EXCESS THERMODYNAMIC FUNCTIONS IN THE CARBON DISULPHIDE–TETRACHLOROETHYLENE SYSTEM

K.Procházka and T.Boublík

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol

The dependence of volume of mixing on composition at 25°C and the liquid–vapour equilibrium at temperatures of 25°C, 35°C, and 45°C were determined experimentally in the carbon disulphide(1)–tetrachloroethylene(2) system. Both data were correlated by equations of the Redlich––Kister type and the dependence of excess thermodynamic functions on composition was established. The first order perturbation theory for convex molecules was used to interpret the experimental data.

Perturbation theories of fluids are at the present time successfully used for the description and prediction of the equilibrium behaviour of simple fluids formed by small nonpolar spherical molecules. With the aim of extending the possibility of prediction of thermodynamic behaviour to a larger group of systems, attention is paid now to the methods which describe the interactions of fluid molecules in terms of hard convex bodies with intermolecular potentials dependent on the shortest distance of the interacting body surfaces[1–5]. As relatively simple convex bodies[6] can be assigned to the molecules of carbon disulphide and tetrachloroethylene, the values of experimentally determined excess thermodynamic functions may serve for the verification of the methods describing the equilibrium behaviour of the nonpolar nonspherical molecule systems.

THEORETICAL

For a system formed by N particles in a volume V at temperature T (with average number density $n = N/V$) we can write[7] for the Helmholtz function F the following perturbation expansion:

$$\beta(F - F^0) = \beta\langle W\rangle_0 - \tfrac{1}{2}\beta^2[\langle W^2\rangle_0 - \langle W\rangle_0^2] + \ldots, \tag{1}$$

where $\beta = (kT)^{-1}$, k is Boltzmann's constant, W the perturbation potential energy, F^0 the Helmholtz function of a reference system, and the symbol $\langle\rangle_0$ denotes a quantity averaged over configurations of the reference system.

With a suitable choice of the reference system the expansion converges rapidly so that the greatest contribution in Eq. (1) is given by the first-order perturbation term.

Recently the perturbation method has been extended to systems with pair potential of noncentral type[4-5]. If the pair potential $w(\varrho)$ depends on the shortest distance ϱ between surfaces of interacting particles, *i.e.* the Kihara-core type of pair potential[1] is concerned, it is possible to write the first-order perturbation term in the following way:

$$\langle W \rangle_0/NkT = \tfrac{1}{2}\beta n \iint w(\varrho)\, g^0(\mathbf{r}_{12}, \boldsymbol{\omega}_{12})\, \mathrm{d}\mathbf{r}_{12}\, \mathrm{d}\boldsymbol{\omega}_{12} \,. \tag{2}$$

If core is a convex body Eq. (2) can be simplified by the transformation to the ϱ, θ, φ coordinates, which results in

$$\langle W \rangle_0/NkT = \tfrac{1}{2}\beta n \int_0^\infty w_{\mathrm{ii}}(\varrho)\, \langle g_{\mathrm{ii}}^0(\varrho) \rangle\, S_{\mathrm{i}+\varrho+\mathrm{i}}\, \mathrm{d}\varrho \,. \tag{3}$$

In Eq. (3) $\langle g^0(\varrho) \rangle$ is the correlation function of reference system (the hard convex body system) averaged over all orientations of particle 2 with regard to the particle 1 and over angles θ and φ connected with the body 1:

$$\iiint g^0(\varrho, \theta, \varphi, \boldsymbol{\omega}_{12})\, \mathbf{u} \left(\frac{\partial \mathbf{r}_{12}}{\partial \theta} \,;\, \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) \mathrm{d}\theta\, \mathrm{d}\varphi\, \mathrm{d}\boldsymbol{\omega}_{12} = \langle g^0(\varrho) \rangle\, S_{\mathrm{i}+\varrho+\mathrm{i}} \,. \tag{4}$$

$S_{\mathrm{i}+\varrho+\mathrm{i}}$ in the last relation is the averaged surface given by the motion of the centre of particle 2 (of the type i) with the shortest surface-to-surface distance ϱ with regard to the particle 1.

