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Predicting Liquid Phase Heat Capacity of Ill-defined Hydrocarbons

by

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Abstract

There are currently no reliable methods for predicting liquid heat capacities of ill-defined hydrocarbons, such as bitumen and heavy crude oils and their partly processed fractions. Estimation techniques for liquid phase isobaric heat capacity of pure compounds include corresponding state and group contribution methods. These techniques require critical properties (T_c, P_c), molecular structure, or physical properties (T_b, ρ, sp gr) to be applied. Molecular structures and critical properties for many industrially relevant organic fluids remain speculative.

In this work, a predictive correlation relating liquid specific heat capacity to absolute temperature and elemental composition was developed. It retained the quadratic form of the Lee-Kesler correlation, but the parameters were redefined as second order power series in a similarity variable based solely on elemental composition. This correlation yields significantly improved heat capacity estimates vis-à-vis prior practice. Since the correlation requires elemental analysis rather than molecular structure, liquid phase heat capacity of ill-defined hydrocarbon fluids, such as bitumen, pure compounds and polymers can be predicted with equal ease. Virtual Materials Group has implemented this correlation in their hydrocarbon refining/petrochemical/natural gas processing simulator (VMGSIM 6.5).

In a further development, a simple correction term, which is a function of reduced temperature and molar mass, was added to the universal correlation to accommodate the critical region. This modification also addressed and resolved the variation of liquid phase isobaric heat capacity among isomers, with differing critical temperatures, at the same absolute temperature. With this modification, one can predict heat capacity of saturated organic liquids (C_{satL}) with 5% average relative deviation from experimental data up to the reduced temperature of 0.99.

Constant pressure heat capacities for liquids are by default evaluated indirectly, in process simulators and in general purpose calculations, using ideal gas isobaric heat capacity values to which equation of state based departure functions are added. As ideal gas heat capacities are known or can be calculated from theory with small uncertainties, and typically comprise 75 % of liquid heat capacity values, the large relative deviations present in departure function calculations appear to be tolerated or ignored. Deviations between indirectly calculated and measured constant pressure liquid heat capacities can exceed 10 % but are typically smaller. Departure function evaluation is the principle source for deviations and uncertainty in these calculations. In this work, departure functions based on the Peng-Robinson and Soave-Redlich-Kwong equations of state are defined and then evaluated. The absolute and relative deviation between the calculated values and experimental data are compared with the Tyagi departure function correlation, and a difference calculation based on accurate and predictive universal correlations for liquid and ideal gas heat capacity. The poor quality of the predictions from typical cubic equations of state, both in magnitude and trend with absolute and relative temperature, are described. The Tyagi correlation is shown to be preferred if (T_c, P_c, ω, M) are available. The difference calculation based on correlations by Dadgostar and Shaw and Laštovka and Shaw is otherwise preferred. The potential use of departure function correlations for constraining the parameterization of equations of state, particularly for ill-defined hydrocarbons, is briefly discussed.

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Nomenclature

a	equation of state parameter
b	equation of state parameter
C_P	isobaric heat capacity
ΔC_P	departure function of isobaric heat capacity
C_P^{exp}	experimental isobaric heat capacity
C_P^{cal}	calculated isobaric heat capacity
C_P°	isobaric ideal gas heat capacity
C_{PL}	isobaric liquid heat capacity
ΔC_{PL}	departure function of isobaric liquid heat capacity
$C_{P,\ solid}$	isobaric solid heat capacity
C_{satL}	saturated liquid heat capacity
C_V	isochoric heat capacity
C_{VL}	isochoric liquid heat capacity
$C_{\sigma L}$	saturated liquid heat capacity with respect to enthalpy
$\Delta C_{\sigma L}$	departure function of saturated liquid heat capacity
H	enthalpy
H°	enthalpy of ideal gas
H_{sg}	enthalpy of saturated vapour
$H_{\sigma L}$	enthalpy of saturated liquid
ΔH_{LV} or ΔH_V	enthalpy of vapourization
K	Watson characterization factor
M	molar mass
M_i	molar mass of chemical element i
m	number of compounds in a dataset
N	number of atoms in a molecule
n	number of elements in a compound AND number of experimental data points for a compound in data sets
P	pressure
P_c	critical pressure
P_r	reduced pressure

P_r^{sat}	reduced saturation vapour pressure
P_{sat}	saturation vapour pressure
p	number of fitted parameters
Q	heat
R	universal gas constant
S	objective function for fitting a correlation
sp gr	specific gravity
T	temperature
T_b	boiling point
T_c	critical temperature
T_{pc}	pseudocritical temperature
T_r	reduced temperature
V_L or $V_{\sigma L}$	saturated liquid volume
V_r	reduced volume
V_{rL}	saturated liquid reduced volume
V_{rV}	saturated vapour reduced volume
V_V	saturated vapour volume
v_i	stoichiometric coefficient for element *i* in a compound
w_i	mass fraction of element *i* in a compound
x_i	mole fraction of element *i* in a compound
ΔZ_V	difference between compressibility factors of saturated vapour and liquid

Greek letters

α	similarity variable
δ	average relative deviation
ε	average absolute deviation
σ	average standard deviation
σ_F	average standard deviation of the fit
ρ	density
ρ_{sLr}	reduced saturated liquid density
ω	acentric factor

Chapter 1
Introduction

Constant pressure heat capacity (C_P) is one of the basic thermodynamic and thermophysical properties, which characterizes a compound. Heat capacity is defined as [1]:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1-1}$$

This definition includes both molar and specific heat capacities, depending on the units used to define enthalpy (H). Heat capacity is directly related to the temperature derivative of basic thermodynamic functions, and as a result, having accurate values for heat capacities is essential for the calculation of the changes in these functions with temperature. Heat capacity is an important and widely used property in chemical engineering for writing energy balances, in thermodynamics for calculating entropy and enthalpy values, and in thermochemistry for measuring changes in enthalpy of reactions at different temperatures. One can evaluate the effect of temperature on phase and reaction equilibria by learning more about the heat capacity. Other important applications for heat capacity are as an indicator of phase transitions and changes in the structure of liquid solutions. One can simply trace these phenomena by observing variations in heat capacity with temperature [2].

Reliable estimation of liquid heat capacity has a significant impact on unit operation design and sizing, and energy integration for the hydrocarbon resource production and refining industry. For instance, a good knowledge about heat capacity of fluids is crucial for an optimum design of individual heat exchangers and heat exchange systems. In the case of deep oil reservoirs, in which petroleum fluids are stored under high temperature and high pressure, the heavy fraction (molecules with 11 or more carbon atoms) dictate the behaviour of the crude oils [3]. The hydrocarbon based energy industry requires reliable energy models for these heavy components of crude oil. For industries dealing with heavy oil and bitumen, such as those located in Alberta, Canada, the challenges in estimating liquid heat capacity are even more significant, as these materials are ill-defined.

1.1 Thesis Objectives

There are several methods for estimating constant pressure liquid heat capacity, including group contribution methods [4],corresponding state principle (CSP) methods [5], and rational approaches [6]. Thermodynamic models have been used rarely to predict calorimetric data, and applying cubic equations of state for representing properties of heavy hydrocarbons and ill-defined compounds is still a field of active research [7]. As Bessières et al. [3] demonstrated, adjustment of equation of state parameters for heavy components effects the reliability of values obtained for liquid heat capacities. Another challenge of estimating liquid heat capacity from equations of state is the format of the departure function, which relates heat capacity of liquids and ideal gases. Apparently, the departure function for calculating heat capacity of liquids currently defined in commercial simulators is identical to the one for heat capacities of real gases, while V_V (vapour volume) is substituted with V_L (liquid volume) in all terms. As an objective of this project, the performance of existing formats for the liquid departure function will be investigated and at the same time an alternative functional form will be proposed and tested for a series of compounds.

The absence of thermophysical property and molecular structure data for ill-defined hydrocarbons renders current direct computational methods and current equation of state based methods for estimating energy properties for these materials impractical at best and inaccurate. Although there has been a tremendous effort made over the past several years, proposed molecular structures and critical properties remain speculative. Thus, another objective is to incorporate a similarity variable, derived from quantum mechanics, for estimating the heat capacity of such liquids. The similarity variable, α, is the number of atoms in a molecule divided by molecular mass [8]. This approach has been successfully used for direct calculation of the heat capacity of organic solids [9, 10], and ideal gases [11]. With this approach, only the elemental analysis of a material need be available to provide accurate heat capacities on a unit mass basis. Use of the similarity variable (α) is expected to reduce the number and uncertainty of parameters arising in heat capacity and energy models for ill-defined liquid hydrocarbons, and to yield improved enthalpy and heat capacity estimates for such fluids vis-à-vis current practice.

1.2 Literature Review

1.2.1 Liquid Heat Capacities, Terms and Definitions

Reid and Sobel [12] defined three different heat capacities of liquids: 1) C_{PL}, the change in enthalpy with temperature at constant pressure, 2) $C_{\sigma L}$, the change in enthalpy of the saturated liquid with temperature, along the saturation curve, $(\frac{dH_{\sigma L}}{dT})$, 3) C_{satL}, the heat required to effect a temperature change while the liquid is kept saturated, $(\frac{dQ}{dT})_{\sigma L}$. The relationships among them are given by definition by [13]:

$$C_{\sigma L} = C_{PL} + [V_{\sigma L} - T(\frac{\partial V}{\partial T})_P](\frac{dP}{dT})_{\sigma L} = C_{satL} + V_{\sigma L}(\frac{dP}{dT})_{\sigma L} \tag{1-2}$$

There are also approximate corresponding state equations available in the literature, which relate C_{PL}, $C_{\sigma L}$, and C_{satL}. For T_r less than 0.8, the different heat capacities can be considered to have the same values [14]. They diverge markedly as the critical point is approached. Most estimation techniques for heat capacity of liquids yield either C_{PL} or $C_{\sigma L}$, while C_{satL} is usually measured experimentally [14].

1.2.2 Estimation Techniques for Liquid Heat Capacity

Methods for estimating liquid heat capacities were categorized into four general groups by Reid et al. [13]: theoretical, group contribution, corresponding states, and Watson's thermodynamic cycle [15]. Reid et al. also argued that reliable estimation procedures for engineering use have not yet been developed, even though Bondi [6, 16] proposed some valuable approximations for high-molecular-weight liquids and polymers. Some of these techniques are discussed in more detail in the following sections.

1.2.2.1Group Contribution Methods

The assumption that is made in these methods is that each molecule is made of various groups, which contribute a specific value to the total molar heat capacity, and that these groups act independently and do not have interactions. Missenard [17] and Chueh and Swanson [18, 19] have suggested values for different groups in order to calculate C_{PL}. Group contributions suggested by Chueh and Swanson can be used to estimate liquid heat capacity at 293 K [13]. Although errors reported for this method rarely exceed 2 to 3 percent, the method is very limited in terms of the temperature range at which the method is valid. Missenard proposed structural increments from -25 to 100°C [13], but his method cannot be used for compounds with double bonds. Moreover, the temperature range is limited to $T_r < 0.75$. Errors for this method are ±5 percent.

Recently, methods that account for dissimilar contributions, considering what an atom is bonded to, have been proposed. An example of these types of methods is that of Růžička and Domalski [4]. This group contribution method can be applied to develop equations for estimating liquid heat capacity from the melting point to the boiling point. The general form of this method is the following:

$$C_{pL} = R[A + B\frac{T}{100} + D(\frac{T}{100})^2] \qquad (1\text{-}3)$$

where R is the gas constant, and T is the temperature in K. Parameters A, B, and D are obtained from equations below:

$$A = \sum_{i=1}^{k} n_i a_i \quad , \quad B = \sum_{i=1}^{k} n_i b_i \quad , \quad D = \sum_{i=1}^{k} n_i d_i \qquad (1\text{-}4)$$

where n_i is the number of groups of type i, k is the total number of different kinds of molecular groups. a_i, b_i, and c_i are given for 114 various groups in “Properties of Gases and Liquids” [14]. This method underestimates liquid heat capacity at higher temperatures.

Needless to say, applying these techniques for estimating liquid heat capacity requires a good knowledge of the molecular structure of compounds. Thus, it is not possible to use group contribution methods for ill-defined hydrocarbons, such as heavy oil and bitumen, for which limited data regarding molecular groups and their quantifications are available.

1.2.2.2 Corresponding States Methods

The Lee-Kesler equation [5] is the base for several Corresponding States Principle (CSP) methods for liquid heat capacity estimation that have been developed:

$$C_P - C_P^{\circ} = \Delta C_P = (\Delta C_P)^{(0)} + \omega(\Delta C_P)^{(1)} \tag{1-5}$$

The simple fluid contribution, $(\Delta C_P)^{(0)}$, and the deviation function, $(\Delta C_P)^{(1)}$, are both listed for different values of reduced temperature and pressure (T_r and P_r). Using these values, one can estimate the heat capacity departure function $C_P - C_P^{\circ}$ for liquids and real gases. Good results have been reported by using an analytical form of the Lee-Kesler heat capacity departure function [5] for calculating liquid heat capacities for hydrocarbons. However, applying this method requires data or good estimates for T_c, P_c, and ω of the compound.

Rowlinson [20] suggested modifications for one of many forms that Bondi [6] has reviewed:

$$\frac{C_{PL} - C_P^{\circ}}{R} = 1.45 + \frac{0.45}{1-T_r} + 4.2775\omega + \frac{6.3\omega(1-T_r)^{1/3}}{T_r} + \frac{0.4355\omega}{1-T_r} \tag{1-6}$$

The Rowlinson-Bondi method is applicable at low values of T_r as well as at values reaching unity [13]. C_P°, T_c, and ω are required to employ this technique. The values estimated by the Rowlinson-Bondi method were compared with the experimental data [13], and the results showed that errors are generally less than 5 percent, but this equation did not work properly for alcohols at low temperatures. In the recent edition of the Properties of Gases and Liquids [14], the first two constants of the Rowlinson-Bondi equation were refitted.

$$\frac{C_{PL} - C_P^{\circ}}{R} = 1.586 + \frac{0.49}{1-T_r} + \omega[4.2775 + \frac{6.3(1-T_r)^{1/3}}{T_r} + \frac{0.4355}{1-T_r}] \tag{1-7}$$

The estimated results for heat capacity of 212 compounds at 298 K were compared to the experimental data. The comparison showed that for 18 of 212 substances the deviations were greater than 10%. C1 to C4 alcohols and acids, water, D_2O, bromoethane, hydrazine, HF, SO_3, N_2O_4, 1,2-oxazole, C_6F_{14}, and isobutyl amine were among these 18 compounds. These compounds are polar and form hydrogen bonds and dimers. Except for these compounds, the average absolute deviation in C_{PL} using the modified version of the Rowlinson-Bondi equation was 2.5 %. Still, C_P°, T_c, and ω of compounds are needed as input so that equation 1-7 can be used to estimate liquid heat capacities.

1.2.2.3 Thermodynamic Cycle Methods

Reid and Sobel [12] defined C_{satL} as:

$$C_{satL} = (\frac{dQ}{dT})_{sL} = C_P^\circ + \phi_0[(\phi_1/\phi_0) - \phi_2 + (\phi_4 P_{vpr}/\Delta Z_v)(\phi_3 + RZ_c/\rho_{sLr})] \tag{1-8}$$

where ρ_{sLr} is the reduced saturated liquid density and ΔZ_v is the difference between compressibility factors of saturated vapour and liquid. The ϕ functions are given as:

$$\phi_0 = \ln P_{br}(1 - P_{br}/T_{br}^3)^{1/2} \tag{1-9}$$

$$\phi_1 = -(1/T_c)[(\partial/\partial T_r)(H^\circ - H_{sg})]_{\mathrm{Pr}} \tag{1-10}$$

$$\phi_2 = [(0.38)(1.04)RT_{br}(1 - T_r)^{-0.62}]/(1 - T_{br})^{1.38} \tag{1-11}$$

$$\phi_3 = (1/T_c)[(\partial/\partial P_r)(H^\circ - H_{sg})]_{T_r} \tag{1-12}$$

$$\phi_4 = [(1.04)T_{br}(1 - T_r)^{0.38}]/[(1 - T_{br})^{1.38} T_r^2] \tag{1-13}$$

The partial derivatives of (H^o – H_{sg}) in equations 1-10 and 1-11 were calculated graphically by Reid and Sobel [12]. The functions ϕ_1 and ϕ_3 were plotted versus reduced temperature for T_r from 0.7 to 0.95, while values of compressibility factors, Z_c, varied from 0.23 to 0.29 with an interval of 0.02. ϕ_2 and ϕ_4 were also plotted against T_r for different T_{br}. Moreover, ΔZ_v was plotted as a function of reduced vapour pressure. Since the ϕ functions, ΔZ_v and ρ_{sLr} were obtained from graphs, the estimated values for C_{satL} deviated significantly from experimental values. Furthermore, this technique cannot be applied for computer calculation [21].

Tyagi [21] observed that saturated liquid heat capacities could be better estimated if the term (H^o – H_{sg}) in the Reid and Sobel expressions could be defined as a function of reduced temperature and reduced pressure. He suggested analytical procedures, using the enthalpy departure from their ideal state, proposed by Lee and Edmister [22] and Stevens and Thodos [23] to estimate the values for functions $dH_{\sigma L}/dT$ and $(dQ/dT)_{sL}$. Among three methods he introduced, Method 1, which appears to be superior to the others is discussed here.

The function $dH_{\sigma L}/dT$ is defined as:

$$C_{\sigma L} = \frac{dH_{\sigma L}}{dT} = \frac{d}{dT}(H_{\sigma L} - H^{\circ}) + C_P^{\circ} \tag{1-14}$$

The following general equation for isothermal enthalpy difference for pure liquids is given by Lee and Edmister [22]:

$$\begin{aligned} \frac{(H_{\sigma L} - H^{\circ})}{RT_c} &= A_2 - A_3T_r - 2A_4T_r^3 - 6A_5T_r^7 + (A_6 - A_7T_r - 2A_8T_r^3)P_r - 3A_9T_r^4P_r^2 \\ &+\omega(A_{10}T_r^2 + A_{11} + A_{12}P_r - 3A_{13}T_r^4P_r^2) \end{aligned} \tag{1-15}$$

where the A_is are generalized constants defined as: $A_1 = 6.32873$; $A_2 = -8.45167$; $A_3 = -6.90287$; $A_4 = 1.87895$; $A_5 = -0.33448$; $A_6 = -0.018706$; $A_7 = -0.2286517$; $A_8 = 0.18940$; $A_9 = -0.002584$; $A_{10} = 8.7015$; $A_{11} = -11.201$; $A_{12} = -0.05044$; $A_{13} = 0.002255$.

Differentiating equation 1-15 with respect to temperature one obtains:

$$\begin{aligned} \frac{d}{dT}(H_{\sigma L} - H^{\circ}) &= R(-A_3 - 6A_4T_r^2 - 42A_5T_r^6 + P_r(-A_7 - 6A_8T_r^2 - 12A_9T_r^3P_r) \\ &+\omega(2A_{10}T_r - 12A_{13}T_r^3P_r^2)) \end{aligned} \tag{1-16}$$

Ideal heat capacity, C_P°, was calculated using the method suggested by Rihani and Doraiswamy [24] in the following form:

$$C_P^{\circ} = a + bT + cT^2 + dT^3 \tag{1-17}$$

where a, b, c, and d are constants. Saturated liquid heat capacity was then calculated by substituting equations 1-16 and 1-17 in equation 1-14. Tyagi [21] compared the results obtained for 46 compounds by this method with experimental values. The Tyagi method is applicable over a reduced temperature range from near the melting point $T_r = 0.45$ to near the critical point $T_r = 0.98$. The absolute deviation from experimental data for this method is less than 3%, while for Reid and Sobel's method, an average error of more than 10% was observed for compounds with Z_c less than 0.23. Moreover, an overall average error of 8.7% was obtained using the method of Reid and Sobel for all the compounds Tyagi tested over the reduced temperature range 0.7-0.95. While the

Tyagi method is preferred over other techniques in this category, it should be noted that the enthalpy departure function has only been validated for pure liquids and this method may not provide reliable results for ill-defined hydrocarbons and mixtures.

1.2.2.4 Thermodynamic Models

To investigate the potential of thermodynamic models for estimating characteristic properties of heavy distillation cuts, Bessières et al. [3] tested existing equations of state and mixing rules available in the literature. They carried out measurements on four narrow distillation cuts, which were obtained from the distillation of the same crude oil, with respective boiling points around 150, 200, 250, and 300°C. The experiments were performed in the pressure range of 0.1 to 40 MPa within the temperature range of 293.15 to 373.15 K using a Setaram C80calorimeter with a custom designed cell for high pressures.

The approach that Bessières et al. took to test the validity of extrapolation for heavy cuts was a comparative study they performed where the predicted values based on existing models were compared with experimental data they measured. Among the different models in the literature, they employed three cubic equations of state: the original form of the Peng-Robinson [25], the modified version of the Peng-Robinson corrected for volume translation [26], and the Soave-Redlich-Kwong equation [27]. They also selected anon-cubic modification of the Peng-Robinson equation of state proposed by Jullian et al. [28]. Two modified Benedict-Webb-Rubin [29] equations of state were also tested: the one introduced by Nishiumi and Saïto (NS) [30], in which all parameters are defined as a function of a centric factor, and the Lee-Kesler correlation [3] which is a corresponding states principle method with two references and three parameters (T_c, P_c, ω). As the distillation cuts included many components, mixing rules should be used in order to apply equations of state. In addition to the usual mixing rules, which combine equation parameters, a number of mixing rules based on the critical properties were tested. The rules proposed by Hankinson and Thomson [31], Lee and Kesler [3], Pedersen et al. [32], Plocker et al.[33], Spencer and Danner [34], Teja [35], Joffe [36] were employed.

A departure function, equation 1-18, defined for heat capacity of real gases [13], was then employed to estimate the heat capacity (C_P) of the liquid phase distillation cuts. The equations of state and mixing rules noted above were used to calculate derivatives arising in equation 1-18.

$$C_P(P,T) = C_P^{\circ}(T) + \int_{\infty}^{V} T\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV - T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \tag{1-18}$$

where C_P° is the ideal gas heat capacity. The very first observation that was applicable to all models used in their study was that the higher the boiling point (the greater the mean molecular mass), the less accurate the prediction became. However, equations of state with parameters fitted to vapour pressures of components with high molecular mass were more successful in predicting the heat capacity of heavy distillation cuts. Bessières et al. [3] concluded that the adjustment of the equation of state parameters to heavy compound properties improves the reliability of heat capacity estimates.

Employing thermodynamic models for predicting heat capacity of ill-defined hydrocarbons is challenging, since the critical properties are not accessible, the mean molar mass is unknown, and the heat capacity of ill-defined hydrocarbons in the ideal gas state, the reference state for such calculations, is unknown. The methods typically used for estimating these properties require molecular structure inputs, and the range of values predicted diverges as molar mass increases, even for pure n-alkanes [37]. The number and uncertainty of parameters is large, and consequently heat capacity estimates for both gases and liquids are inaccurate. Overall, there are no reliable methods for predicting liquid heat capacity values for ill-defined hydrocarbons, such as bitumen and boiling cuts, with any accuracy or certainty.

1.3 Heat Capacity Prediction in Commercial Simulators

The calculation techniques used in commercial process simulators for predicting isobaric ideal gas heat capacities were until recently limited to: (i) group contribution methods for a material with a defined chemical structure, and (ii) Lee-Kesler methods for a compound with an unknown chemical structure. Liquid and real gas heat capacities were then predicted by adding the ideal gas term and the departure function (ΔC_P) (equation 1-18) where (V_L) replaced (V_V). Cubic equations of state, such as Peng-Robinson, are applied to calculate these terms. Ideal gas heat capacity comprises ~ 75% of the heat capacity of liquids remote from normal critical points [3] and the uncertainty of the current methods for calculating ideal gas heat capacity is less than 5% [38]. Accuracy of volumetric prediction by equations of state affects the accuracy of the predicted isobaric liquid heat capacity when using equation 1-18 to evaluate the liquid departure function [39]. The shortcomings of indirect methods for calculating isobaric liquid heat capacity, routinely used in process simulators and general purpose calculations, are investigated in this work.

1.4 Liquid Heat Capacity Experimental Data

Zábranský and Růžička [2] explained the necessity of compiling and assessing experimental data for constant pressure heat capacity of liquids from time to time because calorimetric techniques are updated and also more experimental data are published. As liquid heat capacity experimental data are used extensively in this work, it was critical to select them with the greatest of care. The search for reliable, experimentally measured, unsmoothed data for liquid heat capacity was rigorous. Two cases of inaccurate experimental data reported in the literature are presented.

In Table 1-1, predicted liquid heat capacity values for benzyl acetate ($C_9H_{10}O_2$) by VMGSim at different temperatures are compared with experimental data. At room temperature, liquid heat capacity for benzyl acetate is predicted with almost 50% error.

Table 1-1. Calculated results and experimental data for liquid heat capacities of Benzyl Acetate, $C_9H_{10}O_2$

T[K]	C_{PL} (VMGSim) [J mol^{-1} K^{-1}]	C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]	Deviation (%)
292.7	219.85	250.2	-12.13
298.15	222.76	148.5	50.01
306.0	226.94	154	47.36

The datum reported as the experimental liquid heat capacity of benzyl acetate at 298.15 K is lower than the heat capacity value at 292.7 K. Another way to check these experimental values is to use a correlation presented for constant pressure specific heat capacity for pure crystalline organic solids (equation 1-19) [10].

$$C_P = 3(A_1\alpha + A_2\alpha^2)R(\frac{\theta}{T})^2 \frac{\exp(\frac{\theta}{T})}{[\exp(\frac{\theta}{T}) - 1]^2} + (C_1\alpha + C_2\alpha^2)T + (D_1\alpha + D_2\alpha^2)T^2$$

(1-19)

Liquid heat capacities are by definition larger than those of crystalline solids comprising the same material.

Table 1-2 lists the seven universal coefficients for equation 1-19[8]. Equation 1-19 is a correlation that relates heat capacity of solids (C_P) to temperature (T in K) and similarity variable, α, defined as the number of atoms in a molecule divided by the molecular mass [8].

$$\alpha = \frac{N}{M} = \frac{\sum_{i=1}^{n} \upsilon_i}{\sum_{i=1}^{n} \upsilon_i M_i} = \frac{\sum_{i=1}^{n} x_i}{\sum_{i=1}^{n} x_i M_i} = \frac{\sum_{i=1}^{n} \frac{w_i}{M_i}}{\sum_{i=1}^{n} w_i} \qquad (1\text{-}20)$$

where ν_i is the stoichiometric coefficient for element *i* in a compound consisting of *N* atoms, *n* is the number of elements in a compound, *M* is the molar mass of the compound and M_i is the molar mass of chemical element *i* (g mol^{-1}). Variable x_i is the mole fraction of element *i* in a compound, and w_i is the mass fraction of element *i*. Thus the value of the similarity variable, α, is simply a function of the elemental composition of the compound or mixture.

For benzyl acetate ($C_9H_{10}O_2$):

$$\alpha = \frac{\sum_{i=1}^{n} \upsilon_i}{\sum_{i=1}^{n} \upsilon_i M_i} = \frac{\upsilon_c + \upsilon_H + \upsilon_O}{\upsilon_c \times 12.0107 + \upsilon_H \times 1.00794 + \upsilon_O \times 15.9994} \qquad (1\text{-}21)$$

$$= \frac{9+10+2}{9 \times 12.0107 + 10 \times 1.00794 + 2 \times 15.9994} = 0.1398$$

Table 1-2. Universal coefficients of equation 1-19[10]

coefficient	value
A_1	0.013183
A_2	0.249381
θ	151.8675
C_1	0.026526
C_2	-0.024942
D_1	0.000025
D_2	-0.000123

Applying equation 1-19 for benzyl acetate at room temperature (298.15 K) with $\alpha = 0.1398$ mol g^{-1}, we obtain a value of $C_{P,\ solid} = 1.22 JK^{-1}g^{-1}$. Since generally $C_{P,\ solid}$ is smaller than C_{PL}, we can expect to have a value for liquid heat capacity of benzyl acetate larger than 1.22 $JK^{-1}g^{-1}$ at room temperature. However, as shown in Table 1-3, experimental data for liquid heat capacity is even less than 1 $JK^{-1}g^{-1}$, which is surprisingly low. Thus, in the case of benzyl acetate, we can say that it is the experimental data (at T = 298.15 K and 306 K) that should be re-evaluated rather than the simulator results, since the experimental data are far from what the trend of liquid heat capacity suggest.

Table 1-3. Constant pressure specific heat capacity of benzyl acetate ($C_9H_{10}O_2$) at T = 298.15 K calculated by different methods

$C_{P,solid}$ (equation 1-21) [$JK^{-1}g^{-1}$]	**C_{PL} (experimental) [$JK^{-1}g^{-1}$]**	**C_{PL} (VMGSim) [$JK^{-1}g^{-1}$]**
1.2213	0.9888	1.4833

Among data calculated by VMGSim for liquid heat capacity of different compounds, large deviations of simulator results from experimental data were also observed for n-dotriacontane ($C_{32}H_{66}$) at 348 K. As the Peng-Robinson EOS property package was used to calculate liquid heat capacities, the simulator results for hydrocarbons should not deviate too much from the experimental data. But, as shown in Table 1-4, the deviations are all in the range of (4-8)%, except for n-dotriacontane ($C_{32}H_{66}$), which has much larger error (−25%).

In Figure 1-1, we can see how the experimental data for specific liquid heat capacity of n-alkanes generally increases with their molecular weight. Nevertheless, the experimental value for n-dotriacontane ($C_{32}H_{66}$) with M = 450.87 g mol^{-1} does not follow this trend. Although the temperature, at which liquid heat capacity of n-dotriacontane is reported, is not exactly the same as the others' (353 K), the difference is almost negligible (5 K). Unfortunately, this is the only data available in literature for n-dotriacontane, and no other experimental liquid heat capacity could be found to make the comparison. But, heat capacities of n-alkanes (C_nH_{2n+2}) usually increase with temperature. As an example, for n-octadecane ($C_{18}H_{38}$), at T = 300 K, liquid heat capacity is 564.4 J mol^{-1} K^{-1}, and if we increase the temperature to T = 325 K, it increases to 568 J mol^{-1} K^{-1}. Since the experimental value for n-dotriacontane at T = 348 K is even larger than experimental data for heavier hydrocarbons at higher temperature (T = 350), it would be reasonable to conclude that the experimental data are unreliable and should be re-measured.

