Excess Enthalpies for the Binary Systems *n*-Octane with 2-Methylpentane and 3-Methylpentane

Werner Ameling, Mohammad Aslam Siddiqi, and Klaus Lucas*

Fachgebiet Thermodynamik, Universität-Gesamthochschule-Duisburg, 4100 Duisburg, West Germany

Excess enthalpies for the binary systems *n*-octane with 2-methylpentane and 3-methylpentane are measured at temperatures between 10 and 40 °C and compared to computed values from temperature-dependent vapor–liquid equilibrium (VLE) data for these systems. There is no agreement between these two sets of values, and it is concluded that the published vapor–liquid equilibrium data contain slight systematic errors, which, although not serious for the interpretation and usefulness of the vapor–liquid equilibrium, preclude any reasonable extraction of excess enthalpies in such nearly ideal systems.

In a recent publication (*1*) data for the vapor–liquid equilibrium for the binary systems *n*-octane with 2-methylpentane, 3-methylpentane, and 2,4-dimethylpentane were given over a range of temperatures from 10 to 40 °C. Excess functions were calculated from these data, and the results appeared implausible in view of an extraordinary large temperature dependence of the excess Gibbs free energy, i.e., an implausibly high level of the excess enthalpy. The practical problems in obtaining excess enthalpies from temperature-dependent vapor–liquid equilibria are well recognized. From such experience, it appears that excess enthalpies of about 30% inaccuracy can be obtained from vapor–liquid data of average modern standards for typical systems. The systems considered here are, however, untypical in the sense that they are almost ideal. Clearly, extremely accurate vapor–liquid equilibria over a range of temperatures would be required to extract sensible excess enthalpies. Since the excess enthalpies published in ref *1* appeared to be too high by at least 1 order of magnitude from experience with their relation to molecular interaction, we decided to perform experiments as well as a numerical investigation to clear up the inconsistencies.

Experimental Method and Results

Materials. 2-Methylpentane and 3-methylpentane with reported purity of +99 mol % were obtained from EGA Chemie (Sigma-Aldrich Corp.). *n*-Octane was Fluka puriss. p.a. having a purity of >99.5 mol %. These chemicals were dried over molecular sieve and degassed before use.

Excess Enthalpy Measurements. Excess enthalpies were measured with an isothermal flow calorimeter as described in detail elsewhere (*2*). The calorimeter was tested by measuring the excess enthalpies for the test system cyclohexane + *n*-hexane under various conditions of temperature and pressure. Our results agreed to 1% (2 J/mol) with the established literature values (*2*). The experimental uncertainty for the systems considered here is expected to be 1 J/mol.

Table I. Measured Excess Molar Enthalpy for *n*-Octane (1) + 2-Methylpentane (2)

x_2	h^E, J/mol 10 °C	20 °C	30 °C	40 °C
0.235	18.9	13.5		9.4
0.291				11.1
0.346	23.7	17.6	14.7	
0.399			16.2	
0.451		20.4		14.0
0.502	26.7	20.7	17.4	14.5
0.552	27.2	21.1	17.4	14.2
0.601			17.1	
0.649	26.1	19.8		
0.696			15.4	12.1
0.742	23.5	17.7		
0.787				9.4
0.831	19.5	13.0	10.4	

Table II. Measured Excess Molar Enthalpy for *n*-Octane (1) + 3-Methylpentane (2)

x_2	h^E, J/mol 10 °C	20 °C	30 °C	40 °C
0.238	17.3	13.5	10.2	8.4
0.295				9.7
0.349	22.0	17.5	13.5	
0.403	23.2			11.8
0.455		19.3	15.1	
0.506	24.8	19.3		12.7
0.556	25.0	19.3	15.8	12.7
0.605	24.6			
0.653		17.9	14.6	
0.699				11.2
0.745	21.3	15.0	12.2	
0.790				8.6
0.834		11.1	8.8	

Table III. Constants for Eq 1

	n-octane (1) + 2-methylpentane (2)	*n*-octane (1) + 3-methylpentane (2)
d_1	−399	−414
d_2	142333	145134
e_1	−166	−50
e_2	53200	17362
f_1	−448	−133
f_2	135495	38824

We measured the excess enthalpies of the systems *n*-octane + 2-methylpentane and *n*-octane + 3-methylpentane at temperatures between 10 and 40 °C over the whole composition range. The experimental results are given in Tables I and II and are plotted in Figures 1 and 2. Their composition and temperature dependence was correlated by the equation

$$h^E = x_1x_2[d_1 + d_2/T + (e_1 + e_2/T)(x_2 - x_1) + (f_1 + f_2/T)(x_2 - x_1)^2] \quad (1)$$

and the constants for both systems are given in Table III. The results of this correlating equation are shown as smooth curves in Figures 1 and 2, and it is to be seen that the data are reproduced within their experimental uncertainty.

