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CALCULATION OF THE ENTHALPY OF MIXING FROM VAPOR–LIQUID EQUILIBRIA

ERWIN MÜNSCH
Waeschle Maschinenfabrik GmbH, Postfach 2440, D-7980 Ravensburg (B.R.D.) *

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ABSTRACT

Methods for the calculation of the enthalpy of mixing from isothermal as well as isobaric vapor–liquid equilibria are derived. They make possible a useful estimation of the enthalpy of mixing from a few data, even if the direct differentiation of the free excess enthalpy or vapor pressures does not succeed. They also make possible the calculation of the enthalpy of mixing somewhat outside the temperature range for which measurements of phase equilibria are available. The calculus has been carried out for the systems ammonia/water and benzene/*n*-heptane.

INTRODUCTION

There are two possible methods of calculating the enthalpy of mixing of the liquid phase from vapor–liquid equilibrium data. In both cases, the thermodynamic conditions for the phase equilibrium are used. The vapor–liquid equilibrium of an *m*-component system is defined by the following relations

$$T^{\mathrm{v}} = T^{\mathrm{l}} = T \tag{1}$$

$$p^{\mathrm{v}} = p^{\mathrm{l}} = p \tag{2}$$

$$\mu_i^{\mathrm{v}} = \mu_i^{\mathrm{l}}\ (i = 1, \ldots, m) \tag{3}$$

The first method makes use of the equilibrium conditions for the calculation of the chemical excess potentials μ_i^{E} of the liquid phase. The enthalpy of mixing is then calculable from the temperature dependence of the free excess enthalpy

$$\bar{H}^{\mathrm{E}} = -T^2 \frac{\partial \left(\dfrac{\bar{G}^{\mathrm{E}}}{T}\right)_{p,x_j}}{\partial T} \tag{4}$$

In the second method, the equilibrium conditions are used to derive the differential equations for co-existing phases. These equations show the enthalpy of mixing

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* This paper was written at: Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, D-4630 Bochum (B.R.D.).

is also calculable directly from the temperature dependence of the vapor pressures.

FIRST METHOD

The definition of a thermodynamic excess function implies the definition of the ideal solution, which becomes problematic for regions of state near the phase equilibrium. For the purpose of full differentiability of the excess functions in the whole region of a phase, the ideal solution for a liquid phase (T, p, x_i) is defined in the following manner. The ideal solution is composed of the pure components being liquid at temperature T and pressure p. Under these conditions, the liquid state of a pure component may be only fictitious, then it corresponds to a point on the isotherm, T, extrapolated into the two-phase region. The ideal solution for the vapor phase is defined in a corresponding manner. The equilibrium conditions then yield the chemical excess potential of the component i in the liquid phase at phase equilibrium

$$\mu_i^{\mathrm{E}} = RT \ln \frac{y_i}{x_i} + \int_{p=0}^{p} v_i^{\mathrm{vE}} \, \mathrm{d}p_T + \int_{p_{i0}}^{p} (\bar{V}_i^{\mathrm{v}} - \bar{V}_i^{\mathrm{l}}) \mathrm{d}p_T \equiv RT \ln \gamma_i \tag{5}$$

The excess volume of the vapor phase $\bar{V}^{\mathrm{vE}}$ is rarely known as a function of temperature, pressure, and composition. Therefore, the real behavior of the vapor phase has to be approached by the model of the ideal solution of gases, whereby the first integral of eqn. (5) vanishes. But eqn. (5) can usually be reduced further by use of the ideal gas law for the pure components and by neglecting the molar volume $\bar{V}_i^{\mathrm{l}}$ of the liquid with respect to the molar volume $\bar{V}_i^{\mathrm{v}}$ of the vapor. Then eqn. (5) yields the well-known relation for the activity coefficient

$$\gamma_i \simeq \frac{y_i \, p}{x_i \, p_{i0}} \tag{6}$$

Carrying out the differentiation according to eqn. (4), the pressure need no be held constant, because it influences only slightly the caloric variables of state of liquids. Thus the partial molar enthalpy of mixing in the liquid phase follows by differentiating the activity coefficient given by eqn. (6)

$$h_i^{\mathrm{E}} = -RT^2 \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{x_j} = -RT^2 \left(\frac{\partial \ln \dfrac{y_i \, p}{p_{i0}}}{\partial T} \right)_{x_j} \tag{7}$$

SECOND METHOD

For a change of the equilibrium state, defined by eqns. (1–3), we have the necessary conditions

$$\mathrm{d}T^{\mathrm{v}} = \mathrm{d}T^{\mathrm{l}} = \mathrm{d}T \tag{8}$$

$$\mathrm{d}p^{\mathrm{v}} = \mathrm{d}p^{\mathrm{l}} = \mathrm{d}p \tag{9}$$

$$\mathrm{d}\mu_i^{\mathrm{v}} = \mathrm{d}\mu_i^{\mathrm{l}} \, (i = 1, \ldots, m) \tag{10}$$

Condition (10) is satisfied for each component *i*. Consequently, the following relations also hold.

$$\sum_{i=1}^{m} x_i d(\mu_i^{\mathrm{v}} - \mu_i^{\mathrm{l}}) = 0 \tag{11}$$

$$\sum_{i=1}^{m} y_i \mathrm{d}(\mu_i^{\mathrm{v}} - \mathrm{d}\mu_i^{\mathrm{l}}) = 0 \tag{12}$$

