$

and x_2^i is the "ideal" gas solubility calculated from:

$$\log x_2^i = \frac{\Delta H_v}{4.574}\left(\frac{1}{T} - \frac{1}{T_b}\right) \qquad [13]$$

where ΔH_v is the heat of vaporization of the gas at the boiling point, T_b, and T is the temperature at which the gas solubility is to be determined. Equation 11 gives the best results when gas and solvent molecules are similar in size. For solutions where the molecules differ greatly in size, a correction of the Flory-Huggins type based upon the ratio of molar volumes is introduced which alters Equations 11 to 14 or 15 (Reference 10).

$$-\log x_2 = -\log x_2^i + \frac{0.4343\bar{V}_2 (\delta_1-\delta_2)^2}{RT} + \log\left(\frac{\bar{V}_2}{\bar{V}_1}\right)$$

$$+ 0.4343 \left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right) \qquad [14]$$

In terms of natural logs, Equation 14 is:

$$\ln x_2 = \ln x_2^i - \frac{\bar{V}_2 (\delta_1-\delta_2)^2}{RT} - \left[\ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) + \left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right)\right] \qquad [15]$$

The application of Equations 14 and 15 has been described by Gjaldbaek and the author in a number of publications (References 11 and 12). The pertinent constants for Equation 15 to calculate the gas solubilities in hydrocarbons and perfluorohydrocarbon are given in Table 4-1. Experimental and calculated values using Equations 14 and 15 are shown in Table 4-2, for gases in various solvents.

Figures 4-1 and 4-2 show the effects that the molar volume and solubility parameters have on oxygen (or generally for any other gas). It can be seen that a low molar volume of the liquid phase and matching of the solubility parameters of gas and liquid phase, give the maximum gas in the liquid phase. In practical systems, liquids of low molar volume have high vapor pressure which could be a problem in some process designs.

For more refined calculations on a given gas, the change in the partial molar volume $(\bar{V}_2)$ of the gases dissolved in different liquids needs to be taken into account. The procedure for oxygen can be used as a model. The value of $\bar{V}_2 = 46$ ml/mole for oxygen is the measured value obtained by Horiuti (Reference 12) in benzene and is the value normally used. However, Horiuti's measurements of the partial molar volume of oxygen in other solvents have shown that this quantity depends on the solvent and varies from 56 ml/mole in diethyl ether to 31 ml/mole in water, while in pure liquid oxygen at the boiling point it is 28 ml/mole.

When $\bar{V}_2$ was changed so that values of oxygen solubility calculated from Equation 15 agree for 24 liquid fluorocarbons reported by Clark (Reference 8), it was found that $\bar{V}_2$ varies over the range of 30-50 ml/mole. It can be seen from Figure 4-3 that a reasonable correlation exists between calculated values of $\bar{V}_2$ for these compounds and logarithms of their en-

Table 4-1. Parameters for Calculation of Gas Solubilities

Gas	$\text{Log } X_2^i$ (298.16 K°) (Ideal Solubility X_2^i)	$\bar{V}_2$ ml/mole (Partial Molar Volume)	$\text{Cal}^{1/2}\delta\text{cm}^{-3/2}$ Solubility Parameter
H_2	-3.25964*	37	5.10
N_2	-2.79588	53	5.20
O_2	-2.75355	46	5.70
CO	-2.80967	52	5.80
CO_2	-1.4209	105	3.31
CH_4	-2.40012	52	6.20
CH_3CH_3	-1.48545	66	6.60
$CH_3CH_2CH_3$	-0.92082	89	6.65

*The ΔH_V of H_2 is 216 cal/mole at the boiling point which, from observed data is low, therefore a value of 326.6 cal/mole was used in Equation 13.

