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INDUSTRIAL NEED FOR ACCURATE THERMOPHYSICAL DATA AND FOR RELIABLE PREDICTION METHODS

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Intelligent design of chemical-process equipment requires accurate thermophysical property values for pure components and mixtures including solutions. Databases used by practicing engineers should include the best numbers available and estimated uncertainties of these numbers. Many important property values have not been measured and must be estimated. Care should be exercised in selecting the estimation method. Property values that are a function of temperature, pressure, and/or composition can be correlated using appropriate equations. Such equations and the number of adjustable parameters in these equations should be selected with care. Examples of determining uncertainties, estimation techniques used, and correlating equations are given.

Keywords: *accuracy, correlating equations, databases, experimental values, heat of evaporation, high-temperature NaCl solutions, predicted values, uncertainty, vapor pressures*

Introduction

The intelligent design of industrial chemical processes requires accurate thermophysical data. These data include pure component and mixture values. Three of the authors are involved in maintaining the DIPPR 801 Database [1] that contains pure component data. In order to use the data over wide ranges of conditions, correlating equations are needed. These data can be put into two broad classes: those for pure components and mixtures, including solutions. These data can then be separated into types; those that are constant and those that are functions of temperature, T, pressure, P, and/or composition, x. Examples of thermophysical properties needed by engineers to design processes are shown in Table 1.

Engineers not only need these data, they also need to know the uncertainties associated with the values. The engineer can then design the process to take into account these uncertainties. It is much cheaper to over design the process than to build a plant that produces a product that does not meet

Table 1 Examples of types of data needed by the design engineer

Pure component data		Mixture data
Constant property data (independent of temperature and pressure)	Temperature- and/or pressure-dependent data	Temperature-, pressure-, and/or composition-dependent data
Critical temperature, critical pressure and critical volume	Liquid vapor pressures	Vapor–liquid equilibrium values
Normal boiling temperature, triple point temperature, and melting temperature	Solid vapor pressures	Solid–liquid equilibrium values
Acentric factor	Heat capacities of gases, liquids and solids	Heat capacities of gases, liquids and solids
Molecular mass	Liquid densities	Liquid densities
Standard Gibbs energy of formation, standard enthalpy of formation	Solid densities	Solid densities
Flash point, flammability limits, autoignition temperature	Heats of vaporization and of sublimation	Heats of mixing
	Viscosities of vapors and liquids	Viscosities of vapors and liquids
	Thermal conductivities of vapors, liquids and solids	Thermal conductivities of vapors, liquids and solids

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needed specifications. It is therefore, important that the uncertainties of the values are reported in the databases used by engineers. Assigning an uncertainty is much more involved than finding the standard deviation and confidence intervals of repeated measurements.

The factors that must be taken into account in estimating an uncertainty include the precision of the instruments, the accuracy of the calibrations of the instruments, the methods used, the purities of the materials used, and the agreement among the measurements from various laboratories. The care needed to determine the uncertainties associated with each of these factors has been discussed [2]. The staff in charge of the DIPPR 801 Database [1] expends considerable effort in assigning uncertainties to the values in this database.

Many of the property values found in the databases (including the DIPPR 801 Database) are predicted rather than measured. In such cases, it is important that the most reliable method for a given compound be used to predict a particular property value. Some procedures used include group contribution, corresponding state, molecular dynamics, Monte Carlo positioning and ab initio methods.

Process simulators (e.g., Aspen, Chemcad, Hysis) use correlating equations to calculate property values that are a function of T, P and/or x. Therefore, the uncertainties in the design specifications found using process simulators depend on the accuracy of the correlating equations.

In the following section, new results and some insights derived from the authors' experience managing the DIPPR 801 Database and fitting calorimetric data for high-temperature aqueous solutions are given.

