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Hypothetical Thermodynamic Properties: Application of Correlation Gas-Chromatography to the Evaluation of the Vaporization Enthalpies of Fluorinated Compounds

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Hypothetical Thermodynamic Properties: Application of Correlation Gas-Chromatography to the Evaluation of the Vaporization Enthalpies of Fluorinated Compounds

by

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Darrell W. Hasty

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Contents

Abstract

Relatively little vaporization enthalpy data has been published for fluorinated compounds. The increasing commercial use of fluorinated chemicals and their rapid spreading within our biosphere necessitates a better understanding of their thermodynamic properties and long-term stability. This paper presents an initial attempt at applying correlation gas chromatography (C-GC) to investigate its possible use in deriving the enthalpy of vaporization at 298 K for twenty-seven partially or fully fluorinated compounds. Additionally, the behavior of the *n*-perfluoroalkanes are examined and compared to their hydrocarbon analogues. Although published data for the *n*-perfluoroalkanes as a function of the number of carbons appears to be slightly non-linear, the experimentally determined trend for the fluorinated series is considered linear with a correlation coefficient > 0.98. This linearity mirrors that of similarly sized hydrocarbon *n*-alkanes. Results also indicate that *n*-perfluorinated alkanes behave similarly to hydrocarbon alkanes with vaporization enthalpy values increasing incrementally with the addition of each CF_2 unit to the alkane's chain length.

This work also examines what correlative standards to use with gas chromatography to determine the vaporization enthalpies of different structural classes of fluorinated compounds. Experimental results indicate that *n*-perfluorinated alkanes can successfully be used to evaluate other perfluorinated *n*-alkanes and perfluorocycloalkanes but cannot be used to evaluate perfluoroamines, perfluoroaromatics or the mono substituted 1H–perfluoroalkanes.

Hydrocarbon compounds, both *n*-alkane and aromatic, were also used as standards in an attempt to correlate them with partially and fully perfluorinated compounds. The hydrocarbon *n*-alkanes were found to correlate well with mono fluorinated *n*-alkanes. It was further determined that aromatic hydrocarbons will correlate with partial fluorinated aromatics. However, the same aromatic hydrocarbons do not appear to correlate with fully fluorinated aromatics.

Chapter 1

1.1 Introduction

Today fluorinated compounds are ubiquitous in our daily lives and affect nearly all aspects of it. The strong C–F bond has enabled its wide use in a range of applications from our national defense, which protects us, to the electronics we use for our entertainment. The unusual strength of this bond with its unique properties is nearly bioinert with few living organisms using fluorine in any major chemical cycle. This has provided the opportunity for chemists to create many useful medicines and agrochemicals that have improved our health and standard of living.

However, these same fluorinated compounds are also becoming a concern among environmentalists. Researchers are beginning to discover a darker side with their accumulation in the biosphere. Organofluorine compounds are accumulating in our water, our air and in our bodies because of their high stability and lack of biodegradability. The smaller, lighter perfluorinated alkanes and partially fluorinated compounds have also been found to be accumulating in the atmosphere and have been determined to be greenhouse gas (GHG) contributors. This has led international environmental organizations to call for the restriction to their use.

1.2 Properties of the C–F bond

Fluorine, the most electronegative element in the periodic table, reacts with carbon to form the strongest single bond in organic chemistry. Its 2s and 2p orbitals enable an almost ideal overlap with carbon during bond formation. The resultant $^{\delta+}$C–$^{\delta-}$F bond is highly polarized with a dipole moment of approximately 1.4 Debyes, exhibiting more ionic character than the other halogens, with the highly electronegative fluorine carrying most of the electron density. Even though the C–F bond is highly polarized, it is extremely low in polarizability. [1-2] (Table 1-1.) Fluorine holds tightly to its three lone electron pairs causing it to be a poor hydrogen bond acceptor.[1-3] Crystallographic studies have measured the shortest CF···HX contacts to be around 2.0–2.2 Angstroms.[1-4] Theoretical calculations estimate the strength of the non-bonded CF···HC bond to be around 25% the strength of the typical hydrogen bond. [1-4]

Table 1-1. Comparison of carbon-halogen and carbon-carbon bond characteristics.[1-1][1-5][1-6]

X	C	H	O	F	Cl	Br	I
Bond length (pm) C–X	153	109	142	139	179	194	213
Bond dissociation energy (kJ/mol) C–X	348	412	360.0	484	338	276	238
Electronegativity (Pauling scale)	2.55	2.20	3.44	3.98	3.16	2.96	2.66
Dipole moment, μ (D) C–X	--	(0.4)	0.7	1.41	1.46	1.38	1.19
Van der Waals radius (pm)	170	120	152	147	175	185	198
Atom polarizability, α (10^{-24} cm^3)	--	0.67	0.80	0.56	2.18	3.05	4.7

Fluorine's van der Waals' radius and the C–F bond length fall between hydrogen and oxygen but lie closer to oxygen. While $^{\delta-}$F is closer isosterically to oxygen, its physical properties, size and charge, have enabled fluorine's use as a substituent in drug design. Fluorine is used in medicinal chemistry to adjust a drug's lipophilicity, tune its stereoelectronic structure and, because of its similar size to hydrogen, also employed as a hydrogen mimic enabling the modification of the drug's steric size and effects. [1-7]

1.3 Unusual features of perfluorocarbons

Although perfluorocarbons (PFCs) have highly polar C–F bonds they can also be non-polar. The large intramolecular bond dipoles of the carbon-fluorine bonds cancel each other due to molecular symmetry. Additionally, the fluorines' tight hold on their respective electrons results in the PFCs having very weak intermolecular interactions which causes them to have boiling points that are within ±30 °C of their hydrocarbon analogs even though the fluorinated compounds are four or more times the molecular mass of their hydrocarbon counterparts.[1-8] (Figure 1.1)

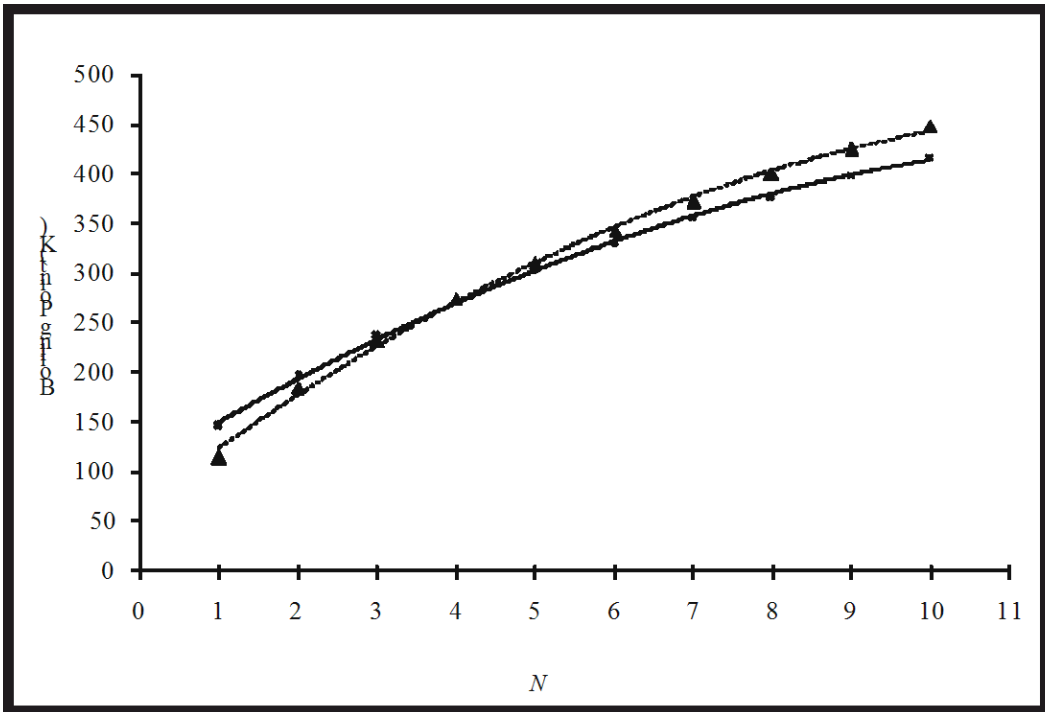


Fig.1.1 Graph of *n*-perfluoroalkanes (■) boiling points compared to homologous *n*-hydrocarbon alkanes (▲). *N* is the number of carbon atoms.

Because perfluorocarbon compounds are neither polar nor polarizable they interact weakly through hydrogen bonding and upon mixing with water and an aliphatic hydrocarbon solvent, liquid perfluoroalkanes will separate into a third immiscible phase. Interestingly, while refusing to mix with water or hydrocarbon solvents, perfluorocarbons such as perfluorodecalin will dissolve oxygen up to 40% by volume and is miscible with carbon dioxide.[1-9] This high oxygen carrying property of fluorinated compounds have encouraged medical researchers since the mid-1960's to try and develop these compounds into a usable blood substitute. [1-10]

Fluorine's strong electrostatic carbon bond and large van der Waals' radius results in steric shielding of the carbon skeleton and defines the shape of the *n*-perfluoroalkane molecule. While *n*-alkane hydrocarbons have zigzag structures with conformational flexibility, the *n*-perfluoroalkanes have spiral structures that are more rigid and rod like due to the steric repulsion and stretching induced by the "hard" fluorines residing on the 1,3-difluoromethylene groups as seen in figure 2.[1-1]

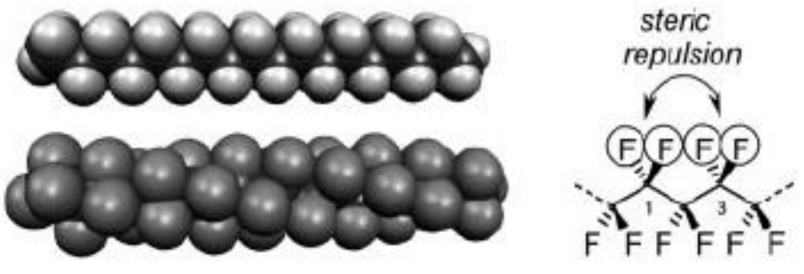


Fig. 2. The zigzag confirmation of octadecane (above) compared with the helical perfluoroctadecane (below). [1-1]

Fluorine's steric shielding of the carbon backbone and C–F bond's stability makes these compounds nearly non-reactive. PFCs are inert to basic hydrolysis since the central carbons are protected against nucleophilic attack. For example, Teflon is non-reactive to molten potassium hydroxide. Generally, it takes strong Lewis acids at high temperatures to decompose PFCs and enable nucleophilic attack of the resulting carbocation. Other methods used to decompose perfluorocarbons are to bring them into contact with molten alkali metals or iron heated to 500 ^{o}C. [1-1]

1.4 A brief history and uses of organofluoride compounds

The first synthesis of elemental fluorine was in 1886 by Henri Moissan. His subsequent research into organofluoride chemistry in the 1890's laid the groundwork for the wide spread development and use of fluorinated compounds. By the 1930's the first commercial application of organofluoride compounds began with the introduction of chlorofluorocarbon (CFC) refrigerants, fire suppressants and aerosols propellants. Two new fluoroplastics were also synthesized: poly(chlorotrifluoroethylene) in 1934 and polytetrafluoroethylene (PTFE, Teflon) in 1938.[1-1]

In 1941 the military found use for fluoroorganic gaskets, lubricants and corrosive resistant coolants in their high-speed uranium centrifuges. The Manhattan Project became fluorine's first large-scale use in the production and separation of fissionable U^{235} from U^{238} in the form of gaseous UF_6 and enabled the creation of the atomic bomb that exploded over Hiroshima in 1945. [1-9]

Minnesota, Mining and Manufacturing (3M) launched the first plant for the production of fluorocarbons in 1951 using the electrochemical fluorination process reported by J.H. Simons in 1949. This paved the way for the increased production of fluorocarbon derivatives with different functional groups. The first sales of fluoropharmaceuticals and agrochemicals began during the 1950's. Meanwhile, the military found a new use for fluorine and began producing their first fluorinated chemical weapons. [1-12]

Starting in the 1980's the electronic industry began using fluorocarbons for photo-resistive work and plasma etching. Today fluorinated compounds' uses have continued to expand as water repellants, flame-retardants, blowing agents for automotive fuel tanks, and cleaning agents for both liquid crystal displays and integrated circuits. Polyfluorinated compounds are increasingly being used in medicine for anesthetics, eye surgery, and as diagnostic imaging agents while research continues into their promising use as a blood substitute. [1-13]

1.5 Buildup of fluorocarbons in the biosphere

The increasing use of fluorocarbons during the twentieth century has led to rising concerns regarding the impact of these compounds on the environment. Refrigerant CFC gases came under suspicion of causing ozone depletion in the atmosphere in 1974. By 1985 a large ozone hole was discovered growing over Antarctic.[1-14] This discovery resulted in the creation of the Montreal Protocol of 1987 banning the commercial use of

CFC gases. [1-15] It is hoped that their elimination will reduce the atmospheric load of chlorofluorocarbons and allow the atmosphere to repair itself. Surprisingly, the replacement refrigerants were hydrofluorocarbons (HFCs) – yet more fluoroorganic compounds. Today these replacement HFCs have been detected in the stratosphere and are under investigation by scientists for their potential long-term effects on our atmosphere. [1-16]

While HFC and PFC gases do not appear to contribute to ozone depletion, they have become a concern as "Greenhouse Gases" (GHGs). Fluorocarbons strongly absorb infrared radiation in the 1000 to 1400 cm^{-1} range. Based on their chemical and thermal stability it is estimated that they have a potential atmospheric "life" of 100 to 1000-years during which they will continue to contribute to atmospheric warming. [1-17][1-18] As a result of these findings the 1997 Kyoto Protocols of the United Nations' Framework Convention on Climate Change (UNFCCC) lists nine PFCs, CF_4 through C_9F_{20}, and the replacement HFC refrigerant gases in use since 1987 as GHGs. Today UNFCCC reports routinely include the atmospheric accumulation of these gases in their listing of all known global warming contributors. [1-19][1-20]

Since fluorinated compounds are very stable and nearly biologically inert, they have also been labeled as highly persistent organic pollutants (POPS) with estimated lives in the biosphere that range from 1000 to 50,000 years.[1-21] Starting in the late 1960's scientists began focusing on the impact of fluorinated compounds that were accumulating in the biosphere. Current studies are finding that the increasing use of perfluorinated chemicals have led to their buildup in the food chain. For example, perfluorooctanesulfonic acid (PFOS) developed and sold by 3M since 1949 and a key ingredient that was used in Scotchguard©, was found present in human blood samples that were collected from around the globe in 1997. The results of this investigation caused 3M to discontinue the manufacture of products containing PFOS in 2001. [1-22] Unfortunately, even with the diminished use of PFOS's over the last decade, current environmental studies have identified it as still present in human breast milk [1-23] and are finding that it continues to accumulate in animals around the world. [1-24] As a consequence of PFOS's pervasiveness in the biosphere the Stockholm Convention in 2009 included it and its salts in the Annex B report as a POP and recommended that this compound be restricted in its global use in order to minimize its environmental impact. [1-21][1-25] [1-26]

1.6 Goals of this study

Curiously, despite the increasing worldwide use of fluorinated compounds and the subsequent environmental accumulation, little thermochemical data has been published in the open literature. The data that is available in the scientific journals is found to be either old or in poor agreement.[1-27][1- 28] The initial aim of this study is to determine if correlation gas-chromatography (C-GC) can be successfully used to determine the vaporization enthalpies of perfluorinated and partially fluorinated hydrocarbons. Successful application of this technique depends on the appropriate selection of the type of standards used to correlate with the compounds under investigation. Previous research with hydrocarbons found that their structure was not a significant factor in their selection as reference standards. Any hydrocarbon - aliphatic, branched cyclic, or aromatic - may be used as standards for correlating with another hydrocarbon. However, it was also found that if functional groups were present the number and nature of the functional groups had to be considered when selecting reference standards. The best correlation results were obtained when the reference standards were in the same chemical family as the compound of interest. [1-29][1-30][1-31]

A secondary goal of this study is to examine how the vaporization enthalpy of the *n*-perfluorinated alkanes behave as a function of the number of CF_2 units within the compound and to compare this with the analogous relationship of the *n*-alkanes to increasing CH_2 units. Figure 3 is a representative plot of the *n*-alkanes (C_5 to C_{30}) vs. their vaporization enthalpies at 298.15 K. [3-31]

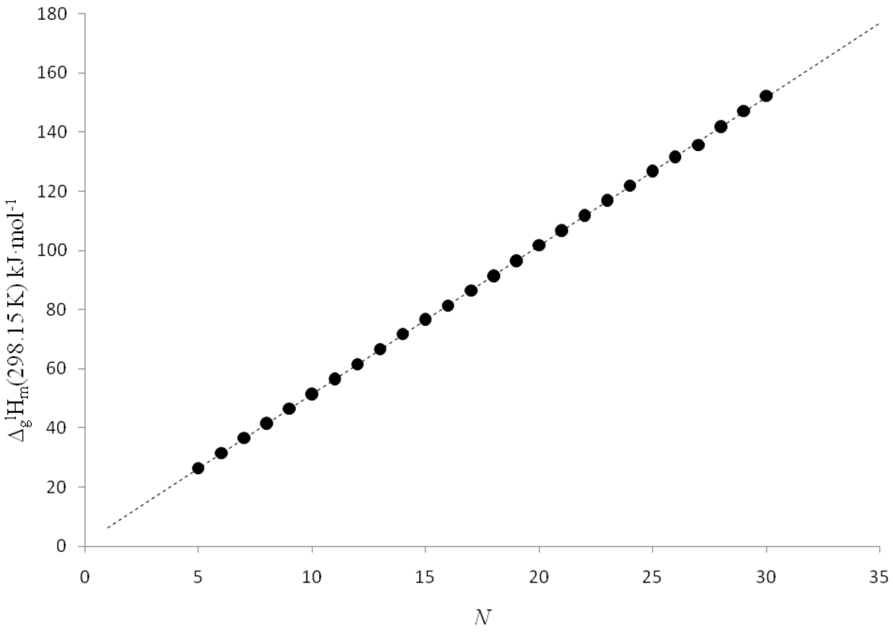


Fig. 3 Vaporization enthalpies, $\Delta_g^l H_m(298.15\ K)$ as a function of the number of carbon atoms (N) for hydrocarbon *n*-alkanes (N = 5 to 30). The dashed line represents the linear regression equation:

$$\Delta_g^l H_m(298.15\ K) = (0.20 \pm 0.00)N - (0.27 \pm 0.03); \qquad r^2 = 0.9999$$

This linear plot of the vaporization enthalpies for these small to intermediate sized hydrocarbons is extraordinarily and is attributed to increasing intermolecular interactions as the molecular size increases with the addition of each methylene group. The size of the incremental increase to $\Delta_g^l H_m$(298 K) with respect to the number of CH_2 units is found to be consistent up to approximately C_{60}. For *n*-alkanes above C_{60} the incremental increase in vaporization enthalpies are observed to diminish with respect to the number of CH_2 units composing the carbon backbone and has been attributed to the flexibility afforded these larger molecules. Unlike the relatively stiff, rod like *n*-perfluoroalkanes, conformational flexibility permits these long *n*-alkane hydrocarbons to fold back upon themselves and interact with different sections within the same molecule. This tendency to flex and bend suggests that as the size of the molecule lengthens the intramolecular interactions should increase at the expense of intermolecular interactions. The proposed hypothesis predicts that at some size, the incremental change of vaporization enthalpy of the *n*-alkanes relative to the increasing number of CH_2 groups will begin to diminish and show curvature as the number of CH_2 groups continues to increase. This hypothesis has been experimentally tested for *n*-alkanes from C_{60} up to C_{92}. [3-33] Figure 4 is a plot of the experimentally determined data and displays this predicted curvature. The fitted quadratic equation for this plot has a correlation coefficient of $r^2 > 0.99$ that supports the hypothesis of a reduction in the incremental change in vaporization enthalpy for large molecules exceeding C_{60}. This hypothesis further suggests that with increasing size the vaporization enthalpy for very large hydrocarbon *n*-alkanes will continue to diminish and should approach zero.

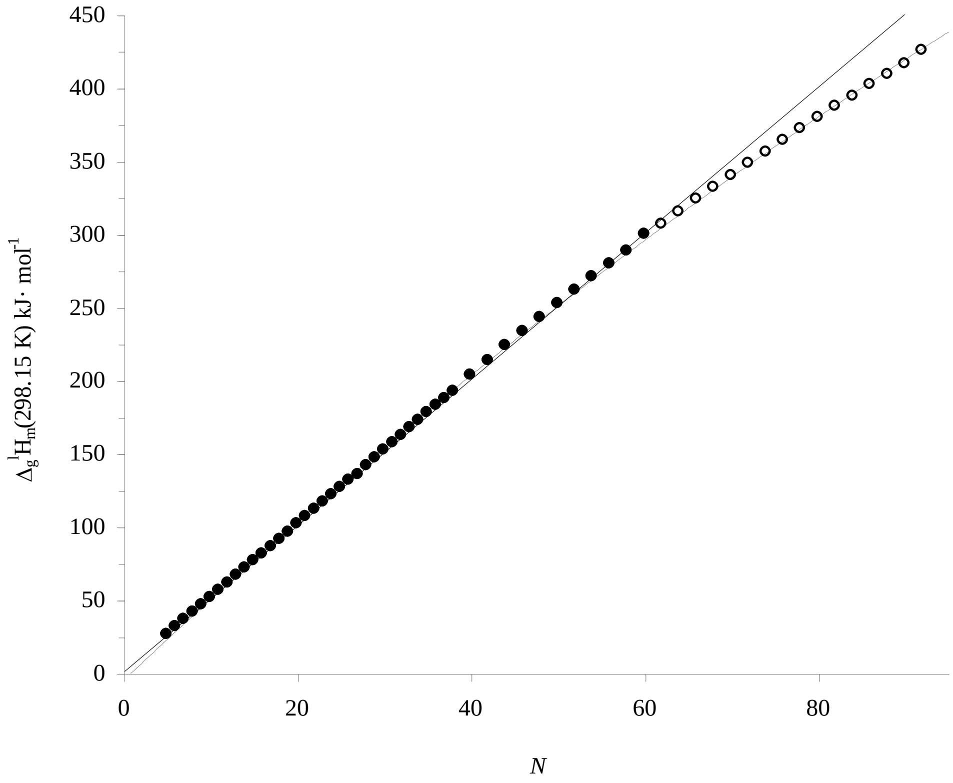


Fig. 4. Vaporization enthalpies as a function of the number of carbon atoms for hydrocarbon *n*-alkanes (*N* = 5 to 92). The straight trend line applies to C_5 to C_{60}. The curved line represents both C_5 to C_{60} and the even n-alkanes from C_{40} to C_{92}.

The linear regression of N = 5 to 60 is given by the equation:

$$\Delta_g^l H_m(298.15\text{ K}) = (5.00 \pm 0.01)\,N + (1.87 \pm 0.32) \qquad r^2 = 0.9998$$

For the full n-alkane series (*N* = 5 to 92) the equation is a second order polynomial give by:

$$\Delta_g^l H_m(298.15\text{ K}) = -\,0.10\,N^2 + 5.60\,N - 4.97 \qquad r^2 = 0.9998$$

A final goal of this work is to evaluate whether fluorine must be treated as a functional group or, due to its size relative to hydrogen, whether it can be treated like a hydrogen atom in the determination of a compound's vaporization enthalpy. As will be described more fully in chapter 3, this initial study has determined that, depending on the number of fluorines present and the structure of the compound, fluorine appears to behave as a functional group, and consideration has to be given to the number of fluorines present in the molecule.

1-1. Kirsh, P.; *Modern Fluoroorganic Chemistry:Synthesis, Reactivity, Applications*, Wiley-VCH, Weinheim, 2004.