Numerical Evaluations from the Gibbs–Helmholtz Equation. The Gibbs–Helmholtz equation

$$\left.\frac{\partial(g^E/T)}{\partial(1/T)}\right|_{p,x} = h^E \quad (2)$$

has been used in ref *1* to predict excess enthalpies from measured vapor–liquid equilibria over the same temperature range as considered here. We have repeated these calcula-

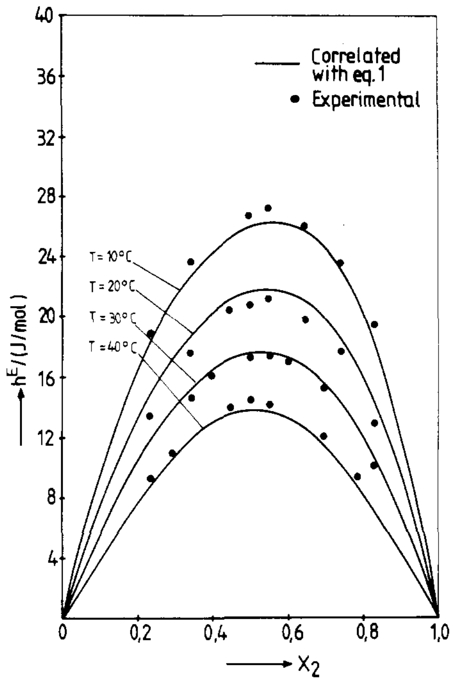

Figure 1. Measured and correlated excess enthalpy for the system *n*-octane (1) + 2-methylpentane (2).

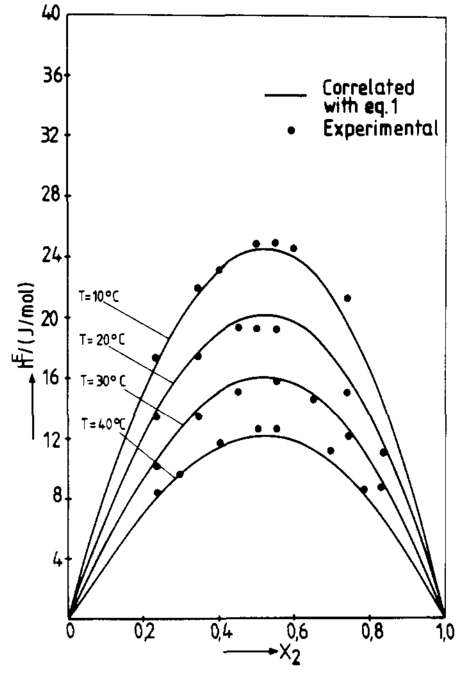

Figure 2. Measured and correlated excess enthalpy for the system *n*-octane (1) + 3-methylpentane (2).

tions with essentially the same results. If the three-parameter Redlich-Kister expansion for the molar excess Gibbs energy

$$g^E = x_1x_2[A + B(x_2 - x_1) + C(x_2 - x_1)^2] \tag{3}$$

is used with the optimization criterion

$$\sum_{i=1}^{M} (p_{\text{exptl}} - p_{\text{calcd}})^2 = \text{min} \tag{4}$$

and the virial coefficients are calculated from a well-known correlation (*3*), Barker's method gives the excess Gibbs free energies for the *n*-octane + 2-methylpentane system shown in Figure 3. Figure 4 shows the g^E/T vs. $1/T$ plot which reveals little scatter and thereby indicates a high precision of the data. Figure 5 finally gives the excess enthalpies obtained by such a regression of the data. Comparison with Figure 1 shows the complete disagreement with the experimental data. Figure 6 shows the vapor-liquid equilibrium as back-calculated from that at 10 °C by using the computed excess enthalpies. The original data are reproduced within their experimental precision, and we conclude that no numerical errors are involved in our processing of the data. Analogous results are found for the system *n*-octane + 3-methylpentane, with the exception that there is considerably more scatter in the g^E/T vs. $1/T$ plot.

