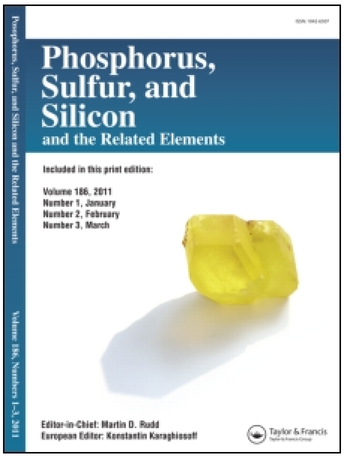

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SOLVENT CHARACTERISTICS OF MOLTEN SULFUR AT 132°C

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SOLVENT CHARACTERISTICS OF MOLTEN SULFUR AT 132°C

by

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ABSTRACT

The activity coefficient of 50 solutes in liquid sulfur have been measured at infinite dilution by gas chromatography. The solvent-solute interactions have been examined in terms of chromatographic models, activity coefficients, and solubility parameter theory. The classification of sulfur with polar chromatographic solvents is examined and attributed to enhanced dispersion of sulfur with compounds which have, relative to alkanes, loosely held electron clouds. Solubility parameter theory is found to provide a basis for the correlation of the behavior of *n*-alkanes in liquid sulfur.

The purpose of the study reported here was to investigate some of the solvent characteristics of liquid sulfur. From the general maxim that "like dissolves like," insight into the solvent nature of sulfur may be gained by a study of "likeness" as measured by the interactions of various solutes in binary solutions of molten sulfur. These interactions have been measured by gas-liquid chromatography.

The results are interpreted in terms of the glc theories of the specific retention volume, in terms of the physical chemical theory of the activity coefficient of the solute at infinite dilution in the solvent and in terms of solubility parameter theory.

The results of this study give only a partial answer to the question of the solvent characteristics of liquid sulfur. The study does:

1) demonstrate the utility of the glc technique in solvent characterization;

2) suggest reasons for the classification of sulfur with moderately polar chromatographic solvents;

3) illustrate that the heightened interactions of sulfur with polar molecules are due to greater dispersion interactions, in the broadest meaning, with the electrons available from the electronegative portions of the polar molecules rather than dipole-induced dipole interactions with the permanent asymmetric charge distributions;

4) indicate at least one class of compounds with which sulfur appears to form regular solutions.

At 132°C, liquid sulfur exists primarily in puckered S_8 rings. Practically no long chain polymers of sulfur are present below 159°C[1]. There are small amounts of other low molecular weight species present; Harris[2] lists the experimental percentage of non-S_8 species in liquid sulfur at 130°C as 6.8%. For practical purposes in this study, liquid sulfur will be approximated as entirely S_8 rings.

Theory

The background and relationships between thermodynamic and chromatographic variables can be found in most modern books on gas chromatography.[3] The following relationships have been used in this report:

1) To a first approximation, the free energy, $\Delta\mu^0$, required to transport a mole of solute from the stationary phase to the mobile phase may be considered as the sum of the chemical potential differences required to move each part of the molecule from one phase to another[4]. For an *n*-alkane

$$\Delta\mu^\circ = 2\Delta\mu^\circ_{CH_3} + (n-2)\Delta\mu^\circ_{CH_2} \qquad (1)$$

where μ° is a standard chemical potential. The $\Delta\mu^\circ$ is related to the specific retention volume, V_g, (retention volume per gram of stationary phase solvent) by[5]

$$\Delta\mu^\circ = RT \ln V_g + \text{constant} \qquad (2)$$

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where R is the gas constant and T is the absolute column temperature.

2) The activity coefficient, γ^∞, of the solute at infinite dilution in the solvent may be calculated[3] from V_g:

$$\gamma^\infty = \frac{273.2\,R}{M_L V_g p^0} \qquad (3)$$

where M_L is the molecular weight of the stationary phase (*e.g.*, sulfur) and p^0 is the vapor pressure of the pure solute at the column temperature, T. The symmetrical definition of the standard states of the components of a solution has been used:

$$p_i = \gamma_i x_i p_i^0 \qquad (4)$$

where x_i is the mole fraction of component i in the solution and p_i is the vapor pressure of i in the solution.