Table 4-2. Comparison of Experimental and Calculated Values for Gases in Various Solvents

The solubilities are in cc of gas per 100 cc of liquid at 25°C.

| Solvent	Solvent V_1 Molar Volume	Solvent δ Solubility Parameter	Oxygen		Hydrogen		Carbon Monoxide		Nitrogen	
			Exp. (10)	Calc'd.	Exp. (10)	Calc'd.	Exp. (10)	Calc'd.	Exp. (9)	Calc'd.
n-C$_7$F$_{16}$	227	5.85	59.2	42.0	15.2	15.0	41.9	33.6	41.9	33.2
n-C$_6$H$_{14}$	132	7.3	36.1	40.0	12.2	12.9			26.2	27.5
(C$_2$H$_5$)$_2$O	105	7.4	46.5	42.6	14.7	13.5	39.6	35.0	29.3	29.3
n-C$_7$H$_{16}$	147	8.1	32.5	30.1	11.0	9.6	23.9	28.9	22.5	18.4
Cyclo-C$_6$H$_{12}$	109	8.2	27.6	32.3	8.5	10.1			17.0	19.8
CCl$_4$	97.1	8.6	30.3	28.8	8.2	9.0	21.9	22.9	16.3	16.7
C$_6$H$_6$	89.3	9.15	22.3	22.8	7.2	7.1	18.5	17.9	12.2	12.2
(CH$_3$)$_2$C=O	74.0	9.3	28.1	23.4	10.0	7.2	25.7	18.4		
C$_6$H$_5$Cl	102	9.5	20.9	17.6	7.6	5.6	15.1	13.4	10.5	8.8
CS$_2$	60.6	10.0	17.6	17.5	6.5	5.4	14.7	13.4	9.0	8.3
1,4-dioxane	86.1	10.0	15.3	14.0	5.5	4.5				
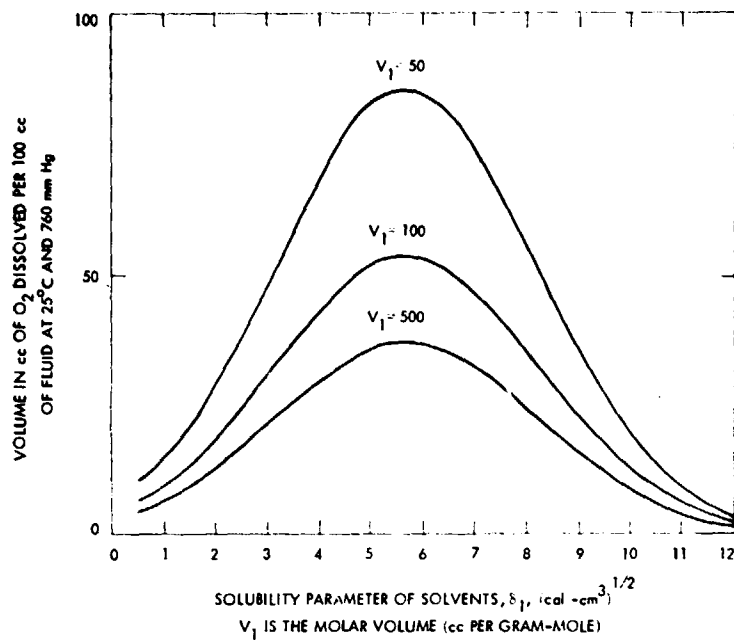
Figure 4-1. Effect of the Solubility Parameter on Oxygen
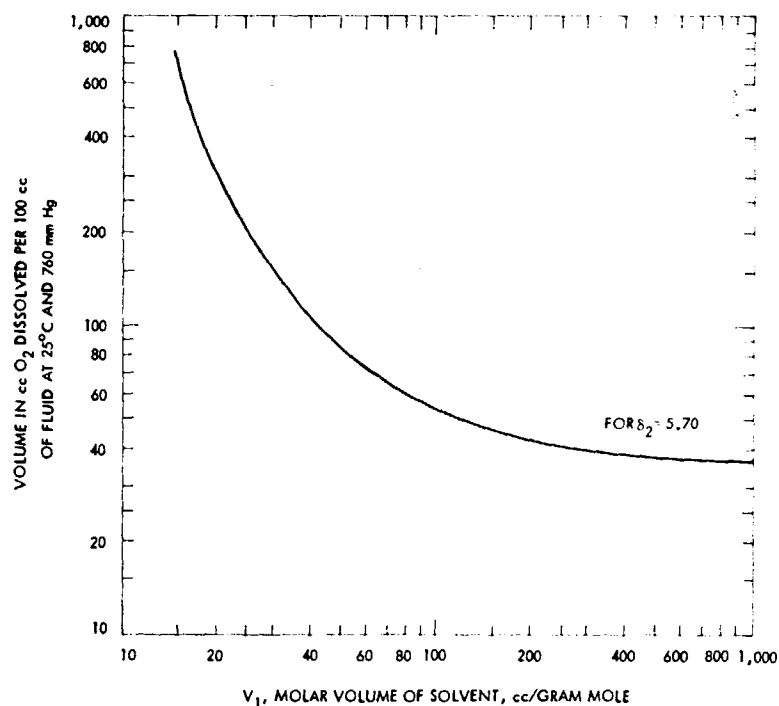Solubility Using Equation 14 or 15 (V = 46 ml)