Results and discussion

Cubic equations of state can be used to predict many fluid properties. The cubic equations of state that most accurately predict these properties are those that incorporate the acentric factor, ω. This factor is defined [3] as

$$\omega = -\log[P^{\mathrm{vap}}(T_r = 0.7/P_c] - 1$$

where P^{vap} is the vapor pressure, T_r is the reduced temperature (T/T_c), T_c is the critical temperature, and P_c is the critical pressure. From Eq. (1), it is apparent that the value of ω is dependent on the vapor pressure curve. Errors in T_c, P_c and normal boiling point, T_{nbp}, reflect the errors in the P^{vap} curve. In this work, a Monte Carlo method was used to determine the error produced in ω due to errors in T_c, P_c, and T_{nbp}. First, it was found that the ω values calculated using predicted vapor pressure curves based only on T_{nbp}, T_c, and P_c (Riedel method [4, 5]) are within 4% of the values found using equations fitted to literature vapor pressure values [1]. This agreement is shown in Table 2 for seven representative compounds.

Second, a large number of normally distributed random T_{nbp}, T_c and P_c values were generated based on the accepted values and estimated uncertainties for each of these constants. Vapor pressure curves were predicted from the sets of T_{nbp}, T_c and P_c values using the method of Riedel [4, 5] and ω was then calculated for each curve. The average and standard deviation of these ω values were then converted to the percent uncertainty. The results of these calculations are shown in Fig. 1.

In Fig. 1, it is seen that the uncertainties in the ω values are strongly dependent on uncertainties in T_{nbp} (Fig. 1a) and T_c (Fig. 1b) but only slightly dependent on uncertainties in P_c (Fig. 1c). As expected, the percent uncertainties in ω values for compounds with a small ω value (i.e., ethane ω=0.00995) are larger than for those with a large ω value (i.e., octane, ω=0.3996, and ethanol, ω=0.6436). It is also seen that small percentage uncertainties in T_{nbp}, T_c and P_c can result in relatively large uncertainties in ω.

These results demonstrate that very accurate measurements of T_c and T_{nbp} are needed to get ω values with low uncertainties, while modest uncertainties in P_c do not cause large errors in ω.

Thermophysical constants for many compounds have not been measured. One reason for this situation is that the conditions needed for some measurements are beyond the capability of the equipment. Another reason is the rapidly expanding number of new

Table 2 Comparison of literature acentric values [1], ω, with those predicted using only T_c, P_c and T_{nbp} [4, 5]

Compound	Literature ω value	Calculated ω value	Difference/%
n-Butane	0.200	0.197	–1.50
l-Pentene	0.235	0.237	0.85
l-Hexanol	0.576	0.571	–0.87
n-Butylbenzene	0.394	0.393	–0.25
2,2,4-Trimethylpentane	0.303	0.304	0.33
trans-2-pentene	0.248	0.246	–0.81
2-Pentyne	0.175	0.181	3.43