3) The deviation of a solution from ideal behavior is expressed as the sum of the contributions to the ln γ^∞ of the solute[6]:

$$\ln \gamma^\infty = \ln \gamma^\infty_{\mathrm{ath}} + \ln \gamma^\infty_{\mathrm{th}} \qquad (5)$$

where $\gamma^\infty_{\mathrm{ath}}$ and $\gamma^\infty_{\mathrm{th}}$ are the athermal and thermal contributions, respectively. The athermal portion accounts for the statistical effect caused by the difference in size between solute and solvent molecules and is calculated approximately by[7]:

$$\ln \gamma^\infty_{\mathrm{ath}} = \ln\left(\frac{V_2}{V_1}\right) + \left(1 - \frac{V_2}{V_1}\right) \qquad (6)$$

where V_2 and V_1 are the molar volumes of the solute and the solvent, respectively.

4) The solubility parameter, δ, of the regular solution theory is a measure of the cohesive energy density of a pure liquid[8a]

$$\delta = (\Delta E^V/V)^{1/2} \qquad (7)$$

where ΔE^V is the energy of vaporization. The $\gamma^\infty_{\mathrm{th}}$ of the solute is related to the solubility parameters of the solute (δ_2) and the solvent (δ_1) by

$$\ln \gamma^\infty_{\mathrm{th}} = \frac{V_2}{RT}(\delta_1 - \delta_2)^2 \qquad (8)$$

for mixing accomplished at constant volume and temperature and in which a regular solution results (the entropy of mixing is ideal). Methods of calculating solubility parameters are given by Hildebrand.[8b]

Experimental Section

A Varian Aerograph 1520 gas chromatograph with a thermal conductivity detector was used with helium as the carrier gas. The injection unit was modified to allow a pre-injection column in the oven to saturate the carrier gas with vapors of the stationary phase.

The injection column inlet pressure was measured at the head of the column to ±1 torr by a mercury manometer, and the outlet pressure was measured by a mercury barometer. The flow rate was determined with a soap bubble flow meter.

Solutes were injected with a Hamilton 701N syringe. The standard sample size was 0.2 $\mu\ell$, and several solutes were injected in smaller quantities to verify that the approximation of zero sample size (infinite dilution) was valid.

Pyridine was chromatographed periodically on the sulfur column to verify that column bleeding was insignificant over the period of experimentation. Samples of pyridine, 1-iodobutane, and *n*-nonane taken before and after passage through the sulfur column were analyzed by ir to verify that there had been no chemical reaction (such as dehydrogenation) between the solutes and the sulfur.

The columns were prepared by standard procedure and were 2 m in length. Dinonyl phthalate (Varian) and squalane (Supelco) solvents were used without additional purification. The sulfur column was prepared from Matheson, Coleman and Bell N.F. sublimed powdered sulfur which was dissolved in carbon disulfide and filtered prior to use. (Larkin, *et al.*, state that in their static solution studies with sulfur, there were no discrepancies between their results using high purity (99.999 + %) sulfur and their results using sublimed sulfur.[9] The solid support was Chromosorb W, 60/80 mesh, AW, DMCS. The sulfur column was 7 mm o.d. glass tubing, and the DNP and squalane columns were 0.25 in o.d. copper tubing. The percentage load was determined by evaporation of samples on a hot plate and in a vacuum oven. The values are given in Table I.

The specific retention volume, V_g, was calculated from retention times by[3]

$$V_g = \frac{3\left[\left(\frac{p_i}{p_o}\right)^2 - 1\right]}{2\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right]} \frac{F}{T_a}\left[1 - \left(\frac{p_w}{p_o}\right)\right]\left(\frac{t_R - t_A}{W_L}\right) 273.2 \qquad (9)$$

where p_i is the column inlet pressure, p_0 is the column outlet pressure, F is the uncorrected flow rate, T_a is the ambient absolute temperature, P_w is the vapor pressure of water at T_a, t_R is the retention time of the solute, t_A is the retention time of air, and W_L is the weight of the stationary phase in the column.