1-2. O'Hagan, D.; Understanding Organofluorine Chemistry. An Introduction to the C–F Bond., *Chem. Soc. Rev.*, **2008**, *37*, 308-319.

1-3. Howard, J. A. K.; Hoy, V. J.; O'Hagan, D.; Smith, G. T.; How Good is Fluorine as a Hydrogen Bond Acceptor?, *Tetrahedron*, **1996**, *52*, 12613-12622.

1-4. Dunnitz, J. D.; Taylor, R.; Organic Fluorine Hardly Ever Accepts Hydrogen Bonds; *Chem.-Eur. J.*, **1997**, *3*, 89-98.

1-5. Lide, D. R., ed.; *CRC Handbook of Chemistry and Physics, Internet Version 2005*, <http://www.hbcpnetbase.com>, CRC Press, Boca Raton, FL, 2005.

1-6. Atkins, P.; Pauala, J.; *Atkins Physical Chemistry,* 8th Ed., Oxford University Press, Oxford, 2006.

1-7. Smart, B. E.; Fluorine Substituent Effects (on Bioactivity); *J. Fluorine Chem.*, **2001**, *109*, 3-11.

1-8. Sandford, G.; Perfluoroalkanes, *Tetrahedron*, **2002,** *59*, 437-454.

1-9. Castro, C. I.; Briceno, J. C.; Perfluorocarbon-Based Oxygen Carriers: Review of Products and Trials; *Artifl. Organs*, **2010**, *34* (8), 622-634.

1-10. Dias, A.M.A.: Freire, M., Coutinho, J.A.P., Marrucho, I.M.; *Solubility of Oxygen in Liquid Perfluorocarbons*, **2004,** (*222–223*), 325–330.

1-11. Okazoe, T.; Overview on the History of Organofluorine Chemistry from the Viewpoint of Material Industry, *Proc. Jpn. Acad*., Ser. B, **2009**, *85*, 276-289.

1-12. Dolbier Jr., W. R.; Fluorine Chemistry at the Millennium, *J. Fluorine Chem.*, 2005, *126*, 157–163

1-13. Lewandowski, G.; Meissner, E.; Milchert, E.; Special Applications of Fluorinated Organic Compounds, *J. Haz. Matl.*, **2006**, *A136*, 385-391.

1-14. Farman, J. C.; Gardiner, B. G.; Shanklin, J. D.; Large Losses of Total Ozone in Antarctica Reveal ClO_x / NO_x interaction, Nature, **1985,** *315*, 207-210.

1-15. Tsai, WT.; Environmental Hazards and Health Risk of Common Liquid Perfluoro-n-alkanes, Potent Greenhouse Gases, *Environment International*, **2009**, *35*, 418–424.

1-16. McCulloch, A.; Fluorocarbons in the Global Environment: A Review of the Important Interactions with Atmospheric Chemistry and Physics, *J. Fluorine Chem.*, **2003**, *123*, 21-29.

1-17. Tsai, WT.; An Overview of Environmental Hazards and Exposure Risk of Hydrofluorocarbons (HFCs), *Chemosphere*, **2005**, *61*, 1539–1547.

1-18. Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007— the Physical Science Basis*. Geneva, Switzerland: IPCC; 2007.

1-19. *Fourth National Report on Human Exposure to Environmental Chemicals*, Executive Summary, Department of Health and Human Services Centers for Disease Control and Prevention National Center for Environmental Health, Atlanta, USA; 2009.

1-20. World Meteorological Organization (WMO), *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System*, 2004.

1-21. Stockholm Convention , *Climate Change and POPS: Predicting the Impacts,* 2011.

1-22. Giesy, J . P.; Kannan, K.; Peer Review: Perfluorochemical Surfactants in the Environment, *Enviro. Sci. Technol.*, **2002**, *36* (7), 146A-152A.

1-23. Tao, L.; Kannan, K.; Wong, C. M.; Arcaro, K.; Butenhoff, J. L.; Perfluorinated Compounds in Human Milk from Massachusetts, U.S.A; *Enviro. Sci. Technol.*, **2008**, *42*, 3096–3101.

1-24. Schiavone, A.; Corolini, S.; Kannan, K.; Tao, L.; Trivelpiece, W.; Torres Jr., D.; Focardi, S.; Perfluorinated Contaminants in Fur Seal Pups and Penguin Eggs from South Shetland, Antarctica, *Sci. Tot. Enviro.*, **2009**, *407*, 3899–3904.

1-25 Swedish Chemicals Inspectorate and the Swedish EPA, *Perfluorooctane Sulfate (PFOS)*: Dossier prepared in support for a nomination of PFOS to the UN-ECE LRTAP Protocol and the Stockholm Convention, August 2004.

1-26. Renner, R.; Piecing Together the Perfluorinated Puzzle, *Anal. Chem.*, **2005**, *77*, 15-16.

1-27. Acree, W.; Chickos, J.S; Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion From 1880 to 2010, J. Phys. Chem. Ref. Data, **2010**, *39*, 043101.

1-28. Dias, A.M.A.; Goncalves, C.M.B.; Cacu, A.I.; Santos, L.M.N.B.F.; Pineiro, M.M.; Vega, L.F.; Coutinho, J.A.P., Marrucho, I.M., Densities and Vapor Pressures of Highly Fluorinated Compounds; *J. Chem. Eng. Data*, **2005**, *50*, 1328-1333.

1-29. Chickos, J.S.; Hosseini, S.; Hesse, D.G.; Determination of Vaporization Enthalpies of Simple Organic Molecules by Correlations of Changes in Gas Chromatographic Net Retention Times, *Thermochimea Acta*, **1995,** *249*, 41-62.

1-30. Chickos, J. S.; Hanshaw, W.; Vapor Pressures and Vaporization Enthalpies of the *n*-Alkanes from C_{21}-C_{30} at T = 298.15 K by Correlation–Gas Chromatography, *J. Chem. Eng. Data* **2004**, *49*, 77–85.

1-31. Chickos, J. S.; Hanshaw, W.; Vapor Pressures and Vaporization Enthalpies of the *n*-Alkanes from C_{31} to C_{38} at T = 298.15 K by Correlation Gas Chromatography, *J. Chem. Eng. Data* **2004**, *49*, 620–630.

1-32. Chickos, J. S.; Wang T.; Sharma, E.; Hypothetical Thermodynamic Properties: Vapor Pressures and Vaporization Enthalpies of the Even *n*-Alkanes from C_{40} to C_{76} at T = 298.15 K by Correlation-Gas Chromatography. Are the vaporization Enthalpies a Linear Function of Carbon Number?, *J. Chem. Eng. Data* **2008**, *53*, 481-491.

1-33. Chickos, J. S.; Dmitry, L.; Hypothetical Thermodynamic Properties: Vapor Pressures and Vaporization Enthalpies of the Even *n*-Alkanes from C_{78} to C_{92} at T = 298.15 K by Correlation-Gas Chromatography, *J. Chem. Eng. Data* **2008**, *53*, 2432-2440.

Chapter 2

2.1 Experimental

All compounds used in this study were obtained from commercial sources and used as purchased. Appendix I list the purities and the companies that provided the samples. Chemicals of high purity were not deemed critical to this study since they were used in mixtures that were subsequently separated by gas chromatography.

Experiments were performed using a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a flame ionization detector and a split-splitless capillary injection inlet system which was ran at a ratio ≈100:1 in order to improve resolution and minimize column loading. The instrument was run isothermally using a Restek RTX-200 capillary column (30 m, 0.25 mm ID.) coated with a cross-bonded trifluoropropyl methyl polysiloxane stationary phase. Helium was used as the carrier gas. All temperatures were measured using a Vernier Temperature probe. Temperatures above ambient were controlled by the HP 5890 to within ±0.1 K. Sub-ambient temperatures were achieved by immersion of the column into a VWR Scientific Products Chiller's tank (model 1166) filled with a 50/50 ethylene glycol–water mixture. This setup enabled temperatures to be controlled within ±0.5 K. HP Chemstation software was employed to record the retention times of all analytes to three decimal places.

Each experimental mixture was composed of a nonretained component, a solution solvent, one or more fluorinated compounds and a minimum of three standards. All solution components in a mixture had published vaporization enthalpy values. The standards used with each mixture were selected so they and the compounds under investigation could be separated throughout the temperature range of the experiment. Methane was bubbled into each sample solution and used as the non-retained reference component except in mixtures 5 and 6. For those two mixtures, which were run above 373 K, perfluorooctane was used as both the nonretained reference and the solvent. At the experimental temperatures of this work, the carrier gas' viscosity increases with increasing temperature. Consequently, the nonretained analyte displayed an increasing dwell time with increasing temperature while the retention time of the remaining analytes decreased. This measurable property was used as a criterion to verify that the nonretained compound is not being retained on the column. The column dwell times of the nonretained analyte was used to determine the dead volume of the column.

All solution mixtures were run twice to verify reproducibility. Each run was composed of seven separate isothermal GC injections at 5 K increments over a temperature range of 30 K. The adjusted retention time, t_a, was obtained by subtracting the nonretained reference's time from each analyte's retention time thereby determining the individual compound's dwell time within the column. The adjusted retention time of each analyte is inversely proportional to its vapor pressure off the column. Plotting the seven adjusted retention times for each individual compound as $\ln(t_a/t_o)$ vs. $1/(T/\mathrm{K})$, where $t_o = 1\mathrm{min}$, and applying a linear regression analysis produced a straight line for each solute. If the correlation coefficient, r^2 was > 0.98 the equation was accepted and considered linear. $R^2 < 0.98$ usually indicate some retention of the non-retained reference.

The slope of each line is equal to $-\Delta_{sol}{}^{g}H_m(T_m)/R$. [2-1][2-2] Multiplying by –R, the molar gas constant, results in a measure of the enthalpy of transfer of the solute from the condensed phase of the column to the gas phase, $\Delta_{sol}{}^{g}H_m(T_m)$, where T_m is the mean temperature of the run. For the rest of this report, $\Delta_{sol}{}^{g}H_m(T_m)$ will be referred to as the enthalpy of transfer. Equation 2-1 illustrates the relationship of the enthalpy of transfer for a solute to the sum of the vaporization enthalpy, $\Delta_l{}^{g}H_m(T_m)$, and the enthalpy of interaction of the analyte on the column, $\Delta_{sol}H_m(T_m)$. Note that in this equation $\Delta_{sol}H_m(T_m)$ is small relative to $\Delta_l{}^{g}H_m(T_m)$ and can essentially be ignored.

$$\Delta_{sol}{}^{g}H_m(T_m) = \Delta_l{}^{g}H_m(T_m) + \Delta_{sol}H_m(T_m) \qquad (2\text{-}1)$$

A plot of $\Delta_l{}^{g}H_m(298.15\text{ K})$ vs. $\Delta_{sol}{}^{g}H_m(T_m)$ for the mixture's three standards results in a linear relationship between the two sets of values. Performing a linear regression analysis on this data produces a correlation equation relating these two enthalpies. This correlation equation was considered acceptable if the $r^2 > 0.98$. The resultant correlation equation was used to calculate the vaporization enthalpies and uncertainties of all the compounds within the mixture. The calculated enthalpies for the compounds under investigation were then compared to the published vaporization enthalpies to determine if a correlation exists between them and the mixture's standards.

Table 2-1 lists a summary of $\Delta_l{}^{g}H_m(298.15\text{ K})$ literature values in column 3 and the corresponding bibliography reference in column 4. Uncertainties are listed when available in the literature.

Table 2-1. Published $\Delta_l^g H_m$(298.15 K) reference values.

Formula	Name	$\Delta_l^g H_m$(298) kJ·mol^{-1}	Ref.
C_6F_6	hexafluorobenzene	36.1±0.1	2-4
C_6F_{14}	perfluorohexane	32.5±0.1	2-4
$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene	37.5	2-5
$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene	37.2	2-5
C_7F_8	octafluorotoluene	40.5 ± 0.2	2-4
C_7F_{16}	perfluoroheptane	36.3 ± 0.3	2-7
$C_7H_5F_3$	trifluorotoluene	37.1	2-5
C_7H_8	toluene	38.1 ± 0.4	2-8
C_7H_{16}	heptane	36.6	2-10
C_8F_{16}	perfluoro-1,3-dimethylcyclohexane	38.6 ± 0.1	2-11
C_8F_{18}	perfluorooctane	41.1 ± 0.1	2-6
C_8HF_{17}	1H-perfluorooctane	43.4 ± 0.2	2-4
C_8H_{10}	*o*-xylene	42.9	2-2
C_9F_{20}	perfluorononane	45.3± 0.2	2-4
C_9H_{12}	mesitylene	47.6	2-12
$C_{10}F_{18}$	*cis*-perfluorodecalin	46.2 ± 0.1	2-11
$C_{10}F_{18}$	*trans*-perfluorodecalin	45.4 ± 0.1	2-11
$C_{10}H_{22}$	decane	51.4	2-10
$C_{10}H_8$	naphthalene	55.0 ± 1.4	2-6
$C_{12}F_{27}N$	perfluorotributylamine	60.3 ± 0.1	2-15
$C_{12}H_{26}$	dodecane	61.5	2-10
$C_{14}H_{30}$	tetradecane	71.7	2-10

For compounds that have published fusion, sublimation or vaporization enthalpy values at temperatures other than 298 K equations 2-2, 2-3, and 2-4 were used to adjust their enthalpies to 298 K. Equation 2-5 relates the thermodynamic enthalpy values of vaporization, sublimation and fusion using the thermodynamic cycle. Previous work has demonstrated that use of these four equations enable the calculation of values that are in good agreement to experimentally measured values of $\Delta_l^g H_m$(298.15 K).[2-3]

Vaporization Enthalpy

$$\begin{aligned}&\Delta_{\mathrm{vap}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) = \Delta_{\mathrm{vap}}H^{\mathrm{o}}_{\mathrm{m}}(\bar{T}/\mathrm{K}) + \\ &\quad 10.58 + 0.26(C_{p,m}(\mathrm{l},\ 298.15\ \mathrm{K})/(\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}))\ \{\bar{T}/\mathrm{K} - 298.15\ \mathrm{K}\}/1000 \qquad (2\text{-}2)\end{aligned}$$

Sublimation Enthalpy

$$\begin{aligned}&\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = \Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}(\bar{T}/\mathrm{K}) + \\ &\quad [0.75 + 0.15(C_{p,m}(\mathrm{s},\ 298.15\ \mathrm{K})/\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}]\ \{\bar{T}/\mathrm{K} - 298.15\}/1000 \qquad (2\text{-}3)\end{aligned}$$

Fusion Enthalpy

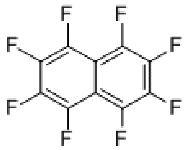
$$\begin{aligned}&\Delta_{\mathrm{fus}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = \Delta_{\mathrm{fus}}H_{\mathrm{m}}(T_{\mathrm{fus}}) + \\ &\quad [0.15\ C_{p,m}(\mathrm{s},\ 298.15\ \mathrm{K}) - 0.26\ C_{p,m}(\mathrm{l},\ 298.15\ \mathrm{K}) - 9.83][(\ T_{\mathrm{fus}}/\mathrm{K} - 298.15]/1000 \qquad (2\text{-}4)\end{aligned}$$

The thermodynamic equality that relates the phase change enthalpies:

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = \Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}{}^{\mathrm{o}}\ (298.15\ \mathrm{K}) - \Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}{}^{\mathrm{o}}\ (298.15\ \mathrm{K}) \qquad (2\text{-}5)$$

Adjustment of thermodynamic values to 298 K is dependent on determining the heat capacity of the liquid, $C_{p,m}(\mathrm{l})$, and/or solid, $C_{p,m}(\mathrm{cr})$. These $C_{p,m}$ values can be estimated using a group additive approach. [2-3]

As an example octafluoronapthalene can be used to illustrate the adjustment of thermodynamic values to 298 K for known fusion and sublimation enthalpy values, $\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}\ (T_m)$ and $\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$.



Examination of the structure finds 8 (C-F) bonds and 10 (>C=) quaternary aromatic sp^2 bonds. Using these 18 groups and the values listed for each group's bond type the liquid and solid heat capacities are calculated [2-3]:

Liquid: $C_{p,m}(l) = 8(16.2) + 10(15.3) = 282.6$ (2-6)

Solid: $C_{p,m}(cr) = 8(24.8) + 10(8.5) = 283.4$ (2-7)

The sublimation enthalpy at 298 K is calculated using data listed in Table 2-3 and equations 2-3:

$$\Delta_{cr}{}^{g}H_m{}^{o}\ (298.15\ K) = 79.4 + [0.75 + (0.15 * 283.4)][308-298]/1000$$

$$= 79.8\ kJ\cdot mol^{-1} \qquad (2\text{-}8)$$

Determining the fusion enthalpy; $\Delta_{cr}{}^{l}H_m{}^{o}$ (298.15 K) with eq. 2-4:

$$\Delta_{cr}{}^{l}H_m{}^{o}\ (298.15\ K) = 17.55 + [(0.15*283.4)-(0.26*282.6)-9.83][359-298]/1000$$

$$= 15.06\ kJ\cdot mol^{-1} \qquad (2\text{-}9)$$

Vaporization enthalpy at 298 K for this compound is derived by applying the thermodynamic cycle (eq. 2-5):

$$\Delta_{l}{}^{g}H_m(298.15\ K) = \Delta_{cr}{}^{g}H_m{}^{o}\ (298.15\ K) - \Delta_{cr}{}^{l}H_m{}^{o}\ (298.15\ K) \qquad (2\text{-}10)$$

$$\Delta_l^g H_m(298.15\ \mathrm{K})/(\mathrm{kJ\cdot mol^{-1}}) = 79.8 - 15.1 = 64.7\ \mathrm{kJ\cdot mol^{-1}} \qquad (2\text{-}11)$$

Table 2.2 lists the compounds that required temperature adjustment calculations of their vaporization enthalpies.

Table 2-2. Temperature adjusted vaporization enthalpies of experimental compounds. Enthalpy values are in kJ·mol^{-1} units.

	$\Delta_{cr}{}^{g}H_m(T_m)$	T_m/K	$\Delta_{cr}{}^{l}H_m(T_m)$	T_{fus}/K	$\Delta_{l}{}^{g}H_m(T_v)$	T_v/K	$C_{p,m}$(l)	$C_{p,m}$(cr)	$\Delta_{cr}{}^{g}H_m$(298 K)	$\Delta_{cr}{}^{l}H_m$(298 K)	$\Delta_{l}{}^{g}H_m$(298 K)	Ref.
perfluoro(methyl)cycloheaxane					35.2	409.7	348.8				35.3	2-8
1-fluoroheptane					54.0	425.5	242.5				35.3	2-16
1-fluorododecane					60.7	426.9	402.0				68.7	2-16
1-fluorotetradecane					61.4	402	465.8				77.7	2-16
perfluoronapthalene	79.4±2.5	308	17.55	359			282.6	283.4	79.83	15.06	64.7	2-17 2-18
perfluorodecane					34.0	420		496.4			51.0	2-13
decafluorobiphenyl					49.9	468		345.6			67.0	2-14
perfluorohexadecane	104.6	295	61.09	402			774.8	763.2	104.46	51.03	53.4	2-19 2-20

2-1. Peacock, L. A., Fuch, R.; Enthalpy of Vaporization Measurements by Gas Chromatography. *J. Am. Chem. Soc.* **1977**, *99*, 5524-5525.

2-2. Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Determination of Vaporization Enthalpies of Simple Organic Molecules by Correlations of Changes in Gas Chromatographic Net Retention Times. *Thermochim. Acta*; **1995**, *249*, 41-61.

2-3. Acree, W.; Chickos, J.S; Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion From 1880 to 2010. *J. Phys. Chem. Ref. Data*, **2010**, *39*, 043101.

2-4. Dias, A.M.A.; Goncalves, C.M.B.; Caco, A.I.; Santos, L.M.N.B.F.; Pineiro, M.M.; Vega, L.F.; Coutinho, J.A.P., Marrucho, I.M., Densities and Vapor Pressures of Highly Fluorinated Compounds. *J. Chem. Eng. Data*, **2005**, *50*, 1328-1333.

2-5. Basarova, P.; Svoboda, V.; Calculation of Heats of Vaporization of Halogenated Hydrocarbons from Saturated Vapour Pressure Data. *Fluid Phase Equilib.*, **1991**, *68*, 13-34.

2-6. Varushchenko, R. M.; Bulgakova, L. L.; Minzabekyants, P. S.; Makarov, K. N.; *Russ. J. Phys. Chem.*, **1981,** *55*, 1480-1482.

2-7. Steele, W. V.; Chirico, R. D.; S. E. Knipmeyer, S. E.; Nguyen, A.; Vapor Pressure, Heat Capacity, and Density along the Saturation Line, Measurements for Cyclohexanol, 2-Cyclohexen-1-one, 1,2-Dichloropropane, 1,4-Di-*tert*-butylbenzene, (±)-2-Ethylhexanoic Acid, 2-(Methylamino)ethanol, Perfluoro-*n*-heptane, and Sulfolane. *J. Chem. Eng. Data*, **1997**, *42*, 1021-1036.

2-8. Rox, M. V.; Temprado, M.; Chickos, J. S.; Nagano, Y.; Critically Evaluated Thermochemical Properties of Polycyclic Aromatic Hydrocarbons. *J. Phys. Chem. Ref. Data*, **2008**, *37* (4), 1855 – 1996.

2-9. Verevkin, S.P.;Thermochemistry of Phenols: Quatification of the Ortho-, Para- and Meta- Interactions in Tert-Alkyl Substituated Phenols. *J. Chem. Thermodyn.*, **1999**, *31*, 559-585.

2-10. Ruzicka, K.; Majer, V.; Simultaneous Treatment of Vapor Pressures and Related Thermal Data Between the Triple Point and Normal Boiling Temperatures for *n*-Alkanes C5 – C20. *J. Phys. Chem. Ref. Data*, **1994**, *23* (1), 1-39.

2-11. Varushchenko, R. M.; Druzhinina, A. I.; Pashchenko, I.L.; Thermodynamics of Vaporization of Some Cyclic Perfluorocarbons. *Fluid Phase Equilibria*, **1996**, *126*, 93-104.

2-12. V. Ruzicka, V.; Zabransky, M.; Ruzicka, K.; Majer, V.; Vapor Pressures for a Group of High-Boiling Alkylbenzenes Under Environmental Conditions. *Thermochim. Acta*, **1994**, *245*, 121-144.

2-13**.** Ermakov, N. V.; Skripov, V. P. Saturation Line Critical Parameters and Reachable Overheat of Perfluoroparaffins. *Zh. Fiz. Khim.*, **1967**, *41*, 77-81.

2-14**.** Back, D. D.; Grzyll, L. R.; Corrigan, M.; DSC Enthalpy of Vaporization Measurements of High Temperature Two-phase Working Fluids. *Thermochim. Acta*, **1996**, *272*, 53-63.

2-15. Varushchenko, R. M.; Droujinina, A. I.; *J. Chem. Thermodyn*. 1995 *27*, 355.

2-16. Li, James C. M.; Rossini, Fredrick D.; Vapor Pressure and Boiling Points of the 1-Fluoroalkanes, 1-Chloroalkanes, 1-Bromoalkanes, and 1-Iodoalkanes, C_1 to C_{20}., *J. Chem. Eng. Data*, **1961**, *6* (2), 268-270.

2-17. Michaud, F.; Negrier, Ph.; Mikailitchenko, D.; Marbeuf, A.; Haget, Y.; Cuevas-Diarte, M.; Oonk, H. A. J.; *Mol. Cryst. Liq. Cryst.*, **1999** *326*, 409 .

