ESTIMATION OF THE EXCESS THERMODYNAMIC FUNCTIONS OF SIMPLE-MOLECULE MIXTURES FROM THE FIRST-ORDER PERTURBATION THEORY

T.BOUBLÍK

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol

First-order perturbation treatment and the new hard sphere equation of state are applied to the calculation of ΔH^E, ΔG^E, and $T\Delta S^E$ of seven binary mixtures: $Ar—N_2$, $Ar—O_2$, $Ar—CO$, $Ar—CH_4$, $CO—CH_4$, $C_5H_{10}—CCl_4$, and $CCl_4—C_6H_{12}$. Results are compared with the experimental data and with the values from the similar treatment where the scaled particle theory equation of state was used.

Perturbation theory of pure fluids[1,2] was found to give a reliable estimation of the properties of liquids, when precise enough description of the hard sphere system was available. In previous communication[3] the perturbation method was applied to the mixture of cyclopentane and carbon tetrachloride. Only the first-order terms in the perturbation treatment were retained to avoid complexity of the relations; the hard sphere equation of state and the radial distribution function from the scaled particle theory (hereinafter referred as SPT)[4] were used in that calculation.

Recently Carnahan and Starling proposed a new hard sphere equation of state for pure fluids[5] that was in a better agreement with the Monte-Carlo data than the SPT-relation (which is identical with the Percus-Yevick (c) equation). The equation was extended for mixtures[6] of hard spheres and relations for the radial distribution functions of the hard spheres at closest approach were obtained.

The effect of an improvement in the description of the hard-sphere behavior on the estimation of the excess functions (within first-order perturbation theory) is followed in this paper on the binary systems of simple, roughly spherical molecules.

THEORETICAL

Exploiting the idea of the thermodynamic cycle where "charging" and "discharging" of the hard spheres by assumed intermolecular potential occurs[7], the following relations for the excess entropy and the energy change associated with mixing the pure components at constant temperature T and pressure P can be found:

$$\Delta S^E = (S_s - S_s^0) - \sum_i x_i(S_i - S_i^0) + (1/T)\left[\sum_i x_i \int_{V_i}^{V*} P_i^0 \, dV - \int_{V_*}^{V_s*} P_s^0 \, dV\right],$$

$$\Delta U^E = (U_s - U_s^0) - \sum_i x_i(U_i - U_i^0). \tag{2}$$

The superscript zero denotes the hard-sphere system, asterisk the perfect gas system (where $P*V* = RT$), and the superscript s a function of the solution with the composition given by the mole fractions x_i.

In the first-order perturbation treatment the "charging" entropy (*i.e.* the difference between entropy for assumed pair potential and the hard-sphere value) for both the pure component and the solution vanishes; the "discharging" energy is just equal to the cohesion energy ΔU_i^{coh},

$$S_i - S_i^0 = 0, \tag{3}$$

$$U_i - U_i^0 = -\Delta U_i^{coh}. \tag{4}$$

The excess entropy can be calculated from the given type of the hard sphere equation of state for pure components and mixture. Here the relations

$$\frac{P_i^0 V}{NkT} = \frac{1 + y_i + y_i^2 - y_i^3}{(1 - y_i)^3} \tag{5}$$

and

$$\frac{P_*^0 V}{NkT} = \frac{6}{\pi}\left[\frac{\xi_0}{(1 - \xi_3)} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^3} + \frac{(3 - \xi_3)\xi_2^3}{(1 - \xi_3)^3}\right] \tag{6}$$

were used for pure components and mixture respectively. N is Avogadro number and the variables y_i and ξ_m are defined by the relations

$$y_i = (\pi N/6V)(2R_i)^3, \tag{7}$$

$$\xi_m = (\pi N/6V)\sum_i x_i(2R_i)^m, \tag{8}$$

where R_i is the radius of the reference hard sphere. Substituting Eqs (7), (8) and (3), in the relation (1) we can obtain the final expression for the excess entropy

$$\frac{T\Delta S}{RT} = \sum_i x_i \left\{\left[\ln\frac{V_s}{V_i} - \left(\frac{\xi_2^3}{\xi_0\xi_3^2} - 1\right)\ln(1 - \xi_3)\right] + \right.$$

$$\left. + 3\left[\frac{y_i}{(1 - y_i)} - \frac{\xi_2(2R_i)}{(1 - \xi_3)}\right] + \left[\frac{y_i}{(1 - y_i)^2} - \frac{\xi_2(2R_i)^2}{\xi_3(1 - \xi_3)^2}\right]\right\}. \tag{9}$$

