THERMODYNAMIC ANALYSIS OF CHEMICAL PROCESSES: ASOG-BASED METHODS FOR THE PREDICTION OF EXCESS ENTHALPY AND EXCESS ENTROPY

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Specific methods for predicting liquid-phase excess enthalpy and excess entropy have been developed. These methods consistently use the ASOG group contribution concept for calculating liquid-phase excess properties. The background of the ASOG-based models and their predictive capabilities are demonstrated.

A detailed procedure for the calculation of mixture enthalpy and entropy of nonideal systems is given. It allows one to estimate changes in enthalpy and entropy that are necessary for the analysis of chemical processes by the second law of thermodynamics.

Introduction

The excess enthalpy and excess entropy are important thermodynamic characteristics of nonideal liquid solutions. In chemical engineering these excess functions have the essential role of estimating mixture enthalpy and entropy, the key properties for thermodynamic analysis of chemical processes.

Analysis based on the second law of thermodynamics[8, 30] has been a subject of intensive research in recent years. Considerable amounts of energy and material resources can be saved by its imaginative application to chemical processes. Until recently, however, direct applications of its principles have not been frequently found in practice[16]. One reason is the difficulties associated with estimating the excess entropy, a physical property not accessible to direct experimental determination.

The purpose of this work is to demonstrate simple predictive methods for liquid-phase excess enthalpy and excess entropy. These two methods are extensions of our previously developed model for estimating excess Gibbs energy based on the ASOG group contribution concept[17, 36]. In the following, the ASOG-based models for the excess functions will be referred as the ASOG-H, the ASOG-S and the ASOG-G, respectively. Because of their importance for the second-law analysis of chemical processes, a detailed procedure for calculating mixture enthalpy and entropy at normal pressure is also demonstrated.

1. Prediction of Liquid Phase Excess Enthalpy by the ASOG-H Method

1.1 The ASOG-H model

Applying the ASOG-G group contribution concept[17] to the Gibbs-Helmholz equation results in the following expression for the excess enthalpy:

$$h^E = \sum_i x_i \sum_k v_{k,i} \left(H_k - H_k^{(i)} \right) \tag{1}$$

where v_{ki} is the total number of atoms other than hydrogen in a group k of a molecule i, H_k is the excess enthalpy of a group k in the solution, and $H_k^{(i)}$ is the excess enthalpy of a group k in the solution of groups consisting a pure component i.

H_k is given by the following equation:

$$\frac{H_k}{RT^2} = \frac{\sum_l X_l b_{k/l}}{\sum_l X_l a_{k/l}} + \sum_l \left(\frac{X_l b_{l/k}}{\sum_m X_m a_{l/m}} \right) - \sum_l \left\{ \frac{X_l a_{l/k}}{\left(\sum_m X_m a_{l/m} \right)^2} \sum_m X_m b_{l/m} \right\} \tag{2}$$

where X_k is the mole fraction of a group k in the solution of groups,

$$X_k = \frac{\sum_i x_i v_{k,i}}{\sum_i x_i \sum_l v_{l,i}} \tag{3}$$

Expressions analogous to Eqs. (2) and (3) hold for $H_k^{(i)}$.

The ASOG-H model uses the following temperature dependence of the group Wilson parameters in Eq. (2):

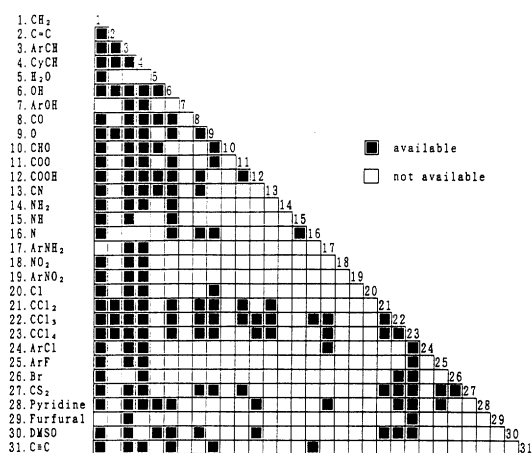$$a_{k/l} = \exp \left(A_{k/l} + B_{k/l} / T + C_{k/l} / T^2 \right) \tag{4}$$

$$b_{k/l} \equiv da_{k/l} / dT = -a_{k/l} \left(B_{k/l} / T^2 + 2C_{k/l} / T^3 \right) \tag{5}$$

Table 1. ASOG group interaction parameters for excess enthalpy

l k		1.CH₂ A	B	C	2.C = C A	B	C	3.ArCH A	B	C
1	CH₂	0.0	0.0	0	−0.9818	239.3	−58515	0.1396	−119.9	10644
2	C = C	−1.5271	−10.9	1018	0.0	0.0	0	−5.2690	2117.8	−280750
3	ArCH	0.5930	84.4	−15297	2.9786	−1494.2	179958	0.0	0.0	0
4	CyCH	0.0056	−26.0	24199	−11.6271	6720.0	−1332822	0.1603	15.2	−9041
5	H₂O	−2.2559	1958.0	−553955	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6	OH	−0.1150	−163.2	−535371	−52.7662	34931.9	−6412995	8.2103	−5187.5	532991

l k		4.CyCH A	B	C	5.H₂O A	B	C	6.OH A	B	C
1	CH₂	−0.1622	149.3	−50463	2.9868	−2395.2	426448	2.7449	−245.4	29345
2	C = C	−0.1002	88.5	−19671	n.a.	n.a.	n.a.	2.7600	−260.9	29271
3	ArCH	0.7283	−0.8	−1687	n.a.	n.a.	n.a.	1.0290	568.0	−75756
4	CyCH	0.0	0.0	0	n.a.	n.a.	n.a.	3.1968	−224.1	28411
5	H₂O	n.a.	n.a.	n.a.	0.0	0.0	0	−3.5353	1884.8	−230186
6	OH	1.3035	−903.5	−519319	−5.0480	603.9	15986	0.0	0.0	0

Fig. 1 Outline of 157 available interaction parameters for excess enthalpy

where $A_{k/l}$, $B_{k/l}$ and $C_{k/l}$ are temperature-independent group interaction parameters. These parameters are the basis for prediction of excess enthalpy by the ASOG-H model.