Table 1-4. Calculated results by VMGSim and experimental data for liquid heat capacities of heavy n-alkanes

<table>
<tr><td colspan="2">C28H58 (n-Octacosane)
M=394.7662 gmol^{-1} α =0.2197 mol g^{-1}</td><td></td><td></td></tr>
<tr><th>T[K]</th><th>C_{PL} (VMGSim) [J mol^{-1} K^{-1}]</th><th>C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]</th><th>Deviation (%)</th></tr>
<tr><td>353 K</td><td>895.68</td><td>937</td><td>-4.41</td></tr>
<tr><td colspan="2">C32H66 (n-Dotriacontane)
M = 450.8734 gmol^{-1} α =0.2129 mol g^{-1}</td><td></td><td></td></tr>
<tr><th>T[K]</th><th>C_{PL} (VMGSim) [J mol^{-1} K^{-1}]</th><th>C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]</th><th>Deviation (%)</th></tr>
<tr><td>348 K</td><td>1016.99</td><td>1356</td><td>-25</td></tr>
<tr><td colspan="2">C33H68 (n-Tritriacontane)
M = 464.9002 gmol^{-1} α =0.2173 mol g^{-1}</td><td></td><td></td></tr>
<tr><th>T[K]</th><th>C_{PL} (VMGSim) [J mol^{-1} K^{-1}]</th><th>C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]</th><th>Deviation (%)</th></tr>
<tr><td>353 K</td><td>1058.88</td><td>1112.5</td><td>-4.82</td></tr>
<tr><td colspan="2">C34H70 (n-Tetratriacontane)
M = 478.927 gmol^{-1} α =0.2172 mol g^{-1}</td><td></td><td></td></tr>
<tr><th>T[K]</th><th>C_{PL} (VMGSim) [J mol^{-1} K^{-1}]</th><th>C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]</th><th>Deviation (%)</th></tr>
<tr><td>353 K</td><td>1091.92</td><td>1149</td><td>-4.97</td></tr>
<tr><td colspan="2">C36H74 (n-Hexatriacontane)
M = 506.9806 gmol^{-1} α =0.2170 mol g^{-1}</td><td></td><td></td></tr>
<tr><th>T[K]</th><th>C_{PL} (VMGSim) [J mol^{-1} K^{-1}]</th><th>C_{PL} (experimental [40]) [J mol^{-1} K^{-1}]</th><th>Deviation (%)</th></tr>
<tr><td>353 K</td><td>1154.86</td><td>1206</td><td>-4.24</td></tr>
</table>

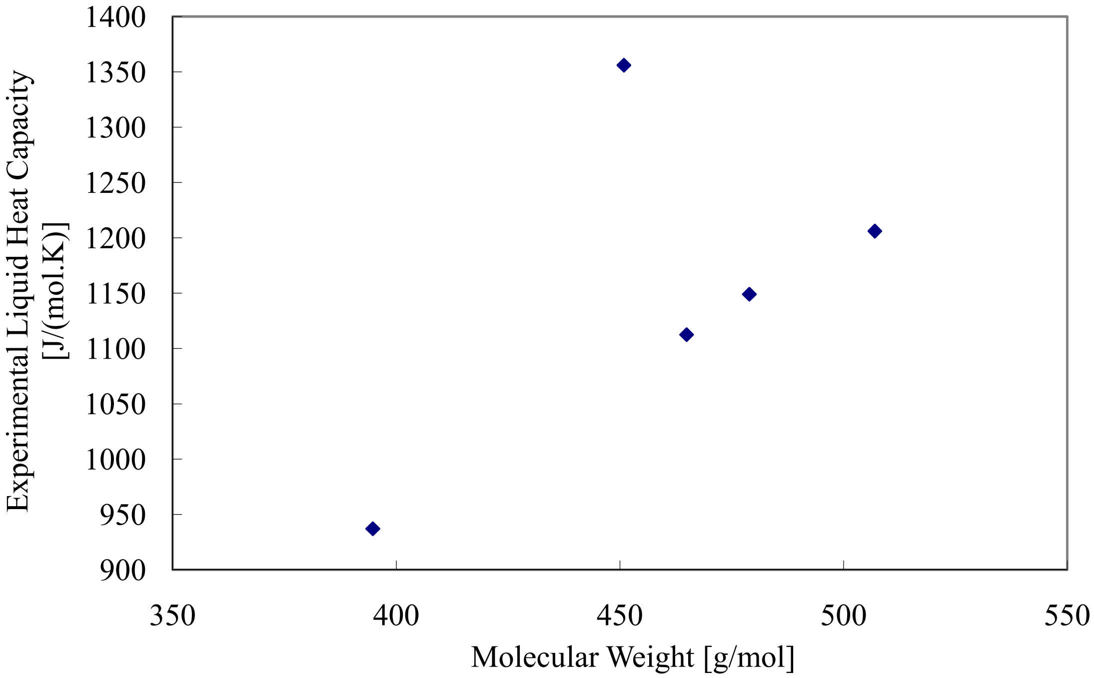

Figure 1-1. Experimental liquid heat capacities of n-alkanes (C_nH_{2n+2}) versus molar mass

1.5 Thesis Outline

There are currently no reliable methods for predicting liquid heat capacities of ill-defined hydrocarbons, such as bitumen and heavy crude oils and their partly processed fractions. The main objective of this research is to develop energy models for predicting liquid heat capacity of ill-defined hydrocarbons. In this chapter, estimation techniques for liquid heat capacity available in the literature are listed, and their shortcomings with regards to compounds with unknown physical properties and molecular structure are discussed. Chapters 2, 3, and 4 address the objectives set for this research. These chapters are in a paper format comprising an introduction, methodology, results and discussion, conclusions, and references. They are self-contained. The sequence of these chapters is consistent with the progress of the research. Chapters 2 and 3 have appeared in print as peer reviewed articles. Chapter 4 has been submitted to Fluid Phase Equilibria for peer review. Chapter 2 concerns the development of a "universal" correlation for the direct calculation of liquid-phase constant pressure heat capacity data (C_{PL}) based on the elemental composition of liquids. Results obtained for a training data set and a test data set are presented. The correlation appears to be preferred over the Lee-Kesler correlation, a common reference equation for engineering calculations, both with respect to overall accuracy and range of application. Reliable heat capacity predictions for ill-defined fluids such as maltenes were made for the first time. Chapter 3 concerns the development of a modified constant pressure heat capacity correlation that accommodates the critical region and the variation of liquid phase isobaric heat capacity among isomers at the same absolute temperature. The results obtained for a training data set and a test data set are presented and compared with results obtained with the universal correlation presented in Chapter 2, and two variants of the Rowlinson-Bondi correlation [14]. The C_P° (ideal gas heat capacity) contribution is calculated using either compound specific correlations or the predictive universal Laštovka-Shaw equation for ideal gases [11]. For pure hydrocarbon liquids where compound specific C_P° correlations, T_c and ω are available, the Rowlinson-Bondi based approach should be used to compute saturated liquid heat capacities. Chapter 4 concerns the definition of departure functions for liquid phase isobaric heat capacity and the relative merits of using equation of state or correlated departure functions versus direct calculation based on the correlations developed in Chapters 2 and 3. Overall conclusions and recommendations for future work comprise Chapter 5.

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Chapter 2

A Predictive Correlation for the Constant-Pressure Specific Heat Capacity of Pure and Ill-defined Liquid Hydrocarbons[*]

2.1 Introduction

For pure compounds, constant pressure liquid heat capacities are typically estimated on the basis of group contribution and corresponding state principles [1, 2]. These techniques require molecular structure or critical properties for estimating liquid heat capacities. Even a more general empirical correlation, such as the widely used Lee-Kesler [3] correlation:

$$C_P = A_1 + A_2 T + A_3 T^2 \tag{2-1}$$

where C_P is the isobaric heat capacity of liquid petroleum fraction in Btu $\mathrm{lb^{-1}R^{-1}}$

$$A_1 = -1.17126 + (0.023722 + 0.024907\mathrm{spgr})\mathrm{K} + (1.14982 - 0.046535\mathrm{K})/\mathrm{spgr} \tag{2-2}$$

$$A_2 = (10^{-4})(1.0 + 0.82463\mathrm{K})(1.12172 - 0.27634/\mathrm{spgr}) \tag{2-3}$$

$$A_3 = (-10^{-8})(1 + 0.82463\mathrm{K})(2.9027 - 0.70958/\mathrm{spgr}) \tag{2-4}$$

and

T_r is the reduced temperature, T/T_{pc}
T is the temperature in degrees Rankine
T_{pc} is the pseudocritical temperature in degrees Rankine
K is the Watson characterization factor = (mean average boiling point)$^{1/3}$/sp gr
sp gr is the specific gravity of the compound at 60 F/ specific gravity of water at 60 F

valid from approximately $0.4 < T_r \leq 0.85$, requires significant property knowledge to be applied in practice.

There are currently no liquid phase specific heat capacity calculation methods available for organic materials with unknown molecular structures, or critical

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[*] N. Dadgostar, J. M. Shaw, Fluid Phase Equilibria 313 (2012) 211-226

properties. Yet, there are numerous industrially relevant fluids for which neither of these sets of physical properties is known or for which proposed molecular structures and critical properties remain speculative. Hydrocarbon resources such as heavy crude oils or bitumen comprising constituents with nominal boiling points exceeding 524 °C, or asphaltenes are excellent examples of challenging and industrially relevant fluids. These materials decompose thermally at temperatures less than their boiling points and are not readily characterized on a molecular of functional group basis. Building on recent successes in establishing predictive correlations for the constant pressure specific heat capacities for ill-defined organic solids [4, 5] and ideal gases [6], the objective of this work is to test the appropriateness of generalizing parameters appearing in a successful liquid phase heat capacity correlation by incorporating a similarity concept, rooted in quantum mechanics, thus rendering the equation capable of estimating liquid heat capacity of ill-defined hydrocarbons in addition to well defined ones.

2.1.1 Predictive Liquid Phase Heat Capacity Correlation Development

2.1.1.1 Similarity Variable

Molecules sorb energy through skeletal and atomistic vibration. Simple molecules possess three fundamental translation and three twisting or bending modes of vibration and 3N-6 fundamental atomistic vibration modes. Atomistic vibration modes dominate, except for the smallest of molecules. If vibration frequency and saturation temperature differences among atoms of different types are ignored, one expects specific heat capacity to be a function of a similarity variable, α, defined as the number of atoms in a molecule divided by the molecular mass [7]:

$$\alpha = \frac{N}{M} = \frac{\sum_{i=1}^{n} \upsilon_i}{\sum_{i=1}^{n} \upsilon_i M_i} = \frac{\sum_{i=1}^{n} x_i}{\sum_{i=1}^{n} x_i M_i} = \frac{\sum_{i=1}^{n} \frac{w_i}{M_i}}{\sum_{i=1}^{n} w_i} \tag{2-5}$$

where ν_i is the stoichiometric coefficient for element i in a compound consisting of N atoms, n is the number of elements in a compound, M is the molar mass of the compound and M_i is the molar mass of chemical element i (g mol^{-1}). Variable x_i is the mole fraction of element i in a compound, and w_i is the mass fraction of element i. Thus the value of the similarity variable, α, is simply a function of the elemental composition of the compound or mixture.

The validity of the similarity variable, α, for predicting the constant pressure specific heat capacities for ill-defined organic solids was evaluated in detail previously [4]. The same principles apply for liquids as illustrated in Figure 2-1 where experimental heat capacity values are compared on three different bases at constant values of the value of the similarity variable (α). Compounds with the same molar masses and elemental compositions but differing molecular structure are compared in Figure 2-1 a. Compounds with differing molar masses and molecular structures but the same elemental compositions are compared in Figure 2-1 b. Compounds with different molar masses, elemental compositions and molecular structures are compared in Figure 2-1 c. Data references are given in Table 2-1. For all three illustrations, the trends with temperature are comparable and the maximum absolute deviation between the measurements is less than 0.2 J K^{-1}g^{-1} and the maximum percentage difference is less than 10 %. Thus, as for solids and ideal gases, the similarity variable (α) appears to be a robust basis for the development of a correlation for constant pressure specific heat capacity for organic liquids. Using this predictive correlation, one needs only temperature and elemental analysis of a compound to predict liquid phase heat capacity at constant pressure. In this work, details of molecular structure are ignored, as they appear to have only a secondary impact on heat capacity values.

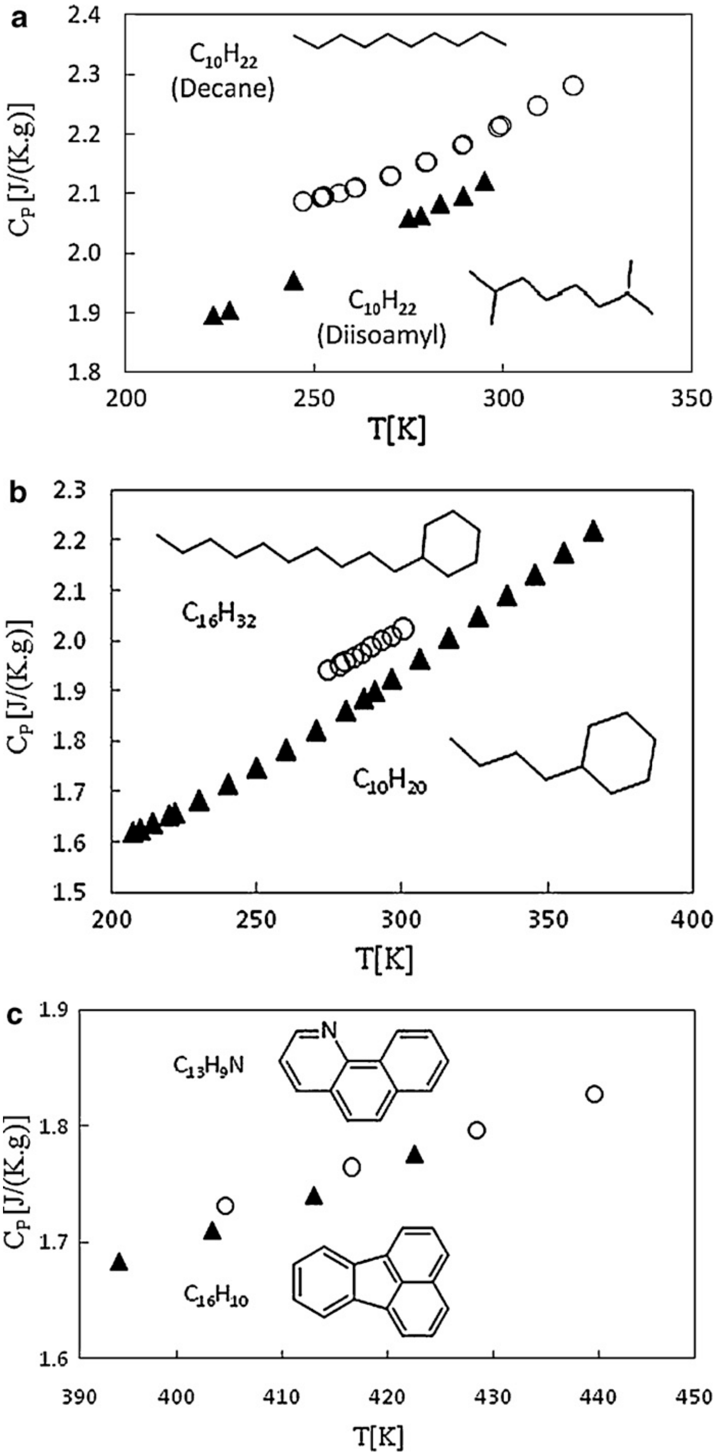

Figure 2-1. Experimental specific liquid heat capacity values for: (a) ▲, 2,7-dimethyloctane, diisoamyl ($C_{10}H_{22}$) and ○, decane ($C_{10}H_{22}$); (b) ▲, butylcyclohexane ($C_{10}H_{20}$) and ○, decylcyclohexane ($C_{16}H_{32}$); (c) ▲, fluoranthene ($C_{16}H_{10}$) and ○, benzo[h]quinoline ($C_{13}H_9N$).

2.1.1.2 Liquid Phase Heat Capacity Definitions

Reid and Sobel [8] provide three definitions for heat capacity of liquids:

1) C_{PL}, the change in enthalpy with temperature at constant pressure, within the liquid phase

2) $C_{\sigma L}$, the change in enthalpy of the saturated liquid with temperature, along the saturation curve, $(\frac{dH_{\sigma L}}{dT})$, and

3) C_{satL}, the heat required to effect a temperature change of a saturated liquid, $(\frac{dQ}{dT})_{\sigma L}$.

These three inter-related definitions possess almost identical numeric values except near the critical point [9]:

$$C_{\sigma L} = C_{PL} + [V_{\sigma L} - T(\frac{\partial V}{\partial T})_P](\frac{dP}{dT})_{\sigma L} = C_{satL} + V_{\sigma L}(\frac{dP}{dT})_{\sigma L} \tag{2-6}$$

There are also approximate corresponding state equations available in the literature, which relate C_{PL}, $C_{\sigma L}$, and C_{satL}. Below $T_r = 0.8$, they can be considered to have the same values [10]. Most estimation techniques for heat capacity of liquids yield either C_{PL} or $C_{\sigma L}$, while C_{satL} is usually measured experimentally [9].

To obtain a universal correlation relating liquid heat capacity to temperature and elemental composition, the quadratic form of the Lee-Kesler correlation was retained and the parameters were redefined as second order power series in the similarity variable α. The predictive correlation for liquid heat capacity has the form:

$$C_{PL} = a_1 + (a_{21}\alpha + a_{22}\alpha^2)T + (a_{31}\alpha + a_{32}\alpha^2)T^2 \tag{2-7}$$

where C_{PL} is the isobaric specific heat capacity of liquids in J $K^{-1}g^{-1}$, T in degrees Kelvin, and α in mol g^{-1}.

The first parameter, a_1, is set equal to the modified Einstein term appearing in the predictive correlation for solid heat capacity [7]. This term accounts for molecular level vibrations that saturate at low temperatures:

$$a_1 = (a_{11}\alpha + a_{12}\alpha^2) \times 3R(\frac{\theta}{T})^2 \frac{\exp(\frac{\theta}{T})}{[\exp(\frac{\theta}{T}) - 1]^2} \tag{2-8}$$

Above 200 K the factor$(3R(\frac{\theta}{T})^2 \frac{\exp(\frac{\theta}{T})}{[\exp(\frac{\theta}{T})-1]^2})$ may be treated as a constant, 24.5 J K^{-1} mol^{-1}, and equation 2-8 becomes:

$$a_1 \cong (a_{11}\alpha + a_{12}\alpha^2) \times 24.5 \tag{2-9}$$

While the Lee-Kesler correlation relates constant pressure heat capacity to temperature and specific gravity, equation 2-7 is a function of temperature only.

As,

$$C_{PL} = C_{VL} + T(\frac{\partial V}{\partial T})_P (\frac{\partial P}{\partial T})_V \tag{2-10}$$

equation2-7 is expected to be valid where the temperature dependent term (C_V) dominates, i.e. where $C_V >> T(\frac{\partial V}{\partial T})_P(\frac{\partial P}{\partial T})_V$. In order to predict constant pressure liquid heat capacity values at temperatures close to the critical point, the correlation would require modification. This is a subject of a future work. For pure compounds, the C_V term dominates for $T_r < 0.95$. Thus the potential range of application of equation 2-7 is from the freezing point up to almost the critical point of fluids. There are no inherent absolute upper or lower temperature bounds.

2.1.2 Heat Capacity Databases

The experimental heat capacity data for liquids, presented in Table 2-1, are distributed into three data sets: a training data set used to regress coefficients appearing in equation 2-7, a test data set used to evaluate the predictive character of the equation 2-7, and a comparison data set used to evaluate the relative performance of equation 2-7 vis-à-vis the Lee-Kesler correlation (equation 2-1). The temperature range for the experimental heat capacity data, the number of data points for each compound, and the literature sources are also noted in Table 2-1. The two-volume monograph entitled *Heat Capacity of Liquids: Critical Review and Recommended Values* by Zábranský et al. [11] and its two supplements [12, 13] were key sources for these experimental data. Non-smoothed experimental data with reported errors of less than 1% were used in this work. Molten polymers were also included in the database [14-16]. In total, 31 compounds, with molar masses ranging from (100.2 to 290.53) g mol^{-1} and temperatures ranging from (196 to 580) K, and 6 polymers with temperatures ranging from (347.61 to 620) K are listed. The training data set comprises 150 heat capacity values for 19 organic compounds (including paraffins, naphthenes, aromatics, sulphur/oxygen/nitrogen derivatives) and 3 molten polymers. The temperature range was from (207 to 590) K. These heat capacity values were used to calculate the six universal coefficients appearing in equation 2-7. A test data set comprising 111 heat capacity values for 12 compounds (including paraffins, naphthenes, aromatics, sulphur/oxygen/nitrogen derivatives) and 3 molten polymers were used to evaluate the predictive character of the correlation. The comparison data set, used to compare the performance of the Lee-Kesler correlation and equation 2-7, comprises 81 heat capacity values for 10 organic compounds (including paraffins, naphthenes, aromatics, and oxygen/nitrogen derivatives). Heat capacities for two ill-defined hydrocarbons, namely Maya pentane maltenes [17] and Athabasca pentane maltenes [18] were also predicted.

Table 2-1. Database and sources for heat capacity data

Compound	Formula	Molar Mass [a] [g mol^{-1}]	α [mol g^{-1}]	Reference [b]	Database	T[K]	C_{PL} [J K^{-1}g^{-1}]	
							Experimental	Calculated (equation 2-7)
alkanes								
Heptane	C_7H_{16}	100.2	0.230	C_P [19]	Test Set & Comparison Set	196.42	2.003	1.775
						208.55	2.007	1.821
						220.61	2.011	1.867
						229.57	2.037	1.901
						238.45	2.057	1.934
						250.18	2.087	1.978
						261.78	2.117	2.022
						270.39	2.147	2.054
						276.2	2.166	2.076
						281.74	2.185	2.097
						287.37	2.199	2.118
						295.68	2.228	2.149
						308.45	2.278	2.196
						317.91	2.318	2.231
						330.38	2.368	2.277
						336.54	2.394	2.299
						342.66	2.421	2.322
2,2,3,3-Tetramethylpentane	C_9H_{20}	128.26	0.226	C_{sat} [20]	Training Set	269.183	1.986	2.033
						275.533	2.015	2.058
						280.277	2.036	2.076
						293.964	2.099	2.127
						301.678	2.132	2.156

						320.554	2.219	2.227
						339.695	2.305	2.298
						352.341	2.365	2.345
2,7-Dimethyloctane, Diisoamyl	$C_{10}H_{22}$	142.28	0.225	C_P [21]	Training Set & Figure 2-1	223.2	1.895	1.849
						227.5	1.904	1.866
						244.5	1.954	1.932
						275	2.059	2.050
						278.2	2.063	2.062
						283.3	2.084	2.082
						289.4	2.096	2.105
						295	2.121	2.126
Decane	$C_{10}H_{22}$	142.28	0.225	C_P [22]	Test Set & Comparison Set	318.15	2.276	2.213
						333.15	2.333	2.269
						348.15	2.393	2.325
						363.15	2.456	2.380
						373.15	2.504	2.416
Decane	$C_{10}H_{22}$	142.28	0.225	C_P [23]	Figure 2-1	247.02	2.087	N/A
						251.7	2.093	
						252.3	2.094	
						252.63	2.096	
						256.53	2.101	
						260.61	2.109	
						261.03	2.110	
						270.08	2.129	
						270.48	2.130	
						279.46	2.152	
						279.82	2.154	
						289.09	2.181	
						289.44	2.183	
						298.59	2.212	
						299.31	2.214	
						309.04	2.247	
						318.62	2.282	

2-Methyldecane	$C_{11}H_{24}$	156.31	0.224	C_{sat} [24]	Training Set	235.442	2.001	1.891
						240.659	2.012	1.912
						248.285	2.027	1.942
						257.243	2.050	1.977
						276.589	2.109	2.051
						295.783	2.174	2.125
						311.95	2.236	2.186
						332.247	2.315	2.262
						342.46	2.357	2.300
						356.085	2.410	2.350
						375.231	2.494	2.420
Tridecane	$C_{13}H_{28}$	184.36	0.222	C_P [25]	Training Set	280.15	2.166	2.058
						288.15	2.182	2.088
						298.15	2.207	2.127
						308.15	2.235	2.165
						318.15	2.265	2.203
Pentadecane	$C_{15}H_{32}$	212.42	0.221	C_P [26]	Test Set & Comparison Test	313.15	2.250	2.179
						333.15	2.313	2.254
						353.15	2.378	2.328
						373.15	2.444	2.402
Hexadecane	$C_{16}H_{34}$	226.45	0.221	C_P [22]	Training Set	318.15	2.263	2.196
						328.15	2.278	2.233
						338.15	2.320	2.271
						348.15	2.351	2.308
						358.15	2.385	2.345
						368.15	2.421	2.382
Octadecane	$C_{18}H_{38}$	254.49	0.220	C_P [27]	Test Set & Comparison Set	306.69	2.247	2.149
						314.63	2.266	2.179
						322.51	2.289	2.209
						330.34	2.312	2.238
						338.13	2.336	2.268
						345.9	2.361	2.297
						353.61	2.388	2.325

						361.27	2.415	2.353
						368.87	2.443	2.381
						376.43	2.468	2.409
						383.66	2.499	2.435
						391.14	2.527	2.462
						398.59	2.553	2.489
naphthenes								
Butylcyclohexane	$C_{10}H_{20}$	140.27	0.214	C_{sat} [28]	Training Set & Figure 2-1	207.52	1.622	1.716
						214.21	1.640	1.744
						221.77	1.660	1.776
						240.1	1.717	1.853
						260.05	1.785	1.935
						280.56	1.861	2.017
						290.54	1.901	2.057
						305.97	1.965	2.117
						325.86	2.049	2.194
						345.43	2.132	2.268
						365.38	2.219	2.342
Decylcyclopentane	$C_{15}H_{30}$	210.4	0.214	C_{sat} [29]	Training Set	258.18	1.930	1.927
						264.82	1.939	1.954
						271.95	1.953	1.983
						282.67	1.980	2.026
						299.44	2.030	2.092
						311.43	2.071	2.139
Decylcyclohexane	$C_{16}H_{32}$	224.34	0.214	C_{sat} [28]	Test Set & Comparison Set & Figure 2-1	274.26	1.940	1.992
						280.27	1.958	2.016
						286.1	1.976	2.040
						293.33	2.000	2.068
						300.48	2.024	2.096
1,1,3-Tricyclohexylpropane	$C_{21}H_{38}$	290.53	0.203	C_P [30]	Training Set	373.15	2.198	2.318
						423.15	2.415	2.492

						483.15	2.633	2.684
Aromatics & Unsaturated Cyclic Hydrocarbons								
Styrene	C_8H_8	104.15	0.154	C_P [31]	Test Set & Comparison Set	246.73	1.614	1.485
						249.91	1.625	1.500
						257.54	1.630	1.535
						276.24	1.686	1.618
						298.54	1.753	1.711
Dimethylbenzene	C_8H_{10}	106.17	0.170	C_{sat} [32]	Training Set	251.989	1.642	1.624
						255.571	1.651	1.640
						262.249	1.668	1.671
						285.471	1.731	1.772
						297.742	1.767	1.824
Naphthalene	$C_{10}H_8$	128.17	0.140	C_{sat} [33]	Training Set	357.439	1.709	1.823
						358.663	1.713	1.827
						362.485	1.724	1.839
						374.966	1.762	1.880
						401.993	1.845	1.961
						427.298	1.921	2.029
1-Methylnaphthalene	$C_{11}H_{10}$	142.2	0.148	C_{sat} [34]	Test Set & Comparison Set	247.97	1.439	1.446
						257.51	1.463	1.490
						266.59	1.487	1.530
						286.39	1.543	1.615
						299.9	1.583	1.671
						310.24	1.615	1.712
						330.8	1.678	1.790
						352.19	1.744	1.867
Anthracene	$C_{14}H_{10}$	178.23	0.135	C_P [35]	Training Set	495	2.249	2.114
						497	2.377	2.117
						498.15	2.355	2.119
						500	2.425	2.122
						502	2.409	2.126

trans-stilbene	$C_{14}H_{12}$	180.24	0.144	C_P [36]	Test Set & Comparison Set	401.61	1.962	1.995
						404.6	1.968	2.003
						407.59	1.976	2.012
						410.57	1.984	2.020
Pyrene	$C_{16}H_{10}$	202.25	0.129	C_{sat} [37]	Training Set	430.7	1.742	1.917
						440.32	1.771	1.939
						449.86	1.798	1.960
						459.3	1.823	1.979
						468.98	1.849	1.998
						478.79	1.878	2.017
Fluoranthene	$C_{16}H_{10}$	202.25	0.129	C_{sat} [37]	Figure 2-1	393.69	1.684	N/A
						403.27	1.711	
						412.97	1.741	
						422.57	1.777	
o-Terphenyl	$C_{18}H_{14}$	230.31	0.139	C_P [38]	Training Set	330.1	1.693	1.714
						336.85	1.712	1.739
						355.6	1.765	1.803
Benzo[a]pyrene	$C_{20}H_{12}$	252.32	0.127	C_{sat} [39]	Test Set	457.23	1.829	1.956
						466.64	1.844	1.975
						476.56	1.873	1.993
						486.48	1.887	2.010
						496.4	1.915	2.027
Compounds with Heteroatoms (N/S/O)								
2-Aminobiphenyl	$C_{12}H_{11}N$	169.23	0.142	C_{sat} [40]	Training Set	295.39	1.755	1.605
						311.507	1.792	1.669
						328.477	1.832	1.733
						329.258	1.834	1.736
						332.326	1.841	1.747
						338.259	1.855	1.768
						358.181	1.904	1.837
						387.095	1.975	1.930