Similarly as in the SPT only the values of the radial distribution function at closest approach are known for the used type of equations of state:

$$G_{ii}(1) = \frac{1}{(1 - y_i)} + \frac{3}{2}\frac{y_i}{(1 - y_i)^2} + \frac{1}{2}\frac{y_i^2}{(1 - y_i)^3} \qquad (10)$$

and

$$G_{ij}(1) = \frac{1}{(1 - \xi_3)} + \frac{6R_iR_j}{(R_i + R_j)}\frac{\xi_2}{(1 - \xi_3)^2} + \frac{8R_i^2R_j^2}{(R_i + R_j)^2}\frac{\xi_2^2}{(1 - \xi_3)^3}, \qquad (11)$$

where $G_{ij}(1) = g_{ij}(R_i + R_j)$.

Because of this limitation it is assumed that molecules interact according to the simple square-well potential model,

$$u_{ij}(r) = \begin{array}{lll} \infty & \text{for} & r < (R_i + R_j) \\ -\varepsilon_{ij} & & (R_i + R_j) < r < (R_i + R_j) + a \\ 0 & & r > (R_i + R_j) + a, \end{array} \qquad (12)$$

where the distance a is the same for every species and so small that the radial distribution function in this range is constant and equal to $G(1)$ and the integral in the expression for the cohesion energy (and ΔU^E) can be approximated as follows

$$\int u_{ij}(r) g_{ij}(r) 4\pi r^2 \, dr = - 4\pi\varepsilon_{ij}a(R_i + R_j)^2 G_{ij}(1). \qquad (13)$$

Under mentioned assumptions ΔU^E can be calculated from the expression

$$\frac{\Delta U^E}{RT} = \sum_i x_i \frac{\Delta U_i^c}{RT} - \frac{2\pi N}{V_s}\sum_i\sum_j x_ix_j\omega_{ij}\left\{\frac{(R_i + R_j)^2}{(1 - \xi_3)} + \right.$$
$$\left. + \frac{6R_iR_j(R_i + R_j)\xi_2}{(1 - \xi_3)^2} + \frac{8R_i^2R_j^2\xi_2^2}{(1 - \xi_3)^3}\right\}, \qquad (14)$$
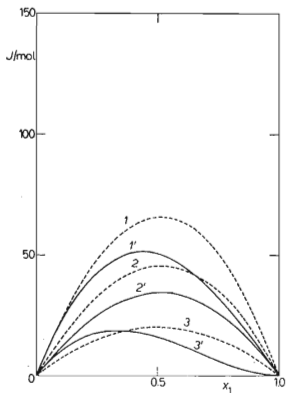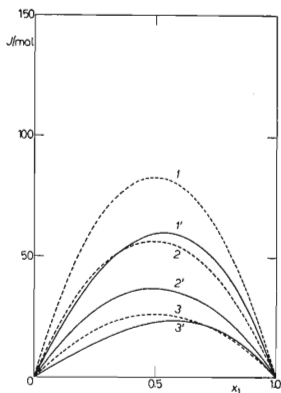
where

$$\omega_{ij} = \varepsilon_{ij}a/kT$$

and

$$\frac{\Delta U_i^c}{RT} = \frac{2\pi N}{V_i}\omega_{ii}(2R_i)^2\left\{\frac{1}{(1 - y_i)} + \frac{3}{2}\frac{y_i}{(1 - y_i)^2} + \frac{1}{2}\frac{y_i^2}{(1 - y_i)^3}\right\}. \qquad (15)$$

