

## PHASE EQUILIBRIA IN THE SYSTEM TETRAHYDROFURAN(1)-WATER(2)

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Vapour-liquid equilibrium at 50 and 70°C, liquid-liquid equilibrium throughout the whole region of limited miscibility and excess molar volume  $V^E$  at 25°C have been determined in the system tetrahydrofuran-water. The system shows great deviations from Raoult's law and the closed-loop region of limited miscibility. For the correlation of the vapour-liquid equilibrium, the modified Redlich-Kister equation has been used. The computation has been carried out according to the recently proposed procedure which has made it possible to obtain such constants of correlation relationship which are not inconsistent with physical reality, *i.e.* with the complete miscibility ( $\partial G^2/\partial x_1^2 > 0$ ) under the experimental conditions.

The system tetrahydrofuran (THF)-water pertains, as far as the thermodynamic behaviour is concerned, to the group of strongly non-ideal binary systems<sup>1,3</sup>. It shows similar characteristic concentration and temperature dependences of excess quantities as aqueous solutions of alcohols and ethers<sup>4,20</sup>. The dependence of excess enthalpy on composition has an S-shaped course<sup>1,5,6</sup> with negative values in the region of higher water concentration. The  $H^E$  increases in whole concentration interval with increasing temperature. The deviations from Raoult's law are positive at the room and higher temperatures<sup>2,3</sup> and the values of excess volume are negative in whole concentration region under these conditions<sup>1,7</sup>.

This work follows on the preliminary communication<sup>8</sup> concerning the existence of closed-loop region of limited miscibility and deals with the phase equilibria (l)-(l) and (l)-(g) in detail. The results have a direct practical application and are as well a contribution to the study of aqueous non-electrolyte solutions. On the basis of the data obtained, some discrepancies in published data and in their interpretation are to be elucidated.

### EXPERIMENTAL

**Materials.** Tetrahydrofuran, an analytical grade reagent (Carlo Erba), was used. It was shaken with ferrous sulphate first and then distilled with sodium on a sixty plate column. In this way obtained product was always dried with  $\text{LiAlH}_4$  and distilled over under vacuum before using. The content of water or other impurities was checked by means of a gas chromatograph (with Porapak Q column packing) and did not exceed 0.01%. Physical constants of tetrahydrofuran used were as follows: n.b.p. 65.93°C (ref.<sup>13</sup> 65.965, ref.<sup>3</sup> 65.72),  $d_4^{25}$  0.8822 (ref.<sup>1</sup> 0.8821, ref.<sup>24</sup> 0.8826),  $n_D^{25}$  1.4051 (ref.<sup>1</sup> 1.4048). The constants of the Antoine equation calculated on the basis

of the data in ref.<sup>13</sup> were:  $A$  6.99589,  $B$  1202.7,  $C$  226.3. Redistilled water with specific conductivity  $\kappa \approx 3 \cdot 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  and refractive index  $n_D^{20} 1.3330$  (ref.<sup>14</sup> 1.3330) was used. The constants of the Antoine equation according to ref.<sup>14</sup> are:  $A$  7.96681,  $B$  1668.2,  $C$  228.

**Liquid-liquid equilibrium.** As the region of limited solubility lies above the normal boiling point of the mixture, the liquid-liquid equilibrium of this system was determined in sealed glass ampoules. The ampoule with the solution of fixed concentration and stirrer (ferrite magnet in Teflon) was after sealing placed into the apparatus which is represented in Fig. 1. Its main parts are thermostatic tube 1 equipped with calibrated thermometer (Anschütz thermometer with scale division of  $0.2^\circ\text{C}$ ) and further the mechanism 2 for lifting the external magnet 3 which carries the stirrer inside the ampoule. The thermostatic tube is connected into the circuit of the thermostat UT 10 filled with silicone oil. During the measurement the temperature of the bath changes continuously and the appearance or disappearance of the second phase (turbidity) in ampoule is observed visually. By the method described, the limited solubility region and the upper and lower critical solution temperatures were determined (Table I).

**Vapour-liquid equilibrium.** The vapour-liquid equilibrium was determined isothermally at the temperature 50 and  $70^\circ\text{C}$  by a dynamical method using the modified Gillespie still<sup>9,10</sup>. To maintain the constant boiling temperature automatically, a regulator with thermistor detecting element<sup>11</sup> was used. It controlled pressure in the system by means of electromagnetic valve on such value that the temperature might be constant during equilibration. An orienting Hg manometer and a 20 l reservoir which moderated pressure impacts were connected to the measuring system. The

