Journal of Thermal Analysis, Vol 29 (1984) 687–695

EXCESS ENTHALPY CALCULATIONS BY MEANS OF EQUATIONS OF STATE

M. Fermeglia and *I. Kikic*

INSTITUTE OF APPLIED CHEMISTRY UNIVERSITY OF TRIESTE, ITALY

The suitability of existing equations of state for the prediction of heat of mixing data is investigated.

Classical cubic equations of state, such as those of Redlich–Kwong and Peng–Robinson, are compared with the more theoretically based equation developed by Carnaham and Starling. Calculations are reported for exothermic and endothermic systems.

It is shown that equations of state can be used to describe heat of mixing data and that the Carnaham–Starling repulsive term seems to give better results than the other models investigated.

The calculation of thermodynamic properties for mixtures has been investigated by many authors.

Christensen [1] and Nagata [2] paid particular attention to the correlation and the prediction of heat of mixing data from vapour–liquid equilibrium (VLE) data: they used different semiempirical excess Gibbs energy models to take into account the non-ideality of the liquid phase.

All the existing excess Gibbs energy models need two or more adjustable parameters obtained from the fitting of experimental data: in order to represent excess enthalpy data, these parameters have to be temperature-dependent since the solution theories on which the models are based do not take into account explicitly a temperature-dependence for the interaction energy. All the temperature-dependent expressions are therefore essentially empirical (linear or quadratic) and have the effect of increasing the number of parameters in the models (4 or 6 in some cases).

Unfortunately, this is not the only limitation in the excess Gibbs energy models: none of the theories for the liquid state has the basic physical meaning necessary to describe the behaviour of different kinds of liquid mixtures.

We therefore turned our attention to thermodynamic models which do not suffer from these basic weaknesses: the equations of state. Many authors are investigating equations of state in order to apply them to high and low-pressure phase equilibria calculations [3–4]. In fact, the thermodynamic models based on an equation of state show some evident advantages with respect to the excess Gibbs energy models, which can be summarized as follows

they are developed from a theoretically based hypothesis concerning the interactions between the molecules;

- they have an explicit temperature-dependence for the pure component parameters, because they must be able to describe the PVT properties of the pure components.

On the other hand, the composition-dependence of the mixture properties depends strongly on the assumptions concerning the mixing and combining rules used to calculate the mixture parameters from those of the pure components.

In this work we present some preliminary calculations showing the suitability of different well-known equations of state in the prediction of heat of mixing data.

Thermodynamics

Equations of state can be used to calculate excess enthalpy [5]. The residual enthalpy H^r is defined as:

$$nH^r = nH(T,P,\underline{n}) - nH^*(T,P,\underline{n}) \tag{1}$$

where H is the molar enthalpy of the mixture, H^* is the ideal gas molar enthalpy and n is the total number of moles present in the mixtures.

Any residual property can be calculated from the Helmholtz function or from its derivatives [6]. The residual enthalpy in particular is calculated from the derivative of the fugacity coefficient (φ_i) with respect to temperature as:

$$nH^r = -RT^2 \sum_i n_i \left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{P,n} \tag{2}$$

If we combine Eqs 1 and 2 we obtain:

$$nH = -RT^2 \sum_i n_i \left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{P,n} + nH^* \tag{3}$$

On the other hand, we know that [5]

$$nH^E = nH - \sum_i n_i H_i^0(T,P) \tag{4}$$

where H^E is the molar excess enthalpy and H_i^0 is the molar enthalpy of the pure component as a liquid.

Combining Eqs 3 and 4 and remembering that for an ideal gas

$$nH^* = \sum_i n_i H_i^*,$$

we obtain:

$$H^E = -RT^2 \sum_i x_i \left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{P,n} + \sum_i (H_i^* - H_i^0)x_i \tag{5}$$

The second term on the right-hand side of Eq. 5 is the pure component heat of vaporization, which can be calculated by means of the Clausius–Clapeyron equation or directly from the equation of state:

$$(H_i^* - H_i^0) = RT^2 \left(\frac{\partial \ln \varphi_i^0}{\partial T}\right)_{P,n} \tag{6}$$

where φ_i^0 is the fugacity coefficient of the pure component i.