Denoting the differential change of a variable of state at constant temperature and constant pressure by δ, the total differential of the chemical potential of any component i reads

$$\mathrm{d}\mu_i = - s_i \mathrm{d}T + v_i \mathrm{d}p + \delta\mu_i \tag{13}$$

With this expression and with eqns. (8 and 9), eqns. (11 and 12) yield

$$- \sum_{i=1}^{m} x_i(s_i^{\mathrm{v}} - s_i^{\mathrm{l}})\mathrm{d}T + \sum_{i=1}^{m} x_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}})\mathrm{d}p + \sum_{i=1}^{m} x_i\, \delta(\mu_i^{\mathrm{v}} - \mu_i^{\mathrm{l}}) = 0 \tag{14}$$

$$- \sum_{i=1}^{m} y_i(s_i^{\mathrm{v}} - s_i^{\mathrm{l}})\mathrm{d}T + \sum_{i=1}^{m} y_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}})\mathrm{d}p + \sum_{i=1}^{m} y_i\, \delta(\mu_i^{\mathrm{v}} - \mu_i^{\mathrm{l}}) = 0 \tag{15}$$

With

$$\mu_i = h_i - Ts_i \tag{16}$$

the equilibrium conditions (1 and 3) yield the relation

$$s_i^{\mathrm{v}} - s_i^{\mathrm{l}} = \frac{h_i^{\mathrm{v}} - h_i^{\mathrm{l}}}{T} \tag{17}$$

Furthermore, the Gibbs–Duhem equation holds for both phases

$$\sum_{i=1}^{m} x_i \delta\mu_i^{\mathrm{l}} = 0 \tag{18}$$

$$\sum_{i=1}^{m} y_i \delta\mu_i^{\mathrm{v}} = 0 \tag{19}$$

With the last three equations, relations (14) and (15) can be transformed to

$$- \sum_{i=1}^{m} x_i(h_i^{\mathrm{v}} - h_i^{\mathrm{l}}) \frac{\mathrm{d}T}{T} + \sum_{i=1}^{m} x_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}})\mathrm{d}p + \sum_{i=1}^{m} x_i \delta\mu_i^{\mathrm{v}} = 0 \tag{20}$$

$$- \sum_{i=1}^{m} y_i(h_i^{\mathrm{v}} - h_i^{\mathrm{l}}) \frac{\mathrm{d}T}{T} + \sum_{i=1}^{m} y_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}})\mathrm{d}p - \sum_{i=1}^{m} y_i \delta\mu_i^{\mathrm{l}} = 0 \tag{21}$$

These equations are the differential equations for co-existing phases for a multicomponent system in the most simple and general form. For the first time, they have been derived in another form by Storonkin[1]. They correspond to the Clausius–Clapeyron equation for pure substances.

The meaning of the coefficient of dp in eqn. (20) is the negative volume change of a system in phase equilibrium if one mole of vapor condenses into such an amount of liquid that thereby the composition of the liquid does not noticeably change. The coefficient of dT/T corresponds to the similar change of enthalpy. On the other hand, the coefficient of dp in eqn. (21) means the volume change of a system if one mole of liquid evaporates into a large vapor phase and, similarly, the coefficient of dT/T holds for the negative enthalpy change. In the following, we treat only eqn. (20) for condensation.

By definition, the differential $\delta\mu_i^{\mathrm{v}}$ is not zero only if the composition changes. Keeping the composition of the vapor phase constant, changes of the phase equilibrium are given by

$$\left(\frac{\partial p}{\partial T}\right)_{y_j} = \frac{1}{T}\,\frac{\sum\limits_{i=1}^{m} x_i(h_i^{\mathrm{v}} - h_i^{\mathrm{l}})}{\sum\limits_{i=1}^{m} x_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}})} \tag{22}$$

For the application of eqn. (22), the same definition of the ideal solution and the same simplifications are used as for the first method. Then, for the partial molar enthalpy in the liquid phase it follows

$$h_i^{\mathrm{l}} = \bar{H}_i^{\mathrm{l}} + h_i^{\mathrm{lE}} \tag{23}$$

According to the model of the ideal solution of gases for the vapor phase it follows

$$h_i^{\mathrm{v}} = \bar{H}_i^{\mathrm{v}} \tag{24}$$

Introducing the enthalpy of vaporization, $\bar{H}_i^{\mathrm{V}}$, of the pure components

$$\bar{H}_i^{\mathrm{V}}(T) \simeq \bar{H}_i^{\mathrm{v}} - \bar{H}_i^{\mathrm{l}} \tag{25}$$

the last three equations yield for the numerator in eqn. (22)

$$\sum_{i=1}^{m} x_i(h_i^{\mathrm{v}} - h_i^{\mathrm{l}}) \simeq \sum_{i=1}^{m} x_i\bar{H}_i^{\mathrm{V}} - \sum_{i=1}^{m} x_i h_i^{\mathrm{lE}} = \sum_{i=1}^{m} x_i\bar{H}_i^{\mathrm{V}} - \bar{H}^{\mathrm{E}} \tag{26}$$

According to the model of the ideal solution of gases for the vapor phase, it follows

$$v_i^{\mathrm{v}} = \bar{V}_i^{\mathrm{v}} \tag{27}$$

Thus the denominator in eqn. (22) reads

$$\sum_{i=1}^{m} x_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}}) = \sum_{i=1}^{m} x_i\bar{V}_i^{\mathrm{v}} - \bar{V}^{\mathrm{l}} \simeq \sum_{i=1}^{m} x_i\bar{V}_i^{\mathrm{V}} - \bar{V}^{\mathrm{E}} \tag{28}$$

with $\bar{V}_i^{\mathrm{V}}$ denoting the volume of vaporization. Using the ideal gas law for the vapor phase, this equation is reduced to

$$\sum_{i=1}^{m} x_i(v_i^{\mathrm{v}} - v_i^{\mathrm{l}}) = \frac{RT}{p} - \bar{V}^{\mathrm{l}} \tag{29}$$

