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On the use of departure function correlations for hydrocarbon isobaric liquid phase heat capacity calculation



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ABSTRACT

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Keywords: Isobaric liquid heat capacity Departure function Calculation Constant pressure heat capacities for pure liquids and mixtures 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 because deviations between indirectly calculated and measured constant pressure liquid heat capacities are typically less than 15% and large deviations are uncommon. For hydrocarbon and petroleum applications, non-cubic equations of state have a limited range of application and a cubic equation of state departure function calculations possesses a systematic skew with respect to absolute and relative temperature. This provides application windows for stand alone departure function correlations: by Tyagi that requires the input properties $(T_{c}, P_{c}, \omega, M)$ at high reduced and absolute temperatures; and a difference calculation based on correlations by Dadgostar and Shaw (for hydrocarbon liquids) and Laštovka and Shaw (for ideal gases) which extend the range of fluids for which liquid state heat capacity departure functions can be evaluated to include poorly defined (T_c and Mare available) individual hydrocarbons or mixtures or ill-defined (only elemental analysis is available) hydrocarbon mixtures. However, none of these approaches provides consistently low deviations from measurements and consequently, direct calculation of liquid phase heat capacities is recommended for detailed engineering calculations.

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1. Introduction

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

$$C_{\rm PL} = C_{\rm P}^{\circ} + \Delta C_{\rm PL} \tag{1}$$

The ideal gas heat capacity comprises \sim 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] and 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 Eq. (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

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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].

Non-cubic equations of state such as the family of equations based on Statistically Associated Fluid Theory (SAFT) or perturbed chain (PC) variants are less commonly used for engineering calculations, and for derivative property prediction in particular due to known limitations related to their functional form as discussed elsewhere [10], in addition to limitations on the number and nature of fluids for which input parameters exist. For example, Villier et al. [10] evaluated a SAFT EOS, a PC–SAFT EOS and a

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Nomenclature	
А	Generalized constants for isothermal enthalpy differ-
 	ence for pure liquids by Lee and Edmister
C_{P}°	Ideal gas isobaric heat capacity
C_{PL}	Liquid phase isobaric heat capacity
ΔC_{PL}	The best required to effect a temperature change while
CsatL	the liquid is kept saturated
с.	The change in enthalpy of the saturated liquid with
CσL	temperature along the saturation curve
٨٢-٢	Departure function for saturated liquid heat capacity
H^{COL}	Enthalpy at given temperature and pressure
Hsø	Enthalpy of saturated gas
$H_{\sigma L}$	Enthalpy of saturated liquid
ΔH_V	Enthalpy of vaporization
Κ	Adjustable parameter for Majer and Svoboda enthalpy
	of vaporization correlation
М	Molar mass of a compound
Mi	Molar mass of chemical element <i>i</i>
N	Number of atoms of a compound
Р Л	Pressure
P _{br} D	Reduced Dolling pressure $(=P_b/P_c)$
г _с Р	Reduced pressure (=P/P)
r _r psat	Reduced saturation pressure (= $P_{\rm c}/P_{\rm c}$)
P	Saturation pressure of a compound at a given
* sat	temperature
Pypr	Vaporization pressure
Q^{ν}	Heat
R	Universal gas constant
Т	Temperature
T _{br}	Reduced boiling temperature $(=T_b/T_c)$
T _c	Critical temperature
$T_{\rm r}$	Reduced temperature $(=T/T_c)$
V	Volume
V _L	Saturated liquid volume
V_V	Difference between the volume of saturated vapor and
Δv_V	liquid
$V_{\sigma L}$	Saturated liquid volume
Zc	Critical compressibility factor
$\Delta Z_{\rm v}$	Difference between the compressibility factors of
-	saturated vapor and liquid
d	constant of kinani and Doralswamy ideal gas heat
Ь	Constant of Ribani and Doraiswamy ideal gas beat
U	canacity method
c	Constant of Rihani and Doraiswamy ideal gas heat
-	capacity method
d	Constant of Rihani and Doraiswamv ideal gas heat
	capacity method
п	Number of elements in a compound
ν_i	Stoichiometric coefficient for element <i>i</i> in a compound
Wi	Mass fraction of element <i>i</i>
x _i	Mole fraction of element <i>i</i> in a compound
α	Similarity variable; and an adjustable parameter for
0	Majer and Svoboda enthalpy of vaporization correlation
δ	Average relative deviation
3	Average absolute deviation
$\rho_{sL_{r}}$	Acentric factor
ക ന	Constants for Reid and Sobel saturated liquid beat
ΨI	canacity equation