From Eqs 5 and 6 we finally obtain an expression for H^E:

$$H^E = RT^2 \sum_i x_i \left(\frac{\partial \ln \varphi_i^0}{\partial T} - \frac{\partial \ln \varphi_i}{\partial T}\right)_{P,n} \tag{7}$$

The derivatives on the right-hand side of Eq. 7 are calculated from the equation of state written in terms of the residual Helmholtz function $nA^r(T, V, n)$. The first and the second derivatives of the residual Helmholtz function are related to the fugacity coefficient and its derivative as follows:

$$RT \ln \varphi_i = \left(\frac{\partial nA^r}{\partial n_i}\right)_{T,V} - RT \ln Z \tag{8}$$

$$RT\left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{P,n} = \left(\frac{\partial^2 nA^r}{\partial T \partial n_i}\right)_V - \frac{1}{T}\left(\frac{\partial nA^r}{\partial n_i}\right)_{T,V} + R - \bar{V}_i \left(\frac{\partial P}{\partial T}\right)_{V,n} \tag{9}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V} - \left(\frac{\partial^2 nA^r}{\partial T \partial V}\right)_n \tag{10}$$

$$\bar{V}_i = -\frac{\left(\frac{\partial P}{\partial n_i}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)_{T,n}} \tag{11}$$

where Z is the compressibility factor and R is the universal gas constant.

Equations of state

The equations of state used in this work are those of Redlich–Kwong (RK) [7], Peng–Robinson (PR) [8] and Carnaham–Starling–Van der Waals (CS) [9]. All these equations are very much like that proposed by Van der Waals in 1873 [10]. They can be split up into two terms: one takes into consideration the attractive forces between the molecules, and the other the repulsive forces. The RK and PR equations have been considered in this work, since they have the same repulsive term but different attractive terms; furthermore, they are widely used in industry and research laboratories. The general form of the RK and PR equations in terms of the compressibility factor is:

$$Z = \frac{V}{V-b} - \frac{aV}{(V^2 + Vcb - (c-1)b^2)RT} \tag{12}$$

The parameters common to the first two models are a and b; c is a third parameter: when $c = 1$ we obtain the RK equation, and if $c = 2$ we have the PR equation. The main disadvantage in using Eq. 12 is that the parameters a and b appear together in the attractive term: one temperature-dependent parameter influences the other [11] and the two parameters obtained from the fitting are strongly correlated.

The CS equation of state overcomes this problem and also has a better theoretical background:

$$Z = \frac{1 + y + y^2 - y^3}{(1-y)^3} - \frac{a}{RTV} \tag{13}$$

where $y = b/4V$.

Table 1 summarizes the equations of state used in terms of the compressibility factor and in terms of the Helmholtz function. The two parameters a and b for the mixture are calculated from a and b for the pure components by means of the mixing and combining rules. The parameter a is generally calculated from the mixing rule:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{14}$$

which is based on the assumption of random mixing. This assumption is correct for mixtures of hydrocarbons of approximately the same size, but it is not correct for mixtures where strong interactions are involved, such as mixtures containing polar compounds.