						415.736	2.046	2.012
						440.488	2.107	2.075
Benzo[h]quinoline	$C_{13}H_9N$	179.22	0.128	C_{sat} [41]	Training Set & Figure 2-1	327.748	1.514	1.612
						331.194	1.524	1.624
						337.096	1.540	1.644
						346.814	1.568	1.677
						369.207	1.632	1.748
						393.489	1.701	1.819
						405.619	1.735	1.852
						428.339	1.797	1.909
Diphenyl Methanone	$C_{13}H_{10}O$	182.21	0.132	C_{sat} [33]	Test Set & Comparison Set	271.421	1.518	1.423
						277.981	1.533	1.450
						288.102	1.558	1.492
						301.814	1.592	1.546
						316.881	1.632	1.603
						331.745	1.671	1.657
						344.931	1.707	1.702
						358.402	1.743	1.746
						373.573	1.784	1.794
						388.99	1.825	1.840
						404.589	1.867	1.883
						429.948	1.933	1.948
1,2,3,4-Tetrahydrodibenzothiophene	$C_{12}H_{12}S$	188.29	0.133	C_{sat} [42]	Test Set	287.635	1.396	1.499
						300.54	1.430	1.550
						315.407	1.471	1.607
						330.789	1.515	1.663
9-Fluorenemethanol	$C_{14}H_{12}O$	196.24	0.138	C_P [43]	Training Set	378.4	2.127	1.868
						381.412	2.193	1.877
						385.714	2.276	1.890
						389.692	2.346	1.902
1,1' -Thiobis(cyclohexane)	$C_{12}H_{22}S$	198.37	0.176	C_{sat} [44]	Training Set	287.6	1.610	1.828
						290.601	1.620	1.840
						307.92	1.676	1.912

						336.785	1.777	2.026
						367.759	1.890	2.140
						398.087	2.005	2.243
						428.059	2.120	2.338
Carboxine	$C_{12}H_{13}NO_2S$	235.302	0.123	C_P [45]	Training Set	367.32	1.844	1.692
						370.32	1.865	1.701
						374.78	1.881	1.714
						377.65	1.899	1.723
						380.54	1.913	1.731
N-Octyl-1-octanamine	$C_{16}H_{35}N$	241.46	0.215	C_{sat} [46]	Test Set & Comparison Set	300	2.107	2.101
						340	2.283	2.254
						380	2.441	2.402
						420	2.586	2.544
						460	2.720	2.680
						500	2.848	2.810
						540	2.979	2.935
						580	3.113	3.055
Ethyl Tridecanoate	$C_{15}H_{30}O_2$	242.398	0.194	C_P [47]	Training Set	275.34	2.006	1.885
						278.01	2.010	1.896
						280.68	2.016	1.908
						283.33	2.018	1.919
						285.99	2.019	1.930
						288.64	2.024	1.941
						291.29	2.030	1.952
						293.93	2.034	1.963
						296.56	2.041	1.974
						299.2	2.046	1.984
						301.82	2.052	1.995
						304.44	2.058	2.006
						307.06	2.066	2.016
						309.67	2.073	2.027

Molten Polymers								
Isotactic Polypropylene	$(C_3H_6)n$	42.08	0.214	[14]	Training Set	450	2.719	2.639
						470	2.777	2.705
						490	2.834	2.770
						510	2.885	2.833
						530	2.932	2.895
						550	2.973	2.955
						570	3.012	3.014
						590	3.048	3.071
Poly(1-butene)	$(C_4H_8)n$	56.11	0.214	[14]	Test Set	420	2.491	2.537
						440	2.550	2.605
						460	2.610	2.672
						480	2.670	2.738
						500	2.729	2.802
						520	2.789	2.864
						540	2.856	2.925
						560	2.927	2.985
						580	2.998	3.043
						600	3.076	3.099
						620	3.158	3.154
Atatic Poly(methyl methacrylate)	$(C_5O_2H_8)n$	100.12	0.150	[14]	Test Set	430	2.131	2.124
						450	2.181	2.176
						470	2.232	2.223
						490	2.282	2.265
						510	2.328	2.304
						530	2.378	2.338
						550	2.424	2.368
Polystyrene	$(C_8H_8)n$	104.15	0.154	[14]	Training Set	420	2.017	2.131
						440	2.077	2.185
						460	2.137	2.236
						480	2.193	2.282

						500	2.246	2.323
						520	2.294	2.361
						540	2.342	2.394
						560	2.386	2.424
						580	2.430	2.449
Poly (oxy-2,6-dimethyl-1,4-phenylene)	$(C_6H_2(CH_3)_2O)n$	120.15	0.141	[15]	Training Set	534.439	2.194	2.252
						544.167	2.213	2.265
Poly (oxyoctamethylene)	$((CH_2)_8O)n$	128.21	0.195	[16]	Test Set	347.61	2.268	2.182
						350.43	2.209	2.193
						353.47	2.224	2.204

2.2 Results and Discussion

2.2.1 Quality of the Fit of the Correlation

Values for the six universal coefficients appearing in equation2-7 were fit using the Ordinary Least Squares (OLS) method and are reported in Table 2-2, where the objective function is the sum of squared residuals (i.e. the difference between the data point (C_P^{exp}) and the correlated point (C_P^{cal})) to be minimized:

$$S = \sum_{i=1}^{m} \sum_{j=1}^{n} (C_P^{\exp} - C_P^{cal})^2 / n \qquad (2\text{-}11)$$

where superscript "exp" represents experimental data, the superscript "cal" stands for the computed value (equation 2-7), parameter *m* is the number of compounds, *n* denotes the number of experimental data for a compound.

Table 2-2. Values for the universal coefficients appearing in equation 2-7

coefficient	value
a_{11}	-0.3416
a_{12}	2.2671
a_{21}	0.1064
a_{22}	-0.3874
a_{31}	-9.8231×10^{-5}
a_{32}	4.182×10^{-4}

Average standard deviation of the fit, σ_F, average relative deviation, δ, and average absolute deviation, ε, reflect the quality of the fit of the correlation for the training set. These parameters, reported in Table 2-3, have the customary definitions:

$$\boldsymbol{\sigma_F = \frac{1}{m}\sum_{i=1}^{m}\sqrt{\sum_{j=1}^{n}\left(C_P^{exp} - C_P^{cal}\right)_j^2/(n-p)}} \qquad (2\text{-}12)$$

$$\boldsymbol{\delta = \frac{1}{m}\sum_{i=1}^{m}\{\frac{\sum_{j=1}^{n}\sqrt{[\left(C_P^{exp} - C_P^{cal}\right)/C_P^{exp}]_j^2}}{n}\}} \qquad (2\text{-}13)$$

$$\boldsymbol{\epsilon} = \frac{1}{m}\sum_{i=1}^{m}\left[\frac{\sum_{j=1}^{n}\sqrt{\left(C_P^{exp}-C_P^{cal}\right)_j^2}}{n}\right] \tag{2-14}$$

where p is the number of fitted parameters.

Average standard deviation (σ) for the test set is defined as

$$\sigma = \frac{1}{m}\sum_{i=1}^{m}\sqrt{\sum_{j=1}^{n}\left(C_P^{exp} - C_P^{cal}\right)_j^2/(n-1)} \tag{2-15}$$

Table 2-3. Quality of the fit of the correlation

	training data set	test data set
number of compounds	22	15
number of $C_{P,liquid}$ values	150	111
σ [J $K^{-1}g^{-1}$]	0.126	0.078
ϵ [J K^{-1} g^{-1}]	0.10	0.07
100δ	5.1	3.5

Calculated liquid heat capacity values obtained using equation 2-7 are also listed in Table 2-1. Average relative deviation (100δ) and average absolute deviation (ε) for compounds in all three data sets (training set, test set, and comparison set) are given in Table 2-4. 9-Fluorenemethanol ($C_{14}H_{12}O$) and Anthracene ($C_{14}H_{10}$) have the largest positive deviations, and 1,1' -Thiobis(cyclohexane) ($C_{12}H_{22}S$) has the largest negative deviations among the 22 compounds in the training set.

Table 2-4. Compounds, their assignment, and fit quality for equation 2-7 and for the Lee-Kesler correlation.

Compound	Formula	Database	Temperature range [K]	This work (equation 2-7)		Lee-Kesler Correlation (equation 2-1)	
				ε J $K^{-1}g^{-1}$	100δ	ε J $K^{-1}g^{-1}$	100δ
Heptane	C_7H_{16}	Test Set & Comparison Set	196.42-342.66	0.112	5.24	0.057	2.73
2,2,3,3-Tetramethylpentane	C_9H_{20}	Training Set	269.18-352.34	0.027	1.30	0.033	1.54
2,7-Dimethyloctane, Diisoamyl	$C_{10}H_{22}$	Training Set	223.2-295	0.016	0.83	0.045	2.24
Decane	$C_{10}H_{22}$	Test Set & Comparison Set	318.15-373.15	0.071	5.24	0.008	0.33
2-Methyldecane	$C_{11}H_{24}$	Training Set	235.44-375.23	0.070	3.24	0.055	2.70
Tridecane	$C_{13}H_{28}$	Training Set	280.15-318.15	0.082	3.76	0.170	7.75
Pentadecane	$C_{15}H_{32}$	Test Set & Comparison Test	313.15-373.15	0.055	2.37	0.026	1.15
Hexadecane	$C_{16}H_{34}$	Training Set	318.15-368.15	0.047	2.02	0.034	1.50
Octadecane	$C_{18}H_{38}$	Test Set & Comparison Set	306.69-398.59	0.069	2.94	0.030	1.32
Butylcyclohexane	$C_{10}H_{20}$	Training Set	207.52-365.38	0.133	7.16	0.047	2.50
Decylcyclopentane	$C_{15}H_{30}$	Training Set	258.18-311.43	0.036	1.82	0.045	2.35
Decylcyclohexane	$C_{16}H_{32}$	Test Set & Comparison Set	274.26-300.48	0.062	3.17	0.020	1.06
1,1,3-Tricyclohexylpropane	$C_{21}H_{38}$	Training Set	373.15-483.15	0.082	3.53	N/A	N/A
Styrene	C_8H_8	Test Set & Comparison Set	246.73-298.54	0.091	5.58	0.148	9.00
Dimethylbenzene	C_8H_{10}	Training Set	251.98-297.74	0.025	1.49	0.084	5.02
Naphthalene	$C_{10}H_8$	Training Set	357.43-427.29	0.114	6.42	0.430	24.27
1-Methylnaphthalene	$C_{11}H_{10}$	Test Set & Comparison Set	247.97-352.19	0.071	4.40	0.169	11.01
Anthracene	$C_{14}H_{10}$	Training Set	495-502	0.243	10.24	0.749	31.66
trans-stilbene	$C_{14}H_{12}$	Test Set & Comparison Set	401.61-410.57	0.034	1.77	0.077	3.93
Pyrene	$C_{16}H_{10}$	Training Set	430.7-478.79	0.158	8.77	0.328	18.14

o-Terphenyl	$C_{18}H_{14}$	Training Set	330.1-355.6	0.028	1.64	0.268	15.56
Benzo[a]pyrene	$C_{20}H_{12}$	Test Set	457.23-496.4	0.122	6.56	N/A	N/A
2-Aminobiphenyl	$C_{12}H_{11}N$	Training Set	295.39-440.48	0.082	4.48	N/A	N/A
Benzo[h]quinoline	$C_{13}H_9N$	Training Set	327.74-428.33	0.109	6.71	0.407	20.59
Diphenyl methanone	$C_{13}H_{10}O$	Test Set & Comparison Set	271.42-429.94	0.033	2.07	0.304	18.30
1,2,3,4-Tetrahydrodibenzothiophene	$C_{12}H_{12}S$	Test Set	287.63-330.78	0.126	8.68	N/A	N/A
9-Fluorenemethanol	$C_{14}H_{12}O$	Training Set	378.4-389.69	0.351	15.61	N/A	N/A
1,1' -Thiobis(cyclohexane)	$C_{12}H_{22}S$	Training Set	287.6-428.05	0.232	12.93	N/A	N/A
Carboxine	$C_{12}H_{13}NO_2S$	Training Set	367.32-380.54	0.168	8.93	N/A	N/A
N-Octyl-1-octanamine	$C_{16}H_{35}N$	Test Set & Comparison Set	300-580	0.037	1.36	0.037	1.39
Ethyl tridecanoate	$C_{15}H_{30}O_2$	Training Set	275.34-309.67	0.078	3.86	N/A	N/A
Isotactic polypropylene	$(C_3H_6)n$	Training Set	450-590	0.043	1.54	N/A	N/A
Poly(1-butene)	$(C_4H_8)n$	Test Set	420-620	0.052	1.91	N/A	N/A
Atatic poly(methyl methacrylate)	$(C_5O_2H_8)n$	Test Set	430-550	0.022	0.96	N/A	N/A
Polystyrene	$(C_8H_8)n$	Training Set	420-580	0.073	3.38	N/A	N/A
Poly (oxy-2,6-dimethyl-1,4-phenylene)	$(C_6H_2(CH_3)_2O)n$	Training Set	534.43 &544.16	0.055	2.50	N/A	N/A
Poly (oxyoctamethylene)	$((CH_2)_8O)n$	Test Set	347.61-353.47	0.040	1.81	N/A	N/A

Relative and absolute deviations of the regressed liquid heat capacity values from experimental values for the training set are summarized in Figure 2-2. For most compounds, the relative deviations decrease as temperature increases as shown in Figure 2-2a, while there is no trend for absolute deviation versus liquid heat capacity values as shown in Figure 2-2b. Figure 2-3 shows that average relative deviations (100.δ) of the correlated liquid heat capacity values from experimental data versus molar masses are distributed normally for the training set. This observation implies that deviations are not necessarily greater for larger compounds. For example, the greatest deviation (15.6%) corresponds to 9-Fluorenemethanol ($C_{14}H_{12}O$) with a molar mass of 196.2 g.mol^{-1}.

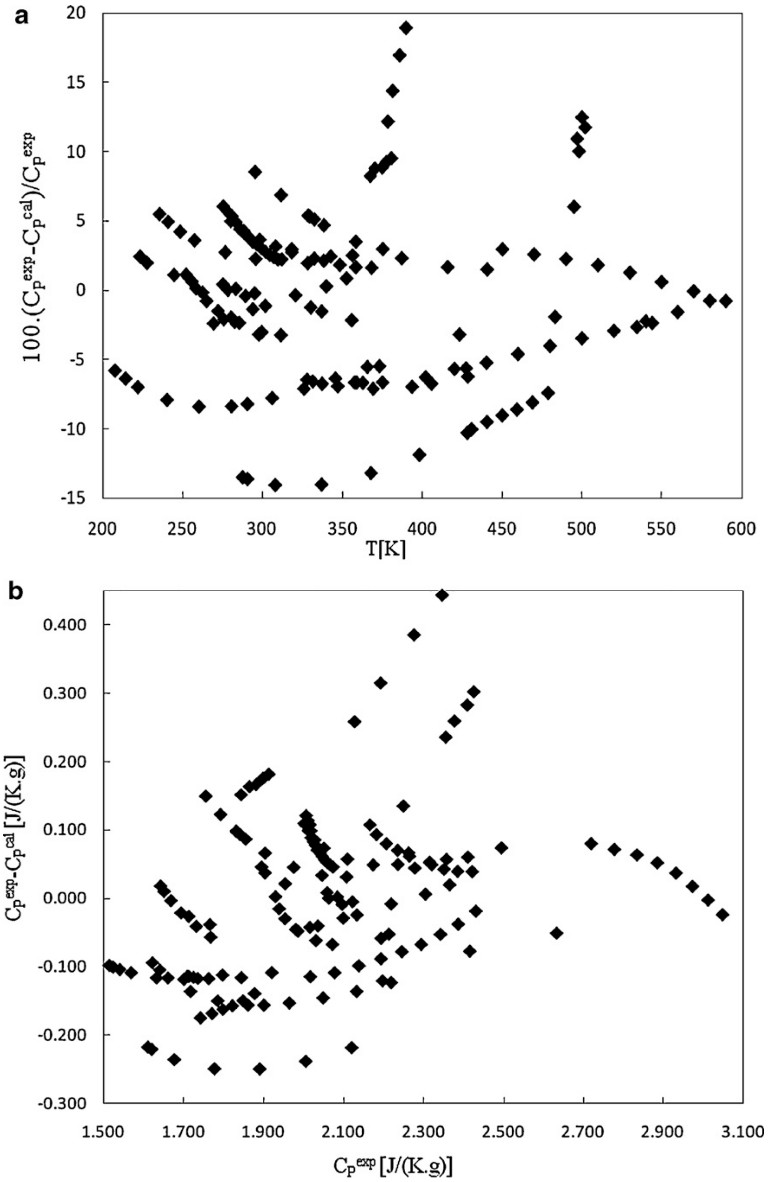

Figure 2-2. Relative deviation (a) and absolute deviation (b) of the correlated liquid heat capacity values from experimental values (training data set).

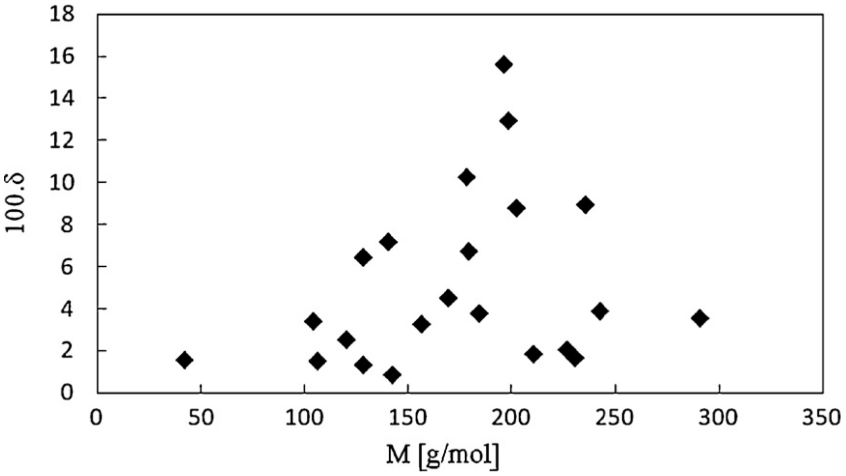

Figure 2-3. Average relative deviation of the correlated liquid heat capacity values from experimental values versus molar mass (training data set).

Average relative deviation (δ), average absolute deviation (ϵ), and average standard deviation (σ) for the test data set are reported in Table 2-3. The trends and values of the various measures of error are comparable to the training data set. Figure 2-4a shows declining relative deviations for most compounds as temperature increases, which is similar to what is observed for the training set in Figure 2-2. For example, the relative deviation for heptane (C_7H_{16}) decreases from 11.4% at 196 K, to 4.1% at 343 K. As with the training data set, the absolute deviations between the predicted and experimental heat capacity values, Figure 2-4b, do not show trends with temperature. Figure 2-5 supports the observation illustrated in Figure 2-3, i.e.: equation 2-7 predicts liquid heat capacity within less than 10% (for the cases evaluated) irrespective of molar mass.

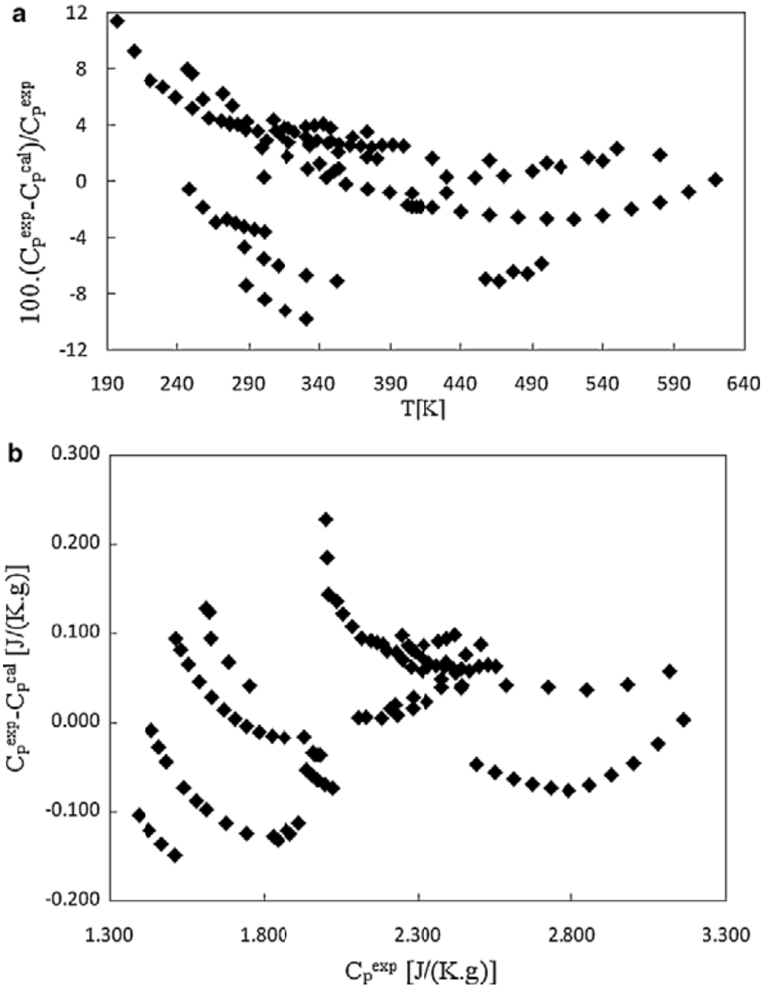

Figure 2-4. Relative deviation (a) and absolute deviation (b) of the predicted liquid heat capacity values from experimental values (test data set).

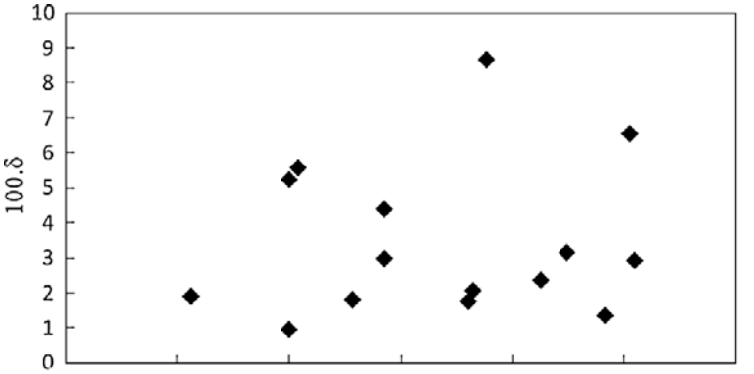

Figure 2-5. Average relative deviation of the predicted liquid heat capacity values from experimental values versus molar mass (test data set).

The coefficients appearing in equation 2-7 are not element specific, or in the case of carbon, carbon type specific. Although such terms arise in group contribution methods for calculating heat capacity, they are of secondary importance as noted in the introduction. While the results are fragmentary, the quality of the fit (training data set and test data set) does not appear to be biased relative to the treatment of heteroatoms (S, O, N) individually or collectively as shown in Figure 2-6, or relative to the treatment of carbon type as shown in Figure 2-7, where the relative errors for all cases fall within the range of aliphatic hydrocarbons. This result is consistent with prior application of the similarity concept to organic solids [4, 5] and ideal gases [6], where within broad limits, the details of molecular structure and the elements present comprise variables of secondary importance.

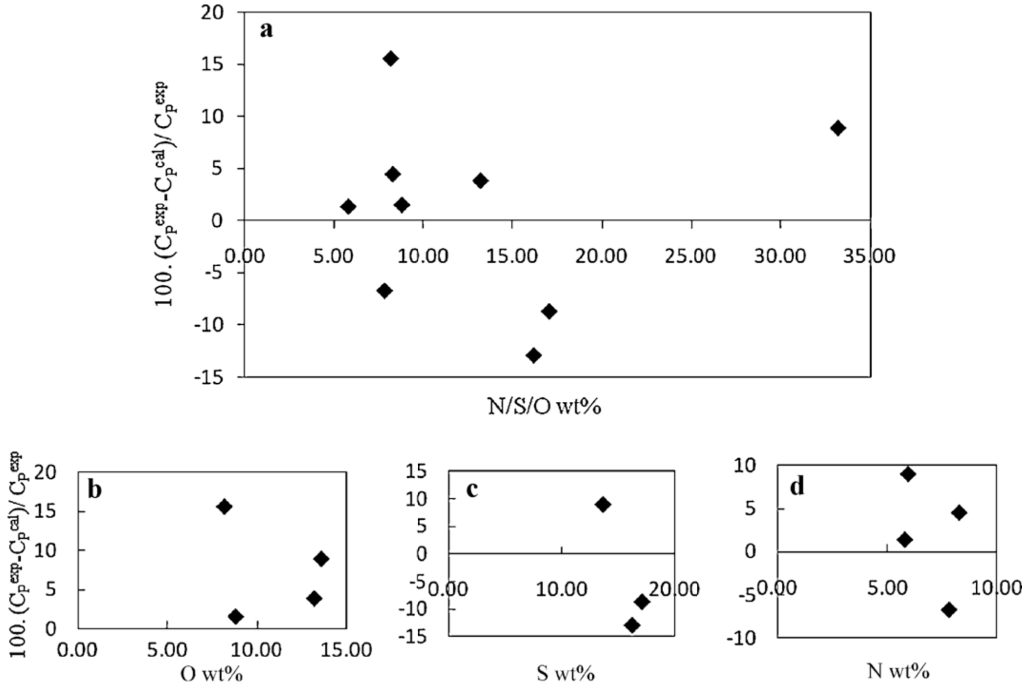

Figure 2-6. Impact of heteroatom content on the relative deviation of predicted liquid heat capacities from experimental values: (a) sum of S + N + O, (b) oxygen, (c) sulphur, and (d) nitrogen.

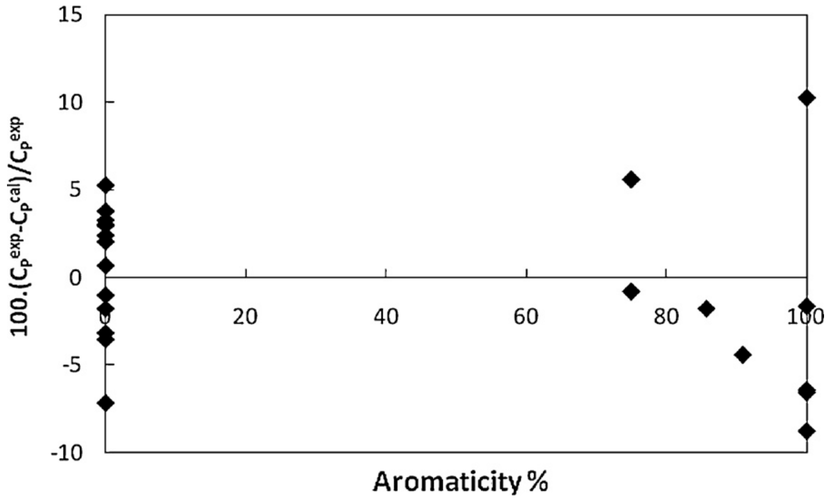

Figure 2-7. Impact of aromatic carbon content on the average relative deviation of predicted liquid heat capacities from experimental values.

The critical temperature (T_c) is available for a number of the compounds listed in both the training and test data sets. For these compounds, absolute and relative deviations of the calculated liquid heat capacity values from experimental values versus reduced temperature, Figure 2-8, show the same trends as for absolute temperature. None of the heat capacity data are in the $T_r > 0.95$ range where equation 2-7 is expected to underestimate values systematically as the data trend to infinity at the critical point. Further, prediction quality appears to be independent of the critical temperature of the liquid as anticipated in section 2.2.1. For liquids with unknown critical properties, equation 2-7 can be applied with confidence.

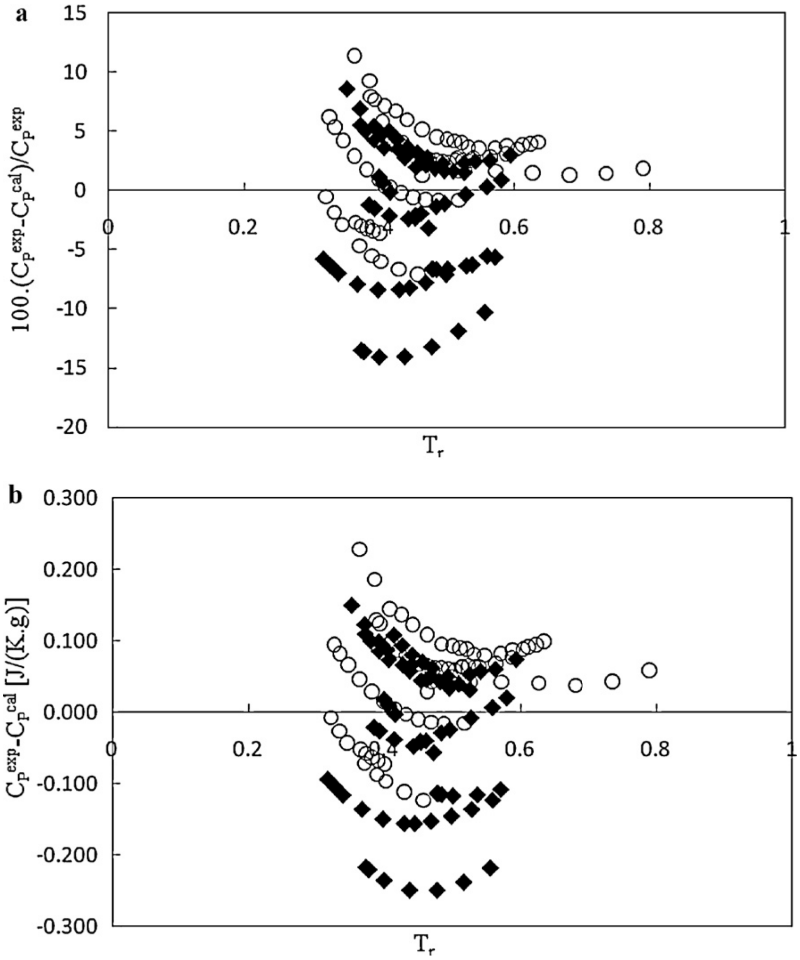

Figure 2-8. Relative deviation (a)and absolute deviation (b) of the calculated liquid heat capacity values from experimental values versus reduced temperature for: ♦, training data set; ○, test data set.