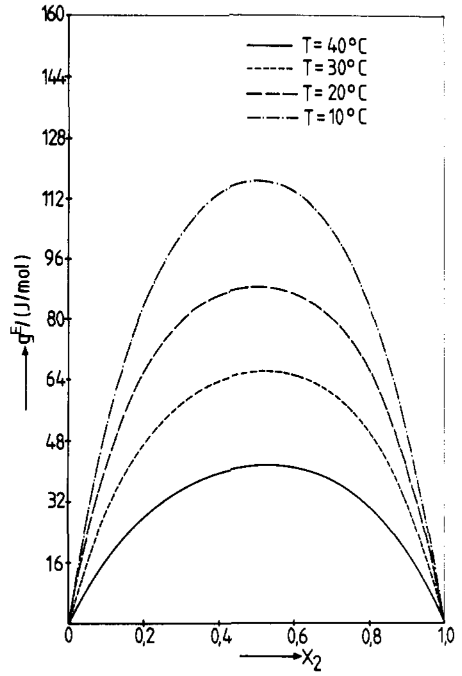

Figure 3. Excess Gibbs free energy for the system *n*-octane (1) + 2-methylpentane (2).

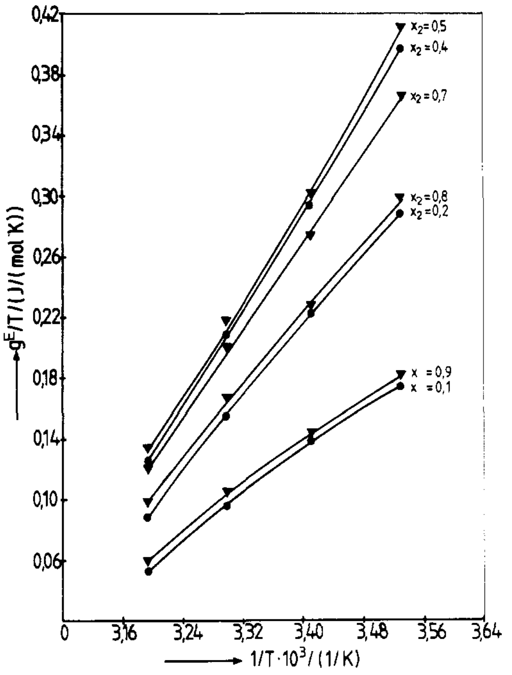

Figure 4. g^E/T vs. $1/T$ for *n*-octane (1) + 2-methylpentane (2) at various mole fractions.

In an effort to study the reasons for this unusually dramatic failure of extracting excess enthalpies from temperature-dependent vapor-liquid equilibria, we assumed a bubble point line, which is a linear connection of the pure-component vapor pressures. This would represent a model system, in which the effects of nonideality in the liquid and in the vapor phase cancel. It can be seen that errors in the experimental pressure of only

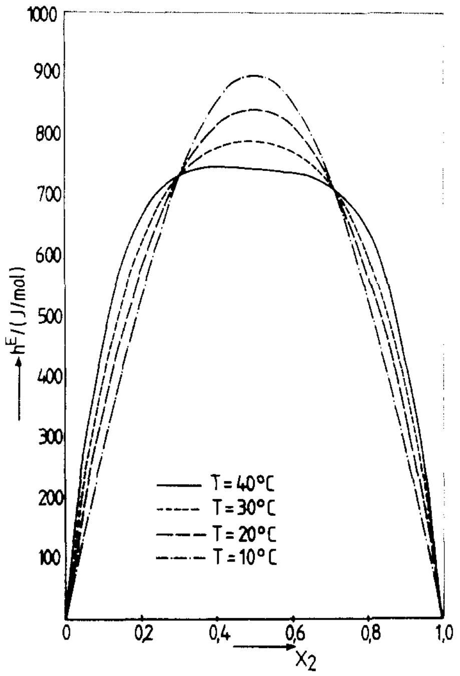

Figure 5. Calculated excess enthalpy for the system *n*-octane (1) + 2-methylpentane (2).