Table 1 Equations of state

	Compressibility factor	Helmholtz function
RK	$= \frac{V}{V-b} - \frac{a}{RT(V+b)}$	$= n \ln\left(\frac{V}{V-b}\right) + \frac{a}{RTb} \ln\left(\frac{V}{V+b}\right)$
PR	$= \frac{V}{V-b} - \frac{aV}{RT(V^2 + 2Vb - b^2)}$	$= n \ln\left(\frac{V}{V-b}\right) + \frac{a}{2\sqrt{2}RTb} \ln\left(\frac{V+b-2b}{V+b+2b}\right)$
CS	$= \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{a}{RTV}$	$= -ny\frac{3y-4}{(1-y)^2} - n^2\frac{a}{RTV}$

The combining rule for the calculation of the a_{ij} in Eq. 14 is:

$$a_{ij} = \alpha_{ij}(a_i a_j)^{1/2} \tag{15}$$

where α_{ij} is a binary adjustable parameter.

The most common mixing rule for the parameter b is:

$$b = \sum_i x_i b_i \tag{16}$$

Equation 16 is a purely empirical expression and a better result can be obtained by using a binary parameter and a combining rule for b_{ij}:

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{17}$$

$$b_{ij} = \frac{\beta_{ij}(b_i + b_j)^3}{8} \tag{18}$$

With the parameters a and b given by Eqs 14 to 18 and the equations of Table 1, one can finally calculate the H^E of Eq. 7.

Results

Christensen et al. [12] showed in their H^E data collection that endothermic mixing is found in 69% of the data sets, with the shape and symmetry of the curves depending very much on the mixture. On the other hand, exothermic mixing is found in about 23% of the data sets. For this reason we selected the following binary systems: acetonitrile–benzene at 45° [13], as an example of an endothermic system; and methanol–water at 25° [12], as an example of an exothermic system.

Figures 1, 2 and 3 show how the equations of state correlate the heat of mixing data for an endothermic system. The numbers in the figures refer to the values of the parameters α and β used in the prediction. All the equations correlate the data sufficiently well when only one parameter is used (one of the parameters is set equal to 1). When the CS equation is used, the experimental data are correlated more or less as well as with the other models, but the binary interaction parameters are closer to unity. Therefore, less arbitrary parameters are needed to represent the data: this is a consequence of the less empirical repulsive term.

Furthermore, all the equations are very sensitive to the values of the parameters and this leads to the conclusion that a prediction of H^E data using parameters from different sources, such as VLE or infinite dilution activity coefficients, is likely to be very difficult.

Figures 4 and 5 show the correlation of the exothermic system using the RK and the CS models, respectively, again we observe that the values of the best parameters are closer to unity when the CS equation is used. We also observe that we need two parameters to represent the system.

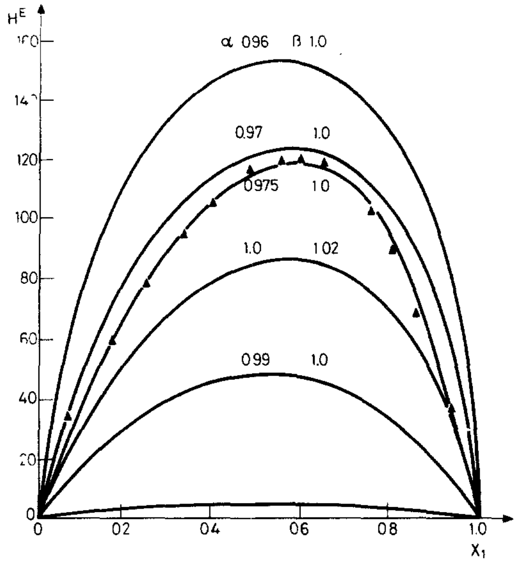

Fig. 1 Comparison between the experimental H^E [cal/mole] and those predicted by means of the RK equation for the acetonitrile (1) benzene (2) system; x_1 is the mole fraction of component one