2-18. Radchenko, L. G.; Kataigorodskii, A. I.; *Zh. Fiz. Khim.*, **1974** *48*, 2702-2074; Eng. Edit. 1595-1597.

2-19. Starkweather, H. W., Melting and Crystalline Transitions in Normal Perfluoroalkanes and Poly(tetrafluoroethylene), *Marcomolecules*, **1986** *19* (4), 1131-1134.

2-20. Bradley, R. S.; Waghorn, G. S. C.; *Proc. Roy. Soc.*, **1951** *A206*, 65-72.

Chapter 3

Results

3.1 *n*-Perfluorocarbons

The GC chromatographs of the *n*-perfluoroalkanes are remarkable. Despite boiling temperatures that are similar to their analogous hydrocarbon alkanes their retention times are surprisingly short in comparison. Peak shapes for these perfluorinated aliphatics was determined to be highly dependent on concentration, flow rate and temperature. Using dilute mixtures, a column pressure set to 3 psi was found to achieve the best separation and enabled sharper peak definition. For mixture 1, which was composed of methane, perfluorohexane, perfluoroheptane, perfluorooctane and perfluorononane, it was also determined that subambient temperatures were needed to accomplish compound separation. Figure 3.1 is shown as an example of a gas chromatograph obtained for mixture 1 at T = 282.1 K.

Table 3.1 below lists the experimentally obtained retention times over the test temperature range, 297.2 K to 266.7 K, for mixture 1 which were subsequently used to calculate the adjusted retention times for the individual components of the solution.

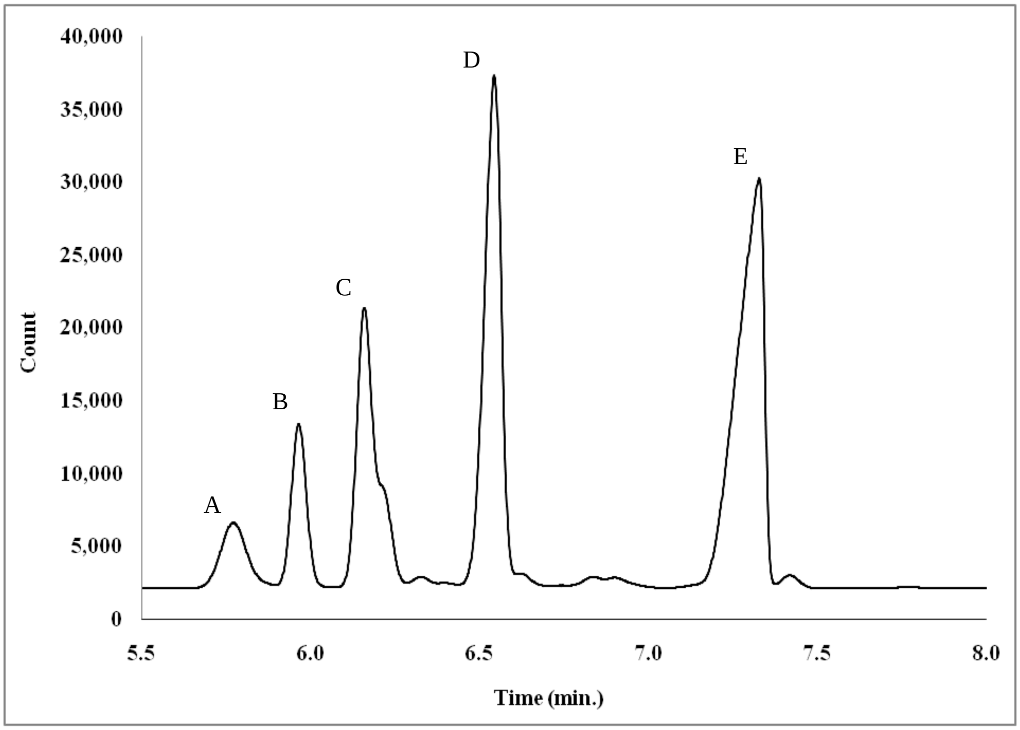


Fig. 3.1. Gas chromatograph trace for mixture 1 containing: methane (A), perfluorohexane (B), perfluoroheptane (C), perfluorooctane (D), and perfluorononane (E) at *T* = 282.1 K

Table 3.1. Unadjusted Retention Times for Mixture 1.

T/K	297.2	292.2	287.2	282.1	276.9	271.8	266.7
Run 1				t/min			
methane[a]	5.994	5.912	5.845	5.770	5.723	5.643	5.583
perfluorohexane	6.129	6.062	6.015	5.964	5.946	5.903	5.885
perfluoroheptane	6.253	6.204	6.179	6.158	6.180	6.188	6.231
perfluorooctane	6.467	6.457	6.485	6.543	6.670	6.807	7.026
perfluorononane[b]	6.875	6.944	7.085	7.326	7.704	8.158	8.853

[a] Nonretained. [b] Mixture solvent.

As mentioned in Chapter 2, each analyte's dwell time is due to its interaction with the column and its vapor pressure on the column. The adjusted retention time (t_a) can be obtained by subtracting the measured nonretained reference's time from each component's actual time, t. A plot of $\ln(t_o/t_a)$ vs. $1/T$, where t_o =1 minute results in a linear relationship where the slope of the derived equation is $-\Delta_{sln}{}^{g}H_m(T_m)/R$. Figure 3.2 is an illustration of the plot for the compounds used in the first run of mixture 1 and is typical for all runs cited in this report.

The five compounds, C_6F_{14} through $C_{10}F_{22}$, were the only *n*-perfluoroalkanes found to have published vaporization enthalpies that were determined reliable enough to be used as standards after adjustment to T = 298.15 K. Sublimation and fusion thermodynamic data for perfluorohexadecane, $C_{16}F_{34}$, was also found in the open literature but after adjustment to T = 298.15 K and application of the thermodynamic cycle the resultant vaporization enthalpy was considered to be in error. It was decided that the enthalpy of sublimation given for $C_{16}F_{34}$ was much too low. As a result this compound was rejected as a standard in evaluating the enthalpies of other compounds (ref. Table 2-2).

Mixture 1, composed of C_6F_{14} though $C_9F_{20,}$ was initially run to determine if a linear correlation actually exists between $\Delta_{sln}{}^{g}H_m(T_m)$ and $\Delta_l{}^{g}H_m(298.15\text{ K})$ as was found for the analogous hydrocarbon counterparts.

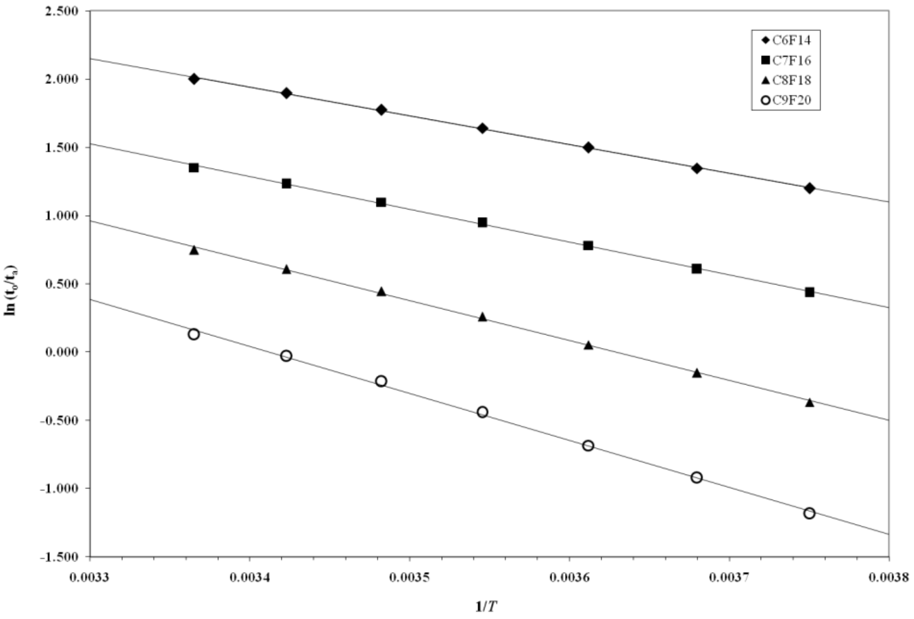


Fig. 3.2 Plot of the natural log of the reciprocal of the adjusted retention times, ln(t_0/t_a) vs. 1/*T* for mixture 1. All four linear equations have correlation coefficients > 0.99: perfluorohexane (♦); perfluoroheptane (■); perfluorooctane (▲); perfluorononane (□). *T* is the temperature of the GC run.

Results from runs 1 and 2 are reported in Table 3.2 and 3.3, respectively. The slopes and intercepts for mixture 1 are listed in columns 2 and 3 and the enthalpies of transfer from the stationary phase of the column to the gas phase are listed in column 4. The equation listed under each table is the derived correlation equation for mixture 1's standards.

Table 3.2. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

mixture 1	slope	intercept	$\Delta_{sln}{}^{g}H_m$(281.9 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.	calcd
perfluorohexane	-2103.8	9.094	17.49	32.5	32.8 ± 3.0
perfluoroheptane	-2402.6	9.454	19.98	36.3 ± 0.3	35.9 ± 3.2
perfluorooctane	-2925.4	10.617	24.32	41.1 ± 0.1	41.3 ± 3.5
Perfluorononane[a]	-3444.0	11.751	28.64	45.3 ± 0.2	46.6 ± 3.9

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.24 ± 0.11) $\Delta_{sln}{}^{g}H_m$(281.9 K) + (11.05 ± 2.28) $r^2 = 0.9923$ (1.1)

[a] Mixture solvent.

Table 3.3. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

mixture 1	slope	intercept	$\Delta_{sln}{}^{g}H_m$(281.9 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Run 2	T/K			lit.[b]	calc
perfluorohexane	-2108.8	9.110	17.53	**32.5**	32.8 ± 3.1
perfluoroheptane	-2401.8	9.451	19.97	**36.3 ± 0.3**	35.9 ± 3.3
perfluorooctane	-2917.4	10.588	24.26	**41.1 ± 0.1**	41.3 ± 3.6
perfluorononane[a]	-3454.1	11.785	28.72	45.3 ± 0.2	46.9 ± 4.0

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.26 ± 0.11) $\Delta_{sln}{}^{g}H_m$(281.9 K) + (10.70 ± 2.37) $r^2 = 0.9919$ (1.2)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Figure 3.3 is a plot of the standards' data from Table 3.2, columns 5 and 6, which confirms that a correlation exists between the published vaporization enthalpy values and the GC derived enthalpies of transfer for these three perfluorinated compounds.

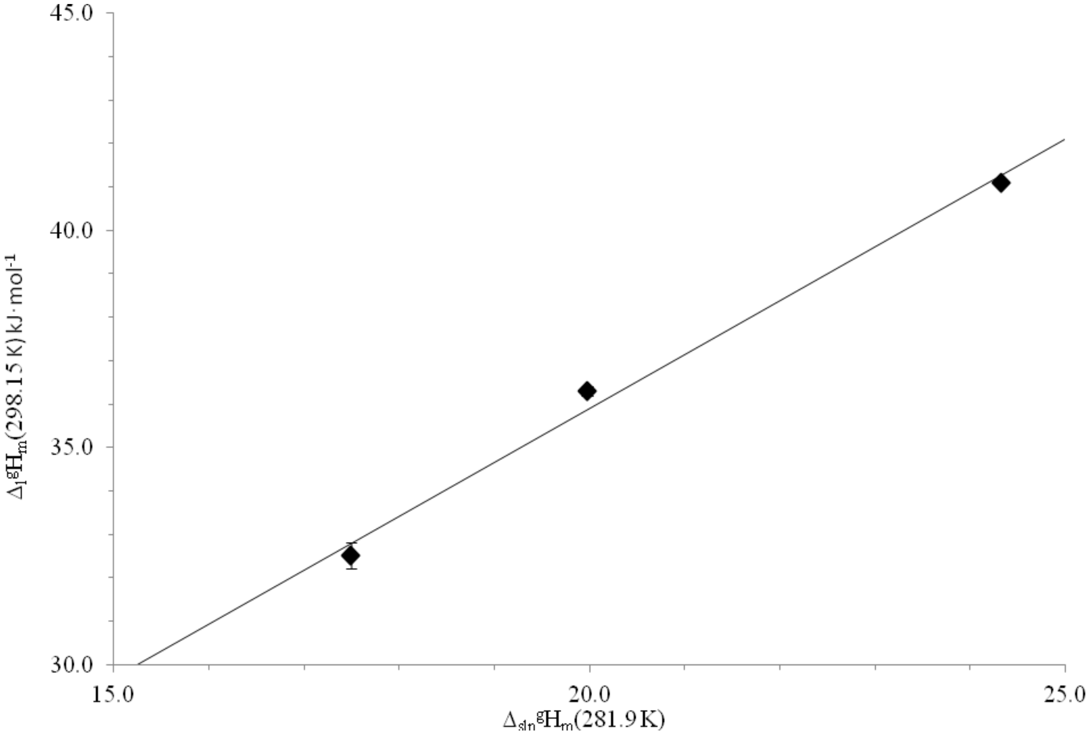


Fig.3.3. Data from run 1 of mixture 1. Correlation plot of published enthalpy of vaporizations, $\Delta_l{}^{g}H_m$(298 K), vs. enthalpy of transfers, $\Delta_{sln}{}^{g}H_m$(281.9 K) for C_6F_{14}, C_7F_{16}, and C_8F_{18}. Uncertainties in published measurements are shown as error bars when available.

The scarcity of experimental vaporization enthalpy data for *n*-perfluoroalkanes obviously provides an impediment for any additional correlations involving larger perfluorinated alkanes. A similar barrier was encountered with hydrocarbon alkanes for lengths > C_{20}. In that study, after confirming correlation linearity of the smaller *n*-alkanes, a “stepladder” approach was employed to evaluate the larger *n*-alkanes. [3-1, 3-2] This same technique was employed with the perfluorinated alkanes. For mixture 2, three smaller *n*-perfluoroalkane standards with known vaporization enthalpies, C_8F_{18}, C_9F_{20} and $C_{10}F_{22}$, were used to determine the correlation equation. This derived equation was then used to calculate the $\Delta_l^gH_m$(298.15 K) values for $C_{12}F_{24}$, $C_{13}F_{28}$, and $C_{14}F_{30}$. The results are reported in column 6 of Tables 3.4 and 3.5. These new $\Delta_l^gH_m$(298.15 K) values for the three larger perfluorinated compounds were subsequently treated as standards for evaluating the next higher *n*-perfluoroalkanes, $C_{15}F_{32}$ and $C_{16}F_{34}$ in mixture 3. A similar stepwise approach was used for mixtures 4 and 5 thereby enabling the evaluation of the remaining two perfluoroalkanes up to $C_{24}F_{50}$.

It should be noted that the limited solubility of the *n*-perfluoroalkanes in conventional solvents necessitated the use of an *n*-perfluoroalkane as a solution solvent. Normally the solvent of a mixture is not used as a standard but due to the limited availability of published vaporization enthalpy data and the limited number of liquid *n*-perfluorocarbon compounds available, either C_8F_{18} or C_9F_{20} was employed in a few of the mixtures as both a solvent and standard. To minimize the risk of accepting poor experimentally derived vaporization enthalpy values for these known compounds when used as a solvent, an arbitrary error limit of ±5% with respect to the literature value was set as the level of acceptance or rejection of a calculated $\Delta_l^gH_m$(298.15 K) value. Solution solvents are noted under each mixture’s data table.

Table 3.4 – 3.11 list the experimentally derived enthalpy data for mixtures 2 through 5 for the *n*-alkanes $C_{12}F_{26}$, $C_{13}F_{28}$, $C_{14}F_{30}$, $C_{15}F_{32}$, $C_{16}F_{34}$, $C_{20}F_{42}$ and $C_{24}F_{50}$.

Table 3.4. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 2	slope	intercept	$\Delta_{sln}{}^{g}H_m$(318.0 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.[b]	calc
perfluorooctane[a]	-2591.1	9.237	21.54	**41.1 ± 0.1**	40.9 ± 5.0
perfluorononane	-2918.6	9.755	24.27	**45.3 ± 0.2**	45.8 ± 5.2
perfluorodecane	-3250.3	10.291	27.03	**51.0**	50.8 ± 5.5
perfluorododecane	-3966.2	11.532	32.98		61.5 ± 6.2
perfluorotridecane	-4338.3	12.200	36.07		67.1 ± 6.6
perfluorotetradecane	-4745.4	12.976	39.46		73.2 ± 7.1

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.80 ± 0.15) $\Delta_{sln}{}^{g}H_m$(318.0 K) + (2.00 ± 3.71) $r^2 = 0.9929$ (2-1)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Table 3.5. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 2	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.9 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 2	T/K			lit.[b]	calc
perfluorooctane[a]	-2639.8	9.397	21.95	**41.1 ± 0.1**	40.8 ± 5.9
perfluorononane	-2959.7	9.889	24.61	**45.3 ± 0.2**	45.8 ± 6.3
perfluorodecane	-3271.8	10.361	27.20	**51.0**	50.7 ± 6.6
perfluorododecane	-3984.6	11.590	33.13		61.9 ± 7.4
perfluorotridecane	-4356.8	12.260	36.23		67.7 ± 7.9
perfluorotetradecane	-4785.1	13.100	39.79		74.4 ± 8.4

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.88 ± 0.18) $\Delta_{sln}{}^{g}H_m$(317.9 K) - (0.53 ± 4.43) $r^2 = 0.9910$ (2-2)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Table 3.6. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 3	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.1 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.[b]	calc
perfluorononane[a]	-2581.2	9.174	21.46	45.3 ± 0.3	43.7 ± 2.7
perfluorododecane	-3648.4	11.018	30.33	**61.7 ± 6.8**	61.6 ± 3.1
perfluorotridecane	-4005.9	11.644	33.31	**67.4 ± 7.2**	67.6 ± 3.3
perfluorotetradecane	-4369.0	12.287	36.33	**73.8 ± 7.7**	73.7 ± 3.4
perfluoropentadecane	-4734.5	12.937	39.36		79.8 ± 3.6
pentafluorohexadecane	-5107.0	13.606	42.46		86.0 ± 3.7

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.02 ± 0.07) $\Delta_{sln}{}^{g}H_m$(338.1 K) + (0.41 ± 2.31) $r^2 = 0.9988$ (3-1)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Table 3.7. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 3	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.1 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 2	T/K			lit.[b]	calc
perfluorononane[a]	-2630.5	9.314	21.87	45.3 ± 0.3	43.6 ± 2.9
perfluorododecane	-3676.3	11.082	30.57	**61.7 ± 6.8**	61.6 ± 3.3
perfluorotridecane	-4027.8	11.688	33.49	**67.4 ± 7.2**	67.6 ± 3.4
perfluorotetradecane	-4382.6	12.305	36.44	**73.8 ± 7.7**	73.7 ± 3.6
perfluoropentadecane	-4742.9	12.939	39.44		79.9 ± 3.8
pentafluorohexadecane	-5106.6	13.583	42.46		86.1 ± 3.9

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.06 ± 0.07) $\Delta_{sln}{}^{g}H_m$(338.1 K) - (1.45 ± 2.44) r^2 = 0.9988 (3-2)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Table 3.8. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 4	slope	intercept	$\Delta_{sln}{}^{g}H_m$(388.7 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.[b]	calc
perfluorotetradecane	-4083.8	11.598	33.95	**73.8 ± 7.7**	73.8 ± 0.3
perfluoropentadecane	-4329.9	11.882	36.00	**79.8 ± 3.7**	79.8 ± 0.4
pentafluorohexadecane	-4591.3	12.220	38.17	**86.1 ± 3.8**	86.1 ± 0.4
perfluoroeicosane	-5756.7	13.955	47.86		114.4 ± 0.4

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.91 ± 0.01) $\Delta_{sln}{}^{g}H_m$(388.7 K) - (25.14 ± 0.25) r^2 = 1.0000 (4-1)

[a] Mixture solvent. [b] Bold values in column 5 used for correlation equation.

Table 3.9. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 4	slope	intercept	$\Delta_{sln}{}^{g}H_m$(388.7 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 2	T/K			lit.[a]	calc
perfluorotetradecane	-4083.8	11.598	33.95	**73.8 ± 7.7**	73.8 ± 0.3
perfluoropentadecane	-4329.9	11.882	36.00	**79.8 ± 3.7**	79.8 ± 0.4
pentafluorohexadecane	-4591.3	12.220	38.17	**86.1 ± 3.8**	86.1 ± 0.4
perfluoroeicosane	-5756.7	13.955	47.86		114.4 ± 0.4

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.70 ± 0.01) $\Delta_{sln}{}^{g}H_m$(388.7 K) - (16.42 ± 0.26) r^2 = 1.0000 (4-2)

[a] Bold values in column 5 used for correlation equation.

Table 3.10. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 5	slope	intercept	$\Delta_{sln}{}^{g}H_m$(398.9 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.[a]	calc
perfluoropentadecane	-4490.0	12.325	37.33	**79.8 ± 0.4**	79.8 ± 0.2
perfluorohexadecane	-4746.0	12.651	39.46	**86.1 ± 3.8**	86.1 ± 0.2
perfluoroeicosane	-5877.2	14.300	48.87	**113.7 ± 0.4**	113.7 ± 0.2
perfluorotetracosane	-7122.7	16.283	59.22		144.1 ± 0.3

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.94 ± 0.00) $\Delta_{sln}{}^{g}H_m$(398.9 K) - (29.79 ± 0.16) r^2 = 1.0000 (5-1)

[a] Bold values in column 5 used for correlation equation.

Table 3.11 Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 5 Run 2	slope T/K	intercept	$\Delta_{sln}{}^{g}H_m$(398.8 K)	$\Delta_l{}^{g}H_m$(298.15 K) lit.[a]	 calc
perfluoropentadecane	-4688.7	12.855	38.98	**79.8 ± 0.4**	79.7 ± 0.7
perfluorohexadecane	-4958.5	13.217	41.23	**86.1 ± 3.8**	86.2 ± 0.7
perfluoroeicosane	-6112.1	14.923	50.82	**113.7 ± 0.4**	113.7 ± 0.8
perfluorotetracosane	-7355.5	16.900	61.16		143.3 ± 0.9

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1}= (2.87 ± 0.01) $\Delta_{sln}{}^{g}H_m$(398.8 K) - (30.05 ± 0.54) r^2 = 1.0000 (5-2)

[a] Bold values in column 5 used for correlation equation.

Table 3.12 columns 2 through 6 is a list of the averaged vaporization enthalpies calculated from two runs for each mixture. Column 7 is the averaged vaporization enthalpy and uncertainty values calculated from columns 2 through 6. Column 8 is the literature values for $\Delta_g{}^{l}H_m$(298).

Table 3.12. Summary of Experimentally Derived Vaporization Enthalpies for Perfluoroalkanes [a, b]

Mixture	1	2	3	4	5	This Work (298 K)	literature (298.15 K)
perfluorohexane						32.8 ± 3.0	**32.5**
perfluoroheptane	35.9					35.9 ± 3.2	**36.3 ± 0.3.**
perfluorooctane	41.3	40.8				41.1 ± 4.5	**41.1 ± 0.1**
perfluorononane	46.8	45.8	43.7			45.4 ± 4.2	**45.3 ± 0.2**
perfluorodecane		50.7				50.7 ± 6.1	**51.0**
perfluorododecane		61.7	61.6			**61.6 ± 5.0**	
perfluorotridecane		67.4	67.6			**67.5 ± 5.3**	
perfluorotetradecane		73.8	73.7	73.8		**73.8 ± 3.9**	
perfluoropentadecane			79.8	79.8	79.8	**79.8 ± 1.5**	
pentafluorohexadecane			86.1	86.1	86.1	**86.1 ± 1.6**	
perfluoroeicosane				113.7	113.7	**113.7 ± 0.5**	
perfluorotetracosane					143.7	**143.7 ± 0.6**	

[a] All values are in kJ·mol^{-1}. [b] Bold values used to plot figure 3.4.