Six molten polymers were included in the database: three in the training data set and three in the test data set. Absolute and relative deviations for these materials are shown in Figure 2-9. The polymers in the training set are isotactic polypropylene ($(C_3H_6)n$), polystyrene ($(C_8H_8)n$), and poly (oxy-2,6-dimethyl-1,4-phenylene) ($(C_6H_2(CH_3)_2O)n$). The polymers in the test data set are poly(1-butene) ($(C_4H_8)n$), atatic poly(methyl methacrylate) ($(C_5O_2H_8)n$), and poly(oxyoctamethylene) ($((CH_2)_8O)n$). The average relative deviations of the predicted heat capacity values for these three latter molten polymers from experimental heat capacity data is less than 2%.

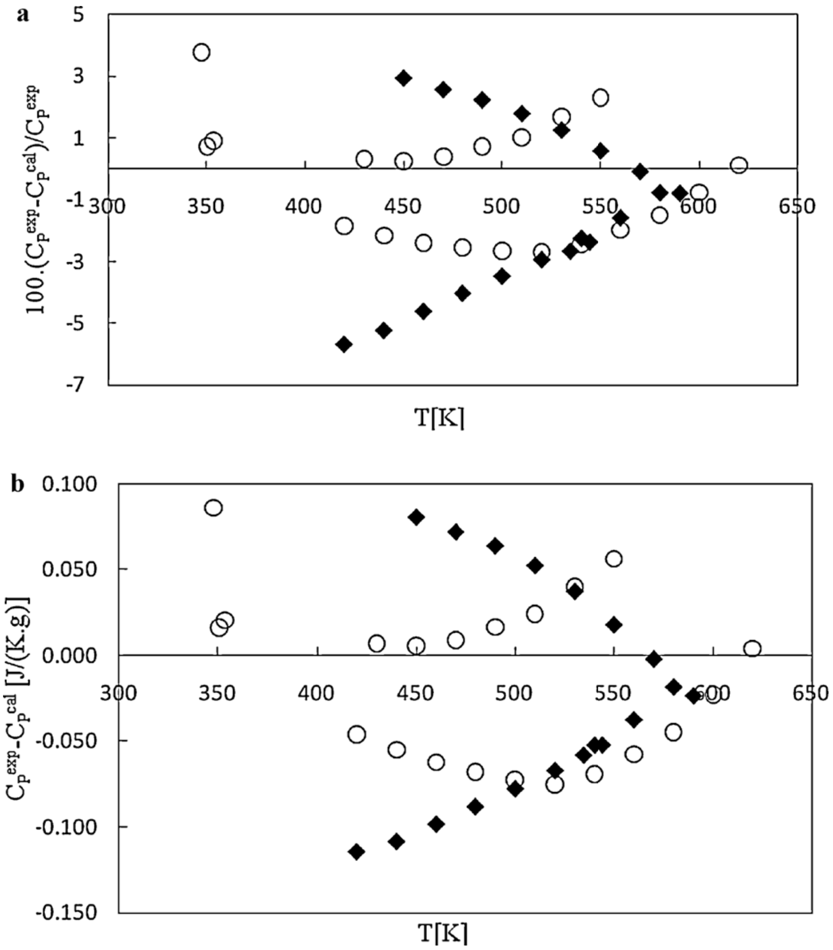

Figure 2-9. Relative deviation (a)and absolute deviation (b) of the calculated liquid heat capacity values from experimental values versus temperature for polymers: ♦, training data set; ○, test data set.

2.2.2 Comparison with the Lee-Kesler Correlation

As the present correlation, equation 2-7, and the Lee-Kesler correlation possess the same functional form, and have overlapping ranges of application, it is possible to make both qualitative and quantitative comparisons between them. The Lee-Kesler correlation cannot be used for a number of compounds listed in the test and training data sets, as boiling point and specific gravity values are not available for them. Thus, even for pure liquids, the present correlation offers advantages over the Lee-Kesler correlation with respect to the range of application. From the perspective of quantitative fit, it is difficult to avoid bias in comparisons between the two correlations because the training set for the Lee-Kesler correlation is not available. The Lee-Kesler correlation is recommended for estimating the isobaric heat capacities of petroleum fractions [3]. One would expect that their training data set comprised n-alkanes (C_nH_{2n+2}) or a plurality of n-alkanes.

The comparison data set is drawn from the test data set for equation 2-7 and comprises 81 data points for 10 organic compounds and should be viewed as illustrative. The compounds comprising the comparison data set, listed in Table 2-1, include paraffins, naphthenes, aromatics, and oxygen/nitrogen derivatives. Boiling point (T_b) and specific gravity (sp gr) values are available in the literature for these compounds. The temperature dependence of the absolute and relative deviations of the predicted liquid heat capacity values from experimental values for the comparison data set are presented in Figure 2-10.

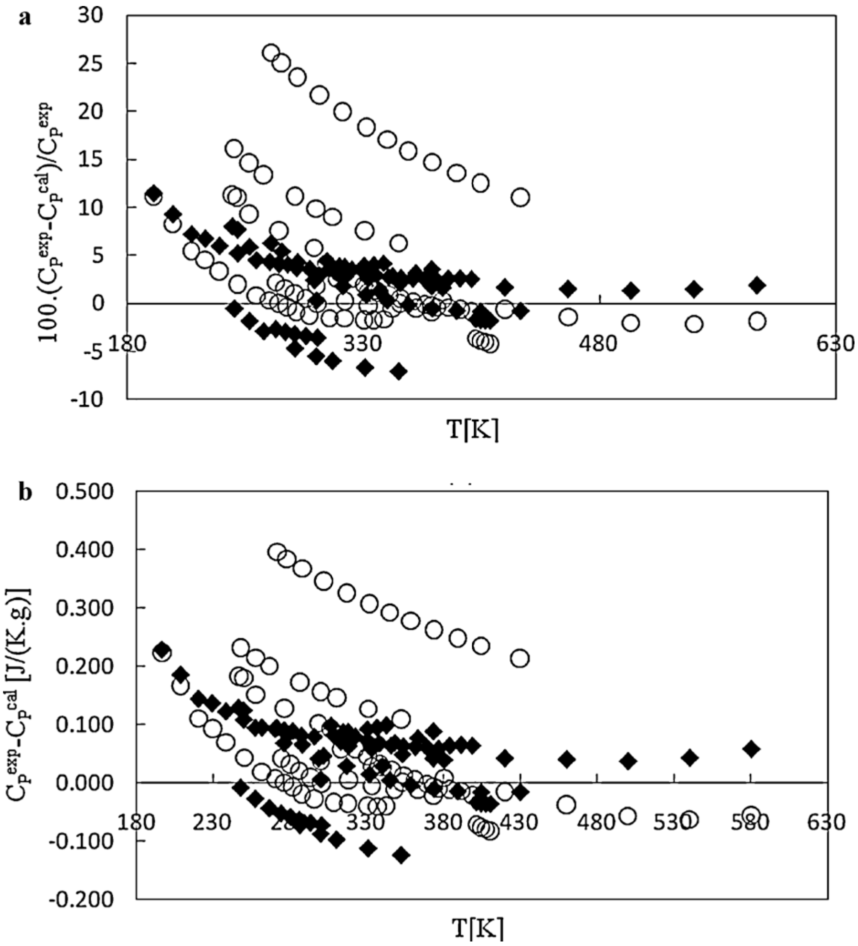

Figure 2-10. Relative deviation (a) and absolute deviation (b) of the predicted liquid heat capacity values from experimental values versus temperature for: ♦, equation 2-7; ○, Lee-Kesler correlation (comparison data set).

Deviation values for individual compounds using both equation 2-7 and the Lee-Kesler correlation (equation 2-1) are listed in Table 2-4. Average standard deviation and average relative deviation values for the comparison data set based on equation 2-7 are 0.07 J $K^{-1}g^{-1}$ and 3.2% respectively. The corresponding values for the Lee-Kesler correlation are 0.10 J $K^{-1}g^{-1}$ and 5.0%. The average relative deviations for the Lee-Kesler correlation appear to be more variable with respect to molecular structure, temperature and molar mass (Figure 2-11) than for equation 2-7, even if the average deviations of the two correlations for the comparison data set are comparable.

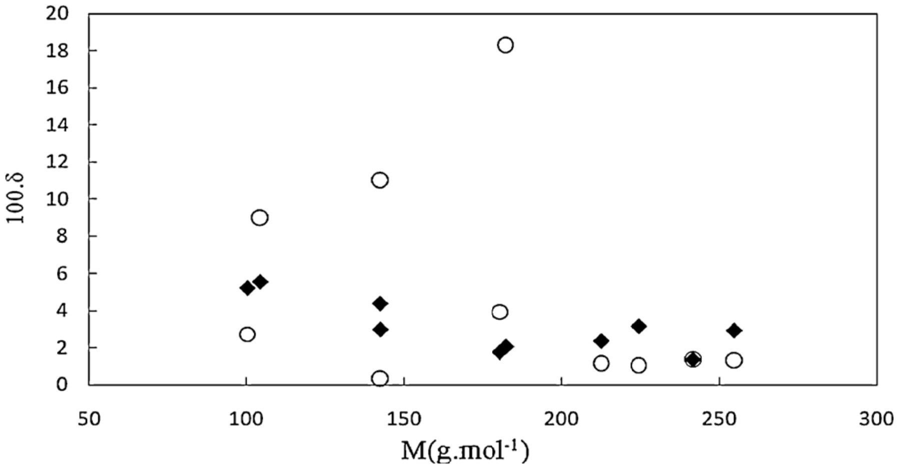

Figure 2-11. Average relative deviation of the predicted liquid heat capacity values from experimental values versus molar mass for: ♦, equation 2-7; ○, Lee-Kesler correlation (comparison data set).

2.2.3 Heat Capacity Prediction for Ill-defined Hydrocarbon Liquids

As noted in the introduction, there are no techniques for predicting liquid heat capacities for hydrocarbons with unknown molecular structure and critical properties. However, to apply equation 2-7, only elemental analysis, a simple and typically available assay, is required to predict liquid heat capacity. On the basis of pure prediction, the average relative deviation for Maya maltenes (Figure 2-12a) is 2.8% and is 6.0% for Athabasca C5 maltenes (Figure 2-12b) from 320 K to 550 K. This is the best temperature range to test the purely predictive quality of the correlation because at lower temperatures the maltenes begin to solidify, and at higher temperatures thermolysis reactions interfere with heat capacity measurements. The quality of the agreement between the predicted and experimental heat capacities is comparable to the fits obtained with the training data set and the predictions realized for the test data set, and remains less than twice the measurement error, ±0.05 J $K^{-1}g^{-1}$ or ~ 2.5 %. This is a key result of the work.

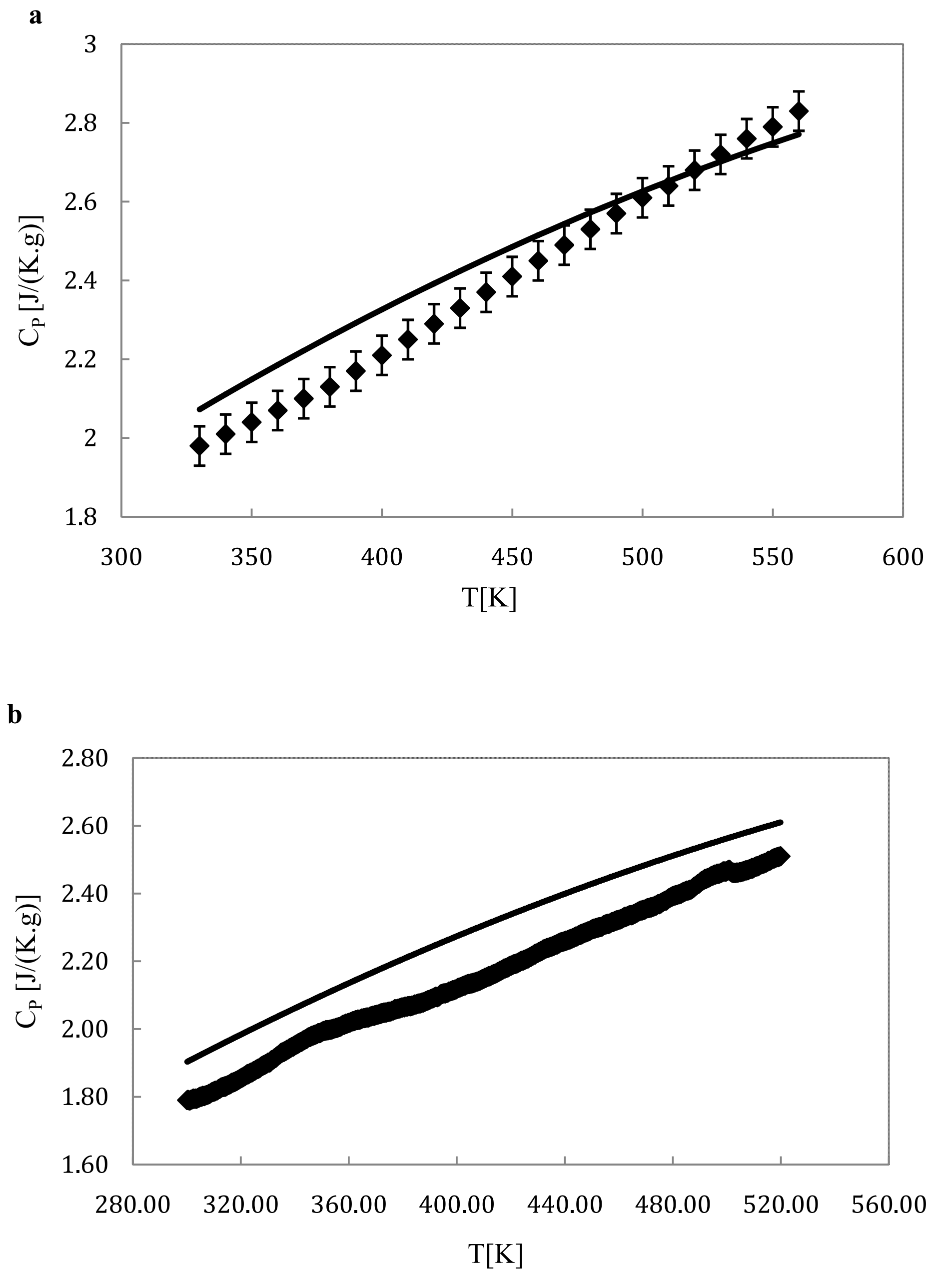

Figure 2-12. Comparison between predicted liquid heat capacity values equation 2-7(—) and experimental values (♦) for (a) Maya pentane maltenes [17] (α = 0.188 [mol/g]) and (b) Athabasca pentane maltenes [18] (α = 0.180 [mol/g]).

2.3 Conclusions

A universal correlation for predicting the heat capacity of hydrocarbons liquids, incorporating a similarity variable, rooted in quantum mechanics, and requiring only fluid specific elemental analysis as an input is presented and validated. The correlation provides heat capacity estimates that are unbiased relative to molecular structure, heteroatom content, carbon aromaticity, and molar mass. The correlation appears to be preferred over alternatives such as the Lee-Kesler equation with respect to ease of use, overall accuracy and range of application. The predictive nature of the correlation is validated for pure organic compounds, and polymer melts, over broad ranges of temperature. Reliable heat capacity predictions for ill-defined fluids such as bitumen and heavy oil were made for the first time.

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Chapter 3
Predictive Correlations for Liquid Heat Capacity - Including the Critical Region†

3.1 Introduction

The Dadgostar-Shaw universal correlation was developed to predict the constant pressure specific heat capacity of pure and ill-defined liquid hydrocarbons [1]. Unlike other predictive techniques, namely group contribution methods [2] and corresponding states methods [3, 4], the universal correlation requires elemental composition rather than the molecular structure and/or physical properties. It enables the prediction of liquid phase heat capacity of organic liquid mixtures with unknown molecular structure (e.g. maltenes, boiling fractions, etc.) as well as providing reliable estimates for large pure hydrocarbon compounds, including aromatics and compounds with heteroatoms (e.g. nitrogen, oxygen, sulfur), and molten polymers.

The universal correlation (equation 3-1) retains the successful quadratic temperature form of the Lee-Kesler correlation [5], and includes six universal coefficients:

$$C_{PL} = 24.5(a_{11}\alpha + a_{12}\alpha^2) + (a_{21}\alpha + a_{22}\alpha^2)T + (a_{31}\alpha + a_{32}\alpha^2)T^2 \tag{3-1}$$

C_{PL} is the isobaric specific heat capacity of a liquid (J K^{-1} g^{-1}), T is temperature (K), and α, has the units mol g^{-1}. The values of the coefficients are listed in Table 3-1.

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†N. Dadgostar, J. M. Shaw, Fluid Phase Equilibria 344 (2013) 139-151

Table 3-1. Values for the coefficients appearing in equation 3-1 and equation 3-10.

coefficient	value
a_{11}	-0.3416
a_{12}	2.2671
a_{21}	0.1064
a_{22}	-0.3874
a_{31}	-9.8231×10^{-5}
a_{32}	4.182×10^{-4}
b_1	1.6704
b_2	0.5509

The similarity variable (α) defined as the number of atoms in a molecule divided by molecular mass is rooted in quantum mechanics (equation 3-2):

$$\alpha=\frac{N}{M}=\frac{\sum_{i=1}^{n}\upsilon_i}{\sum_{i=1}^{n}\upsilon_i M_i}=\frac{\sum_{i=1}^{n}x_i}{\sum_{i=1}^{n}x_i M_i}=\frac{\sum_{i=1}^{n}\frac{w_i}{M_i}}{\sum_{i=1}^{n}w_i} \tag{3-2}$$

where ν_i is the stoichiometric coefficient for element *i* in acompound consisting of *N* atoms, *n* is the number of elements in a compound, *M* is the molar mass of the compound and M_i is the molar mass of chemical element *i* ($\mathrm{gmol^{-1}}$). Variable x_i is the mole fraction of element *i* in a compound, and w_i is the mass fraction of element *i*. Thus the value of the similarity variable, α, is simply a function of the elemental composition of the compound or mixture. The validity of the similarity variable approach for predicting the constant pressure specific heat capacities for ill-defined organic liquids and solids was discussed in detail previously [1, 6]. The heat capacities of diverse pure, mixed and ill-defined hydrocarbons possessing molar masses exceeding ~ 100 g $\mathrm{mol^{-1}}$ were well represented across available data bases and the absolute relative deviations between predicted and measured heat capacity values were within 0.08 on average for solids and 0.05 on average for liquids.

As,

$$C_{PL} = C_{VL} + T(\frac{\partial V}{\partial T})_P(\frac{\partial P}{\partial T})_V \quad (3\text{-}3)$$

equation 3-1 is expected to be valid where the temperature dependent term (C_V) dominates, i.e. where $C_V >> T(\frac{\partial V}{\partial T})_P(\frac{\partial P}{\partial T})_V$. Modification is required to accommodate the critical region and the consequent variation of liquid phase isobaric heat capacity among isomers or compounds possessing the same value of α but differing critical temperatures at the same absolute temperature. While deviations among compounds sharing a similarity variable are typically small for a broad range of industrially relevant conditions, the deviation of predicted values by the Dadgostar-Shaw universal correlation from the experimental liquid heat capacity data becomes significant at temperatures close to the critical point as illustrated for n-heptane in Figure 3-1. In this work, modifications to the successful form of the Dadgostar-Shaw correlation are explored to address these two sources of deviation from experimental data. Computational outcomes are compared with two variants of the Rowlinson-Bondi computational approach.

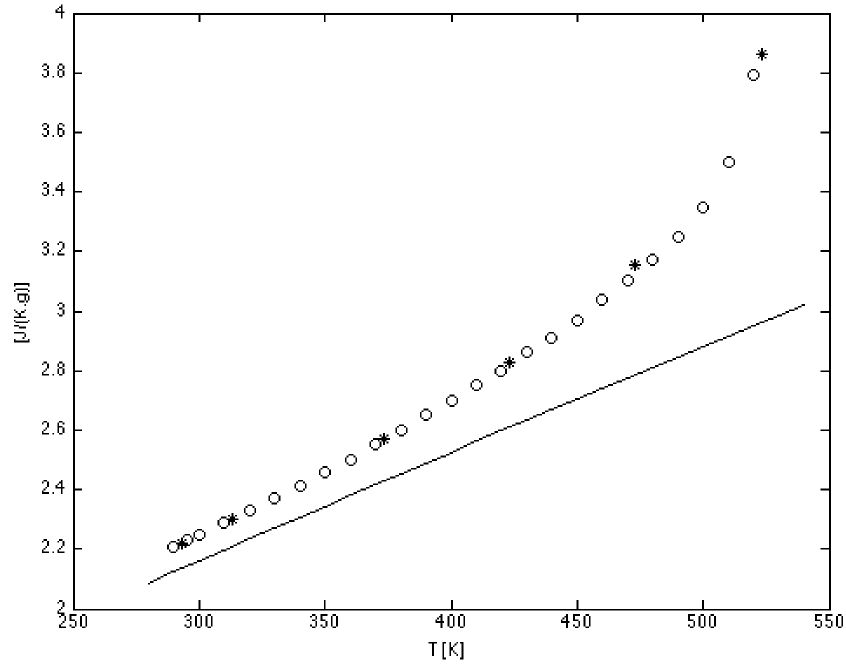

Figure 3-1. Deviation of predicted liquid phase heat capacity values by equation 3-1 (—) from experimentally measured data by: ○, Douglas et al. [7]; *, Mel'nikov et al. [8] for n-heptane.

3.1.1 Correlation Modification Methodology

A reliable baseline is required to address deviations arising in the critical region. Four baselines were evaluated. Deviations of the baselines from experimental data were tracked for low and intermediate molar mass compounds and these deviations were then modeled using a reduced temperature dependent term.

3.1.1.1 Baseline Evaluation

The baselines evaluated include:

1- A polymer baseline, comprising only experimental heat capacity data for molten polymers. By definition, these data include a broad range of temperatures but are remote from critical point effects. The diversity of molecular forms and ranges of the similarity variable are however constrained.

2- A polymer + large pure compound ($M > 200$ g mol^{-1}) baseline, where the polymer data are augmented with heat capacity data for additional compounds remote from their critical points (revised baseline).
3- The Dadgostar-Shaw universal correlation[1].
4- The heat capacity data set used to define the Dadgostar-Shaw universal correlation + additional data for molten polymers at higher temperatures (critical baseline).

All four baselines share the same functional form (equation 3-1). The main difference among them is the nature and number of compounds used to fit parameters. Table 3-2 lists the compounds used in the baseline data sets. The relative performance of these baselines is illustrated in Figure 3-2 where the predicted liquid heat capacity values for n-heptane are compared with experimental data. The polymer-only baseline performs poorly at lower temperatures, while the other three baselines perform equivalently over a broad range of temperatures. These two outcomes were observed for numerous test cases. Thus, the Dadgostar-Shaw universal correlation was adopted as the baseline for tracking deviations between predicted and measured heat capacity values in the critical region.

Table 3-2. Databases for baseline evaluation (Unless otherwise noted, P = 1 atm for the isobaric heat capacity measurements.)

Compound	Formula	M [g mol^{-1}]	α [mol g^{-1}]	Reference	Baseline	T[K]	C_{PL}[J K^{-1} g^{-1}]_Experimental
Alkanes							
Pentadecane	$C_{15}H_{32}$	212.42	0.221	[9]	Revised	313.15	2.250
						333.15	2.313
						353.15	2.378
						373.15	2.444
Hexadecane[a]	$C_{16}H_{34}$	226.45	0.221	[10]	Universal,Revised, Critical	318.15	2.263
						328.15	2.278
						338.15	2.320
						348.15	2.351
						358.15	2.385
						368.15	2.421
Octadecane	$C_{18}H_{38}$	254.49	0.22	[11]	Revised	306.69	2.247
						314.63	2.266
						322.51	2.289
						330.34	2.312
						338.13	2.336
						345.9	2.361
						353.61	2.388
						361.27	2.415
						368.87	2.443
						376.43	2.468
						383.66	2.499
						391.14	2.527
						398.59	2.553
Naphthenes							

Decylcyclopentane	$C_{15}H_{30}$	210.4	0.214	[12]	Universal,Revised, Critical	258.18	1.930
						264.82	1.939
						271.95	1.953
						282.67	1.980
						299.44	2.030
						311.43	2.071
Decylcyclohexane	$C_{16}H_{32}$	224.34	0.214	[13]	Revised	274.26	1.940
						280.27	1.958
						286.1	1.976
						293.33	2.000
						300.48	2.024
1,1,3-Tricyclohexylpropane	$C_{21}H_{38}$	290.53	0.203	[14]	Universal,Revised, Critical	373.15	2.198
						423.15	2.415
						483.15	2.633
Aromatics & Unsaturated Cyclic Hydrocarbons							
Pyrene	$C_{16}H_{10}$	202.25	0.129	[15]	Universal,Revised, Critical	430.7	1.742
						440.32	1.771
						449.86	1.798
						459.3	1.823
						468.98	1.849
						478.79	1.878
Fluoranthene	$C_{16}H_{10}$	202.25	0.129	[15]	Revised	393.69	1.684
						403.27	1.711
						412.97	1.741
						422.57	1.777
o-Terphenyl	$C_{18}H_{14}$	230.31	0.139	[16]	Universal,Revised, Critical	330.1	1.693
						336.85	1.712
						355.6	1.765

Benzo[a]pyrene	$C_{20}H_{12}$	252.32	0.127	[17]	Revised	457.23	1.829
						466.64	1.844
						476.56	1.873
						486.48	1.887
						496.4	1.915
Compounds with Heteroatoms (N/S/O)							
Carboxine	$C_{12}H_{13}NO_2S$	235.302	0.123	[18]	Universal,Revised, Critical	367.32	1.844
						370.32	1.865
						374.78	1.881
						377.65	1.899
						380.54	1.913
N-Octyl-1-octanamine	$C_{16}H_{35}N$	241.46	0.215	[19]	Revised	300	2.107
						340	2.283
						380	2.441
						420	2.586
						460	2.720
						500	2.848
						540	2.979
						580	3.113
Ethyl Tridecanoate	$C_{15}H_{30}O_2$	242.398	0.194	[20]	Universal,Revised, Critical	275.34	2.006
						278.01	2.010
						280.68	2.016
						283.33	2.018
						285.99	2.019
						288.64	2.024
						291.29	2.030
						293.93	2.034
						296.56	2.041

						299.2	2.046
						301.82	2.052
						304.44	2.058
						307.06	2.066
						309.67	2.073
Molten Polymers[b]							
Polyethylene	$(CH_2)n$	14.03	0.214	[21]	Polymer, Revised, Critical	420	2.564
						430	2.594
						440	2.620
						450	2.650
						460	2.677
						470	2.707
						480	2.743
						490	2.773
						500	2.805
						510	2.835
						520	2.868
						530	2.901
						540	2.931
						550	2.964
						560	2.994
						570	3.026
						580	3.059
						590	3.092
						600	3.122
						610	3.155
						620	3.187
						630	3.220

Isotactic Polypropylene	$(C_3H_6)n$	42.08	0.214	[21]	Polymer, Revised, Critical	450	2.719
						460	2.749
						470	2.777
						480	2.804
						490	2.834
						500	2.862
						510	2.885
						520	2.909
						530	2.932
						540	2.953
						550	2.973
						560	2.993
						570	3.012
						580	3.031
						590	3.048
						600	3.062
Poly(oxyethylene)	$((CH_2)_{20})n$	44.05	0.159	[22]	Revised, Critical	300	2.031
						310	2.044
						320	2.056
						330	2.069
						340	2.081
						350	2.094
						360	2.106
cis Poly(1-butenylene), Polybutadiene	$(C_4H_6)n$	54.09	0.185	[23]	Revised, Critical	260	1.829
						270	1.862
						273	1.872
						280	1.894
						290	1.927

						298	1.954
						300	1.960
						310	1.993
						320	2.026
						330	2.059
						340	2.092
						350	2.125
						360	2.158
						370	2.191
						380	2.224
						390	2.256
						400	2.289
						410	2.322
						420	2.355
						430	2.388
						440	2.421
						450	2.454
Poly-1-butene	$(C_4H_8)n$	56.1	0.214	[24]	Revised	410	2.463
						420	2.494
						430	2.522
						440	2.553
						450	2.583
						460	2.613
						470	2.642
						480	2.672
						490	2.702
						500	2.731
						510	2.761

						520	2.791
						530	2.829
						540	2.859
						550	2.897
						560	2.929
						570	2.963
						580	3.000
						590	3.037
						600	3.078
						610	3.119
						620	3.160
						630	3.201
Poly(oxytetramethylene)	$((CH_2)_4O)n$	72.1	0.180	[22]	Revised, Critical	280	1.943
						290	1.965
						300	1.989
						310	2.011
						320	2.033
						330	2.055
						340	2.079
Poly(methyl acrylate)	$(C_4H_6O_2)n$	86.09	0.139	[25]	Revised, Critical	300	1.784
						310	1.784
						320	1.802
						330	1.816
						340	1.839
						350	1.861
						360	1.874
						370	1.890
						380	1.904

						390	1.918
						400	1.955
						410	1.979
						420	2.005
						430	2.030
						440	2.036
						450	2.040
						460	2.073
						470	2.089
						480	2.104
						490	2.125
						500	2.135
Poly(oxy-1,4-phenylene)	$(C_6H_4O)n$	92.1	0.119	[22]	Revised, Critical	590	2.025
						600	2.042
						610	2.060
						620	2.077
Poly(methyl methacrylate)	$(C_5H_8O_2)n$	100.12	0.150	[21]	Polymer, Revised, Critical	410	2.077
						420	2.106
						430	2.131
						440	2.156
						450	2.181
						460	2.207
						470	2.232
						480	2.257
						490	2.282
						500	2.307
						510	2.328
						520	2.353

						530	2.378
						540	2.399
						550	2.424
Poly(oxymethyleneoxytetramethylene)	$(C_5H_{10}O_2)n$	102.13	0.166	[22]	Revised, Critical	300	1.905
						310	1.923
						320	1.941
						330	1.958
						340	1.975
						350	1.994
						360	2.010
Polystyrene	$(C_8H_8)n$	104.15	0.154	[21]	Polymer, Revised, Critical	400	1.932
						410	1.985
						420	2.017
						430	2.049
						440	2.077
						450	2.105
						460	2.137
						470	2.165
						480	2.193
						490	2.218
						500	2.246
						510	2.270
						520	2.294
						530	2.318
						540	2.342
						550	2.362
						560	2.386
						570	2.410

						580	2.430
						590	2.451
nylone 6	$(C_6H_{11}ON)n$	113.16	0.168	[26]	Revised, Critical	510	2.589
						520	2.609
						530	2.628
						540	2.648
						550	2.667
						560	2.686
						570	2.706
						580	2.725
						590	2.745
						600	2.764
Ploy(oxy-2,6-dimethyl-1,4-phenylene)	$(C_6H_2(CH_3)_2O)n$	120.15	0.141	[27]	Revised, Critical	534.439	2.194
						544.167	2.213
Poly(oxyoctamethylene)	$((CH_2)_8O)n$	129.21	0.195	[28]	Revised	347.61	2.268
						350.43	2.209
						353.47	2.224
Poly(ethylene terephthalate)	$(C_{10}H_8O_4)n$	192.12	0.115	[26]	Revised, Critical	360	1.761
						370	1.777
						380	1.793
						390	1.808
						400	1.823
						540	2.041
						550	2.057
						560	2.073
						570	2.088
						580	2.103
						590	2.119

nylon 6,6	$(C_{12}H_{22}O_2N_2)n$	226.31	0.168	[26]	Revised, Critical	550	2.690
						560	2.710
						570	2.731
						580	2.752
						590	2.772
						600	2.793
Poly(oxy-2,6-diphenyl-1,4-phenylene)	$(C_{18}H_{12}O)n$	244.29	0.127	[22]	Revised, Critical	780	2.759
						790	2.776
						800	2.795
						810	2.817
						820	2.840
Poly(4,4'-isopropylidenediphenylene carbonate)	$(C_{16}H_{14}O_3)n$	254.29	0.130	[29]	Revised, Critical	420	1.899
						430	1.916
						440	1.939
						450	1.957
						460	1.979
						470	2.002
						480	2.019
						490	2.046
						500	2.064
						510	2.073
						520	2.109
						530	2.127
						540	2.145
						550	2.172
poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene)	$(C_{27}H_{22}O_4S)n$	442.54	0.122	[23]	Revised, Critical	460	1.834
						470	1.913
						480	1.992

[a] Experimental isobaric heat capacity data of hexadecane were reported at P=1 bar.