Figure 4-2. Degree of Change of Oxygen Solubility
with Molar Volume (Equation 14 or 15,
V_2 = 46 ml)

tropies of vaporization at 25°C, if the cyclic structures are treated
separately. The equations of the least squares fit for the data and their
correlation coefficients are:

Open chain compounds:

$$\bar{V}_2 = -19.85 + 15.90 \ln\Delta S_v^{298} \qquad r^2 = 0.8999 \qquad [16]$$
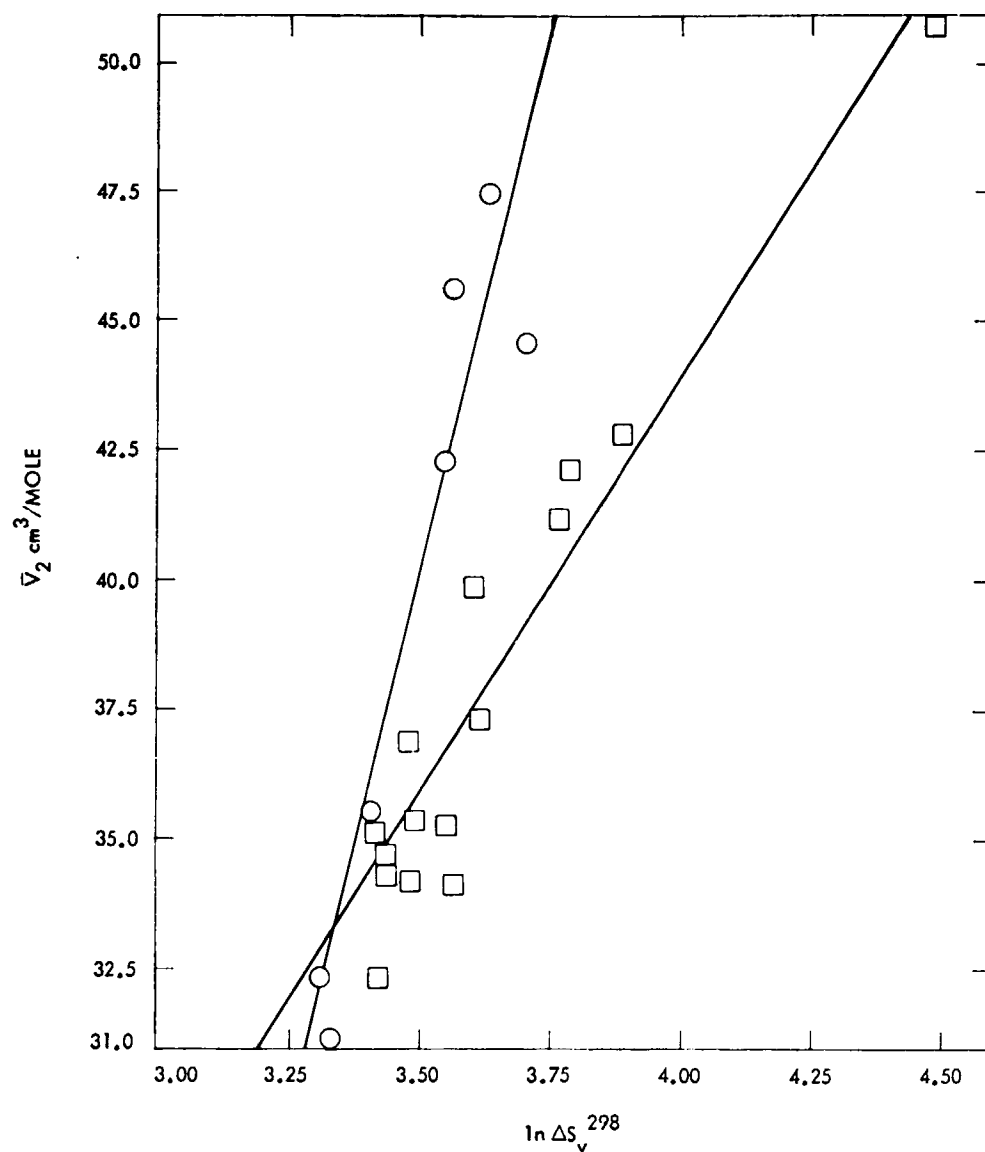