1.2 Determination of ASOG-H group interaction parameters

The group interaction parameters in Eqs. (4) and (5) have been determined for 31 groups, including CH₂, C = C, ArCH, CyCH and H₂O[15]. An outline of the current state of the ASOG-H parameter table with 157 available entries is presented in **Fig. 1**. The experimental data used to determine the group interaction parameters were taken from Christensen et al.[6] In all, 517 excess enthalpy data sets for 325 binary systems and spanning the temperature range of 288-348 K were included in the determination. The Marquardt method[22] was used to minimize the following objective function:

$$F_{obj} = \sum_{s}\sum_{t}\left\{\left|h^E_{t(\exp)} - h^E_{t(\text{cal})}\right|\right\}^2_s \tag{6}$$

where t stands for the number of data points and s is the number of data sets. If excess enthalpy data for a binary system were available at only two temperatures, the $C_{k/l}$ in Eqs. (4) and (5) was set to the value of zero. For illus-

tration, the group interaction parameters of the six groups CH₂, C = C, ArCH, CyCH, H₂O and OH are shown in **Table 1**.

1.3 Excess enthalpy predictions

The available group interaction parameters of the ASOG-H model were used to predict excess enthalpy in the following systems: 224 binary systems (364 data sets); 57 ternary systems (66 data sets); and 1 quaternary and one quinary system (one data set each). Examples of predicted excess enthalpy for binary systems are shown in **Figs. 2-6**. Figure 2 illustrates the performance of the ASOG-H model for typical aqueous systems. In Fig. 2, $\Delta 1$ denotes the maximum absolute deviation (J/mol), and $\Delta 2$ is the average arithmetic deviation (%). For systems with a changing sign of the excess enthalpy, the following definition of $\Delta 2$ was used:

$$\Delta 2 = \sum_{t}\left\{\left|h^E_{t(\exp)} - h^E_{t(\text{cal})}\right| / h^E_{\exp,\,\max}\right\} \times 100 \tag{7}$$

where t is the number of data points and $h^E_{\exp,\,\max}$ is the maximum value of experimental excess enthalpy in a given data set.

The performance of the ASOG-H model for binary systems showing endothermic and exothermic effects on mixing is demonstrated in Figs. 3-5. The systems with a changing sign of the excess enthalpy are covered in Fig. 6. Examples of excess enthalpy predictions for the three ternary systems 1-propanol + 1-pentanol + 1-octane, benzene + cyclohexane + 1-heptane, and ethanol + 1-propanol + water are shown in **Fig. 7**.

2. Calculation of Liquid and Vapor Phase Enthalpy of Nonideal Systems

The liquid-phase enthalpy H^L of a nonideal system at normal pressure ($P = 101.3$ kPa) is given by the following relation:

$$H^L - \sum_i x_i H_{0,\,i} = \sum_i x_i \int_{T_0}^{T} Cp_i^L\, dT + h^E \tag{8}$$

where $H_{0,\,i}$ is the enthalpy of a pure component liquid at a reference temperature T_0. Pure-component molar heat
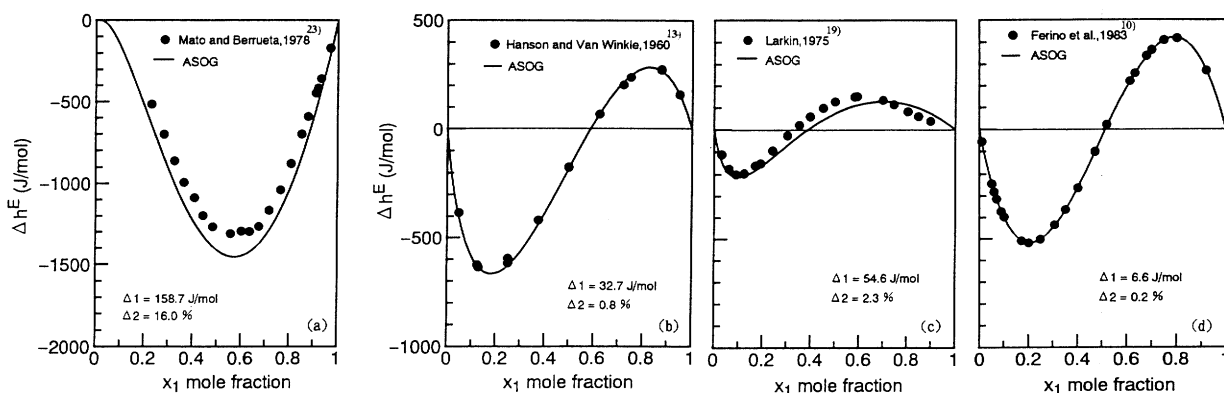
Fig. 2 Predicted results for excess enthalpy of systems including water: (a), Water (1) -Pyridine (2) 298.15 K; (b), Acetone (1) -Water (2) 298.15K; (c), Ethanol (1) -Water (2) 353.15 K; (d), Acetaldehyde (1) -Water (2) 298.15 K; ($\Delta1$), maximum absolute deviation; ($\Delta2$), average arithmetic deviation
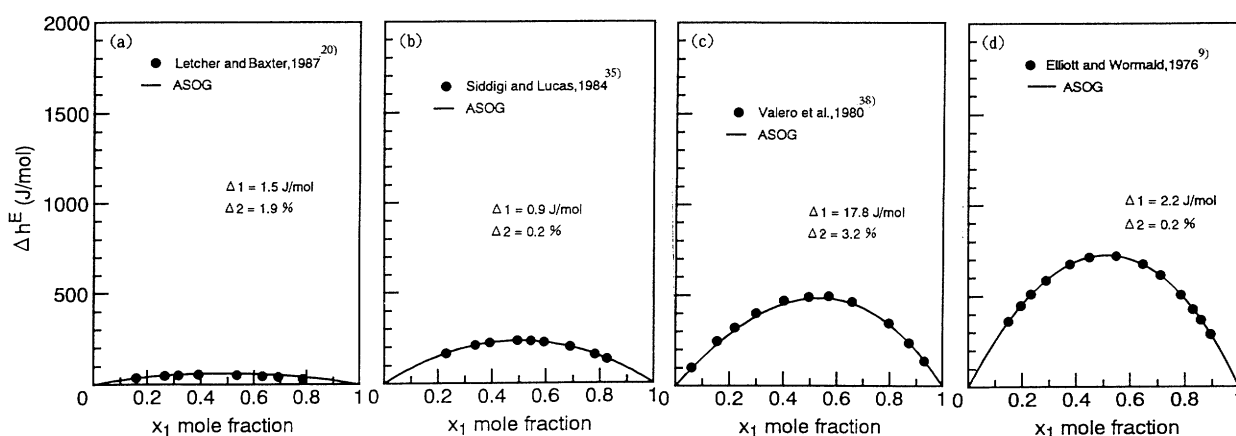