Neglecting also the molar volume of the liquid phase in comparison with that of the vapor phase, eqn. (22) yields, in connection with eqns. (26 and 29), for the enthalpy of mixing in the liquid phase

$$\bar{H}^{\mathrm{E}} = \sum_{i=1}^{m} x_i \bar{H}_i^{\mathrm{V}} - RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_{y_j} \tag{30}$$

THEORETICAL INTERRELATION BETWEEN BOTH METHODS

Applying the same simplifications as used for the derivation of eqns. (7 and 30) to the Clausius–Clapeyron equation, we have

$$\frac{\mathrm{d} \ln p_{i0}}{\mathrm{d}T} = \frac{\bar{H}_i^{\mathrm{V}}}{RT^2} \tag{31}$$

So, from eqn. (7)

$$\bar{H}^{\mathrm{E}} = RT^2 \left[\sum_{i=1}^{m} x_i \frac{\mathrm{d} \ln p_{i0}}{\mathrm{d}T} - \sum_{i=1}^{m} x_i \left(\frac{\partial \ln y_i p}{\partial T}\right)_{x_j} \right] \tag{32}$$

Equation (30) can be rewritten by using eqn. (31)

$$\bar{H}^{\mathrm{E}} = RT^2 \left[\sum^{m} x_i \frac{\mathrm{d} \ln p_{i0}}{\mathrm{d}T} - \left(\frac{\partial \ln p}{\partial T}\right)_{y_j} \right] \tag{33}$$

Comparison of eqns. (32 and 33) yields

$$\left(\frac{\partial \ln p}{\partial T}\right)_{y_j} = \left(\frac{\partial \ln p}{\partial T}\right)_{x_j} + \sum_{i=1}^{m} x_i \left(\frac{\partial \ln y_i}{\partial T}\right)_{x_j} \tag{34}$$

This relation between the different vapor pressure curves of mixtures holds for the same assumptions as needed for eqns. (7 and 30).

Equations (32 and 33) show that, for the calculation of enthalpies of mixing, complete measurements of phase equilibria are needed because all variables T, p, x_i and y_i must be known. The differentiations according to eqns. (32 and 33) have to be done for constant composition of the liquid or vapor phase. But usually phase equilibria are measured at constant temperature or pressure. Therefore the experimental data have to be interpolated graphically or numerically. If the evaluation of the results does not satisfy, the reason for that has to be seen more often in the insufficient thermodynamic consistency of the data than in the assumptions of eqns. (32 and 33). Because in both methods the enthalpy of mixing results as a difference of several differential quotients, they have to be calculated with high precision.

For $m = 2$, let $x_2 = x$ and $y_2 = y$, then eqn. (34) reads

$$\left(\frac{\partial \ln p}{\partial T}\right)_y = \left(\frac{\partial \ln p}{\partial T}\right)_x - \frac{y - x}{y(1 - y)}\left(\frac{\partial y}{\partial T}\right)_x \tag{35}$$

Application of the differentiation rule

$$\left(\frac{\partial \ln p}{\partial T}\right)_y = \left(\frac{\partial \ln p}{\partial T}\right)_x - \left(\frac{\partial \ln p}{\partial y}\right)_T \left(\frac{\partial y}{\partial T}\right)_x \tag{36}$$

yields the well-known relation

$$\left(\frac{\partial \ln p}{\partial y}\right)_T = \frac{y - x}{y(1 - y)} \tag{37}$$

In the special case of binary systems, the isothermal data of the boiling point curve suffice for the calculation of the enthalpy of mixing because eqn. (37) enables the calculation of the isothermal dew-point curve from boiling data provided the assumptions of eqn. (37) are fulfilled.

In many cases, measurements of phase equilibria are available only for two or three isotherms or isobars. Then, the evaluation of the enthalpy of mixing according to eqns. (32) or (33) mostly fails. But further manipulation of these equations can provide a satisfying evaluation of the enthalpy of mixing. Introducing the partial pressure

$$p_i = y_i p \tag{38}$$

eqn. (32) reads, for a binary system

$$\bar{H}^{\mathrm{E}} = -RT^2\left[(1 - x)\left(\frac{\partial \ln \frac{p_1}{p_{10}}}{\partial T}\right)_x + x\left(\frac{\partial \ln \frac{p_2}{p_{20}}}{\partial T}\right)_x\right] \tag{39}$$

For a binary system, eqn. (33) yields

$$\bar{H}^{\mathrm{E}} = RT^2\left[x\frac{\partial \ln \frac{p_{20}}{p_{10}}}{\mathrm{d}T} - \left(\frac{\partial \ln \frac{p}{p_{10}}}{\mathrm{d}T}\right)_y\right] \tag{40}$$

Applying the chain rule of differential calculus with respect to eqn. (31), both equations can be transformed to

$$\bar{H}^{\mathrm{E}} = -\bar{H}_1^{\mathrm{V}}\left[(1 - x)\left(\frac{\partial \ln \frac{p_1}{p_{10}}}{\partial \ln p_{10}}\right)_x + x\left(\frac{\partial \ln \frac{p_2}{p_{20}}}{\partial \ln p_{10}}\right)_x\right] \tag{41}$$

and

$$\bar{H}^{\mathrm{E}} = \bar{H}_1^{\mathrm{V}}\left[x\frac{\mathrm{d} \ln \frac{p_{20}}{p_{10}}}{\mathrm{d} \ln p_{10}} - \left(\frac{\partial \ln \frac{p}{p_{10}}}{\partial \ln p_{10}}\right)_y\right] \tag{42}$$

The new relations (41) and (42) have the advantage that the differential quotients are now almost independent of temperature. This has been shown by Othmer[2-4] (see also Figs. 1–6). After interpolating the equilibrium data for certain compositions, the differential quotients of eqns. (41) or (42) can be calculated simply by linear regression with any pocket calculator.

