Simple and Controlled Extrapolation of Vapor Pressures toward the Triple Point

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Although experimental vapor pressures are abundant in the medium-pressure range ($p_{sat} \approx 5-100$ kPa), their values are scarce and uncertain at lower pressures due to experimental difficulties in determining the data. Reliable values are, however, required by technology (separation processes dealing with mixtures containing high molar mass compounds) and environmental concerns (transport and fate of high-boiling pollutants). The ability of frequently used vapor-pressure equations to extrapolate the data at medium pressures toward the triple-point temperature was tested on three groups of compounds (polar and nonpolar organic chemicals, n-alkanes, and 1-alkanols) for which reliable experimental data in the low-pressure range were available. Results of a simple extrapolation were compared with those from a simultaneous correlation of vapor pressures in the medium-pressure range and the differences between heat capacity of an ideal gas and that of the liquid available at lower temperatures. The latter is generally more reliable, as it is controlled by the exact thermodynamic constraints linking vapor pressures and the thermal data. The extent of improvement when using simultaneous correlation was examined, as well as the influence of the quality of input data on the results of extrapolation. Extrapolated values were compared with experimental vapor pressures and calorimetric enthalpies of vaporization that were selected from literature and free of any important systematic errors.

Introduction

Vapor-pressure data p_{sat} for organic compounds in the low-pressure range are needed for a variety of chemical engineering and thermodynamic calculations. This article focuses on the problem of extrapolating vapor-pressure data available near atmospheric pressure toward the region of low pressures and examines to what extent the use of related thermal data can improve the results of the extrapolation procedure.

In this article, the low-pressure range is understood to mean all pressures below 1 kPa. For many organic compounds, the vapor pressure at the triple-point temperature T_t is far below 1 kPa, and the temperature interval corresponding to p_{sat} in the low-pressure range is for an organic liquid generally larger than 100 K.

For high boiling compounds of large molar mass, the temperature interval of vapor pressures in the low-pressure range covers partly or fully the range of environmental temperatures that extend from about 223 to 323 K. Many chemicals listed as pollutants are in fact higher boiling organic compounds; their vapor pressures at ambient temperatures are needed for estimating transport to the atmosphere and solubility in the aquatic environment. For that reason, the ability to accurately determine p_{sat} at low pressures is of prime importance from an environmental point of view.

Reliable vapor-pressure data in the low-pressure range can be used for determining enthalpies of vaporization ΔH_{vap} of high boiling compounds at 298.15 K; the vaporization data play an important role in various thermochemical and thermodynamic calculations for converting different enthalpic quantities between the gaseous and liquid states. Good-qual-

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ity calorimetric data are rare near room temperatures for compounds of high molar mass. Direct measurements are complicated and interpretation of experimental results is complex; this problem has been discussed in detail by Majer and Svoboda (1985). At low pressures the deviations of vapor volume from ideal gas behavior are negligible and enthalpies of vaporization can be obtained from the Clausius–Clapeyron equation, provided vapor-pressure data are known with sufficient accuracy.

Various approaches to experimental determination of vapor pressures were reviewed by Ambrose (1975). The main experimental techniques for determination of vapor pressures in the low-pressure range are the saturation method using a carrier gas and two techniques based on molecular effusion (weighing effusion and torsion effusion methods). Gas–liquid chromatography has also been used, but it is not easy to give the resulting data a rigorous thermodynamic interpretation. Direct static measurement of vapor pressure is a universal technique that can be used over a wide pressure range down to 1 Pa; the most accurate data reported in the low-pressure range were obtained by this technique. However, in general, experimental vapor pressures below 1 kPa are scarce and usually of low reliability; the vapor pressure data in the low-pressure range are rarely consistent at their upper temperature limit with p_{sat} values obtained by different techniques at higher temperatures. The reasons for this are the experimental difficulties in determining p_{sat} at low pressures; a slight contamination of samples by lower boiling compounds or incomplete degassing can cause important systematic errors. Differences of several tens of percent between the data from different literature sources are quite common.

Vapor-pressure data in the medium-pressure range (1 to 150 kPa) are, on the other hand, abundant and much more reliable than in the low-pressure range. Measurements are less complicated to perform, and high-quality p_{sat} data can be obtained near the normal boiling temperature, T_b, with an error below one-hundredth percent. Easy access to data is always a significant advantage; besides tabulations of evaluated data in the "nonopen" literature (*TRC Thermodynamic Tables*, DIPPR project, ESDU items, etc.) several compilations were published over the last 20 years (Ohe, 1976; Dykyj and Repáš, 1979; Dykyj et al., 1984; McGarry, 1983; Boublík et al., 1984; Reid et al., 1987; Boublík and Aim, 1996) that present experimental and/or recommended data for a large quantity of compounds. For that reason it is worthwhile to examine the methods for extrapolating the p_{sat} data available in the medium-pressure range toward the triple point temperature and to assess the reliability of this procedure.

The simplest approach is an extrapolation from vapor pressures measured in the medium pressure range using an equation with an optimum number of parameters. The input data must be reliable and available over a sufficiently wide temperature interval in order to allow a meaningful extrapolation. The form of the correlation equation used can also largely affect the results; suitability of some relationships for such an extrapolation was tested by Scott and Osborn (1979). A somewhat more sophisticated method was proposed by Ambrose et al. (1981) who suggested a procedure of simultaneously fitting the data and subjecting the resulting parameters to several semiempirical constraints. This approach improves the ability of the correlation equation to extrapolate to higher and lower pressures and was used for the description of the vapor pressure curve between the triple and critical points; for instance the constrained data were obtained by McGarry (1983) for over 250 important compounds.

An alternative approach regarding extrapolation towards low pressures is a combination of p_{sat} in the medium pressure range with the related thermal data by which we understand enthalpy of vaporization ΔH_{vap} and the heat capacity difference ΔC^0_{vap}. The latter quantity is defined as

$$\Delta C^0_{vap} = C^0_p - C^1_p, \tag{1}$$

where C^0_p denotes the heat capacity of an ideal gas and C^1_p that of the liquid. Vapor pressures are related to the thermal properties by the exact thermodynamic relationships, which allow a controlled extrapolation of p_{sat} data in the medium-pressure range down to the triple-point temperature T_t, provided the thermal data are available in the temperature range below that of the p_{sat} data. In extrapolations enthalpies of vaporization cannot always be used effectively, as reliable calorimetric values at temperatures corresponding to p_{sat} in the low-pressure range are available only for a limited number of compounds. On the other hand, heat-capacity differences are more readily accessible since they can be calculated for many compounds in a wide temperature range down to the triple-point temperature by combining calorimetric and spectroscopic data. The simultaneous correlation of medium vapor pressures and ΔC^0_{vap} values can also be useful for determining the frequently required values of ΔH_{vap} at 298.15 K for high boiling compounds. Further combination of the vapor pressure calculated at T_t with the enthalpies of phase transition (solid–liquid, solid–solid) and differences between the heat capacity of an ideal gas and that of the solid makes it possible to calculate vapor pressures along the vapor–solid saturation line.

The method using the thermal data for extrapolating vapor pressures was first described by King and Al-Najjar (1974), and further developed by Ambrose and Davies (1980) and Růžička and Majer (1986). Several authors have discussed the thermodynamic basis and applicability of this method (Mosselman and van Vugt, 1982; Ambrose, 1985; Majer et al., 1988, 1989; Lichtenstein, 1989), and several attempts were made to use this approach for the development of predictive equations (Rogalski, 1985; Guthrie, 1986; King and Mahmud, 1986; Vetere, 1988, 1991). We have recently used this procedure for correlating and examining consistency of data for several groups of compounds (Růžička and Majer, 1994, 1996; Růžička et al., 1994).

The simultaneous treatment of vapor pressures and the related thermal data has, however, never been extensively used in the past. The reason is obviously the necessity of compiling and evaluating experimental data for several different properties; most potential users have neither the expertise nor the time to make such an effort. This task has been, however, substantially facilitated over the last few years by the publication of several comprehensive compilations listing the evaluated data for thermal properties in the form of correlating equations. Calorimetric enthalpies of vaporization were compiled and the recommended data produced for over 650 compounds by Majer and Svoboda (1985), and experimental heat

capacities of liquid were evaluated and correlated as a function of temperature for more than 1,600 compounds by Zábranský et al. (1996); both these projects were conducted under the auspices of the International Union of Pure and Applied Chemistry (IUPAC). Frenkel et al. (1994) evaluated ideal gas properties for over 2,000 organic compounds and reported recommended values of C_p. Bureš et al. (1992) published a temperature correlation of thermodynamic properties of ideal gas (including spectroscopic C_p^0 values) for 3,000 organic compounds. The availability of these and other sources made the use of thermal data in the correlation more user-friendly, and this approach deserves to be examined in more detail.

This article presents the results of a project whose objective was to test the performance of the most frequently used vapor-pressure equations in extrapolating vapor-pressure data from the medium-pressure range down to the triple-point temperature. Quantitative information was also obtained, showing to what extent the extrapolation can be improved by including the thermal data, and the suitability of different equations for such a simultaneous correlation was evaluated. Attention was also paid to the influence of errors in the input data to the extrapolation in the low-pressure region.

Vapor-Pressure Equations

In this study we have tested four types of empirical relationships that were most frequently used in the literature for the correlation of vapor-pressure data. The tested forms of equation types 2 to 5 are listed with the assigned codes in Table 1.

Antoine equation

$$\ln p_{\text{sat}} = A_1 + \frac{A_2}{T + A_3}. \tag{2}$$

This relationship has been most frequently used for the vapor-pressure correlation of data measured in a limited temperature range (usually several tens of kelvins). It has been stated several times in the literature that the extrapolation capabilities of the Antoine equation are limited (King and Al-Najjar, 1974; Scott and Osborn, 1979; Majer et al., 1989). Nevertheless, this relationship appears to be routinely used in engineering calculations for extrapolating beyond the range of experimental data. This is due mainly to the fact that most compilations of vapor pressures present parameters of the Antoine equation, which are available in the literature for over 5,000 compounds. It is therefore worthwhile to gain a quantitative idea of how this relationship performs compared to other equations.

Quasi-polynomial equations

Under quasi-polynomial equations we understand the form

$$\ln p_{\text{sat}} = \sum_{i=k}^{m} A_i \cdot T^i + A_{\ln} \ln T, \tag{3}$$

where i is usually changing between -1 and 6 and some parameters A_i are equal to zero. Different forms of Eq. 3 have been used for simultaneously correlating vapor pressures and thermal data; the four- and five-parameter forms are the most common, with A_{-1} and A_0 always differing from zero. A four-parameter relationship QL1 was employed for C_1 to C_{16} n-alkanes (King and Al-Najjar, 1974; King and Mahmud, 1986), and a five-parameter form QL12 was used for polar compounds (Ambrose and Davies, 1980; Růžička and Majer, 1986). The former expression was also used for representing temperature dependence of p_{sat} data in the DIPPR tables (Daubert and Danner, 1989) together with two additional four-parameter forms QL2 and QL6. The last stated form is usually denoted in the literature as the Riedel equation.

All four of the above-mentioned quasi-polynomial equations contain nonzero parameters multiplying terms T^{-1}, T^0, and $\ln T$. The last term can be expressed as a linear combination of the preceding two terms over a relatively wide temperature interval; this can lead to ill-conditioning of the parameters (Ambrose et al., 1970; Voňka et al., 1980). In this case, the experimental data can be correctly represented but the equation might fail in extrapolations. The four-parameter equation Q12 without the logarithmical term (denoted sometimes in the literature as the Cragoe equation) does not present this danger and was used as an alternative to the other four-parameter forms.

Wagner equations

The logarithm of the ratio of p_{sat} and the critical pressure p_c (reduced vapor pressure) is expressed as an expansion in $\tau = (1 - T/T_c)$, where T_c is the critical temperature

$$\ln\left(\frac{p_{\text{sat}}}{p_c}\right) = \frac{T_c}{T} \sum_{i=1}^{m} A_i \left(1 - \frac{T}{T_c}\right)^{\alpha_i}. \tag{4}$$

Exponents α_i have fixed values that were determined by the methods of statistical analysis (Wagner, 1973). The number of adjustable parameters is usually four; five adjustable parameters were used exceptionally for correlations of accurate data in a wide temperature range. In all versions of the Wagner equation the first two exponents α_i are equal to 1 and 2, respectively. The four-parameter forms W25 and W36 have been used most often. The Wagner equations have become very popular for correlating vapor pressures up to the critical temperature, and several articles present parameters for certain groups of substances (e.g., McGarry, 1983; Reid et al., 1987; Ambrose and Walton, 1989; Boublík and Aim, 1996).