Fig. 3 Predicted results for excess enthalpy of endothermic systems: (a), Hexane (1) -Hexene (2) 298.15 K; (b), Chloroform (1) - Tetrachloromethane (2) 293.15 K; (c), Hexane (1) -1-Chloro butane (2) 298.15 K; (d), Benzene (1) -Cyclohexane (2) 323.15 K; ($\Delta1$), maximum absolute deviation; ($\Delta2$), average arithmetic deviation
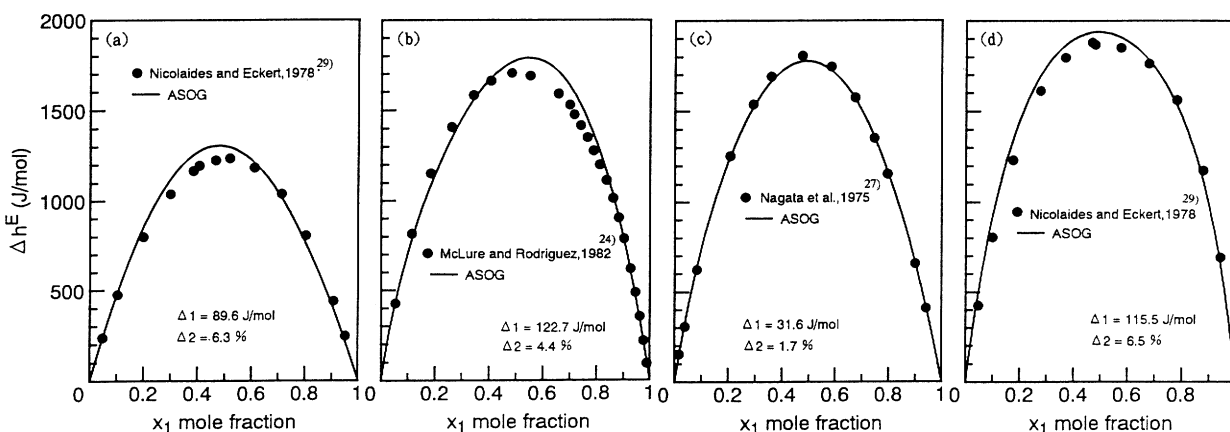

Fig. 4 Predicted results for excess enthalpy of endothermic systems: (a), Acetone (1) -Ethanol (2) 323.15 K; (b), Nitrilebutane (1)- Tetradecane (2) 298.15 K; (c), Methylacetate (1) -Hexane (2) 318.15 K; (d), Cyclohexane (1) -Aniline (2) 308.15 K; ($\Delta1$), maximum absolute deviation; ($\Delta2$), average arithmetic deviation

capacities of liquids Cp_i^L have been compiled and correlated by Zabransky et al.[39]

The liquid-phase excess enthalpy h^E in Eq. (8) can be calculated by the ASOG-H method described in sections 1.1-1.3. Equation (8) can be also used to estimate enthalpy of a saturated liquid mixture at its bubble tem-

perature T_b.

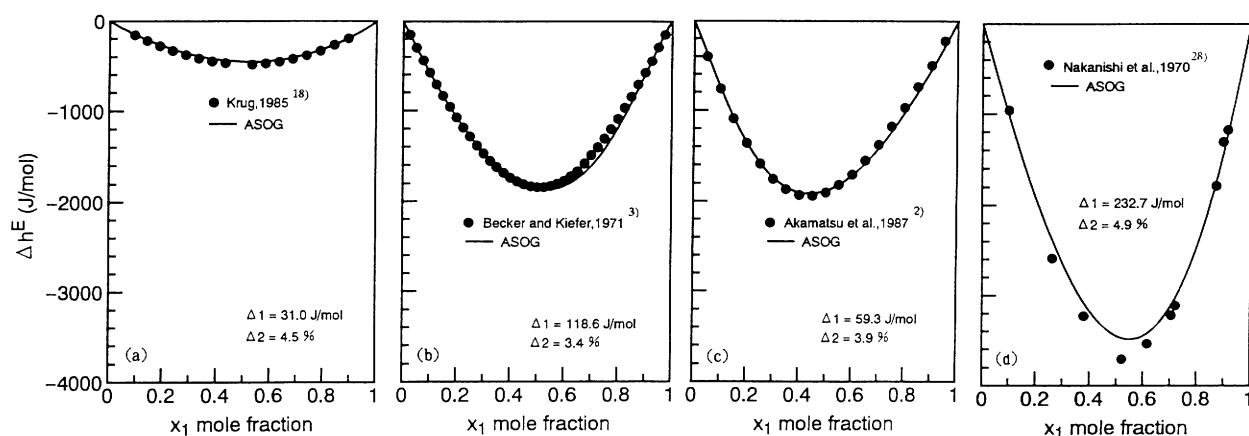The vapor-phase enthalpy H^V of a nonideal system at normal pressure is given by Eq. (9):