Accurate measurements of enthalpies of vaporization for the pure substances are rare, therefore calculation from vapor pressure equations according to eqn. (31) is preferable. As a simple and accurate vapor pressure equation, the Antoine equation is serviceable

$$\log p_{i0} = A_i - \frac{B_i}{t + C_i} \tag{43}$$

with

$$\bar{H}_i^{\mathrm{V}} = RT^2 \frac{B_i \ln 10}{(t + C_i)^2} \tag{44}$$

The constants of the Antoine equation have been calculated for many substances by API (Project 44)[5]. Another suitable vapor pressure equation with only three parameters reads

$$\log p_{i0} = -\frac{A_i}{T} + B_i + C_i \log T \tag{45}$$

with

$$\bar{H}_i^{\mathrm{V}} = R(A_i \ln 10 + C_i T) \tag{46}$$

The constants of these equations have also been calculated for many substances (see Landolt-Börnstein[6]).

CORRECTIONS FOR REAL GAS BEHAVIOR

An approximation to the real behavior of the vapor phase can be obtained by applying the model of the ideal solution of gases; then we obtain the activity coefficient at phase equilibrium from eqn. (5), with restriction to the second virial coefficients and by neglect of the pressure dependence of the molar liquid volume in the range from p_{i0} to p, in the form

$$\gamma_i = \frac{y_i p}{x_i p_{i0}} \exp\left\{\frac{(B_i - \bar{V}_i^{\mathrm{l}})(p - p_{i0})}{RT}\right\} \equiv \frac{y_i p}{x_i p_{i0}} r_i \tag{47}$$

Then, eqn. (41) for the calculation of the enthalpy of mixing by the first method changes to

$$\bar{H}^{\mathrm{E}} = RT^2 \frac{\mathrm{d} \ln p_{10}}{\mathrm{d}T} \left[(1 - x)\left(\frac{\partial \ln \frac{p_1 r_1}{p_{10}}}{\partial \ln p_{10}}\right)_x + x\left(\frac{\partial \ln \frac{p_2 r_2}{p_{20}}}{\partial \ln p_{10}}\right)_x\right] \tag{48}$$

For the second method we also neglect the volume of mixing $\overline{V}^{\mathrm{E}}$ of the liquid phase. Then we obtain from eqns. (28, 26 and 22), using the Clausius–Clapeyron equation

$$\overline{H}^{\mathrm{E}} = T \sum_{i=1}^{m} x_i \overline{V}_i^{\mathrm{V}} \frac{\mathrm{d} \ln p_{i0}}{\mathrm{d}T} \left[p_{i0} - p \left(\frac{\partial \ln p}{\partial \ln p_{i0}} \right)_{y_j} \right] \tag{49}$$

with

$$\overline{V}_i^{\mathrm{V}} = \frac{RT}{p_{i0}} + B_i - \overline{V}_i^{\mathrm{l}}$$

In view of the uncertainty of the equilibrium data, corrections for real gas behavior are not necessary at moderate pressures.

COMPARISON OF BOTH METHODS

In the first method [eqn. (41)], the assumption of temperature-independent differential quotients is problematic because then the temperature dependence of the enthalpy of mixing would correspond to that of the enthalpy of vaporization of pure substances [$\overline{H}_{\mathrm{I}}^{\mathrm{V}}$ in eqn. (41)]. The expression in the bracket of eqn. (41) would be a function only of composition; therefore, all $\overline{H}^{\mathrm{E}}(x)$ curves at different temperatures would be similar. Thus, if the $\overline{H}^{\mathrm{E}}(x)$ curves vary with temperature, the differential quotients of eqn. (41) cannot be independent of temperature. In any case, a graphical examination by a double logarithmic plot of the data is advisable.

By the second method, according to eqn. (42), only one differential quotient needs to be calculated. But in the case of extreme forms of the dew point curves, e.g. ammonia/water, the calculation of the enthalpy of mixing may be possible only for a part of the concentration range. Furthermore, the second method has the disadvantage that the equilibrium compositions of the two phases have to be known for that temperature, for which the enthalpy of mixing is to be calculated. If necessary, these compositions can be calculated for any temperature by interpolation or extrapolation from the equilibrium data.