Cox equations

The logarithm of the ratio of p_{sat} to an arbitrarily selected vapor pressure p_0 corresponding to the temperature T_0 is expressed as an exponential of a polynomial expansion in temperature.

$$\ln\left(\frac{p_{\text{sat}}}{p_0}\right) = \left(1 - \frac{T_0}{T}\right) \exp\left(\sum_{i=0}^{m} A_i T^i\right). \tag{5}$$

In the original relationship (Cox, 1936) the number of adjustable parameters A_i was three, but up to nine parameters have been used for describing highly accurate vapor pressures over a wide temperature range (Scott and Osborn, 1979). The most frequently used reference condition for T_0 and p_0 is the normal boiling point or the critical point. The

Table 1. List of Tested Vapor-Pressure Equations with Expressions Corresponding to $\Delta H'$ and $\Delta C'$

Eq. Code	$\ln p_{sat}$	$\Delta H' = RT^2\left(\frac{d \ln p}{dT}\right)_{sat} = -R\left(\frac{d \ln p}{d(1/T)}\right)_{sat}$	$\Delta C' = 2RT\left(\frac{d \ln p}{dT}\right)_{sat} + RT^2\left(\frac{d^2 \ln p}{dT^2}\right)_{sat}$
ANT	$A_1 + \frac{A_2}{A_3 + T}$	$-RT^2 \frac{A_2}{(A_3+T)^2}$	$-\frac{2RA_2A_3T}{(A_3+T)^3}$
QL1	$A_{ln} \ln T + \frac{A_{-1}}{T} + A_0 + A_1 T$	$R(-A_{-1} + A_{ln}T + A_1T^2)$	$R(A_{ln} + 2A_1T)$
QL2	$A_{ln} \ln T + \frac{A_{-1}}{T} + A_0 + A_2 T^2$	$R(-A_{-1} + A_{ln}T + 2A_2T^3)$	$R(A_{ln} + 6A_2T^2)$
QL6	$A_{ln} \ln T + \frac{A_{-1}}{T} + A_0 + A_6 T^6$	$R(-A_{-1} + A_{ln}T + 6A_6T^7)$	$R(A_{ln} + 42A_6T^6)$
Q12	$\frac{A_{-1}}{T} + A_0 + A_1T + A_2T^2$	$R(-A_{-1} + A_1T^2 + 2A_2T^3)$	$2RT(A_1 + 3A_2T)$
QL12	$A_{ln} \ln T + \frac{A_{-1}}{T} + A_0 + A_1T + A_2T^2$	$R(-A_{-1} + A_{ln}T + A_1T^2 + 2A_2T^3)$	$R(A_{ln} + 2A_1T + 6A_2T^2)$
W25	$\ln p_c + \frac{T_c}{T}(A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^5)$	$-RT\left[A_1 + 1.5A_2\tau^{0.5} + 2.5A_3\tau^{1.5} + 5\tau^4 + \ln\left(\frac{p_{sat}}{p_c}\right)\right]$	$R\frac{T}{T_c}(0.75A_2\tau^{-0.5} + 3.75A_3\tau^{0.5} + 20A_4\tau^3)$
W36	$\ln p_c + \frac{T_c}{T}(A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6)$	$-RT\left[A_1 + 1.5A_2\tau^{0.5} + 3A_3\tau^2 + 6\tau^5 + \ln\left(\frac{p_{sat}}{p_c}\right)\right]$	$R\frac{T}{T_c}(0.75A_2\tau^{-0.5} + 6A_3\tau + 30A_4\tau^4)$
C3b	$\ln p_b + \left(1 - \frac{T_b}{T}\right)\exp(A_0 + A_1T + A_2T^2)$	$R[T_b + (T - T_b)(A_1T + A_2T^2)]\exp(A_0 + A_1T + A_2T^2)$	$RT\exp(A_0 + A_1T + A_2T^2)$ $[2A_1 + 4A_2T + (T - T_b)(2A_2 + (A_1 + 2A_2)^2)]$
C4b	$\ln p_b + \left(1 - \frac{T_b}{T}\right)\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$	$R[T_b + (T - T_b)(A_1T + A_2T^2 + A_3T^3)]$ $\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$	$RT\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$ $[2A_1 + 4A_2T + 6A_3T + (T - T_b)(2A_2 + 6A_3T + (A_1 + 2A_2 + 6A_3T^2)^2)]$
C3c	$\ln p_c + \left(1 - \frac{T_c}{T}\right)\exp(A_0 + A_1T + A_2T^2)$	$R[T_c + (T - T_c)(A_1T + A_2T^2)]\exp(A_0 + A_1T + A_2T^2)$	$RT[\exp(A_0 + A_1T + A_2T^2)$ $[2A_1 + 4A_2T + (T - T_c)(2A_2 + (A_1 + 2A_2)^2)]$
C4c	$\ln p_c + \left(1 - \frac{T_c}{T}\right)\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$	$R[T_c + (T - T_c)(A_1T + A_2T^2 + A_3T^3)]$ $\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$	$RT\exp(A_0 + A_1T + A_2T^2 + A_3T^3)$ $[2A_1 + 4A_2T + 6A_3T + (T - T_c)(2A_2 + 6A_3T + (A_1 + 2A_2 + 6A_3T^2)^2)]$

$\tau = 1 - T/T_c$.

Cox equation has been used frequently for data fitting, particularly in publications from the Bartlesville laboratory of the Bureau of Mines (today's NIPER). Due to its high flexibility the equation is useful for the correlation over a wide temperature range, and the ability of the three-parameter form to extrapolate toward low pressures was emphasized in the literature (Scott and Osborne, 1979).

Thermodynamic Background of the Data Correlation

Thermodynamic background for the temperature correlation of vapor pressures and the related thermal data has been described in the literature (Majer et al., 1989; Růžička and Majer, 1994; Růžička et al., 1994) and will be reviewed only briefly here. The parameters of a selected correlation equation can be determined by minimizing a general objective function:

$$S = \sum_{i=1}^{t} \frac{(\ln p_{\text{sat}}^{\text{exp}} - \ln p_{\text{sat}}^{\text{sm}})_i^2}{\sigma_i^2 \ln p_{\text{sat}}} + K_H^2 \sum_{j=1}^{u} \frac{(\Delta H'^{\text{exp}} - \Delta H'^{\text{sm}})_j^2}{\sigma_j^2 \Delta H'} + K_C^2 \sum_{k=1}^{v} \frac{(\Delta C'^{\text{exp}} - \Delta C'^{\text{sm}})_k^2}{\sigma_k^2 \Delta C'} \quad (6)$$

The three individual sums correspond to the contribution of vapor pressures, enthalpies of vaporization, and heat-capacity differences; indices t, u, v indicate the number of data points for each property. In the case when $u = v = 0$, the preceding equation reduces to the common formula for the weighted least squares fitting of vapor pressures alone; K_H, K_C are the factors allowing one to modify the weight of the thermal properties in the correlation—their values differ from unity when the number of data points for individual properties is disproportional or when some data inconsistency is observed. The variances $\sigma^2 \ln p_{\text{sat}}$, $\sigma^2 \Delta H'$, and $\sigma^2 \Delta C'$ are estimated from the expected errors of experimental data points.

The quantities with the superscript "sm" are expressed from the selected vapor-pressure equation ($P_{\text{sat}}^{\text{sm}}$); the quantities $\Delta H'^{\text{sm}}$ and $\Delta C'^{\text{sm}}$ are given by equations

$$\Delta H' = RT^2 \left(\frac{d \ln p}{dT} \right)_{\text{sat}} = -R \left(\frac{d \ln p}{d(1/T)} \right)_{\text{sat}} \quad (7)$$

and

$$\Delta C' = R \left[\frac{d}{dT} T^2 \left(\frac{d \ln p}{dT} \right) \right]_{\text{sat}} = 2RT \left(\frac{d \ln p}{dT} \right)_{\text{sat}} + RT^2 \left(\frac{d^2 \ln p}{dT^2} \right)_{\text{sat}} \quad (8)$$

The expressions for $\Delta H'$ and $\Delta C'$ corresponding to the tested forms of Eqs. 2 to 5 are listed in Table 1. Simple polynomials result from the quasi-polynomial equations, while expressions obtained from the Wagner and Cox equations are much more complex. When passing from the expression for p_{sat} to that for $\Delta C'$, the number of adjustable parameters is reduced by two for all quasi-polynomial equations, by one for the Antoine and Wagner equations, and remains unchanged for the Cox equations. This can play a role in the simultaneous fitting of vapor pressures and the thermal data in the cases where the temperature variation of $\Delta C'$ is complex, and hence a flexible relationship is required for its description.

The quantities with the superscript "exp" relate to experimental vapor pressures ($P_{\text{sat}}^{\text{exp}}$) and thermal data. Considering the form of Eqs. 7 and 8, $\Delta H'^{\text{exp}}$ and $\Delta C'^{\text{exp}}$ can be calculated from ΔH_{vap} and ΔC_{vap}^0 as follows:

$$\Delta H' = \frac{\Delta H_{\text{vap}}}{1 + \frac{p_{\text{sat}}}{RT}(B - V^0)}, \quad (9)$$

$$\Delta C' = \Delta C_{\text{vap}}^0 - T p_{\text{sat}} \frac{d^2 B}{dT^2} - 2T \frac{d(B - V^0)}{dT} \left(\frac{dp}{dT} \right)_{\text{sat}} - T(B - V^0) \left(\frac{d^2 p}{dT^2} \right)_{\text{sat}}, \quad (10)$$

where B is the second virial coefficient and the pressure dependence of the molar volume V^0 is neglected. For ideal gas behavior, $\Delta H'$ and $\Delta C'$ are equal to ΔH_{vap} and ΔC_{vap}^0, respectively. This means that at sufficiently low pressures the primed quantities and the thermal data are practically identical and the importance of the pVT correction terms is increasing with increasing vapor pressure. At the normal boiling temperature, the quantities $\Delta H'$ and $\Delta C'$ differ from ΔH_{vap} and ΔC_{vap}^0 typically by about 5 and 40%, respectively. The possibilities of accurately determining the pVT correction terms in Eqs. 9 and 10 are limited for most compounds. In order to avoid distortion of the correlation through uncertainty in estimating the vapor nonideality, it is necessary to confine thermal data to the region where correction terms are not important, that is, $T < T_b - 40$ and $T < T_b - 80$ for ΔH_{vap} and ΔC_{vap}^0, respectively.

Methodology of Testing Extrapolation Capabilities of Vapor-Pressure Equations

The objective of this test was to determine the possibilities of the different equations being used to extrapolate from the medium-pressure range in the direction of the triple point under the two different regimes:

(a) Extrapolation using the parameters of a vapor-pressure equation determined from the p_{sat} data in the medium-pressure range alone (denoted as "simple extrapolation")

(b) Extrapolation using the parameters of a vapor-pressure equation determined by a simultaneous correlation of the p_{sat} data in the medium-pressure range and the heat-capacity differences ΔC_{vap}^0 relating to lower temperatures (denoted as "controlled extrapolation"). Extrapolations using ΔH_{vap} as an input quantity were not tested because little calorimetric data were available in the low vapor-pressure range.

Three types of tests were performed for the selected groups of organic compounds:

1. The vapor pressures in the medium-pressure range were first correlated alone and subsequently simultaneously with the heat-capacity differences. Comparison of deviations

in both types of correlation allows one to evaluate the ability of an equation to fit both vapor pressure and thermal data satisfactorily (Table 2).

2. Simple and controlled extrapolation of the data from the medium-pressure range was performed to obtain the temperature corresponding to $p_{sat} = 1$ Pa, and the results were compared with the "best" values derived from the literature. In those cases where the vapor pressure at the triple point is higher than 1 Pa, the comparison was performed at T_t (Table 3 and Appendix B).

3. The enthalpy of vaporization at 298.15 K for higher boiling compounds was calculated using simple and controlled extrapolation of the data in the medium-pressure range, and comparison with the "best" literature values was carried out (Table 4 and Appendix C). ΔH_{vap} at 298.15 K is often required in applications, and it is interesting to examine the reliability of its determination from the extrapolated vapor pressures. In addition, the amount of reliable vapor-pressure measurements at low pressures is highly limited, and the use the ΔH_{vap} at 298.15 K as a tested quantity allows one to perform tests for a larger number of compounds.

To make extrapolations for individual compounds comparable, the data in the medium-pressure range were considered in all tests only at temperatures where $p_{sat} > 10$ kPa. Our policy was to work primarily with highly reliable input data in order to see what the limits of individual equations are for the ideal case. Subsequently, we have also tried to get some feeling for how the uncertainty in vapor pressures and the thermal data can influence the results of extrapolation.

Database

To perform the preceding tests it was necessary to establish a database of substances where the needed data were available. This was an intricate task; to include a compound in the data base, the following requirements had to be fulfilled simultaneously:

(a) Reliable data must be available for vapor pressures near $p_{sat} = 1$ Pa and/or for the enthalpy of vaporization at temperature of 298.15 K (or in its close vicinity). This temperature must be well below the lower temperature limit of the data used in the medium-pressure range.

(b) High-quality vapor pressures must be available in the medium-pressure range.

(c) Spectroscopic heat capacities of an ideal gas and calorimetric heat capacities of liquid must be available at temperatures corresponding to low p_{sat}. As the spectroscopic C_p^0 data are usually tabulated at temperatures starting near 273.15 K, it is mainly the high boiling compounds that may be selected.

The number of substances satisfying all three criteria is limited. In order to better distinguish how the correlation equations perform for different types of compounds, we have performed the tests on three distinct groups of substances.

Selected polar and nonpolar compounds (a1 and a2)

This group covers a variety of polar and nonpolar organic structures and consists of two subgroups: (a1) substances for which reliable p_{sat} data in the low-pressure range were available; and (a2) higher boiling compounds where good calorimetric ΔH_{vap} values are available near the room temperature. There are no identical substances in the two subgroups with the exception of 2-methylheptane, 3,4-dithiahexane, and ethylbenzene, for which both experimental p_{sat} and ΔH_{vap} are available with good accuracy in the low-pressure range.