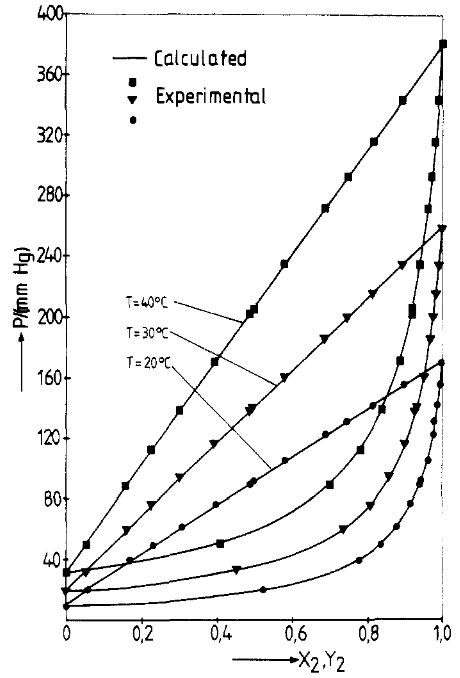

Figure 6. VLE for the system *n*-octane (1) + 2-methylpentane (2) back-calculated from that at 10 °C by using the computed excess enthalpy.

a few mmHg would lead to such a result. In that case, the computed excess enthalpies for an equimolar mixture of *n*-octane + 2-methylpentane would be −76.6 J/mol at 10 °C and −152.7 J/mol at 40 °C. It is clear from these numbers that the computation of excess enthalpies from vapor–liquid equilibria is extremely sensitive to systematic errors in the pressure measurement for this system. We conclude that such systematic errors are present in the data of ref *1*, which, although probably not serious for the interpretation and usefulness of the vapor–liquid equilibrium, preclude any sensible evaluation of the excess functions, in particular the excess enthalpy. Analogous findings apply to the system *n*-octane + 3-methylpentane.

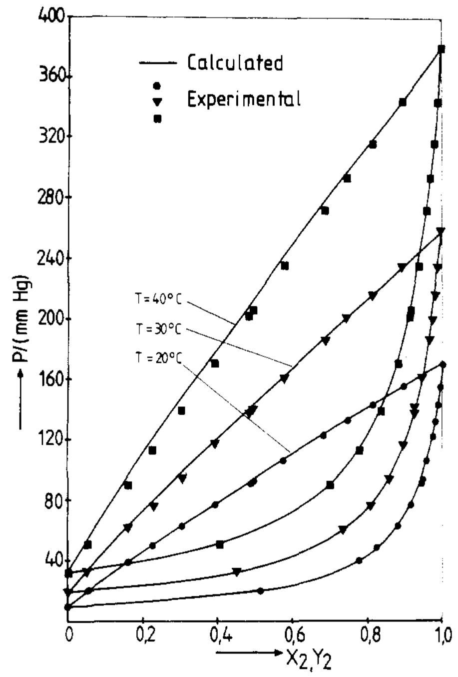

Figure 7. Predicted VLE for the system *n*-octane (1) + 2-methylpentane (2) using the experimental excess enthalpy and the VLE data of ref *1* at 10 °C.

Finally, we have computed the vapor–liquid equilibrium at 20, 30, and 40 °C, using our experimental excess enthalpies and the vapor–liquid equilibrium data of ref *1* at 10 °C. The result is shown in Figure 7, and it can be seen that errors in the pressure of about 6 mmHg, i.e., 3%, account for the observed inconsistencies. Entirely analogous results are obtained when the 40 °C isotherm of ref *1* is used together with our enthalpy data to predict the vapor–liquid equilibrium at 10 °C. We conclude that, in systems that are nearly ideal, an unusual experimental accuracy is required in vapor–liquid equilibrium measurements if the Gibbs–Helmholtz equation is to give even the right order of magnitude of excess enthalpies.

Glossary

A, B, C	constants in expansions of g^E
d_1, d_2, e_1, e_2, f_1, f_2	constants in expansions of h^E
g^E	excess Gibbs free energy, J/mol
h^E	excess enthalpy, J/mol
P_{exptl}	experimental values of the total pressure, mmHg
P_{calcd}	calculated values of the total pressure, mmHg
T	temperature, K
x	mole fraction in liquid
y	mole fraction in vapor

Registry No. Octane, 111-65-9; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0.

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(2) Siddiqi, M. A.; Lucas, K. *J. Chem. Thermodn.* **1982**, *14*, 1183.
(3) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.

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