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Heat capacity estimations using equations of state

Roland Solimando and Marek Rogalski

Laboratoire de Thermodynamique Chimique et Appliquée, INPL-ENSIC, B.P. 451, 54001 Nancy Cedex (France)

Lucie Coniglio

Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, 13288 Marseille Cedex 9 (France)

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Abstract

Five equations of state accurately expressing the vapor pressures of hydrocarbons were used to estimate ΔC_p, the difference between liquid and ideal gas heat capacities. It was observed that two equations of state giving equally accurate vapor pressures can yield very different ΔC_p estimates. The consequences are investigated and discussed.

INTRODUCTION

The heat capacity is a fundamental physical property of chemical species with which it is possible to establish most of their thermodynamic characteristics. In this study, we investigate whether selected equations of state (EOS) accurately express the heat capacities of hydrocarbons or more specifically ΔC_p, i.e. the difference between the real fluid and ideal gas heat capacities. The parameters of the currently used equations of state have usually been based on the *PVT* and vapor pressure experimental data. Calculating the ΔC_p involves a double differentiation of all temperature dependent terms of a given equation of state and constitutes a severe test of its thermodynamic consistency. In comparing two EOS yielding similar vapor pressure and volume calculations, it is possible to judge their physical soundness by checking the degree of agreement between the estimated and the experimental heat capacity. In this study, several semi-empirical EOS often used in chemical engineering calculations were investigated.

Correspondence to: M. Rogalski, Laboratoire de Thermodynamique Chimique et Appliquée, INPL-ENSIC, B.P. 451, 54001 Nancy Cedex, France.

DATA BASE

Only hydrocarbons were considered in this study. A set of data including compounds with various molecular structures (*n*-alkanes, isoalkanes, naphthenes and aromatics) and differing in their molecular size and volatility was drawn up. All the *n*-alkanes from ethane up to *n*-hexadecane were considered.

Vapor pressures, liquid heat capacities and liquid volumes of these compounds are known. Experimental heat capacity data have often been determined in the low temperature range (100–200 K). At these temperatures the vapor pressures were usually unknown. The heat capacities in almost the full liquid range (from the triple point up to temperatures around the critical point) were available, however, in the case of a few compounds (cyclohexane, *n*-heptane). The list of compounds and references to the sources of the selected data are given in Table 1. To establish the ΔC_p values, the liquid heat capacities and ideal gas heat capacities were needed. The literature from which the experimental liquid heat capacities were drawn is specified in Table 2. The ideal gas heat capacities were calculated using the Planck–Einstein function fitted to data published in TRC Tables (Coniglio et al. [43]).

EQUATION CHOICE

Five EOS were considered in this study: COR (chain-of-rotators), proposed by Chien et al. [44], PHCT$_{\mathrm{BDP}}$ (perturbed hard chain theory), proposed by Beret and Prausnitz [45] and developed by Donohue and Prausnitz [46], the modified form of the same equation PHCT$_{\mathrm{GLP}}$, presented by Gmehling et al. [47]; BACK (Boublik, Alder, Chen and Kreglewski), presented by Chen and Kreglewski [48] and the Peng–Robinson equation with the modifications proposed by Rauzy [49]. The corresponding formulae are presented in the Appendix. The first four EOS were derived by applying the perturbation theory. This promising theoretical approach has proved to be useful and had led numerous authors to propose new equations of state. Different formulations were obtained based on different theoretical and empirical assumptions. These topics will not be discussed in the present study. Characteristic parameters (three with PHCT$_{\mathrm{BDP}}$, PHCT$_{\mathrm{GLR}}$ and COR and four with BACK) were determined by fitting these equations to experimental vapor pressure and liquid density data. In the case of the PHCT and COR equations, these parameters were the characteristic temperature T^*, the close packed volume v^* and the parameter c related to the number of degrees of freedom associated with the external vibration and rotation modes of molecules. It is worth noting that parameter c is correlated with ΔC_p. As discussed by Bagley et al. [50], ΔC_p is correlated with external molecular