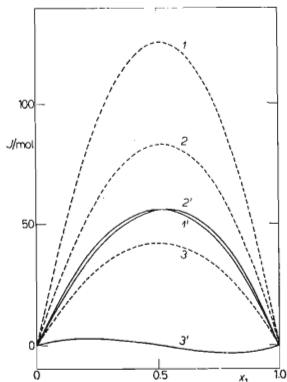First-order perturbation theory (together with the special kind of square-well poten-

tial) fails to predict the $P - V - T$ behavior of liquid precisely enough. For this reason the expression for ΔV^E is not given.
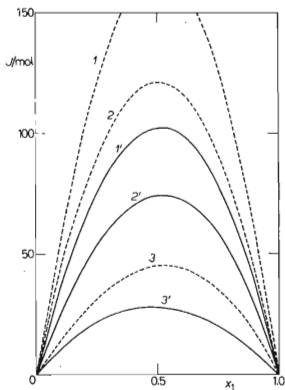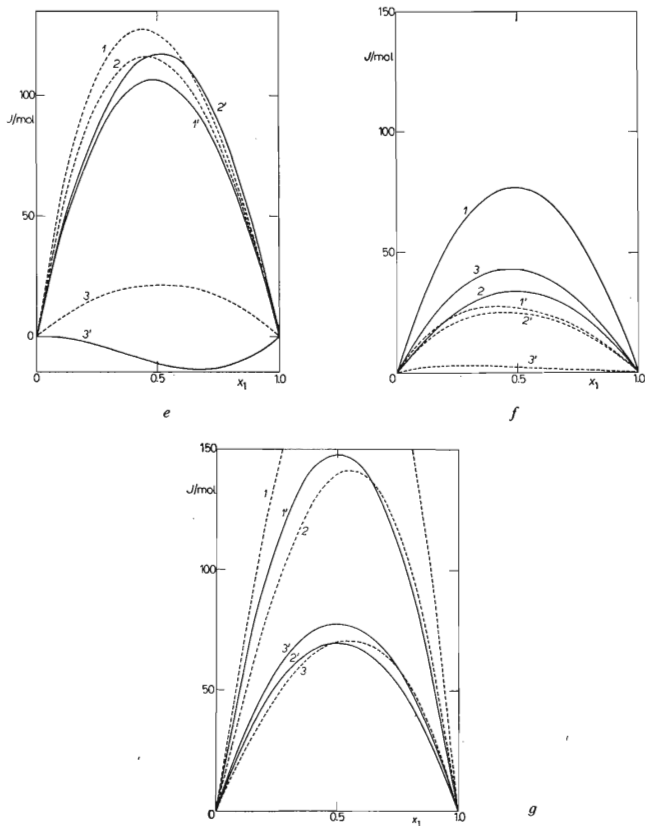
FIG. 1

Comparison of the Calculated and Smoothed Experimental Excess Thermodynamic Functions

a Argon–nitrogen at −189·33°C; *b* argon–oxygen at −189·33°C; *c* argon–carbon monoxide at −190·00°C; *d* argon–methane at −181·95°C; *e* carbon monoxide–methane at −182·48°C; *f* cyclopentane–carbon tetrachloride at 25·00°C; *g* carbon tetrachloride–cyclohexane at 25·00°C. *1*, *2*, *3* calculated ΔH^E, ΔG^E and $T \Delta S^E$ functions, resp.; *1'*, *2'*, *3'* corresponding experimental functions.

TABLE I

Excess Thermodynamic Functions of Equimolar Mixtures from the Scaled Particle Theory and this Work

Source of data	ΔH^{E}	ΔG^{E}, J/mol	$T \Delta S^{E}$
argon–nitrogen, $-189 \cdot 33°C$			
Exptl.	50·52	34·36	16·16
SPT	64·86	44·56	20·29
This work	65·74	45·37	20·37
argon–oxygen, $189 \cdot 33°C$			
Exptl.	59·83	37·08	22·75
SPT	86·27	59·26	27·01
This work	83·05	56·80	26·25
argon–carbon monoxide, $-180 \cdot 00°C$			
Exptl.	56·48	56·65	—0·17
SPT	127·90	85·00	42·90
This work	126·02	83·53	42·49
argon–methane, $-181 \cdot 95°C$			
Exptl.	102·90	74·72	28·18
SPT	170·63	124·51	46·12
This work	166·52	121·49	45·03
carbon monoxide–methane, $-182 \cdot 48°C$			
Exptl.	106·17	117·17	—11·00
SPT	123·46	113·40	10·07
This work	125·50	115·40	10·10
cyclopentane–carbon tetrachloride, $25 \cdot 00°C$			
Exptl.	77·14	34·08	43·06
SPT	25·92	23·72	2·20
This work	27·26	24·93	2·34
cyclohexane–carbon tetrachloride, $25 \cdot 00°C$			
Exptl.	148·00	69·78	78·22
SPT	215·50	143·42	72·08
This work	210·27	139·73	70·54