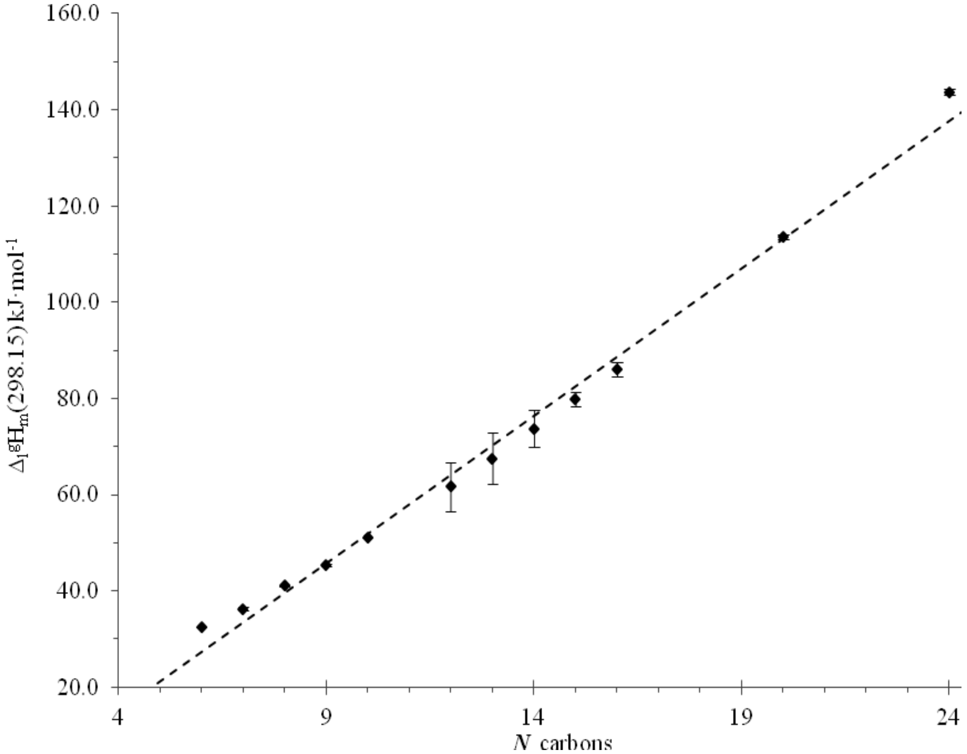


Fig. 3.4. Vaporization enthalpies of the perfluorocarbons in this study, C_6F_{14} through $C_{24}F_{50}$, as a function of the number of carbon atoms (*N*). The dashed line represents the linear regression equation 3.1. The bold values shown in Table 3.12 were used for plotting.

Figure 3.4 above is a plot of the published enthalpy values for C_6 through C_{10} and the experimentally determined $\Delta_l{}^gH_m(298\ K)$ averages C_{12} through C_{24} as listed in Table 3.12 vs. the number of carbon atoms (*N*) in the compound. The linear regression equation of the data is:

$$\Delta_l{}^gH_m(298.15)\ \text{kJ·mol}^{-1} = (6.13 \pm 0.18)\,N - (9.35 \pm 2.55) \qquad r^2 = 0.9911 \qquad (3.1)$$

The correlation relationship is > 0.98 and can be considered linear. However, a visual examination of the chart suggests that a better fit might be a polynomial equation. A regression analysis of this same data as a second order equation produces:

$$\Delta_l{}^gH_m(298.15)\ )\ \mathrm{kJ\cdot mol^{-1}} = (0.10)\ N^2 + (3.15\ )\ N + 9.30 \qquad r^2 = 0.9999 \qquad (3.2)$$

While this equation may fit the data better (r^2=0.9999) care should be taken in forming any definite conclusions. The extrapolated data used for the perfluorinated alkanes with >10 carbon atoms are completely dependent on the accuracy of the published vaporization enthalpies for alkanes C_6 to C_{10}. Any inaccuracy of the known standards will affect the accuracy of any extrapolated measurements derived from them.

Using only the published enthalpy of vaporization data of the first five *n*-perfluoroalkanes as a function of the number of carbon atoms the following second order equation was obtained:

$$\Delta_l{}^gH_m(298.15)\ )\ \mathrm{kJ\cdot mol^{-1}} = 0.229\ N^2 + 0.943\ N + 18.61 \qquad r^2 = 0.9990 \qquad (3.3)$$

Comparison plots of equations 3.2 and 3.3 can be seen in Figure 3.5. It is apparent from the chart that the positive curvature of the experimental data follows the curvature seen in the five standards. The question that needs to be resolved is whether the experimental data's curvature is an artifact as a result of the standards' non-linearity or do the perfluorinated *n*-alkanes actually, in fact, demonstrate this behavior? Complicating the resolution of this issue is the limited number of *n*-perfluoroalkanes available. Currently, there are no compounds available between $C_{16}F_{30}$ and $C_{20}F_{42}$ or any larger than $C_{24}F_{50}$ to aid in clarifying this question.

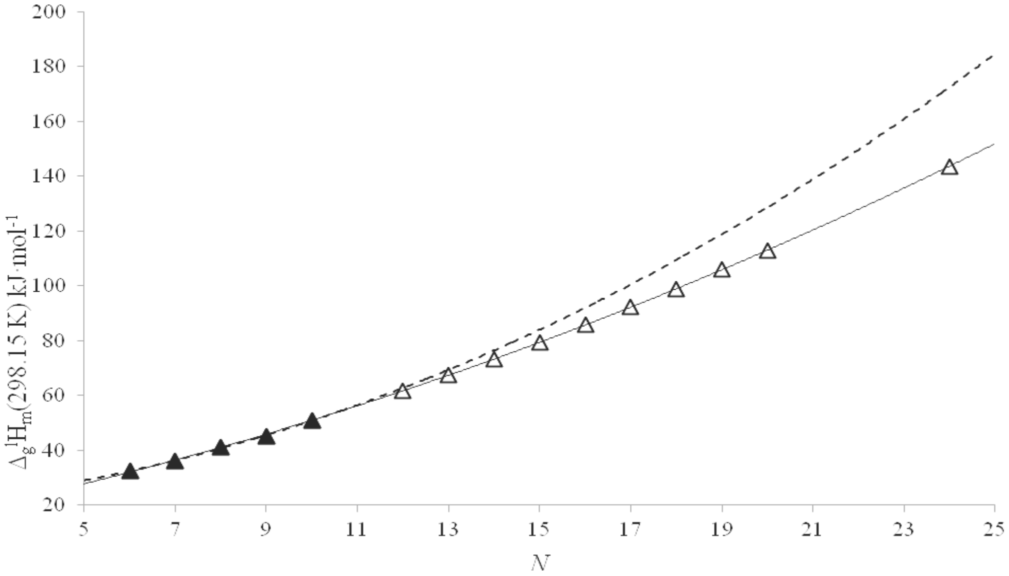


Fig. 3.5. Comparison plot of published vaporization enthalpies of C_6F_{14} to $C_{10}F_{22}$ (▲, dashed line from Eq. 3.3) and the C-GC vaporization enthalpies derived in this work , Table 3.12 (Δ, solid line from Eq. 3.2.) vs. the number of carbon atoms, *N*.

The easiest resolution of this issue would require using a different method to again measure and verify the vaporization enthalpy of the compounds that deviate most from linearity, i.e. the lowest two standards C_6F_{14} and C_7F_{16}. It would also add clarity if a larger alkane was measured such as $C_{16}F_{34}$. The results would enable the determination of the curved or linear relationship of the vaporization enthalpy to the number of carbons in these fluorinated compounds.

The inconclusive nature of the *n*-perfluoroalkanes' vaporization of enthalpy relationship with regard to the number of carbons they contain makes comparison to hydrocarbon *n*-alkanes more difficult but a few similarities still exists between the two series and are worth noting. Table 3.13 lists the experimental data from this work and the literature data for the analogous hydrocarbons.

Carbons	Perfluorinated alkanes	Hydrocarbon alkanes
N	$\Delta_g^l H_m$(298.15 K)	$\Delta_g^l H_m$(298.15 K)
6	32.5	31.5
7	36.3	36.6
8	41.1	41.6
9	45.3	46.6
10	50.7	51.4
12	61.6	61.5
13	67.5	66.7
14	73.8	71.7
15	79.8	76.8
16	86.1	81.4
20	113.7	101.8
24	143.7	121.9

Table 3.13. Perfluoro-*n*-alkane vaporization enthalpy data from Table 3.12 (bold values) and the published data for the analogous *n*-hydrocarbon alkanes.

A plot of these two sets of data is presented in Figure 3.6. For comparison purposes, the linear regression curve for each of these series is shown. As noted in chapter 1, previous work with *n*-hydrocarbon alkanes have indicated that the enthalpy verses carbon relationship is linear over the limited carbon chain length examined in this study. Although the graph indicates the vaporization enthalpy for *n*-perfluorocarbons less than *N* = 9 should be lower than the analogous hydrocarbon n-alkanes this is not supported in the published literature. It was previously stated, care needs to be taken for these lower perfluorocarbon compounds as the lower two perfluorocarbons' published measurements are suspect.

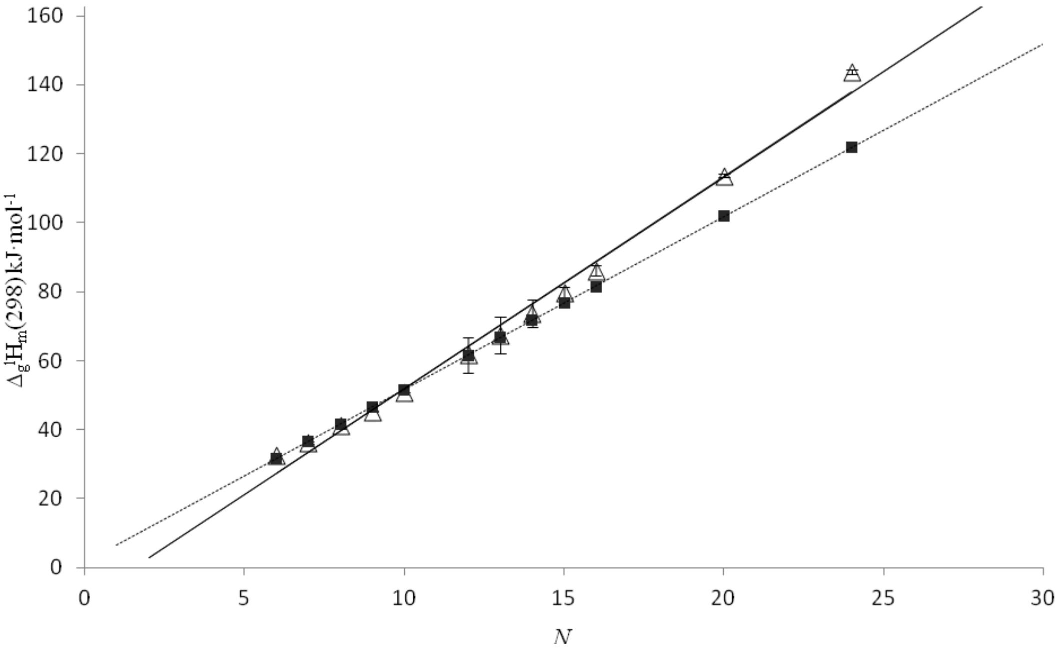


Fig. 3.6. Comparison plot of vaporization enthalpies vs. number of carbon atoms (*N*) for *n*-perfluorinated (Δ, solid line from eq. 3.1) and *n*-hydrocarbon alkanes (■, dashed line).

What figure 3.6 does indicates is that both the hydrocarbon and perfluorinated *n*-alkanes demonstrate increasing vaporization enthalpy as carbon length increases. Additionally, the perfluorinated *n*-alkane series' rate of increase for $\Delta_l^g H_m$(298.15 K) is larger than the equivalent hydrocarbon alkane series. The plot also suggests that for $N > 13$ the vaporization enthalpy is larger for the perfluoroalkane when compared to its analogous hydrocarbon.

The above study indicates that C-GC can be used successfully with perfluorinated *n*-alkanes to determine the vaporization enthalpy of other perfluorinated *n*-alkanes. The question now becomes - how well will these same fluorinated alkanes correlate with different structural classes of perfluorinated compounds? To answer this question three different perfluorinated classes (cycloalkanes, aromatics and amines) were examined.

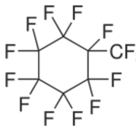
Vaporization enthalpy values used for *n*-perfluoroalkane standards are highlighted in bold in Table 3.12, columns 7 and 8. Where possible four standards were used if $r^2 > 0.99$, otherwise the solvent was eliminated as a standard and only 3 perfluoroalkane standards were employed.

3.2 Perfluorocycloalkanes

These initial investigations attempted to investigate whether the *n*-perfluorinated alkanes would correlate with the cycloalkanes: perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane and the bicyclic, perfluorodecalin.

Initial trial runs on these three cycloalkanes found they needed to be run at about the same temperature range but it was also determined that peak interference would occur between them and the standards. In order to minimize peak overlap between solutes three different mixtures, each composed of different perfluoroalkane standards and/or solvent were ran.

3.2.1 Perfluoromethylcyclohexane (C_7F_{14})



Perfluoromethylcyclohexane was run with three perfluorinated *n*-alkanes in a solution of C_9F_{20}. The low boiling point of this compound and the associated standards (C_6F_{14} and

C_7F_{16}) necessitated running the GC column below ambient temperature to achieve peak separation. Column temperatures ranged from T = (276.8 to 307.2) K with T_m = 292 K.

Examination of Figure 3.7 below shows that perfluoromethylcyclohexane correlates with the *n*-perfluorinated alkane standards. The correlation equation for the trend line is:

$$\Delta_l{}^gH_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}=(1.41\pm0.09)\Delta_{sln}{}^gH_m(292.0\text{ K})+(8.29\pm2.20);\;\; r^2=0.9916 \quad (3.4)$$

Calculation of the theoretical enthalpy of vaporization using this equation and the $\Delta_{sln}{}^gH_m$(292.0 K) value listed for this compound in Table 3.14 gives $\Delta_g{}^lH_m$(298) = (37.3±2.9) kJ·mol^{-1}. This value is approximately 6% higher than the published vaporization enthalpy value of 35.3 kJ·mol^{-1} but both agree within the experimental uncertainty.

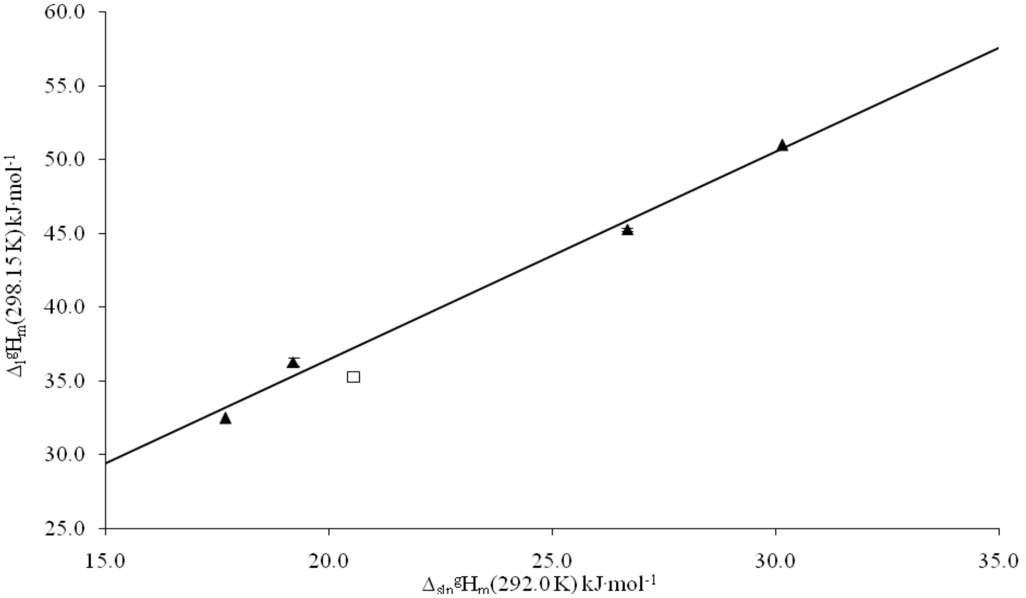


Fig. 3.7. Mixture 8. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m= 292 K. Standards (C_6F_{14}, C_7F_{16}, C_9F_{20}, and $C_{10}F_{22}$) are represented by triangles (▲) and perfluoromethylcyclohexane is represented as a square (□).

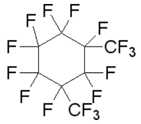
Table 3.14. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 8 Run 1	slope T/K	intercept	$\Delta_{sln}{}^{g}H_m$(292.0 K)	$\Delta_l{}^{g}H_m$(298.15 K) lit.[c]	 calc
n-C_6F_{14}	-2127.3	9.175	17.69	**32.5**	33.2 ± 2.7
n-C_7F_{16}	-2310.9	9.139	19.21	**36.3 ±0.3**	35.3 ± 2.8
C_7F_{14}[a]	-2474.3	9.063	20.57	35.3	37.3 ± 2.9
n-C_9F_{20}[b]	-3209.4	10.945	26.68	**45.3 ± 0.2**	45.9 ± 3.3
n-$C_{10}F_{22}$	-3624.4	11.745	30.14	**51.0**	50.7 ± 3.5

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.41 ± 0.09) $\Delta_{sln}{}^{g}H_m$(292.0 K) + (8.29 ± 2.20) r^2 = 0.9916 (15)

[a] perfluoromethylcyclohexane. [b] Mixture solvent. [c] Bold values in column 5 used for correlation equation.

3.2.2 Perfluoro-1,3-dimethylcyclohexane (C_8F_{16})



Perfluoro-1,3-dimethylcyclohexane was also found to correlate with the n-perfluoroalkane standards with which it was ran. Compared to perfluoromethylcyclohexane, this dimethylcyclohexane demonstrates an even smaller variance (+3.5%) between its calculated value of (40.1±0.5) kJ·mol^{-1} and its published vaporization enthalpy value (38.6±0.1) kJ·mol^{-1}.

Figure 3.8 is a plot of the enthalpy of solution ($\Delta_{sln}{}^{g}H_m$(322.8 K)) values verses the published enthalpy of vaporization values at T = 298 K. The correlation equation is:

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.85\pm0.01)\Delta_{sln}{}^{g}H_m(322.8\ K)+(1.03\pm0.43);\ r^2 = 0.9999 \quad (3.5)$$

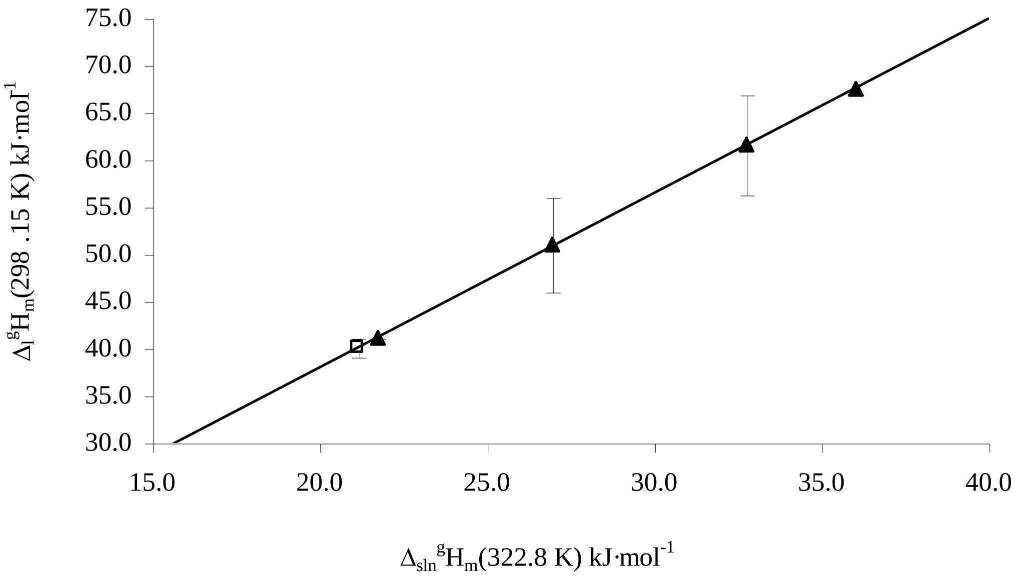


Fig. 3.8. Mixture 9. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m= 322.8 K. Standards (C_8F_{18}, $C_{10}F_{22}$, $C_{12}F_{26}$, and $C_{13}F_{28}$) are represented by triangles (▲) and perfluoro-1,3-dimethylcyclohexane is represented by a square (□).

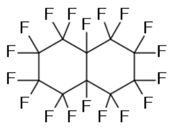
Table 3.15. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 9	slope	intercept	$\Delta_{sln}{}^gH_m$(322.8 K)	$\Delta_l{}^gH_m$(298.15 K)	
Run 1	T/K			lit.[c]	calc
n-C_8F_{18}[b]	-2615.3	9.802	21.75	**41.1 ± 0.1**	41.2 ± 0.5
C_8F_{16}[a]	-2543.5	8.915	21.15	38.6 ± 0.1	40.1 ± 0.5
n-$C_{10}F_{22}$	-3242.8	10.749	26.96	**51.0**	50.8 ± 0.6
n-$C_{12}F_{26}$	-3939.9	11.928	32.76	**61.6 ± 5.0**	61.6 ± 0.6
n-$C_{13}F_{28}$	-4333.6	12.657	36.03	**67.5 ± 5.3**	67.6 ± 0.7

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.85 ± 0.01) $\Delta_{sln}{}^gH_m$(322.8 K) + (1.03 ± 0.43) r^2 = 0.9999   (17)

[a] perfluoro-1,3-dimethylcyclohexane. [b] Mixture solvent. [c] Bold values in column 5 used for correlation equation.

3.2.3 *cis/trans* Perfluorodecalin ($C_{10}F_{18}$)



Perfluorodecalin was mixed in a solution of C_8F_{18} containing the n-perfluoroalkanes C_9F_{20}, $C_{10}F_{22}$ and $C_{13}F_{28}$ as standards. GC column temperatures ranged from T = (302.7 to 333.0) K with an average T_m = 317.8 K.

Figure 3.9 is a correlation plot of the standards and the perfluorodecalin isomers. Using correlation equation 3.9, the calculated vaporization enthalpy values of (49.1±1.8) kJ·mol^{-1} for the *trans* and (49.9±1.8) kJ·mol^{-1} for *cis* perfluorodecalin are ~8% higher than the published enthalpies. The uncertainties in the values of the standards as shown in Figure 3.9 indicate that both perfluorodecalin isomers correlate with the hydrocarbon n-alkanes. The chart also illustrates that the two isomers readily separate even though they have a published vaporization enthalpy difference between them of just 0.8 kJ·mol^{-1}. Interestingly, the calculated vaporization enthalpy values derived from the correlation equation also produces the same difference of 0.8 kJ·mol^{-1}.