[b] In the case of polymers, molar masses of their monomers are listed. Accordingly, the similarity variable (α) is calculated for monomers

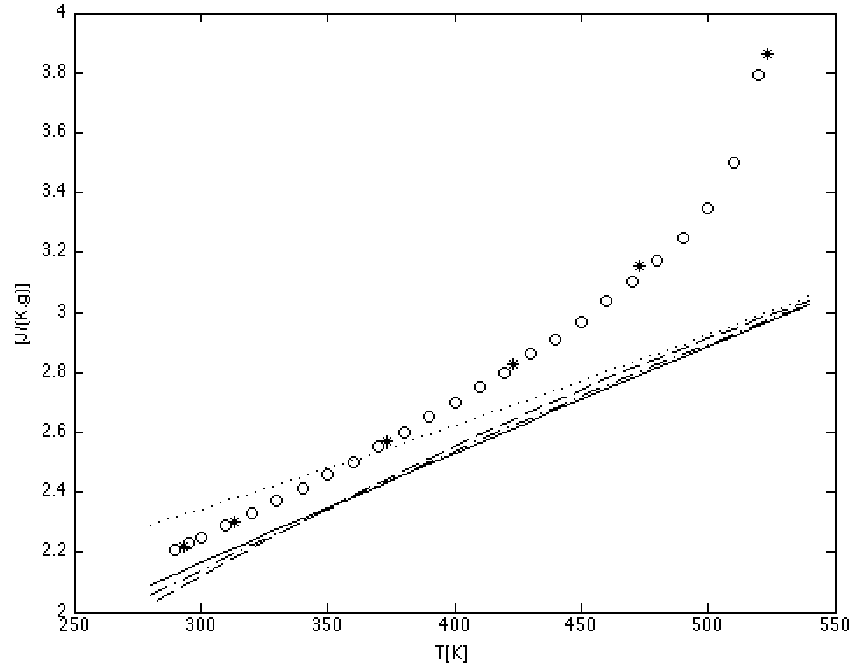

Figure 3-2. Deviation of predicted liquid phase heat capacity values by: (:), Polymer Baseline; (--), Revised Baseline; (-), Dadgostar-Shaw universal correlation; (-.), Critical Baseline from experimentally measured data by: ○, Douglas et al. [7];*, Mel'nikov et al. [8] for n-heptane.

3.1.1.2 Formulating the Deviation Term Valid for the Critical Region

Reid and Sobel [30] provide three definitions for heat capacity of liquids:

1) C_{PL}, the change in enthalpy with temperature at constant pressure, within the liquid phase

2) $C_{\sigma L}$, the change in enthalpy of the saturated liquid with temperature, along the saturation curve, $(\frac{dH_{\sigma L}}{dT})$, and

3) C_{satL}, the heat required to effect a temperature change of a saturated liquid, $(\frac{dQ}{dT})_{\sigma L}$.

These three inter-related definitions possess almost identical numeric values except near the critical point [31]:

$$C_{\sigma L} = C_{PL} + [V_{\sigma L} - T(\frac{\partial V}{\partial T})_P](\frac{dP}{dT})_{\sigma L} = C_{satL} + V_{\sigma L}(\frac{dP}{dT})_{\sigma L} \tag{3-4}$$

There are also approximate corresponding state equations available in the literature, which relate C_{PL}, $C_{\sigma L}$, and C_{satL}. Below $T_r \sim 0.8$, these three heat capacities are indistinguishable numerically [4]. Most estimation techniques for heat capacity of liquids yield either C_{PL} or $C_{\sigma L}$, while C_{satL} is usually measured experimentally [4].

C_{satL} and C_{PL} can be related by re-arranging equation 3-4:

$$C_{satL} = C_{PL} - T(\frac{\partial V}{\partial T})_P(\frac{dP}{dT})_{\sigma L} \tag{3-5}$$

As the Dadgostar-Shaw universal correlation nominally predicts C_{VL}, deviations between experimental liquid phase heat capacity (C_{satL}) values and the values predicted by the Dadgostar-Shaw universal correlation baseline (C_{VL}) becomes:

$$C_{satL} - C_{VL} = T(\frac{\partial V}{\partial T})_P[(\frac{\partial P}{\partial T})_V - (\frac{dP}{dT})_{\sigma L}] \tag{3-6}$$

Equation 3-6, simply derived by combining equations 3-3 and 3-5, was used to track and model deviations in the critical region.

3.1.2 Modeling Deviations in the Critical Region

3.1.2.1 Selection of the Form of the Deviation Term

As the critical point of a fluid is approached, C_{satL} (equation 3-6) approaches infinity, and deviations between a model and data become large. Even a simple equation of state, such as the van der Waals equation of state:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \tag{3-7}$$

can provide leading dependencies for a deviation term applicable in the critical region. By substituting derivatives of the van der Waals equation of state (equation 3-7) into equation 3-6 one obtains, on a mass basis:

$$C_{satL} = C_{VL} + \frac{R}{M[\frac{-(3V_{rL}-1)^2}{4V_{rL}^3 T_r}+1]} - \frac{\Delta H_{LV}}{MT_C(V_{rV}-V_{rL})[\frac{3}{4}(\frac{1-3V_{rL}}{V_{rL}^3}+\frac{4T_r}{(3V_{rL}-1)})]} \tag{3-8}$$

where M is the molar mass, V_r is the reduced molar volume, T_r is the reduced temperature, and ΔH_{LV} is the enthalpy of vaporization. While both the second and third terms, on the right hand side of the equation approach infinity at the critical point, the third term can be neglected as the value of enthalpy of vaporization trends to zero at the critical point and this term is small compared to the second term. Therefore, the second term, explicit in molar mass (M), reduced temperature (T_r) and reduced saturated liquid volume V_{rL} is the starting point for modeling the deviations at the critical region. As V_{rL} is a polynomial function of (T_r-1) where the powers include 1/2, 1, 3/2 and 2 [32], and the correction term must reduce to zero remote from the critical point, a simple empirical term for addressing ($C_{satL} - C_{VL}$) deviations in the critical region that meets these criteria is proposed

$$C_{satL} - C_{VL} = b_1 \frac{R}{M}\left[\frac{1}{(1-T_r)^{b_2}} - 1\right] \tag{3-9}$$

where R is the gas constant possessing the units ($JK^{-1}mol^{-1}$), and M is the molar mass with the units ($g\ mol^{-1}$). The dimensionless coefficients, b_1 and b_2, are expected to be of order unity and 0.5 respectively.

3.1.2.2 Liquid Heat Capacity Data at Higher Temperatures

There are few reliable experimental data reported for heat capacity of organic liquids near their critical points. Reid and Sobel [30] listed experimental heat capacities for 15 saturated liquids at higher temperatures. More recently, Domalski and Hearing [33] compiled data on the heat capacities and entropies of organic compounds for 2503 organic compounds. They listed the value of heat capacity at room temperature, the temperature range over which experimental measurements are available, and more importantly evaluated each entry. After investigating these references and confirming that the data were experimentally measured (C_{satL}) values and unsmoothed, a training set comprising 113 data points for 5 compounds, was selected (Table 3-3). The selection was rigorous. C_{satL} is calculated by thermodynamic relations in many studies. For example, C_{VL} for a two-phase system (saturated liquid + vapour) is measured at high temperature. C_{satL} values are then reported after small corrections are applied to address thermal expansion. For cases where the corrections were estimated with theoretical relations, the reported saturated liquid heat capacity data were not used in either the training data set or the test data set.

3.2 Results and Discussion

3.2.1 Quality of the Fit of the Correlation

The training data set, listed in Table 3-3, was used to obtain coefficients b_1 and b_2 by non-linear regression. An ordinary least squares (OLS) method, similar to the approach taken for developing the universal correlation [1] was applied. The variety of compounds and the precision of the experimental data were the most important criteria used to select the training data set. In addition to the physical properties, experimental heat capacity data (C_{satL}) and references, predicted heat capacity values for both the Dadgostar-Shaw universal (equation 3-1) and the modified correlation (equation 3-10) are shown.

$$C_{satL} = 24.5(a_{11}\alpha + a_{12}\alpha^2) + (a_{21}\alpha + a_{22}\alpha^2)T + (a_{31}\alpha + a_{32}\alpha^2)T^2 + b_1 \frac{R}{M}[\frac{1}{(1-T_r)^{b_2}} - 1]$$

(3-10)

where C_{satL} is the saturated liquid heat capacity in (J K^{-1} g^{-1}); T is in Kelvin; α is in (mol g^{-1}); R is in ($JK^{-1}mol^{-1}$); and M is in (g mol^{-1}). The coefficient values, b_1 and b_2, are included in Table 3-1.

The statistical measures that are used to evaluate the quality of the fit of the correlation are average standard deviation (σ_F), average relative deviation (δ), and average absolute deviation (ε). The customary definitions of these parameters were given previously [1], and their values for the training set are reported for both equations 3-1 and 3-10 in Table 3-4. A test set comprising of 49 data points for 4 compounds was prepared (Table 3-5) and the statistical measures of the quality of fit are also listed in Table 3-4. The modified correlation out performs the unmodified correlation (average relative deviation (100δ) for the test set doubles if the universal correlation is applied) because the data are weighted in the critical region. The inclusion of the critical correction term increases the predicted heat capacity values close to critical points ($T_r > 0.8$). At lower reduced temperatures, the impact of the correction term is smaller. Table 3-6 lists compounds from the test set used in the development of the Dadgostar-Shaw universal correlation [1], for which the critical properties were available. By comparing average absolute and relative deviations of the universal correlation and the modified correlation for the eight compounds listed in Table 3-6, one can appreciate the slight improvement in predicted liquid heat capacity values by adding the correction term even remote from critical temperatures. To place the impact in context, the correction term is less than 0.05 J K^{-1} g^{-1} for larger compounds (M > 350 g mol^{-1}) even at reduced temperatures as high as 0.8. Therefore, the main applications of the modified Dadgostar-Shaw correlation is for smaller molecules at higher reduced temperatures, and where the liquid heat capacity of isomers can be discriminated at fixed absolute temperature. Applications at high absolute temperature, for larger hydrocarbons, where the hydrocarbons are subject to thermolysis reactions, and where equation 3-10 can be used to establish a reliable baseline for enthalpies of reaction, are also anticipated. It is worth mentioning that below $T_r \sim 0.8$, the modified Dadgostar-Shaw correlation can be used to calculate both C_{PL} and C_{satL}, since they are almost identical at this temperature range. Above $T_r > 0.8$, C_{satL} can be converted to C_{PL} either theoretically (using equation 3-4) or empirically by corresponding state equations available in the literature.

Table 3-3. Training set for the modified Dadgostar-Shaw correlation (equation 3-10)

Compound	Formula	Molar mass [g mol^{-1}]	α [mol g^{-1}]	T_c [K]	Reference	T [K]	T_r	Experimental Data	Calculated Values [J K^{-1} g^{-1}]	
								C_{satL} [J K^{-1} g^{-1}]	Dadgostar-Shaw Universal Correlation (equation 3-1)	Modified Dadgostar-Shaw Correlation (equation 3-10)
Alkanes										
Ethane	C_2H_6	30.069	0.266	305.32	[34]	200.029	0.66	2.50	2.0207	2.3891
						202.057	0.66	2.51	2.0253	2.4027
						202.127	0.66	2.51	2.0255	2.4031
						204.49	0.67	2.52	2.0309	2.4193
						204.866	0.67	2.52	2.0318	2.4220
						206.723	0.68	2.53	2.0361	2.4351
						208.85	0.68	2.54	2.0410	2.4504
						209.372	0.69	2.55	2.0422	2.4543
						211.363	0.69	2.56	2.0469	2.4691
						213.835	0.70	2.57	2.0527	2.4880
						215.978	0.71	2.59	2.0578	2.5049
						218.259	0.71	2.61	2.0633	2.5234
						220.536	0.72	2.62	2.0688	2.5425
						222.647	0.73	2.63	2.0739	2.5607
						225.058	0.74	2.65	2.0798	2.5821
						229.541	0.75	2.69	2.0908	2.6242
						231.507	0.76	2.71	2.0957	2.6436
						233.988	0.77	2.73	2.1019	2.6690
						236.091	0.77	2.75	2.1072	2.6914
						238.894	0.78	2.77	2.1143	2.7226
						240.641	0.79	2.80	2.1188	2.7429
						243.704	0.80	2.82	2.1267	2.7802
						244.814	0.80	2.84	2.1295	2.7943
						247.726	0.81	2.87	2.1371	2.8329
						248.469	0.81	2.88	2.1390	2.8431
						252.414	0.83	2.94	2.1494	2.9006
						257.059	0.84	3.01	2.1617	2.9759
						260.02	0.85	3.06	2.1697	3.0291
						260.744	0.85	3.06	2.1716	3.0429
						261.383	0.86	3.07	2.1733	3.0552

						264.754	0.87	3.15	2.1825	3.1248
						269.456	0.88	3.25	2.1954	3.2363
						274.128	0.90	3.37	2.2083	3.3694
						274.528	0.90	3.39	2.2094	3.3821
						279.261	0.91	3.55	2.2227	3.5528
						283.62	0.93	3.75	2.2351	3.7553
						283.946	0.93	3.75	2.2360	3.7728
						288.238	0.94	4.05	2.2484	4.0478
						291.779	0.96	4.34	2.2586	4.3668
						292.479	0.96	4.44	2.2607	4.4451
						292.539	0.96	4.44	2.2608	4.4521
						295.236	0.97	4.87	2.2687	4.8300
						296.55	0.97	5.05	2.2726	5.0756
						296.661	0.97	5.08	2.2729	5.0989
						298.389	0.98	5.56	2.2780	5.5329
						300.295	0.98	6.24	2.2837	6.2590
						300.55	0.98	6.36	2.2844	6.3889
						301.473	0.99	7.06	2.2872	6.9660
Heptane	C_7H_{16}	100.202	0.229	540.2	[7]	290	0.54	2.21	2.1233	2.1965
						295	0.55	2.23	2.1419	2.2174
						300	0.56	2.25	2.1605	2.2385
						310	0.57	2.29	2.1975	2.2807
						320	0.59	2.33	2.2345	2.3231
						330	0.61	2.37	2.2713	2.3658
						340	0.63	2.41	2.3080	2.4089
						350	0.65	2.46	2.3446	2.4523
						360	0.67	2.50	2.3811	2.4963
						370	0.68	2.55	2.4175	2.5408
						380	0.70	2.60	2.4538	2.5859
						390	0.72	2.65	2.4899	2.6319
						400	0.74	2.70	2.5260	2.6788
						410	0.76	2.75	2.5619	2.7268
						420	0.78	2.80	2.5977	2.7763
						430	0.80	2.86	2.6334	2.8275
						440	0.81	2.91	2.6690	2.8810
						450	0.83	2.97	2.7045	2.9374
						460	0.85	3.04	2.7399	2.9976
						470	0.87	3.10	2.7751	3.0631

						480	0.89	3.17	2.8103	3.1359
						490	0.91	3.25	2.8453	3.2198
						500	0.93	3.35	2.8802	3.3215
						510	0.94	3.50	2.9150	3.4553
						520	0.96	3.79	2.9497	3.6583
Naphthenes										
Propene	C_3H_6	42.08	0.214	364.85	[35]	299.82	0.82	2.3504	2.0922	2.6156
						305.37	0.84	2.4057	2.1138	2.6803
						310.93	0.85	2.4769	2.1354	2.7515
						316.48	0.87	2.5543	2.1568	2.8314
						322.04	0.88	2.6493	2.1781	2.9225
						327.59	0.90	2.7657	2.1993	3.0292
						333.15	0.91	2.9239	2.2203	3.1582
						338.71	0.93	3.1843	2.2413	3.3212
						344.26	0.94	3.6033	2.2621	3.5403
cis-2-butene	C_4H_8	56.106	0.214	435.5	[36]	299.82	0.69	2.3161	2.0922	2.3152
						305.37	0.70	2.3463	2.1138	2.3478
						310.93	0.71	2.3760	2.1354	2.3811
						316.48	0.73	2.4120	2.1568	2.4151
						322.04	0.74	2.4459	2.1781	2.4499
						327.59	0.75	2.4882	2.1993	2.4856
						333.15	0.76	2.5380	2.2203	2.5225
						338.71	0.78	2.5949	2.2413	2.5606
						344.26	0.79	2.6577	2.2621	2.6002
						349.82	0.80	2.7217	2.2829	2.6415
						355.37	0.82	2.7896	2.3035	2.6849
						360.93	0.83	2.8632	2.3240	2.7308
						366.48	0.84	2.9428	2.3443	2.7797
Aromatics										
naphthalene	$C_{10}H_8$	128.171	0.140	748.3	[37]	360	0.48	1.72	1.8260	1.8732
						380	0.51	1.78	1.8899	1.9416
						400	0.53	1.84	1.9493	2.0060
						420	0.56	1.90	2.0042	2.0664
						440	0.59	1.96	2.0547	2.1230
						460	0.61	2.02	2.1008	2.1757
						480	0.64	2.08	2.1424	2.2247
						500	0.67	2.13	2.1795	2.2702
						520	0.69	2.19	2.2123	2.3123

						540	0.72	2.25	2.2406	2.3514
						560	0.75	2.30	2.2644	2.3878
						580	0.78	2.36	2.2838	2.4219
						600	0.80	2.41	2.2987	2.4547
						620	0.83	2.47	2.3092	2.4871
						640	0.86	2.52	2.3153	2.5212
						660	0.88	2.58	2.3169	2.5602
						680	0.91	2.66	2.3141	2.6108
						700	0.94	2.76	2.3068	2.6888

Table 3-4. Statistical measures for the modified Dadgostar-Shaw correlation (equation 3-10).

	training data set	test data set
number of compounds	5	4
number of $C_{P,\mathrm{liquid}}$ values	113	49
σ [J $K^{-1}g^{-1}$]	0.096	0.131
ϵ [J $K^{-1}g^{-1}$]	0.090	0.113
100δ	3.58	4.91

3.2.2 Isomers

A second objective of this work is to adapt the Dadgostar-Shaw universal correlation so that the liquid heat capacity for isomers can be distinguished. Isomers possess the same molar masses and elemental compositions and consequently the same similarity variable values (α), but differing molecular structures, which leads to different critical temperatures. The modified correlation distinguishes such differences as it has a reduced temperature dependent term, and therefore does not predict identical values for liquid heat capacity of isomers at fixed absolute temperature. Figure 3-3 shows experimental data and predicted values for 1-butene and cis-2-butene. Both the universal and modified Dadgostar-Shaw correlations were used. The improvement in predicted liquid heat capacity for these isomers using the modified Dadgostar-Shaw correlation over a wide temperature range is clear.

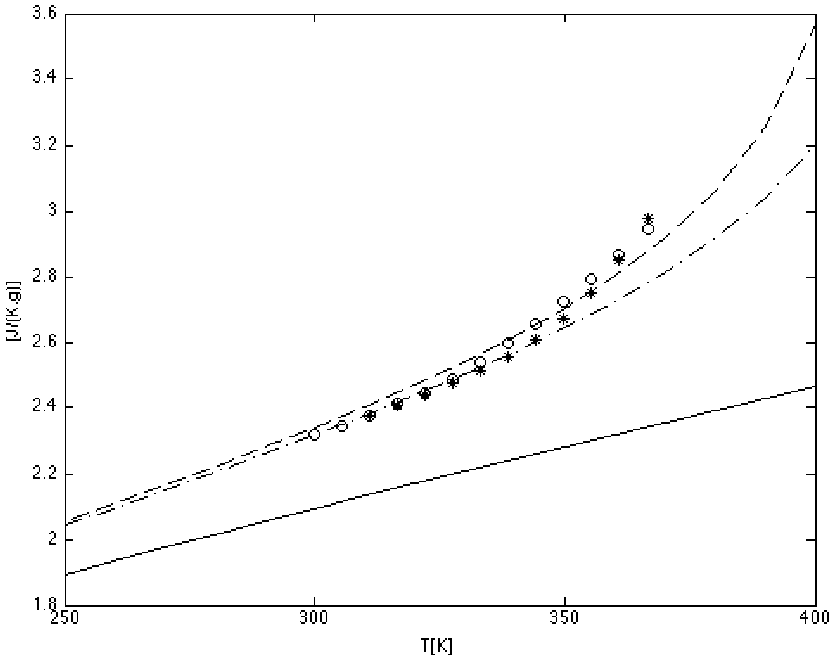

Figure 3-3.Deviation of predicted liquid phase heat capacity values by Dadgostar-Shaw universal correlation (—) and modified Dadgostar-Shaw correlation for 1-butene (--) and cis-2-butene (-.) from experimental data of 1-butene [40], *; and cis-2-butene [37],○.

Table 3-5. Test set for the modified Dadgostar-Shaw correlation (equation 3-10)

Compound	Formula	Molar mass [g mol^{-1}]	α [mol g^{-1}]	T_c [K]	Ref.	T [K]	T_r	Experimental Data	Predicted Values [J K^{-1} g^{-1}]	
								C_{satL} [J K^{-1} g^{-1}]	Dadgostar-Shaw Universal Correlation (equation 3-1)	Modified Dadgostar-Shaw Correlation (equation 3-10)
Alkanes										
Isobutane	C_4H_{10}	58.122	0.241	407.84	[38]	294.26	0.72	2.36	2.1864	2.4307
						310.92	0.76	2.50	2.2450	2.5334
						327.59	0.80	2.66	2.3040	2.6502
						344.26	0.84	2.85	2.3633	2.7895
						360.92	0.88	3.10	2.4229	2.9704
						377.59	0.93	3.43	2.4828	3.2455
Naphthenes										
1-butene	C_4H_8	56.106	0.214	419.13	[39]	310.93	0.74	2.38	2.1348	2.4092
						316.48	0.76	2.41	2.1562	2.4460
						322.04	0.77	2.44	2.1775	2.4840
						327.59	0.78	2.47	2.1987	2.5235
						333.15	0.79	2.51	2.2198	2.5647
						338.71	0.81	2.56	2.2408	2.6078
						344.26	0.82	2.61	2.2616	2.6534
						349.82	0.83	2.67	2.2823	2.7019
						355.37	0.85	2.75	2.3029	2.7539
						360.93	0.86	2.85	2.3234	2.8104
						366.48	0.87	2.98	2.3438	2.8725
Aromatics										
p-xylene	C_8H_{10}	106.165	0.170	616.17	[40]	293.15	0.48	1.70	1.8033	1.8592
						313.15	0.51	1.76	1.8852	1.9478
						333.15	0.54	1.82	1.9634	2.0334
						353.15	0.57	1.89	2.0379	2.1161
						373.15	0.61	1.96	2.1086	2.1962
						393.15	0.64	2.04	2.1757	2.2739
						413.15	0.67	2.11	2.2391	2.3494
						433.15	0.70	2.19	2.2987	2.4232
						453.15	0.74	2.26	2.3547	2.4960
						473.15	0.77	2.34	2.4069	2.5686
						493.15	0.80	2.43	2.4554	2.6424
						513.15	0.83	2.52	2.5002	2.7198
						533.15	0.87	2.63	2.5414	2.8052
						553.15	0.90	2.75	2.5788	2.9073
						573.15	0.93	2.89	2.6125	3.0486
2,7-	$C_{12}H_{12}$	156.223	0.154	775	[37]	380	0.49	1.86	2.0083	2.0483

dimethylnaphthalene						400	0.52	1.92	2.0709	2.1147
						420	0.54	1.98	2.1294	2.1771
						440	0.57	2.04	2.1836	2.2358
						460	0.59	2.10	2.2337	2.2908
						480	0.62	2.16	2.2796	2.3421
						500	0.65	2.22	2.3213	2.3898
						520	0.67	2.28	2.3589	2.4340
						540	0.70	2.34	2.3923	2.4749
						560	0.72	2.41	2.4215	2.5127
						580	0.75	2.47	2.4465	2.5477
						600	0.77	2.52	2.4673	2.5802
						620	0.80	2.58	2.4840	2.6108
						640	0.83	2.64	2.4965	2.6404
						660	0.85	2.69	2.5048	2.6702
						680	0.88	2.74	2.5089	2.7026
						700	0.90	2.81	2.5089	2.7418

Table 3-6. Performance of the Dadgostar-Shaw universal correlation and the modified Dadgostar-Shaw correlation for a group of compounds from the test set for the Dadgostar-Shaw universal correlation [1]

Compound	Formula	Temperature Range (T_r)	Dadgostar-Shaw Universal Correlation (equation 3-1) [J $K^{-1}g^{-1}$]		Modified Dadgostar-Shaw Correlation (equation 3-10) [J $K^{-1}g^{-1}$]	
			ε [J $K^{-1}g^{-1}$]	100δ	ε [J $K^{-1}g^{-1}$]	100δ
Decane	$C_{10}H_{22}$	0.52-0.60	0.072	3.00	0.059	2.45
Pentadecane	$C_{15}H_{32}$	0.44-0.53	0.055	2.38	0.047	2.01
Octadecane	$C_{18}H_{38}$	0.41-0.53	0.070	2.94	0.062	2.61
Decylcyclohexane	$C_{16}H_{32}$	0.37-0.40	0.063	3.17	0.069	3.46
Styrene	C_8H_8	0.39-0.47	0.092	5.58	0.084	5.13
1-Methylnaphthalene	$C_{11}H_{10}$	0.32-0.46	0.071	4.41	0.077	4.75
Diphenyl Methanone	$C_{13}H_{10}O$	0.33-0.52	0.033	2.08	0.033	2.07
N-Octyl-1-octanamine	$C_{16}H_{35}N$	0.41-0.79	0.037	1.37	0.023	0.86
Average Deviations			0.062	3.12	0.057	2.92

3.2.3 Comparisons with Rowlinson-Bondi Based Methods

Rowlinson [41] suggested modifications for one of many forms that Bondi [42] considered:

$$\frac{C_{PL}-C_P^{\circ}}{R}=1.45+\frac{0.45}{1-T_r}+4.2775\omega+\frac{6.3\omega(1-T_r)^{1/3}}{T_r}+\frac{0.4355\omega}{1-T_r} \tag{3-11}$$

Equation 3-11 is applicable for pure hydrocarbons from their melting points up to reduced temperature values approaching unity [31]. The ideal gas heat capacity, C_P°, the critical temperature, T_c, and the acentric factor, ω, are required to calculate C_{PL}. The estimated C_{PL} values calculated using equation 3-11 generally differ by less than 5 percent from experimental data, except for alcohols at low temperatures, where the errors are significantly higher [31].

In a recent edition of the Properties of Gases and Liquids [4], the first two constants appearing in equation 3-11 were refitted to obtain:

$$\frac{C_{PL}-C_P^{\circ}}{R}=1.586+\frac{0.49}{1-T_r}+\omega[4.2775+\frac{6.3(1-T_r)^{1/3}}{T_r}+\frac{0.4355}{1-T_r}] \tag{3-12}$$

where the estimated C_{PL} values for the heat capacity of 212 compounds at 298 K were compared to experimental data. C_P° values at T = 298.15 K were reproduced from Appendix A of [43]. Some values were tabulated by Thermodynamics Research Centre (TRC) College Station, TX, USA. Others were calculated using:

$$\frac{C_P^{\circ}}{R}=a_{\circ}+a_1T+a_2T^2+a_3T^3+a_4T^4 \tag{3-13}$$

where R is the gas constant ($JK^{-1}mol^{-1}$), and T is absolute temperature (K). The temperature ranges at which ideal gas heat capacity data were fitted and the values of its five parameters (a_0-a_4) appearing in equation 3-13 are also listed in Appendix A [43]. Thus the Rowlinson-Bondi method for computing C_{PL}, comprising equations 3-12 and 3-13 is compound-specific and can only be used over the range of applicability of the ideal gas heat capacity correlation, equation 3-13. For 18 of 212 compounds the deviations were greater than 10%. C1 to C4 alcohols and acids, water, D_2O, bromoethane, hydrazine, HF, SO_3, N_2O_4, 1,2-

oxazole, C_6F_{14}, and isobutyl amine were among these 18 compounds. Most of these compounds form hydrogen bonds and dimers. Except for these compounds, the average absolute deviation in C_{PL} using equations 3-12 and 3-13 was 2.5 %. So, while the accuracy is excellent, compound specific ideal gas heat capacity (C_P°) critical temperature (T_c), and acentric factor (ω) values are required to employ the Rowlinson-Bondi approach for estimating liquid heat capacities. Thus it has a restricted range of application both with respect to temperature and compounds vis-à-vis the modified Dadgostar-Shaw correlation.