Similarly to pure substance the perturbation expansion of the first order can be written for mixture as well

$$(F_{\mathrm{s}} - F_{\mathrm{s}}^0)/NkT = \tfrac{1}{2}\beta n \sum_{\mathrm{i},\mathrm{j}} x_\mathrm{i} x_\mathrm{j} \int_0^\infty w_{\mathrm{ij}}(\varrho)\, \langle g_{\mathrm{ij}}^0(\varrho) \rangle\, S_{\mathrm{i}+\varrho+\mathrm{j}}\, \mathrm{d}\varrho \,. \tag{5}$$

As the function $\langle g_{\mathrm{ij}}^0(\varrho) \rangle$ is known only at the contact point[4] (*i.e.* for $\varrho = 0$) the square--well-core potential with a very narrow interval $\varDelta$ is considered in which the correlation function remains practically constant. In this case for the difference of the Helmholtz functions $(F_{\mathrm{s}} - F_{\mathrm{s}}^0)$ the relation[5] can be obtained

$$(F_{\mathrm{s}} - F_{\mathrm{s}}^0)/NkT = -\tfrac{1}{2}n \sum_{\mathrm{i},\mathrm{j}} x_\mathrm{i} x_\mathrm{j} a_{\mathrm{ij}} S_{\mathrm{i}+\mathrm{j}} \,, \tag{6}$$

and for a pure substance analogously

$$(F_\mathrm{i} - F_\mathrm{i}^0)/NkT = -\tfrac{1}{2}n a_{\mathrm{ii}} S_{\mathrm{i}+\mathrm{i}} \,, \quad a_{\mathrm{ij}} = \varepsilon_{\mathrm{ij}} \varDelta/kT \,. \tag{7}, (8)$$

The averaged surface S_{i+j} is given by the surfaces S_i, S_j and by the $(1/4\pi)$-multiples of integrals of mean curvature R_i, R_j of single components, *i.e.*

$$S_{i+j} = S_i + S_j + 8\pi R_i R_j \,. \tag{9}$$

F_i^0 and F_s^0 and further thermodynamic functions of the reference system of hard convex bodies can be determined from a corresponding equation of state[4],

$$\beta P_s^0/n = 1/(1-v) + rs/n(1-v)^2 + qs^2/3n(1-v)^3 \,; \tag{10}$$

for the averaged correlation function the polynom was then found

$$\langle g_{ij}(0)\rangle \, S_{i+j} = A_{ij}(S_i + S_j + 8\pi R_i R_j) + B_{ij}(S_j + 4\pi R_i R_j) + C_{ij}S_j \,, \tag{11}$$

where the coefficients A_{ij}, B_{ij}, and C_{ij} are expressed in terms of the quantities r, s, q, v for which in case of a mixture (with the number density n_i for the component i) holds[5]

$$r = \sum n_k R_k \,, \quad s = \sum n_k S_k \,, \quad q = \sum n_k R_k^2 \,, \quad v = \sum n_k V_k \,, \quad n = \sum n_k \,. \tag{12}$$

The knowledge of thermodynamic and correlation functions of reference system for mixture and pure components allows then the computation of excess functions of the system studied with a given composition, temperature and pressure.

It appears that the excess entropy, in case of the first order perturbation expansion with the temperature- and density independent choice of the reference body size, is given only by contributions of reference systems of hard convex bodies, so that it holds

$$\Delta S^E/Nk = \sum_i x_i \left\{ \ln \frac{\mathscr{V}_s(1-v)}{\mathscr{V}_i(1-y_i)} + 3\left[\frac{\alpha_i y_i}{(1-y_i)} - \frac{rs}{3n(1-v)} \right] + \right.$$
$$\left. + \frac{3}{2}\left[\frac{\alpha_i^2 y_i^2}{(1-y_i)^2} - \frac{qs^2}{9n(1-v)^2} \right] \right\} \,, \tag{13}$$

where $y_i = nV_i$, $\alpha_i = R_i S_i/3V_i$, and $\mathscr{V}_s$ and $\mathscr{V}_i$ are molar volumes of the solution and the component i.

Unlike the excess entropy, the other excess functions are given also by the combination of the first-order perturbation terms, so that the final relations are somewhat more complicated.

