

## EXCESS THERMODYNAMIC FUNCTIONS IN THE CARBON DISULPHIDE-CYCLOPENTANE SYSTEM

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Vapour-liquid equilibrium data at 288·15, 298·15, and 308·15 K and volume of mixing at 298·15 K were measured in the carbon disulphide(1)-cyclopentane(2) system. The excess Gibbs free energy, as determined from the vapour-liquid equilibrium measurements, and the excess volume were correlated by the three-constant Redlich-Kister expansion.

As a part of systematic study of binary mixtures containing nonpolar molecules, several systems formed by carbon disulphide, tetrachloromethane, tetrachloroethylene and cyclopentane have been recently investigated<sup>1-3</sup>. The importance of these systems dwells in the fact that simple convex cores may be easily assigned to their molecules, which enables one to apply a recently proposed perturbation expansion for systems of convex particles<sup>4</sup>. This work supplements existing experimental data on excess thermodynamic functions of mixtures suitable for verifying relations which follow from the theory of systems containing nonspherical and nonpolar molecules.

### EXPERIMENTAL

*Materials used.* Carbon disulphide, A.R. grade (Laborchemie, Apolda) was shaken subsequently with aqueous solution of  $\text{KMnO}_4$ , water, mercury, and saturated solution of  $\text{HgSO}_4$ . After washings with water it was dried and fractionated:  $n_D^{15}$  1·63182 (1·6319 (ref.<sup>5</sup>)),  $d_4^{20}$  1·26315 (1·2632 (ref.<sup>5</sup>)),  $t_{\text{b.p.}}$  46·21°C (46·25 (ref.<sup>6</sup>)). Cyclopentane, pure grade (Fluka), was shaken with sulphuric and nitric acids, dried and fractionated:  $n_D^{20}$  1·4065 (1·40645 (ref.<sup>6</sup>)),  $d_4^{25}$  0·7403 (0·74045 (ref.<sup>6</sup>)),  $t_{\text{b.p.}}$  49·26 (49·262 (ref.<sup>6</sup>)).

*Experimental technique.* For determining the vapour-liquid equilibrium, a Gillespie recirculation equilibrium still<sup>7</sup> was used. It was connected to an equipment maintaining the pressure with an accuracy of  $\pm 0\cdot1$  Torr. The composition of equilibrium phases in the  $\text{CS}_2$ - $\text{C}_5\text{H}_{10}$  system was determined refractometrically from the following calibration curve:

$$n_D^{20} = 1\cdot40650x_1 + 1\cdot62770(1 - x_1) + x_1(1 - x_1)[-0\cdot11620 - 0\cdot02937(2x_1 - 1) - 0\cdot00956(2x_1 - 1)^2], \quad (1)$$

where  $x_1$  is the mole fraction of  $\text{CS}_2$ . The volumes of mixing were measured in an earlier described dilatometer<sup>3</sup> which made it possible to determine the excess volume of an equimolar mixture with a 2% error.

TABLE I  
Excess Volumes in the CS<sub>2</sub>-C<sub>5</sub>H<sub>10</sub> System at 298.15 K

$x$	$V^E$ cm <sup>3</sup> /mol	Deviation $V^E$	$x$	$V^E$ cm <sup>3</sup> /mol	Deviation $V^E$
0.1026	0.0919	-0.0011	0.5782	0.2699	-0.0041
0.1721	0.1440	-0.0008	0.6674	0.2452	-0.0003
0.2403	0.1867	-0.0002	0.7034	0.2301	0.0011
0.3211	0.2255	0.0013	0.7257	0.2192	0.0020
0.3222	0.2264	0.0009	0.7547	0.2050	0.0013
0.4105	0.2549	0.0015	0.8185	0.1658	0.0008
0.4732	0.2666	0.0005	0.8715	0.1279	-0.0017
0.5258	0.2711	-0.0016	0.9196	0.0846	-0.0010

TABLE II  
Vapour-Liquid Equilibrium in the CS<sub>2</sub>-C<sub>5</sub>H<sub>10</sub> System at 288.15 K