TABLE 1

Vapor pressure calculation results obtained with selected equations of state

Compound	Pressure (bar)		$\delta_r(P_s)$ (%)					Ref.
	Min	Max	PR_c	COR	$PHCT_{GLP}$	$PHCT_{BDP}$	BACK[a]	
Ethane	2.00	37.65	0.30	0.24	0.34	0.19	0.28	1
Propane	0.02	39.68	0.53	0.47	0.46	1.04	0.35	1–3
n-Butane	0.01	31.09	0.47	0.24	0.13	1.01	0.34	1,4,5
i-Butane	0.01	33.63	1.61	1.96	0.73	1.78	0.24	1,4
n-Pentane	0.004	30.52	0.43	0.16	0.34	1.14	0.64	1,6,7
2,3-Dimethylbutane	0.20	28.47	0.21	0.08	0.31	0.45	0.63	1,7
n-Hexane	0.12	24.25	0.44	0.26	0.24	0.82	0.56	1,7,8
2-Methylpentane	0.17	24.52	0.28	0.10	0.27	0.46	0.66	1,7
Cyclohexane	0.09	27.68	0.98	0.44	0.44	1.04	0.80	7,9–11
Methylcyclopentane	0.12	1.02	0.54	0.02	0.06	0.12	–	7
Benzene	0.08	38.69	1.17	0.67	0.66	1.45	0.51	7,12,13
2,4-Dimethylpentane	0.08	24.87	0.42	0.16	0.22	0.93	0.63	1,14
n-Heptane	0.06	24.97	0.45	0.24	0.34	0.66	0.79	1,7
2-Methylhexane	0.02	24.66	0.41	0.17	0.29	0.99	0.77	1,14,15
n-Octane	0.08	20.00	0.33	0.16	0.23	0.78	0.68	1,7
i-Octane	0.06	22.11	0.33	0.07	0.21	0.83	0.60	1,7
Toluene	0.009	37.07	0.72	0.22	0.49	1.43	0.79	1,12,16
Methylcyclohexane	0.06	1.04	0.69	0.05	0.10	0.18	–	7,17
Ethylcyclopentane	0.06	1.01	0.50	0.04	0.08	0.19	–	14
Ethylcyclohexane	0.06	1.04	2.19	0.05	0.11	0.21	–	7
Ethylbenzene	0.03	30.39	0.56	0.25	0.34	1.22	0.69	7,12,18
o-Xylene	0.06	30.42	0.35	0.06	0.21	0.85	0.78	7,12
m-Xylene	0.06	29.85	0.39	0.16	0.26	0.74	0.78	7,12
p-Xylene	0.06	29.94	0.51	0.18	0.27	0.68	0.94	7,12,19
n-Nonane	0.06	19.96	0.47	0.48	0.46	0.39	0.75	1,14
1,2,4-Trimethylbenzene	0.06	26.81	0.54	0.55	0.60	0.33	0.83	12,14
n-Decane	0.02	2.70	1.17	0.66	0.98	1.63	–	7,20,21
n-Undecane	0.07	1.05	0.20	0.10	0.12	0.25	–	22
n-Dodecane	0.02	1.04	1.76	1.41	1.71	2.36	–	7,20
n-Tetradecane	0.07	1.03	1.30	0.86	1.00	1.64	–	20,22
n-Hexadecane	0.001	1.01	1.94	2.08	2.26	3.10	–	23,24
Naphthalene	0.01	1.03	0.40	0.15	0.23	0.37	–	22,25
Mean deviation %			0.68	0.38	0.45	0.97	0.66	

[a] Vapor pressure data higher than 1 atm were used with the BACK equation.