EXPERIMENTAL

Chemicals. Carbon disulphide, an analytical reagent (Laborchemie, Apolda), was shaken with aqueous $KMnO_4$ solution, then with water, mercury and with saturated aqueous $HgSO_4$ solu-

tion. After washing with distilled water, it was dried by means of $CaCl_2$ and distilled: n_D^{15} 1·63182 (1·6319 (ref.[8])), d_4^{20} 1·26315 (1·2632 (ref.[8])), $t_{n.b.p.}$ 46·21°C (46·25 (ref.[9])).

Tetrachloroethylene, for IR spectroscopy (Fluka), was dried by means of $CaCl_2$ and distilled under vacuum: n_D^{20} 1·50577 (1·50566 (ref.[10])), d_4^{20} 1·62280 (1·62272 (ref.[9])), $t_{n.b.p.}$ 121·05°C (120·97 (ref.[9])).

Apparatus and methods of measurements. Vapour–liquid equilibrium was measured in an equilibrium recirculation still of the Gillespie type with stirring the liquid and the condensate[11]. The apparatus was connected to a vacuum station maintaining the pressure in the system with an accuracy of ± 0.1 Torr. Temperature was measured by a platinum thermometer connected into the circuit of Mueller bridge (Leeds and Northrup). Pressure was determined from boiling points of redistilled water in the Swietoslawski ebulliometer connected to the vacuum station. The composition of equilibrium phases in the $CS_2(1)$–$C_2Cl_4(2)$ system was determined refractometrically. Refractive index at wave length corresponding to the sodium D line was measured by a Zeiss immersion refractometer which allows to determine the measured quantity with an accuracy of $\pm 2 . 10^{-5}$. The dependence of refractive index on the composition of mixture at 20°C was correlated by the least square method:

$$n_D^{20} = 1.62775x_1 + 1.50577(1 - x_1) + x_1(1 - x_1)\left[-0.08820 - 0.03013(2x_1 - 1) - 0.00918(2x_1 - 1)^2\right].\tag{14}$$

The mean error in the determination (on repeating the refractometric analysis several times) of the equilibrium phase compositions amounted to $\pm 0.07\%$. Saturated vapour pressures of pure components, P_i^0, were determined at temperatures of 25°C, 35°C, and 45°C in the arrangement identical with the equilibrium measurement, a good agreement being obtained with the data obtained by the standard ebulliometric method[6] (± 0.1 Torr). The volumes of mixing were mea-
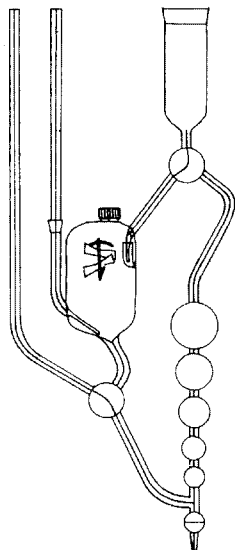

FIG. 1

Schematic Diagram of the Dilatometer Used

sured in a dilatometer proposed by Pflug and Benson[12] with a modified charging part. A schematic diagram of the apparatus is evident from Fig. 1. During measurements the dilatometer was immersed in a thermostat maintaining the temperature of 25°C with an accuracy of ± 0.001°C. The overall error in the excess colume determination for the equimolar mixture is estimated to be 2%.

RESULTS AND DISCUSSION

The experimental data on molar volumes of mixing as a function of the CS_2 mole fraction are presented in Table I. The experimental data were correlated by an em-

TABLE I

Excess Volumes in the CS_2–C_2Cl_4 System at 298·15 K

x	V^E, cm^3/mol	x	V^E, cm^3/mol
0·0258	0·0636	0·4756	0·5106
0·0567	0·1336	0·5430	0·4947
0·1189	0·2553	0·5951	0·4706
0·2042	0·3718	0·6218	0·4544
0·2207	0·3893	0·6446	0·4410
0·2406	0·4087	0·7751	0·3210
0·2815	0·4441	0·8856	0·1777
0·3392	0·4797	0·9461	0·0855