$x$	$y$	$P$ Torr	$G^E$ J/mol	Deviation		
				$y$	$P$	$G^E$
0.0000	0.0000	210.96	0.00	—	—	—
0.0365	0.0585	215.90	28.66	-0.0018	0.09	-1.33
0.0425	0.0660	216.46	33.22	-0.0004	0.26	-1.70
0.0741	0.1095	220.00	56.52	0.0013	0.42	0.15
0.1584	0.2170	229.08	112.69	0.0020	0.20	-1.23
0.2836	0.3522	239.21	179.04	0.0024	0.72	5.46
0.3054	0.3738	241.58	188.37	0.0021	-0.08	-1.94
0.3650	0.4292	245.25	210.26	0.0021	0.10	0.59
0.3820	0.4450	246.62	215.50	0.0014	-0.28	-2.48
0.4916	0.5372	251.64	237.81	0.0013	-0.11	0.22
0.5818	0.6089	254.55	239.91	0.0008	-0.24	-0.35
0.5919	0.6166	254.98	239.15	0.0009	-0.45	-2.24
0.7044	0.7052	255.64	215.92	-0.0001	0.16	3.71
0.7627	0.7525	255.64	192.35	-0.0001	-0.15	0.69
0.8130	0.7962	254.88	165.09	-0.0007	-0.29	-0.94
0.8377	0.8188	254.12	149.21	-0.0010	-0.21	-0.49
0.8838	0.8634	252.50	114.99	-0.0012	-0.37	-2.42
0.9790	0.9715	245.35	24.00	-0.0002	0.49	5.28
1.0000	1.0000	243.88	0.00	—	—	—

## RESULTS AND DISCUSSION

Experimental concentration dependences of the excess volume in the carbon disulphide(1)–cyclopentane(2) system at 298·15 K are in Table I. The data were correlated by the following three-constant expansion

$$X^E = x_1(1 - x_1) [C_1 + C_2(2x_1 - 1) + C_3(2x_1 - 1)^2], \quad (2)$$

where  $X^E$  denotes an excess thermodynamic function and  $C_1, C_2, C_3$  constants in the expansion. Constants in the expansion of the excess volume are given in the first row of Table V, whereas deviations between correlated and experimental data may be found in the last column of Table I. The standard deviation in  $V^E$  is 0·0017 cm<sup>3</sup>/mol.

Tables II–IV summarize experimental data on the vapour–liquid equilibrium determined at 288·15, 298·15, and 308·15 K. The tables comprise equilibrium liquid and vapour compositions (in mole fractions of CS<sub>2</sub>) together with the total pressure (in Torr). The equilibrium data were used for computing values of the excess enthalpy; the state behaviour of the vapour phase was described by a virial expansion including only the second virial coefficient whose values were taken from the literature<sup>8</sup>.

TABLE III

Vapour–Liquid Equilibrium in the CS<sub>2</sub>–C<sub>5</sub>H<sub>10</sub> System at 298·15 K

<i>x</i>	<i>y</i>	<i>P</i> Torr	<i>G</i> <sup>E</sup> J/mol	Deviation		
				<i>y</i>	<i>P</i>	<i>G</i> <sup>E</sup>
0·0000	0·0000	317·80	0·00	—	—	—
0·0607	0·0902	328·79	47·00	−0·0006	0·11	−1·97
0·0749	0·1082	330·71	57·24	0·0008	0·44	−0·36
0·1265	0·1748	337·96	92·04	0·0005	0·84	3·91
0·1594	0·2150	342·82	112·29	−0·0005	0·44	2·38
0·2175	0·2788	350·56	144·32	0·0004	−0·18	−1·62
0·2836	0·3472	358·17	174·96	−0·0003	−0·76	−3·99
0·3077	0·3705	359·77	184·56	−0·0003	−0·07	0·99
0·3661	0·4256	364·89	204·27	−0·0011	−0·20	1·30
0·3841	0·4405	366·52	209·31	0·0001	−0·45	−0·90
0·4930	0·5330	373·66	228·79	0·0004	−0·83	−2·56
0·5937	0·6140	376·52	228·72	0·0008	0·18	4·42
0·7052	0·7038	378·64	205·75	0·0005	−0·48	0·39
0·7630	0·7517	378·18	183·24	0·0006	−0·58	−0·32
0·8377	0·8184	376·07	142·21	0·0002	−0·80	−2·14
0·9720	0·9640	364·89	30·23	−0·0011	−0·06	0·47
1·0000	1·0000	361·39	0·00	—	—	—

Values of  $G^E$  obtained in this manner were correlated by the three-constant Redlich-Kister expansion (constants in the expansion of  $G^E/RT$  at 288.15, 298.15, and 308.15 K are collected in Table V); differences between correlated and experimental values of the vapour phase composition, pressure and excess Gibbs free energy are together with smoothed  $G^E$  values also given in Tables II–IV.