TABLE 2

ΔC_p estimations obtained with selected equations of state using parameters established with vapor pressure data

Compound	Temperature (K)		$\delta(\Delta C_p)$ (%)			Ref.
	min	max	PR_c	COR	$PHCT_{GLP}$	
Ethane	100	280	13.3	8.4	6.0	26
Propane	100	350	15.8	9.6	6.6	27
n-Butane	145	380	11.7	6.2	5.9	28
i-Butane	120	380	15.1	9.5	8.3	29
n-Pentane	149	303	14.1	4.2	10.7	30
2,3-Dimethylbutane	145	310	28.1	9.9	21.8	31,32
n-Hexane	178	301	15.4	3.9	15.2	30,32
2-Methylpentane	140	310	21.4	3.0	16.3	31,32
Cyclohexane	280	523	13.0	11.1	16.7	33
Methylcyclopentane	140	308	25.9	3.9	16.3	32
Benzene	279	500	15.7	9.7	15.1	34
2,4-Dimethylpentane	154	310	20.4	3.5	17.1	31
n-Heptane	183	519	16.5	5.2	11.4	31,33
2-Methylhexane	155	300	21.6	4.3	18.9	31
n-Octane	216	300	18.2	6.4	21.2	30,35
i-Octane	166	320	15.2	3.4	11.9	35
Toluene	178	500	15.8	5.4	15.3	34,36
Methylcyclohexane	155	308	27.5	2.9	16.9	32,33
Ethylcyclopentane	160	302	35.3	16.9	29.5	37
Ethylcyclohexane	167	299	27.8	1.6	14.9	38
Ethylbenzene	178	300	23.0	3.9	16.8	34
o-Xylene	248	300	13.9	4.5	13.3	39
m-Xylene	225	310	15.6	3.5	15.5	39
p-Xylene	286	570	13.3	4.5	9.5	39,40
n-Nonane	220	320	18.9	8.7	23.3	30
1,2,4-Trimethylbenzene	229	300	17.1	3.6	17.0	39
n-Decane	250	320	18.5	10.0	22.2	41
n-Undecane	248	310	21.5	13.0	27.5	30
n-Dodecane	264	320	20.8	12.7	25.5	30
n-Tetradecane	279	300	24.5	16.6	30.5	30
n-Hexadecane	291	320	22.7	17.3	29.3	30
Naphthalene	357	371	17.3	6.1	18.2	42
Mean deviation, %			18.5	6.6	14.6	

rotations. Consequently, if the physical significance of the parameter c is preserved, ΔC_p will be accurately formulated. On the contrary, any wrong ΔC_p estimates obtained will prove that the model is not quite consistent.

In the case of the BACK equation, four parameters were adjusted with the experimental data. The first parameter α is associated with the molecular shape and defined according to the convex hard body concept developed by Boublik [51]. Three further parameters u^0, v^0 and η are necessary to determine T^* and v^*, which were taken to be temperature dependent.

Lastly, an empirical development of the van der Waals theory, the Peng–Robinson equation [52] was considered. Cubic EOS, because of their simplicity and the qualitatively satisfactory description they give of the *PVT* properties of fluids, have received much attention. Their common characteristic feature is a single temperature dependent term, the $a(T)$ function, which can be selected in such a way that the vapor pressures are perfectly formulated. Liquid heat capacities are usually satisfactorily estimated using each equation of state capable of accounting accurately for the vapor pressures. In particular, ΔC_p can be estimated using a cubic equation of state with a suitable $a(T)$ function, as demonstrated by Rogalski et al. [53]. The temperature domain where reliable ΔC_p results can be expected will usually be smaller, however, than that covered by the experimental data used. This is a common feature of empirical models. For this reason we have used in this study the $a(T)$ function proposed by Soave [54]. This expression, yielding only fair vapor pressures, is valid in wide temperature ranges and can accurately express second virial coefficients at supercritical temperatures. Given this wide validity range, we had grounds for hoping that the ΔC_p estimates would be broadly satisfactory with this equation.

DATA REDUCTION

Characteristic parameters of all equations studied were determined in the case of 32 selected compounds. They were obtained by fitting selected EOS simultaneously to experimental vapor pressure and liquid volume data (except for the Peng–Robinson equation, with which only vapor pressure data were used). A universal computer algorithm for dealing with complex equations of state, that of Solimando [55], was used to carry out the calculations. The vapor pressure results obtained with the five EOS studied are given in Table 1. The parameters determined can be found in the study by Solimando.