The linear regression equation is plotted in figure 3.9:

$$\Delta_l{}^gH_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.90\pm 0.04)\Delta_{sln}{}^gH_m(317.8\text{ K}) - (1.08\pm 1.32);\quad r^2 = 0.9995 \quad (3.6)$$

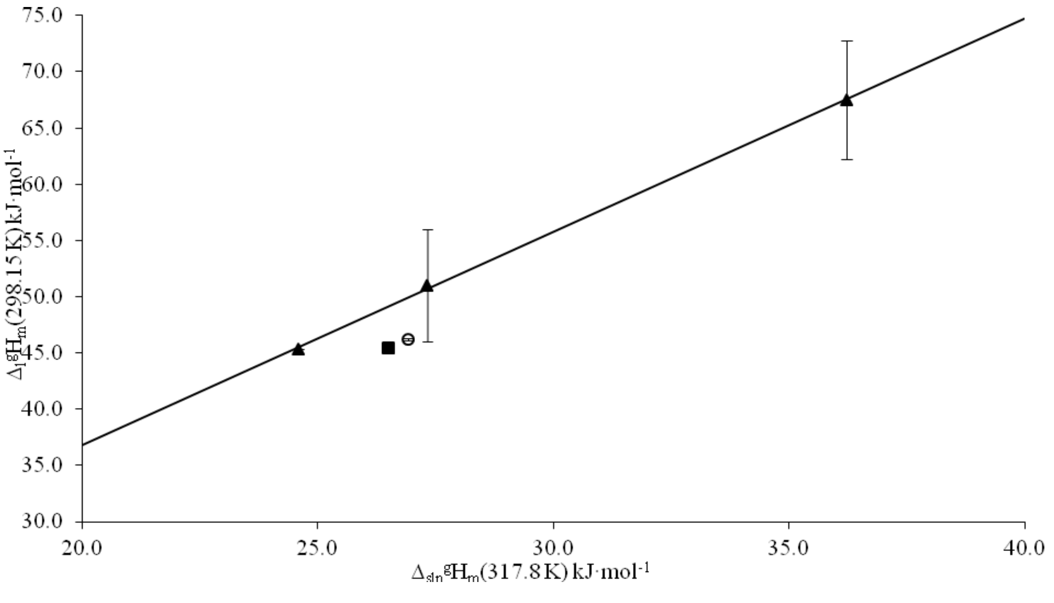


Fig. 3.9. Mixture 10. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m= 317.8 K. Standards (C_9F_{20}, $C_{10}F_{22}$, and $C_{13}F_{28}$) are represented by triangles (▲), *cis*-perfluorodecalin is represented by a circle (○) and *trans*-perfluorodecalin is represented as a square (■).

Table 3.16. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 10 Run 1	slope T/K	intercept	$\Delta_{sln}{}^{g}H_m$(317.8 K)	$\Delta_l{}^{g}H_m$(298.15 K) lit.[c]	 calc
n-C_8F_{18}[b]	-2924.9	10.740	24.32	41.1 ± 0.1	45.0 ± 1.7
n-C_9F_{20}	-2957.9	10.341	24.59	**45.3 ± 0.2**	45.5 ± 1.7
n-$C_{10}F_{22}$	-3285.6	10.862	27.32	**51.0**	50.7 ± 1.8
cis-$C_{10}F_{18}$[a]	-3185.7	9.519	26.49	45.4 ± 0.1	49.1 ± 1.8
trans-$C_{10}F_{18}$[a]	-3237.3	9.522	26.92	46.2 ± 0.1	49.9 ± 1.8
n-$C_{13}F_{28}$	-4356.8	12.713	36.22	**67.5 ± 5.3**	67.6 ± 2.1

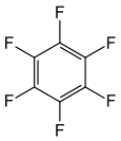
$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.90 ± 0.04) $\Delta_{sln}{}^{g}H_m$(317.8 K) **-** (1.08 ± 1.32) r^2 = 0.9995 (19)

[a] perflurodecalin. [b] Mixture solvent. [c] Bold values in column 5 used for correlation equation.

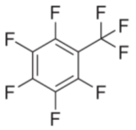
In summary, these three mixtures indicate that n-perfluoroalkanes and perfluorocycloalkanes will successful correlate and should enable the use of C-GC in determining the vaporization enthalpies of other unknown perfluorinated cycloalkanes.

3.3 Perfluorinated aromatics

Hexafluorobenzene (C_6F_6)



Octafluorotoluene (C_7F_8)



The perfluorinated aromatics hexafluorobenzene and octafluorotoluene were dissolved in C_8F_{18} along with the n-perfluoroalkane standards $C_{12}F_{26}$, $C_{13}F_{28}$ and $C_{14}F_{30}$. All four alkanes, solvent and standards, were used to calculate the correlation equation (Eq.3.7) which is plotted in Figure 3.10.

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1}=(1.95\pm0.03)\Delta_{sln}{}^{g}H_m(333.1\ K)+(0.07\pm1.02);\ \ r^2=0.9995 \quad (3.7)$$

As can be observed from the Figure below, the perfluorinated aromatics correlate poorly with the perfluorinated *n*-alkanes with errors above.

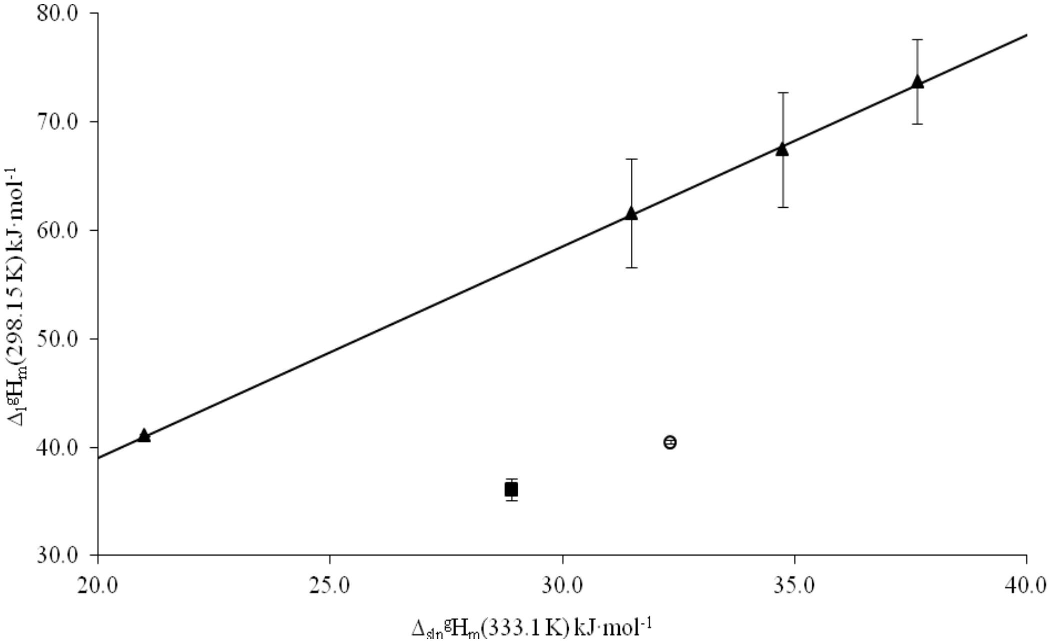


Fig. 3.10. Mixture 11. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m= 333.1 K. Standards (C_8F_{18}, $C_{12}F_{26}$, $C_{13}F_{28}$, and $C_{14}F_{30}$) are represented by triangles (▲), octafluorotoluene by a circle (o) and hexafluorobenzene by as a square (■).

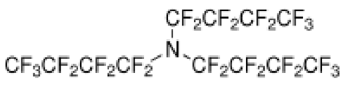
Table 3.17. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 11 Run 1	slope T/K	intercept	$\Delta_{sln}{}^gH_m$(333.1 K)	$\Delta_l{}^gH_m$(298.15 K) lit.[d]	 calc
C_8F_{18}[c]	-2527.4	9.277	21.01	**41.1 ± 0.1**	41.1 ± 1.2
$C_{12}F_{26}$	-3786.5	11.218	31.48	**61.6 ± 5.0**	61.5 ± 1.4
$C_{13}F_{28}$	-4177.5	11.935	34.73	**67.5 ± 5.3**	67.9 ± 1.5
$C_{14}F_{30}$	-4525.9	12.537	37.63	**73.8 ± 3.9**	73.5 ± 1.6
C_6F_6[a]	-3475.4	9.060	28.90	36.1 ± 0.1	56.5 ± 1.4
C_7F_8[b]	-3887.2	9.941	32.32	40.5 ± 0.2	63.2 ± 1.5

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.95 ± 0.03) $\Delta_{sln}{}^gH_m$(333.1 K) - (0.07 ± 1.02) r^2 = 0.9995 (21)

[a] hexafluorobenzene [b] octafluorotoluene [c] Mixture solvent.
[d] Bold values in column 5 used for correlation equation.

3.4 Perfluorotributylamine ($(C_4F_9)_3N$)



In mixture 7, three perfluoroalkane standards ($C_{14}F_{30}$, $C_{15}F_{32}$, and $C_{16}F_{34}$) and the solvent, C_8F_{18}, were correlated with perfluorotributylamine. Figure 3.11 presents a correlation plot of the experimental data. The data point for the amine falls slightly outside the error bars associated with the standards and in this case it is not clear whether the perfluoroamine correlates with the *n*-perfluoroalkane standards. Its calculated vaporization enthalpy value (66.3±5.7) kJ·mol^{-1} is 10% higher than its cited literature value (60.3 kJ·mol^{-1}).

The correlation equation for the data is:

$$\Delta_l{}^gH_m(298.15\text{ K})/\text{kJ·mol}^{-1}=(2.33\pm0.12)\Delta_{sln}{}^gH_m(338.8\text{ K})-(7.96\pm4.17);\ r^2=0.9946 \quad (3.8)$$

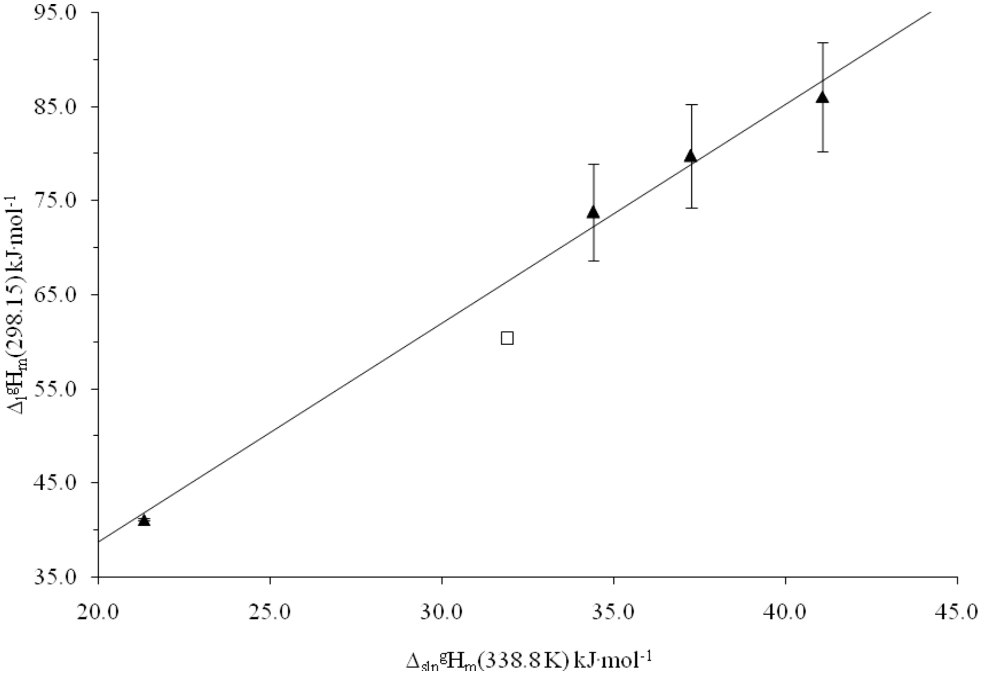


Fig. 3.11. Mixture 7. Correlation plot of $\Delta_g{}^lH_m(298\text{ K})$ as a function of the enthalpy of transfer at T_m= 338.8 K. Standards (C_8F_{18}, $C_{14}F_{30}$, $C_{15}F_{32}$, and $C_{16}F_{34}$) are represented by triangles (▲)and perfluorotributylamine is represented as a square (□).

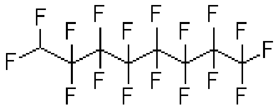
Table 3.18. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 7	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.8 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Run 1	T/K			lit.[c]	calc
C_8F_{18}[b]	-2565.9	9.606	21.33	**41.1 ± 0.1**	41.8 ± 4.9
$C_{12}F_{27}N$[a]	-3831.9	11.707	31.86	60.3 ± 0.1	66.3 ± 5.7
$C_{14}F_{30}$	-4138.2	12.030	34.41	**73.8 ± 3.9**	72.3 ± 5.9
$C_{15}F_{32}$	-4480.1	12.611	37.25	**79.8 ± 1.5**	78.9 ± 6.2
$C_{16}F_{34}$	-4939.5	13.520	41.07	**86.1 ± 1.6**	87.8 ± 6.5

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.33 ± 0.12) $\Delta_{sln}{}^{g}H_m$(338.8 K) **-** (7.96 ± 4.17) r^2 = 0.9946 (13)

[a] perfluorotributylamine. [b] Mixture solvent. [c] Bold values in column 5 used for correlation equation.

3.5 1-H Perfluorooctane (C_8HF_{17})



1H-perfluorooctane was examined to determine what effect a single hydrogen atom has on the compound's correlation with *n*-perfluoroalkanes. Figure 3.12 indicates that the addition of only one hydrogen on a terminal carbon alters the intermolecular forces of this *n*-alkane enough that it will no longer correlate with the *n*-perfluoroalkane standards. Unlike the standards used, this compound has a dipole moment associated with its structure and probably interacts with the column more strongly relative to the standards. It was determined that 1H-perfluorooctane will not correlate with the n-perfluoroalkanes. The calculated vaporization enthalpy value (57.5 ± 1.3 kJ·mol^{-1})was in error with respect to the published values by ~32.5%

The linear correlation equation for this mixture is:

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1}=(1.89±0.03)$\Delta_{sln}{}^{g}H_m$(317.8 K)+(1.38±0.86); r^2=0.9994 (3.9)

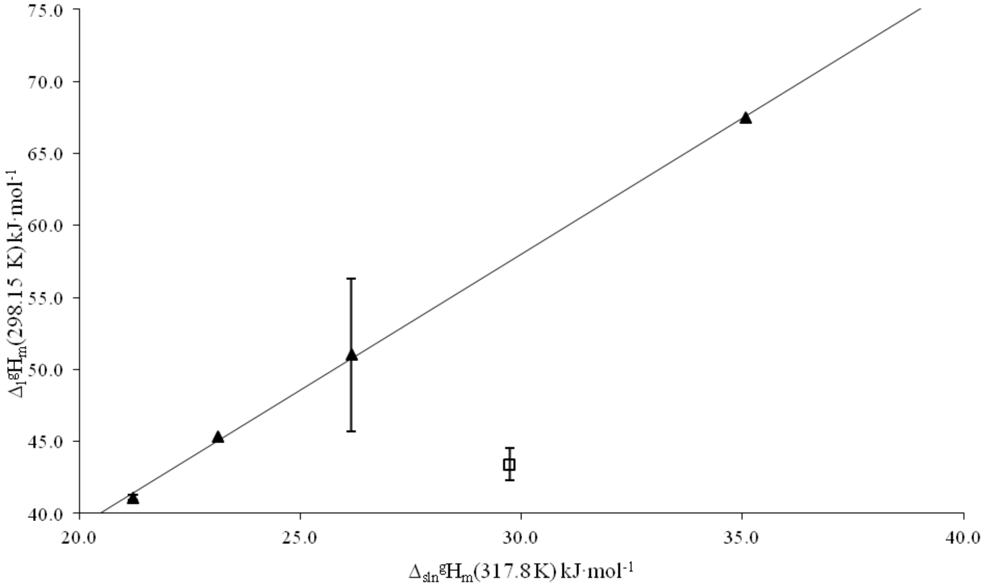


Fig. 3.12. Mixture 6. Correlation plot of $\Delta_g{}^lH_m(298\ K)$ as a function of the enthalpy of transfer at T_m = 317.8 K. Standards (C_8F_{18}, C_9F_{20}, $C_{10}F_{22}$, and $C_{13}F_{28}$) are represented by triangles (▲), and 1H-perfluorooctane is represented as a square (□).

Table 3.19. Enthalpies of Transfer and Vaporization ($kJ\cdot mol^{-1}$)

Mixture 6	slope	intercept	$\Delta_{sln}{}^gH_m(317.8\ K)$	$\Delta_l{}^gH_m(298.15\ K)$	
Run 1	T/K			lit.[c]	calc
C_8F_{18}[b]	-2551.1	9.585	21.21	**41.1 ± 0.1**	41.4 ± 1.1
C_9F_{20}	-2783.5	9.803	23.14	**45.3 ± 0.2**	45.1 ± 1.1
$C_{10}F_{22}$	-3145.0	10.437	26.15	**51.0**	50.8 ± 1.2
C_8HF_{17}[a]	-3575.3	10.908	29.73	43.4 ± 1.1	57.5 ± 1.3
$C_{13}F_{28}$	-4217.3	12.297	35.07	**67.5 ± 5.3**	67.6 ± 1.4

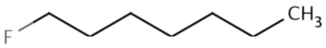
$\Delta_l{}^gH_m(298.15\ K)/kJ\cdot mol^{-1} = (1.89 \pm 0.03)\ \Delta_{sln}{}^gH_m(317.8\ K) + (1.38 \pm 0.86)$ $r^2 = 0.9994$ (11)

[a] 1H-perfluorooctane. [b] Mixture solvent. [c] Bold values in column 5 used for correlation equation.

While perfluorinated alkanes are insoluble in hydrocarbons, partially fluorinated hydrocarbons will easily dissolve. Similarly, the fully and partially fluorinated aromatics readily dissolve in hydrocarbon aromatics. The solubility of these fluorinated compound classes in hydrocarbons affords an opportunity to investigate whether hydrocarbons can be used as standards in evaluating some of these fluorinated compounds' vaporization enthalpies. The following sections, 3.6 and 3.7, present the results of this investigation.

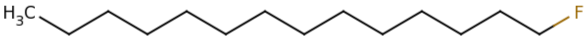
3.6 Monofluorinated *n*-alkanes

1F-fluoroheptane ($C_7H_{15}F$)



1F-fluorododecane ($C_{12}H_{25}F$)

1F-fluorotetradecane ($C_{14}H_{29}F$)



Mixture 12 was composed of four hydrocarbons (C_7H_{16}, ($C_{10}H_{22}$, $C_{12}H_{26}$, $C_{14}H_{30}$) and the three 1F *n*-alkanes listed above. The vaporization enthalpies used for the 1F compounds was calculated using the experimentally derived constants for the Antoine equation provided by Li and Rossini. [3-1] Seven equally spaced vapor pressures were calculated over a temperature range of 30 degrees as close to T = (405 to 440) K as was allowed by the publication's cited pressure range for each of these compounds. Using this pressure data a regression plot of ln(P) vs. 1/T was performed. The resultant slopes from these three equations when divided by the molar gas constant provided the vaporization enthalpies for each 1F compound. The resultant vaporization enthalpies were subsequently adjusted to 298 K. (ref. Table 2.2). Figure 3.13 is a plot of the enthalpy of solution vs. the published vaporization enthalpies adjusted to 298 K. All four hydrocarbons used in the solution were employed to derive the correlation equation. As can be observed, the monofluorinated compounds correlate well with the hydrocarbon standards. The calculated vaporization enthalpies for 1F-fluoroheptane (42.8±0.2 $kJ\cdot mol^{-1}$), 1F- fluorododecane (67.7±0.3 $kJ\cdot mol^{-1}$) and 1F-fluorotetradecane (77.7±0.3 $kJ\cdot mol^{-1}$) have less than a 1.5% error from the published vaporization enthalpies. These results indicate that C-GC should be successful in deriving or confirming other 1F *n*-alkane vaporization enthalpies.

The correlation equation for the hydrocarbon standards is:

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.396\pm0.005)\Delta_{sln}{}^{g}H_m(424.2\ K) + (2.339\pm0.193); \quad r^2=1.0000 \qquad (3.10)$$

Of interest is the linearity of the 1F compound themselves. The correlation equation for the terminal 1F *n*-alkanes is:

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.383\pm0.035)\Delta_{sln}{}^{g}H_m(424.2\ K) + (3.439\pm1.556); \quad r^2=0.9994 \qquad (3.11)$$

This suggests that, like the hydrocarbon *n*-alkanes, they could be used to extrapolate other homologous 1F compounds in the series.

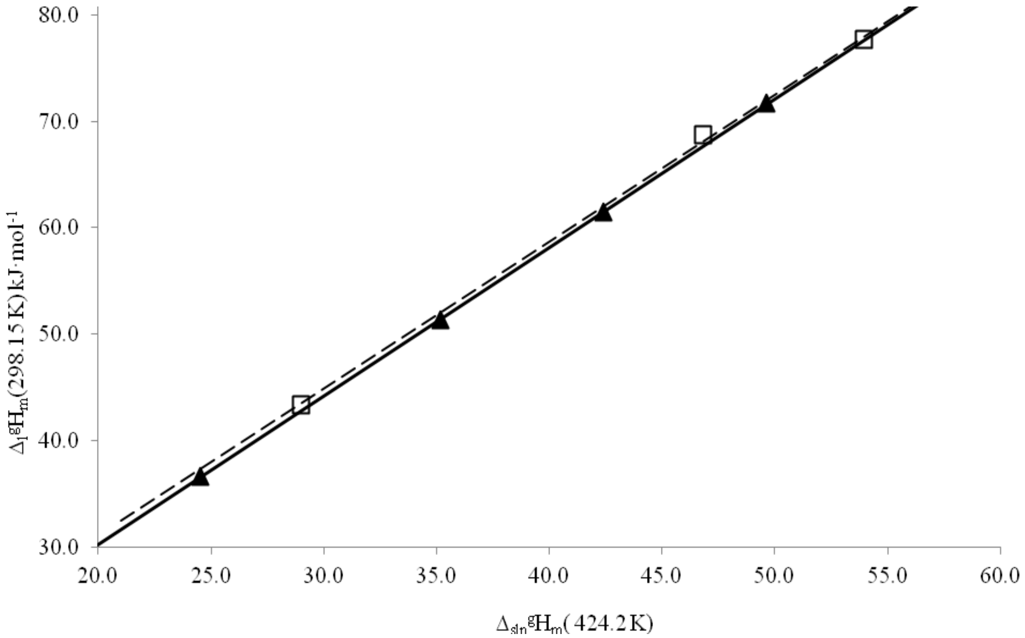


Fig. 3.13. Mixture 12. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m =424.4 K. The hydrocarbon *n*-alkane standards (C_7H_{16}, $C_{10}H_{22}$, $C_{12}H_{26}$ and $C_{14}H_{30}$) are represented by triangles (▲) and the 1F-fluoroalkanes ($C_7H_{15}F$, $C_{12}H_{25}F$, and $C_{14}H_{29}F$) are represented by (□).

Table 3.20. Enthalpies of Transfer and Vaporization ($kJ\cdot mol^{-1}$)

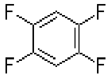
Mixture 12 Run 1	slope T/K	intercept	$\Delta_{sln}{}^gH_m$(424.2 K)	$\Delta_l{}^gH_m$(298.15 K) lit.[e]	 calc
n-C_7H_{16}[d]	-2947.1	8.156	24.50	**36.6**	36.6 ± 0.2
$C_7H_{15}F$ [a]	-3487.1	8.765	28.99	43.4	42.8 ± 0.2
n-$C_{10}H_{22}$	-4232.9	9.664	35.19	**51.4**	51.5 ± 0.3
n-$C_{12}H_{26}$	-5102.0	10.735	42.42	**61.5**	61.6 ± 0.3
$C_{12}H_{25}F$ [b]	-5629.7	11.326	46.81	68.7	67.7 ± 0.3
n-$C_{14}H_{30}$	-5968.9	11.808	49.63	**71.7**	71.6 ± 0.3
$C_{14}H_{29}F$ [c]	-6488.0	12.381	53.94	77.7	77.7 ± 0.3

$\Delta_l{}^gH_m(298\ K)/kJ\cdot mol^{-1} = (1.40 \pm 0.00)\ \Delta_{sln}{}^gH_m(424.2\ K) + (2.34 \pm 0.19)$ $r^2 = 1.0000$ (23)

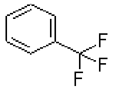
[a] 1F- fluoroheptane. [b] 1F-fluorododecane. [c] 1F-fluorotatradecane. [d] Mixture solvent. [e] Bold values in column 5 used for correlation equation.