TABLE I

Injection Column Specifications

	DNP	Squalane	Sulfur
Liquid phase weight percentage,			
Of Chromosorb W, %	20.336	20.082	18.749
Of coated Chromosorb W, %	16.900	16.724	15.789
Coated Chromosorb W, g	12.7963	11.8712	10.1520
Liquid Phase, g	2.1626	1.9853	1.6029

Results and Discussion

In Table II are listed the values of γ^∞ for all the solutes of this study in molten sulfur and the values of γ_{th}^∞ calculated from these values and the molar volumes. (Since ratios of molar volumes were required, the molar volumes used were primarily those at 25°C (several were at 20°C), since this data was more readily available.) Since the molar volumes of most of these solutes are about the order of magnitude of the molar volume of sulfur, the athermal correction is relatively small. The listing is in the order of increasing values of γ^∞. All values of γ_{th}^∞ are greater than unity, indicating only positive deviations from the ideal behavior of Raoult's Law. Halogenated compounds (with the exception of fluorinated compounds), aromatic compounds, ring compounds, and carbon disulfide have small values of γ_{th}^∞, indicating solutions that more closely approach ideal behavior. The *n*-alkanes, fluorinated compounds, and alcohols show large positive deviations from ideal behavior. (With such large values of γ_{th}^∞ in a GLC experiment, one should be aware of the possibility of liquid surface adsorption effects.[10])

In Table II the increased ideality as the atomic number of a halogen is increased is apparent. Somewhat similar is the decrease in γ_{th}^∞ as the size of an aromatic system is increased from the six π electrons of benzene to the ten π electrons of naphthalene or to the twelve π electrons of biphenyl. The greater delocalization of the π electrons of naphthalene is seen to enhance the interaction with sulfur over that of the nonfused aromatic system of biphenyl.

The addition of hydrocarbon segments to a molecule appears to cause an increase in nonideality of solution in sulfur, as indicated by the increased value of γ_{th}^∞. This effect can be seen in the sets of *n*-bromoalkanes, *n*-iodoalkanes, and aromatic compounds, as relisted in Table III. This effect is consistent with the large values of γ_{th}^∞ for the *n*-alkanes. The substitution of atoms from the second-row elements for a carbon

TABLE II

Values of the Experimental γ^∞ and the Experimental γ_{th}^∞ for the Solutes in Sulfur at 131-132°C

Solute	Exp. γ^∞	Exp. γ_{th}^∞
Methylene iodide	1.36	1.52
Carbon disulfide	1.46	1.87
Methyl iodide	2.19	2.75
Bromoform	2.3	2.5
Iodobenzene	3.11	3.16
Ethylene bromide	3.8	4.1
p-Dibromobenzene	4.19	4.26
Bromobenzene	4.90	5.04
Naphthalene	5.29	5.31
1-Iodobutane	5.33	5.40
Biphenyl	6.1	6.1
Ethyl bromide	6.12	7.06
1,5-Cyclooctadiene	6.70	6.73
Pyridine	6.80	7.60
Chlorobenzene	6.98	7.24
1,2,3,4-Tetrachlorobenzene	6.99	–
Benzene	7.15	7.71
Chloroform	7.2	8.1
p-Dichlorobenzene	7.28	7.34
Methylene chloride	8.00	9.98
1-Bromo-4-fluorobenzene	8.18	8.49
Toluene	9.03	9.25
Carbon tetrachloride	9.21	9.67
Benzyl chloride	9.44	9.55
o-Xylene	9.53	9.58
1-Bromobutane	10.5	10.7
cis-Hydrindane	10.9	10.9
1,4-Dioxane	11.9	13.0
Fluorobenzene	14.8	15.6
1-Chlorobutane	19.7	20.3
2-Octyne	26	26
m-Difluorobenzene	30.9	32.2
1-Nitropropane	38	41
2-Pentanone	38.4	39.4
1-Butanol	43.7	46.6
n-Hexane	48.7	48.8
n-Heptane	59.5	59.8
2-Methyl-2-pentanol	64.8	64.9
n-Octane	68.3	69.7
n-Nonane	74.5	77.9
n-Decane	90.7	98.1
n-Undecane	110	124
1,2,3,4-Tetrafluorobenzene	111	–
n-Dodecane	134	158
n-Tridecane	166	206
n-Tetradecane	198	260
n-Pentadecane	244	341
n-Hexadecane	282	421
m-Fluorobenzotrifluoride	361	362
n-Octadecane	373	638