Analysis of the results afforded some interesting information about the efficiency of the equations considered. Upon inspecting the overall differences between experimental and calculated vapor pressures obtained with 32 compounds, it became clear that BACK and $\mathrm{PHCT_{BDP}}$ yield the least satisfactory results. Moreover, the BACK equation cannot be used to reproduce low vapor pressures (the results summarized in Table 1 were obtained with superatmospheric data only). The idea of taking the characteristic temperature T^* and the close packed volume v^*, to be temperature dependent parameters seems to have caused this difficulty. Consequently, the vapor pressures of heavy compounds could not be expressed with this equation.

The results obtained with the PHCT_{BDP} equation were more regular but, in the majority of cases, substantially poorer than those obtained with PHCT_{GLP}. It is worth noting the very consistent results obtained with the modified Peng–Robinson equation. Small changes in the $a(T)$ function proposed by Soave [54] (the use of 0.44 instead of 0.5 in eqn. (A2)) made it possible to improve perceptibly the low pressure representation. The best results were obtained with the COR and PHCT_{GLP} equations. The overall mean deviations obtained in these two cases were nearly identical but the COR equation seems to yield better results in the low pressure range.

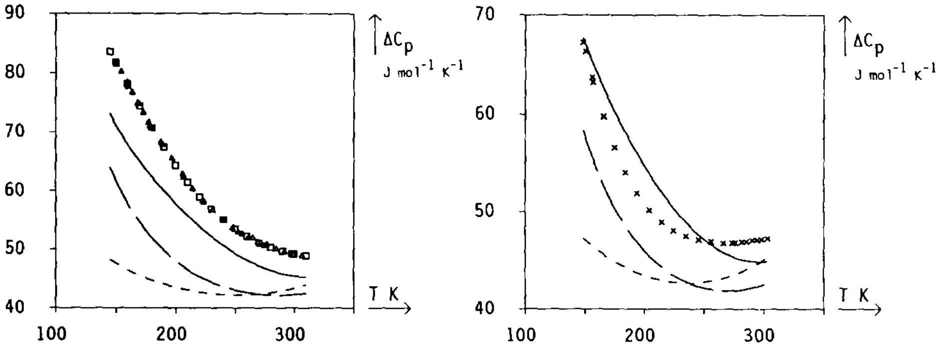
On the basis of these results, we concluded that only three equations: PHCT_{GLP}, COR and the modified Peng–Robinson equation, are suitable for studying ΔC_p.

HEAT CAPACITY CALCULATIONS

The difference between the liquid and ideal gas heat capacity ΔC_p was calculated with each EOS considered, using expressions derived from the general thermodynamic relationship

$$\Delta C_p = -RT(\partial P/\partial T)_v^2/(\partial P/\partial v)_T + T\,\partial^2/\partial T^2\left[\int (P - RT/v)\,\mathrm{d}v\right] \qquad (1)$$

and parameter values determined with vapor pressures and liquid volumes. The results were compared with ΔC_p values derived from experimental data, and the corresponding deviations are listed in Table 2. As can be seen from this table, the ΔC_p estimates obtained with the COR equation were the most accurate. The fact that the overall mean deviation in the ΔC_p was twice as high with PHCT_{GLP} is surprising in view of the



(a) (b)

Fig. 1. Heat capacity estimation in the low temperature range using (——) COR, (— — —) PHCT_{BDP} and (- - -) PR_c equations of state. (a) 2,3-Dimethylbutane; □, TRC Tables [31], Δ, Douslin et al. [32]. (b) *n*-Pentane; ×, Messerly et al. [30].