Fig. 5 Predicted results for excess enthalpy of exothermic systems: (a), Diethylether (1) -Tetrachloromethane (2) 298.15 K; (b), Chloroform (1) -Dibutylether (2) 298.15 K; (c), Acetone (1) -Chloroform (2) 298.15 K; (d), Methanol (1) -Butylamine (2) 318.15 K; ($\Delta 1$), maximum absolute deviation; ($\Delta 2$), average arithmetic deviation
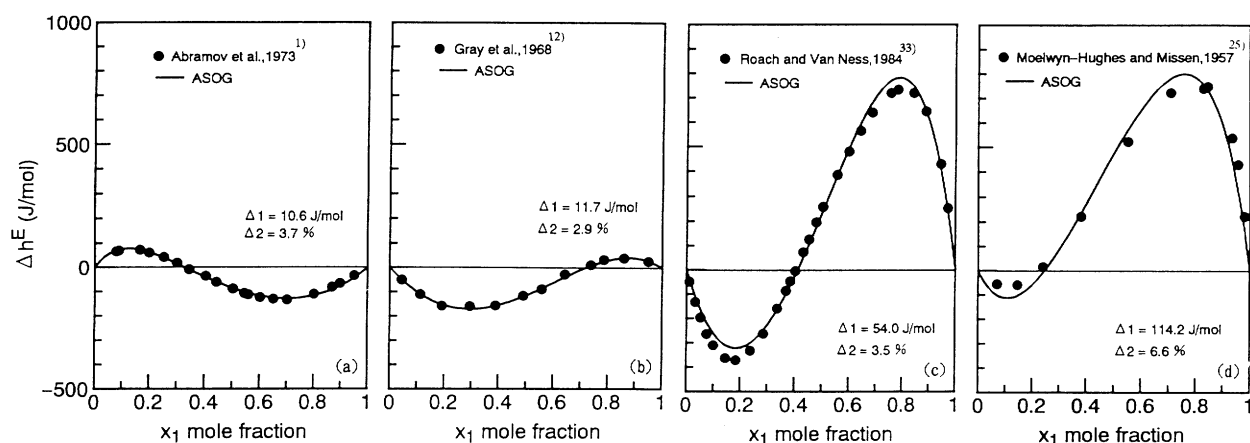

Fig. 6 Predicted results for excess enthalpy of systems with a change of sign: (a), Methanol (1) -Aceticacid (2) 298.15 K; (b), Tetrachloromethane (1) -Pyridine (2) 298.15 K; (c), Chloroform (1) -Ethanol (2) 298.15 K;(d), Dichloromethane (1) -Methanol (2) 308.15 K; ($\Delta 1$), maximum absolute deviation; ($\Delta 2$), average arithmetic deviation
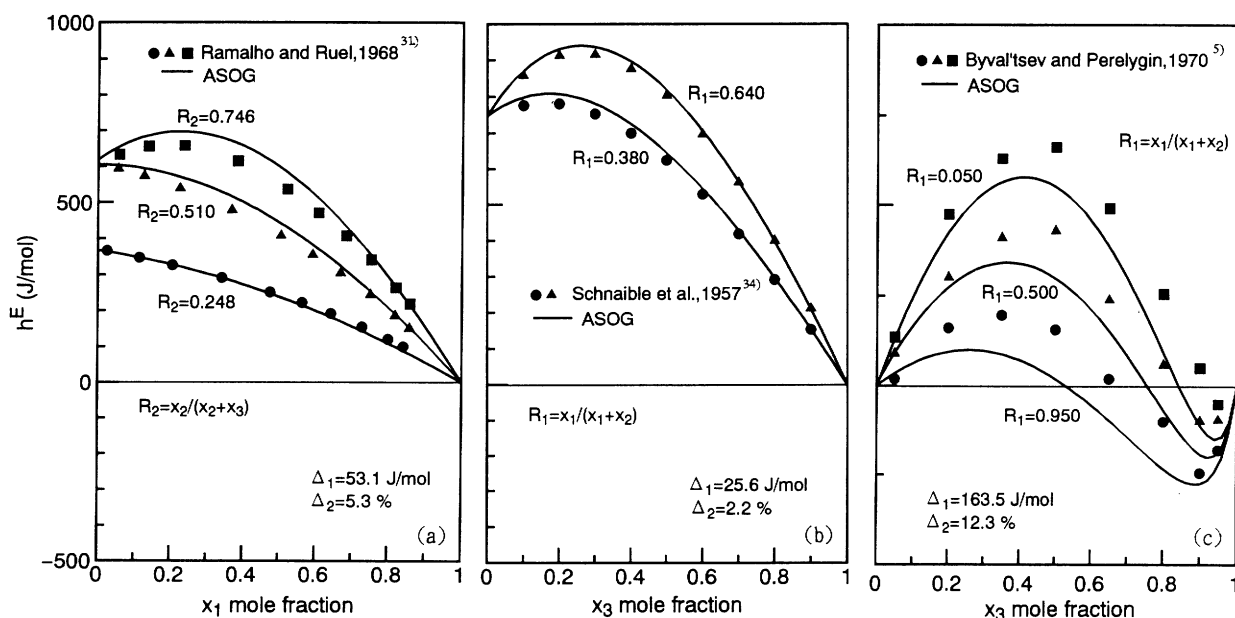