(a1) A total of 17 compounds was selected for testing the extrapolation from the medium-pressure range to a temperature corresponding to $p_{sat} = 1$ Pa or T_t. The corresponding temperature (or pressure) were determined from the Cox equation with three adjustable parameters that were determined by fitting together the data in the low- and medium-pressure range selected from the literature. We have used only those sources of experimental p_{sat} data in the low-pressure range where the occurrence of systematic errors was not likely. For that reason, the choice of the experimental data at low pressures was limited to those obtained primarily by the static method in the laboratories reputed to carry out highly reliable vapor-pressure measurements: the Bartlesville Laboratory of the Bureau of Mines—later NIPER, USA (11 substances); the National Bureau of Standards, USA (1 substance); the National Physical Laboratory in Teddington, UK (4 substances); and the University of Utrecht, Netherlands (1 substance). It was necessary in some cases to extrapolate toward lower temperatures, as the experimental data for most test substances start above the temperature used in the test. However, this procedure should not increase the error in the data significantly; the extrapolation interval was short (usually less than 40 K) compared to the overall temperature interval where the experimental vapor pressures were included in the correlation (typically over 150 K). In the case of the three phenolic compounds, the experimental p_{sat} data are available for the vapor–solid equilibria close to and below the triple-point temperature T_t to which they were extrapolated (by less than 6 K). We believe that the "best" data obtained by this procedure are reliable to better than 5% at $p_{sat} = 1$ Pa and to better than 3% for compounds where p_{sat} at the triple-point temperature is larger than 1 Pa.

(a2) A total of 32 compounds was selected to test calculation of ΔH_{vap} by extrapolating vapor pressures to 298.15 K. For these compounds reliable calorimetric values were available in the literature and usually showed an error below 0.5%; all the recommended data for ΔH_{vap} were taken from the compilation by Majer and Svoboda (1985).

In both groups a1 and a2 reliable vapor pressures in the medium-pressure range were used with typical uncertainty around 0.01% in p_{sat} near T_b. The values of C_p^l (estimated error below 1%) were generated from cubic splines using parameters taken from the monograph by Zábranský et al. (1996). For most compounds the source of ideal gas heat capacities was the compilation of Bureš et al. (1992), where the recommended data are listed starting with a temperature of 273.15 K. The TRC Thermodynamic Tables were used for those compounds where the C_p^0 data were needed at lower temperatures. In all cases, a five-parameter equation (Bureš et al., 1981) was used for the analytical description of the C_p^0 data as a function of temperature. More detailed information regarding input data for the individual polar and nonpolar compounds is given in Appendix A.

n-Alkanes and 1-alkanols (groups b and c)

The groups b and c cover 10 *n*-alkanes (C_7 to C_{16}) and 8

1-alkanols (C_2 to C_{12}), respectively; they were included as two separate groups for their importance and specific behavior. In addition it was also possible to examine how the reliability of extrapolation evolves in a homologous series of compounds. This was particularly visible in tests with ΔH_{vap} at 298.15 K, where the extrapolation interval increases with the increasing length of the hydrocarbon chain. All the tests used the data from the review articles by Růžička and Majer (1994, 1996), where the recommended values resulted from the simultaneous treatment of vapor pressures and the thermal data with a special effort to achieve a consistency within a homologous series. Only a concise description of the data sources is given in the following paragraph, since detailed information is available in the reviews by Růžička and Majer (1994, 1996).

For the groups of *n*-alkanes the recommended vapor pressures are based mainly on the measurements performed in the medium-pressure range at the National Bureau of Standards (Willingham et al., 1945; Forziati et al., 1949; Camin et al., 1954; Camin and Rossini, 1955), except for *n*-decane, where the NIPER data from the Bartlesville laboratory (Chirico et al., 1989b) were preferred covering both low and medium pressures. For *n*-alkanes C_{11} and higher, data in the medium-pressure range were complemented by the measurements performed in the low-pressure range from the University of Lyon, France (Allemand et al., 1986a,b; Sasse et al., 1988; Jose, 1993). In the case of 1-alkanols the p_{sat} data from the National Physical Laboratory in Teddington (Ambrose and Sprake, 1970; Ambrose et al., 1974) were used, covering both the low- and medium-pressure range. The recommended vapor-pressure data for both groups of compounds were also affected to some extent by inclusion of the thermal data selected from the same sources as for the groups (a). Three- and four-parameter Cox equations were used for obtaining the recommended data. According to our analysis, the "best" data used for tests at $p_{sat} = 1$ Pa are reliable in most cases to 5% (for *n*-decane to 2%). The best ΔH_{vap} values at 298.15 K have errors of less than 1%.

For all tested compounds the method proposed by Tsonopoulos (1974) was used for estimating the vapor nonideality terms in Eqs. 9 and 10. Use of this the method required knowledge of critical temperatures and pressures that were also needed as parameters in some correlation equations (W25, W36, C3c, and C4c). All the T_c and p_c values were taken from the databank of thermodynamic quantities CDATA (1993). In Eqs. C3b and C4b the correlation results were practically identical when using the normal boiling temperature T_b as an adjustable parameter, or with a fixed value consistent with the data in the medium-pressure range.

Results of Tests and Discussion

The global results of the equation tests are presented for the groups of compounds a1, a2, b and c in Tables 2 to 4. All results were obtained by averaging over all the compounds in the group, while a specific information for each particular compound can be found in Appendices B and C.

Ability of equations to fit vapor pressures and heat-capacity differences

Table 2 gives quantitative comparison regarding performance of the tested equations in correlating vapor-pressure data in the medium-pressure range alone, and simultaneously with the heat capacity data. The listed values, $\bar{d}_w$, were calculated from the average weighted deviations of correlation d_w defined as

$$d_w = \left(\frac{\sum_{i=1}^{n_x} [(X^{exp} - X^{sm})/\sigma^2 X]_i^2}{n_x} \right)^{1/2}, \qquad (11)$$

Table 2. Average Weighted Deviation of Correction $\bar{d}_w$ (Eq. 11) for p_{sat} and ΔC^0_{vap}

	$\bar{d}_w$											
	ANT	QL1	QL2	QL6	Q12	QL12	W25	W36	C3b	C4b	C3c	C4c
	a1. Polar/Nonpolar Compounds ($\Delta\bar{T}$ = 78 K, $\Delta\bar{T}$ = *201K*)											
p_{sat}	1.40	0.76	0.75	0.76	0.75	0.93	0.76	0.76	0.75	0.66	1.11	0.76
p_{sat}	*78.7*	*1.01*	*0.87*	*1.94*	*1.44*	*0.95*	*0.93*	*0.96*	*0.96*	*0.86*	*2.44*	*0.91*
ΔC^0_{vap}	*252.0*	*1.44*	*0.87*	*3.19*	*1.83*	*0.14*	*0.73*	*0.66*	*0.90*	*0.19*	*7.51*	*0.60*
	a2. Polar/Nonpolar Compounds ($\Delta\bar{T}$ = 62 K, $\Delta\bar{T}$ = *144 K*)											
p_{sat}	0.66	0.49	0.49	0.48	0.48	0.48	0.49	0.49	0.48	0.44	0.59	0.49
p_{sat}	*31.3*	*0.86*	*0.85*	*1.17*	*0.94*	*0.53*	*0.76*	*0.72*	*0.86*	*0.52*	*1.51*	*0.72*
ΔC^0_{vap}	*68.3*	*0.40*	*0.35*	*0.93*	*0.71*	*0.14*	*0.23*	*0.20*	*0.37*	*0.16*	*5.76*	*0.17*
	b. *n*-Alkanes ($\Delta\bar{T}$ = 75 K, $\Delta\bar{T}$ = *222 K*)											
p_{sat}	0.48	0.35	0.34	0.31	0.32	0.29	0.35	0.34	0.33	0.27	0.35	0.37
p_{sat}	*113.0*	*0.50*	*0.35*	*2.31*	*1.32*	*0.37*	*0.37*	*0.36*	*0.46*	*0.39*	*0.91*	*0.41*
ΔC^0_{vap}	*130.0*	*0.26*	*0.27*	*3.89*	*2.94*	*0.13*	*0.31*	*0.24*	*0.73*	*0.21*	*1.13*	*0.36*
	c. 1-Alkanols ($\Delta\bar{T}$ = 60 K, $\Delta\bar{T}$ = *211 K*)											
p_{sat}	3.27	0.20	0.20	0.21	0.20	0.20	0.21	0.21	0.20	0.20	1.07	0.21
p_{sat}	*916*	*3.03*	*2.61*	*2.10*	*3.41*	*0.66*	*2.92*	*3.20*	*3.90*	*0.69*	*53.9*	*2.98*
ΔC^0_{vap}	*460*	*7.93*	*6.96*	*5.18*	*11.9*	*0.39*	*8.74*	*10.6*	*11.3*	*0.64*	*59.3*	*9.68*

$\Delta\bar{T}$ corresponds to the temperature range of correlation. Values of $\bar{d}_w$ and $\Delta\bar{T}$ were obtained by averaging over all substances in the group; the values in italics correspond to the simultaneous fitting of p_{sat} and ΔC^0_{vap} data.

Table 3. Vapor Pressures at the Temperature Corresponding to $p_{sat} = 1$ Pa or the Triple-Point Temperature (Whichever Is Higher): Simple vs. Controlled Extrapolation

	$\bar{d}_r$ (%)											
	ANT	QL1	QL2	QL6	Q12	QL12	W25	W36	C3b	C4b	C3c	C4c
a1. Pol./Nonpol.	22.8	7.5	6.9	8.4	7.9	47.4	9.6	11.9	7.2	30.1	4.5	10.
$\Delta\bar{T} = 124$ K	*21.6*	*2.7*	*2.6*	*6.0*	*5.2*	*3.4*	*2.3*	*2.4*	*3.2*	*3.3*	*3.5*	*2.2*
b. n-Alkanes	33.7	5.0	2.8	12.2	8.4	114.7	5.3	6.0	3.7	63.5	3.1	5.3
$\Delta\bar{T} = 140$ K	*50.4*	*3.6*	*0.9*	*8.9*	*7.3*	*3.8*	*1.7*	*1.7*	*1.4*	*3.4*	*0.7*	*0.9*
c. 1-Alkanols	63.6	18.1	15.6	12.9	12.0	15.1	16.5	20.8	16.8	17.2	24.5	16.0
$\Delta\bar{T} = 125$ K	*54.8*	*12.0*	*10.5*	*9.4*	*8.6*	*2.7*	*13.2*	*13.8*	*11.6*	*2.8*	*7.2*	*13.0*

$\bar{d}_r$ is the percent deviation, $\Delta\bar{T}$ is the extrapolation interval. Values of $\bar{d}_r$ and $\Delta\bar{T}$ were obtained by averaging over all substances in the group; the values in italics correspond to the simultaneous fitting of p_{sat} and ΔC^0_{vap} data.

where n_x is the overall number of data points for a given property X (p_{sat} or ΔC^0_{vap}) and the variance $\sigma^2 X_i$ is estimated as the squared expected error σX_i of each experimental point used in the correlation [$\sigma^2 X_i = (\sigma X_i^{exp})^2$]. The values of $d_w \leq 1$ correspond to an adequate fit within the expected error limits of experimental data. By comparing d_w values for p_{sat} in the simple and simultaneous correlation one can obtain quantitative information to determine to what extent the inclusion of the thermal data affects the fit of the high-precision vapor pressures in the medium-pressure range. We can also expect that the equation will fail in extrapolating vapor pressures toward the triple point for those cases where $\bar{d}_w$ is far above unity for the fit of ΔC^0_{vap}. To make the tests for individual compounds comparable the parameter K_c in Eq. 6 was always unity.

It is apparent from Table 2 that all equations (with the exception of the Antoine equation for 1-alkanols) represent adequately the vapor-pressure data in the medium-pressure range. In the simultaneous correlation most equations perform comparably for *n*-alkanes and two groups of polar and nonpolar compounds; the results are somewhat better in the group a2 compared to a1 due to the shorter temperature interval of correlation in the former group. The Antoine equation always fails in the simultaneous fitting, and its performance is clearly inferior to all other tested relationships. From the quasi-polynomial equations forms QL6 and Q12 do not represent the data satisfactorily, especially in the case of *n*-alkanes. The three-parameter Cox equation with the fixed critical point C3c is not sufficiently flexible to describe both p_{sat} and ΔC^0_{vap} data for polar and nonpolar substances.

For the group of 1-alkanols most equations fail in the simultaneous correlation. The reason is obviously a more complex temperature variation of heat-capacity difference for hydrogen-bonded liquids (Růžička and Majer, 1996) compared to nonpolar and slightly polar compounds where the function $C' = f(T)$ is only slightly curved (Ambrose and Davies, 1980) and close to a straight line for *n*-alkanes (King and Al-Najjar, 1974; Růžička and Majer, 1994). The only two equations that are flexible enough to simultaneously represent the p_{sat} and ΔC^0_{vap} data for 1-alkanols are the five-parameter relationship QL12 and the four-parameter Cox equation with the fixed normal boiling temperature C4b. The Cox equation with the fixed critical point C4c gives much less satisfactory results; it has lower flexibility compared to form C4b since it is constrained by T_c and p_c, which are far above the range of the fitted data. The same is true for both forms of the Wagner equation that behave for all groups of tested compounds similar to form C4c. An example for 1-octanol in Figure 1 illustrates the performance of different equations in describing $\Delta C'$ as a function of temperature for hydrogen-bounded compounds.