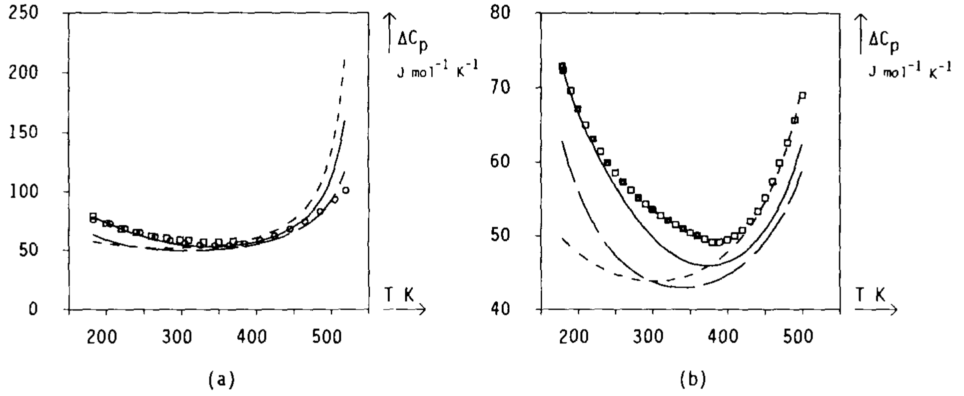


Fig. 2. Heat capacity estimation up to temperatures close to the critical point using (——) COR, (— — —) $PHCT_{BDP}$ and (- - -) PR_c equations of state. (a) *n*-Heptane; ○, Stephan et al. [33], □, TRC Tables, [31]. (b) Toluene; □, TRC Tables [34], ⊠, Scott et al. [36].

nearly equally satisfactory vapor pressure modeling obtained with the two equations. The least satisfactory results, as expected, were obtained with the Peng–Robinson equation of state.

It seemed interesting to discuss in greater detail the efficiency of three of the equations considered. The results obtained at very low temperatures (between 150 and 300 K) on 2,3-dimethylbutane and *n*-pentane are plotted in Fig. 1. In both cases, the vapor pressure data used to determine the equation parameters were measured at substantially higher temperatures. As expected, unsatisfactory results were obtained at low temperatures with the Peng–Robinson equation. The results obtained with $PHCT_{GLP}$ and COR results were systematically biased, but the general pattern of the ΔC_p curve was preserved. The ΔC_p of *n*-heptane and toluene within a nearly all liquid phase range were plotted in Fig. 2. In the

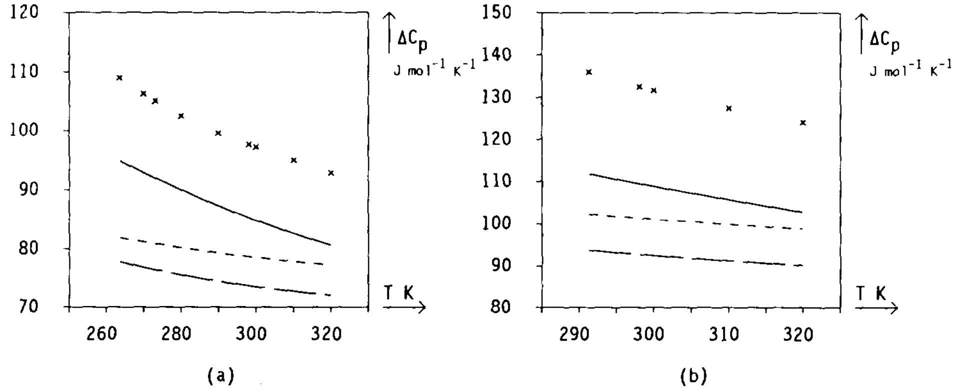


Fig. 3. Heat capacities of long chain *n*-alkanes estimated with (——) COR, (— — —) $PHCT_{BDP}$ and (- - -) PR_c equations of state. (a) *n*-Dodecane; ×, Messerly et al. [30]. (b) *n*-Hexadecane; ×, Messerly et al. [30].

case of *n*-heptane the results obtained with the COR equation were in excellent agreement with the experimental data, but PHCT_{GLP} was found to be more accurate in the vicinity of the critical point. In the case of toluene, it should be noted that the COR equation accounts very well for the ΔC_p shape in all temperature ranges and that the Peng–Robinson equation gives an excellent agreement above 420 K.

In the case of heavy hydrocarbons, seriously biased results were obtained with all three equations considered (Fig. 3). Here, the best results were obtained with the COR equation which, moreover, satisfactorily models the slope of the experimental curve.

CONCLUSION

This study on ΔC_p estimation using various equations of state led us to conclude definitely that the COR equation yields the most accurate estimations. This conclusion was based on a large set of experimental data in wide temperature ranges. In view of the fact that the PHCT_{GLP} and COR equations give similar vapor pressure results, the fact that the latter equation gave much more satisfactory heat capacities confirms its physical consistency and soundness.