Fig. 7 Predicted results for excess enthalpy of ternary systems: (a), 1-Propanol (1) -1-Pentanol (2) -1-Octane (3) 298.15 K; (b), Benzene (1) -cyclohexane (2) -Heptane (3) 298.15 K; (c), Ethanol (1) -1-Propanol (2) -Water (3) 333.15 K; ($\Delta 1$), maximum absolute deviation; ($\Delta 2$), average arithmetic deviation
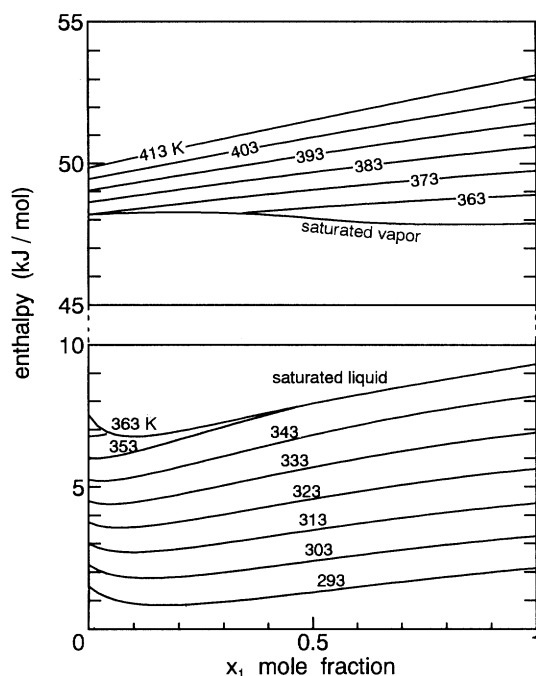
Fig. 8 Calculated liquid-and vapor-phase enthalpy for ethanol(1) + water (2) system at 101.3 kPa

Fig. 9 Calculated liquid-and vapor-phase enthalpy for chloroform (1) + methanol (2) at 101.3 kPa

$$H^V - \sum_i y_i H_{0,i} = \sum_i y_i \int_{T_0}^{T_{B_i}} Cp_i^L \, dT + \sum_i y_i h_i^{evp}$$
$$+ \sum_i y_i \int_{T_{B_i}}^{T} Cp_i^V \, dT + h^{E(V)} \qquad (9)$$

where T_{Bi} is the normal boiling temperature of a pure-component liquid. The parameters of the Antoine equation or the Wagner equation listed in Gmehling and Onken[11] and Reid et al.[32] can be used for estimating vapor pressures and boiling temperatures of pure liquids. Pure-component enthalpies of vaporization h_i^{evp} have been collected by Majer and Svoboda[21].

At moderate pressures, the vapor-phase excess enthalpy $h^{E(V)}$ can be calculated by the virial equation of state truncated after the second virial coefficient,

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \qquad (10)$$

with

$$B = \sum_j \sum_k y_j y_k B_{jk} \qquad (11)$$

For $h^{E(V)}$ the virial equation of state gives

$$h^{E(V)} = \left\{ \left(B - T \frac{dB}{dT} \right) - \sum_i y_i \left(B_{ii} - T \frac{dB_{ii}}{dT} \right) \right\} P \qquad (12)$$

The second virial coefficient correlation by Tsonopoulos[37] can be used for calculating vapor-phase excess properties.

The vapor-phase isobaric heat capacity of a pure component i, (Cp_i^V) is given by the virial equation of state as

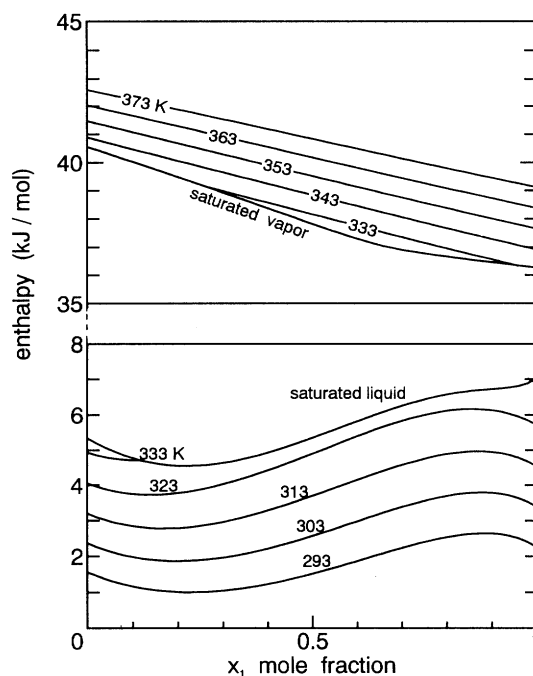$$Cp_i^V = Cp_i^{idealgas} - T \frac{d^2 B_{ii}}{dT^2} P \qquad (13)$$

Equation (9) can be also be used to estimate the enthalpy of a saturated vapor mixture at its dew temperature T_d. The ASOG-G method[17, 36] is a suitable model for estimating bubble and dew point temperatures of saturated mixtures.

The reference temperature used in this study is 273.15 K.

The above method for the determination of liquid-and vapor-phase enthalpy is illustrated in **Figs. 8** and **9** for the binary systems ethanol + water and chloroform + methanol at 101.3 kPa.

3. Prediction of Liquid Phase Excess Entropy by the ASOG-S Method

3.1 Determination of liquid phase excess entropy data of binary systems

The excess entropy (s^E) can be determined by the fundamental thermodynamic relation

$$s^E = (h^E - g^E) / T \qquad (14)$$

using experimental excess enthalpy data h^E and the excess Gibbs energy g^E calculated from vapor-liquid equilibrium data under isothermal conditions (VLET).