Performance of equations in simple and controlled extrapolation

Results of simple and controlled vapor-pressure extrapolation to a temperature corresponding to $p_{sat} = 1$ Pa (or T_t) are summarized in Table 3. Similarly, Table 4 presents the results of calculating ΔH_{vap} at 298.15 K from the extrapolated vapor pressures. In both tables the percent deviations of the extrapolated values from the recommended ones are pre-

Table 4. Enthalpies of Vaporization at 298.15 K: Simple vs. Controlled Extrapolation

	$\bar{d}_r$ (%)											
	ANT	QL1	QL2	QL6	Q12	QL12	W25	W36	C3b	C4b	C3c	C4c
a2. Pol./Nonpol.	2.2	1.1	1.0	1.1	1.1	3.7	1.2	1.3	1.1	3.8	0.9	1.2
$\Delta\bar{T} = 53$ K	*1.6*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*	*0.8*
b. n-Alkanes	7.1	0.8	0.4	1.7	1.1	17.6	0.9	1.0	0.5	12.7	0.3	0.8
$\Delta\bar{T} = 101$ K	*4.4*	*0.5*	*0.1*	*1.2*	*1.0*	*0.5*	*0.2*	*0.2*	*0.2*	*0.4*	*0.1*	*0.1*
c. 1-Alkanols	14.9	3.7	2.9	1.7	1.7	2.5	4.4	5.1	3.5	2.6	3.5	4.5
$\Delta\bar{T} = 80$ K	*5.5*	*1.1*	*0.9*	*1.0*	*0.8*	*0.4*	*1.3*	*1.4*	*1.0*	*0.4*	*0.5*	*1.3*

$\bar{d}_r$ is the percent deviation, $\Delta\bar{T}$ is the extrapolation interval. Values of $\bar{d}_r$ and $\Delta\bar{T}$ were obtained by averaging over all substances in the group; the values in italics correspond to the simultaneous fitting of p_{sat} and ΔC^0_{vap} data.

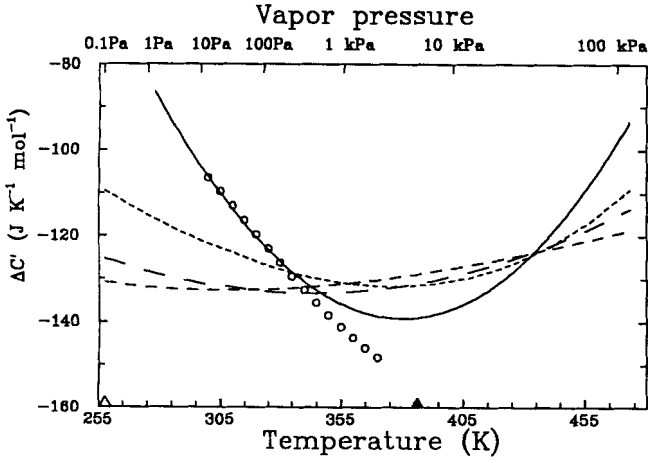

Figure 1. Variation of $\Delta C'$ with temperature for 1-octanol; calculation from Eq. 8 using different equations with parameters obtained by the simultaneous fitting of experimental p_{sat} and ΔC^0_{vap} data.

—— Eq. C4b; ---- Eq. C3b; ------ Eq. W25; —— Eq. Q12; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ▲ the lower limit of experimental p_{sat} data included in the correlation.

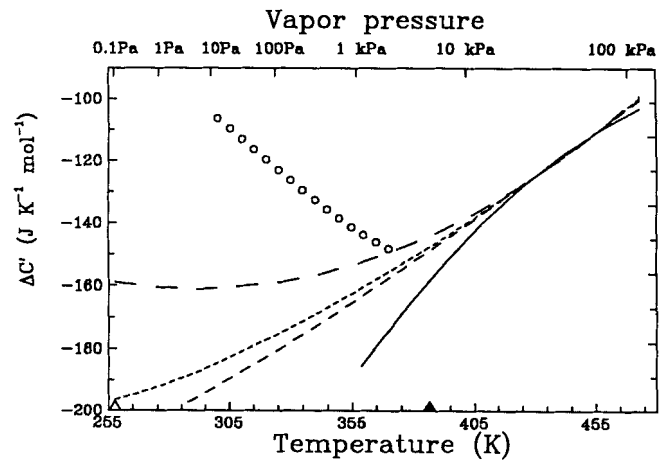

Figure 2. Variation of $\Delta C'$ with temperature for 1-octanol; calculation from Eq. 8 using different equations with parameters obtained by the fitting of the p_{sat} data in the medium pressure range alone.

—— Eq. C4b; ---- Eq. C3b; ------ Eq. W25; —— Eq. Q12; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ▲ the lower limit of experimental p_{sat} data included in the correlation.

sented averaged over the group of compounds. It is apparent that deviations in the ΔH_{vap} test are always lower due to generally shorter extrapolation intervals. As expected performance of the Antoine equation is again inferior compared to all other tested equations that extrapolate generally much better for groups of *n*-alkanes and polar and nonpolar compounds than for 1-alkanols.

Regarding the simple extrapolation, there are no substantial differences between individual equations except for the most flexible relationships QL12 and C4b, which obviously overfit vapor pressures in the medium-pressure range and fail completely in low-pressure predictions. For most equations the errors in extrapolated p_{sat} are below 10% for groups a1 and b and up to 20% in group c. For the calculation of ΔH_{vap} at 298.15 K the deviations are not important for groups a2 and b (usually below 1.5%) and do not exceed 5% for group c. For compounds other than 1-alkanols, the quasi-polynomial form QL2 and the three-parameter Cox equations C3b and C3c seem to give somewhat better results in the simple extrapolation than the other tested equations. The latter three-parameter equation is clearly superior to all four-parameter equations that also have the fixed critical point (W25, W36, and C4c); the higher number of parameters can be a handicap when extrapolating from vapor-pressure data in the medium-pressure range alone. In the simple extrapolation, none of the tested equations can predict adequately vapor-pressure data in the low-pressure range for 1-alkanols. This is also illustrated in Figure 2, showing to what extent the individual equations deviate in extrapolation from the real shape of the $\Delta C'$ function obtained in the low-pressure range from the thermal data.

In the controlled extrapolation, most tested relationships behave comparably for *n*-alkanes and polar and nonpolar compounds. Deviations are generally below 4% in the vapor-pressure tests and 1% in the enthalpy of vaporization tests; higher deviations were observed for the quasi-polynomial equations QL6 and Q12, which do not seem to be suitable for extrapolation toward low pressures. A good performance of the three-parameter Cox equation constrained by the critical point C3c is noticeable; a distortion of the input data observed in the simultaneous correlation (Table 2) does not seem to impair its extrapolation capability. For 1-alkanols, most equations do not give satisfactory results in the controlled extrapolation; deviations in p_{sat} are typically near 10%. Two exceptions are forms QL12 and C4b where errors in extrapolated data are usually below 3%; contrary to the simple extrapolation for which both forms are unsuitable, their high flexibility is clearly beneficial in the simultaneous fit for hydrogen-bonded compounds.

Effect of data quality on the extrapolation results

All test results presented in Tables 2 to 4 were obtained with substances where reliable vapor pressures in the medium-pressure range were available in the literature. The listed deviations indicate that except for 1-alkanols a properly chosen equation in a simple extrapolation can give values that are satisfactory for engineering applications. In *reality*, however, the input data are often unreliable, and it is interesting to examine how the quality of vapor pressures in the medium-pressure range affect the extrapolation and to what extent the use of thermal data can improve the accuracy of the extrapolated values. As an example, simple and controlled extrapolations for one *n*-alkane, two polar compounds, and one 1-alkanol are compared where input data of varying quality were available. Figures 3 to 6 present for these compounds the $\Delta C'$ function calculated as a function of temperature using different data sources; the Cox equation C3b

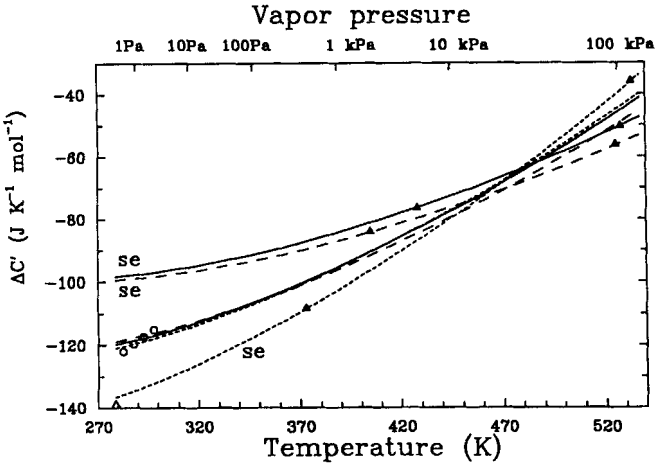

Figure 3. Variation of $\Delta C'$ with temperature for tetradecane; calculation from Eq. 8 using different vapor pressure sources.

—— Camin and Rossini (1955); ---- Kneisl and Zondlo (1987); —— Morgan and Kobayashi (1994); curves denoted "se" relate to simple extrapolation from the p_{sat} data in the medium-pressure range, all other curves correspond to the simultaneous correlation; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ▲ the lower and upper limits of the p_{sat} data included in the correlation.

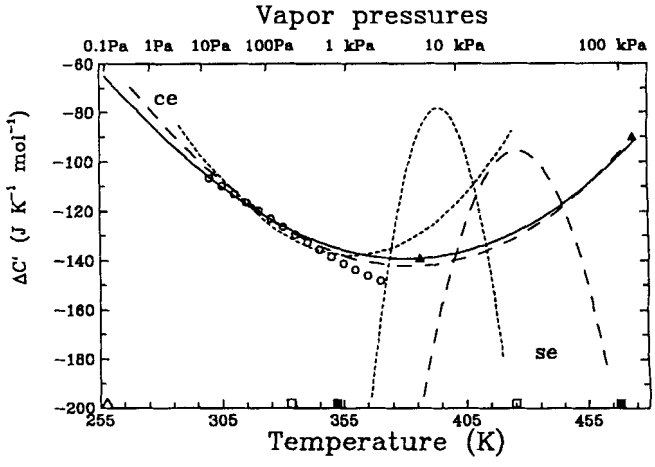

Figure 5. Variation of $\Delta C'$ with temperature for 1-octanol; calculation from Eq. 8 using different vapor pressure sources.

—— Ambrose and Sprake (1970); --- Butler et al. (1935); —— Kemme and Kreps (1969); curves denoted "se" relate to simple extrapolation from the p_{sat} data in the medium-pressure range alone, curves denoted "ce" correspond to the simultaneous correlation; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ▲, □, ■ the lower and upper limits of the p_{sat} data from the cited sources.

was used in tests for all compounds except 1-octanol where the correlation was performed with form C4b. A sound extrapolation can be expected when the $\Delta C'$ line calculated from Eq. 8 approaches the line obtained from the thermal data (Eq. 10) at low pressures.

For tetradecane (Figure 3) the high-quality vapor pressures from NBS by Camin and Rossini (1955) are compared with less reliable data by Kneisl and Zondlo (1987) and by Morgan and Kobayashi (1994). The errors in a simple extrapolation to a temperature corresponding to $p_{sat} = 1$ Pa are 1.4, 14.0, and

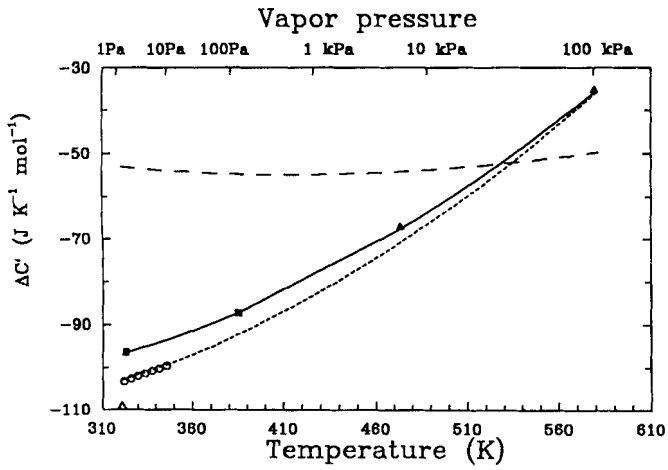

Figure 4. Variation of $\Delta C'$ with temperature for diphenyl methanone; calculation from Eq. 8 using different vapor pressure sources.

— combination of the p_{sat} data in the low- (de Kruif et al., 1983) and medium- (Dreisbach and Shrader, 1949) pressure ranges; ------ simultaneous correlation of the p_{sat} data in the medium-pressure range and ΔC^0_{vap} values at lower temperatures; —— simple extrapolation from the p_{sat} data in the medium-pressure range; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ■ the lower and upper limits of the p_{sat} data in the low-pressure range; ▲ the lower and upper limits of the p_{sat} data in the medium-pressure range.