As the Rowlinson-Bondi correlation (equations3-12 and 3-13) yields C_{PL} values, a correction is needed to accommodate the critical region, and corresponding state principle relations, valid for $T_r < 0.99$, were applied [4]:

$$\frac{C_P - C_\sigma}{R} = \exp(20.1T_r - 17.9) \tag{3-14}$$

$$\frac{C_\sigma - C_{sat}}{R} = \exp(8.655T_r - 8.385) \tag{3-15}$$

By combining equations 3-12, 3-14 and 3-15, C_{sat} becomes:

$$C_{satL} = \frac{R}{M_w} \times \{\frac{C_P^{\circ}}{R} + 1.586 + \frac{0.49}{1-T_r} + \omega[4.2775 + \frac{6.3(1-T_r)^{1/3}}{T_r} + \frac{0.4355}{1-T_r}] - \exp(20.1T_r - 17.9) - \exp(8.655T_r - 8.385)\}$$

(3-16)

Equation 3-16, is referred to as the Rowlinson-Bondi + critical correction correlation in this work. As C_P° values are not correlated for all pure hydrocarbons, two variants of equation 3-16 were used to calculate C_{satL}, namely equation 3-13 (compound specific correlations), and the recent Laštovka-Shaw universal correlation (equation 3-17) for ideal gas heat capacity [44]:

$$C_P^{\circ} =$$

$$\left(1.25 + \frac{0.58 - 1.25}{1 + \exp\left(\frac{\alpha - 0.17338003}{0.014}\right)}\right) + (0.73917383 + 8.88308889\alpha)\left(-\frac{(1188.28051 + 1813.04613\alpha)}{T}\right)^2 \frac{\exp\left(-\frac{(1188.28051 + 1813.04613\alpha)}{T}\right)}{\left[1 - \exp\left(-\frac{(1188.28051 + 1813.04613\alpha)}{T}\right)\right]^2} +$$

$$(0.0483019 + 4.35656721\alpha)\left(-\frac{(2897.01927 + 5987.80407\alpha)}{T}\right)^2 \frac{\exp\left(-\frac{(2897.01927 + 5987.80407\alpha)}{T}\right)}{\left[1 - \exp\left(-\frac{(2897.01927 + 5987.80407\alpha)}{T}\right)\right]^2}$$

(3-17)

where C_P° is the constant pressure heat capacity of an ideal gas in (J K^{-1} g^{-1}), T is in Kelvin, and α is in (mol g^{-1}). Like the Dadgostar-Shaw universal correlation, equation 3-17 relates constant pressure heat capacity of ideal gases to absolute temperature and the value of the similarity variable. α. The second variant of the Rowlinson-Bondi based method (equations 3-16 and 3-17) generalizes this approach as it eliminates the link to compound-specific C_P° values or compound specific correlations.

Deviation values for the compounds in the test set are listed in Table 3-7 for the critical region corrected but compound-specific Rowlinson-Bondi method (equations 3-16 and 3-13), the more general variant (equations 3-16 and 3-17) and the modified Dadgostar-Shaw correlation (equation 3-10). Average absolute deviation (ε) and average relative deviation for the test set based on equation 3-10 are 0.11 (J K^{-1} g^{-1}) and 4.9%, respectively. These statistical values for the compound-specific Rowlinson-Bondi method are 0.07 (J K^{-1} g^{-1}) and 2.7%, and for the generalized Rowlinson-Bondi method are 0.09 (J $K^{-1}g^{-1}$) and 3.5%. The original Rowlinson-Bondi approach is the most precise method for predicting liquid heat capacity close to critical points if all of the inputs required (coefficients for equation 3-13, acentric factor, molar mass, and critical temperature) are available. However, for heavy hydrocarbons, ill-defined components, and mixtures, this is not the case. Further, even though less compound-specific information is required to use the modified Dadgostar-Shaw correlation [T_c, M, α] than the other two approaches (Rowlinson-Bondi compound specific correlation [T_c, M, ω, $a_{\circ}$- a_4] and Rowlinson-Bondi generalized correlation [T_c, M, α, ω]), the accuracy is comparable as shown in Figure 3-4.

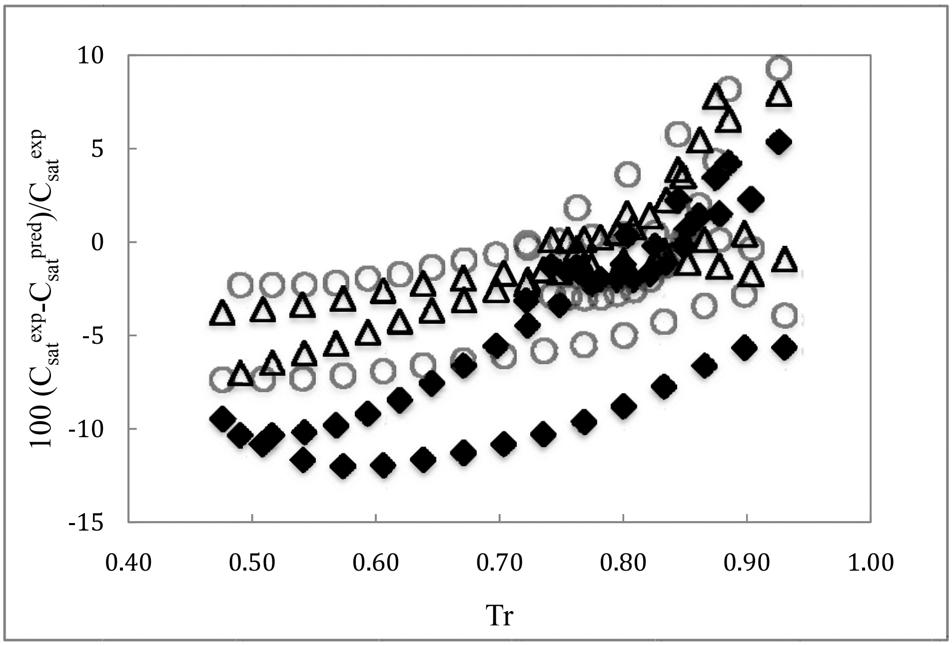

Figure 3-4. Relative deviation of predicted liquid heat capacity values from experimental data for compound of test set by: Rowlinson-Bondi compound-specific, (Δ); modified Dadgostar-Shaw correlation, (♦); and Rowlinson-Bondi generalized equation, (○).

Table 3-7. Statistical measures for the comparison data set

Compound	Formula	Temperature Range (T_r)	Rowlinson-Bondi compound-specific (equations 3-13 and 3-16) [J $K^{-1}g^{-1}$]		Modified Dadgostar-Shaw (equation 3-10) [J $K^{-1}g^{-1}$]		Rowlinson-Bondi generalized (equations 3-16 and 3-17) [J $K^{-1}g^{-1}$]	
			ε [J $K^{-1}g^{-1}$]	100.δ	ε [J $K^{-1}g^{-1}$]	100.δ	ε [J $K^{-1}g^{-1}$]	100.δ
Isobutane	C_4H_{10}	0.72-0.93	0.115	3.76	0.083	2.79	0.147	4.80
1-butene	C_4H_8	0.74-0.87	0.057	2.04	0.045	1.71	0.063	2.42
p-xylene	C_8H_{10}	0.48-0.93	0.037	1.86	0.206	9.60	0.122	5.72
2,7-dimethylnaphthalene	$C_{12}H_{12}$	0.49-0.90	0.069	3.20	0.119	5.53	0.023	1.06

3.2.4 Liquid Mixtures

The Dadgostar-Shaw universal correlation [1] is applicable for ill-defined heavy hydrocarbons such as maltenes. The correction term, which is a function of reduced temperature (T_r) and molar mass (M), was added to cover the larger deviations in the critical region and to resolve the issue of isomers. Two new inputs, T_r and M are accessible for pure compounds and mixtures with low molar masses and T_r can be estimated for high molar mass mixtures [3, 45]. Few studies have been conducted on measuring heat capacity of mixtures at temperatures close to their critical points and for the case of mixtures of light alkanes, the saturated heat capacity data are difficult to obtain [46]. It is not possible to comment on the performance of the modified Dadgostar-Shaw correlation for low molar mass hydrocarbon mixtures in the critical region. Attempts to use Rowlinson-Bondi based calculation approaches and other corresponding states principle methods for mixtures, have met with limited success [47, 48] due to their complexity. Thus the application niches for the Dadgostar-Shaw universal correlation and the modified Dadgostar-Shaw correlation are liquid hydrocarbon mixtures irrespective of whether the components are well defined as molecular species or are ill-defined hydrocarbon species.

3.3 Conclusions

A simple correction term, which is a function of molar mass and reduced temperature, is introduced to accommodate the deviation of predicted liquid heat capacity values obtained using the Dadgostar-Shaw universal correlation in the critical region. The correction term extends the application of this correlation to small molecules and provides reliable saturated liquid heat capacity estimates over a broader range of reduced temperatures. The modified Dadgostar-Shaw correlation discriminates liquid heat capacity of isomers at fixed absolute temperatures and does not impact prediction quality for pure or mixed hydrocarbons with large molar masses where specific heat capacity is only a function of elemental composition and absolute temperature. The modified Dadgostar-Shaw correlation predicts liquid heat capacity at high reduced temperatures with an accuracy approaching Rowlinson-Bondi based calculation procedures, and offers a comparative advantage over such computational approaches for mixtures and ill-defined hydrocarbon liquids where all required inputs are not available.

3.4 References

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Chapter 4
Departure Functions for Hydrocarbon Isobaric Liquid Phase Heat Capacity[‡]

4.1 Introduction

Liquid phase isobaric heat capacity, C_{PL}, like other thermodynamic properties, can be calculated directly or by a perturbation from the ideal gas state, C_P°, by adding a departure function, ΔC_{PL}:

$$C_{PL} = C_P^{\circ} + \Delta C_{PL} \tag{4-1}$$

The ideal gas heat capacity comprises ~ 75% of the heat capacity of liquids remote from normal critical points [1] and the uncertainty of current methods for calculating ideal gas heat capacity is less than 5% by correlation [2] or by quantum mechanical calculation [3]. Therefore, much of the deviation of predicted liquid-phase isobaric heat capacity values from experimental data, based on the use of equation 4-1, are attributable to the nature and form of the departure function. Typically, the departure function is derived using an equation of state. For such cases, errors can exceed 10 % [1]. The significance of the role played by the departure function in determining the uncertainty of liquid-phase heat capacity values in this way appears to be under appreciated. A compound specific departure function correlation by Tyagi [4] requiring the same inputs as equations of state (T_c, P_c, ω) did emerge but has not been widely adopted. Liquid phase constant pressure heat capacity values continue to be calculated indirectly, for the most part in process simulators and in general purpose calculations, despite this apparent shortcoming because until recently direct calculation methods for liquid phase constant pressure heat capacity, based on group contribution [5],corresponding state principles [6] and theoretical methods [7] presented a fragmented and frequently inaccurate suite of options [8, 9]. Further, there are numerous industrially relevant organic fluids such as boiling fractions and residual oils, for which required input properties needed to exploit these methods:

[‡] N. Dadgostar, J. M. Shaw, has been submitted to Fluid Phase Equilibria

molecular structures, critical properties, and basic physical properties, are unavailable to practitioners or remain speculative.

In this contribution the performance of different functional forms proposed in the literature for the liquid-phase constant-pressure heat-capacity departure-function are evaluated. These comprise a conventional form originally given for real gases along with thermodynamic models for calculating the temperature and volume derivatives [1, 10] and an unconventional form based on the temperature derivative of the enthalpy of vaporization [4, 11, 12]. Further, accurate elemental composition based correlations developed for predicting heat capacity of ideal gases and liquids [3, 9] are used to investigate the potential of using difference calculations based on them to constrain equation of state departure functions for liquid phase heat capacity.

4.2 Expressions for Departure Functions

Reid and Sobel [11] defined three heat capacities for liquids: 1) C_{PL}, the change in enthalpy with temperature at constant pressure, 2) $C_{\sigma L}$, the change in enthalpy of the saturated liquid with temperature, along the saturation curve, $(\frac{dH_{\sigma L}}{dT})$, and 3) C_{satL}, the heat required to effect a temperature change while the liquid is kept saturated, $(\frac{dQ}{dT})_{\sigma L}$. These different heat capacity measures are inter-related [10]:

$$C_{\sigma L} = C_{PL} + [V_{\sigma L} - T(\frac{\partial V}{\partial T})_P](\frac{dP}{dT})_{\sigma L} = C_{satL} + V_{\sigma L}(\frac{dP}{dT})_{\sigma L} \tag{4-2}$$

The volume and temperature derivatives in equation 4-2 tend to be small remote from the critical point. C_{PL}, $C_{\sigma L}$, and C_{satL} values can be considered to have the same values for $T_r < 0.8$ [13]. As most indirect estimation techniques yield either C_{PL} or $C_{\sigma L}$ [13], departure functions are needed for both cases even though at $T_r < 0.8$, the departure function values for isobaric liquid heat capacity ($\Delta C_{PL} = C_{PL}$ -

C_P°) and for the saturated liquid heat capacity ($\Delta C_{\sigma L}= C_{\sigma L}-C_P^\circ$) are indistinguishable numerically.

4.2.1 Departure Function of Isobaric Liquid Heat Capacity (ΔC_{PL})

The conventional form of the departure function for isobaric liquid heat capacity was initially derived for real gases as [10]:

$$\Delta C_p = -T\int_V^\infty \left(\frac{d^2P}{dT^2}\right)_V dV - T\left(\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}\right) - R \qquad (4\text{-}3)$$

Equation 4-3 was later used to calculate ΔC_{PL} [1] by substituting the volume of saturated vapour (V_V) with the volume of saturated liquid (V_L) for any volume (V) term. Equations of state, such as the Peng-Robinson or Soave-Redlich-Kwong equations, are used to calculate the temperature and volume derivatives and it is this form that is typically encountered, for example, in chemical engineering process simulators.

Majer and Svoboda [12] took a different approach. They based their departure function on the enthalpy of vapourization (ΔH_V) and the virial equation for volume and volume derivative prediction to develop a method to calculate ΔC_{PL} from the temperature dependence of the enthalpy of vapourization:

$$C_P^\circ - C_P^l = \left(\frac{\partial \Delta H_V}{\partial T}\right)_P = \left(\frac{d\Delta H_V}{dT}\right)_{sat} - \frac{\Delta H_V}{T}\left[1-\frac{T}{\Delta V_V}\left(\frac{\partial \Delta V_V}{\partial T}\right)_P\right] + T\int_0^{P_{sat}} \left(\frac{\partial^2 V^g}{\partial T^2}\right)_P dP \qquad (4\text{-}4)$$

Equation 4-4 is often referred to as an unconventional parameterization of the ΔC_{PL} departure function. As they later explained [14], the second and third terms on the right hand side of equation 4-4 are negligible at low pressure, where the behaviour of the vapour phase can be treated as ideal, and equation 4-4 can be truncated to:

$$C_P^\circ - C_P^l = \left(\frac{d\Delta H_V}{dT}\right)_{sat} \qquad (4\text{-}5)$$

There are a variety of empirical correlations that relate enthalpy of vapourization to reduced temperature [14]. Among them, Majer and Svoboda [12] proposed:

$$\Delta H_V = K(1-T_r)^{\alpha} \qquad (4\text{-}6)$$

where the two adjustable parameters, K and α, are fit to large experimental data sets for enthalpy of vapourization for individual compounds. There are few such data sets, but if available, $(\frac{d\Delta H_V}{dT})_{sat}$ can be evaluated with less than 1% error [12]. More general departure function based approaches [13, 15] can be used to estimate (ΔH_V) but not $(\frac{d\Delta H_V}{dT})_{sat}$ because the forms of these functions do not fulfill the following requirements [14]:

1- $(\frac{d\Delta H_V}{dT})_{sat}$ must go to minus infinity as the system approaches the critical point.

2- ΔH_V must be a concave function of temperature above the normal boiling point.

Thus the unconventional parameterization of the ΔC_{PL} departure function has not been broadly adopted.

4.2.2 Departure Function for Saturated Liquid Heat Capacity ($\Delta C_{\sigma L}$)

Reid and Sobel [11] defined C_{satL} as:

$$C_{satL} = (\frac{dQ}{dT})_{sL} = C_P^{\circ} + \phi_0[(\phi_1/\phi_0) - \phi_2 + (\phi_4 P_{vpr}/\Delta Z_v)(\phi_3 + RZ_c/\rho_{sLr})] \qquad (4\text{-}7)$$

where ρ_{sLr} is the reduced saturated liquid density and ΔZ_v is the difference between the compressibility factors of saturated vapour and liquid.

The ϕ functions are given as:

$$\phi_0 = \ln P_{br}(1 - P_{br}/T_{br}^3)^{1/2} \qquad (4\text{-}8)$$

$$\phi_1 = -(1/T_c)[(\partial/\partial T_r)(H^{\circ} - H_{sg})]_{\mathrm{Pr}} \qquad (4\text{-}9)$$

$$\phi_2 = [(0.38)(1.04)RT_{br}(1-T_r)^{-0.62}]/(1-T_{br})^{1.38} \qquad (4\text{-}10)$$

$$\phi_3 = (1/T_c)[(\partial/\partial P_r)(H^\circ - H_{sg})]_{T_r} \tag{4-11}$$

$$\phi_4 = [(1.04)T_{br}(1-T_r)^{0.38}]/[(1-T_{br})^{1.38}T_r^2] \tag{4-12}$$

The partial derivatives of ($H^o - H_{sg}$) in equations (4-9) and (4-11) were calculated graphically by Reid and Sobel [11]. The functions ϕ_1 and ϕ_3 were plotted versus reduced temperature for T_r from 0.7 to 0.95, while values of compressibility factors, Z_c, varied from 0.23 to 0.29 with an interval of 0.02. ϕ_2 and ϕ_4 were also plotted against T_r for different T_{br}. Moreover, ΔZ_v was plotted as a function of reduced vapour pressure. Since the ϕ functions, ΔZ_v and ρ_{sLr} were all obtained from graphs, the estimated values for C_{satL} could deviate from experimental values significantly. Further, this technique cannot be applied for computer calculation [4].

Tyagi [4] observed that saturated liquid heat capacities can be better estimated if the term ($H^o - H_{sg}$) in the Reid and Sobel expressions were defined as a function of reduced temperature and reduced pressure. He then suggested analytical procedures, using the enthalpy departure from the ideal gas state, proposed by Lee and Edmister [16] and Stevens and Thodos [17] to estimate the values for functions $dH_{\sigma L}/dT$ and $(dQ/dT)_{sL}$. Among three methods introduced, Method 1, preferred from the perspective of the current work, is discussed. The function $dH_{\sigma L}/dT$ is defined as:

$$C_{\sigma L} = \frac{dH_{\sigma L}}{dT} = \frac{d}{dT}(H_{\sigma L} - H^\circ) + C_P^\circ \tag{4-13}$$

A general equation for isothermal enthalpy difference for pure liquids is given by Lee and Edmister [16]:

$$\frac{(H_{\sigma L}-H^{\circ})}{RT_c} = A_2 - A_3T_r - 2A_4T_r^3 - 6A_5T_r^7 + (A_6 - A_7T_r - 2A_8T_r^3)P_r - 3A_9T_r^4P_r^2 + \omega(A_{10}T_r^2 + A_{11} + A_{12}P_r - 3A_{13}T_r^4P_r^2) \tag{4-14}$$

where the A_is are generalized constants:

$A_1 = 6.32873$; $A_2 = -8.45167$; $A_3 = -6.90287$; $A_4 = 1.87895$; $A_5 = -0.33448$;

$A_6 = -0.018706$; $A_7 = -0.286517$; $A_8 = 0.18940$; $A_9 = -0.002584$; $A_{10} = 8.7015$;

$A_{11} = -11.201$; $A_{12} = -0.05044$; $A_{13} = 0.002255$.

Differentiating equation 4-14 with respect to temperature, one obtains:

$$\frac{d}{dT}(H_{\sigma L}-H^{\circ}) = R(-A_3 - 6A_4T_r^2 - 42A_5T_r^6 + P_r(-A_7 - 6A_8T_r^2 - 12A_9T_r^3P_r) + \omega(2A_{10}T_r - 12A_{13}T_r^3P_r^2)) \tag{4-15}$$

The ideal gas heat capacity, C_P°, was calculated using the method suggested by Rihani and Doraiswamy [18]:

$$C_P^{\circ} = a + bT + cT^2 + dT^3 \tag{4-16}$$

where a, b, c, and d are constants.

Tyagi [4] then compared the results for $C_{\sigma L}$ values calculated for 46 compounds by this method with experimental values. Since this method is continuous, no error was introduced from graphical interpretation and the absolute deviation from experimental saturated liquid heat capacities for this method was found to be less than 3% over the reduced temperature range 0.45 to 0.98. Acknowledging the advantages of Tyagi's method compared to other techniques in this category, equation 4-15 was used to calculate the departure function for saturated liquid heat capacity, $\Delta C_{\sigma L} = d(H_{\sigma L} - H^{\circ})/dT$ where the reduced pressure (P_r) in equation 4-15 was calculated by a Guggenheim-type expression developed by Quintales et al. [19]:

$$LnP_r^{sat} = 3.64 - \frac{3.67}{T_r} \tag{4-17}$$

4.2.3 Universal Constant Pressure Heat Capacity Correlation Approach for ΔC_{PL}

To explore the potential of using accurate and predictive universal constant pressure heat capacity correlations for ideal gases and for liquids to predict departure functions, correlations developed for liquids [9] (equation 4-18) and ideal gases [3] (equation 4-19) are used:

$$C_{satL} = 24.5(-0.3416\alpha + 2.2671\alpha^2) + (0.1064\alpha - 0.3874\alpha^2)T + (-9.8231\times10^{-5}\alpha + 4.182\times10^{-4}\alpha^2)T^2$$
$$+1.6704\frac{R}{M}\left[\frac{1}{(1-T_r)^{0.5509}} - 1\right]$$

(4-18)

$$C_P^{\circ} = (1.25 + \frac{0.58-1.25}{1+\exp(\frac{\alpha-0.17338003}{0.014})}) + (0.73917383 + 8.88308889\alpha)(-\frac{(1188.28051+1813.04613\alpha)}{T})^2 \frac{\exp(-\frac{(1188.28051+1813.04613\alpha)}{T})}{[1-\exp(-\frac{(1188.28051+1813.04613\alpha)}{T})]^2}$$
$$+(0.0483019 + 4.35656721\alpha)(-\frac{(2897.01927+5987.80407\alpha)}{T})^2 \frac{\exp(-\frac{(2897.01927+5987.80407\alpha)}{T})}{[1-\exp(-\frac{(2897.01927+5987.80407\alpha)}{T})]^2}$$

(4-19)

where C_{satL} is the saturated liquid heat capacity in (J K^{-1} g^{-1}); T is in Kelvin; α is in (mol g^{-1}); R is 8.314 $JK^{-1}mol^{-1}$; Mis the molar mass in (g mol^{-1}); $C_P^{\circ}$is the isobaric specific heat capacity of an ideal gas (J K^{-1} g^{-1}).

The Dadgostar-Shaw correlation (equation 4-18) and the Laštovka-Shaw correlation (equation 4-19) are based solely on elemental composition and are generalized in terms of a similarity variable. The similarity variable (α) defined as the number of atoms in a molecule divided by molecular mass is rooted in quantum mechanics:

$$\alpha = \frac{N}{M} = \frac{\sum_{i=1}^{n}\upsilon_i}{\sum_{i=1}^{n}\upsilon_i M_i} = \frac{\sum_{i=1}^{n}x_i}{\sum_{i=1}^{n}x_i M_i} = \frac{\sum_{i=1}^{n}\frac{w_i}{M_i}}{\sum_{i=1}^{n}w_i} \qquad (4\text{-}20)$$

where ν_i is the stoichiometric coefficient for element i in a compound consisting of N atoms, n is the number of elements in a compound, M is the molar mass of the compound and M_i is the molar mass of chemical element i (g mol^{-1}). Variable x_i is the mole fraction of element i in a compound, and w_i is the mass fraction of element i. Thus the value of the similarity variable, α, is simply a function of the elemental composition of the compound or mixture.

While developed for saturated liquid heat capacity (C_{satL}) and valid for T_r values approaching unity, equation 4-18 can be applied to calculate C_{PL} at $T_r < 0.8$ as well because all three measures of liquid heat capacity are numerically indistinguishable at lower reduced temperatures. The departure function for isobaric heat capacity based on this approach is:

$$\Delta C_{PL}\left|\text{universal} = C_{PL}\right|\text{mod D-S} - C_P^\circ\left|\text{L-S}\right. \tag{4-21}$$

C_{PL} |mod D-S is the isobaric liquid heat capacity calculated using equation 4-18 and C_P°|L-S is the isobaric ideal gas heat capacity obtained from equation 4-19.

4.3 Databases and Tabulated Calculations

Experimental values for departure functions, defined as the difference between the experimental constant pressure liquid heat capacity and reliable constant pressure heat capacity values for ideal gases, drawn from the NIST/TRC Web Thermo Tables [20], were used to evaluate the performance of different methods for determining heat capacity departure functions for liquids. Table 4-1 lists experimental departure function values for 21 compounds and a total of 199 data points drawn from data sets used in developing and testing the universal and modified Dadgostar-Shaw correlation for liquid phase heat capacities [8, 9] along with their physical and critical properties. Liquid heat capacity experimental data were carefully chosen from reliable references. The critical properties required to estimate the departure functions were taken from reliable databases [21, 22]. While the preference was to only work with the experimental data reported for the critical properties, a few compounds with estimated critical temperature (T_c) and/or critical pressure (P_c) were included to extend the temperature range and increase the number of data points. Estimated critical properties are denoted by * in the table. Four approaches for calculating the departure function for liquids were evaluated. Results for three approaches from the literature: the conventional departure function (equation 4-3) along with the Peng-Robinson equation of state [23]; the conventional departure function (equation 4-3) along with the Soave-Redlich-Kwong equation of state [24]; the Tyagi method for calculating the departure function of saturated liquid (equation 4-15) are reported in Table 4-2. The reduced temperature range for the comparisons is restricted to $T_r < 0.8$. This limitation is necessary, as at higher temperatures, differences among the definitions cause the departure function values to diverge. Results for the universal correlation approach (equation 4-21) are presented in Table 4-3 where compounds present in the training sets for correlation development (equations 4-18 and 4-19) are distinguished from compounds that are part of the test data sets. Computed values for individual data points are presented as supplemental data – Table S1.