Figure 4-3. Relationship Between $\ln\Delta S_v^{298}$ and $\bar{V}_2$
for Cyclic (o) and Open Chain (□)
Fluorochemicals

Cyclic Compounds:

$$\bar{V}_2 = -100.15 + 39.90 \; \ln\Delta S_v^{298} \qquad\qquad r^2 = 0.8910 \qquad\qquad [17]$$

By using Equation 16 or 17 in conjunction with Equation 15, it is possible to predict the oxygen solubility of 22 compounds to ±4 ml and 14 of these to within ±2 ml of their experimentally determined values. Since Equations 16 and 17 are empirical and we have not measured the partial molar volume of oxygen in these solvents, no physical interpretation of this relationship is attempted. Some compounds with their calculated oxygen solubility and corresponding experimentally measured values are presented in Table 5-1.

Therefore, to estimate the solubility of oxygen in a fluorochemical from its structure alone, ΔE_v^{298} and V are estimated from Table 2-1. δ_1 is calculated from Equation 12, ΔH_v^{298} is calculated from Equation 6, and ΔS_v^{298} (= $\Delta H_v^{298}/T$) is then determined. From ΔS_v^{298} and either Equation 16 or 17, $\bar{V}_2$ is estimated. Then, using the estimated δ_1, $\bar{V}_2$, V_1 and the constants x_2^i and δ_2 in Equation 15, the mole fraction of oxygen, x_2, is obtained. This can be converted to cm^3 of $O_2/100$ ml of liquid at 25°C by:

$$cm^3 \; O_2/100 \text{ ml of liquid} = \frac{100 \cdot x_2 \cdot 24465}{V_1} \qquad\qquad [18]$$

Table 4-2 presents a sample calculation of all the physical properties discussed in this paper for a perfluoromethyldecalin.

SECTION V

MISCIBILITY OF LIQUID SYSTEMS

In general, solubility, or miscibility of two liquids, is to be expected if there is a decrease in the free energy of mixing Viz,

$$\Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{19}$$

Inasmuch as the entropy of mixing ΔS_{mix} is always positive (i.e., $-T\Delta S_{mix} < 0$), the enthalpy of mixing ΔH_{mix} will virtually determine solubility. The latter term for nonpolar substances is positive and its magnitude is proportional to the difference of the respective solubility parameters δ (i.e., square root of the cohesive energy density):

$$\Delta H_{mix} \sim (\delta_1 - \delta_2)^2 \tag{20}$$

Thus, the closer the solubility parameter values, the smaller the ΔH_{mix} will be and, consequently, the greater the decrease in ΔF_{mix}.

For the condition of liquid immiscibility the following approximation is obtained:
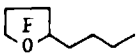
$$\Delta H_{mix} \sim V (\delta_1 - \delta_2)^2 > 2 \ RT \tag{21}$$

If an approximation is made for V, when $V_1 \neq V_2$, as the arithmetic mean of V_1 and V_2 is used, then the expression becomes:

$$\frac{(V_1 + V_2)}{2} (\delta_1 - \delta_2)^2 > 2 \ RT \tag{22}$$

These equations or approximations are to be regarded as a first order estimation or guide in the selection of possible heat exchange fluid systems.