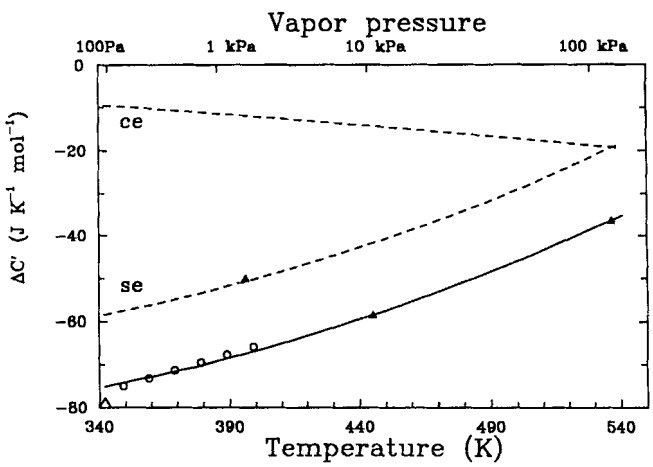

Figure 6. Variation of $\Delta C'$ with temperature for 1,1'-biphenyl; calculation from Eq. 8 using different vapor pressure sources.

—— Chirico et al. (1989a); --- curves denoted "se" and "ce" relate to the simple extrapolation from the p_{sat} data in the medium-pressure range alone, and to the simultaneous correlation, respectively (Nasir et al., 1980); curve denoted "se" relates to the simple extrapolation from the p_{sat} data in the medium-pressure range alone, curve denoted "ce" corresponds to the simultaneous correlation; ○ experimental ΔC^0_{vap}, identical with $\Delta C'$ from Eq. 10 within experimental errors; Δ triple-point temperature; ▲ the lower and upper limits of the p_{sat} data included in the correlation.

-7.6%, and they change in extrapolation controlled by the ΔC^0_{vap} data to -1.2, -4.6, and 0.7%, respectively.

For diphenyl methanone, $\Delta C'$ calculated from vapor pressures in the medium-pressure range (Dreisbach and Shrader, 1949) alone is compared in Figure 4 with the values obtained by including either reliable p_{sat} data at low pressures (de Kruif et al., 1983) or the thermal data. In the two latter cases the $\Delta C'$ lines are close to each other and the difference in p_{sat} at T_t is about 6%. On the other hand, the $\Delta C'$ line corresponding to simple extrapolation has a completely different orientation and the difference of the triple-point vapor pressure from the experimental value is about 34%.

For 1-octanol, Figure 5 compares the $\Delta C'$ line corresponding to the simultaneous correlation of high-quality p_{sat} data at medium pressures (Ambrose and Sprake, 1970) with the values obtained from the vapor-pressure sources of lower quality (Butler et al., 1935; Kemme and Kreps, 1969). It is obvious that both latter sources fail completely in the simple extrapolation where the differences from the recommended vapor-pressure data approach 100% near $p_{sat} = 1$ Pa. The simultaneous fitting with the ΔC^0_{vap} data allows a decrease in the error in the vapor pressure to 12.5 and 1.4%, respectively.

In the preceding three examples, the inclusion of thermal data always had a positive effect on the extrapolation results. This is not, however, generally the case; when the temperature derivatives of p_{sat} at medium pressures in Eq. 8 are completely incompatible at their lower temperature limit with the ΔC^0_{vap} data, the controlled extrapolation can be quite misleading. This behavior can be illustrated with an example for 1,1'-biphenyl. The highly precise vapor pressures in the medium-pressure range from the Bartlesville laboratory (Chirico et al., 1989a) are consistent with the experimental ΔC^0_{vap} data, and differ both in simple and controlled extrapolations by less than 1% from the recommended p_{sat} value at the triple point. On the other hand, the values obtained by the simple and controlled extrapolations using the data by Nasir et al. (1980) differ by 56 and 104%, respectively. The deterioration of extrapolation results after inclusion of thermal data is reflected by a completely erroneous temperature variation of $\Delta C'$ calculated from Eq. 8 (Figure 6). Severe consistency problems between the p_{sat} data at medium pressures and thermal data can be expected when the $\Delta C'$ line resulting from the simultaneous fit does not agree with that obtained from the heat capacities only.

Conclusions

The following conclusions can be made on the basis of the preceding test results.

Extrapolation of vapor pressures

When a suitable correlation equation is used (see below), a simple extrapolation of reliable vapor pressures in the medium-pressure range toward lower temperatures appears quite promising for nonpolar and polar compounds without specific interactions. However, for hydrogen-bonded compounds all correlation equations give poor results. For all types of compounds the simple extrapolation becomes generally very uncertain when only low-quality p_{sat} data are available in the medium-pressure range.

The inclusion of thermal data always improves extrapolated results when reliable input data are used. This is particularly true for hydrogen-bonded compounds where a highly flexible equation is necessary for a good description of vapor pressure and thermal data simultaneously. A controlled extrapolation should be used with caution when vapor pressures in the medium-pressure range are of uncertain quality. While inclusion of thermal data can be of substantial help in cases when the p_{sat} values are scanty and/or scattered, the reliability of extrapolation will not improve when the slope of experimental vapor pressures is completely erroneous and hence incompatible with the thermal data. For that reason, when working with uncertain sources, the simultaneous correlation is valuable primarily as a consistency test of vapor pressures and the related thermal data. Such a test allows one to evaluate whether a combination of different input data exists at all, for which the controlled extrapolation can be promising.

Extrapolation for determining enthalpy of vaporization

The enthalpy of vaporization at 298.15 K can be calculated from extrapolated vapor pressures with reasonable accuracy provided good-quality data are available and a suitable correlation equation is selected. For many high boiling compounds the extrapolation interval is below 100 K and the differences between simple extrapolation and that controlled by ΔC^0_{vap} data are not considerable for nonpolar and polar compounds without specific interactions. The controlled extrapolation brings an important improvement for high boiling hydrogen-bonded compounds and in most cases when a limited amount of vapor pressure data are used as the input. Generally speaking, the percent errors in the extrapolation of p_{sat} and ΔH_{vap} are comparable to an identical temperature. This means that the temperature derivative of the vapor pressure obtained in extrapolation is not subject to a significant higher error than the extrapolated p_{sat} value itself.

Type of vapor-pressure equation

The type of correlation equation used affects results of an extrapolation to a considerable extent; it is always necessary to select a relationship with an optimum number of adjustable parameters. While in a simple extrapolation using too many parameters can be dangerous due to overfitting of the vapor-pressure data, a highly flexible relationship is indispensable in the extrapolation controlled by the thermal data when temperature dependence of ΔC^0_{vap} is strongly nonlinear. For that reason, the five-parameter quasi-polynomial equation QL12 and the four-parameter Cox equation C4b should never be used in a simple extrapolation from the experimental data over a limited temperature range; these two equations are, on the other hand, very useful in the controlled extrapolation of vapor pressures for hydrogen-bonded compounds.

The Antoine equation clearly shows the poorest performance from all the tested equations; it fails for most types of compounds both in simple and controlled extrapolation and is not even able to describe adequately the p_{sat} data in the medium-pressure range for compounds with specific interactions. The Antoine equation has a very low flexibility and its use should always be abandoned when the temperature interval of correlation becomes large (say above 50 K) and any

kind of extrapolation is foreseen. The only effective way of using the Antoine equation is determination of two (or more) parameter sets, corresponding to different temperature intervals, with forced continuity of p_{sat} and its first temperature derivative at the boundaries (*TRC Thermodynamic Tables*).

Regarding the four-parameter quasi-polynomial equations tested in this study, the form QL2 should be preferred while the Riedel equation QL6 and the Cragoe equation Q12 should be avoided. All five tested forms are unreliable when used on alkanols.

The Wagner equations require the use of critical parameters that provide for the realistic prediction of the vapor-pressure saturation line up to the critical temperature. However, this constraint limits the flexibility of the relationship in low-pressure extrapolations and is both useless and inconvenient for high boiling chemicals that decompose below or near the normal boiling temperature.

The Cox equations can be considered to be the most useful equations for extrapolations toward low pressures; the possibility of changing both the number of parameters and the reference condition T_0 and p_0 allows one to obtain different forms suitable for particular applications. The three-parameter form with the normal boiling point C3b is very dependable in both simple and controlled extrapolation for all organic liquids with the exception of hydrogen-bonded compounds. In the latter case, the four-parameter equation C4b gives very good results for extrapolation when vapor pressures and the thermal data are fitted simultaneously. For compounds decomposing below the normal boiling temperature, a vapor pressure corresponding to a lower temperature can always be used as a reference condition. On the other hand, the use of the critical point allows one to transform the Cox equations into a relationship suitable for description of the complete vapor pressure line. The form C4c is comparable to the Wagner equation and behaves similarly in correlation and extrapolation toward low pressures.

It should be kept in mind that it is highly dangerous to use flexible equations with more than three parameters in extrapolations when the experimental data are scanty and/or of low quality.

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Appendix A

Table A1. Summary of Data Sources for Polar/Nonpolar Compounds

Compound	CAS Reg. No.	Heat Capacities: No. of Pts.	Heat Capacities: T_{min} K	Heat Capacities: T_{max} K	Vapor Pressures*: No. of Pts.	Vapor Pressures*: T_{min} K	Vapor Pressures*: T_{max} K	Vapor Pressures*: p_{min} Pa	Vapor Pressures*: p_{max} Pa	References
a1: Vapor Pressure Tests										
2-Methylheptane	592-27-8	6	200.0	250.0	11	233.2	283.1	2.5E+1	1.2E+3	Osborn and Douslin, 1974
					28	314.8	391.7	6.4E+3	1.0E+5	Willingham et al., 1945
3-Methylheptane	589-81-1	6	200.0	250.0	11	238.2	288.1	3.7E+1	1.5E+3	Osborn and Douslin, 1974
					30	315.8	392.9	6.4E+3	1.0E+5	Willingham et al., 1945
2-Methyldecane	6975-98-0	6	236.0	286.0	9	273.1	293.1	1.1E+1	5.8E+1	Osborn and Douslin, 1974
					14	386.0	462.3	9.6E+3	1.0E+5	Osborn and Douslin, 1974
Ethylbenzene	100-41-4	6	180.0	230.0	16	273.1	296.6	2.6E+2	1.2E+3	Scott and Brickwedde, 1945
					16	339.2	416.0	9.6E+3	1.2E+5	Osborn and Scott, 1980
1,1'-Biphenyl	92-52-4	6	349.0	399.0	13	350.0	410.0	1.5E+2	2.9E+3	Chirico et al., 1989a
					19	400.8	536.6	2.0E+3	1.2E+5	Chirico et al., 1989a
Isoquinoline	119-65-3	6	299.0	349.0	12	313.1	403.1	2.7E+1	3.5E+3	Steele et al., 1988
					16	430.5	524.5	9.6E+3	1.2E+5	Steele et al., 1988
Quinoline	91-22-5	6	275.0	325.0	19	298.1	385.6	1.1E+1	2.0E+5	Steele et al., 1988
					16	425.3	518.3	9.6E+3	1.2E+5	Steele et al., 1988
Phenol†	108-95-2	6	313.0	353.0	1	314.0		1.8E+2		Biddiscombe and Martin, 1958
					32	394.3	455.3	1.4E+4	1.0E+5	Biddiscombe and Martin, 1958
2-Methylphenol†	95-48-7	6	304.0	354.0	1	304.1		7.0E+1		Biddiscombe and Martin, 1958
					24	411.7	465.5	2.0E+4	1.0E+5	Biddiscombe and Martin, 1958
3-Methylphenol	108-39-4	6	285.0	335.0	12	284.1	312.2	6.8E+0	5.8E+1	Biddiscombe and Martin, 1958
					25	409.0	476.9	1.2E+4	1.1E+5	Biddsicombe and Martin, 1958
4-Methylphenol†	106-44-5	6	307.0	357.0	1	307.8		4.0E+1		Biddiscombe and Martin, 1958
					22	397.3	476.1	7.5E+3	1.0E+5	Biddiscombe and Martin, 1958
Diphenyl methanone	119-61-9	7	322.0	346.0	25	323.0	385.6	1.6E+0	1.3E+2	de Kruif et al. 1983
					8	473.6	579.2	6.3E+3	1.0E+5	Dreisbach and Shrader, 1949
Dibenzofuran	132-64-9	6	361.0	411.0	14	358.1	433.1	9.0E+1	3.1E+3	Chirico et al., 1990
					16	465.6	567.0	9.6E+3	1.2E+5	Chirico et al., 1990
3,4-Dithiahexane	110-81-6	4	273.0	303.0	15	273.1	353.1	1.0E+2	9.1E+3	Osborn and Douslin, 1966
					10	373.7	434.0	2.0E+4	1.2E+5	Osborn and Douslin, 1966
1-Heptanethiol	1639-09-4	6	273.0	323.0	8	273.1	293.1	2.8E+1	1.3E+2	Osborn and Douslin, 1966
					16	374.8	457.2	9.6E+3	1.2E+5	Osborn and Douslin, 1966
Benzo[*b*]thiophene	95-15-8	6	300.0	350.0	8	310.0	380.0	6.6E+1	2.9E+3	Chirico et al., 1991b
					19	371.3	501.9	2.0E+3	1.2E+5	Chirico et al., 1991b
Dibenzothiophene	132-65-0	6	377.0	427.0	12	375.0	470.0	4.1E+1	3.2E+3	Chirico et al., 1991a
					19	457.2	614.0	2.0E+3	1.2E+5	Chirico et al., 1991a
a2: Enthalpy of Vaporization Tests										
2-Methylheptane	592-27-8	6	200.0	250.0	23	325.4	391.7	1.0E+4	1.0E+5	Willingham et al., 1945
Ethylcyclohexane	1678-91-7	3	273.0	293.0	17	335.8	405.9	1.0E+4	1.0E+5	Willingham et al., 1945
Propylcyclopentane	2040-96-2	6	273.0	323.0	17	336.0	405.0	1.0E+4	1.0E+5	Willingham et al., 1945
1-Octene	111-66-0	4	273.0	303.0	15	328.7	395.4	1.0E+4	1.0E+5	Forziati et al., 1950
1-Decene	872-05-9	6	273.0	323.0	14	371.7	444.7	1.0E+4	1.0E+5	Forziati et al., 1950
1-Dodecene	112-41-4	4	273.0	303.0	17	409.4	487.6	1.0E+4	1.0E+5	Forziati et al., 1950
1,4-Dimethylbenzene	106-42-3	6	288.0	308.0	15	344.0	418.2	1.1E+4	1.2E+5	Osborn and Douslin, 1974
Ethylbenzene	100-41-4	6	180.0	230.0	15	342.2	416.0	1.1E+4	1.2E+5	Osborn and Scott, 1980
1-Fluoro-4-methylbenzene	352-32-9	6	273.0	323.0	10	340.8	396.1	2.0E+4	1.2E+5	Scott et al., 1962
1,2-Ethanediamine	107-15-3	6	293.0	343.0	14	335.1	395.7	1.2E+4	1.2E+5	Messerly et al., 1975
Butanenitrile	109-74-0	6	273.0	323.0	11	332.9	395.0	1.4E+4	1.1E+5	Meyer and Hotz, 1973
Pyridine	110-86-1	6	273.0	318.0	10	340.4	394.5	2.0E+4	1.2E+5	Osborn and Douslin, 1968
2-Methylpyridine	109-06-8	6	273.0	323.0	10	352.9	408.9	2.0E+4	1.2E+5	Osborn and Douslin, 1968
3-Methylpyridine	108-99-6	6	273.0	323.0	15	350.2	423.9	1.1E+4	1.2E+5	Osborn and Douslin, 1968
4-Methylpyridine	108-89-4	6	283.0	318.0	15	351.3	425.1	1.1E+4	1.2E+5	Osborn and Douslin, 1968
2,3-Dimethylpyridine	583-61-9	6	258.0	308.0	22	372.7	435.6	1.5E+4	1.0E+5	Coulson et al., 1959
2,4-Dimethylpyridine	108-47-4	6	248.0	298.0	25	363.4	433.0	1.1E+4	1.1E+5	Coulson et al., 1959
3,5-Dimethylpyridine	591-22-0	6	266.0	316.0	21	382.7	445.9	1.5E+4	1.0E+5	Coulson et al., 1959
Methoxybenzene	100-66-3	6	304.0	324.0	15	383.0	433.1	2.7E+4	1.2E+5	Collerson et al., 1965
Cyclopentanol	96-41-3	4	275.0	299.0	13	358.6	414.3	1.2E+4	1.0E+5	Ambrose and Ghiassee, 1987
Cyclohexanol	108-93-0	4	297.0	332.0	15	375.2	439.9	1.2E+4	1.2E+5	Ambrose and Ghiassee, 1987
Cyclopentanone	120-92-3	1	298.2		11	339.8	409.2	1.1E+4	1.2E+5	Meyer and Hotz, 1976
					13	342.2	407.3	1.3E+4	1.1E+5	Ambrose and Ghiassee, 1987
Cyclohexanone	108-94-1	3	273.0	293.0	15	362.8	430.1	1.3E+4	1.1E+5	Meyer and Hotz, 1973
					13	360.6	428.8	1.2E+4	1.0E+5	Ambrose and Ghiassee, 1987
2-Hexanone	591-78-6	6	273.0	323.0	18	336.9	406.9	1.1E+4	1.2E+5	Ambrose et al., 1975
3-Hexanone	589-38-8	5	273.0	313.0	16	348.7	402.7	2.0E+4	1.2E+5	Collerson et al., 1965
2-Methoxyethanol	109-86-4	4	298.0	328.0	13	357.1	395.3	2.4E+4	9.5E+4	Dohnal and Novotná, 1996
3,4-Dithiahexane	110-81-6	6	273.0	303.0	10	373.7	434.0	2.0E+4	1.2E+5	Osborn and Douslin, 1966
1-(Methylthio)butane	628-29-5	6	273.0	323.0	10	346.9	403.0	2.0E+4	1.2E+5	Osborn and Douslin, 1966
2,2'-Thiobispropane	625-80-9	6	273.0	323.0	15	328.2	399.6	1.1E+4	1.2E+5	Osborn and Douslin, 1966
Nitromethane	75-52-5	6	273.0	323.0	10	328.8	380.1	2.0E+4	1.2E+5	McCullough et al., 1954