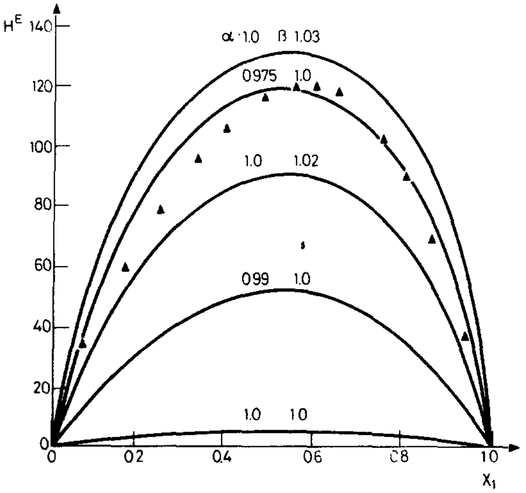

Fig. 2 Comparison between the experimental H^E [cal/mole] and those predicted by means of the PR equation for the acetonitrile (1) benzene (2) system; x_1 is the mole fraction of component one

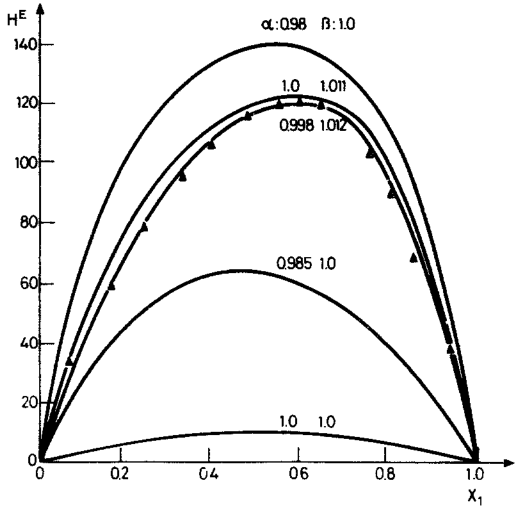

Fig. 3 Comparison between the experimental H^E [cal/mole] and those predicted by means of the CS equation for the acetonitrile (1) benzene (2) system; x_1 is the mole fraction of component one

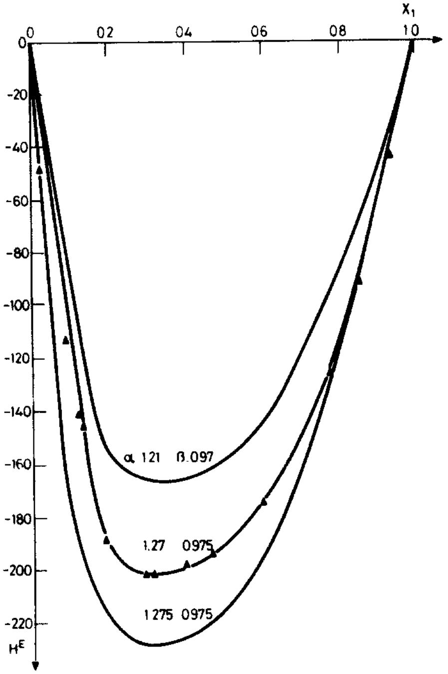

Fig. 4 Comparison between the experimental H^E [cal/mole] and those predicted by means of the RK equation for the methanol (1) water (2) system; x_1 is the mole fraction of component one

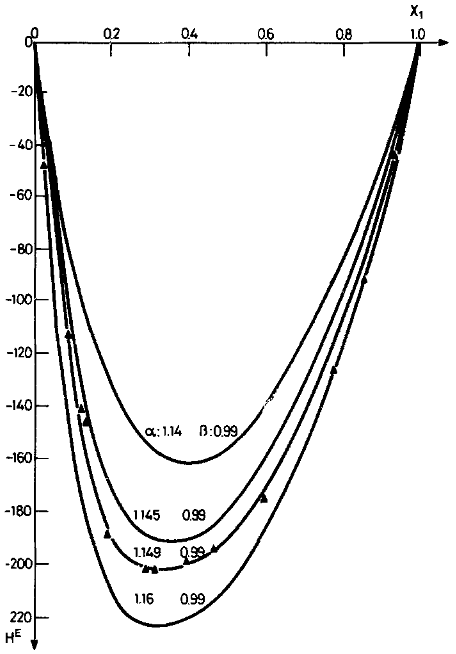

Fig. 5 Comparison between the experimental H^E [cal/mole] and those predicted by means of the CS equation for the methanol (1) water (2) system; x_1 is the mole fraction of component one

Conclusions

Equations of state can generally describe the concentration-dependence of the excess enthalpy quite satisfactorily, even if only one parameter is used: no assumption is made about the temperature-dependence of the adjustable parameters.