TABLE III

Variation of the Experimental γ_{th}^{∞} with the Addition of Hydrocarbon Segments for some Solutes in Sulfur at 131-132°C

Solute	Exp. γ_{th}^{∞}	Dipole Moments[21] (D)
n-Bromoalkanes		
Ethyl bromide	7.06	1.90
1-Bromobutane	10.7	2.17
n-Iodoalkanes		
Methyl iodide	2.75	1.62
1-Iodobutane	5.40	2.10
Aromatic hydrocarbons		
Benzene	7.71	0
Toluene	9.25	0.37
o-Xylene	9.58	0.62

TABLE IV

Values of δ_1 for Molten Sulfur Calculated by Solubility Parameter Theory from Values of the Experimental γ_{th}^{∞} and Values of δ_2 for the *n*-Alkanes as Solutes at 131°C

Solute	δ_2^a (cal/cc)$^{1/2}$ 25°C	δ_1 (cal/cc)$^{1/2}$
n-Hexane	7.27	12.1
n-Heptane	7.43	12.2
n-Octane	7.55	12.1
n-Nonane	7.65	12.1
n-Decane	7.72	12.1
n-Undecane	7.79	12.1
n-Dodecane	7.84	12.1
n-Tridecane	7.89	12.1
n-Tetradecane	7.93	12.1
n-Pentadecane	7.96	12.1
n-Hexadecane	7.99	12.1
n-Octadecane	8.04	12.0
Average		12.1 ± 0.0

[a] Calculated from values of ΔH_2^V and V_2 at 25°C from Ref. (18) by

$$\delta_2 = \left(\frac{\Delta H_2^V - RT}{V_2}\right)^{1/2}.$$

in a saturated hydrocarbon does provide outer nonbonding electrons, but the electrons appear to be too tightly held to be effective in enhancing the interaction with sulfur. Pyridine with its nitrogen has a γ_{th}^{∞} of 7.60 compared to benzene with a γ_{th}^{∞} of 7.71. The oxygen-containing compounds (2-pentanone, 1-butanol, and 2-methyl-2-pentanol) have values of γ_{th}^{∞} in Table II almost as large as those for the *n*-alkanes with the same number of non-hydrogen atoms. Fluorinated compounds have relatively large values of γ_{th}^{∞}. The solubility studies of various workers using static methods also indicate that halogenated compounds, aromatic compounds, and Lewis bases seem to be more soluble in molten sulfur than other substances.[1,9,11-16] These observations are consistent with the suggestion of Wiewiorowski and Touro[17] that the S_8 ring of molten sulfur behaves as a Lewis acid.

In general, the γ_{th}^{∞} for a solute in sulfur is a function of the size of the electron cloud of the solute and the looseness with which the electrons are held. As the size of the cloud increases, the deviation of the solution from ideal behavior decreases.

Solubility parameter theory provides a model for the interpretation of γ_{th}^{∞} in terms of the properties of the solute and the solvent. The homologous series of *n*-alkanes tested in molten sulfur, while forming extremely nonideal solutions, might be expected to form regular solutions, since only dispersion interactions might be anticipated between an *n*-alkane and sulfur. From the solubility parameters of the *n*-alkanes and the experimental values of γ_{th}^{∞}, the values of the solubility parameter δ_1 of sulfur were calculated and are listed in Table IV. (Since the equations of regular solution theory are merely zero-order approximations, it is sufficient to have self-consistent values of δ and V_2 at approximately 25°C even though the calculation is being performed to determine ln γ_{th}^{∞} at quite a different temperature[19] (here 131-132°C).) The consistent value of 12.1 for sulfur falls within the range of 11.7 to 13.6 reported from static solution studies.[1,20a,21]