3.7 Partially and fully fluorinated aromatics

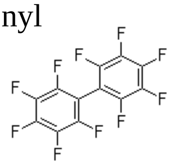
1,2,4,5-tetrafluorobenzene



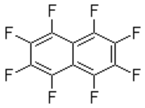
trifluorotoluene



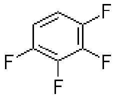
decafluorobiphenyl



octafluoronaphthalene



1,2,3,4-tetrafluorobenzene



Previous C-GC work has demonstrated that aromatic hydrocarbons, both single and multi-ringed with or without alkyl substituents, correlate well with each other. In order to expand the C-GC investigation of fluorinated aromatics, the five compounds shown above were run with hydrocarbon aromatics as standards. Two mixtures, 13 and 14, were evaluated using the same solvent, standards and temperature range *T* = (400 and 430) K to determine if a correlation was feasible for these two different aromatic classes.

Mixture 13 contained the aromatic hydrocarbons, toluene, o-xylene and naphthalene and two partially fluorinated aromatic hydrocarbons, 1,2,4,5-tetrafluorobenzene and trifluorotoluene.

The correlation equation for the standards in mixture 13 is:

$$\Delta_l{}^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.23\pm0.07)\Delta_{sln}{}^g H_m(414.5\ \text{K}) + (4.74\pm2.29)$$

$$r^2=0.9969 \qquad (3.12)$$

Figure 3.14 is a plot of the results for mixture 13. Using equation 3.12, the calculated vaporization enthalpies for 1,2,4,5-tetrafluorobenzene and trifluorotoluene are found to be within experimental error. Differences of approximately 5% or less with the published literature values (5.1% and 1.1%, respectively) were obtained. This indicates that these two partial fluorinated aromatics have a strong correlation with the aromatic hydrocarbons.

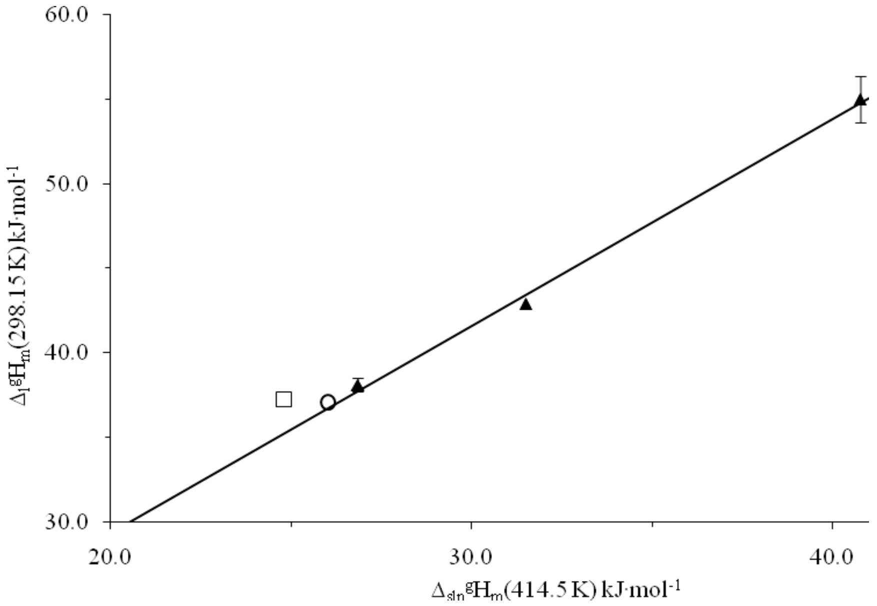


Fig. 3.14. Mixture 13. Correlation plot of $\Delta_g{}^lH_m(298\ K)$ as a function of the enthalpy of transfer at $T_m = 414.5$ K. The aromatic hydrocarbon standards (toluene, o-xylene and naphthalene) are represented by (▲), the fluoroaromatics: 1,2,4,5-tetrafluorobenzene is represents by (□), and trifluorotoluene by (o).

Table 3.21 Enthalpies of Transfer and Vaporization ($kJ{\cdot}mol^{-1}$)

Mixture 13	slope	intercept	$\Delta_{sln}{}^gH_m(414.5\ K)$	$\Delta_l{}^gH_m(298.15\ K)$	
Run 1	*T*/K			lit.[d]	calc
$C_6H_2F_4$[a]	-2986.9	8.243	24.83	37.2	35.3 ± 2.9
$C_7H_5F_3$[b]	-3127.8	8.273	26.01	37.1	36.7 ± 2.9
C_7H_8	-3229.0	8.125	26.85	**38.1 ± 0.4**	37.7 ± 2.9
C_8H_{10}	-3788.0	8.777	31.50	**42.9**	43.4 ± 3.2
C_9H_{12}[c]	-4249.3	9.540	35.33	47.6	48.2 ± 3.3
$C_{10}H_8$	-4901.4	9.758	40.75	**55.0 ± 1.4**	54.8 ± 3.6

$\Delta_l{}^gH_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.23 \pm 0.07)\ \Delta_{sln}{}^gH_m(414.5\ K) + (4.74 \pm 2.29)$ $r^2 = 0.9969$ (25)

[a] 1,2,4,5-tetrafluorobenzene. [b] trifluorotoluene. [c] Mixture solvent. [d] Bold values in column 5 used for correlation equation.

For mixture 14 the correlation equation for the standards is:

$$\Delta_l{}^gH_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}=(1.22\pm0.07)\Delta_{sln}{}^gH_m(415.0\text{ K})+(5.03\pm2.20);\ r^2=0.9971 \quad (3.13)$$

This solution includes the hydrocarbon standards toluene, o-xylene and naphthalene along with the fluorinated aromatics 1,2,3,4-tetrafluorobenzene and decafluorobiphenyl. Figure 3.5 is the correlation plot for mix 14. It suggests 1,2,3,4-tetrafluorobenzene correlates well with aromatic hydrocarbons. The calculated vaporization enthalpy is within the experimental uncertainty and deviates from the published literature value by just 1.3 kJ·mol^{-1} (3.5 %).

The plot also shows that the two fully-fluorinated aromatics, perfluoronapthalene and biphenyl have a questionable correlation with the aromatic hydrocarbon standards. The calculated vaporization enthalpy values for decafluorobiphenyl (58.0±3.6 kJ·mol^{-1}) and octafluoronapthalene (60.2±3.7 kJ·mol^{-1}) are too low by +13.4% and +7.0%, respectively, when compared to their published values. Both of these perfluorinated aromatics fall outside the uncertainty limits of the standards and are considered as non-correlative.

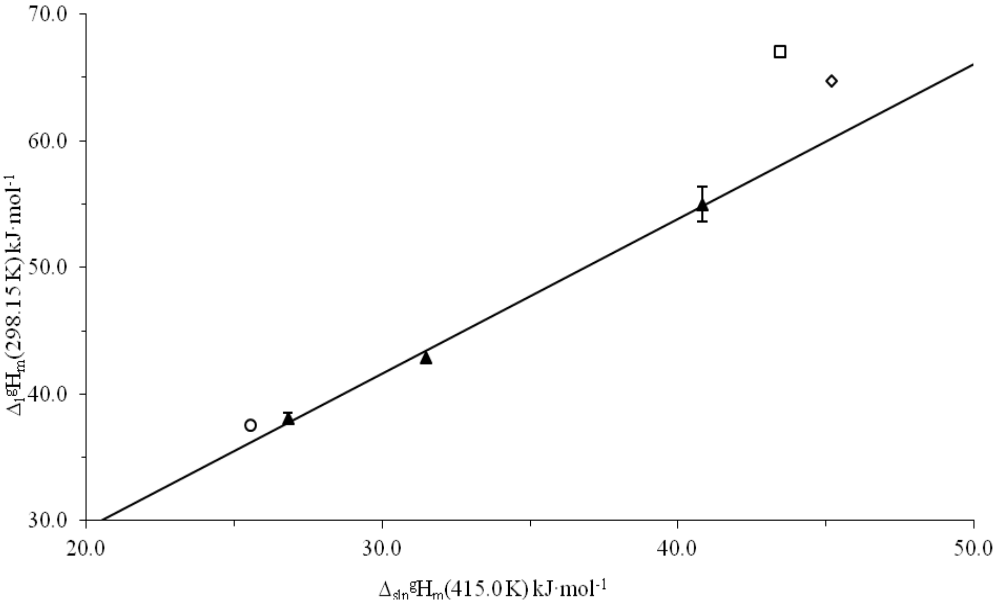


Fig. 3.15. Mixture 14. Correlation plot of $\Delta_g{}^lH_m$(298 K) as a function of the enthalpy of transfer at T_m =415.0 K. The aromatic hydrocarbon standards (toluene, o-xylene and naphthalene) are represented by (▲), the fluoroaromatics: 1,2,3,4-tetrafluorobenzene is represents by (o), octafluoronapthalene by (◊) and decafluorobiphenyl by (□).

Table 3.22. Enthalpies of Transfer and Vaporization (kJ·mol^{-1})

Mixture 14	slope	intercept	$\Delta_{sln}{}^gH_m$(415.0 K)	$\Delta_l{}^gH_m$(298.15 K)	
Run 1	T/K			lit.[d]	calc
$C_6H_2F_4$[a]	-3071.2	8.29	25.54	37.5	36.2 ± 2.8
C_7H_8	-3225.3	8.15	26.82	**38.1 ± 0.4**	37.7 ± 2.8
C_8H_{10}	-3785.6	8.80	31.48	**42.9**	43.4 ± 3.0
C_9H_{12}[d]	-4450.4	10.02	37.00	47.6	50.2 ± 3.3
$C_{10}F_8$[b]	-5436.3	11.66	45.20	64.7	60.2 ± 3.7
$C_{12}F_{10}$[c]	-5225.7	10.88	43.45	67.0	58.0 ± 3.6
$C_{10}H_8$	-4909.9	9.80	40.82	**55.0 ± 1.4**	54.8 ± 3.5

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.22 ± 0.07) $\Delta_{sln}{}^gH_m$(415.0 K) + (5.03 ± 2.20) r^2 = 0.9971 (27)

[a] 1,2,3,4-tetrafluorobenzene [b] octafluoronapthalene [c] decafluorobiphenyl [d] Mixture solvent. [e] Bold values in column 5 used for correlation equation.

3-1. Li, James C. M.; Rossini, Fredrick D.; Vapor Pressure and Boiling Points of the 1-Fluoroalkanes, 1-Chloroalkanes, 1-Bromoalkanes, and 1-Iodoalkanes, C_1 to C_{20}., *J. Chem. Eng. Data*, **1961**, *6* (2), 268-270.

Chapter 4

4.1 Conclusion

This study confirms that correlation gas chromatography can successfully be used to determine the enthalpy of vaporization of perfluorinated compounds if proper care is taken in the selection of the standards. When deciding what standards are to be use the controlling factor appears to be number of fluorines present on the compounds being examined.

This work has determined that *n*-perfluorocarbon standards will correlate well with other *n*-perfluorocarbons within the homologous series and with perfluorocycloalkanes. They were also found to correlate marginally with perfluoroamines but would not correlate with 1H-*n*-perfluoroalkanes or the perfluoroaromatics.

This study also determined that 1F-hydrocarbon *n*-alkanes would correlate well with their analogous hydrocarbon n-alkanes. It was observed that the presence of a single fluorine atom as a substituent does not significantly alter the molecular properties enough to prevent correlation with these *n*-alkane standards.

Additional work was conducted to examine whether partially or fully fluorinated aromatics would correlate with aromatic hydrocarbons. It was found that the number of fluorines in the compound has a significant influence on their correlation with these hydrocarbon standards. Partially fluorinated aromatics correlate well with aromatic hydrocarbons but fully fluorinated aromatics will not correlate with aromatic hydrocarbons.

Appendix I

Chemical sources and purities

CAS #	Formula	Name	Source	% Purity
392-56-3	C_6F_6	hexafluorobenzene	Sigma-Aldrich	≥99
355-42-0	C_6F_{14}	perfluorohexane	Sigma-Aldrich	≥98
551-62-2	$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene	Sigma-Aldrich	≥99
327-54-8	$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene	Sigma-Aldrich	≥99
434-64-0	C_7F_8	octafluorotoluene	Sigma-Aldrich	≥98
355-02-2	C_7F_{14}	perfluoro(methylcyclohexane)	Sigma-Aldrich	≥90
355-57-9	C_7F_{16}	perfluoroheptane	Sigma-Aldrich	≥85
98-8-8	$C_7H_5F_3$	trifluorotoluene	Sigma-Aldrich	≥99
108-88-3	C_7H_8	toluene	Baxter	≥98
661-11-0	$C_7H_{15}F$	1-fluoroheptane	Sigma-Aldrich	≥98
142-82-5	C_7H_{16}	heptane	Sigma-Aldrich	≥99
335-27-3	C_8F_{16}	perfluoro-1,3-dimethylcyclohexane	Sigma-Aldrich	≥80
307-34-6	C_8F_{18}	perfluorooctane	Sigma-Aldrich	≥98
335-65-9	C_8HF_{17}	1H- perfluorooctane	Sigma-Aldrich	≥99
703-87-7	$C_8H_6F_4$	2,3,5,6 -tetrafluoro-p-xylene	Sigma-Aldrich	≥99
443-82-3	C_8H_9F	3-fluoro-o-xylene	Sigma-Aldrich	≥99
95-47-6	C_8H_{10}	o-xylene	Eastman Kodak	≥95
375-96-2	C_9F_{20}	perfluorononane	Sigma-Aldrich	≥97
108-67-8	C_9H_{12}	mesitylene	MCB	≥95
313-72-4	$C_{10}F_8$	octafluoronapthalene	Sigma-Aldrich	≥96
306-94-5	$C_{10}F_{18}$	perfluorodecalin (cis/trans)	Sigma-Aldrich	≥95
307-45-9	$C_{10}F_{22}$	perfluorodecane	SynQuest	≥95
124-18-5	$C_{10}H_{22}$	decane	Sigma-Aldrich	≥99
91-20-3	$C_{10}H_8$	naphthalene	Sigma-Aldrich	≥99
434-90-2	$C_{12}F_{10}$	decafluorobiphenyl	Sigma-Aldrich	≥99
307-59-5	$C_{12}F_{26}$	perfluorododecane	SynQuest	≥97
311-89-7	$C_{12}F_{27}N$	perfluorotributylamine	Sigma-Aldrich	≥99
334-68-9	$C_{12}H_{25}F$	1-fluorododecane	Sigma-Aldrich	≥99

CAS #	Formula	Name	Source	% Purity
112-40-3	$C_{12}H_{26}$	dodecane	Eastman Kodak	≥98
376-03-4	$C_{13}F_{28}$	perfluorotridecane	SynQuest	≥98
307-62-0	$C_{14}F_{30}$	perfluorotetradecane	SynQuest	≥97
2264-03-1	$C_{15}F_{32}$	perfluoropentadecane	Sigma-Aldrich	≥95
593-33-9	$C_{14}H_{29}F$	1-fluorotetradecane	Sigma-Aldrich	≥96
629-59-4	$C_{14}H_{30}$	tetradecane	Sigma-Aldrich	≥99
355-49-7	$C_{16}F_{34}$	perfluorohexadecane	SynQuest	≥97
37589-57-4	$C_{20}F_{42}$	perfluoroeicosane	SynQuest	≥97
1766-41-2	$C_{24}F_{50}$	perfluorotetracosane	Sigma-Aldrich	≥99

Baxter Healthcare Corp., McGraw Park, IL

Eastman Chemical Co., Rochester, NY

Sigma -Aldrich Chemical Co., St. Louis, MO

SynQuest, PO Box 309, Alachua, FL

Appendix II

Supplemental Information

Hypothetical Thermodynamic Properties: Application of Correlation Gas-Chromatography to the Evaluation of the Vaporization Enthalpies of Fluorinated Compounds

Bold values were used as correlation standards.

All enthalpies are reported in kJ·mol^{-1}

Table 1.1A. Retention Times

Run 1		*T*/K	297.2	292.2	287.2	282.1	276.9	271.8	266.7
Mix1						t_r/min			
CH_4	methane(a)		5.994	5.912	5.845	5.770	5.723	5.643	5.583
C_6F_{14}	perfluorohexane		6.129	6.062	6.015	5.964	5.946	5.903	5.885
C_7F_{16}	perfluoroheptane		6.253	6.204	6.179	6.158	6.180	6.188	6.231
C_8F_{18}	perfluorooctane		6.467	6.457	6.485	6.543	6.670	6.807	7.026
C_9F_{20}	perfluorononane(b)		6.875	6.944	7.085	7.326	7.704	8.158	8.853

(a) non-retained component (b) mixture solvent

Table 1.2A. Enthalpies of Transfer and Vaporization

Run 1	slope	intercept	$\Delta_{sln}{}^{g}H_m$(281.9 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix1	*T*/K			lit	calc
C_6F_{14}	-2103.8	9.094	17.49	**32.5**	32.8 ± 3.0
C_7F_{16}	-2402.6	9.454	19.98	**36.3 ± 0.3**	35.9 ± 3.2
C_8F_{18}	-2925.4	10.617	24.32	**41.1 ± 0.1**	41.3 ± 3.5
C_9F_{20}	-3444.0	11.751	28.64	45.3 ± 0.2	46.6 ± 3.9

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.24 ± 0.11) $\Delta_{sln}{}^{g}H_m$(281.9 K) + (11.05 ± 2.28) $r^2 = 0.9923$ (1)

Table 1.1B. Retention Times

Run 2		*T*/K	297.2	292.2	287.2	282.1	276.9	271.7	266.7
Mix1						t_r/min			
CH_4	methane(a)		5.973	5.910	5.854	5.778	5.722	5.641	5.584
C_6F_{14}	perfluorohexane		6.107	6.060	6.025	5.972	5.947	5.901	5.885
C_7F_{16}	perfluoroheptane		6.229	6.203	6.189	6.167	6.182	6.185	6.230
C_8F_{18}	perfluorooctane		6.440	6.460	6.497	6.557	6.668	6.809	7.016
C_9F_{20}	perfluorononane(b)		6.835	6.957	7.104	7.357	7.697	8.190	8.833

(a) non-retained component (b) mixture solvent

Table 1.2B. Enthalpies of Transfer and Vaporization

Run 2	slope	intercept	$\Delta_{sln}{}^{g}H_m$(281.9 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix1	T/K			lit	calc
C_6F_{14}	-2108.8	9.110	17.534	**32.5**	32.8 ± 3.1
C_7F_{16}	-2401.8	9.451	19.970	**36.3 ± 0.3**	35.9 ± 3.3
C_8F_{18}	-2917.4	10.588	24.256	**41.1 ± 0.1**	41.3 ± 3.6
C_9F_{20}	-3454.1	11.785	28.719	45.3 ± 0.2	46.9 ± 4.0

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.26 ± 0.11) $\Delta_{sln}{}^{g}H_m$(281.9 K) + (10.70 ± 2.37) r^2 = 0.9919 (2)

Table 2.1A. Retention Times

Run 3		T/K	302.9	308.0	313.0	318.0	323.0	328.1	333.2
Mix 2						t_r/min			
CH_4	methane$^{(a)}$		7.774	7.846	7.918	7.995	8.073	8.159	8.237
C_8F_{18}	perfluorooctane$^{(b)}$		8.279	8.286	8.303	8.332	8.369	8.422	8.469
C_9F_{20}	perfluorononane		8.665	8.603	8.570	8.556	8.561	8.584	8.608
$C_{10}F_{22}$	perfluorodecane		9.338	9.148	9.015	8.925	8.868	8.840	8.827
$C_{12}F_{26}$	perfluorododecane		12.569	11.697	11.044	10.550	10.179	9.902	9.699
$C_{13}F_{30}$	perfluorotridecane		16.173	14.465	13.172	12.220	11.489	10.936	10.530
$C_{14}F_{30}$	perfluorotetradecane		22.550	19.369	16.800	14.986	13.610	12.582	11.827

(a) non-retained component (b) mixture solvent

Table 2.1B. Enthalpies of Transfer and Vaporization

Run 3	slope	intercept	$\Delta_{sln}{}^{g}H_m$(318.0 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 2	T/K			lit	calc
C_8F_{18}	-2591.1	9.237	21.54	**41.1 ± 0.1**	40.9 ± 5.0
C_9F_{20}	-2918.6	9.755	24.27	**45.3 ± 0.2**	45.8 ± 5.2
$C_{10}F_{22}$	-3250.3	10.291	27.03	**51.0**	50.8 ± 5.5
$C_{12}F_{26}$	-3966.2	11.532	32.98		61.5 ± 6.2
$C_{13}F_{30}$	-4338.3	12.200	36.07		67.1 ± 6.6
$C_{14}F_{30}$	-4745.4	12.976	39.46		73.2 ± 7.1

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.80 ± 0.15) $\Delta_{sln}{}^{g}H_m$(318.0 K) + (2.00 ± 3.71) r^2=0.9929 (3)

Table 2.2A. Retention Times

Run 4		*T*/K	302.7	307.9	312.9	318.0	323.0	328.1	333.2
Mix 2						t_r/min			
CH_4	methane[(a)]		7.846	7.850	7.910	7.997	8.074	8.155	8.235
C_8F_{18}	perfluorooctane[(b)]		8.356	8.290	8.293	8.333	8.368	8.411	8.466
C_9F_{20}	perfluorononane		8.745	8.608	8.559	8.555	8.563	8.573	8.602
$C_{10}F_{22}$	perfluorodecane		9.424	9.156	9.005	8.923	8.869	8.831	8.822
$C_{12}F_{26}$	perfluorododecane		12.713	11.724	11.034	10.539	10.190	9.894	9.694
$C_{13}F_{30}$	perfluorotridecane		16.390	14.490	13.164	12.195	11.504	10.926	10.521
$C_{14}F_{30}$	perfluorotetradecane		23.085	19.367	16.782	14.930	13.640	12.568	11.814

(a) non-retained component (b) mixture solvent

Table 2.2B. Enthalpies of Transfer and Vaporization

Run 4	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.9 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 2	*T*/K			lit	calc
C_8F_{18}	-2639.8	9.40	21.95	**41.1 ± 0.1**	40.8 ± 5.9
C_9F_{20}	-2959.7	9.89	24.61	**45.3 ± 0.2**	45.8 ± 6.3
$C_{10}F_{22}$	-3271.8	10.36	27.20	**51.0**	50.7 ± 6.6
$C_{12}F_{26}$	-3984.6	11.59	33.13		61.9 ± 7.4
$C_{13}F_{30}$	-4356.8	12.26	36.23		67.7 ± 7.9
$C_{14}F_{30}$	-4785.1	13.10	39.79		74.4 ± 8.4

$\Delta_{l}{}^{g}H_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.88 \pm 0.18)\ \Delta_{sln}{}^{g}H_m(317.9\ K) - (0.53 \pm 4.43)$ $r^2 = 0.9910$ (4)