TABLE II

Vapour–Liquid Equilibrium in the CS_2–C_2Cl_4 System at 298·15 K

x	y	P, Torr	Dev, G^E
0·1233	0·7905	76·33	-0.0113
0·1607	0·8355	93·35	-0.0097
0·2251	0·8822	121·31	-0.0076
0·2574	0·8977	134·58	-0.0045
0·3346	0·9234	164·14	-0.0022
0·4724	0·9508	209·87	0·0804
0·5822	0·9622	241·56	-0.0820
0·7092	0·9752	275·88	0·0113
0·7918	0·9822	298·34	0·0111
0·8823	0·9898	324·22	0·0173
0·9285	0·9937	338·23	0·0114

pirical equation of the Redlich–Kister type[11]. Constants of the equation were evaluated by the weighted least square method and are given in Table V.

The data characterizing the equilibrium between the liquid and vapour phases in the $CS_2(1)$–$C_2Cl_4(2)$ system at 25°C, 35°C, and 45°C are summarized in Tables II − IV.

TABLE III

Vapour–Liquid Equilibrium in the CS_2–C_2Cl_4 System at 308·15 K

x	y	P, Torr	Dev . G^E
0·1024	0·7200	98·54	—0·0223
0·1929	0·8388	155·37	—0·0087
0·2666	0·8837	198·21	—0·0054
0·3015	0·8982	217·32	—0·0018
0·3334	0·9102	234·13	0·0867
0·3918	0·9238	263·32	—0·0781
0·4734	0·9412	301·03	0·0063
0·5799	0·9567	346·10	0·0010
0·6977	0·9701	392·23	0·0141
0·7850	0·9789	427·41	—0·0038
0·8757	0·9877	464·57	—0·0051
0·9285	0·9928	487·39	—0·0172

TABLE IV

Vapour–Liquid Equilibrium in the CS_2–C_2Cl_4 System at 318·15 K

x	y	P, Torr	Dev . G^E
0·1272	0·7329	163·40	—0·0231
0·1650	0·7853	195·33	—0·0127
0·2355	0·8461	252·23	—0·0044
0·2985	0·8797	300·11	—0·0042
0·3369	0·8950	327·94	0·0035
0·3923	0·9134	366·38	0·0728
0·4734	0·9306	419·31	—0·0683
0·5751	0·9495	481·09	0·0074
0·6967	0·9659	550·69	0·0055
0·7964	0·9774	606·84	0·0020
0·8754	0·9861	652·49	0·0057
0·9279	0·9918	684·13	—0·0065

By using the experimental data, the concentration dependence of activity coefficients γ_i of components in the liquid phase were calculated. On calculating, the non-ideality of the vapour phase behaviour was considered. Logarithms of activity coefficients were calculated on the basis of the relation[13]

$$RT \ln \gamma_i = RT \ln \left(P y_i / P_i^0 x_i \right) + \left(B_{ii} - V_i^0 \right) \left(P - P_i^0 \right) + P \delta y_{3-i}^2, \qquad (15)$$

where x_i and y_i are mole fractions of the i-th component in the liquid or the vapour phase, respectively, T is absolute temperature, and R is gas constant. P denotes total pressure and P_i^0 are saturated vapour pressures of pure substances at the given temperature. Second virial coefficients at the given temperature are denoted by B_{ii} and V_i^0 stands for volumes of components in the liquid state. The quantity δ is defined by the relation $\delta = 2B_{12} - B_{11} - B_{22}$.

TABLE V

Constants in the Redlich–Kister Expansion of Excess Functions

Function	A	B	C
$(\Delta G^E / RT)_{298.15}$	0·4770	0·1206	−0·0453
$(\Delta G^E / RT)_{308.15}$	0·4479	0·1019	−0·0443
$(\Delta G^E / RT)_{318.15}$	0·4114	0·0938	−0·0156
$(\Delta H^E / RT)_{298.15}$	0·8228	0·5575	−0·0252
$\Delta V_{298.15}^E$, cm^3/mol	2·0211	−0·3898	0·0972

TABLE VI

Comparison of Theoretical and Experimental Values of Excess Thermodynamic Functions of the CS_2–C_2Cl_4 System at 298·15 K