To a first approximation, ln V_g, for members of an homologous series of compounds as solutes in a stationary liquid phase at constant column conditions will have a linear relationship with the number of carbon atoms in the solutes (see eqs 1 and 2). The use of ln V_g by chromatographers is equivalent to the use of $-\ln \gamma$ as can be seen from eq 3. This linear relationship follows from Martin's theory of the additivity of the group chemical potentials of a compound.[4] Figure 1† illustrates this relationship for the series of *n*-alkanes chromatographed on the sulfur column. In Table V are the slope and intercept from the least squares fit of this data (ln V_g vs. carbon number) along with the values for *n*-alkanes chromatographed on a squalane

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† Figure not available at time of going to press. It is hoped that the figure can be reproduced in a later issue.

TABLE V

Slopes and Intercepts of the Lines[a] of ln V_g vs. Carbon Number for the *n*-Alkanes

Stationary Liquid Phase	Slope *m*	Intercept *b*
Squalane	0.697	−1.04
DNP	0.654	−1.27
Sulfur	0.495	−3.85

[a] $\ln V_g = m$ (carbon number) $+ b$

column and on a DNP column. The latter two columns were used to check experimental procedures and to provide a basis for comparison of solvent natures. The slope of each of these lines is directly proportional to $\Delta\mu^0_{CH_2}$ the free energy change in the transfer of a mole of methylene groups from the stationary phase to the mobile phase. The slopes in Table V indicate that the solvent interactions per methylene group decrease in the order squalane > DNP > sulfur. This classes sulfur with the moderately polar chromatographic solvents used for stationary phases (*e.g.* Tricresyl phosphate and Triton X100 are similar to sulfur on chromatographic "polarity"scales). The large number of electrons available on sulfur as a third row element and its greater polarizability allow an enhanced dispersion interaction with molecules which share this characteristic. This is evidenced by the high solubility parameter which it possesses. The differences between sulfur and squalane as solvents for *n*-alkanes can be seen in their solubility parameters of 12.1 and 7.95 resp.

When the solubility parameter of sulfur is predicted from the values of δ_2 and of γ^∞_{th} of compounds other than *n*-alkanes, the results fall within the range of 12.9 to 15.1, as listed in Table VI. Regular solution theory[8a] assumes that the molecules are spherically symmetric. The solute-solvent interaction is assumed to be the geometric mean of the solute-solute and solvent-solvent interactions. The failure of solubility parameter theory with the set of compounds in Table VI may be attributed largely to deviations from the geometric mean. Table VI also reports thermal activity coefficients calculated on the basis of sulfur having a solubility parameter of 12.1. Comparison with the experimental values of γ^∞_{th} dramatically illustrates the failure of solubility parameter theory as a general quantitative tool. Nevertheless, the consistency within the data for the *n*-alkanes in liquid sulfur suggests that this area might be a fruitful one for further investigation.

TABLE VI

Values of δ_1 for Sulfur Calculated by Solubility Parameter Theory from Values of δ_2 and Values of the Experimental γ^∞_{th} for Some Solutes at 131–132°C and γ^∞_{th} Values Calculated from $\delta_1 = 12.1$

Solute	δ_1 (cal/cc)$^{1/2}$	δ_2^a (cal/cc)$^{1/2}$ 25°C	Calc. γ^∞_{th} ($\delta_1 = 12.1$)	Exp. γ^∞_{th}
Carbon disulfide	12.9	10.0	1.39	1.87
o-Xylene	12.9	9.0	4.18	9.58
Carbon tetrachloride	12.9	8.6	4.32	9.67
Toluene	13.0	8.9	3.85	9.25
Naphthalene	13.2	9.9	2.07	5.31
Bromoform	13.4	10.5	1.31	2.5
Benzene	13.4	9.15^b	2.59	7.71
Chlorobenzene	13.4	9.5^b	2.33	7.24
Ethyl bromide	13.5	8.9	2.57	7.06
Methyl iodide	13.5	9.9	1.45	2.75
Methylene iodide	13.8	11.8	1.01	1.52
Chloroform	13.9	9.3	2.18	8.1
Ethylene bromide	13.9	10.4	1.37	4.1
1,4-Dioxane	14.9	10.0^b	1.59	13.0
Methylene chloride	15.2	9.8	1.52	9.98
Pyridine	15.2	10.7^b	1.21	7.60

[a] From Ref. (8c).