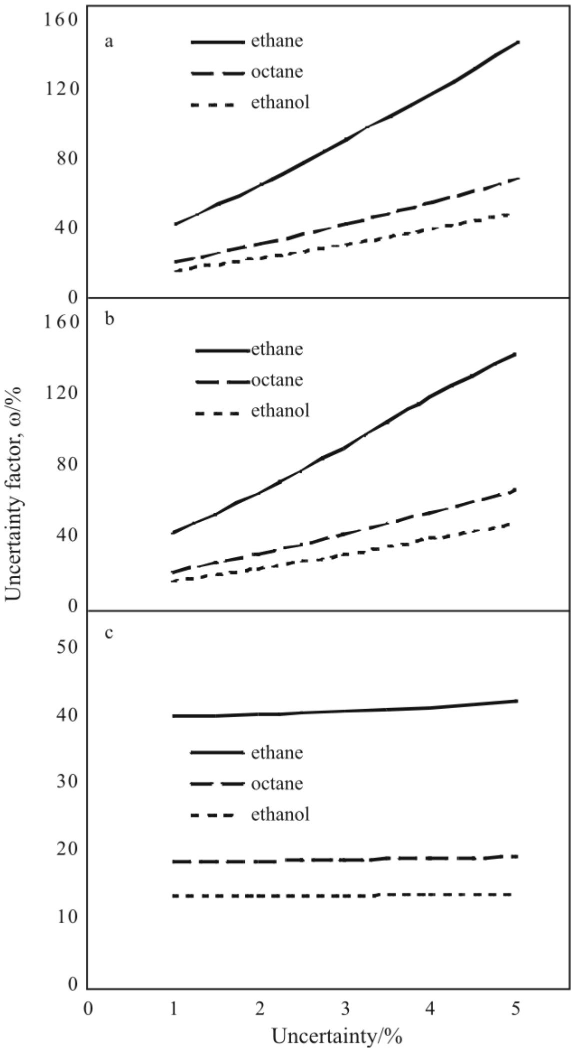

Fig. 1 Plot of % uncertainty in ω *vs.* percent uncertainties in a $=T_c$, b $=T_{nbp}$ and c $=P_c$. The percent uncertainties in T_c, T_{nbp} and P_c are varied, while the uncertainties in the remaining two quantities are held constant at 1%

industrially important compounds. Property measurements are difficult for some compounds due to their decomposition at temperatures below those of the desired measurements, their corrosive nature, and/or danger in handling them. In cases where measured values are not available, estimations can be made using accepted prediction techniques. Techniques commonly used include group contribution methods, molecular dynamics simulations, Monte Carlo simulations, ab initio calculations, and interpolation or extrapolation of thermophysical values for molecules consisting of similar functional groups and structure.

The most commonly used estimation techniques are based on group contribution methods [6]. These methods are based on the assumption that the contribution of a chemical 'group' to a given property is dependent only on that group and sometimes its nearest neighboring groups for all compounds in which it occurs. The advantages of group contribution methods are that they are relatively simple and the best of them are the most accurate estimation techniques available. The disadvantages of group-contribution methods are 1) they are difficult to apply to large, complex molecules; 2) the contributions of some groups have not been determined; 3) the accuracy of a given method is uncertain when applied to a new compound with a chemical structure much different than those of the compounds used to regress the contribution of the groups; 4) they generally cannot be used to predict differences between the properties of isomers and 5) the regressed value of a group that exists in only a few molecules cannot be determined reliably.

Caution is required when using a new group contribution technique. Sometimes the stated accuracy of a method applies only to the results for molecules used in the parameter regression. Poor results may be obtained when using the new method on compounds quite different from those used to regress the parameters. Marrero and Pardillo [7] developed excellent group contribution methods to estimate T_c and P_c values. A review by Yan *et al.* [8] showed this method was superior to other methods for a set of simple molecules. However, when this method was used to estimate T_c and P_c for more complex molecules, sometimes it gave very poor results. For example, the errors in T_c values calculated for *n*-alcanes with more than 20 carbons increase markedly with chain length, reaching 20% for C_{30}. An in depth study of T_c and P_c predictive methods is being conducted by the authors.

One needs to compare the predicted property value for a compound in a given chemical family (e.g., alkanes, alcohols, aldehydes, etc.) with the measured value before using the method for that family of compounds. In the case of complex molecules (a molecule that contains groups from more than one family), one must determine if the predicted value is reasonable.

Molecular dynamics and Monte Carlo methods depend heavily on the intermolecular potential used and generally do not give the accuracy needed unless the potential has been determined using measured values. Another problem with using these methods to predict properties is that they require large amounts of computational resources. Of the two, Monte Carlo methods use fewer computer resources at the expense of reduced accuracy. Rowley *et al.* have predicted viscosity [9, 10], and thermal conductivity [11] using molecular dynamics calculations. At least two conclusions can be drawn from their results. First, quantitative agreement between the measured and calculated values is obtained only when the parameters in the potential function are regressed using experimental data. Second, the amount of computer time needed to make the calculations is large, but improved techniques have significantly reduced the required time [10]. It is anticipated that in the future the intermolecular potential can be determined a priori and continued reduction in computer time will be achieved.