Table 4-1. List of compounds used for evaluating the performance of departure function methods, along with critical properties and experimental departure function values

Compound	Formula	Molar mass [g mol^{-1}]	α [mol g^{-1}]	T_c [K]	P_c [bar]	ω	T [K]	Experimental liquid heat capacity [J K^{-1}g^{-1}]	Ideal gas heat capacity [J K^{-1}g^{-1}]	Experimental Departure Function [J K^{-1}g^{-1}]
Ethane	C_2H_6	30.069	0.266	305.32	48.72	0.1	200.029	2.499	1.407	1.092
							202.057	2.508	1.411	1.096
							202.127	2.509	1.411	1.098
							204.49	2.524	1.417	1.107
							204.866	2.520	1.418	1.101
							206.723	2.533	1.423	1.110
							208.85	2.542	1.428	1.113
							209.372	2.546	1.430	1.116
							211.363	2.560	1.435	1.125
							213.835	2.574	1.442	1.132
							215.978	2.590	1.448	1.142
							218.259	2.606	1.455	1.152
							220.536	2.623	1.461	1.162
							222.647	2.632	1.468	1.164
							225.058	2.654	1.475	1.179
							229.541	2.687	1.489	1.198
							231.507	2.707	1.496	1.212
							233.988	2.726	1.504	1.223
							236.091	2.747	1.511	1.236
							238.894	2.774	1.520	1.254
							240.641	2.796	1.526	1.269
							243.704	2.824	1.536	1.287
Isobutane	C_4H_{10}	58.122	0.466	407.8	36.4	0.184	294.26	2.357	1.645	0.712
							310.92	2.5	1.724	0.776
							327.59	2.659	1.803	0.856
Heptane	C_7H_{16}	100.202	0.229	540.2	27.4	0.35	290	2.213	1.613	0.600
							295	2.231	1.635	0.596
							300	2.250	1.657	0.593
							310	2.288	1.701	0.588
							320	2.328	1.745	0.582
							330	2.369	1.790	0.579

							340	2.412	1.835	0.577
							350	2.456	1.880	0.576
							360	2.501	1.925	0.576
							370	2.548	1.970	0.578
							380	2.596	2.014	0.582
							390	2.645	2.059	0.586
							400	2.696	2.103	0.593
							410	2.748	2.146	0.602
							420	2.802	2.190	0.612
							430	2.857	2.231	0.626
2,2,3,3-Tetramethylpentane	C_9H_{20}	128.259	0.226	607.5	27.41	0.305	269.183	1.986	1.492	0.494
							275.533	2.015	1.528	0.487
							280.277	2.036	1.555	0.481
							293.964	2.099	1.630	0.469
							301.678	2.132	1.672	0.460
							320.554	2.219	1.771	0.448
							339.695	2.305	1.870	0.435
							352.341	2.365	1.934	0.431
Decane	$C_{10}H_{22}$	142.286	0.225	617.7	21.1	0.492	247.02	2.087	1.422	0.665
							251.7	2.093	1.441	0.652
							252.3	2.094	1.444	0.650
							252.63	2.096	1.445	0.651
							256.53	2.101	1.460	0.641
							260.61	2.109	1.477	0.632
							261.03	2.11	1.479	0.631
							270.08	2.129	1.517	0.612
							270.48	2.13	1.518	0.612
							279.46	2.152	1.556	0.596
							279.82	2.154	1.557	0.597
							289.09	2.181	1.598	0.583
							289.44	2.183	1.600	0.583
							298.59	2.212	1.640	0.572
							299.31	2.214	1.642	0.572
							309.04	2.247	1.686	0.561
							318.15	2.276	1.727	0.549
							333.15	2.333	1.795	0.538
							348.15	2.393	1.862	0.531
							363.15	2.456	1.931	0.525

							373.15	2.504	1.976	0.528
2-methyldecane	$C_{11}H_{24}$	156.313	0.224	631.76*	19.48*	0.507	235.442	2.001	1.345	0.656
							240.659	2.012	1.368	0.644
							248.285	2.027	1.402	0.625
							257.243	2.05	1.443	0.607
							276.589	2.109	1.532	0.577
							295.783	2.174	1.621	0.553
							311.95	2.236	1.697	0.539
							332.247	2.315	1.792	0.523
							342.46	2.357	1.840	0.517
							356.085	2.41	1.903	0.507
							375.231	2.494	1.991	0.503
Tridecane	$C_{13}H_{28}$	184.367	0.222	675	16.8	0.617	280.15	2.166	1.553	0.613
							288.15	2.182	1.588	0.594
							298.15	2.207	1.633	0.574
							308.15	2.235	1.677	0.558
							318.15	2.265	1.722	0.543
Pentadecane	$C_{15}H_{32}$	212.421	0.221	708	14.8	0.686	313.15	2.25	1.697	0.553
							333.15	2.313	1.787	0.526
							353.15	2.378	1.879	0.499
							373.15	2.444	1.969	0.475
Hexadecane	$C_{16}H_{34}$	226.448	0.221	723	14	0.717	318.15	2.263	1.720	0.543
							328.15	2.278	1.765	0.513
							338.15	2.32	1.809	0.511
							348.15	2.351	1.854	0.497
							358.15	2.385	1.898	0.487
							368.15	2.421	1.942	0.479
Octadecane	$C_{18}H_{38}$	254.502	0.220	747	12.7*	0.811	306.69	2.247	1.666	0.581
							314.63	2.266	1.701	0.565
							322.51	2.289	1.737	0.552
							330.34	2.312	1.773	0.539
							338.13	2.336	1.808	0.528
							345.9	2.361	1.844	0.517
							353.61	2.388	1.879	0.509
							361.27	2.415	1.914	0.501
							368.87	2.442	1.948	0.494
							376.43	2.468	1.982	0.486
							383.66	2.499	2.015	0.484

							391.14	2.527	2.048	0.479
							398.59	2.552	2.081	0.471
cis-2-butene	C_4H_8	56.108	0.214	435.58	42.06	0.203	299.82	2.316	1.436	0.880
							305.37	2.346	1.458	0.889
							310.93	2.376	1.479	0.897
							316.48	2.412	1.501	0.911
							322.04	2.446	1.523	0.923
							327.59	2.488	1.545	0.943
							333.15	2.538	1.567	0.971
							338.71	2.595	1.589	1.005
							344.26	2.658	1.612	1.046
							349.82	2.722	1.634	1.088
1-butene	C_4H_8	56.108	0.214	419.59	40.2	0.187	310.93	2.378	1.578	0.800
							316.48	2.408	1.601	0.807
							322.04	2.439	1.623	0.816
							327.59	2.474	1.646	0.828
							333.15	2.514	1.668	0.846
Butylcyclohexane	$C_{10}H_{20}$	140.27	0.214	653.1	25.7*	0.274	207.52	1.622	1.063	0.559
							214.21	1.640	1.094	0.546
							221.77	1.660	1.129	0.531
							240.1	1.717	1.216	0.501
							260.05	1.785	1.312	0.473
							280.56	1.861	1.411	0.450
							290.54	1.901	1.459	0.442
							305.97	1.965	1.535	0.430
							325.86	2.049	1.630	0.418
							345.43	2.132	1.725	0.407
							365.38	2.219	1.819	0.400
Decylcyclohexane	$C_{16}H_{32}$	224.432	0.214	751.25*	16.5*	0.663	274.26	1.939	1.432	0.507
							280.27	1.958	1.460	0.498
							286.1	1.975	1.488	0.487
							293.33	1.999	1.522	0.477
							300.48	2.023	1.556	0.467
Styrene	C_8H_8	104.152	0.154	635	38.4	0.297	246.73	1.614	0.955	0.659
							249.91	1.625	0.967	0.658
							257.54	1.63	0.997	0.633
							276.24	1.686	1.070	0.616
							298.54	1.753	1.156	0.597

Dimethylbenzene	C_8H_{10}	106.168	0.170	630.3	37.32	0.31	251.989	1.642	1.082	0.560
							255.571	1.651	1.094	0.556
							262.249	1.668	1.119	0.549
							285.471	1.731	1.202	0.530
							297.742	1.767	1.246	0.521
p-xylene	C_8H_{10}	106.168	0.170	616.2	35.11	0.322	293.15	1.699	1.169	0.530
							313.15	1.758	1.247	0.511
							333.15	1.821	1.325	0.496
							353.15	1.890	1.402	0.488
							373.15	1.962	1.477	0.485
							393.15	2.036	1.550	0.486
							413.15	2.111	1.622	0.489
							433.15	2.187	1.692	0.495
							453.15	2.263	1.760	0.503
							473.15	2.343	1.826	0.517
							493.15	2.429	1.889	0.539
Naphthalene	$C_{10}H_8$	128.174	0.140	748.4	40.5	0.302	360	1.718	1.262	0.455
							380	1.779	1.334	0.445
							400	1.840	1.404	0.436
							420	1.900	1.471	0.429
							440	1.960	1.535	0.424
							460	2.019	1.597	0.422
							480	2.077	1.657	0.420
							500	2.135	1.714	0.421
							520	2.192	1.769	0.423
							540	2.248	1.821	0.427
							560	2.303	1.871	0.432
							580	2.357	1.918	0.439
							600	2.411	1.964	0.447
1-methylnaphthalene	$C_{11}H_{10}$	142.201	0.148	772	36	0.342	299.9	1.583	1.129	0.455
							310.24	1.615	1.168	0.447
							330.8	1.678	1.245	0.433
							352.19	1.744	1.324	0.419
2,7-dimethylnaphthalene	$C_{12}H_{12}$	156.228	0.154	775	31.7*	0.42	380	1.856	1.486	0.370
							400	1.916	1.555	0.361
							420	1.976	1.621	0.355
							440	2.036	1.685	0.351
							460	2.098	1.746	0.352

							480	2.159	1.804	0.355
							500	2.221	1.860	0.361
							520	2.283	1.914	0.369
							540	2.344	1.966	0.378
							560	2.406	2.016	0.390
							580	2.465	2.064	0.401
							600	2.523	2.110	0.413
							620	2.58	2.154	0.426
N-Octyl-1-octanamine	$C_{16}H_{35}N$	241.463	0.215	734	12.6	0.819	300	2.107	1.619	0.488
							340	2.283	1.802	0.481
							380	2.441	1.971	0.470
							420	2.586	2.137	0.449
							460	2.72	2.294	0.426
							500	2.848	2.443	0.405
							540	2.979	2.588	0.391
							580	3.113	2.721	0.392

[*] Estimated critical properties

Table 4-2. Deviations of the predicted departure functions from the experimental values reported in Table 4-1 for three methods

Compound	Formula	T_r Range	(DF) + PR EoS		(DF) + SRK EoS		Tyagi correlation for $\Delta C_{\sigma L}$	
			ε [J $K^{-1}g^{-1}$]	100δ	ε [J $K^{-1}g^{-1}$]	100δ	ε [J $K^{-1}g^{-1}$]	100δ
Ethane	C_2H_6	0.66-0.80	0.050	4.2	0.140	11.81	0.037	3.28
Isobutane	C_4H_{10}	0.72-0.80	0.017	2.11	0.080	10.23	0.023	2.96
Heptane	C_7H_{16}	0.54-0.80	0.060	10.20	0.035	5.88	0.018	2.97
2,2,3,3-Tetramethylpentane	C_9H_{20}	0.44-0.58	0.118	25.28	0.078	16.64	0.014	2.92
Decane	$C_{10}H_{22}$	0.40-0.60	0.159	26.42	0.110	18.19	0.092	15.06
2-methyldecane*	$C_{11}H_{24}$	0.37-0.59	0.161	27.80	0.115	19.73	0.105	17.74
Tridecane	$C_{13}H_{28}$	0.42-0.47	0.172	29.80	0.125	21.60	0.146	25.11
Pentadecane	$C_{15}H_{32}$	0.44-0.53	0.135	26.13	0.091	17.49	0.113	21.72
Hexadecane	$C_{16}H_{34}$	0.44-0.51	0.136	26.81	0.092	18.03	0.122	23.91
Octadecane**	$C_{18}H_{38}$	0.41-0.53	0.149	28.67	0.103	19.78	0.150	28.61
cis-2-butene	C_4H_8	0.69-0.80	0.100	10.52	0.049	5.11	0.090	9.28
1-butene	C_4H_8	0.74-0.79	0.023	2.71	0.081	9.83	0.004	0.45
Butylcyclohexane**	$C_{10}H_{20}$	0.32-0.56	0.169	35.23	0.131	27.16	0.057	11.37
Decylcyclohexane*	$C_{16}H_{32}$	0.37-0.40	0.122	24.92	0.077	15.76	0.128	26.11
Styrene	C_8H_8	0.39-0.47	0.213	33.65	0.161	25.37	0.061	9.56
Dimethylbenzene	C_8H_{10}	0.40-0.47	0.122	22.34	0.070	12.77	0.023	4.22
p-xylene	C_8H_{10}	0.48-0.80	0.044	8.70	0.037	7.26	0.049	9.76
Naphthalene	$C_{10}H_8$	0.48-0.80	0.056	12.91	0.036	8.23	0.011	2.46
1-methylnaphthalene	$C_{11}H_{10}$	0.39-0.46	0.102	23.15	0.060	13.73	0.009	2.07
2,7-dimethylnaphthalene**	$C_{12}H_{12}$	0.49-0.80	0.011	2.84	0.039	10.42	0.057	15.45
N-Octyl-1-octanamine	$C_{16}H_{35}N$	0.41-0.79	0.057	12.70	0.041	9.68	0.067	15.18
average deviations			0.104	18.9	0.083	14.5	0.065	11.9

* T_c and P_c estimated, ** P_c estimated.

Table 4-3. Deviations of the predicted departure functions from the experimental values reported in Table 4-1 for the universal approach

Compound	Formula	T_r range	Universal Approach (ΔC_{PL})	
			ε [J $K^{-1}g^{-1}$]	100δ
Pure Prediction				
Isobutane	C_4H_{10}	0.72-0.80	0.084	11.1
Pentadecane	$C_{15}H_{32}$	0.44-0.53	0.012	2.3
Octadecane**	$C_{18}H_{38}$	0.41-0.53	0.022	4.2
1-butene	C_4H_8	0.74-0.79	0.031	3.8
Decylcyclohexane*	$C_{16}H_{32}$	0.37-0.40	0.026	5.5
Styrene	C_8H_8	0.39-0.47	0.039	6.3
p-xylene	C_8H_{10}	0.48-0.80	0.140	28.0
2,7-dimethylnaphthalene**	$C_{12}H_{12}$	0.49-0.80	0.202	55.1
N-Octyl-1-octanamine	$C_{16}H_{35}N$	0.41-0.79	0.010	2.2
		average deviations	0.063	13.2
Present in the training sets of D-S correlations and/or L-S correlation				
Ethane	C_2H_6	0.66-0.80	0.040	3.3
Heptane	C_7H_{16}	0.54-0.80	0.021	3.5
2,2,3,3-Tetramethylpentane	C_9H_{20}	0.44-0.58	0.111	24.1
Decane	$C_{10}H_{22}$	0.40-0.60	0.037	5.9
2-methyldecane*	$C_{11}H_{24}$	0.37-0.59	0.041	6.9
Tridecane	$C_{13}H_{28}$	0.42-0.47	0.032	5.3
Hexadecane	$C_{16}H_{34}$	0.44-0.51	0.009	1.8
cis-2-butene	C_4H_8	0.69-0.80	0.193	20.1
Butylcyclohexane**	$C_{10}H_{20}$	0.32-0.56	0.082	18.0
Dimethylbenzene	C_8H_{10}	0.40-0.47	0.063	11.7
Naphthalene	$C_{10}H_8$	0.48-0.80	0.153	35.5
1-methylnaphthalene	$C_{11}H_{10}$	0.39-0.46	0.211	48.2
		average deviations	0.083	15.3
		Overall average deviations	0.074	14.4

4.4 Discussion

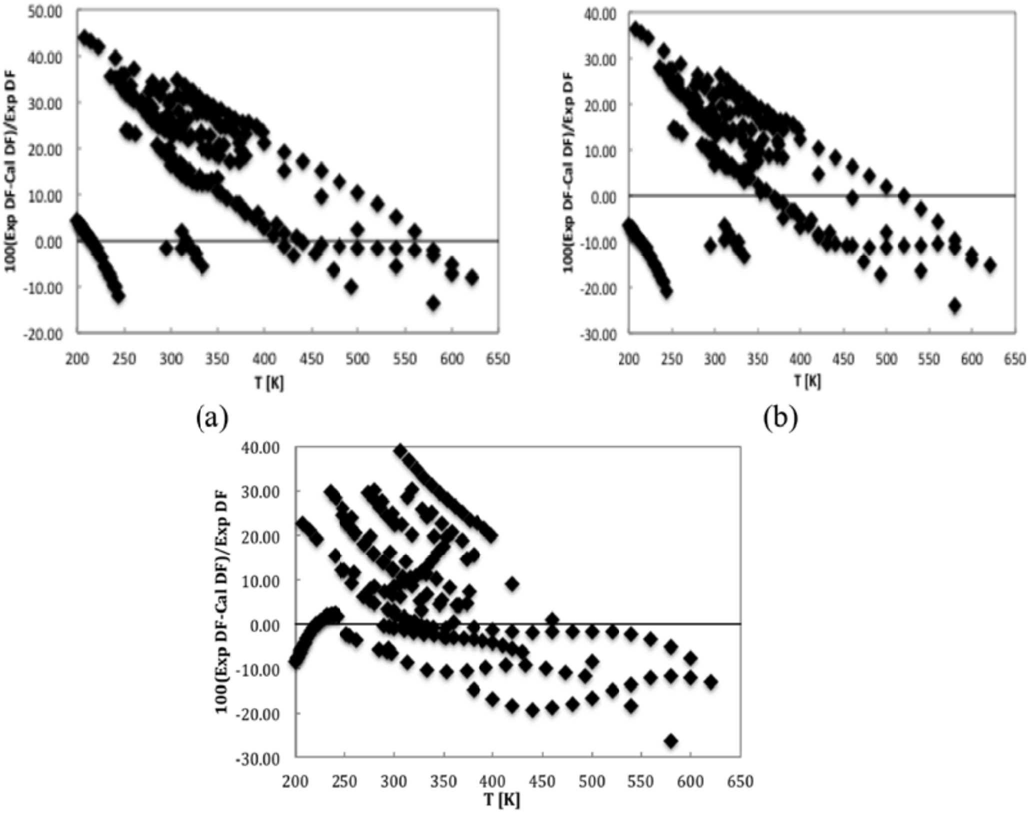
4.4.1 ΔC_{PL}, $\Delta C_{\sigma L}$ Departure Function Calculation Options Available in the Literature

The average relative deviation (100δ) and average absolute deviation (ε) for the conventional departure function of isobaric liquid heat capacity (ΔC_{PL}) (equation 4-3) based on the Peng-Robinson [23] and Soave-Redlich-Kwong [24] equations of state are given in Table 4-2. For both cases, more than 70% of the compounds have average relative deviations larger than 10%. The performance of the Soave-Relich-Kwong equation is slightly better than the performance of the Peng-Robinson equation where the average absolute deviation and average relative deviation for the conventional departure function and Soave-Redlich-Kwong equation of state are 0.083 J K^{-1} g^{-1} and 14.5%, respectively and 0.104 J K^{-1} g^{-1} and 18.9% for the Peng-Robinson equation of state. For the Tyagi correlation, equation 4-15, used to calculate ($\Delta C_{\sigma L}$) fewer compounds (less than 50%) possess average relative deviations larger than 10%, and this generalized method, with an average absolute deviation of 0.065 J K^{-1} g^{-1} and an average relative deviation of 11.9% is preferred over the two equation of state approaches.

The relationships between absolute and relative deviations for departure functions with absolute and reduced temperature are important from both theoretical and practical perspectives. They are explored in greater detail in Figures 4-1 to 4-4 for the equations of state and Tyagi correlation available in the literature. The relative deviations of the calculated departure function values from the experimental departure function data for the three methods are presented as functions of absolute temperature in Figure 4-1 and reduced temperature in Figure 4-2. Absolute deviations are presented in Figures 4-3 as functions of absolute temperature and in Figure 4-4 as functions of reduced temperature.

For both of the equation of state approaches, Figures 4-1a and b to Figures 4-4 a and b, there is a systematic underestimation of departure function values, in both absolute and relative terms at low absolute and reduced temperature, where positive relative deviations as high as 40%, and absolute deviations as high as

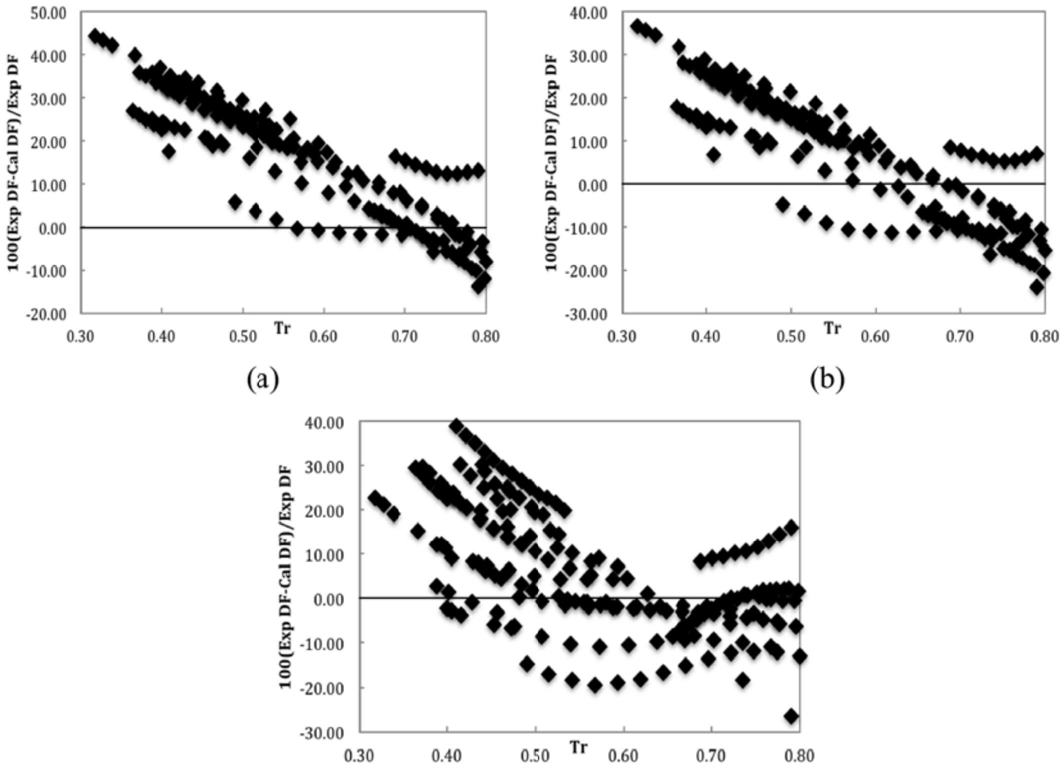
0.247 J K^{-1} g^{-1} arise. At higher absolute and reduced temperatures, the deviations for these methods decrease. At $T_r > 0.7$, as shown in Figures 4-2 a and b and Figures 4-4 a and b, they systematically overestimate departure function values. As the accuracy of volumetric prediction affects the accuracy of isobaric liquid heat capacity prediction using equations of state [25], this overestimation becomes worse at higher reduced temperatures. While not the focus of this work, the deviations between the calculated departure function values and the experimental ones, based on both equations of state, could be reduced significantly through the inclusion of a linear correction term that is a function of reduced temperature. The behaviour of the Tyagi generalized correlation is comparable but the errors are smaller both in absolute and relative terms and appear bounded at higher temperatures. However, as the variation of the deviations for the Tyagi method are less systematic with respect to absolute and relative temperature, the potential for linearly corrected equation of state based departure function calculations to outperform the Tyagi correlation is evident.



(a) (b)

(c)

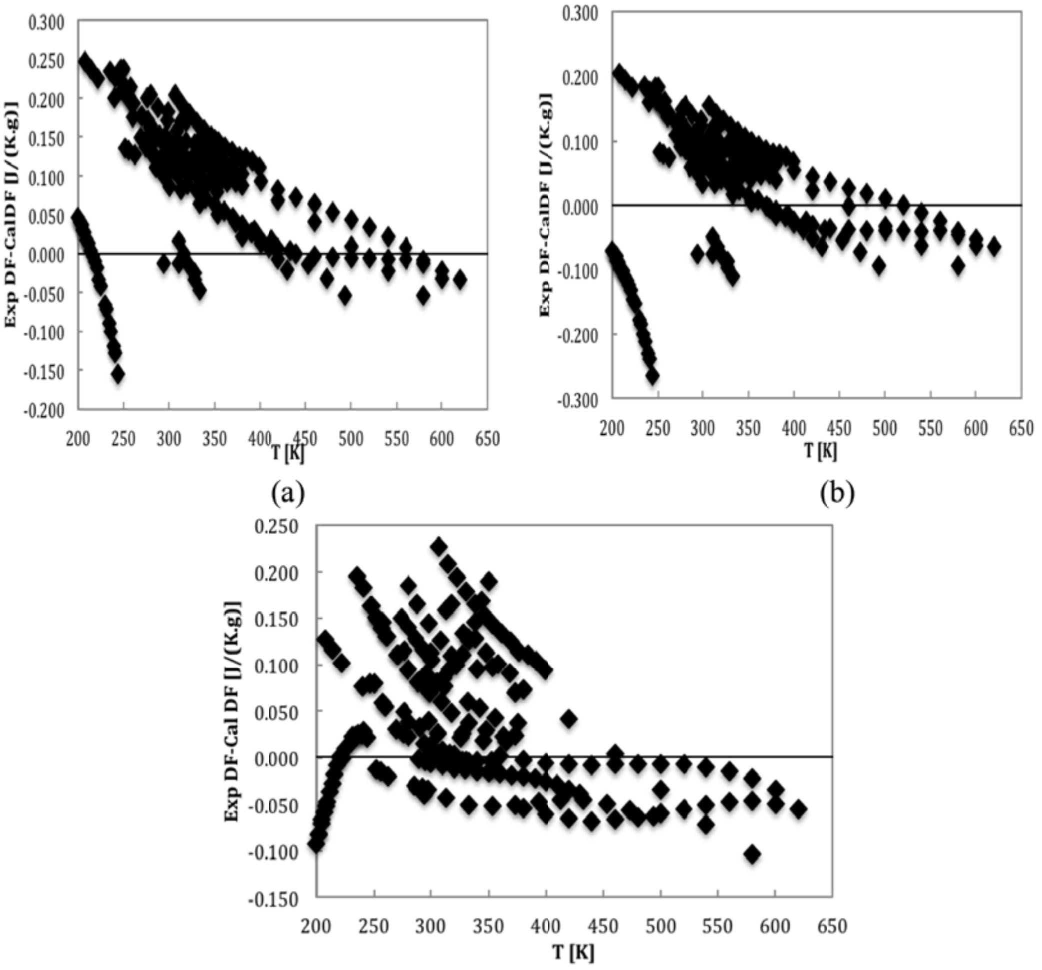
Figure 4-1. Relative deviations of calculated departure function values from experimental departure function data listed in Table 4-1 as a function of absolute temperature for: (a) conventional departure function (equation 4-3) and the Peng-Robinson equation of state, (b) conventional departure function and the Soave-Redlich-Kwong equation of state, (c) the Tyagi correlation for saturated liquid departure function (equation 4-15).



(a) (b)

(c)

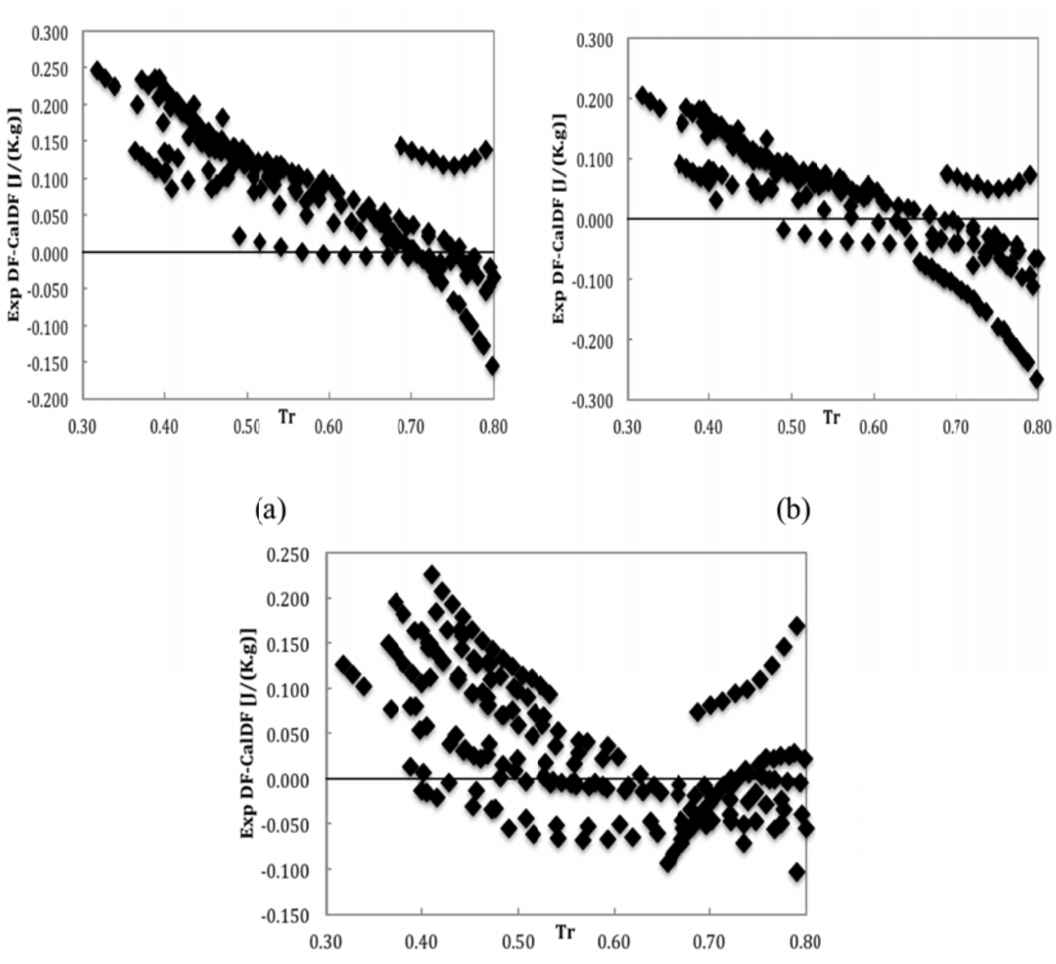
Figure 4-2. Relative deviations of calculated departure function values from experimental departure function data listed in Table 4-1 as a function of reduced temperature for: (a) conventional departure function (equation 4-3) and the Peng-Robinson equation of state, (b) conventional departure function and the Soave-Redlich-Kwong equation of state, (c) the Tyagi correlation for saturated liquid departure function (equation 4-15).



(a) (b)

(c)

Figure 4-3. Absolute deviations of calculated departure function values from experimental departure function data listed in Table 4-1 as a function of absolute temperature for: (a) conventional departure function (equation 4-3) and the Peng-Robinson equation of state, (b) conventional departure function and the Soave-Redlich-Kwong equation of state, (c) the Tyagi correlation for saturated liquid departure function (equation 4-15).



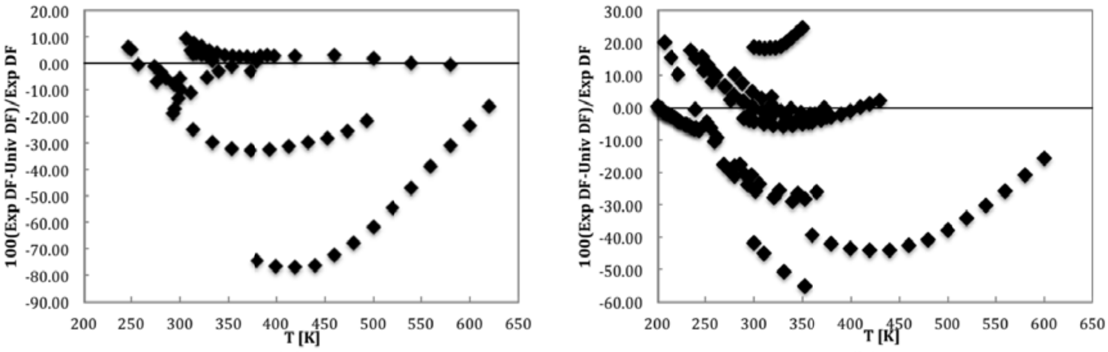
(a) (b)

(c)

Figure 4-4. Absolute deviations of calculated departure function values from experimental departure function data listed in Table 4-1 as a function of reduced temperature for: (a) conventional departure function (equation 4-3) and the Peng-Robinson equation of state, (b) conventional departure function and the Soave-Redlich-Kwong equation of state, (c) the Tyagi correlation for saturated liquid departure function (equation 4-15).