[b] From Ref. (20a).

TABLE VII

Slopes and intercepts of the lines[a] of ln V_g versus number of nonhydrogen atoms for homologous series in sulfur, 131-132°C

Series	Slope, *m*	Intercept, *b*
n-Alkanes	0.495	−3.85
n-Bromoalkanes	0.525	−1.29
n-Iodoalkanes	0.443	0.55

[a] $\ln V_g = m$ (nonhydrogen atom number) + *b*.

The relationships between ln V_g (or $-\ln \gamma_{\text{th}}^{\infty}$) and the non-hydrogen atom number for the three homologous series, *n*-alkanes, *n*-bromoalkanes, and *n*-iodoalkanes are given in terms of the slopes and intercepts of these lines (ln V_g *vs*. nonhydrogen atom number) in Table VII. The slopes of the three lines should be approximately equal since each slope is proportional to $\Delta\mu^0_{CH_2}$. The small variation is due in part to the inclusion of the one and two carbon members of the halide series. The *intercepts* are proportional to the difference in the free energy required to transport the terminal halide from the molten sulfur to the mobile phase and the free energy required to transport a terminal methyl group. The large difference between the halide groups indicates that the net solute-solvent interactions for a terminal iodide group are greater than for a terminal bromide group, which, in turn, are greater than for a terminal methyl group. This strongly suggests that the increased interaction is due to the halide itself and is not due to any dipole resulting from the presence of the halide within the molecule. That the increased interaction of sulfur with increased atomic number of a halogen must be a dispersion type of interaction, and not a dipole-induced dipole effect, can be seen by a comparison of groups of halogenated compounds of similar dipole moment.

TABLE VIII

Variation of the Experimental $\gamma_{\text{th}}^{\infty}$ with the kind of Halogen for Some Solutes in Sulfur at 131-132°C

Solutes	Exp. $\gamma_{\text{th}}^{\infty}$	Dipole Moments (D)
Halobutanes		
1-Chlorobutane	20.3	2.06
1-Bromobutane	10.7	2.17
1-Iodobutane	5.40	2.10
Dihalomethanes		
Methylene chloride	9.98	1.62
Methylene iodide	1.52	1.09
Trihalomethanes		
Chloroform	8.1	1.06
Bromoform	2.5	1.00
Halobenzenes		
Fluorobenzene	15.6	1.60
Chlorobenzene	7.24	1.72
Bromobenzene	5.04	1.71
Iodobenzene	3.16	1.72

The thermal part of the activity coefficient and dipole moments for various groups of halogenated compounds are listed in Table VIII. Decreased interactions are indicated by large values of $\gamma_{\text{th}}^{\infty}$, while a value of unity indicates that the interaction is the same as found between S_8 molecules in pure sulfur. From this table it may be noted that members of the groups halobutanes, trihalomethanes, halobenzenes, and p-dihalobenzenes have essentially no differences in dipole moments between members of a given set, yet the solute sulfur interactions increase markedly with increasing atomic number of the halogen.

APPENDICES

Data References

Appendix I

Physical Constants for the Calculation of the Vapor Pressures of the Solutes

Method A: Antoine-type equation

$$\ln p_2^0 = 2.303\left\{A_1 - \left[\frac{B_1}{(C_1 + t_2)}\right]\right\}$$

where A_1, B_1, and C_1 are constants for a given solute; and t_2 is the column temperature (°C).

Ref. (18): *n*-alkanes, benzene, 1-butanol, 2-pentanone, 2-methyl-2-pentanol, toluene, *o*-xylene, naphthalene.