Ab initio methods, in theory, should give accurate results. However, such methods take much more computer time and memory than molecular dynamics or Monte Carlo methods. Results using ab initio methods have significant errors because of the limitations of the numerical methods used to solve the Schrödinger wave equation. Ab initio methods are used in the DIPPR 801 database [1] when other methods are not available to predict dipole moments, van der Waals volumes and areas, and ideal gas heat capacities (C_P^{IG}) and entropies.

Many pure component properties such as liquid vapor pressures depend on T. Other pure component properties such as C_P depend on T and P. All mixture properties depend on the x values of the mixture and usually on the T and P values of the mixture. Correlating equations for these properties are used in simulation programs. Property values calculated using correlating equations in process simulators need to be accurate over wide T, P and x ranges. Since property values cannot be measured at every T, P and x value, these correlating equations are useful in calculating reliable quantities at conditions other than those of the measurements.

It is important to use the appropriate equations with the proper number of parameters to correlate these properties. Selection of the appropriate equation for a given property is often aided by a sound knowledge of the theoretical and empirical behavior of the compounds and mixtures. The number of adjustable parameters in a given equation should be judiciously selected. Adding additional adjustable parameters to a correlating equation usually results in a better fit of the raw data. However, many times this better fit is illusory because the resulting better agreement is due to the fitting of experimental scatter. Thus, the use of this equation to find values at extrapolated conditions or to find derivatives with respect to T, P or x gives poor results. On the other hand, correlating equations with too few parameters may not account for important physical and/or chemical relationships.

An example where too many parameters are present is seen when applying two different Wagner vapor pressure equations [6] to correlate the vapor pressure of ethanol. The normal Wagner equation [6] (Eq. (1))

$$\ln(P_r)=\frac{A\tau+B\tau^{1.5}+C\tau^{3}+D\tau^{6}}{1-\tau} \tag{1}$$

has been used successfully to correlate liquid vapor pressures. In Eq. (1), $\tau=1-T_r$. However, Eq. (1) does not adequately fit the vapor pressures of normal alcohols of chain lengths of four carbons and above. Wagner developed Eq. (2) [6] specifically for alcohols.

$$\ln(P_r)=\frac{A\tau+B\tau^{1.5}+C\tau^{2.5}+D\tau^{5}+E\tau^{6}}{1-\tau} \tag{2}$$

Equation (2) has one more adjustable parameter than is found in Eq. (1). Equations (1) and (2) were fitted to the logarithms of the vapor pressures of ethanol [1]. As expected, the logarithms of the vapor pressures as correlated by Eq. (2) gave a slightly smaller mean squared error (($3.50\cdot10^{-5}$) than did the logarithms of those using Eq. (1) ($5.50\cdot10^{-5}$).

An additional test for the validity of any given vapor pressure equation involves comparing experimental liquid heat capacities (C_P^{liq}) with those found using the equation,

$$C_P^{liq}=C_P^{vap}-\frac{d\Delta_{vap}H(T)}{dT} \tag{3}$$

where the heat of vaporization [$\Delta_{vap}H(T)$] is derived by applying the Clapeyron equation to the given vapor pressure equation and is the heat capacity of the vapor.

The results of applying this test to Eqs (1) and (2) in the case of ethanol are shown in Fig. 2. It is apparent that in the case of ethanol, the inclusion of one additional parameter results in inaccurate derivatives.

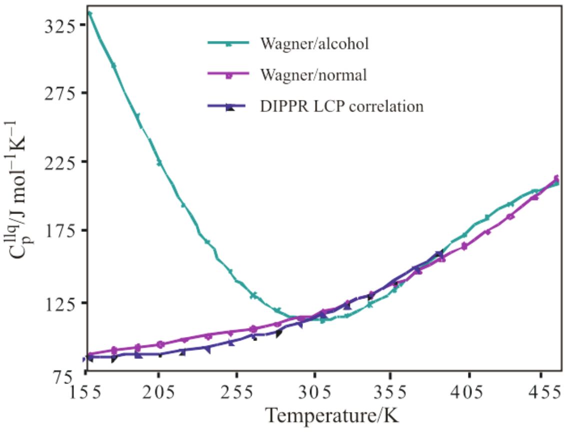

Fig. 2 Plot of C_P^{liq} *vs.* T for the measured value (DIPPR correlation) and values calculated using Eq. (3) with the normal Wagner equation and the Wagner equation for alcohols