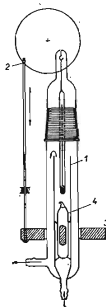


FIG. 1

Apparatus for Determination of Liquid-Liquid Equilibrium

1 Thermostatic tube, 2 mechanism for lifting the magnet, 3 magnet, 4 ampoule with sample and ferrite magnetic stirrer.

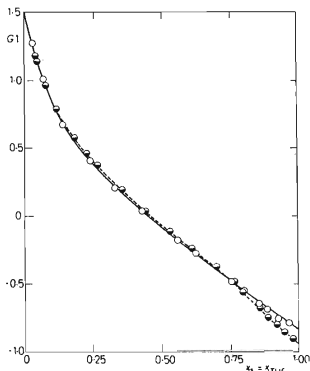


FIG. 2

Thermodynamic Consistency According to Redlich and Kister

$t$ :  $\circ$   $70^\circ\text{C}$ ,  $\bullet$   $50^\circ\text{C}$ .

measurement was made in the inert nitrogen atmosphere and if need there was, even under overpressure. Because of a quicker establishing of equilibrium, the space of the equilibrium vapour phases was stirred by magnetic stirrers. In order to eliminate the loss by evaporation of the more volatile component a cooler in which cooling water with the temperature  $1-2^{\circ}\text{C}$  from a special cooling circuit circulated, was placed above the receiver of the vapour phase. Temperature was measured by calibrated standard thermometers. The equilibrium pressure was measured indirectly, *i.e.* by measuring the boiling point of water in an ebullimeter connected parallel to the Gillespie still *via* a trap. The temperature in the ebullimeter was measured, as well, by the calibrated standard thermometers with an accuracy of  $\pm 0.02^{\circ}\text{C}$  and the pressures corresponding to the temperature measured were taken over from the literature<sup>1,2</sup>. The analysis of the equilibrium phases was carried out by measuring the density with pycnometers on the basis of the predetermined dependence  $d = d(x_{\text{THF}})$ . In the region of higher THF concentration, this dependence (Table II) differs to a certain extent from the formerly published data<sup>1</sup>.

TABLE I  
Liquid-Liquid Equilibrium in the THF-Water System  
Concentration dependence of temperature<sup>a</sup> along the boundary curve of limited miscibility.

THF, mass%	28.1	29.0	30.2	30.7	32.2	35.0	36.1	40.5	40.8	41.5	44.2
$t, ^{\circ}\text{C}$	102.5	92.9	89.5	87.9	83.3	78.9	78.6	n	75.4	n	73.4
	110.5	119.3	n	127.8	n	132.9	n	136.1	n	136.5	n
THF, mass%	48.0	48.1	48.6	49.9	50.0	50.7	51.6	53.0	53.8	54.0	55.7
$t, ^{\circ}\text{C}$	72.2	72.25	72.3	n	n	72.3	72.1	n	71.8	n	72.1
	n	n	n	137.1	137.0	n	n	136.8	n	136.7	n
THF, mass%	56.9	57.3	59.8	62.2	63.3	64.8	66.3	68.2	68.6	69.6	71.0
$t, ^{\circ}\text{C}$	n	72.3	72.8	73.4	n	74.8	n	78.2	78.3	79.9	83.0
	135.6	n	n	n	130.9	n	126.2	n	n	n	113.0

<sup>a</sup> As the system has the closed-loop region of limited miscibility two values of temperature pertain to each concentration in the Table; n denotes that the temperature was not determined.

TABLE II  
Dependence of Density and Excess Molar Volume on Composition at  $25^{\circ}\text{C}$

$x_{\text{THF}}$	$d_4^{25}$	$V^E$ $\text{cm}^3 \text{mol}^{-1}$	$x_{\text{THF}}$	$d_4^{25}$	$V^E$ $\text{cm}^3 \text{mol}^{-1}$
0.000	0.9971	0.000	0.527 <sub>2</sub>	0.9146 <sub>5</sub>	-0.758
0.142 <sub>7</sub>	0.9712	-0.657	0.712 <sub>4</sub>	0.8990	-0.521
0.199 <sub>1</sub>	0.9601	-0.763	0.819 <sub>1</sub>	0.8918	-0.320
0.273 <sub>4</sub>	0.9465	-0.815	0.906 <sub>9</sub>	0.8868 <sub>5</sub>	-0.178
0.423 <sub>5</sub>	0.9258	-0.828	1.000	0.8822	0.000

## RESULTS

*Liquid-Liquid Equilibrium*

The results of the determination of the (l)-(l) equilibrium in the system THF-water are presented in Table I. The values of the critical solution temperatures, LCST =  $71.8 \pm 0.15^\circ\text{C}$ , UCST =  $137.1 \pm 0.15^\circ\text{C}$  and the corresponding concentrations  $(w_{\text{THF}})_{\text{LCST}} = 0.53$ ,  $(w_{\text{THF}})_{\text{UCST}} = 0.48$  were determined according to the Cailletet-Mathias rule.