The following criteria were applied to the selection of experimental data sets from the collections of excess enthalpy[6, 7] and VLET[11]:

(1) Binary excess enthalpy and VLET data measured at isothermal conditions in the temperature range of 293.15-363.15 K;

(2) VLET data sets covering the whole composition range and containing at least 10 data points;

(3) VLET data sets showing the thermodynamic

Table 2. Collected data of liquid phase excess entropy and its deviation for 36 systems*

No.	system	Temp. Renge K	Deviation Δave[a] J/mol	Deviation Δmax[b] J/mol
1	acetaldehyde + water	298.15	15.1	52.3
2	acetone + benzene	298.15-318.15	12.3	50.3
3	acetone + carbon tetrachloride	318.15	3.6	16.3
4	acetone + chloroform	293.15-323.15	8.5	53.9
5	acetone + cyclohexane	298.15	18.1	45.5
6	acetone + n-hexane	293.15-298.15	18.4	68.3
7	acetone + water	298.15-308.15	38.1	184.3
8	benzene + acetonitrile	298.15-318.15	11.4	64.1
9	benzene + aniline	323.15	14.1	63.8
10	benzene + cyclohexane	298.15-343.15	13.0	69.7
11	benzene + n-heptane	293.15-318.15	17.1	71.3
12	benzene + n-butanol	298.15-318.15	25.2	77.1
13	benzene + nitroethane	298.15	34.1	99.3
14	carbon disulfide + cyclohexane	298.15	3.5	19.0
15	carbon disulfide + chloroform	298.15	5.1	16.2
16	carbon tetrachloride + benzene	313.15-331.15	6.0	21.7
17	carbon tetrachloride + cyclohexane	313.15-318.15	2.4	8.4
18	carbon tetrachloride + n-heptane	298.15	4.4	23.0
19	carbon tetrachloride + pyridine	293.15-298.15	7.6	36.7
20	chloroform + cabon tetrachloride	298.15-323.15	3.6	11.3
21	chloroform + n-heptane	298.15	2.5	10.4
22	chloroform + n-hexane	298.15-308.15	8.2	32.5
23	ethanol + benzene	298.15-318.15	15.0	66.3
24	ethanol + cyclohexane	293.15-318.15	8.7	76.5
25	ethanol + water	298.15-343.15	14.7	77.2
26	ethyl acetate + cyclohexane	298.15-308.15	39.4	142.3
27	methanol + benzene	308.15-318.15	27.5	102.8
28	methanol + water	298.15-323.15	26.4	106.3
29	methyl acetate + cyclohexane	308.15-313.15	18.5	75.0
30	n-hexane + benzene	298.15-313.15	30.6	117.8
31	n-hexane + cyclohexane	298.15-308.15	5.6	37.0
32	n-hexane + n-butanol	298.15	17.9	76.2
33	n-hexane + n-propanol	318.15	15.1	63.5
34	n-hexene + benzene	298.15	4.4	13.0
35	water + dimethylsulfoxide	298.15	40.0	147.7
36	water + pyridine	323.15-362.15	24.4	86.7

[a] average absolute deviation $= \sqrt{\left(\Delta_{ave(g^E)}\right)^2 + \left(\Delta_{ave(h^E)}\right)^2}$

[b] maximum absolute deviation $= |\Delta_{max(g^E)}| + |\Delta_{max(h^E)}|$
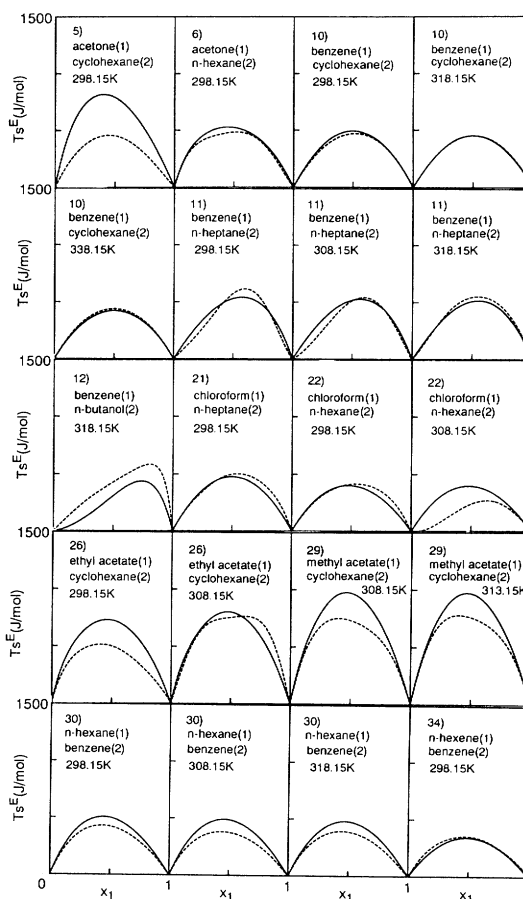
* Hayashi, H. and K. Kojima: Ind. Eng. Chem. Res., 32, 2187 (1993)

Fig. 10 Predicted results of excess entropy for binary systems with positive deviation; (—) ASOG; (...) excess entropy data

consistency (+, +) in the point and area tests according to the DECHEMA compilation[11] and Moon[26];

(4) Excess enthalpy data sets covering the whole composition range and containing at least 10 data points. The above conditions were satisfied for the 36 systems shown in **Table 2**[14]. For determination of the excess entropy, 96 data sets of VLET and 120 data sets of excess enthalpy were finally included.