Table 5-1. Calculated Oxygen Solubility in Fluorochemicals

Compound	[1] b.p.°C	[2] $D_2 25$	[3] ΔH_v^{298}	[4] V	[5] δ	[6] ΔS_v^{298}	[7] $\bar{V}_2$ calc.	[8] O_2 solub. calcd/lit.
(hexagon with F)	76.3	1.788	8150	195.7	6.21	27.34	31.85	58.1/57.2
$CF_3CHF[OCF_2CF(CF_3)]_2F$	104.4	1.656	9147	272.9	5.60	30.68	34.59	52.4/55.7
$CF_3(CF_2)_7Br$	140.5	1.890	10,595	264.0	6.16	35.54	36.92	49.1/52.7
$(CF_3)_2CF(CF_2)_4Cl$	108	1.77	9,283	228.2	6.17	31.14	35.82	52.7/52.7
$(CF_3)_2CFO(CF_2)_5CF_3$	121	1.721	9,789	292.9	5.60	32.83	35.66	50.6/52.5
(structure F O)	102	1.783	9,057	233.3	6.02	30.38	36.06	51.3/52.2
$(CF_3)_2CF(CF_2)_4Br$	120	1.977	9,749	227.1	6.35	32.70	35.60	51.1/51.4
$CF_3CHF[OCF_2CF(CF_3)]_3F$	152	1.738	11,096	355.6	5.43	37.22	37.66	47.0/47.3
$(CF_3)_2CF(CF_2)_6Cl$	151	1.83	11,051	275.4	6.16	37.07	37.59	48.0/45.6
$[(CF_3)_2CFO(CF_2)_4-]_2$	199	1.820	13,342	423.1	5.49	44.75	40.59	43.2/41.8
F F (structure)	160	1.972	11,455	259.6	6.47	38.42	45.43	39.9/38.4
$CF_3CHF[OCF_2CF(CF_3)]_9F$	399	1.848	26,477	873.4	5.44	88.80	51.48	32.9/33.3

1,2: Literature values from (Reference 8).

3: From lit. b.p. and Equation 4.

4: From lit. D and Equation 7.

5: From ΔH_v^{298} and Equation 12.

6: From ΔH_v^{298}

7: From ΔS_v^{298} and Equation 16 or 17.

8: From Equations 15 and 18.

Table 5-2. Sample Calculations of Physical Properties
from Chemical Structure

From Table 2-1.	ΔE_v^{298} cal/mole	V^{298} cm^3/mole
7 x CF$_2$ =	5481	161.7
3 x CF	-1188	-45.0
1 x CF$_3$	1933	54.8
2 x 6 atom ring =	4544	79.8
	$\Sigma = 10,770$	$\Sigma = 251.3$

1. $\Delta E_v^{298} = 10,770$ cal/mole

2. $V_1^{298} = 251.3$ cm^3/mole (molar volume)

3. $\delta_1 = 6.55$ from Equation 12 (solubility parameter)

4. $\Delta H_v^{298} = \Delta E_v^{298} + RT = 10,770 + 592 = 11,362$ cal/mole
   (heat of vaporization)

5. T_b °K = 431 or 158°C from Equation 5 (Boiling point at 760 torr)

6. $D_4^{25} = 2.04$ from Equation 7 (density)

7. VP torr = 6.1 from Equation 9 using perfluorochemical α, β values
   (vapor pressure)

8. $\Delta S_v^{298} = \dfrac{\Delta H_v^{298}}{298.15} = 38.11$ cal/mole-°K (entropy)

9. $\bar{V}_2 = 45.11$ cm^3/mole from Equation 17

10. Mole fraction of dissolved O_2 @ 25°C: $X_2 = 4.111 \times 10^{-3}$ from Equation 15, cm^{3}O$_2$/100 cm^3 of liquid = 40.0 from Equation 18

SECTION VI.

CALCULATIONS

By use of a small programmable hand calculator it is possible to screen new schemes of gas separation for candidate thermochemical cycles.

Copies of the programs written for the Hewlett-Packard HP67 or HP97 are available by request from the author for the calculations done in this paper.

SECTION VII

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