There are some cases where additional parameters are needed to describe the thermodynamics of the system. An example is seen in the addition of two parameters to an accepted correlating equation for $\Delta_{vap}H$ for a pure liquid. The general DIPPR 801 equation [1] for $\Delta_{vap}H$ is

$$\Delta_{vap}H(T)=A(1-T_r)^{(B+CT_r+DT_r^2+ET_r^3)} \tag{4}$$

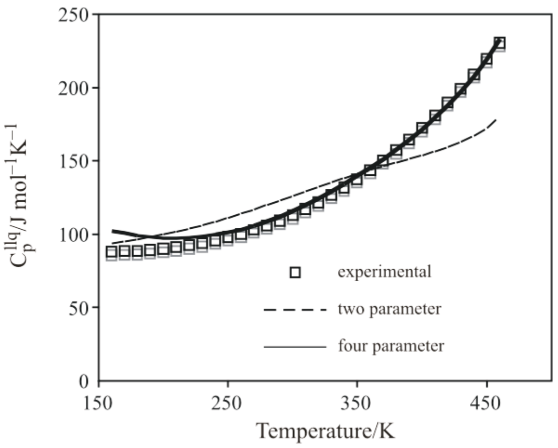

Fig. 3 Plot of C_P^{liq} *vs.* T for ethanol showing comparison between the ability of two-parameter and four-parameter $\Delta_{vap}H$ equations to give proper T-derivative (Eq. (3))

Prior to 1998, most of the $\Delta_{vap}H$ values were correlated using only parameters A and B in Eq. (4) because the improvement in the agreement between the calculated and measured values was very small when using more parameters than A and B. A test was made to see if, in the case of ethanol, the C_P^{liq} values determined by subtracting the temperature derivatives of $\Delta_{vap}H$ from C_P^{vap} values [Eq. (3)] agreed with the measured C_P^{liq} values. It was found that inclusion of the parameters C and D was needed to obtain good agreement as shown in Fig. 3. Use of parameter E did not improve the fit.

Some correlating equations do not adequately represent the properties of a chemical system because they do not include term(s) representing significant chemistry or physics occurring in the system. An example is found in the case of aqueous NaCl solutions at high T values. As T increases, salts in aqueous solutions become more associated. In their model of high-T NaCl solutions, Anderko and Pitzer [12] assumed that the contribution of the dissociation of NaCl was negligible and hence did not include any terms for this chemical reaction in their model. Even at high temperatures, this assumption is correct only at very high NaCl concentrations and/or low solution densities. They regressed their model using density and phase equilibrium data and were able to fit these data very well. However, using their model to predict heats of dilution ($\Delta_{dil}H$) of NaCl solutions resulted in poor agreement with measured values. The addition of terms that account explicitly for the dissociation of NaCl(aq) [13] resulted in much better agreement between the calculated and measured $\Delta_{dil}H$ values as shown in Figs 4 and 5 [13, 14].

The RI model [13] includes a term for the dissociation of NaCl while the RIII model [14] includes terms for the dissociation of NaCl and the effect due to change in the ionic strength of the solution.