*Two references are given for the compounds used in vapor-pressure tests (*a1*), relating to the low- and medium-pressure ranges, respectively.
†Experimental data on sublimation pressures were extrapolated for determining the triple-point pressure.

Table A2. Parameters of the Cox Equation C3b for the Group of Polar/Nonpolar Compounds (*a1*)

Compound	A_0	$A_1 \times 10^3$	$A_2 \times 10^6$	T_0 (K)	p_0 (kPa)
2-Methylheptane	2.833146	−1.772199	1.6533900	390.778	101.325
3-Methylheptane	2.845814	−1.845088	1.7595290	392.047	101.325
2-Methyldecane	3.006981	−2.031933	1.7215000	462.329	101.325
Ethylbenzene	2.838919	−1.750831	1.6402190	409.310	101.325
1,1′-Biphenyl	2.933904	−1.460358	1.0177320	528.382	101.325
Isoquinoline	2.857368	−1.293496	0.9156198	516.348	101.325
Quinoline	2.866184	−1.358681	0.9998938	510.251	101.325
Phenol	3.041585	−1.611786	1.0448870	454.988	101.325
2-Methylphenol	3.103677	−2.050171	1.6059540	464.153	101.325
3-Methylphenol	3.102269	−1.843543	1.3193760	475.387	101.325
4-Methylphenol	3.144500	−1.973006	1.4218560	475.095	101.325
Diphenylmethanone	3.041900	−1.630197	1.1393050	579.195	101.325
Dibenzofuran	2.861700	−1.210425	0.7996136	558.268	101.325
3,4-Dithiahexane	2.867326	−1.760531	1.5919500	427.122	101.325
1-Heptanethiol	2.876240	−1.564468	1.2274450	450.064	101.325
Benzo[*b*]thiopene	2.833815	−1.339815	1.0009210	494.010	101.325
Dibenzothiophene	2.870847	−1.127660	0.6888106	604.570	101.325

Parameters are valid in the region between the triple and normal boiling points and were determined by correlating the p_{sat} data from the sources listed in Table A1.

Appendix B

The following two tables summarize the results of simple and controlled extrapolation of vapor pressures toward the temperature corresponding to $p_{sat} = 1$ Pa or the triple-point temperature (whichever is higher). d_r is the percent deviation of the extrapolated vapor pressure from the recommended value; T_e is the temperature corresponding to $p_{sat} = 1$ Pa and/or the triple-point temperature (in the latter case, the corresponding p_{sat} is listed after a slash as p_e); ΔT is the extrapolation interval (difference between the lower temperature limit of p_{sat} used in correlation and T_c). The values in italics correspond to the simultaneous fitting of p_{sat} and ΔC^0_{vap} data (controlled extrapolation).

Table B1. Vapor Pressures: Test Results with the Antoine and Quasipolynomial Equations

Compound	T_e/p_e K/Pa	ΔT K	d_r (%) ANT		QL1		QL2		QL6		Q12		QL12	
Polar/Nonpolar Compounds (*a1*)														
2-Methylheptane	204.67	120	−37.5	*23.8*	−22.4	*−4.9*	−17.8	*−7.9*	−4.6	*−16.9*	−9.7	*−15.6*	78.4	*−8.0*
3-Methylheptane	205.46	120	−35.7	*25.8*	−16.5	*−3.2*	−11.9	*−6.3*	0.9	*−15.5*	−3.8	*−14.2*	69.6	*−6.4*
2-Methyldecane	249.86	139	−32.2	*42.8*	5.1	*6.0*	9.5	*2.0*	21.7	*−9.6*	18.1	*−8.0*	−33.0	*6.7*
Ethylbenzene	214.31	127	−30.7	*64.9*	−6.0	*6.3*	*−1.6*	*1.7*	10.6	*−10.9*	6.7	*−12.0*	−16.0	*2.8*
1-1′-Biphenyl	342.10/92.6	102	−7.4	*−7.2*	−1.7	*−1.0*	−0.9	*−0.7*	1.4	*1.1*	0.6	*0.2*	0.0	*−0.4*
Isoquinoline	299.62/9.4	134	−17.9	*−11.8*	−0.5	*0.8*	1.0	*0.2*	5.2	*−0.1*	4.2	*−1.2*	19.0	*0.3*
Quinoline	271.25	157	−31.0	*−22.3*	6.5	*4.1*	9.0	*3.4*	15.5	*4.9*	15.0	*2.0*	87.8	*4.4*
Phenol	314.03/189.7	80	−11.4	*10.1*	3.6	*−1.3*	3.7	*−1.6*	4.1	*−2.8*	4.4	*−2.5*	104.4	*−2.1*
2-Methylphenol	304.20/69.5	107	−11.8	*12.4*	−7.1	*−0.8*	−5.5	*−1.7*	*−0.7*	*−5.1*	−2.9	*−3.8*	−4.7	*−3.8*
3-Methylphenol	285.40/5.9	123	−31.6	*42.0*	5.5	*1.6*	7.0	*0.1*	11.3	*−5.5*	11.0	*−4.4*	65.9	*−5.2*
4-Methylphenol	307.94/39.4	103	−16.9	*23.3*	2.9	*3.4*	3.8	*2.7*	6.5	*0.1*	5.9	*0.7*	21.8	*0.0*
Diphenylmethanone	321.03/1.4	152	−25.6	*41.3*	31.5	*−0.9*	31.7	*−4.2*	32.3	*−15.1*	35.4	*−12.3*	1471.*	*5.2*
Dibenzofuran	355.31/76.5	114	−7.2	*−6.6*	−1.7	*−0.6*	−0.9	*−0.6*	1.4	*0.4*	0.5	*−0.4*	−3.1	*−0.6*
3,4-Dithiahexane	225.00	148	−29.3	*8.2*	−1.3	*5.3*	3.6	*3.8*	17.2	*−1.4*	12.9	*0.5*	215.7	*3.3*
1-Heptanethiol	239.36	138	−41.7	*−10.4*	−9.2	*−4.9*	−5.3	*−6.2*	5.7	*−10.1*	2.6	*−9.4*	−32.2	*−5.9*
Benzo[*b*]thiophene	304.48/44.7	109	−9.5	*−5.0*	−3.1	*0.2*	−2.0	*−0.4*	1.2	*−1.2*	0.0	*−1.5*	−6.0	*−0.9*
Dibenzothiophene	371.82/34.3	136	−10.4	*−9.5*	−2.7	*−1.2*	−1.6	*−1.1*	1.7	*0.6*	0.5	*−0.6*	0.0	*−1.0*
***n*-Alkanes (*b*)**														
Heptane	194.47	114	−30.9	*45.1*	−5.5	*3.3*	−1.2	*1.7*	10.7	*−3.1*	6.8	*−2.4*	−5.0	*1.9*
Octane	216.37/2.0	116	−26.7	*19.6*	−2.0	*1.5*	1.1	*0.4*	10.0	*−3.5*	7.4	*−2.4*	82.8	*0.1*
Nonane	226.17	128	−33.6	*24.0*	−1.5	*1.4*	2.7	*−0.9*	14.4	*−7.6*	10.9	*−6.2*	−28.6	*1.2*
Decane	243.50/1.4	131	−32.9	*−24.2*	−5.0	*−0.8*	−1.0	*−1.6*	10.3	*0.9*	6.6	*−2.2*	16.0	*−1.5*
Undecane	254.71	141	−32.3	*39.1*	1.3	*4.5*	5.7	*1.3*	18.4	*−7.8*	14.4	*−6.2*	455.8	*4.4*
Dodecane	267.75	144	−34.0	*30.9*	−4.4	*4.6*	0.4	*1.0*	14.3	*−9.7*	9.3	*−7.8*	73.2	*3.3*
Tridecane	280.31	150	−35.1	*79.2*	−16.6	*4.9*	−11.3	*0.5*	4.2	*−13.7*	−2.4	*−10.7*	204.5	*7.9*
Tetradecane	292.24	154	−34.3	*89.7*	−5.5	*6.1*	−0.8	*1.3*	12.6	*−14.3*	7.8	*−11.3*	4293.*	*3.8*
Pentadecane	303.58	158	−38.0	*98.8*	−5.7	*4.9*	−1.0	*0.0*	12.7	*−16.0*	7.7	*−13.1*	135.2	*9.0*
Hexadecane	314.05	162	−39.0	*53.7*	−2.2	*4.2*	2.1	*0.0*	14.8	*−12.6*	10.5	*−10.7*	31.2	*4.6*
1-Alkanols (c)														
Ethanol	199.40	107	−40.5	*54.0*	3.0	*1.3*	2.1	*0.6*	−0.2	*−1.1*	3.6	*1.9*	−28.8	*−0.8*
1-Propanol	213.61	119	−65.7	*93.8*	−11.7	*−7.3*	−12.4	*−5.8*	−14.4	*0.1*	−10.0	*−9.1*	4.1	*−0.6*
1-Butanol	227.70	123	−76.1	*80.6*	−16.4	*−2.6*	−16.6	*−0.4*	−17.3	*7.1*	−13.2	*−3.4*	−4.4	*4.0*
1-Pentanol	240.73	115	−78.8	*53.5*	−19.7	*0.9*	−19.5	*3.1*	−19.0	*10.2*	−15.8	*0.5*	−9.4	*3.3*
1-Octanol	275.51	130	−79.5	*12.0*	−28.9	*14.2*	−25.2	*13.6*	−14.0	*11.2*	−17.4	*10.4*	−44.4	*−1.0*
1-Decanol	296.21	136	−62.3	*85.0*	−33.8	*37.3*	−27.6	*33.9*	−7.6	*22.8*	−17.4	*23.9*	−13.9	*−0.7*
1-Dodecanol	314.94	144	−42.2	*−4.6*	−13.4	*20.7*	−5.9	*16.3*	18.1	*13.2*	6.4	*10.6*	0.8	*8.2*

* Value was omitted in calculation of $\bar{d}_r$ in Table 3. For equation codes see Table 1.