Standard deviations of the different properties at 288.15, 298.15, and 308.15 K are equal to 0.0015, 0.0007, and 0.0009 for the vapour phase composition, 0.35, 0.57

TABLE IV  
Vapour-Liquid Equilibrium in the  $CS_2$ - $C_5H_{10}$  System at 308.15 K

$x$	$y$	$P$ Torr	$G^E$ J/mol	Deviations		
				$y$	$P$	$G^E$
0.0000	0.0000	464.25	0.00	—	—	—
0.0372	0.0555	473.25	29.08	-0.0007	0.97	0.93
0.0749	0.1061	481.87	56.67	0.0004	0.66	-0.57
0.1321	0.1781	493.13	94.92	0.0005	0.84	1.73
0.1614	0.2112	498.74	112.83	0.0019	0.58	0.07
0.2221	0.2788	509.54	146.24	0.0013	-0.14	-1.64
0.3095	0.3677	521.72	185.42	0.0002	-0.08	1.06
0.3847	0.4380	531.11	210.29	-0.0007	-0.97	-1.44
0.4881	0.5255	539.63	230.05	0.0005	-0.76	0.19
0.5932	0.6119	545.17	231.20	-0.0004	-0.94	0.44
0.7059	0.7028	546.82	208.27	-0.0003	-1.04	0.26
0.7630	0.7516	545.58	185.90	-0.0013	-0.90	0.71
0.8127	0.7949	543.52	159.95	-0.0009	-1.00	0.06
0.8377	0.8178	542.09	144.47	-0.0007	-1.15	-0.72
0.9735	0.9640	526.10	29.18	0.0005	-1.22	-2.00
1.0000	1.0000	520.41	0.00	—	—	—

TABLE V  
Constants in the Redlich-Kister Expansions of the Excess Functions

Function $X^E$	$C_1$	$C_2$	$C_3$
$V_{298.15}^E, \text{cm}^3/\text{mol}$	1.0764	0.0898	-0.0293
$(G^E/RT)_{288.15}$	0.3984	0.0776	0.0158
$(G^E/RT)_{298.15}$	0.3701	0.0620	0.0219
$(G^E/RT)_{308.15}$	0.3609	0.0661	0.0201

and 0.98 Torr for the pressure, and 2.65, 2.55, and 1.18 J/mol for the excess free energy.

Smoothed experimental values of  $V^E$  and  $G^E$  at 298.15 K were compared with results of computations of the excess thermodynamic functions by the perturbation theory of molecular liquids containing convex molecules<sup>4</sup>. The following geometric functionals were used for  $\text{CS}_2$  and  $\text{C}_5\text{H}_{10}$  in the computations:  $R_c = 2.376 \text{ \AA}$ ,  $S_c = 63.375 \text{ \AA}^2$ ,  $V_c = 42.121 \text{ \AA}^3$ ,  $R_c = 2.718 \text{ \AA}$ ,  $S_c = 89.392 \text{ \AA}^2$ , and  $V_c = 74.363 \text{ \AA}^3$ ; the interaction parameters  $a_{ii}$  were set equal to  $a_{11} = 1.550 \text{ \AA}$ ,  $a_{22} = 1.500 \text{ \AA}$ ,  $a_{12} = (a_{11}a_{22})^{1/2}$ .

In a manner<sup>4</sup> described earlier, the following values of the excess functions were obtained for the  $\text{CS}_2$ — $\text{C}_5\text{H}_{10}$  equimolar mixture at 298.15 K:  $V^E = 0.11 \text{ cm}^3/\text{mol}$  (exptl.  $0.27 \text{ cm}^3/\text{mol}$ ),  $H^E = 207.6 \text{ J/mol}$ , and  $G^E = 128.3 \text{ J/mol}$  ( $229.4 \text{ J/mol}$ ).

It follows from the comparison of the theoretical and experimental values of  $V^E$  and  $G^E$  that the perturbation theory<sup>4</sup> of molecular liquids formed by nonspherical molecules leads to a good prediction of thermodynamic behaviour of solutions containing nonpolar substances.

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