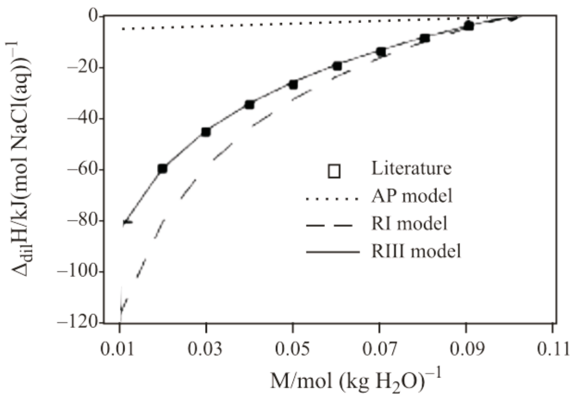

Fig. 4 Plot of $\Delta_{dil}H$ for a NaCl solution *vs.* NaCl concentration at 370°C and 24.7 MPa showing comparison of measured $\Delta_{dil}H$ values with those calculated using the Anderko–Pitzer, RI and RIII models [14]. Reprinted with permission from the American Chemical Society

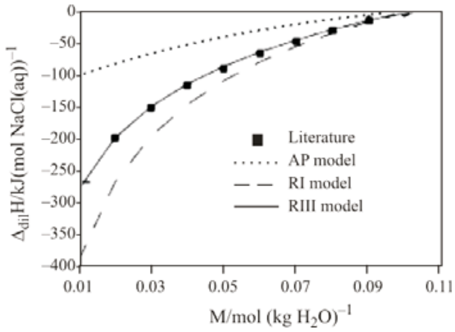

Fig. 5 Plot of $\Delta_{dil}H$ for a NaCl solution *vs.* NaCl concentration at 380°C and 24.7 MPa showing comparison of measured $\Delta_{dil}H$ values with those calculated using the Anderko–Pitzer, RI and RIII models [14]. Reprinted with permission from the American Chemical Society

As seen in Figs 4 and 5, the $\Delta_{dil}H$ values calculated using the AP model are in better agreement with the literature values at 380°C and 24.7 MPa than at 370°C and 24.7 MPa. This is due to increased ion association [14].

The addition of terms accounting for NaCl dissociation also resulted in better agreement between the calculated and measured densities over the entire density range [14] as seen in Fig. 6. As expected, the AP model shows the best agreement with experimental densities at high and low densities. At the high densities, the concentration of the NaCl is high resulting in a high fraction of association. At low densities, the solution is very dilute (mostly water) and the AP model fits the properties of water well.

The improved agreement between experimental $\Delta_{dil}H$ and density values and those calculated using the RIII model (Figs 4–6) shows the value of incorporating term(s) for the association of NaCl in this case.

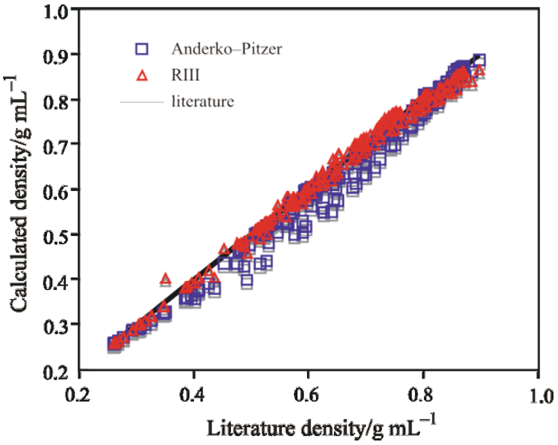

Fig. 6 Plot of calculated *vs.* literature densities of NaCl(aq) solutions at 350 to 450°C, 17 to 38 MPa, and 0.0025 to 3.1 molal NaCl [14]. Reprinted with permission from the American Chemical Society

Conclusions

There is a need for accurate thermophysical data, reliable prediction techniques, and correlating equations that can be used to calculate values that are in close agreement with those found experimentally. A knowledge of the uncertainties associated with measured, predicted and calculated values is essential when designing a given chemical process. Examples have been presented that demonstrate the care that must be taken in evaluating data, in using predicted values, and in developing correlating equations. Proper evaluation of the uncertainties requires more than calculating the averages and standard deviations of the measurements. Careful attention must be given to include the proper physics and/or chemistry in correlating equations. Reliable data are needed not only for design purposes but also for checking correlating equations. These correlating equations should be validated using different types of data to insure that the values calculated using these equations agree with experimental values within the uncertainties of the measurements.

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