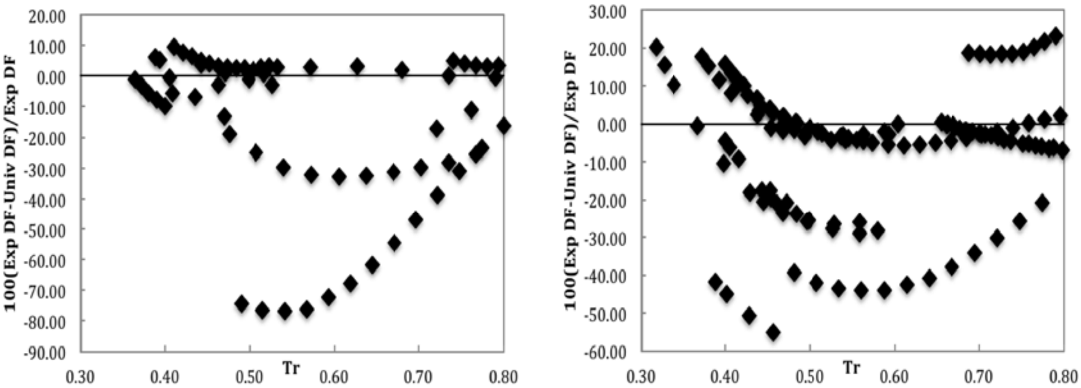
4.4.2 Universal Correlation Approach for Liquid Phase Departure Function Calculation: ΔC_{PL}

The elemental composition based correlations, equations 4-18 and 4-19, were developed for direct prediction of liquid and ideal gas isobaric heat capacities. These accurate and predictive correlations have been shown to be reliable and easy to use for both pure compounds and ill-defined hydrocarbons [3, 8, 9]. Here they are combined, as equation 21, to explore their joint potential for reducing the error associated with departure function evaluation, for improving the form of the liquid departure function, and for constraining equation of state parameters for use with ill-defined hydrocarbons where characterization remains ambiguous. Average absolute deviations and average relative deviations for this approach are reported in Table 4-3. The results obtained for the 21 compounds are grouped into two data sets: compounds present in the training data sets for one or both of the correlations and compounds only present in test data sets. Outcomes are reported separately. The statistical measures for these two sets are comparable. Average absolute deviations and average relative deviation for the nine compounds in the test data set are 0.063 J K^{-1} g^{-1} and 13.2%, respectively. For compounds in the training data set, the absolute and relative deviation values are 0.083 J K^{-1} g^{-1} and 15.3% respectively. With over all deviations of 0.074 J K^{-1} g^{-1} and 14.4%, with fewer than 40 % of the compounds having average deviations exceeding 10 %, this approach is preferred over the equation of state approaches and is comparable to the Tyagi approach for the range of compounds evaluated. Figures 4-5 a and b and Figures 4-6 a and b show the absolute deviations for both data sets versus absolute and reduced temperature respectively. The deviations remain bounded but there is no systematic pattern of over or underestimation.



(a) (b)

Figure 4-5. Deviations of calculated departure function values, this work (equation 4-21), from the experimental departure function data listed in Table 4-1 versus absolute temperature for: (a) compounds that are not in any training sets used for developing Dadgostar-Shaw correlations [8, 9] for liquids and Laštovka – Shaw correlation [3] for ideal gases: pure prediction (b) compounds that are present in at least one training set.



(a) (b)

Figure 4-6. Deviations of calculated departure function values, this work (equation 4-21), from the experimental departure function data listed in Table 4-1 versus reduced temperature for: (a) compounds that are not in any training sets used for developing Dadgostar-Shaw correlations [8, 9] for liquids and Laštovka – Shaw correlation [3] for ideal gases: pure prediction (b) compounds that are present in at least one training set.

4.4.3 General Discussion

Far from the critical point, the ideal gas constant pressure heat capacity comprises approximately 75% of the constant pressure heat capacity of liquids [1] and the departure function comprises the balance of the value. As ideal gas heat capacities are well defined and estimation methods for them typically possess small errors, little attention is paid to the impact of the form of departure functions and the error introduced by them in the calculation of liquid phase heat capacities. The relative errors for individual compounds or data points may be large, but it is important to note that the impact of these errors on the uncertainty of liquid heat capacity values tends to be modest in both absolute and relative terms as a consequence of the dominance of the ideal gas contribution to liquid heat capacity. For example, a 40 % error in 25 % of the value introduces a 10 % over all error. In the critical region, the departure function, which approaches infinity at the critical point irrespective of the definition, dominates and the impact of uncertainty introduced by this term is significant. Further, care must be taken with respect to the use and the meaning of heat capacity departure functions as illustrated in Figure 4-7 for heptane. The departure functions ΔC_{satL} (C_{satL}- C_P°) and $\Delta C_{\sigma L}$ for heptane are well represented by equation 4-21 and the Tyagi correlation (equation 4-15) respectively while equation 4-3 combined with the Peng-Robinson and Soave-Redlich-Kwong equations of state both overestimate the ΔC_{PL} departure function even at $T_r < 0.8$. The Tyagi correlation, valid up to $T_r < 0.98$, and equation 4-21, valid for T_r approaching unity, diverge from one another above $T_r > 0.96$. The value of C_P° for heptane at $T_c = 540.2$ is 2.666 J K^{-1} g^{-1} and is significantly smaller than the predicted departure function values above $T_r > 0.99$. Deviations of ΔC_{satL}, $\Delta C_{\sigma L}$, and ΔC_{PL} calculated departure functions for heptane from the experimental ΔC_{satL} values are shown in Figure 4-8. Experimental saturated liquid heat capacities for heptane are available up to $T_r = 0.96$. The universal approach has a narrower range of deviations compared to the other approaches, and at $T_r > 0.96$ its trend is in agreement with the theory (see Figure 4-7). However, in the absence of experimental data at higher reduced temperatures, it cannot be verified quantitatively.

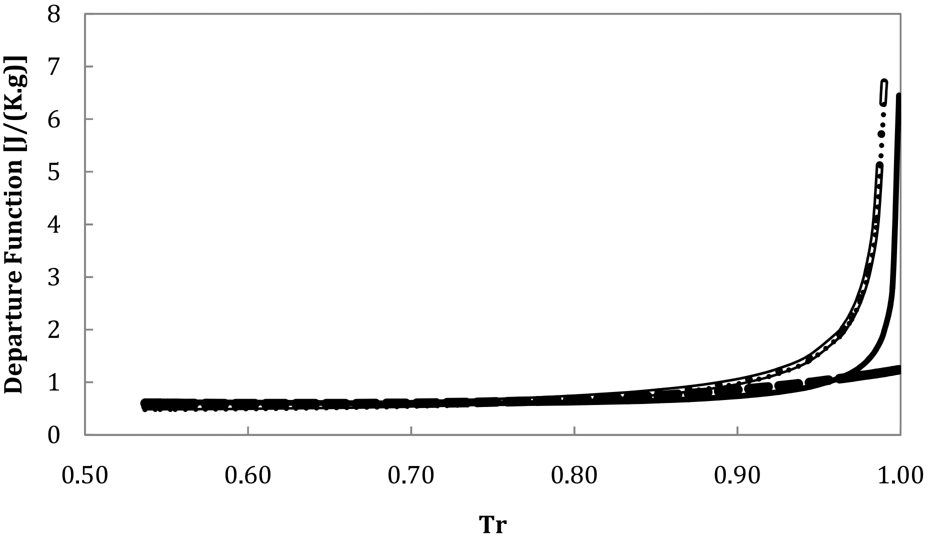


Figure 4-7. Liquid state departure function predictions for heptane: (--), the Tyagi correlation (equation 4-15) $\Delta C_{\sigma L}$; (−), the universal correlation (equation 4-21)ΔC_{satL}; the conventional formulation of the departure function (equation 4-3) combined with (••) the Peng-Robinson equation of state and (−•) the Soave-Redlich-Kwong equation of state ΔC_{PL}.

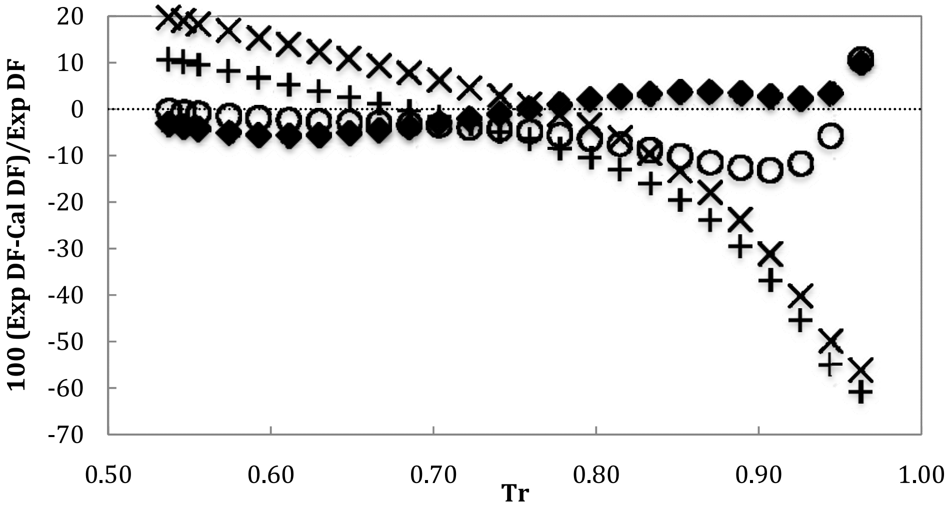


Figure 4-8. Deviations of calculated departure functions from ΔC_{satL}experimental data for heptane: (○), the Tyagi correlation (equation 4-15) $\Delta C_{\sigma L}$; (♦), the universal correlation (equation 4-21) ΔC_{satL}; the conventional formulation of the departure function (equation 4-3) combined with (×), the Peng-Robinson equation of state and (+), Soave-Redlich-Kwong equation of state ΔC_{PL}.

The poor quality of the predictions from typical cubic equations of state, both the magnitudes and the trends with absolute and relative temperature, was unexpected. Both the Peng-Robinson and the Soave-Redlich-Kwong equations of state underestimate the values of departure functions at low temperature and overestimate them at high temperature. Thus the heat capacity of liquids is systematically underestimated at low temperature (and low reduced temperature) and systematically overestimated at high temperature (and high reduced temperature). This is of particular concern, as equation of state approaches such as these, are typical defaults for process simulation, that skew heat duties in process flow sheets, from both unit operation design and heat integration perspectives.

As equation of state based computational approaches and the Tyagi correlation require the same input data (T_c, P_c, ω, M), the Tyagi correlation is clearly preferred, where these inputs are available. If these inputs must be estimated or are unknown, the universal elemental composition based approach is preferred. For this correlation only the elemental composition is required for $T_r < 0.8$. Elemental composition is known by definition for all pure compounds or mixtures, and is readily measured for industrial fluids. Further, most industrial processes operate at $T_r < 0.8$ and for large hydrocarbon molecules which pyrolize well below their critical temperature. At high-reduced temperature (up to $T_r = 0.99$), T_c and M are needed. Thus the niche for application of equation 4-21 is clearly delineated and it offers the prospect of heat capacity departure function calculation quality on a par with that realized for well-defined molecules for ill-defined fluids or fluids for which critical or other properties are missing or unavailable.

Finally the unexpectedly large deviations between the experimental and computed heat capacity departure functions, irrespective of the definition and computational method, suggests that equation 4-21 or its truncated equivalent applicable below $T_r = 0.8$, may only provide a check or a general constraint on equations of state models intended to represent the volumetric and phase behaviour of ill-defined hydrocarbon mixtures or large hydrocarbon molecules. Close agreement between model and experiment cannot be expected. Evaluation of how best to make use of this finding will be the subject of future work.

4.5 Conclusions

Departure functions for constant pressure heat capacity were defined. The unconventional parameterization attributed to Majer and Svoboda was found to be difficult to generalize. Shortcomings in the conventional parameterization approach were delineated. In particular, the poor and skewed fit of the cubic equation of state departure function relative to experimental data is illustrated with the Peng Robinson and the Soave-Redlich-Kwong equations of state for twenty-one diverse compounds. Departure functions values were systematically underestimated at low temperature and over estimated at high temperature. For reduced temperatures less than 0.8, average absolute and relative deviations with respect to data were found to be large. The Tyagi correlation, which requires the same inputs as the equation of state calculations, is preferred as it possesses lower average relative and absolute deviations and better performance at higher temperatures than the equation of state based calculations. A difference calculation based on accurate correlations for the heat capacity of liquids and ideal gases by Dadgostar and Shaw, and Laštovka and Shaw, gave a performance nearly equivalent to the Tyagi correlation and is preferred over the Tyagi correlation if the inputs (T_c, P_c, ω) are unknown or are estimated. For reduced temperatures exceeding 0.8, there are few data and the distinctions among departure functions being evaluated and comparisons with data must be carefully made. However, the Tyagi correlation for $\Delta C_{\sigma L}$ and the difference calculation for ΔC_{satL} appear to be complementary. Use of heat capacity departure function correlations to refine equation of state parameterization is complicated by the poor agreement between the models and experiment and will be the subject of a future work. Empirical modification of equation of state based departure functions for isobaric heat capacity is also a subject of future work.

Supplemental Data:

Table S1: Computed constant pressure heat capacity departure function values for liquids based on the conventional formulation of the departure function (equation 4-3) plus the Peng-Robinson and Soave-Redlich-Kwong equations of state, a departure function correlation by Tyagi (equation 4-15), and a difference calculation based on correlations by Dadgostar-Shaw and Laštovka-Shaw (equation 4-21).

4.6 References

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Chapter 5
Conclusions and Recommendations for Future Work

5.1 Conclusions

A predictive correlation relating liquid specific heat capacity to absolute temperature and elemental composition was developed. It retained the quadratic form of the Lee-Kesler correlation, but the parameters were redefined as second order power series in a similarity variable based solely on elemental composition. The Dadgostar-Shaw universal correlation provides heat capacity estimates that are unbiased relative to molecular structure, heteroatom content, carbon aromaticity, and molar mass. The correlation appears to be preferred over alternatives such as the Lee-Kesler equation with respect to ease of use, overall accuracy and range of application. The heat capacities of diverse pure, mixed and ill-defined hydrocarbons possessing molar masses exceeding ~ 100 g mol^{-1} were well represented across available data bases and the average relative deviations between predicted and measured heat capacity values were within 5% for liquids.Virtual Materials Group (VMG) has already implemented this correlation in the latest version of their hydrocarbon refining/petrochemical/natural gas processing simulator.

The resulting predictive correlation valid where the temperature dependent term (C_V) dominates, i.e. where $C_V >> T(\partial V/\partial T)_P(\partial P/\partial T)_V$, requires modification to accommodate the critical region and the consequent variation of liquid phase isobaric heat capacity among isomers at the same absolute temperature. The Dadgostar-Shaw universal correlation was validated as a reliable baseline. Deviations of experimental data from the baseline were tracked for low and intermediate molar mass compounds and these deviations were then modeled by introducing a simple correction term, which is a function of reduced temperature and molar mass. The correction term extends the application of this correlation to small molecules and provides reliable saturated liquid heat capacity estimates over a broader range of reduced temperatures. The inclusion of the critical correction term increases the predicted heat capacity values close to critical points ($T_r > 0.8$). At lower reduced temperatures, the impact of the correction term is smaller. The main applications of the modified Dadgostar-Shaw correlation (universal correlation + correction term) is for smaller molecules at higher reduced temperatures, and where the liquid heat capacity of isomers can be discriminated at fixed absolute temperature. Applications at high absolute temperature, for larger hydrocarbons, where the hydrocarbons are subject to thermolysis reactions are also anticipated. The modified Dadgostar-Shaw correlation predicts liquid heat capacity at high reduced temperatures with an accuracy approaching Rowlinson-Bondi based calculation procedures, and offers a comparative advantage over such computational approaches for mixtures and ill-defined hydrocarbon liquids where all required inputs are not available.

The performances of current forms of the liquid departure function are evaluated. The poor quality of the predictions from typical cubic equations of state, both the magnitudes and the trends with absolute and relative temperature, was unexpected. Both the Peng-Robinson and the Soave-Redlich-Kwong equations of state underestimate liquid departure function at low temperature and over estimate at high temperature. Tyagi’s method for saturated liquid departure function is superior to the combination of the conventional form for the isobaric liquid departure function and cubic equations of state. A difference calculation based on accurate correlations for the heat capacity of liquids and ideal gases by Dadgostar and Shaw, and Laštovka and Shaw, gave a performance nearly equivalent to the Tyagi correlation and is preferred over the Tyagi correlation if the inputs (T_c, P_c, ω) are unknown or are estimated.

5.2 Recommendations for Future Work

Generalizing the Lee-Kesler empirical correlation and redefining its three parameters as second order power series of the similarity variable, we developed the Dadgostar-Shaw universal correlation. The training set included data points for a variety of compounds (paraffins, naphthenes, aromatics, sulphur/oxygen/nitrogen derivatives, molten polymers) at a broad range of temperature. The main objective for developing the Dadgostar-Shaw universal correlation was to investigate the potential of energy models in predicting liquid heat capacity. While on average one can predict isobaric liquid heat capacity for hydrocarbons within 5%, deviations of the predicted heat capacity from the experimental data can be higher for specific compounds (e.g. aromatics, highly polar molecules). This correlation can be adjusted for the development of high-accuracy fluid-specific correlations where warranted by customizing one or more of the universal coefficients. The significance of its six universal coefficients can be tested, and the design of the correlation can be optimized for each category of compounds.

Implementing elemental composition based predictive correlations for ideal gases and liquids heat capacities in commercial software, such as VMGSim, is an active field of research. Currently, the experimental elemental analysis is required as an input. However, there are other bases defined to calculate the elemental analysis, such as an American Petroleum Institute (API) standard. In practice, dissonances have been reported between computed and measured elemental analysis. As a result, the current techniques for calculating the elemental composition should be reviewed and revised.

As was discussed in this work, the conventional formats for the liquid departure functions are not complete and can severely underestimate (> 40%) these values even at room temperature. Therefore, the links between elemental composition based correlations for ideal gases and liquids are missing, and require improvement. Furthermore, heat capacity departure function correlations can be used to refine equation of state parameterization. While re-parameterizing equations of state is complicated by the poor agreement between the models and experiment, empirical modification of equation of state based departure functions for isobaric heat capacity can be explored in the future.

Supplemental Data

Table S1. Computed constant pressure heat capacity departure function values for liquids based on the conventional formulation of the departure function (equation 4-3) plus the Peng-Robinson and Soave-Redlich-Kwong equations of state, a departure function correlation by Tyagi (equation 4-15), and a difference calculation based on correlations by Dadgostar-Shaw and Laštovka-Shaw (equation 4-21).

Compound	Formula	Molar mass $[\mathrm{g\ mol^{-1}}]$	α $[\mathrm{mol\ g^{-1}}]$	T_c [K]	P_c [bar]	ω	T [K]	Eq. 4-3 + PR EoS $[\mathrm{J\ K^{-1}g^{-1}}]$	Eq. 4-3 + SRK EoS $[\mathrm{J\ K^{-1}g^{-1}}]$	Eq. 4-15 (Tyagi) $[\mathrm{J\ K^{-1}g^{-1}}]$	(Eq. 4-21) $[\mathrm{J\ K^{-1}g^{-1}}]$
Ethane	C_2H_6	30.069	0.266	305.32	48.72	0.1	200.029	1.046	1.163	1.185	1.089
							202.057	1.056	1.173	1.180	1.099
							202.127	1.057	1.174	1.179	1.099
							204.49	1.07	1.186	1.173	1.112
							204.866	1.072	1.188	1.173	1.114
							206.723	1.083	1.199	1.169	1.123
							208.85	1.096	1.212	1.165	1.135
							209.372	1.099	1.215	1.164	1.137
							211.363	1.112	1.227	1.162	1.148
							213.835	1.129	1.244	1.160	1.162
							215.978	1.145	1.259	1.159	1.175
							218.259	1.162	1.276	1.160	1.188
							220.536	1.18	1.294	1.162	1.202
							222.647	1.198	1.311	1.164	1.215
							225.058	1.22	1.332	1.169	1.231
							229.541	1.264	1.376	1.182	1.261
							231.507	1.284	1.396	1.189	1.276
							233.988	1.312	1.424	1.201	1.294
							236.091	1.337	1.449	1.212	1.311
							238.894	1.373	1.484	1.229	1.334
							240.641	1.397	1.508	1.241	1.349
							243.704	1.442	1.553	1.265	1.377
Isobutane	C_4H_{10}	58.122	0.466	407.8	36.4	0.184	294.26	0.724	0.788	0.752	0.832
							310.92	0.789	0.852	0.778	0.862
							327.59	0.881	0.943	0.830	0.902
Heptane	C_7H_{16}	100.202	0.229	540.2	27.4	0.35	290	0.482	0.535	0.602	0.620
							295	0.483	0.535	0.600	0.619
							300	0.485	0.536	0.599	0.619

							310	0.488	0.539	0.596	0.617
							320	0.493	0.543	0.594	0.615
							330	0.498	0.548	0.592	0.612
							340	0.505	0.554	0.591	0.609
							350	0.513	0.561	0.592	0.605
							360	0.522	0.569	0.593	0.603
							370	0.532	0.58	0.597	0.600
							380	0.545	0.591	0.602	0.599
							390	0.559	0.605	0.609	0.598
							400	0.576	0.622	0.619	0.599
							410	0.596	0.641	0.631	0.601
							420	0.619	0.664	0.647	0.606
							430	0.647	0.691	0.665	0.613
2,2,3,3-Tetramethylpentane	C_9H_{20}	128.259	0.226	607.5	27.41	0.305	269.183	0.344	0.386	0.463	0.581
							275.533	0.343	0.385	0.461	0.582
							280.277	0.343	0.384	0.459	0.582
							293.964	0.343	0.383	0.455	0.581
							301.678	0.343	0.383	0.452	0.579
							320.554	0.345	0.384	0.445	0.572
							339.695	0.349	0.387	0.439	0.561
							352.341	0.352	0.39	0.435	0.554
Decane	$C_{10}H_{22}$	142.286	0.225	617.7	21.1	0.492	247.02	0.443	0.496	0.501	0.560
							251.7	0.442	0.493	0.502	0.564
							252.3	0.441	0.493	0.502	0.564
							252.63	0.441	0.493	0.502	0.564
							256.53	0.44	0.491	0.502	0.567
							260.61	0.439	0.49	0.502	0.569
							261.03	0.438	0.489	0.502	0.569
							270.08	0.436	0.486	0.502	0.572
							270.48	0.436	0.486	0.502	0.572
							279.46	0.434	0.483	0.502	0.573
							279.82	0.433	0.483	0.502	0.573
							289.09	0.432	0.48	0.502	0.573
							289.44	0.432	0.48	0.502	0.572
							298.59	0.43	0.478	0.502	0.571
							299.31	0.43	0.478	0.502	0.570
							309.04	0.43	0.477	0.502	0.567
							318.15	0.429	0.476	0.502	0.563

							333.15	0.43	0.476	0.502	0.555
							348.15	0.431	0.476	0.502	0.545
							363.15	0.434	0.479	0.503	0.536
							373.15	0.437	0.481	0.504	0.529
2-methyldecane	$C_{11}H_{24}$	156.313	0.224	631.76*	19.48*	0.507	235.442	0.421	0.471	0.461	0.540
							240.659	0.418	0.468	0.461	0.546
							248.285	0.415	0.464	0.462	0.553
							257.243	0.412	0.46	0.462	0.559
							276.589	0.406	0.453	0.463	0.564
							295.783	0.402	0.448	0.463	0.563
							311.95	0.4	0.445	0.464	0.557
							332.247	0.4	0.443	0.464	0.546
							342.46	0.4	0.443	0.464	0.539
							356.085	0.402	0.443	0.465	0.530
							375.231	0.405	0.446	0.467	0.517
Tridecane	$C_{13}H_{28}$	184.367	0.222	675	16.8	0.617	280.15	0.409	0.458	0.428	0.549
							288.15	0.407	0.454	0.429	0.549
							298.15	0.404	0.451	0.431	0.546
							308.15	0.401	0.448	0.432	0.543
							318.15	0.399	0.445	0.434	0.538
Pentadecane	$C_{15}H_{32}$	212.421	0.221	708	14.8	0.686	313.15	0.383	0.429	0.395	0.532
							333.15	0.379	0.424	0.398	0.520
							353.15	0.376	0.419	0.402	0.505
							373.15	0.374	0.417	0.406	0.489
Hexadecane	$C_{16}H_{34}$	226.448	0.221	723	14	0.717	318.15	0.374	0.42	0.379	0.525
							328.15	0.372	0.417	0.381	0.519
							338.15	0.37	0.414	0.383	0.512
							348.15	0.368	0.412	0.385	0.505
							358.15	0.366	0.41	0.386	0.497
							368.15	0.365	0.408	0.388	0.489
Octadecane	$C_{18}H_{38}$	254.502	0.220	747	12.7*	0.811	306.69	0.378	0.427	0.355	0.526
							314.63	0.375	0.423	0.357	0.522
							322.51	0.373	0.421	0.359	0.517
							330.34	0.371	0.418	0.361	0.512
							338.13	0.369	0.415	0.363	0.506
							345.9	0.367	0.413	0.365	0.501
							353.61	0.365	0.411	0.366	0.495

							361.27	0.364	0.409	0.368	0.488
							368.87	0.363	0.408	0.370	0.482
							376.43	0.362	0.406	0.372	0.476
							383.66	0.361	0.405	0.374	0.470
							391.14	0.36	0.404	0.375	0.464
							398.59	0.36	0.403	0.377	0.458
cis-2-butene	C_4H_8	56.108	0.214	435.58	42.06	0.203	299.82	0.736	0.805	0.806	0.715
							305.37	0.751	0.819	0.808	0.724
							310.93	0.767	0.835	0.811	0.733
							316.48	0.785	0.853	0.816	0.743
							322.04	0.805	0.872	0.824	0.753
							327.59	0.827	0.893	0.833	0.764
							333.15	0.851	0.917	0.845	0.776
							338.71	0.878	0.944	0.860	0.789
							344.26	0.908	0.973	0.878	0.804
							349.82	0.942	1.007	0.899	0.820
1-butene	C_4H_8	56.108	0.214	419.59	40.2	0.187	310.93	0.784	0.85	0.794	0.761
							316.48	0.807	0.872	0.804	0.774
							322.04	0.832	0.897	0.816	0.787
							327.59	0.861	0.925	0.832	0.802
							333.15	0.893	0.957	0.851	0.818
Butylcyclohexane	$C_{10}H_{20}$	140.27	0.214	653.1	25.7*	0.274	207.52	0.312	0.355	0.432	0.447
							214.21	0.31	0.352	0.431	0.461
							221.77	0.307	0.348	0.429	0.476
							240.1	0.302	0.342	0.425	0.504
							260.05	0.298	0.336	0.419	0.523
							280.56	0.295	0.332	0.413	0.532
							290.54	0.294	0.331	0.409	0.533
							305.97	0.294	0.33	0.404	0.531
							325.86	0.295	0.329	0.397	0.525
							345.43	0.297	0.331	0.390	0.516
							365.38	0.3	0.333	0.383	0.505
Decylcyclohexane	$C_{16}H_{32}$	224.432	0.214	751.25*	16.5*	0.663	274.26	0.37	0.416	0.357	0.513
							280.27	0.368	0.413	0.358	0.514
							286.1	0.366	0.41	0.360	0.514
							293.33	0.363	0.407	0.361	0.514
							300.48	0.361	0.405	0.362	0.512

Styrene	C_8H_8	104.152	0.154	635	38.4	0.297	246.73	0.423	0.477	0.579	0.619
							249.91	0.422	0.476	0.578	0.624
							257.54	0.42	0.473	0.575	0.636
							276.24	0.417	0.468	0.568	0.658
							298.54	0.415	0.465	0.558	0.676
Dimethylbenzene	C_8H_{10}	106.168	0.170	630.3	37.32	0.31	251.989	0.425	0.478	0.573	0.586
							255.571	0.424	0.477	0.572	0.591
							262.249	0.422	0.475	0.569	0.600
							285.471	0.419	0.47	0.560	0.622
							297.742	0.418	0.468	0.555	0.630
p-xylene	C_8H_{10}	106.168	0.170	616.2	35.11	0.322	293.15	0.428	0.479	0.562	0.630
							313.15	0.429	0.478	0.555	0.639
							333.15	0.432	0.48	0.547	0.643
							353.15	0.438	0.484	0.541	0.645
							373.15	0.446	0.491	0.536	0.645
							393.15	0.457	0.501	0.534	0.644
							413.15	0.472	0.515	0.535	0.643
							433.15	0.491	0.534	0.541	0.643
							453.15	0.517	0.558	0.553	0.644
							473.15	0.549	0.59	0.573	0.648
							493.15	0.593	0.633	0.602	0.657
Naphthalene	$C_{10}H_8$	128.174	0.140	748.4	40.5	0.302	360	0.341	0.381	0.454	0.635
							380	0.342	0.381	0.448	0.632
							400	0.344	0.382	0.442	0.626
							420	0.347	0.385	0.437	0.619
							440	0.352	0.389	0.433	0.611
							460	0.358	0.395	0.429	0.601
							480	0.367	0.402	0.428	0.591
							500	0.377	0.412	0.428	0.580
							520	0.389	0.424	0.431	0.568
							540	0.405	0.439	0.437	0.556
							560	0.424	0.457	0.447	0.543
							580	0.448	0.481	0.462	0.530
							600	0.479	0.511	0.482	0.518
1-methylnaphthalene	$C_{11}H_{10}$	142.201	0.148	772	36	0.342	299.9	0.341	0.383	0.442	0.645
							310.24	0.338	0.38	0.440	0.649
							330.8	0.335	0.376	0.437	0.652

							352.19	0.333	0.373	0.433	0.651
2,7-dimethylnaphthalene	$C_{12}H_{12}$	156.228	0.154	775	31.7*	0.42	380	0.348	0.387	0.424	0.645
							400	0.348	0.386	0.422	0.637
							420	0.349	0.387	0.421	0.629
							440	0.352	0.388	0.420	0.619
							460	0.355	0.391	0.419	0.608
							480	0.36	0.395	0.420	0.596
							500	0.367	0.401	0.421	0.584
							520	0.375	0.409	0.425	0.570
							540	0.385	0.419	0.430	0.556
							560	0.398	0.431	0.438	0.541
							580	0.414	0.447	0.449	0.526
							600	0.435	0.466	0.463	0.511
							620	0.46	0.491	0.482	0.495
N-Octyl-1-octanamine	$C_{16}H_{35}N$	241.463	0.215	734	12.6	0.819	300	0.402	0.455	0.376	0.516
							340	0.39	0.44	0.387	0.496
							380	0.383	0.43	0.397	0.466
							420	0.381	0.427	0.408	0.437
							460	0.385	0.428	0.421	0.413
							500	0.395	0.437	0.439	0.397
							540	0.413	0.454	0.462	0.390
							580	0.446	0.486	0.496	0.393

* Estimated critical properties