THE BENZENE/*n*-HEPTANE SYSTEM

The calculus is based on the isothermal equilibrium measurements of Werner and Schuberth[7] at 20 °C, Harris and Dunlop[8] at 25 °C, Palmer and Smith[9] at 45 °C, and Fu and Lu[10] at 75 °C. Furthermore, the isobaric measurements of Sieg[11] in the range from 300 to 760 Torr have been used. The data, graphically interpolated for certain compositions, are plotted in Figs. 1–3 according to eqns. (41) and (42). Additionally, Figs. 1 and 2 show the isobaric measurements of Hloušek and Hala[12]. For reasons of the graphical representation, log p_2/p_{10} has been plotted instead of log p/p_{10} in Fig. 3 for constant composition of the vapor phase. The slopes of the representative curves are the same. As the figures show, the differential quotients of

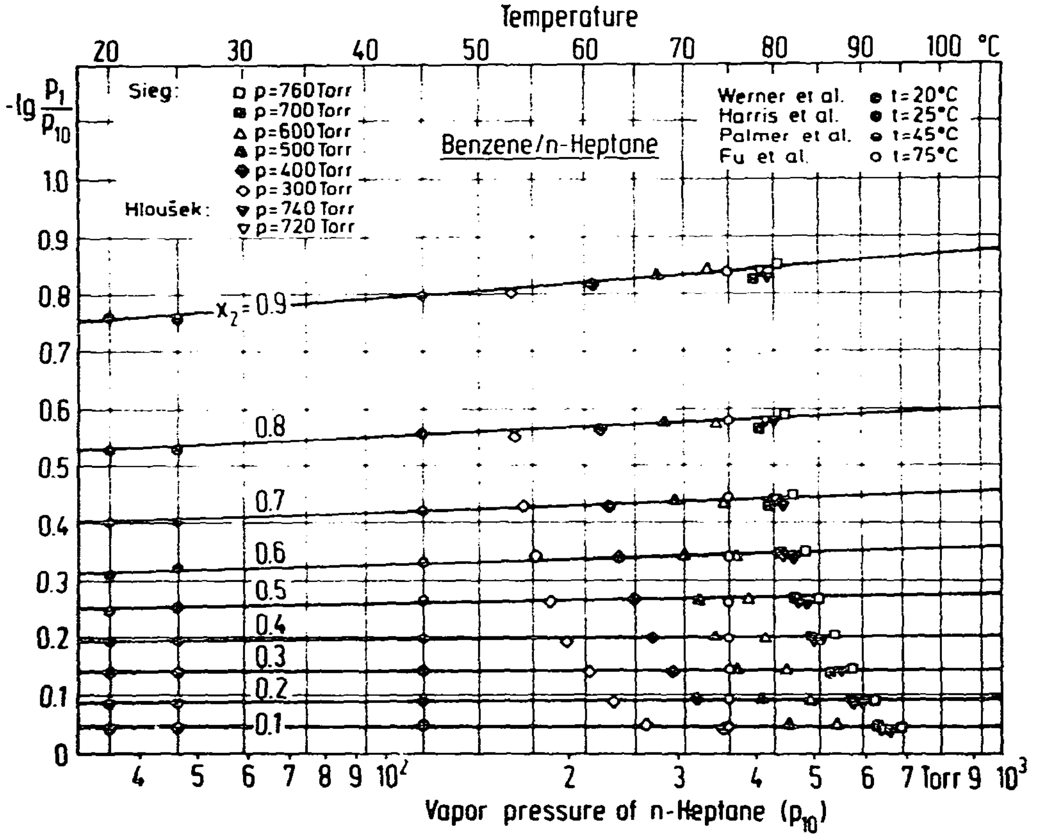

Fig. 1. Lines of constant composition of the liquid phase in the log p_1/p_{10} vs. p_{10} plot.

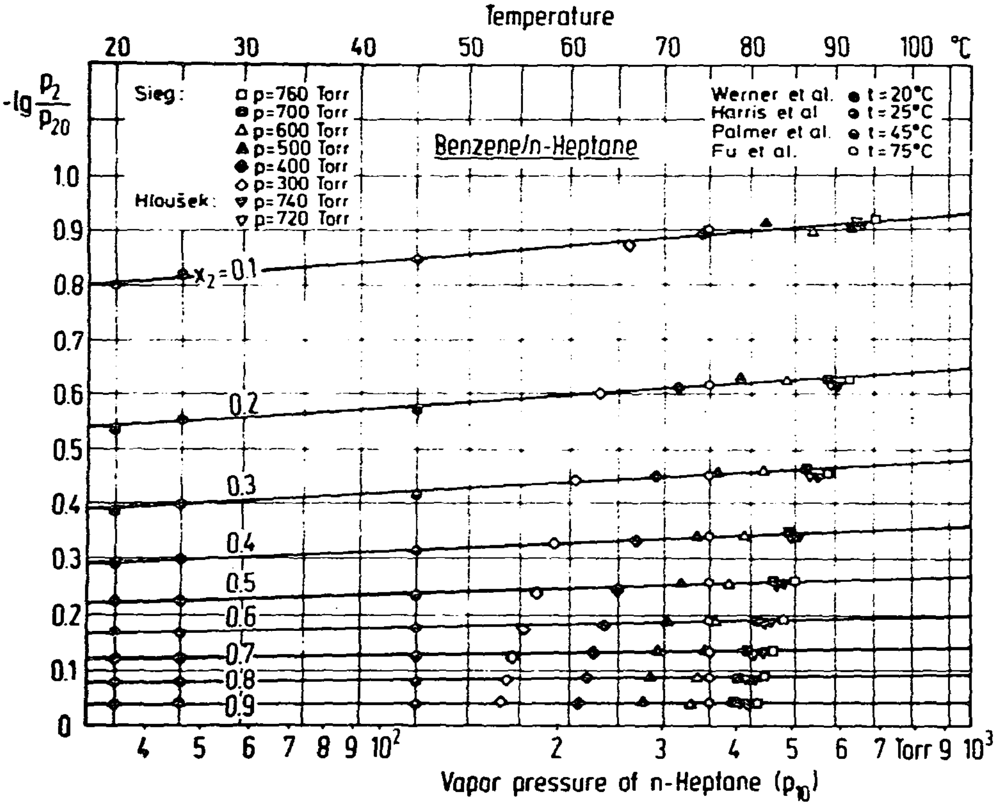

Fig. 2. Lines of constant composition of the liquid phase in the log p_2/p_{20} vs. p_{10} plot.