Ref. (22): 1-chlorobutane, 1-bromobutane, 1-iodobutane, methylene chloride, ethyl bromide, methyl iodide, methylene iodide.

Ref. (23): iodobenzene, *p*-dichlorobenzene.

Ref. (24, 25): *p*-dibromobenzene.

Method B: Variation of the Clausius-Clapeyron equation:

$$\ln\left(\frac{p_2^0}{p_1^0}\right) = \left[\frac{\Delta H^V (T_2 - T_1)}{R T_2 T_1}\right]$$

Solute	Ref. ΔH^V	Ref. T_1
Pyridine	(26b)	(26b)
Carbon disulfide	(27)	(27)
Carbon tetrachloride	(27)	(22)
m-Fluorobenzotrifluoride	(28)	(29)

where ΔH^V is the heat of vaporization of the solute at n.b.p., $p_1^0 = 760$ torr., T_2 is the absolute column temperature, T_1 is the absolute n.b.p., R is the gas constant.

Method C: Variation of the Clausius-Clapeyron equation:

$$\ln\left(\frac{p_2^0}{p_1^0}\right) = \left[\frac{T_1(T_2 - T_1)}{p_1^0 T_2\left(\frac{dt}{dp}\right)}\right]$$

where (dt/dp) is at n.b.p.

Ref. (18): 2-octyne, biphenyl.

Ref. (22): 1-nitropropane, chloroform, ethylene bromide, bromoform.

Method D: Antoine-type equation:

$$\ln p_2^0 = 2.303\left[\left(\frac{-0.2185\,A_2}{T_2}\right) + B_2\right]$$

where A_2 and B_2 are constants for a given solute.

Ref. (30): 1,4-Dioxane, 1,2,3,4-tetrachlorobenzene, benzyl chloride.

Method E: Variation of the Clausius-Clapeyron equation

$$\ln\left(\frac{p_2^0}{p_4^0}\right) = \frac{T_3(T_2 - T_4)\ln\left(\frac{p_3^0}{p_4^0}\right)}{T_2(T_3 - T_4)}$$

where p_3^0 and p_4^0 are vapor pressures of the pure solute at the absolute temperatures T_3 and T_4, respectively.

Ref. (26b): *Cis*-hydrindane, fluorobenzene, chlorobenzene, bromobenzene.

Method F: Variation of the Clausius-Clapeyron equation in which ΔH^V at n.b.p. is estimated by the Hildebrand Rule[20b]:

$$\Delta H^V = 17.0\,T_1 + 0.009\,T_1^2$$

Then ΔH^V is used in Method B.

Ref. (29): *m*-difluorobenzene, 1-bromo-4-fluorobenzene, 1,5-cyclooctadiene.

Ref. (31): 1-bromo-4-fluorobenzene.

Ref. (32): 1,2,3,4-tetrafluorobenzene.

Appendix II

Molar Volumes (at 25°C, except as noted)

Given:

Ref. (18): *n*-alkanes, 1-butanol, 2-pentanone, 2-methyl-2-pentanol, 2-octyne.

Ref. (8c): benzene, carbon disulfide, carbon tetrachloride, toluene, *o*-xylene, naphthalene, methylene chloride, chloroform, ethyl bromide, ethylene bromide, bromoform, methyl iodide, methylene iodide, sulfur.

Ref. (20a): pyridine, chlorobenzene, 1,4 dioxane.

Calculated: from molar weights [Ref. (30)] and densities:

Ref. (22): 1-nitropropane, 1-iodobutane.

Ref. (23): fluorobenzene.

Ref. (25): *p*-dichlorobenzene.

Ref. (26b): *cis*-hydrindane, bromobenzene, benzyl chloride.

Ref. (29): 1-bromo-4-fluorobenzene, m-fluorobenzotrifluoride.

Ref. (30): 1-chlorobutane (20°C), 1-bromobutane (20°C).

Ref. (31): biphenyl, *m*-difluorobenzene, *p*-dibromobenzene (20°C).

Ref. (26a): iodobenzene.

Ref. (33): 1,5-cyclooctadiene.

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