Table 3.1A. Retention Times

Run 5		*T*/K	323.0	328.0	333.1	338.1	343.2	348.2	353.3
Mix 3						t_r/min			
CH_4	methane[(a)]		5.142	5.195	5.250	5.307	5.358	5.407	5.459
C_9F_{20}	perfluorononane[(b)]		5.456	5.463	5.489	5.519	5.549	5.581	5.615
$C_{12}F_{26}$	perfluorododecane		6.478	6.304	6.184	6.099	6.037	5.993	5.963
$C_{13}F_{30}$	perfluorotridecane		7.301	6.960	6.710	6.526	6.386	6.281	6.201
$C_{14}F_{30}$	perfluorotetradecane		8.639	8.004	7.533	7.186	6.916	6.710	6.551
$C_{15}F_{32}$	perfluoropentadecane		10.806	9.661	8.817	8.199	7.717	7.350	7.063
$C_{16}F_{34}$	pentafluorohexadecane		14.352	12.303	10.829	9.765	8.934	8.306	7.818

(a) non-retained component (b) mixture solvent

Table 3.1B. Enthalpies of Transfer and Vaporization

Run 5	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.1K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 3	T/K			lit	calc
C_9F_{20}	-2581.2	9.174	21.46	45.3 ± 0.2	43.7 ± 2.7
$C_{12}F_{26}$	-3648.4	11.018	30.33	**61.7 ± 6.8**	61.6 ± 3.1
$C_{13}F_{30}$	-4005.9	11.644	33.31	**67.4 ± 7.2**	67.6 ± 3.3
$C_{14}F_{30}$	-4369.0	12.287	36.33	**73.8 ± 7.7**	73.7 ± 3.4
$C_{15}F_{32}$	-4734.5	12.937	39.36		79.8 ± 3.6
$C_{16}F_{34}$	-5107.0	13.606	42.46		86.0 ± 3.7

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.02 ± 0.07) $\Delta_{sln}{}^{g}H_m$(338.1 K) + (0.41 ± 2.31) $r^2 = 0.9988$ (5)

Table 3.2A. Retention Times

Run 6		T/K	322.9	327.9	333.1	338.1	343.2	348.2	353.3
Mix 3						t_r/min			
CH_4	methane(a)		5.280	5.341	5.384	5.437	5.485	5.530	5.583
C_9F_{20}	perfluorononane(b)		5.598	5.613	5.625	5.652	5.674	5.701	5.742
$C_{12}F_{26}$	perfluorododecane		6.653	6.476	6.337	6.247	6.173	6.121	6.098
$C_{13}F_{30}$	perfluorotridecane		7.501	7.150	6.877	6.685	6.532	6.415	6.341
$C_{14}F_{30}$	perfluorotetradecane		8.876	8.222	7.721	7.359	7.076	6.855	6.699
$C_{15}F_{32}$	perfluoropentadecane		11.108	9.928	9.044	8.396	7.897	7.510	7.225
$C_{16}F_{34}$	pentafluorohexadecane		14.726	12.648	11.114	9.994	9.142	8.488	7.998

(a) non-retained component (b) mixture solvent

Table 3.2B. Enthalpies of Transfer and Vaporization

Run 6	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.1K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 3	T/K			lit	calc
C_9F_{20}	-2630.5	9.314	21.871	45.3 ± 0.2	43.6 ± 2.9
$C_{12}F_{26}$	-3676.3	11.082	30.567	**61.7 ± 6.8**	61.6 ± 3.3
$C_{13}F_{30}$	-4027.8	11.688	33.489	**67.4 ± 7.2**	67.6 ± 3.4
$C_{14}F_{30}$	-4382.6	12.305	36.439	**73.8 ± 7.7**	73.7 ± 3.6
$C_{15}F_{32}$	-4742.9	12.939	39.435		79.9 ± 3.8
$C_{16}F_{34}$	-5106.6	13.583	42.459		86.1 ± 3.9

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.06 ± 0.07) $\Delta_{sln}{}^{g}H_m$(338.1 K) **-** (1.45 ± 2.44) $r^2 = 0.9988$ (6)

Table 4.1A. Retention Times

Run 7		T/K	373.4	378.6	383.7	388.8	394.1	399.0	404.1
Mix 4						t_r/min			
C_8F_{18}	perfluorooctane$^{(a, b)}$		5.792	5.830	5.876	5.892	5.940	5.998	6.039
$C_{14}F_{30}$	perfluorotetradecane		6.312	6.275	6.260	6.225	6.232	6.254	6.265
$C_{15}F_{32}$	perfluoropentadecane		6.549	6.473	6.425	6.364	6.350	6.355	6.352
$C_{16}F_{34}$	pentafluorohexadecane		6.879	6.742	6.649	6.550	6.508	6.488	6.465
$C_{20}F_{42}$	perfluoroeicosane		10.147	9.330	8.718	8.219	7.868	7.604	7.386

(a) non-retained component (b) mixture solvent

Table 4.1B. Enthalpies of Transfer and Vaporization

Run 7	slope	intercept	$\Delta_{sln}{}^{g}H_m$(388.7 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 4	T/K			lit	calc
$C_{14}F_{30}$	-4083.8	11.598	33.95	**73.8 ± 7.7**	73.8 ± 0.3
$C_{15}F_{32}$	-4329.9	11.882	36.00	**79.8 ± 3.7**	79.8 ± 0.4
$C_{16}F_{34}$	-4591.3	12.220	38.17	**86.1 ± 3.8**	86.1 ± 0.4
$C_{20}F_{42}$	-5756.7	13.955	47.86		114.4 ± 0.4

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.91 ± 0.01) $\Delta_{sln}{}^{g}H_m$(388.7 K) - (25.14 ± 0.25) $r^2 = 1.0000$ (7)

Table 4.2A. Retention Times

Run 8		T/K	373.5	378.6	383.6	388.7	393.8	398.9	404.0
Mix 4						t_r/min			
C_8F_{18}	perfluorooctane$^{(a, b)}$		5.715	5.772	5.828	5.900	5.936	5.934	5.995
$C_{14}F_{30}$	perfluorotetradecane		6.229	6.214	6.210	6.236	6.233	6.191	6.221
$C_{15}F_{32}$	perfluoropentadecane		6.462	6.409	6.374	6.374	6.351	6.292	6.308
$C_{16}F_{34}$	pentafluorohexadecane		6.787	6.677	6.597	6.560	6.508	6.423	6.420
$C_{20}F_{42}$	perfluoroeicosane		10.008	9.236	8.653	8.222	7.868	7.531	7.332

(a) non-retained component (b) mixture solvent

Table 4.2B. Enthalpies of Transfer and Vaporization

Run 8	slope	intercept	$\Delta_{sln}{}^{g}H_m$(388.7 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 4	T/K			lit	calc
$C_{14}F_{30}$	-4013.5	11.418	33.37	**73.8 ± 7.7**	73.8 ± 0.4
$C_{15}F_{32}$	-4281.5	11.760	35.60	**79.8 ± 3.7**	79.8 ± 0.4
$C_{16}F_{34}$	-4560.4	12.146	37.92	**86.1 ± 3.8**	86.1 ± 0.4
$C_{20}F_{42}$	-5757.4	13.966	47.87		113.0 ± 0.4

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (2.70 ± 0.01) $\Delta_{sln}{}^{g}H_m$(388.7 K) - (16.42 ± 0.26) $r^2 = 1.0000$ (8)

Table 5.1A. Retention Times

Run 9		T/K	383.7	388.8	393.8	398.9	404.0	409.0	414.1
Mix 5						t_r/min			
C_8F_{18}	perfluorooctane$^{(a,b)}$		5.759	5.741	5.730	5.605	5.727	5.787	5.773
$C_{15}F_{32}$	perfluoropentadecane		6.302	6.202	6.127	5.941	6.025	6.050	6.003
$C_{16}F_{34}$	perfluorohexadecane		6.523	6.385	6.279	6.065	6.131	6.141	6.081
$C_{20}F_{42}$	perfluoroeicosane		8.564	8.014	7.593	7.113	7.002	6.867	6.685
$C_{24}F_{50}$	perfluorotetracosane		15.693	13.459	11.803	10.310	9.551	8.917	8.319

(a) non-retained component (b) mixture solvent

Table 5.1B. Enthalpies of Transfer and Vaporization

Run 9	slope	intercept	$\Delta_{sln}{}^{g}H_m$(398.9 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 5	T/K			lit	calc
$C_{15}F_{32}$	-4490.0	12.325	37.33	**79.8 ± 3.7**	79.8 ± 0.2
$C_{16}F_{34}$	-4746.0	12.651	39.46	**86.1 ± 3.8**	86.1 ± 0.2
$C_{20}F_{42}$	-5877.2	14.300	48.87	**113.7 ± 0.4**	113.7 ± 0.2
$C_{24}F_{50}$	-7122.7	16.283	59.22		144.1 ± 0.3

$\Delta_l{}^{g}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.94 \pm 0.00)\ \Delta_{sln}{}^{g}H_m(398.9\text{ K}) - (29.79 \pm 0.16)$ $r^2 = 1.0000$ (9)

Table 5.2A. Retention Times

Run 10		T/K	383.5	388.7	393.8	398.9	404.0	409.1	414.1
Mix 5						t_r/min			
C_8F_{18}	perfluorooctane$^{(a,b)}$		5.700	5.673	5.644	5.515	5.448	5.433	5.468
$C_{15}F_{32}$	perfluoropentadecane		6.233	6.129	6.035	5.844	5.731	5.681	5.687
$C_{16}F_{34}$	perfluorohexadecane		6.452	6.308	6.185	5.966	5.832	5.767	5.761
$C_{20}F_{42}$	perfluoroeicosane		8.464	7.918	7.478	6.993	6.662	6.448	6.331
$C_{24}F_{50}$	perfluorotetracosane		15.515	13.281	11.641	10.132	9.096	8.371	7.880

(a) non-retained component (b) mixture solvent

Table 5.2B. Enthalpies of Transfer and Vaporization

Run 10	slope	intercept	$\Delta_{sln}{}^{g}H_m$(398.8 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 5	T/K			lit	calc
$C_{15}F_{32}$	-4688.7	12.855	38.98	**79.8 ± 3.7**	79.7 ± 0.7
$C_{16}F_{34}$	-4958.5	13.217	41.23	**86.1 ± 3.8**	86.2 ± 0.7
$C_{20}F_{42}$	-6112.1	14.923	50.82	**113.7 ± 0.4**	113.7 ± 0.8
$C_{24}F_{50}$	-7355.5	16.900	61.16		143.3 ± 0.9

$\Delta_l{}^{g}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.87 \pm 0.01)\ \Delta_{sln}{}^{g}H_m(398.8\text{ K}) - (32.05 \pm 0.54)$ $r^2 = 1.0000$ (10)

Table 6.1A. Retention Times

Run 11		T/K	302.6	307.7	312.7	317.8	322.8	327.9	333.0
Mix 6						t_r/min			
CH_4	methane[(a)]		4.807	4.854	4.905	4.955	5.007	5.052	5.101
C_8F_{18}	perfluorooctane[(b)]		5.129	5.124	5.141	5.168	5.193	5.216	5.249
C_9F_{20}	perfluorononane		5.361	5.321	5.306	5.308	5.313	5.321	5.340
$C_{10}F_{22}$	perfluorodecane		5.776	5.659	5.584	5.538	5.505	5.482	5.476
C_8HF_{17}	1H-perfluorooctane		7.317	6.890	6.582	6.363	6.185	6.051	5.953
$C_{13}F_{28}$	perfluorotridecane		10.057	8.946	8.152	7.597	7.144	6.822	6.566

(a) non-retained component (b) mixture solvent

Table 6.1B. Enthalpies of Transfer and Vaporization

Run 11	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.8 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 6	T/K			lit	calc
C_8F_{18}	-2551.1	9.585	21.21	**41.1 ± 0.1**	41.4 ± 1.1
C_9F_{20}	-2783.5	9.803	23.14	**45.3 ± 0.2**	45.1 ± 1.1
$C_{10}F_{22}$	-3145.0	10.437	26.15	**51.0**	50.8 ± 1.2
C_8HF_{17}	-3575.3	10.908	29.73	43.4 ± 1.1	57.5 ± 1.3
$C_{13}F_{28}$	-4217.3	12.297	35.07	**67.5 ± 5.3**	67.6 ± 1.4

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.89 ± 0.03) $\Delta_{sln}{}^{g}H_m$(317.8 K) + (1.38 ± 0.86) $r^2 = 0.9994$ (11)

Table 6.2A. Retention Times

Run 12		T/K	302.5	307.6	312.7	317.7	322.8	327.8	332.9
Mix 6						t_r/min			
CH_4	methane[(a)]		4.913	4.915	4.960	4.990	5.012	5.073	5.101
C_8F_{18}	perfluorooctane[(b)]		5.238	5.197	5.203	5.203	5.201	5.237	5.250
C_9F_{20}	perfluorononane		5.489	5.404	5.374	5.348	5.324	5.342	5.340
$C_{10}F_{22}$	perfluorodecane		5.917	5.748	5.655	5.581	5.517	5.503	5.477
C_8HF_{17}	1H-perfluorooctane		7.503	7.017	6.671	6.417	6.206	6.070	5.952
$C_{13}F_{28}$	perfluorotridecane		10.366	9.184	8.290	7.697	7.211	6.835	6.565

(a) non-retained component (b) mixture solvent

Table 6.2B. Enthalpies of Transfer and Vaporization

Run 12	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.7 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 6	T/K			lit	calc
C_8F_{18}	-2609.2	9.753	21.69	**41.1 ± 0.1**	40.9 ± 1.1
C_9F_{20}	-2924.5	10.228	24.32	**45.3 ± 0.2**	45.7 ± 1.1
$C_{10}F_{22}$	-3262.5	10.791	27.13	**51.0**	50.8 ± 1.2
C_8HF_{17}	-3691.1	11.260	30.69	43.4 ± 1.1	57.3 ± 1.3
$C_{13}F_{28}$	-4358.2	12.722	36.24	**67.5 ± 5.3**	67.5 ± 1.4

$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1} = (1.83 ± 0.03) $\Delta_{sln}{}^{g}H_m$(317.7 K) + (1.22 ± 0.86) $r^2 = 0.9994$ (12)

Table 7.1A. Retention Times

Run 13		T/K	323.8	328.6	333.7	338.7	343.8	348.8	353.8
Mix 7			t_r/min						
CH_4	methane[(a)]		5.010	5.079	5.131	5.182	5.235	5.278	5.333
C_8F_{18}	perfluorooctane[(b)]		5.197	5.245	5.279	5.313	5.354	5.381	5.429
$C_{12}F_{27}N$	heptacosafluorotributylamine		6.162	6.034	5.928	5.851	5.804	5.765	5.755
$C_{14}F_{30}$	perfluorotetradecane		7.153	6.832	6.576	6.381	6.240	6.126	6.056
$C_{15}F_{32}$	perfluoropentadecane		8.460	7.855	7.382	7.023	6.754	6.545	6.396
$C_{16}F_{34}$	perfluorohexadecane		10.761	9.625	8.710	8.054	7.554	7.187	6.907

(a) non-retained component (b) mixture solvent

Table 7.1B. Enthalpies of Transfer and Vaporization

Run 13	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.8 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 7	T/K			lit	calc
C_8F_{18}	-2565.9	9.606	21.33	**41.1 ± 0.1**	41.8 ± 4.9
$C_{12}F_{27}N$	-3831.9	11.707	31.86	60.3 ± 0.1	66.3 ± 5.7
$C_{14}F_{30}$	-4138.2	12.030	34.41	**73.8 ± 3.9**	72.3 ± 5.9
$C_{15}F_{32}$	-4480.1	12.611	37.25	**79.8 ± 1.5**	78.9 ± 6.2
$C_{16}F_{34}$	-4939.5	13.520	41.07	**86.1 ± 1.6**	87.8 ± 6.5

$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (2.33 \pm 0.12)\ \Delta_{sln}{}^{g}H_m(338.8\ K) - (7.96 \pm 4.17)$ $r^2 = 0.9946$ (13)

Table 7.2A. Retention Times

Run 14		T/K	323.6	328.7	333.7	338.7	343.7	348.8	353.8
Mix 7			t_r/min						
CH_4	methane[(a)]		5.180	5.137	5.182	5.233	5.285	5.327	5.386
C_8F_{18}	perfluorooctane[(b)]		5.370	5.304	5.332	5.366	5.409	5.435	5.484
$C_{12}F_{27}N$	heptacosafluorotributylamine		6.349	6.095	5.994	5.914	5.864	5.825	5.811
$C_{14}F_{30}$	perfluorotetradecane		7.375	6.908	6.651	6.451	6.304	6.192	6.115
$C_{15}F_{32}$	perfluoropentadecane		8.716	7.938	7.469	7.105	6.824	6.616	6.460
$C_{16}F_{34}$	perfluorohexadecane		10.983	9.685	8.844	8.150	7.627	7.277	6.971

(a) non-retained component (b) mixture solvent

Table 7.2B. Enthalpies of Transfer and Vaporization

Run 14	slope	intercept	$\Delta_{sln}{}^{g}H_m$(338.7 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 7	T/K			lit	calc
C_8F_{18}	-2463.5	9.279	20.48	**41.1 ± 0.1**	41.4 ± 2.6
$C_{12}F_{27}N$	-3805.0	11.613	31.64	60.3 ± 0.1	66.5 ± 3.0
$C_{14}F_{30}$	-4151.8	12.056	34.52	**73.8 ± 3.9**	73.0 ± 3.1
$C_{15}F_{32}$	-4494.1	12.638	37.37	**79.8 ± 1.5**	79.3 ± 3.3
$C_{16}F_{34}$	-4908.2	13.417	40.81	**86.1 ± 1.6**	87.1 ± 3.4

$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (2.24 \pm 0.06)\ \Delta_{sln}{}^{g}H_m(338.7\ K) - (4.52 \pm 2.20)$ $r^2 = 0.9984$ (14)

Table 8.1A. Retention Times

Run 15		T/K	307.2	302.2	297.1	292.1	287.1	281.9	276.8
Mix 8						t_r/min			
CH_4	methane[(a)]		6.079	6.022	5.946	5.891	5.817	5.764	5.699
C_6F_{14}	perfluorohexane		6.184	6.141	6.080	6.042	5.987	5.958	5.927
C_7F_{14}	perfluoroheptane		6.279	6.248	6.202	6.183	6.152	6.153	6.159
C_7F_{14}	perfluoromethylcyclohexane		6.454	6.438	6.420	6.436	6.450	6.513	6.606
C_9F_{20}	perfluorononane[(b)]		6.687	6.746	6.817	6.938	7.079	7.308	7.627
$C_{10}F_{22}$	perfluorodecane		7.133	7.308	7.528	7.842	8.230	8.804	9.564

(a) non-retained component (b) mixture solvent

Table 8.1B. Enthalpies of Transfer and Vaporization

Run 15	slope	intercept	$\Delta_{sln}{}^{g}H_m$(292.0 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 8	T/K			lit	calc
C_6F_{14}	-2127.3	9.175	17.69	**32.5**	33.2 ± 2.7
C_7F_{14}	-2310.9	9.139	19.21	**36.3 ±0.3**	35.3 ± 2.8
C_7F_{14}	-2474.3	9.063	20.57	35.3	37.3 ± 2.9
C_9F_{20}	-3209.4	10.945	26.68	**45.3 ± 0.2**	45.9 ± 3.3
$C_{10}F_{22}$	-3624.4	11.745	30.14	**51.0**	50.7 ± 3.5

$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.41 ± 0.09) $\Delta_{sln}{}^{g}H_m$(292.0 K) + (8.29 ± 2.20) r^2 = 0.9916 (15)

Table 8.2A. Retention Times

Run 16		T/K	307.2	302.2	297.2	292.1	287.1	282.0	276.8
Mix 8						t_r/min			
CH_4	methane[(a)]		6.080	6.015	5.962	5.899	5.830	5.768	5.699
C_6F_{14}	perfluorohexane		6.188	6.136	6.095	6.049	6.002	5.963	5.924
C_7F_{14}	perfluoroheptane		6.283	6.242	6.218	6.189	6.167	6.158	6.155
C_7F_{14}	perfluoromethylcyclohexane		6.456	6.433	6.435	6.443	6.464	6.518	6.604
C_9F_{20}	perfluorononane[(b)]		6.695	6.734	6.833	6.933	7.091	7.321	7.645
$C_{10}F_{22}$	perfluorodecane		7.147	7.288	7.547	7.821	8.241	8.834	9.547

(a) non-retained component (b) mixture solvent

Table 8.2B. Enthalpies of Transfer and Vaporization

Run 16	slope	intercept	$\Delta_{sln}{}^{g}H_m$(292.0 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 8	T/K			lit	calc
C_6F_{14}	-2052.8	8.914	17.07	**32.5**	33.0 ± 2.6
C_7F_{14}	-2270.4	8.997	18.88	**36.3 ±0.3**	35.5 ± 2.7
C_7F_{14}	-2464.7	9.029	20.49	35.3	37.6 ± 2.8
C_9F_{20}	-3222.0	10.987	26.79	**45.3 ± 0.2**	46.1 ± 3.2
$C_{10}F_{22}$	-3618.7	11.725	30.09	**51.0**	50.5 ± 3.4

$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1} = (1.34± 0.09) $\Delta_{sln}{}^{g}H_m$(292.0 K) + (10.08 ± 2.11) r^2 = 0.9914 (16)

Table 9.1A. Retention Times

Run 17		*T*/K	307.7	312.8	317.7	322.8	327.9	333.0	338.0
Mix 9						t_r/min			
CH_4	methane(a)		4.887	4.923	4.965	5.002	5.047	5.097	5.137
C_8F_{18}	perfluorooctane(b)		5.161	5.159	5.170	5.184	5.215	5.237	5.264
C_8F_{16}	perfluoro-1,3-dimethylcyclohexane		5.412	5.379	5.365	5.357	5.367	5.375	5.386
$C_{10}F_{22}$	perfluorodecane		5.702	5.607	5.541	5.497	5.477	5.460	5.452
$C_{12}F_{26}$	perfluorododecane		7.306	6.896	6.551	6.312	6.149	6.009	5.903
$C_{13}F_{28}$	perfluorotridecane		9.064	8.313	7.590	7.130	6.811	6.535	6.321

(a) non-retained component (b) mixture solvent

Table 9.1B. Enthalpies of Transfer and Vaporization

Run 17	slope	intercept	$\Delta_{sln}{}^gH_m$(322.8 K)	$\Delta_l{}^gH_m$(298.15 K)	
Mix 9	*T*/K			lit.	calc
C_8F_{18}	-2615.3	9.802	21.75	**41.1 ± 0.1**	41.2 ± 0.5
C_8F_{16}	-2543.5	8.915	21.15	38.6 ± 0.1	40.1 ± 0.5
$C_{10}F_{22}$	-3242.8	10.749	26.96	**51.0**	50.8 ± 0.6
$C_{12}F_{26}$	-3939.9	11.928	32.76	**61.6 ± 5.0**	61.6 ± 0.6
$C_{13}F_{28}$	-4333.6	12.657	36.03	**67.5 ± 5.3**	67.6 ± 0.7

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.85 ± 0.01) $\Delta_{sln}{}^gH_m$(322.8 K) + (1.03 ± 0.43) $r^2 = 0.9999$ (17)

Table 9.2A. Retention Times

Run 18		*T*/K	307.6	312.7	317.7	322.8	327.9	333.0	338.0
Mix 9						t_r/min			
CH_4	methane(a)		4.930	4.955	4.989	5.029	5.060	5.108	5.145
C_8F_{18}	perfluorooctane(b)		5.205	5.192	5.207	5.217	5.223	5.250	5.275
C_8F_{16}	perfluoro-1,3-dimethylcyclohexane		5.458	5.414	5.397	5.386	5.376	5.387	5.397
$C_{10}F_{22}$	perfluorodecane		5.751	5.641	5.579	5.527	5.484	5.472	5.464
$C_{12}F_{26}$	perfluorododecane		7.351	6.904	6.602	6.348	6.146	6.016	5.916
$C_{13}F_{28}$	perfluorotridecane		9.091	8.242	7.657	7.176	6.790	6.535	6.335