Function	$x = 0.2$		$x = 0.5$		$x = 0.8$	
	calc	exp	calc	exp	calc	exp
ΔG^E, J/mol	93·7	154·0	140·7	295·6	85·2	211·4
ΔH^E, J/mol	186·6	190·1	289·3	509·5	182·5	455·4
$T \Delta S^E$, J/mol	92·9	36·1	148·6	214·3	97·3	244·0
ΔV^E cm^3, /mol	0·11	0·37	0·17	0·50	0·11	0·29

The values of second virial coefficients for CS_2 were found in the literature[14]. However, for C_2Cl_4 measured values are not available and the second virial coefficients had to be estimated from the generalized equation[15]

$$B_{ii} = (RT_{ci}/P_{ci}) [f_0(T_r) + \omega_i f_1(T_r)] , \qquad (16)$$

where T_{ci} and P_{ci} denote critical temperature and critical pressure, respectively, T_r is reduced temperature $T_r = T/T_{ci}$ and the functions $f_0(T_r)$ and $f_1(T_r)$ are defined by the following relations:

$$f_0(T_r) = 0.1445 - 0.33T_r^{-1} - 0.1385T_r^{-2} - 0.0121T_r^{-3} , \qquad (17)$$

$$f_1(T_r) = 0.073 - 0.46T_r^{-1} - 0.5T_r^{-2} - 0.097T_r^{-3} - 0.0073T_r^{-8} . \qquad (18)$$

The symbol ω_i denotes acentric factor defined by the equation

$$\omega_i = - \log P_r^{(0.7)} - 1 , \qquad (19)$$

where $P_r^{(0.7)}$ is reduced saturated vapour pressure of a substance (P^0/P_{ci}) at a reduced temperature $T_r = T/T_{ci} = 0.7$.

Inasmuch as C_2Cl_4 decomposes at higher temperatures and therefore its critical constants are not determinable experimentally, they had to be estimated by means of the Lydersen method[15].

The cross virial coefficient was calculated by means of equations

$$V_{c12} = [1/2(V_{c1}^{1/3} + V_{c2}^{1/3})]^3 , \quad T_{c12} = (T_{c1}T_{c2})^{1/2} (V_{c1}V_{c2}/V_{c12}^2) ,$$
$$\omega_{12} = 1/2[\omega_1 + \omega_2] , \qquad (20)-(22)$$

$$B_{12}/V_{c12} = f_0(T_r)/0.291 + \omega_{12}[0.274f_0(T_r) + f_1(T_r)]/[0.231 - 0.8\omega_{12}] . \quad (23)$$

The excess free enthalpy was calculated from the relation

$$\Delta G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 . \qquad (24)$$

The data on $\Delta G^E/RT$ were fitted to the Redlich–Kister expansion

$$\Delta G^E/RT. = x_1 x_2 [A + B(2x_1 - 1) + C(2x_1 - 1)^2] , \qquad (25)$$

whose constants, listed for temperatures of 298·15, 308·15, and 318·15K in Table V, were determined by the least square method. The measured experimental x-y-P data

are presented in Tables II–IV. In the fourth column of the Tables, the quantity $(\Delta G^E)_{exp} - (\Delta G^E)_{cor}/(\Delta G^E)_{cor}$ is given which has the meaning of the relative deviation of the experimental values $(\Delta G^E)_{exp}$ from the values smoothed $(\Delta G^E)_{cor}$.

The insertion of the correction for nonideality of the vapour phase is necessary because both components (especially C_2Cl_4) exhibit in the vapour phase at the given temperatures considerable deviations from ideal behaviour. Taking this correction into account, the deviations in composition and in pressure are reduced three to six times. At the same time ΔG^E decreases as much as by 10%.

An error is brought into the calculation of excess free enthalpy by an inaccuracy with which the values of second virial coefficients are determined. For CS_2 this inaccuracy amounts to ± 50 cm^3. A higher uncertainty undergoes the determination of virial coefficients of C_2Cl_4 which is based solely on generalized methods. It is to be expected that this error does not exceed ± 150 cm^3. The total error connected with this corresponds to about $\pm 1\%$. The experimental data of measurements of volumes of mixing are summarized in Table I. These data were correlated by the equation of the Redlich–Kister type, too. The constants of correlation relations for ΔV^E, ΔG^E, and ΔH^E (which were obtained from the temperature dependence of ΔG^E course) are presented in Table V.