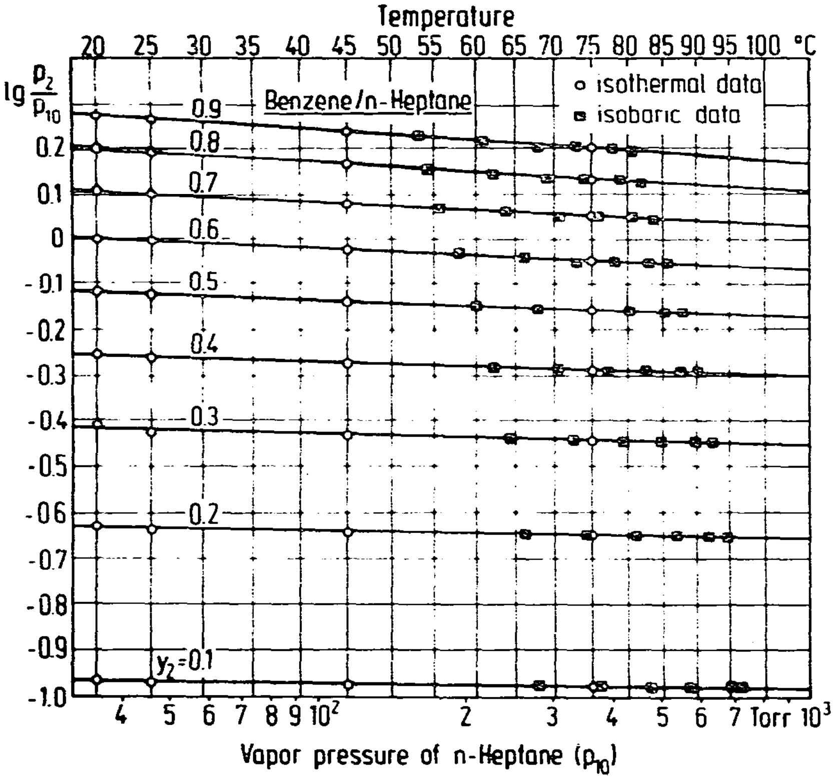

Fig. 3. Lines of constant composition of the vapor phase in the log p_2/p_{10} vs. p_{10} plot.

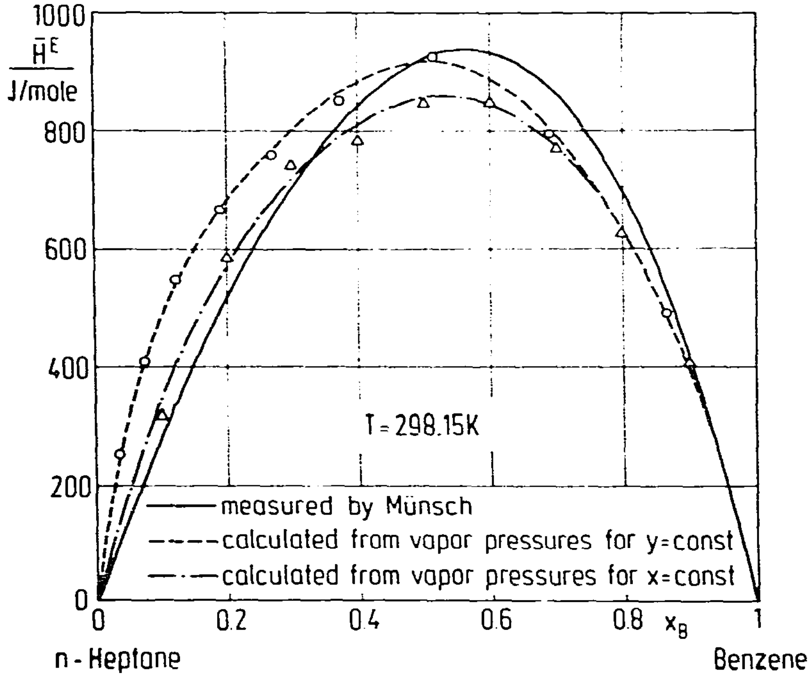

Fig. 4. Comparison of measured and calculated enthalpy of mixing of the benzene/*n*-heptane system at 25 °C.