(a) non-retained component (b) mixture solvent

Table 9.2B. Enthalpies of Transfer and Vaporization

Run 18	slope	intercept	$\Delta_{sln}{}^gH_m$(322.8 K)	$\Delta_l{}^gH_m$(298.15 K)	
Mix 9	*T*/K			lit.	calc
C_8F_{18}	-2621.8	9.808	21.80	**41.1 ± 0.1**	41.1 ± 0.2
C_8F_{16}	-2535.8	8.886	21.08	38.6 ± 0.1	39.8 ± 0.2
$C_{10}F_{22}$	-3247.0	10.757	27.00	**51.0**	51.0 ± 0.2
$C_{12}F_{26}$	-3924.4	11.880	32.63	**61.6 ± 5.0**	61.7 ± 0.2
$C_{13}F_{28}$	-4292.0	12.534	35.69	**67.5 ± 5.3**	67.5 ± 0.2

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.90 ± 0.00) $\Delta_{sln}{}^gH_m$(322.8 K) **-** (0.27 ± 0.14) $r^2 = 1.0000$ (18)

Table 10.1A. Retention Times

Run 19	T/K	302.7	307.8	312.8	317.8	322.8	327.9	333.0
Mix 10		t_r/min						
CH_4	methane(a)	4.912	4.952	5.017	5.062	5.118	5.163	5.216
C_8F_{18}	perfluorooctane(b)	5.253	5.251	5.265	5.274	5.299	5.325	5.362
C_9F_{20}	perfluorononane	5.477	5.441	5.429	5.418	5.420	5.430	5.453
$C_{10}F_{22}$	perfluorodecane	5.907	5.792	5.713	5.654	5.616	5.594	5.592
$C_{10}F_{18}$	perfluorodecalin (trans)	7.657	7.263	6.958	6.717	6.528	6.382	6.275
$C_{10}F_{18}$	perfluorodecalin (cis)	8.157	7.674	7.299	7.002	6.768	6.585	6.448
$C_{13}F_{28}$	perfluorotridecane	10.307	9.232	8.363	7.766	7.295	6.942	6.681

(a) non-retained component (b) mixture solvent

Table 10.1B. Enthalpies of Transfer and Vaporization

Run 19	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.8 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 10	T/K			lit	calc
C_8F_{18}	-2924.9	10.740	24.32	41.1 ± 0.1	45.0 ± 1.7
C_9F_{20}	-2957.9	10.341	24.59	**45.3 ± 0.2**	45.5 ± 1.7
$C_{10}F_{22}$	-3285.6	10.862	27.32	**51.0**	50.7 ± 1.8
$C_{10}F_{18}$	-3185.7	9.519	26.49	45.4 ± 0.1	49.1 ± 1.8
$C_{10}F_{18}$	-3237.3	9.522	26.92	46.2 ± 0.1	49.9 ± 1.8
$C_{13}F_{28}$	-4356.8	12.713	36.22	**67.5 ± 5.3**	67.6 ± 2.1

$\Delta_{l}{}^{g}H_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.90 \pm 0.04)\ \Delta_{sln}{}^{g}H_m(317.8\ K) - (1.08 \pm 1.32)$ $r^2 = 0.9995$ (19)

Table 10.2A. Retention Times

Run 20	T/K	302.6	307.7	312.7	317.7	322.8	327.9	333.0
Mix 10		t_r/min						
CH_4	methane(a)	4.806	4.848	4.886	4.939	4.984	5.020	5.079
C_8F_{18}	perfluorooctane(b)	5.117	5.115	5.118	5.142	5.164	5.178	5.221
C_9F_{20}	perfluorononane	5.356	5.313	5.284	5.282	5.284	5.280	5.309
$C_{10}F_{22}$	perfluorodecane	5.775	5.654	5.561	5.511	5.475	5.441	5.445
$C_{10}F_{18}$	perfluorodecalin (trans)	7.497	7.100	6.778	6.548	6.366	6.209	6.110
$C_{10}F_{18}$	perfluorodecalin (cis)	7.987	7.501	7.111	6.825	6.600	6.407	6.279
$C_{13}F_{28}$	perfluorotridecane	10.093	9.042	8.155	7.547	7.128	6.759	6.504

(a) non-retained component (b) mixture solvent

Table 10.2B. Enthalpies of Transfer and Vaporization

Run 20	slope	intercept	$\Delta_{sln}{}^{g}H_m$(317.8 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 10	T/K			lit	calc
C_8F_{18}	-2594.3	9.753	21.57	41.1 ± 0.1	41.2 ± 1.5
C_9F_{20}	-2882.5	10.136	23.97	**45.3 ± 0.2**	45.5 ± 1.6
$C_{10}F_{22}$	-3228.4	10.711	26.84	**51.0**	50.7 ± 1.7
$C_{10}F_{18}$	-3178.6	9.523	26.43	45.4 ± 0.1	50.0 ± 1.6
$C_{10}F_{18}$	-3230.7	9.528	26.86	46.2 ± 0.1	50.7 ± 1.7
$C_{13}F_{28}$	-4351.3	12.722	36.18	**67.5 ± 5.3**	67.6 ± 1.9

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.81 ± 0.04) $\Delta_{sln}{}^{g}H_m$(317.8 K) + (2.25 ± 1.23) r2 = 0.9995 (20)

Table 11.1A. Retention Times

Run 21		T/K	318.0	323.0	328.0	333.2	338.2	343.2	348.3
Mix 11						t_r/min			
CH_4	methane[(a)]		6.313	6.366	6.428	6.484	6.542	6.597	6.672
C_8F_{18}	perfluorooctane[(b)]		6.580	6.602	6.632	6.668	6.707	6.745	6.805
$C_{12}F_{26}$	perfluorododecane		8.324	8.031	7.799	7.643	7.517	7.430	7.385
$C_{13}F_{28}$	perfluorotridecane		9.671	9.098	8.621	8.320	8.054	7.865	7.743
$C_{14}F_{30}$	perfluorotetradecane		11.825	10.764	9.906	9.340	8.862	8.514	8.270
C_6F_6	hexafluorobenzene (HFB)		12.842	11.841	11.050	10.416	9.913	9.504	9.191
C_7F_8	octafluorotoluene (OFT)		16.200	14.497	13.144	12.096	11.260	10.597	10.083

(a) non-retained component (b) mixture solvent

Table 11.1B. Enthalpies of Transfer and Vaporization

Run 21	slope	intercept	$\Delta_{sln}{}^{g}H_m$(333.1 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 11	T/K			lit	calc
C_8F_{18}	-2527.4	9.277	21.01	**41.1 ± 0.1**	41.1 ± 1.2
$C_{12}F_{26}$	-3786.5	11.218	31.48	**61.6 ± 5.0**	61.5 ± 1.4
$C_{13}F_{28}$	-4177.5	11.935	34.73	**67.5 ± 5.3**	67.9 ± 1.5
$C_{14}F_{30}$	-4525.9	12.537	37.63	**73.8 ± 3.9**	73.5 ± 1.6
C_6F_6	-3475.4	9.060	28.90	36.1 ± 0.1	56.5 ± 1.4
C_7F_8	-3887.2	9.941	32.32	40.5 ± 0.2	63.2 ± 1.5

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.95 ± 0.03) $\Delta_{sln}{}^{g}H_m$(333.1 K) **-** (0.07 ± 1.02) r^2 = 0.9995 (21)

Table 11.2A. Retention Times

Run 22		*T*/K	317.6	322.9	328.0	333.0	338.0	343.1	348.1
Mix 11						t_r/min			
CH_4	methane(a)		6.000	6.002	6.062	6.117	6.177	6.238	6.301
C_8F_{18}	perfluorooctane(b)		6.247	6.222	6.258	6.294	6.331	6.377	6.427
$C_{12}F_{26}$	perfluorododecane		7.904	7.563	7.361	7.202	7.095	7.022	6.980
$C_{13}F_{28}$	perfluorotridecane		9.145	8.540	8.137	7.820	7.597	7.430	7.317
$C_{14}F_{30}$	perfluorotetradecane		11.180	10.098	9.353	8.779	8.361	8.045	7.817
C_6F_6	hexafluorobenzene (HFB)		12.229	11.180	10.436	9.836	9.363	8.988	8.689
C_7F_8	octafluorotoluene (OFT)		15.413	13.663	12.407	11.411	10.636	10.021	9.532

(a) non-retained component (b) mixture solvent

Table 11.1B. Enthalpies of Transfer and Vaporization

Run 22	slope	intercept	$\Delta_{sln}{}^{g}H_m(332.8\ K)$	$\Delta_l{}^{g}H_m(298.15\ K)$	
Mix 11	*T*/K			lit	calc
C_8F_{18}	-2477.6	9.192	20.60	**41.1 ± 0.1**	41.0 ± 1.1
$C_{12}F_{26}$	-3758.7	11.199	31.25	**61.6 ± 5.0**	61.8 ± 1.3
$C_{13}F_{28}$	-4120.4	11.834	34.26	**67.5 ± 5.3**	67.7 ± 1.4
$C_{14}F_{30}$	-4471.0	12.441	37.17	**73.8 ± 3.9**	73.4 ± 1.5
C_6F_6	-3477.4	9.126	28.91	36.1 ± 0.1	57.3 ± 1.3
C_7F_8	-3877.5	9.974	32.24	40.5 ± 0.2	63.8 ± 1.3

$\Delta_l{}^{g}H_m(298.15\ K)/kJ \cdot mol^{-1} = (1.96 \pm 0.03)\ \Delta_{sln}{}^{g}H_m(332.8\ K) + (0.66 \pm 0.94)$ $r^2 = 0.9995$ (22)

Table 12.1A. Retention Times

Run 23		*T*/K	409.1	414.1	419.2	424.2	429.3	434.3	439.3
Mix 12						t_r/min			
CH_4	methane(a)		3.124	3.152	3.175	3.199	3.227	3.249	3.273
C_7H_{16}	heptane(b)		3.508	3.504	3.503	3.499	3.501	3.502	3.509
$C_7H_{15}F$	1-fluoroheptane		3.910	3.860	3.819	3.780	3.752	3.727	3.712
$C_{10}H_{22}$	decane		5.097	4.888	4.725	4.593	4.445	4.330	4.241
$C_{12}H_{26}$	dodecane		8.809	8.022	7.394	6.855	6.391	6.005	5.680
$C_{12}H_{25}F$	1-fluorododecane		14.552	12.776	11.416	10.233	9.237	8.402	7.684
$C_{14}H_{30}$	tetradecane		19.310	16.648	14.603	12.868	11.400	10.199	9.179
$C_{14}H_{29}F$	1-fluorotetradecane		35.568	29.758	25.444	21.764	18.710	16.216	14.094

(a) non-retained component (b) mixture solvent

Table 12.1B. Enthalpies of Transfer and Vaporization

Run 23	slope	intercept	$\Delta_{sln}{}^{g}H_m$(424.2 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 12	T/K			lit	calc
C_7H_{16}	-2947.1	8.156	24.50	**36.6**	36.6 ± 0.2
$C_7H_{15}F$	-3487.1	8.765	28.99	43.4	42.8 ± 0.2
$C_{10}H_{22}$	-4232.9	9.664	35.19	**51.4**	51.5 ± 0.3
$C_{12}H_{26}$	-5102.0	10.735	42.42	**61.5**	61.6 ± 0.3
$C_{12}H_{25}F$	-5629.7	11.326	46.81	68.7	67.7 ± 0.3
$C_{14}H_{30}$	-5968.9	11.808	49.63	**71.7**	71.6 ± 0.3
$C_{14}H_{29}F$	-6488.0	12.381	53.94	77.7	77.7 ± 0.3

$\Delta_l{}^{g}H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.40 \pm 0.00)\ \Delta_{sln}{}^{g}H_m(424.2\text{ K}) + (2.34 \pm 0.19)$ $r^2 = 1.0000$ (23)

Table 12.2A. Retention Times

Run 24		T/K	408.9	414.0	419.0	424.0	429.2	434.3	439.3
Mix 12						t_r/min			
CH_4	methane$^{(a)}$		3.136	3.150	3.179	3.198	3.224	3.250	3.273
C_7H_{16}	heptane$^{(b)}$		3.523	3.502	3.502	3.492	3.501	3.503	3.508
$C_7H_{15}F$	1-fluoroheptane		3.926	3.858	3.819	3.773	3.753	3.729	3.712
$C_{10}H_{22}$	decane		5.123	4.889	4.717	4.571	4.443	4.331	4.242
$C_{12}H_{26}$	dodecane		8.860	8.036	7.387	6.879	6.396	6.003	5.683
$C_{12}H_{25}F$	1-fluorododecane		14.674	12.832	11.393	10.336	9.252	8.395	7.699
$C_{14}H_{30}$	tetradecane		19.456	16.715	14.569	12.979	11.403	10.192	9.199
$C_{14}H_{29}F$	1-fluorotetradecane		35.979	29.973	25.364	22.104	18.774	16.203	14.150

(a) non-retained component (b) mixture solvent

Table 12.2B. Enthalpies of Transfer and Vaporization

Run 24	slope	intercept	$\Delta_{sln}{}^{g}H_m$(424.1 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 12	T/K			lit	calc
C_7H_{16}	-2924.5	8.109	24.32	**36.6**	36.5 ± 0.2
$C_7H_{15}F$	-3461.9	8.708	28.78	43.4	42.8 ± 0.3
$C_{10}H_{22}$	-4221.9	9.643	35.10	**51.4**	51.5 ± 0.3
$C_{12}H_{26}$	-5091.2	10.710	42.33	**61.5**	61.6 ± 0.3
$C_{12}H_{25}F$	-5627.9	11.321	46.79	68.7	67.8 ± 0.3
$C_{14}H_{30}$	-5958.8	11.784	49.54	**71.7**	71.6 ± 0.3
$C_{14}H_{29}F$	-6485.0	12.371	53.92	77.7	77.7 ± 0.4

$\Delta_l{}^{g}H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.39 \pm 0.01)\ \Delta_{sln}{}^{g}H_m(424.1\text{ K}) + (2.68 \pm 0.27)$ $r^2 = 0.9999$ (24)

Table 13.1A. Retention Times

Run 25		T/K	399.2	404.1	409.3	414.4	419.4	424.3	429.8
Mix 13						t_r/min			
CH_4	methane$^{(a)}$		3.061	3.087	3.103	3.127	3.158	3.180	3.206
$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene		3.531	3.512	3.490	3.482	3.484	3.481	3.481
$C_7H_5F_3$	trifluorotoluene		3.710	3.672	3.633	3.611	3.601	3.586	3.577
C_7H_8	toluene		4.031	3.959	3.892	3.844	3.811	3.777	3.751
C_8H_{10}	*o*-xylene		5.113	4.899	4.716	4.567	4.448	4.341	4.250
C_8H_9F	3-flouro-*o*-xylene		5.326	5.076	4.868	4.694	4.557	4.433	4.329
C_9H_{12}	mesitylene$^{(b)}$		6.113	5.722	5.429	5.161	4.971	4.785	4.631
$C_{10}H_8$	naphthalene		15.588	13.762	12.293	11.046	10.027	9.162	8.442

(a) non-retained component (b) mixture solvent

Table 13.1B. Enthalpies of Transfer and Vaporization

Run 25	slope	intercept	$\Delta_{sln}{}^{g}H_m$(414.5 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 13	T/K			lit	calc
$C_6H_2F_4$	-2986.9	8.243	24.83	37.2	35.3 ± 2.9
$C_7H_5F_3$	-3127.8	8.273	26.01	37.1	36.7 ± 2.9
C_7H_8	-3229.0	8.125	26.85	**38.1 ± 0.4**	37.7 ± 2.9
C_8H_{10}	-3788.0	8.777	31.50	**42.9**	43.4 ± 3.2
C_8H_9F	-3933.3	9.042	32.70	n/a	44.9 ± 3.2
C_9H_{12}	-4249.3	9.540	35.33	47.6	48.2 ± 3.3
$C_{10}H_8$	-4901.4	9.758	40.75	**55.0 ± 1.4**	54.8 ± 3.6

$\Delta_{l}{}^{g}H_m$(298.15 K)/kJ·mol^{-1} = (1.23 ± 0.07) $\Delta_{sln}{}^{g}H_m$(414.5 K) + (4.74 ± 2.29) $r^2 = 0.9969$ (25)

n/a Not used due to no published vaporization enthalpy value.

Table 13.2A. Retention Times

Run 26		T/K	399.2	404.3	409.2	414.2	419.2	424.2	429.3
Mix 13						t_r/min			
CH_4	methane$^{(a)}$		3.060	3.088	3.115	3.140	3.162	3.184	3.212
$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene		3.529	3.513	3.503	3.495	3.487	3.484	3.487
$C_7H_5F_3$	trifluorotoluene		3.708	3.673	3.646	3.624	3.603	3.589	3.583
C_7H_8	toluene		4.029	3.961	3.904	3.857	3.814	3.780	3.757
C_8H_{10}	*o*-xylene		5.109	4.902	4.727	4.580	4.451	4.344	4.257
C_8H_9F	3-fluoro-*o*-xylene		5.324	5.082	4.878	4.708	4.559	4.438	4.337
C_9H_{12}	mesitylene$^{(b)}$		6.084	5.728	5.424	5.170	4.973	4.785	4.632
$C_{10}H_8$	naphthalene		15.583	13.783	12.299	11.069	10.042	9.173	8.450

(a) non-retained component (b) mixture solvent

Table 13.2B. Enthalpies of Transfer and Vaporization

Run 26	slope	intercept	$\Delta_{sln}{}^{g}H_m$(414.2 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 13	T/K			lit	calc
$C_6H_2F_4$	-3044.6	8.386	25.31	37.2	35.4 ± 2.7
$C_7H_5F_3$	-3182.4	8.409	26.46	37.1	36.8 ± 2.7
C_7H_8	-3281.4	8.254	27.28	**38.1 ± 0.4**	37.8 ± 2.8
C_8H_{10}	-3841.2	8.908	31.94	**42.9**	43.4 ± 3.0
C_8H_9F	-3990.2	9.182	33.18	n/a	44.9 ± 3.0
C_9H_{12}	-4298.2	9.664	35.74	47.6	48.0 ± 3.1
$C_{10}H_8$	-4971.4	9.930	41.34	**55.0 ± 1.4**	54.8 ± 3.4

$\Delta_{l}{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.21 \pm 0.06)\ \Delta_{sln}{}^{g}H_m(414.2\ \mathrm{K}) + (4.63 \pm 2.16)$ $r^2 = 0.9973$ (26)

n/a Not used due to no published vaporization enthalpy value.

Table 14.1A. Retention Times

Run 27		T/K	399.7	404.9	410.0	415.1	420.2	425.2	430.3
Mix 14						t_r/min			
CH_4	methane[(a)]		2.908	2.930	2.969	2.989	3.002	3.032	3.067
$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene		3.453	3.424	3.416	3.396	3.375	3.379	3.381
C_7H_8	toluene		3.831	3.763	3.720	3.669	3.622	3.604	3.585
$C_8H_6F_4$	2,3,5,6-tetrafluoro-*p*-xylene		4.752	4.550	4.404	4.269	4.141	4.053	3.977
C_8H_{10}	*o*-xylene		4.865	4.660	4.508	4.365	4.232	4.143	4.063
C_9H_{12}	mesitylene[(b)]		5.919	5.555	5.284	5.081	4.818	4.582	4.421
$C_{10}F_8$	octafluoronaphthalene		9.896	8.779	7.926	7.250	6.624	6.115	5.713
$C_{12}F_{10}$	decafluorobiphenyl		11.897	10.501	9.448	8.626	7.819	7.124	6.593
$C_{10}H_8$	naphthalene		14.911	13.154	11.786	10.691	9.652	8.763	8.059

(a) non-retained component (b) mixture solvent

Table 14.1B. Enthalpies of Transfer and Vaporization

Run 27	slope	intercept	$\Delta_{sln}{}^{g}H_m$(415.0 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)	
Mix 14	T/K			lit	calc
$C_6H_2F_4$	-3071.2	8.29	25.54	37.5	36.2 ± 2.8
C_7H_8	-3225.3	8.15	26.82	**38.1 ± 0.4**	37.7 ± 2.8
$C_8H_6F_4$	-3949.1	9.27	32.83	n/a	45.1 ± 3.1
C_8H_{10}	-3785.6	8.80	31.48	**42.9**	43.4 ± 3.0
C_9H_{12}	-4450.4	10.02	37.00	47.6	50.2 ± 3.3
$C_{10}F_8$	-5436.3	11.66	45.20	64.7	60.2 ± 3.7
$C_{12}F_{10}$	-5225.7	10.88	43.45	67.0	58.0 ± 3.6
$C_{10}H_8$	-4909.9	9.80	40.82	**55.0 ± 1.4**	54.8 ± 3.5

$\Delta_{l}{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.22 \pm 0.07)\ \Delta_{sln}{}^{g}H_m(415.0\ \mathrm{K}) + (5.03 \pm 2.20)$ $r^2 = 0.9971$ (27)

n/a Not used due to no published vaporization enthalpy value.

Table 14.2A. Retention Times

Run 27		T/K	399.5	404.7	409.9	414.9	420.0	425.1	430.2
Mix 14						t_r/min			
CH_4	methane[(a)]		3.052	3.080	3.107	3.129	3.153	3.164	3.198
$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene		3.626	3.600	3.577	3.560	3.546	3.526	3.530
C_7H_8	toluene		4.025	3.957	3.897	3.849	3.807	3.762	3.745
$C_8H_6F_4$	2,3,5,6-tetrafluoro-*p*-xylene		4.982	4.781	4.606	4.465	4.343	4.231	4.156
C_8H_{10}	*o*-xylene		5.104	4.897	4.718	4.571	4.443	4.326	4.245
C_9H_{12}	mesitylene[(b)]		6.118	5.769	5.415	5.187	4.973	4.773	4.622
$C_{10}F_8$	octafluoronaphthalene		10.366	9.217	8.265	7.525	6.904	6.388	5.980
$C_{12}F_{10}$	decafluorobiphenyl		12.419	11.008	9.799	8.884	8.090	7.436	6.908
$C_{10}H_8$	naphthalene		15.599	13.797	12.273	11.065	10.027	9.155	8.438

(a) non-retained component (b) mixture solvent

Table 14.2B. Enthalpies of Transfer and Vaporization

Run 28	slope	intercept	$\Delta_{sln}{}^{g}H_m$(414.8 K)	$\Delta_l{}^{g}H_m$(298.15 K)	
Mix 14	T/K			lit	calc
$C_6H_2F_4$	-3063.7	8.23	25.47	37.5	36.2 ± 2.4
C_7H_8	-3223.2	8.10	26.80	**38.1 ± 0.4**	37.8 ± 2.4
$C_8H_6F_4$	-3926.8	9.17	32.65	n/a	45.0 ± 2.6
C_8H_{10}	-3767.5	8.71	31.32	**42.9**	43.4 ± 2.6
C_9H_{12}	-4287.7	9.61	35.65	47.6	48.7 ± 2.7
$C_{10}F_8$	-5416.6	11.57	45.04	64.7	60.2 ± 3.2
$C_{12}F_{10}$	-5193.3	10.77	43.18	67.0	57.9 ± 3.1
$C_{10}H_8$	-4893.2	9.72	40.68	**55.0 ± 1.4**	54.9 ± 3.0

$\Delta_l{}^{g}H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.23 \pm 0.06)\ \Delta_{sln}{}^{g}H_m(414.8\text{ K}) + (4.86 \pm 1.88)$ $r^2 = 0.9979$ (28)

n/a Not used due to no published vaporization enthalpy value.