The experimental data of VLET and excess enthalpy were correlated by the Redlich-Kister equation with temperature-dependent parameters:

$$\frac{g^E}{RT} = x_1 x_2 \sum_{i=0}^{5} \left\{ A_i (x_1 - x_2)^i \right\} \tag{15}$$

$$A_i = a_{i,0} + \frac{a_{i,1}}{T/T_0} + \frac{a_{i,2}}{(T/T_0)^2} \tag{15a}$$

$$h^E = x_1 x_2 \sum_{i=0}^{5} \left\{ B_i (x_1 - x_2)^i \right\} \tag{16}$$

$$B_i = b_{i,0} + \frac{b_{i,1}}{T/T_0} + \frac{b_{i,2}}{(T/T_0)^2} \tag{16a}$$

For correlating excess enthalpies of systems containing alcohols (with the exception of aqueous systems), Eq. (17) was used instead.

$$h^E = \frac{x_1 x_2}{\sum_{i=0}^{5} \left\{ B_i (x_i - x_2)^i \right\}} \tag{17}$$

$$B_i = b_{i,0} + \frac{b_{i,1}}{T/T_0} + \frac{b_{i,2}}{(T/T_0)^2} \tag{17a}$$

The coefficients $a_{i,k}$ in Eq. (15a) are temperature-independent parameters of the excess Gibbs energy, and the coefficients $b_{i,k}$ in Eqs. (16a) and (17a) are temperature-independent parameters of the excess enthalpy. T_0 is a reference temperature of 273.15 K. For correlating the excess Gibbs energy, the ideal vapor phase was assumed. The Wagner equation[32] was used to estimate the vapor pressures of pure components.

The average deviations of correlating experimental data by Eqs. (15-17) were less than 10 % for the excess Gibbs energy and less than 5 % for the excess enthalpy[14]. Table 2 gives deviations of the correlated
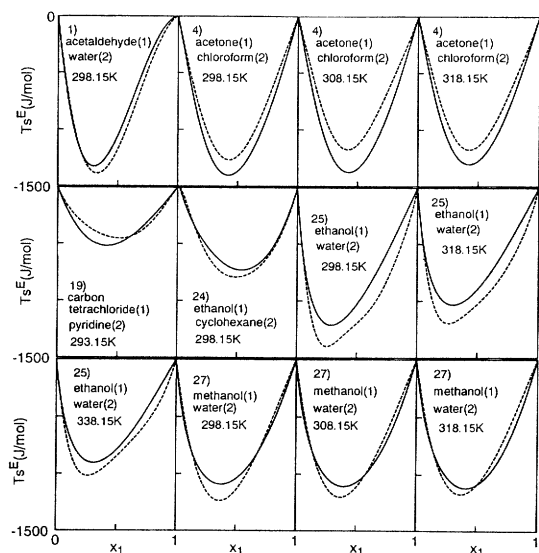
Fig. 11 Predicted results of excess entropy for binary systems with negative deviation; (—) ASOG; (...)excess entropy data

Fig. 12 Predicted results of excess entropy for binary systems with a change of sign; (—) ASOG; (...) excess entropy data

excess entropy determined by Eq. (14) for individual binary systems. The absolute average deviation of excess entropy for the 36 collected systems was less than 40 J/mol.

3.2 Excess entropy predictions by the ASOG-S method

Following Eq. (14), liquid-phase excess entropy was predicted by a combination of the ASOG-G method for estimating excess Gibbs energy and the ASOG-H method for the excess enthalpy. Although the resulting ASOG-based predictive method for the excess entropy is not an independent model, for simplicity it is referred here as the ASOG-S method. **Figures 10** and **11** show the predicted excess entropy for binary mixtures in which the excess entropy has either positive or negative value. **Figure 12** demonstrates the performance of the ASOG-S method for systems with a changing sign of the excess entropy.

Overall comparison of correlated and predicted excess entropy for 36 systems gives an average deviation of 28 %.

4. Calculation of Liquid and Vapor Phase Entropy of Nonideal Systems

The liquid-phase entropy S^L of a nonideal system at normal pressure ($P = 101.3$ kPa) is given by the following relation:

$$S^L - \sum_i x_i S_{0,i} = \sum_i x_i \int_{T_0}^{T} \frac{Cp_i^L}{T} dT + s^E$$
$$- R \sum_i x_i \ln x_i \qquad (18)$$

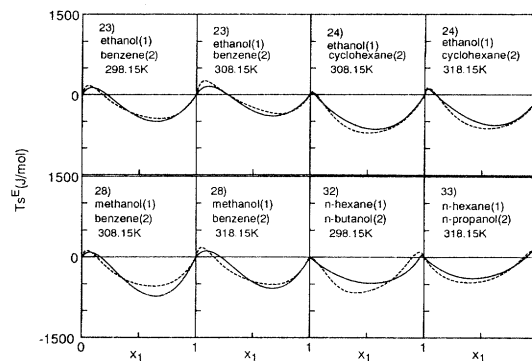where $S_{0,i}$ is the entropy of a pure-component liquid at a

reference temperature T_0. The liquid-phase excess entropy s^E in Eq. (18) can be calculated by the ASOG-S method described in section 3.2. Equation (18) can be also used to estimate the entropy of a saturated liquid mixture at its bubble point temperature T_b.

The vapor-phase entropy S^V of a nonideal system at normal pressure is given by Eq. (19)

$$S^V - \sum_i y_i S_{0,i} = \sum_i y_i \int_{T_0}^{T_{B_i}} \frac{Cp_i^L}{T} dT + \sum_i y_i \frac{h_i^{evp}}{T_{B_i}}$$
$$+ \sum_i y_i \int_{T_{B_i}}^{T} \frac{Cp_i^V}{T} dT + s^{E(V)} - R \sum_i y_i \ln y_i \qquad (19)$$

where T_{Bi} is the boiling temperature of a pure-component liquid at normal pressure. Equation (19) can also be used to estimate the entropy of a saturated vapor mixture at its dew point temperature T_d.

Assuming the virial equation of state, Eq. (10), the vapor-phase excess entropy $s^{E(V)}$ can be calculated as

$$s^{E(V)} = \left(\frac{dB}{dT} - \sum_i y_i \frac{dB_{ii}}{dT} \right) P \qquad (20)$$

The physical meaning of other properties in Eqs. (18-20) and recommended methods for their estimation can be found in section 2.