cubic + association (CPA) EOS for the prediction of isobaric liquid heat capacity of selected *n*-alkane and *n*-alkanol compounds systematically. They encountered deviations as high as 28% for small *n*-alkanes with a SAFT EOS at low temperatures ($T_r = 0.5$). For such large deviations to arise in isobaric liquid heat capacity values, errors greater than 100% in predicted derivatives (dP/dV and dP/dT must be present. Further, the PC-SAFT EOS, while providing good agreement with isobaric liquid phase heat capacities for *n*-alkanes at saturation, predicts that heat capacity increases rather than decreases at elevated pressure. The departure function of the isobaric heat capacity for saturated liquid decane at T_r = 0.5 is underestimated by 19% for CPA, over estimated by 12% for the SAFT, and less than 2% deviation using the PC-SAFT approaches evaluated. The corresponding impacts on the isobaric heat capacity are small -5% for CPA, +3% for SAFT and nil for PC-SAFT. At higher temperatures, $T_r = 0.7$ and $T_r = 0.9$, predicted values for isobaric heat capacity of liquids for the SAFT and PC-SAFT approaches deviate less from experimental data for compounds tested than for the CPA EOS. These outcomes may reflect variations in tuning procedures used for parameter identification because property data underlying parameter selection (vapor pressures, enthalpies of vaporization, saturated liquid densities, and liquid heat capacities) typically available at room temperature, and around the boiling point, approximately $T_r = 0.7$, are prioritized differently during regression. Consequently, it is difficult to parse issues related to the functional form of non-cubic EOS and parameter fitting procedures, even for the PC-SAFT case cited above, because training and test data sets appear to be conflated. Data used to fit parameters for a compound in one citation can become predictions in another distantly related or unrelated citation, skewing the perception of relative performance. Parameters for cubic equations of state are fit to vapor pressures, critical pressure and temperature and derivative properties comprise pure prediction.

As this contribution focuses on industrial application, where frequently minimal fluid specific data are available, the performance of two functional forms for the liquid-phase constant-pressure heatcapacity departure-function are evaluated from the perspective of range of application as much as performance. The two forms comprise a conventional form originally given for real gases along with cubic thermodynamic models for calculating the temperature and volume derivatives [1,11] and an unconventional form based on the temperature derivative of the enthalpy of vaporization [4,12,13]. As there are numerous industrially relevant organic fluids such as boiling fractions and residual oils, for which required input properties needed to exploit any of the EOS methods: molecular structures, critical properties, basic physical properties, are unavailable to practitioners or remain speculative, 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.

2. Expressions for departure functions

Reid and Sobel [12] 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, $(dH_{\sigma L}/dT)$, (3) C_{satL} , the heat required to effect a temperature change while the liquid is kept saturated, $(dQ/dT)\sigma L$. These different heat capacity measures are inter-related [12]:

$$C_{\sigma\Lambda} = C_{\rm PL} + \left[V_{\sigma\Lambda} - T \left(\frac{\partial V}{\partial T} \right)_P \right] \left(\frac{dP}{dT} \right)_{\sigma\Lambda} = C_{\rm satL} + V_{\sigma\Lambda} \left(\frac{dP}{dT} \right)_{\sigma\Lambda}$$
(2)

The volume and temperature derivatives in Eq. (2) tend to be small, remote from the critical point. C_{PL} , $C_{\sigma L}$, and C_{satL} values can be

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