NUMERICAL CALCULATIONS

Excess functions ΔH^{E}, ΔG^{E}, and $T \Delta S^{\mathrm{E}}$ were calculated from Eqs (9), (15), (16), and (17)

$$\Delta H^{\mathrm{E}} = \Delta U^{\mathrm{E}} + P \, \Delta V^{\mathrm{E}} , \qquad (16)$$

$$\Delta G^{\mathrm{E}} = \Delta H^{\mathrm{E}} - T \, \Delta S^{\mathrm{E}} . \qquad (17)$$

for seven binary mixtures, formed by simple-molecule liquids, exploiting molar volumes, calculated from densities given in the literature and molecular parameters determined from the relations (15) and (18) for the cohesion energy and vaporization entropy of pure components

$$\frac{\Delta S_i^{\mathrm{V}}}{R} = \frac{\Delta H_i^{\mathrm{V}}}{R T} = \frac{2 B_{ii} P_i^{\mathrm{sat}}}{R T} - \ln \frac{P_i^{\mathrm{sat}} V_i}{R T} + \frac{4 y_i - 3 y_i^2}{(1 - y_i)^2} , \qquad (18)$$

where ΔH_i^{V} is the vaporization heat, P_i^{sat} the vapor pressure and B_{ii} the second virial coefficient of the component i.

The mentioned determination of parameters R_i and ω_{ii} from the properties of pure components is necessary because for the used type of square-well potential the parameters are unknown even for the common compounds. Moreover it is believed that the errors due to the limitation of the (first-order) perturbation theory and due to the special kind of the potential compensate themselves to great deal. Heats of vaporization were calculated from the Antoine vapor pressure equation at given temperature and the cohesion energies from the relation (19)

$$U_i^{\mathrm{coh}} = \Delta H_i^{\mathrm{V}} + P_i^{\mathrm{sat}}(V_i - 3 B_{ii}) - R T . \qquad (19)$$

For the cross-terms ω_{ii} the combining rule

$$\omega_{ij} = (\omega_{ii} \omega_{jj})^{1/2} \qquad (20)$$

was used.

In Fig. 1 the comparison is given of the calculated and experimental[8] excess thermodynamic functions ΔH^{E}, ΔG^{E}, and $T \Delta S^{\mathrm{E}}$ for binary system argon–nitrogen at $-189.33°C$, argon–oxygen ($-189.33°C$), argon–carbon monoxide ($-190.00°C$), argon–methane ($-181.95°C$), carbon monoxide–methane ($-182.48°C$), cyclopentane–carbon tetrachloride ($25.00°C$), and carbon tetrachloride–cyclohexane ($25.00°C$). Experimental values are given in full lines, theoretical in broken lines. Values of the excess functions at mole fraction $x_1 = 0.5$ are listed in the Table I.

DISCUSSION

From Fig. 1 and Table I it follows that the used hard sphere equation of state together with the first order perturbation treatment give a fair estimation of the excess functions ΔG^{E}, H^{E} and $T \Delta S^{\mathrm{E}}$ for the mixtures of simple molecules. The agreement is worse for the non-spherical, complex molecules. This conclusion is valid both for the SPT- and the here discussed treatment. Only moderate improvement in the estimation of the thermodynamic functions of real systems results when more precise hard sphere equation of state (and the contact distribution function) is used. The

main sources of the discrepancies are the unsufficient model of pair interactions, the semiempirical mixing rule for ω_{1j}, the limitation of the perturbation relations to the first-order terms only, and the inaccuracy in the determination of molecular parameters.

Advantages of the proposed method remain the simplicity of the derived relations, the small number of parameters, determined from densities and the vapor pressure equations of pure components, and the fact that no parameter adjustable to thermodynamic functions of the solution is present.

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