The above method for the determination of liquid- and vapor-phase entropy is illustrated in **Figs. 13** and **14** for the binary systems ethanol + water and chloroform + methanol at 101.3 kPa.

Conclusions

Specific methods for predicting liquid-phase excess enthalpy and excess entropy have been developed. They consistently use the ASOG group contribution concept for calculating liquid-phase excess properties. The background of the ASOG-based models and their predictive capabilities are demonstrated.

A detailed procedure for the calculation of mixture enthalpy and entropy of nonideal systems at normal pressure is given. The procedure allows estimation of changes of enthalpy and entropy which are necessary for
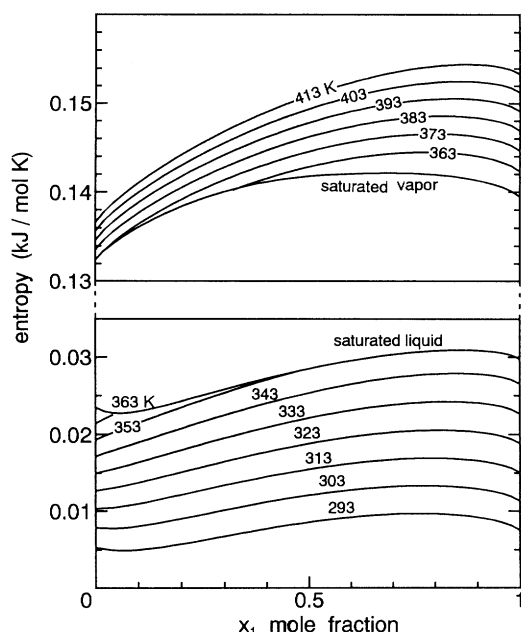
Fig. 13 Calculated liquid-and vapor-phase entropy for ethanol (1) + water (2) system at 101.3 kPa
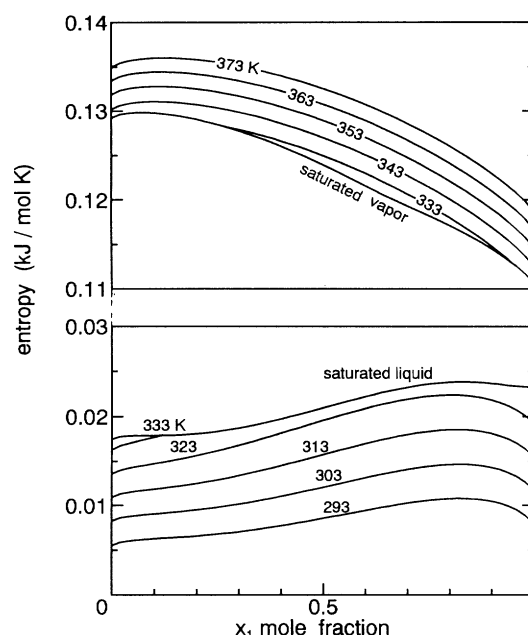

Fig. 14 Calculated liquid-and vapor-phase entropy for chloroform (1) + methanol (2) system at 101.3 kPa

the analysis of chemical processes by the second law of thermodynamics.

Nomenclature

$A_{k/l}, B_{k/l}, C_{k/l}$	=	group interaction parameters of ASOG-H model	[-]
$a_{i,0}, a_{i,1}, a_{i,2}$	=	temperature-independent parameters for excess Gibbs energy in Eq. (14a)	[-]
$a_{k/l}, b_{k/l}$	=	ASOG group Wilson parameters of ASOG-H model	[-]
B	=	second virial coefficient	[m³/mol]
$b_{i,0}, b_{i,1}, b_{i,2}$	=	temperature-independent parameters for excess enthalpy in eqs. (15a) and (16a)	[-]
Cp_i^L	=	molar heat capacity of liquid for pure component i	[J/(mol·K)]
Cp_i^V	=	molar heat capacity of vapor for pure component i	[J/(mol·K)]
$Cp_i^{ideal\ gas}$	=	molar heat capacity of ideal gas for pure component i	[J/(mol·K)]
g^E	=	excess Gibbs energy	[J/mol]
H_k	=	excess enthalpy of group k in solution of groups	[J/mol]
$H_k^{(i)}$	=	excess enthalpy of group k in pure component i	[J/mol]
H^L	=	liquid-phase enthalpy	[J/mol]
H^V	=	vapor-phase enthalpy	[J/mol]
$H_{0,i}$	=	enthalpy of pure liquid component i at reference state	[J/mol]
h^E	=	excess enthalpy of liquid mixture	[J/mol]
$h^{E(V)}$	=	excess enthalpy of vapor mixture	[J/mol]
h_i^{evp}	=	enthalpy of vaporization for pure component i	[J/mol]
P	=	pressure	[kPa]
R	=	gas constant	[J/(mol·K)]
S^L	=	liquid-phase entropy	[J/(mol·K)]
S^V	=	vapor-phase entropy	[J/(mol·K)]
$S_{0,i}$	=	entropy of pure liquid component i at reference state	[J/(mol·K)]
s^E	=	excess entropy of liquid mixture	[J/(mol·K)]
$s^{E(V)}$	=	excess entropy of vapor mixture	[J/(mol·K)]
T	=	absolute temperature	[K]

T_0	=	reference temperature	[K]
X_k	=	mole fraction of group k in solution of group	[-]
x_i	=	liquid mole fraction of component i	[-]
y_i	=	vapor mole fraction of component i	[-]
$v_{k,i}$	=	total number of atoms other than hydrogen in group k of molecule i	[-]

\<Subscripts\>

exp	=	experimental data
cal	=	calculated by ASOG

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