When the Carnaham and Starling repulsive term is used, although together with a very simple attractive term, it is possible to predict the behaviour of both the exo- and endothermic systems with binary adjustable parameters which are close to unity. This allows us to conclude that the CS repulsive term has greater physical meaning than the other repulsive terms.

Further studies are necessary to describe systems with strong interactions between the molecules. Better results will be obtained for these systems when a more sophisticated model for the attractive term is available. The work of Mollerup [14] and Whiting [15] seems to be very promising in this respect.

* * *

The authors thank the CNR: "Progetto finalizzato chimica fine e secondaria" for financial support.

References

1 J. J. Christensen and R. W. Hanks, I. Chem. E. Symp. Series, 56 (1979).

2 I. Nagata and T. Yamada, IEC Proc. Des. Dev., 11 (1972) 574.

3 H. Wenzel, R. A. S. Moorwood and M. Baumgartner, Fluid Phase Equilibria, 9 (1982) 225.

4 I. Kikic, P. Alessi and M. Fermeglia, Fluid Phase Equilibria, 14 (1983) 363.

5 J. M. Prausnitz, Molecular Thermodynamics of Fluid Phase Equilibria, Prentice Hall, New Jersey, 1969.

6 J. Mollerup, SEP 8112 Danmarks Tekniske Hojskole Chem., 1981.

7 O. Redlich and J. N. S. Kwong, Annual Review, 44 (1949) 233.

8 D. Y. Peng and D. B. Robinson, IEC Fundam., 15 (1976) 59.

9 N. F. Carnaham and K. E. Starling, J. Phys. Chem., 51 (1969) 635.

10 J. D. Van der Waals, Doctorial Dissertation, Leiden, 1873.

11 M. Fermeglia and J. Mollerup, published in Chem. Eng. Sci., 1984.

12 C. Christensen, J. Gmehling and P. Rasmussen, Paper presented in CHISA'81, Prague.

13 D. A. Palmer and B. D. Smith, J. Chem. Eng. Data, 17 (1972) 71.

14 J. Mollerup, Fluid Phase Equilibria, 7 (1981) 121.

15 W. B. Whiting and J. M. Prausnitz, Spring National Meeting AIChE J., Houston, 1981.

Zusammenfassung — Die Eignung von bekannten Zustandsgleichungen zur Vorhersage von Mischungswärmen wird untersucht. Klassische Zustandsgleichungen 3. Grades, wie die von Redlich—Kwong und Peng—Robinson werden mit der mehr theoretisch fundierten Gleichung von Carnaham und Starling verglichen. Berechnungen werden für exotherme und endotherme Systeme angegeben. Es wird gezeigt, daß die Zustandsgleichungen zur Beschreibung von Mischungswärmen verwendet werden können und das Abstoßungsglied von Carnaham—Starling bessere Resultate als andere untersuchte Modelle ergibt.

Резюме — Исследована применимость существующих уравнений состояния для определения теплот смешения. Классические кубические уравнения состояния, такие как уравнения Редлих—Квонга и Пенг—Робинсона, сопоставлены с более теоретически обоснованным уравнением Кэрнехема и Старлинга. Приведены расчеты для экзотермических и эндотермических систем. Показано, что уравнения состояния могут быть использованы для описания данных по теплотам смешения и что отталкивающий множитель Кэрнехема—Старлинга дает лучшие результаты по сравнению с другими исследованными моделями.