Table B2. Vapor Pressures: Test Results with the Wagner and Cox Equations

Compound	T_c/p_c K/Pa	ΔT K	d_r (%) W25		W36		C3b		C4b		C3c		C4c	
Polar/Nonpolar Compounds (*a2*)														
2-Methylheptane	204.67	120	−25.5	*−7.3*	−30.1	*−6.5*	−15.2	*−10.8*	55.4	*−8.3*	−1.0	*−7.7*	−24.3	*−8.0*
3-Methylheptane	205.46	120	−18.5	*−5.6*	−22.3	*−4.6*	−9.1	*−9.3*	45.8	*−6.5*	2.1	*−5.5*	−16.9	*−6.1*
2-Methyldecane	249.86	139	8.3	*3.2*	11.0	*3.8*	12.3	*−0.8*	−26.7	*6.6*	6.6	*1.7*	14.6	*1.8*
Ethylbenzene	214.31	127	−6.4	*0.7*	−9.7	*2.6*	2.0	*−4.4*	−12.7	*1.9*	10.5	*1.6*	−4.9	*0.8*
1,1′-Biphenyl	342.10/92.6	102	−1.6	*−0.8*	−1.9	*−0.7*	−0.4	*−0.4*	0.0	*−0.4*	0.7	*0.7*	−1.2	*−0.6*
Isoquinoline	299.62/9.4	134	−0.8	*0.5*	−2.1	*1.0*	2.5	*−0.6*	16.0	*0.1*	7.6	*6.7*	−0.7	*0.6*
Quinoline	271.25	157	11.3	*2.7*	13.1	*3.0*	12.1	*2.3*	75.3	*3.8*	8.4	*7.7*	14.0	*2.4*
Phenol	314.03/189.7	80	6.0	*−2.0*	7.6	*−2.1*	4.1	*−1.8*	−17.4	*−2.0*	−4.3	*−0.1*	7.0	*−2.1*
2-Methylphenol	304.20/69.5	107	−8.1	*−1.5*	−9.5	*−1.4*	−5.3	*−2.0*	−7.3	*−3.8*	−0.3	*−2.0*	−8.0	*−1.6*
3-Methylphenol	285.40/5.9	123	9.6	*−1.0*	12.4	*−0.1*	8.3	*−1.0*	57.4	*−5.1*	0.2	*−0.2*	12.4	*−0.6*
4-Methylphenol	307.94/39.4	103	6.5	*1.8*	8.8	*1.3*	4.3	*2.3*	28.9	*0.0*	−4.0	*4.8*	8.3	*1.2*
Diphenylmethanone	321.03/1.4	152	44.2	*−0.8*	56.4	*1.4*	34.1	*−6.2*	788*	*5.6*	18.2	*−9.6*	50.4	*0.0*
Dibenzofuran	355.31/76.5	114	−1.4	*−0.6*	−1.5	*−0.5*	−0.3	*−0.6*	−2.8	*−0.6*	0.1	*0.0*	−0.8	*−0.6*
3,4-Dithiahexane	225.00	148	4.7	*3.7*	6.3	*3.7*	7.6	*2.5*	103.8	*3.4*	4.1	*3.2*	9.6	*3.0*
1-Heptanethiol	239.36	138	−5.5	*−6.2*	−4.0	*−6.3*	−2.3	*−7.4*	−27.0	*−5.9*	−6.6	*−6.9*	−0.9	*−7.0*
Benzo[*b*]thiophene	304.48/44.7	109	−2.9	*−0.4*	−3.4	*−0.2*	−1.2	*−0.9*	−5.7	*−1.0*	0.9	*0.7*	−2.5	*−0.5*
Dibenzothiophene	371.82/34.3	136	−2.2	*−1.1*	−2.5	*−0.9*	−0.7	*−1.0*	−0.1	*−1.1*	0.1	*0.0*	−1.4	*−1.0*
***n*-Alkanes (*b*)**														
Heptane	194.47	114	−5.6	*1.8*	−8.1	*2.1*	2.0	*−0.1*	−4.5	*2.0*	8.0	*−0.9*	−3.4	*1.5*
Octane	216.37/2.0	116	−0.4	*0.7*	−0.4	*0.8*	3.5	*−0.7*	70.2	*0.1*	5.1	*−0.6*	2.3	*0.3*
Nonane	226.17	128	0.4	*−0.2*	0.8	*0.2*	5.6	*−2.6*	−21.5	*1.4*	4.1	*−1.2*	4.8	*−1.0*
Decane	243.50/1.4	131	−3.6	*−1.4*	−3.0	*−1.2*	1.3	*−2.1*	13.7	*−1.8*	0.6	*0.2*	0.7	*−2.0*
Undecane	254.71	141	5.7	*2.1*	9.7	*2.3*	8.2	*−0.8*	131.6	*4.2*	2.8	*0.4*	12.6	*0.7*
Dodecane	267.75	144	−3.4	*2.0*	−2.0	*2.0*	2.4	*−1.1*	69.8	*2.7*	1.5	*0.3*	2.7	*0.2*
Tridecane	280.31	150	−21.7	*1.8*	−25.6	*1.9*	−10.4	*−1.7*	127.2	*7.3*	−0.1	*−0.9*	−18.4	*0.0*
Tetradecane	292.24	154	−5.6	*3.8*	−3.5	*4.2*	0.4	*−0.9*	1803*	*2.6*	5.8	*−1.3*	0.1	*2.1*
Pentadecane	303.58	158	−5.7	*1.6*	−3.1	*1.4*	0.1	*−2.1*	106.5	*7.9*	−1.7	*−0.5*	1.3	*−0.6*
Hexadecane	314.05	162	−1.0	*1.6*	3.5	*1.0*	3.2	*−1.7*	26.7	*3.7*	−1.6	*−0.7*	6.8	*−0.8*
1-Alkanols (*c*)														
Ethanol	199.40	107	9.3	*3.8*	16.2	*4.0*	3.5	*2.2*	−34.0	*0.2*	−6.9	*−4.1*	11.0	*4.0*
1-Propanol	213.61	119	−2.5	*10.1*	8.4	*−10.8*	−10.3	*−8.8*	13.2	*1.5*	−24.0	*−3.3*	1.7	*−9.8*
1-Butanol	227.70	123	−4.4	*−9.6*	9.6	*−13.6*	−14.3	*−3.7*	2.0	*4.5*	−34.2	*−1.4*	3.8	*−12.4*
1-Pentanol	240.73	115	−6.6	*−8.4*	7.4	*−13.9*	−17.6	*−0.3*	−10.0	*2.7*	−41.9	*−9.3*	4.2	*−13.5*
1-Octanol	275.51	130	−24.9	*8.6*	−21.3	*5.5*	−27.2	*−12.8*	−44.9	*−1.1*	−40.5	*−1.1*	−19.6	*5.2*
1-Decanol	296.21	136	−42.8	*28.3*	−49.6	*23.8*	−33.3	*33.7*	−15.7	*−0.7*	−16.3	*20.5*	−45.9	*22.5*
1-Dodecanol	314.94	144	−24.9	*23.2*	−33.2	*25.0*	−11.2	*19.5*	−0.5	*8.6*	7.6	*10.5*	−26.6	*23.4*

*Value was omitted in calculation of $\bar{d}_r$ in Table 3. For equation codes see Table 1.

Appendix C

The following two tables summarize results of simple and controlled extrapolations for obtaining ΔH_{vap} at 298.15 K. d_r is the percent deviation of the calculated enthalpy of vaporization from the recommended value of ΔH_{vap} (Majer and Svoboda, 1985; Růžička and Majer, 1994, 1996); ΔT is the extrapolation interval (the difference between the lower temperature limit of p_{sat} used in correlation and 298.15 K). The values in italics correspond to the simultaneous fitting of p_{sat} and ΔC^0_{vap} data (controlled extrapolation).

Table C1. Enthalpy of Vaporization: Test Results with the Antoine and Quasipolynomial Equations

Compound	ΔH_{vap} kJ·mol^{-1}	ΔT K	d_r (%) ANT		QL1		QL2		QL6		Q12		QL12	
Polar/Nonpolar Compounds (*a2*)														
2-Methylheptane	39.67	27	0.6	*−2.6*	0.7	*−0.1*	0.6	*0.1*	0.3	*0.9*	0.4	*0.7*	−0.7	*0.1*
Ethylcyclohexane	40.56	37	0.5	*0.2*	−0.2	*−0.6*	−0.3	*−0.6*	−0.7	*−0.5*	−0.5	*−0.5*	0.7	*−0.5*
Propylcyclopentane	41.08	37	1.1	*0.6*	0.6	*0.4*	0.4	*0.4*	0.1	*0.5*	0.2	*0.5*	0.3	*0.4*
1-Octene	40.39	30	0.6	*0.3*	−0.4	*−0.1*	−0.5	*0.0*	−0.7	*0.1*	−0.6	*0.1*	−2.4	*−0.1*
1-Decene	50.43	73	2.5	*0.4*	0.0	*−0.6*	−0.3	*−0.4*	−1.2	*0.0*	−0.9	*−0.1*	−1.1	*−0.3*
1-Dodecene	60.78	111	5.6	*1.2*	0.3	*−1.6*	−0.4	*−1.3*	−2.3	*−0.7*	−1.7	*−0.6*	−9.7	*−1.0*
1,4-Dimethylbenzene	42.40	45	0.9	*−1.1*	0.1	*−0.2*	0.0	*−0.1*	−0.5	*0.2*	−0.3	*0.1*	−0.7	*0.0*
Ethylbenzene	42.24	44	1.1	*−4.3*	0.4	*−0.3*	0.3	*0.1*	−0.2	*1.2*	0.0	*1.2*	0.8	*0.0*
1-Fluoro-4-methylbenzene	39.42	42	0.8	*0.1*	0.0	*0.2*	−0.1	*0.2*	−0.3	*0.3*	−0.2	*0.3*	−3.2	*0.2*
1,2-Ethanediamine	44.98	36	3.0	*2.6*	1.6	*1.8*	1.5	*1.9*	1.2	*1.9*	1.3	*1.9*	2.0	*1.9*
Butanenitrile	38.91	34	1.7	*1.3*	1.5	*0.4*	1.4	*0.4*	1.2	*0.4*	1.3	*0.4*	1.7	*0.5*
Pyridine	40.15	42	0.8	*−0.6*	0.0	*−0.2*	−0.1	*−0.2*	−0.4	*−0.1*	−0.2	*−0.1*	−1.3	*−0.2*
2-Methylpyridine	42.48	54	1.1	*−0.5*	0.3	*−0.2*	0.2	*−0.2*	−0.3	*0.0*	−0.1	*−0.1*	−2.9	*−0.1*
3-Methylpyridine	44.55	52	1.2	*−0.1*	−0.5	*−0.3*	−0.6	*−0.2*	−1.0	*0.0*	−0.9	*−0.1*	−1.7	*−0.3*
4-Methylpyridine	44.80	53	1.3	*−1.0*	−0.7	*−0.4*	−0.8	*−0.4*	−1.2	*0.0*	−1.1	*−0.1*	−3.3	*−0.4*

(Continued)

Table C1. Enthalpy of Vaporization: Test Results with the Antoine and Quasipolynomial Equations (Continued)