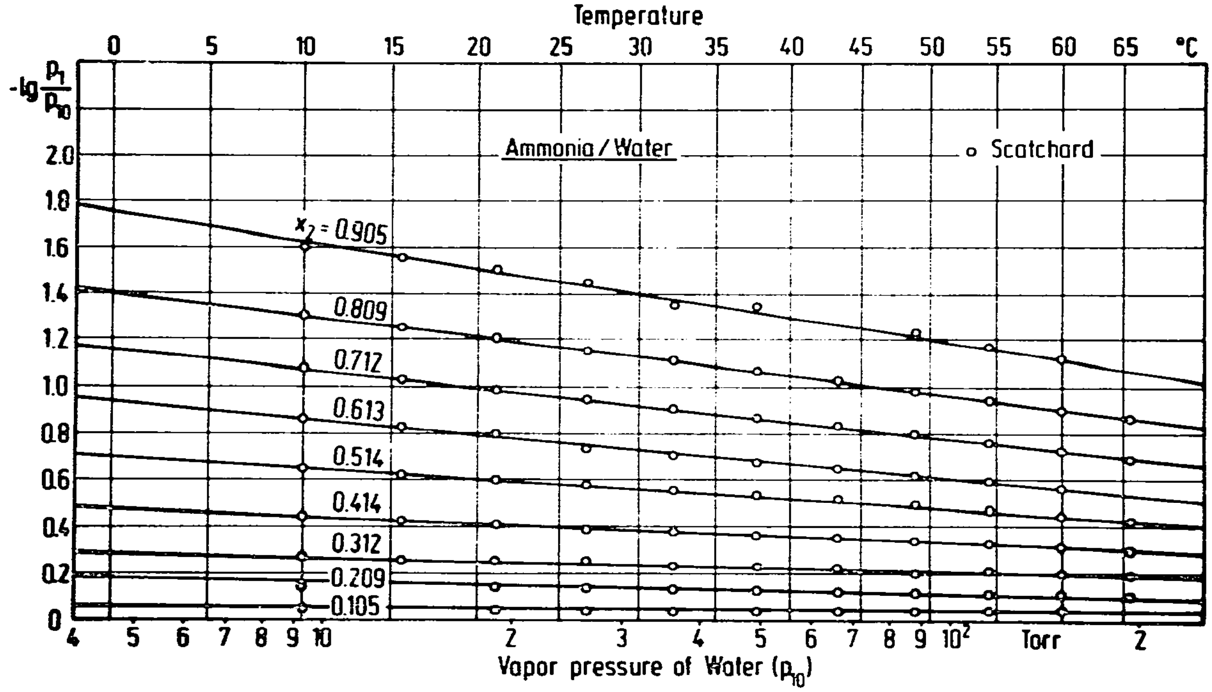

Fig. 5. Lines of constant composition of the liquid phase in the log p_1/p_{10} vs. p_{10} plot.

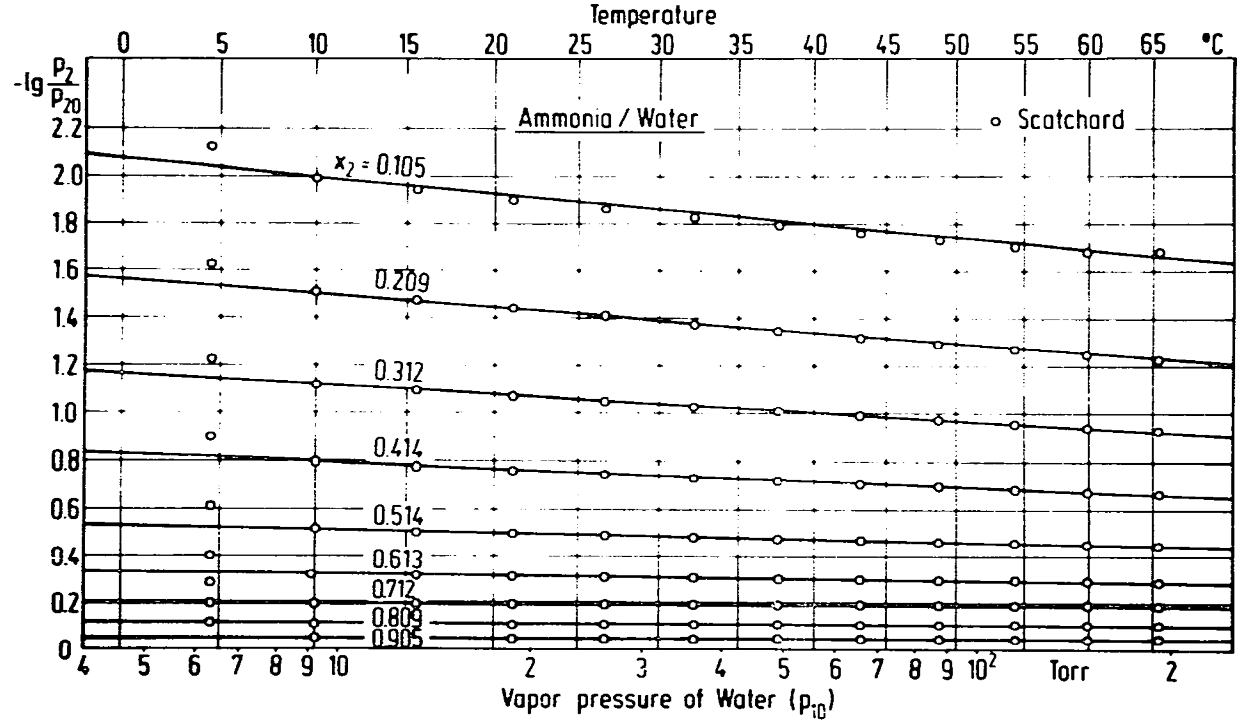

Fig. 6. Lines of constant composition of the liquid phase in the log p_2/p_{20} vs. p_{10} plot.