The satisfactory results obtained at moderate and high reduced temperatures with the Peng–Robinson equation stem from the validity of the Soave function over a wide temperature range (except at low reduced temperatures).

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APPENDIX

The formulas defining the equations of state used in this study are given and briefly discussed below.

Modified version of the Peng–Robinson equation (volume corrected Peng–Robinson equation PR_c) proposed by Rauzy [49]

$$P = RT/(v - b) - a(T)/[v(v + 4.82843b)] \tag{A1}$$

$$a(T) = a_c[1 + m(1 - T_r^{0.44})]^2 \tag{A2}$$

$$a_c = 0.45724RT_c^2/P_c^2 \tag{A3}$$

$$b = 0.045572RT_c/P_c \tag{A4}$$

For volume calculations, these equations should be used with volume correction; see Péneloux et al. [56]. In this study, the volumes were not calculated and consequently only the parameter m was tuned.

Perturbed hard chain theory equations

Two equations of state derived from the perturbed hard chain theory were considered. The first was the version proposed by Beret and Prausnitz [45] and developed by Donohue and Prausnitz [46] ($\mathrm{PHCT_{BDP}}$). The second was that proposed by Gmehling, Liu and Prausnitz [47] ($\mathrm{PHCT_{GLP}}$). Both equations have the same general form

$$Z = 1 + c[(4y - 2y^2)/(1 - y)^3] + c\sum_{n=1}^{N}\sum_{m=1}^{M} mD_{n,m}(T^*/T)^n(v^*/v)^m \tag{A5}$$

with

$$y = 0.7405v^*/v \tag{A6}$$

In the case of the $\mathrm{PHCT_{BDP}}$ equation, the double sum is defined with $N = 4$ and $M = 6$, and in that of the $\mathrm{PHCT_{GLD}}$ equation with $N = 2$ and $M = 5$. The total number of universal parameters $D_{n,m}$ is 21 with the former equation and 10 with the latter. Universal parameters were established by the authors using selected experimental data and molecular dynamics results. Three parameters were adjusted with these equations: c, a parameter expressing the degree of freedom associated with the external molecular rotations, v^*, the close packed volume and T^*, the characteristic temperature.

The general form of the chain of rotators equation (COR) proposed by Chien et al. [44]

$$\begin{aligned} Z = {} & 1 + (4y - 2y^2)/(1-y)^3 + 0.5c(\alpha - 1) \\ & \times [3y + 3\alpha y^2 - (\alpha + 1)y^3]/(1-y)^3 \\ & + [1 + 0.5c(B_0 + B_1)T^*/T + B_2 T/T^*)] \\ & \times \sum_{n=1}^{4} \sum_{m=1}^{6} m D_{n,m} (T^*/T)^n (v^*/v)^m \end{aligned} \qquad \text{(A7)}$$

where y is defined by eqn. (A6). The total number of universal parameters ($D_{n,m}$, B_0, B_1, B_2) established by the authors was 27. As in the case of the PHCT equations, c, T^* and v^* were adjusted in the study.

The Boublik, Alder, Chen and Kreglewski equation (BACK) [48]

$$\begin{aligned} Z = {} & 1 + (4y - 2y^2)/(1-y)^3 + (\alpha - 1) \\ & \times [3y + 3\alpha y^2 - (\alpha + 1)y^3]/(1-y)^3 \\ & + \sum_{n=1}^{4} \sum_{m=1}^{9} m D_{n,m} (T^*/T)^n (v^*/v)^m \end{aligned} \qquad \text{(A8)}$$

where y is defined by eqn. (A6). The characteristic temperature and the close packed volume are temperature dependent in this case

$$T^* = g(u^0, \eta, T) \qquad \text{(A9)}$$

$$v^* = h(u^0, v^0, T) \qquad \text{(A10)}$$

The number of universal parameters specified by the authors is 24. Four parameters were adjusted in this study: α, u^0, v^0 and η. The first, α, characterizes the molecular shape. The last three parameters are used to establish T^* and v^*.