Compound	ΔH_{vap} kJ·mol^{-1}	ΔT K	d_r (%) ANT		QL1		QL2		QL6		Q12		QL12	
Polar/Nonpolar Compounds (*a2*)														
2,3-Dimethylpyridine	47.73	74	2.4	−2.2	−0.9	−0.4	−1.1	−0.2	−1.5	0.3	−1.4	0.2	−3.6	−0.3
2,4-Dimethylpyridine	47.48	65	0.9	−2.7	−3.3	−0.9	−3.3	−0.7	−3.3	0.0	−3.5	−0.2	−3.1	−1.0
3,5-Dimethylpyridine	49.48	84	1.8	−2.9	−1.1	−0.8	−1.3	−0.6	−1.9	0.1	−1.8	−0.1	−7.2	−0.5
Methoxybenzene	46.90	84	3.4	3.4	1.8	3.7	1.5	3.7	0.5	3.5	0.9	3.8	8.3	3.4
Cyclopentanol	57.60	60	6.7	−2.0	−1.4	−2.9	−1.3	−3.0	−1.3	−3.2	−1.6	−2.8	−28.8	−2.2
Cyclohexanol	62.01	77	15.4	9.5	6.6	−1.7	5.9	−1.5	3.9	−0.8	4.7	−1.2	1.0	−0.7
Cyclopentanone	42.72	41	−0.6	−0.7	−1.5	−0.7	−1.6	−0.7	−1.9	−0.7	−1.8	−0.7	−1.3	−0.9
Cyclohexanone	45.06	62	2.7	1.7	1.4	0.8	1.1	1.0	0.5	1.3	0.7	1.3	−4.6	1.1
2-Hexanone	43.14	38	0.4	0.0	−0.4	−0.3	−0.5	−0.3	−0.9	−0.2	−0.7	−0.2	−0.6	−0.3
3-Hexanone	42.47	50	0.5	−0.3	−0.3	−0.8	−0.4	−0.8	−0.9	−0.5	−0.7	−0.6	1.2	−0.7
2-Methoxyethanol	45.17	58	3.6	3.0	3.7	3.3	3.5	3.4	2.9	3.7	3.2	3.5	9.2	3.4
3,4-Dithiahexane	45.18	75	2.3	−0.9	0.9	0.4	0.6	0.6	−0.2	1.3	0.2	1.1	−5.6	0.7
1-(Methylthio)butane	40.46	48	1.8	1.0	0.8	0.9	0.7	0.9	0.3	1.1	0.5	1.0	3.0	0.9
2,2′-Thiobispropane	39.60	30	0.7	0.6	0.0	0.2	0.0	0.2	−0.3	0.3	−0.2	0.3	−0.5	0.2
Nitromethane	38.27	30	0.0	−0.4	−0.4	−0.2	−0.4	−0.2	−0.5	−0.1	−0.5	−0.1	−1.1	−0.2
***n*-Alkanes (*b*)**														
Heptane	36.58	11	0.2	−2.5	0.1	−0.1	0.0	0.0	−0.1	0.3	0.0	0.1	0.0	−0.1
Octane	41.56	34	0.7	−2.4	0.0	−0.2	−0.1	−0.1	−0.4	0.4	−0.3	0.3	−1.7	0.0
Nonane	46.50	56	1.6	−3.0	0.0	−0.2	−0.2	0.0	−0.9	0.9	−0.6	0.7	1.6	−0.2
Decane	51.42	76	3.1	1.9	0.4	0.0	0.1	0.1	−1.0	0.0	−0.6	0.3	−1.4	0.1
Undecane	56.58	97	4.2	−4.1	−0.2	−0.6	−0.7	−0.2	−2.1	1.0	−1.6	0.8	−20.2	−0.6
Dodecane	61.54	113	6.4	−2.9	0.7	−0.6	−0.1	−0.1	−2.0	1.3	−1.4	1.1	−8.5	−0.4
Tridecane	66.68	132	8.8	−7.4	3.1	−0.7	2.0	−0.1	−1.1	1.9	0.1	1.5	−22.1	−1.1
Tetradecane	71.76	148	11.2	−8.1	1.3	−0.9	0.2	−0.2	−2.6	2.0	−1.8	1.7	−88.7	−0.6
Pentadecane	76.77	163	15.4	−8.7	1.4	−0.8	0.1	−0.1	−3.1	2.2	−2.2	1.9	−23.6	−1.3
Hexadecane	81.09	178	19.2	−2.8	1.0	−0.5	−0.4	0.1	−3.6	1.6	−2.9	1.5	−8.3	−0.5
1-Alkanols (*c*)														
Ethanol	42.37	8	0.5	−2.4	0.0	−0.2	0.0	−0.2	0.0	0.0	0.0	−0.4	0.1	0.0
1-Propanol	47.29	35	3.1	−5.3	0.6	−0.4	0.6	0.3	0.7	0.0	0.6	0.5	0.3	0.1
1-Butanol	52.14	53	6.8	−6.2	1.1	0.2	1.2	0.0	1.2	−0.6	1.0	0.3	0.6	−0.3
1-Pentanol	56.94	58	10.6	−5.5	1.8	−0.1	1.8	−0.3	1.7	−1.1	1.5	0.0	1.0	−0.3
1-Octanol	71.40	108	26.8	1.5	5.9	−1.4	5.0	−1.3	2.7	−1.1	3.4	−1.0	10.1	0.1
1-Decanol	81.23	134	29.0	−3.3	10.4	−3.7	8.2	−3.4	2.6	−2.2	4.9	−2.4	3.9	0.1
1-Dodecanol	91.13	161	27.6	14.2	6.0	−1.4	3.4	−1.1	−2.8	−2.0	−0.4	−1.2	1.3	−1.6

For equation codes see Table 1.

Table C2. Enthalpy of Vaporization: Test Results with the Wagner and Cox Equations

Compound	ΔH_{vap} kJ·mol^{-1}	ΔT K	d_r (%) W25		W36		C3b		C4b		C3c		C4c	
Polar/Nonpolar Compounds (*a2*)														
2-Methylheptane	39.67	27	0.8	0.1	0.9	0.0	0.5	0.3	−0.6	0.1	−0.1	0.3	0.7	0.1
Ethylcyclohexane	40.56	37	−0.3	−0.6	−0.3	−0.6	−0.4	−0.5	0.5	−0.5	−0.4	−0.4	−0.4	−0.5
Propylcyclopentane	41.08	37	0.6	0.4	0.6	0.4	0.4	0.4	0.4	0.4	0.0	0.2	0.5	0.4
1-Octene	40.39	30	−0.6	0.0	−0.7	0.0	−0.5	0.0	−2.0	−0.1	−0.3	−0.2	−0.7	0.0
1-Decene	50.43	73	0.1	−0.5	0.2	−0.5	−0.5	−0.3	−1.0	−0.3	−0.9	−0.7	−0.1	−0.5
1-Dodecene	60.78	111	0.4	−1.4	0.5	−1.4	−0.7	−1.1	−9.8	−1.0	−1.1	−1.2	−0.3	−1.2
1,4-Dimethylbenzene	42.40	45	0.1	−0.1	0.1	−0.1	−0.2	0.0	−0.6	0.0	−0.5	0.1	0.0	−0.1
Ethylbenzene	42.24	44	0.5	0.1	0.6	0.0	0.1	0.5	0.7	0.0	−0.3	0.3	0.4	0.1
1-Fluoro-4-methylbenzene	39.42	42	−0.1	0.2	−0.2	0.2	−0.1	0.2	−2.8	0.2	−0.1	0.1	−0.2	0.2
1,2-Ethanediamine	44.98	36	1.3	1.9	1.2	1.9	1.4	1.9	1.9	1.9	2.2	2.1	1.2	1.9
Butanenitrile	38.91	34	1.5	0.4	1.5	0.5	1.4	0.4	1.7	0.6	1.2	1.0	1.4	0.5
Pyridine	40.15	42	0.0	−0.2	0.0	−0.2	−0.2	−0.2	−0.9	−0.2	−0.4	0.2	−0.1	−0.2
2-Methylypridine	42.48	54	0.4	−0.2	0.5	−0.2	0.1	−0.1	−1.9	−0.1	−0.4	−0.2	0.3	−0.2
3-Methylypridine	44.55	52	−0.6	−0.3	−0.6	−0.3	−0.7	−0.2	−1.7	−0.3	−0.7	−0.4	−0.7	−0.2
4-Methylpyridine	44.80	53	−0.9	−0.4	−1.0	−0.4	−0.9	−0.3	−2.9	−0.4	−0.6	−0.3	−1.1	−0.3
2,3-Dimethylpyridine	47.73	74	−1.5	−0.2	−1.8	−0.2	−1.3	−0.1	−3.7	−0.3	−0.3	−0.1	−1.7	−0.1
2,4-Dimethylypridine	47.48	65	−4.1	−0.7	−4.7	−0.8	−3.4	−0.5	−3.5	−1.1	−1.4	−0.5	−4.4	−0.7
3,5-Dimethylpyridine	49.48	84	−1.5	−0.6	−1.7	−0.7	−1.5	−0.4	−11.7	−0.5	−1.2	−0.4	−1.7	−0.6
Methoxybenzene	46.90	84	1.9	3.7	2.1	3.6	1.2	3.8	4.7	3.5	0.6	0.9	1.7	3.7
Cyclopentanol	57.60	60	−2.1	−2.5	−2.7	−2.2	−1.5	−2.8	−20.2	−2.2	0.3	−1.6	−2.6	−2.2
Cyclohexanol	62.01	77	7.5	−1.8	8.5	−1.8	6.3	−1.6	0.9	−0.7	3.6	2.5	8.3	−1.8
Cyclopentanone	42.72	41	−1.5	−0.7	−1.4	−0.8	−1.7	−0.7	−1.3	−0.9	−2.0	−1.8	−1.5	−0.7
Cyclohexanone	45.06	62	1.3	0.9	1.3	0.9	1.0	1.1	−3.8	1.1	0.5	0.6	1.2	1.0
2-Hexanone	43.14	38	−0.5	−0.3	−0.5	−0.3	−0.6	−0.3	−0.6	−0.3	−0.6	−0.5	−0.6	−0.3
3-Hexanone	42.47	50	−0.2	−0.8	−0.2	−0.8	−0.5	−0.7	1.3	−0.7	−0.8	−0.8	−0.4	−0.7
2-Methoxyethanol	45.17	58	3.6	3.4	3.7	3.4	3.4	3.4	24.9	3.4	3.7	3.5	3.4	3.8
3,4-Dithiahexane	45.18	75	0.6	0.7	0.5.	0.7	0.4	0.8	−3.5	0.7	0.7	0.7	0.3	0.7
1-(Methylthio)butane	40.46	48	0.7	0.9	0.7	0.9	0.6	1.0	3.0	0.9	0.8	0.9	0.6	0.9
2,2′-Thiobispropane	39.60	30	0.0	0.2	−0.1	0.2	−0.1	0.3	−0.4	0.2	0.0	0.1	−0.1	0.3
Nitromethane	38.27	30	−0.4	−0.2	−0.5	−0.2	−0.4	−0.2	−0.9	−0.2	−0.2	−0.1	−0.5	−0.2

(Continued)

Table C2. Enthalpy of Vaporization: Test Results with the Wagner and Cox Equations (Continued)

Compound	ΔH_{vap} kJ·mol^{-1}	ΔT K	d_r (%) W25		W36		C3b		C4b		C3c		C4c	
n-Alkanes (*b*)														
Heptane	36.58	11	0.1	*−0.1*	0.1	*−0.1*	0.0	*0.0*	0.1	*−0.1*	−0.1	*0.2*	0.0	*−0.1*
Octane	41.56	34	−0.1	*−0.1*	−0.1	*−0.1*	−0.2	*0.1*	−1.7	*0.0*	−0.3	*0.1*	−0.1	*0.0*
Nonane	46.50	56	−0.1	*−0.1*	−0.1	*−0.1*	−0.4	*0.2*	1.2	*−0.3*	−0.3	*0.2*	−0.3	*0.0*
Decane	51.42	76	0.3	*0.1*	0.2	*0.1*	−0.1	*0.2*	−1.2	*0.1*	−0.1	*0.0*	−0.1	*0.2*
Undecane	56.58	97	−0.7	*−0.3*	−1.1	*−0.3*	−1.0	*0.1*	−10.1	*−0.5*	−0.3	*−0.1*	−1.5	*−0.1*
Dodecane	61.54	113	0.6	*−0.3*	0.3	*−0.3*	−0.4	*0.2*	−8.2	*−0.3*	−0.2	*−0.1*	−0.4	*0.0*
Tridecane	66.68	132	4.4	*−0.3*	5.4	*−0.3*	1.7	*0.2*	−16.0	*−1.0*	0.0	*0.1*	3.6	*0.0*
Tetradecane	71.76	148	1.4	*−0.5*	1.0	*−0.6*	−0.1	*0.1*	−62.9	*−0.4*	−1.1	*0.1*	0.1	*−0.3*
Pentadecane	76.77	163	1.4	*−0.3*	0.8	*−0.3*	−0.2	*0.2*	−19.1	*−1.1*	0.2	*0.0*	−0.5	*0.0*
Hexadecane	81.09	178	0.5	*−0.1*	−0.8	*−0.1*	−0.8	*0.3*	−6.9	*−0.4*	0.4	*0.2*	−1.8	*0.2*
1-Alkanols (*c*)														
Ethanol	42.37	8	0.0	*−0.4*	−0.1	*−0.4*	0.0	*−0.4*	0.2	*0.0*	0.1	*0.0*	0.0	*−0.4*
1-Propanol	47.29	35	0.4	*0.5*	0.2	*0.5*	0.6	*0.5*	0.1	*−0.1*	1.2	*−0.1*	0.3	*0.4*
1-Butanol	52.14	53	0.6	*0.8*	0.1	*1.2*	1.1	*0.3*	0.3	*−0.4*	2.6	*−0.3*	0.3	*1.1*
1-Pentanol	56.94	58	0.8	*0.9*	0.0	*1.5*	1.6	*0.0*	1.1	*−0.3*	4.5	*0.5*	0.1	*1.5*
1-Octanol	71.40	108	5.0	*−0.9*	4.2	*−0.6*	5.5	*−1.3*	10.3	*0.1*	8.7	*1.5*	3.8	*−0.6*
1-Decanol	81.23	134	13.7	*−3.0*	17.2	*−2.7*	10.3	*−3.4*	4.5	*0.1*	5.9	*−0.3*	15.7	*−2.5*
1-Dodecanol	91.13	161	10.0	*−2.2*	14.2	*−2.7*	5.3	*−1.5*	1.7	*−1.6*	1.1	*0.6*	11.6	*−2.6*

For equation codes see Table 1.

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