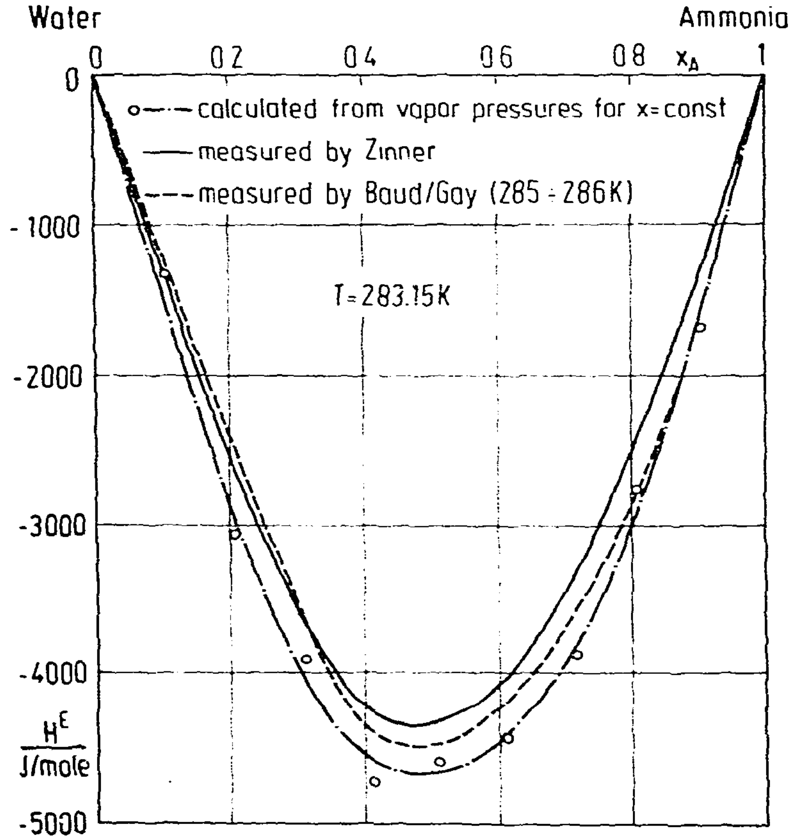

Fig. 7. Comparison of calculated and measured enthalpy of mixing of the ammonia/water system at 10°C.

eqns. (41) and (42) can be considered as independent of temperature. They have been calculated by linear regression.

The temperature range of the equilibrium data reaches from 20 to 95°C. The enthalpy of mixing has been calculated for 25°C and compared with the data measured by Münsch[13]. There is satisfactory agreement of calculated and measured data (Fig. 4). For the enthalpy of vaporization, the value of API-Project 44[5], according to eqn. (44), has been used for the calculus.

THE AMMONIA/WATER SYSTEM

The calculus for the ammonia/water system may be used as an example for strongly non-ideal mixtures. The calculus is based on the isothermal equilibrium data of Scatchard et al.[14]. The calculus has been carried out with the assumption of an ideal vapor phase, according to eqn. (41). Nevertheless the calculated enthalpies of mixing are in satisfactory agreement (Fig. 7) to the measurements by Baud and Gay[15] and Zinner[16]. Because of the extreme form of the dew point curves, the second method according to eqn. (42) allows the calculation of the enthalpy of mixing only in the range of $x_A < 0.25$; therefore it has not been carried out.

CONCLUSIONS

In order to calculate the enthalpy of mixing according to eqn. (33), the vapor pressure curves of the benzene/*n*-heptane system have been fitted by Antoine equations for constant compositions of the vapor phase. Although the same data, as used for the calculus according to eqn. (42), are represented by the Antoine equations with a precision of 2×10^{-3} in the temperature range from 20 to 75°C and 10^{-2} beyond that, the resulting $\bar{H}^E(x)$ curve is so severely deformed that its representation in Fig. 4 has been omitted.

Thus the manipulations leading to eqns. (41) and (42) reduce not only the process of calculation, but also increase the accuracy of the results. The search for equations which describe the temperature dependence of activity coefficients or vapor pressures, then becomes unnecessary.

As a further example, a similar calculation has been carried out for the benzene/1,2-dichloroethane system elsewhere[13].

NOMENCLATURE

B_i	second virial coefficient of pure component i (m^3).
$\bar{G}^E$	molar excess free enthalpy of mixing (J $mole^{-1}$).
$\bar{H}^E$	molar excess enthalpy of mixing (J $mole^{-1}$).
$\bar{H}_i$	molar enthalpy of pure component i at system temperature (J $mole^{-1}$).
$\bar{H}_i^V$	molar enthalpy of vaporization of pure component i at system temperature (J $mole^{-1}$).
h_i	partial molar enthalpy of component i (J $mole^{-1}$).
p	total pressure (N m^{-2}).
p_i	partial pressure of component i (N m^{-2}).
p_{i0}	saturated vapor pressure of pure component i at system temperature (N m^{-2}).
R	gas constant (8.314 J $mole^{-1}$ K).
r_i	real gas correction of activity coefficient γ_i.
s_i	partial molar entropy of component i (J $mole^{-1}$ K^{-1}).
T	temperature, absolute (K).
$\bar{V}_i$	molar volume of pure component i at system temperature (m^3 $mole^{-1}$).
$\bar{V}_i^V$	molar volume of vaporization of pure component i at system temperature (m^3 $mole^{-1}$).
v_i	partial molar volume of component i (m^3 $mole^{-1}$).
x_i	liquid phase mole fraction, component i.
y_i	vapor phase mole fraction, component i.

Greek letters

γ_i	activity coefficient of component i at phase equilibrium.
μ_i	chemical potential of component i (J $mole^{-1}$).

Indices or subscripts

E excess function (in the liquid phase, if not indicated additionally).
V vaporization.
l liquid phase.
v vapor phase.
j at constant composition of a phase.

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