The smoothed experimental data on ΔV^E, ΔG^E, and ΔH^E were used to test the above described theoretical procedure. Convex cores were assigned to the molecules of CS_2 and C_2Cl_4: the CS_2 core is a rod connecting the S-atom centres, the C_2Cl_4 core is a rectangle connecting the Cl-atom centres. The parallel convex bodies are characterized by their thicknesses $\xi_{CS_2} = 1.60$ Å and $\xi_{C_2Cl_4} = 1.52$ Å which were determined from the correlations of heats of vaporization of both substances at 25°C. Geometric functionals of the representative convex bodies have the following values: for CS_2 — $R_C = 2.376$ Å, $S_C = 63.375$ Å^2, $V_C = 42.121$ Å^3; for C_2Cl_4 — $R_C = 3.041$ Å, $S_C = 105.51$ Å^2, and $V_C = 86.702$ Å^3. The parameter a_{ii} determined from cohesive energy has the values: for CS_2 1.550 Å, for C_2Cl_4 1.410 Å; the cross term a_{12} was determined by means of the rule: $a_{12} = (a_{11}a_{22})^{1/2}$. The comparison of the calculated and theoretical values of excess thermodynamic functions of the CS_2–C_2Cl_4 system at 298.15K is carried out in Table VI.

From the comparison it follows that the perturbation theory of solutions (of convex molecules) with a very simple model of pair interaction represents the thermodynamic behaviour of the binary CS_2–C_2Cl_4 system altogether fairly well; for all excess functions it gives right values as to the sign and order of magnitude. In accordance with the fact that entropy depends only on the repulsive interaction (which is in this procedure relatively well expressed) the best agreement of calculated and theoretical data for $T\Delta S^E$ was found. On the contrary, the simplified description of attractive forces brings about larger deviations in the determination of volume and heat of mixing.

It may be said altogether that analogously to the systems studied formerly, the perturbation method (with the reference system of hard convex bodies) yields also for the CS_2–C_2Cl_4 system a good prediction of equilibrium behaviour of solutions. It is very likely that the use of a more realistic pair potential to describe intermolecular interactions would bring an improvement of the excess function prediction; however this use is restrained by hitherto unknown course of averaged distribution function in a wider interval of surface-to-surface distances.

REFERENCES

1. Kihara T.: Advan. Chem. Phys. *5*, 147 (1963).
2. Gibbons R.: Mol. Phys. *17*, 81 (1969).
3. Gibbons R.: Mol. Phys. *18*, 809 (1970).
4. Boublík T.: Mol. Phys. *27*, 1415 (1974).
5. Boublík T.: This Journal *39*, 2333 (1974).
6. Boublík T., Aim K.: This Journal *37*, 3513 (1972).
7. Boublík T., Nezbeda I., Hlavatý K.: *Statistická termodynamika kapalin a kapalných směsí.* Academia, Prague 1974.
8. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds.* Elsevier, Amsterdam, Vol. I, 1950, Vol. II, 1963.
9. Dreisbach R. R.: *Physical Properties of Chemical Compounds.* Publ. Am. Chem. Soc., Washinton, Vol. I, 1955, Vol. II, 1959, Vol. III, 1961.
10. Perrin D. D., Armarego W. L. F., Perrin D. R.: *Purification of Laboratory Chemicals.* Pergamon Press, Oxford 1966.
11. Hála E., Pick J., Fried V., Vilim O.: *Vapour–Liquid Equilibrium,* 2nd Ed. Pergamon Press, London 1967.
12. Pflug H. D., Benson G. C.: Can. J. Chem. *46*, 287 (1968).
13. Haase R.: *Thermodynamik der Mischenphasen.* Springer, Berlin 1956.
14. Dymond J. H., Smith E. B.: *The Virial Coefficients of Gases.* Clarendon Press, Oxford 1969.
15. Reid R. C., Sherwood T. K.: *The Properties of Gases and Liquids.* McGraw-Hill, New York 1966.

Translated by J. Linek.