*Correlation of Vapour-Liquid Equilibrium Data*

The equilibrium data were correlated in a form of the dependence of the ratio of activity coefficients on composition calculated from the relation

$$\gamma_1/\gamma_2 = x_2 y_1 P_2^0 / x_1 y_2 P_1^0, \quad (1)$$

where  $\gamma_i$  are activity coefficients of components,  $y_i$  and  $x_i$  mole fractions in the vapour and liquid phase, resp., and  $P_i^0$  vapour pressures of pure components at a given temperature. The values of the vapour pressure of THF were calculated from the Antoine equation whose constants were determined from the Scott experimental data<sup>13</sup>. The constants of the Antoine equation for water were taken over from the literature<sup>14</sup>. (Considering that the data on the  $P$ - $V$ - $T$  behaviour of the mixture THF-water are not at disposal, the real behaviour of the vapour phase could not be respected. An influence upon  $\gamma_1/\gamma_2$  caused by the real behaviour of the vapour phase will be, however, little in comparison with the non-ideality in the liquid phase.) From the Redlich-Kister test it follows that the data obtained are thermodynamically consistent (Fig. 2). The dependence of excess thermodynamic functions of this system on composition expressed by mole fractions is asymmetrical<sup>1,2,5,6</sup> and therefore the use of the Redlich-Kister equation is not suitable<sup>15-17</sup>. The symmetry of the curve which bounds the region of limited miscibility<sup>8</sup> in the coordinates temperature - mass fraction indicates that the application of the Redlich-Kister equation in the form

$$Q = G^E/2 \cdot 303RT = w_1 w_2 [b + c(w_1 - w_2) + d(w_1 - w_2)^2 + e(w_1 - w_2)^3 + \dots] \quad (2)$$

should be more suitable. The concentrations  $w_i$  are defined by the relation

$$w_1 = x_1/(x_1 + \alpha x_2), \quad w_2 = 1 - w_1. \quad (3)$$

The quantity  $\alpha$  is considered as adjustable parameter. In case of  $\alpha = M_2/M_1$ ,  $w_i$  turns into the mass fraction. From Eq (2) the relations can be obtained

$$\log(\gamma_1/\gamma_2) = Q1 = \alpha(x_1 + \alpha x_2)^{-2} [(w_2 - w_1)Z + w_1 w_2 Z1], \quad (4)$$

$$G11 = 0.4343x_1^{-1}x_2^{-1} + 2\alpha(\alpha - 1)(x_1 + \alpha x_2)^{-3} [(w_2 - w_1)Z + w_1 w_2 Z1] + \\ + \alpha^2(x_1 + \alpha x_2)^{-4} [-2Z + 2(w_2 - w_1)Z1 + w_1 w_2 Z11], \quad (5)$$

$$G111 = 0.4343(x_2^{-2} - x_1^{-2}) + 6\alpha(1 - \alpha)^2(x_1 + \alpha x_2)^{-4} [(w_2 - w_1)Z + w_1 w_2 Z1] + \\ + 6\alpha^2(\alpha - 1)(x_1 + \alpha x_2)^{-5} [-2Z + 2(w_2 - w_1)Z1 + w_1 w_2 Z11] + \\ + \alpha^3(x_1 + \alpha x_2)^{-6} [-6Z1 + 3(w_2 - w_1)Z11] + w_1 w_2 Z111], \quad (6)$$

where

$$G11 = 1/(2.303RT) (\partial^2 G/\partial x_1^2),$$

$$G111 = 1/(2.303RT) (\partial^3 G/\partial x_1^3),$$

$$Z = b + c(w_1 - w_2) + d(w_1 - w_2)^2 + e(w_1 - w_2)^3 + \dots,$$

$$Z1 = \partial Z/\partial w_1 = 2[c + 2d(w_1 - w_2) + 3e(w_1 - w_2)^2 + \dots],$$

$$Z11 = \partial^2 Z/\partial w_1^2 = 8[d + 3e(w_1 - w_2) + \dots],$$

$$Z111 = \partial^3 Z/\partial w_1^3 = 48e + \dots$$

These relations will be needed for further calculations. The activity coefficients alone are to be determined from the relations

$$\log \gamma_1 = Q + x_2 Q1; \quad \log \gamma_2 = Q - x_1 Q1. \quad (7)$$

The constants of the modified Redlich-Kister equation (2) for chosen values  $\alpha$  were evaluated by the least square method minimizing the deviations of the ratio of activity coefficients.

The dependence of the mean deviation

$$\sigma = \sum_{i=1}^N |(y_i)_{\text{exp}} - (y_i)_{\text{calc}}|/N, \quad (8)$$

where  $N$  is the number of experimental points, on the chosen  $\alpha$  is represented in Fig. 3. The curves 1, 2, and 3 correspond to the mean deviations for the case the constant  $b$ , the constants  $b$  and  $c$ , and the constants  $b$ ,  $c$ , and  $d$ , resp., are considered and refer to the 50°C isotherm. The curve 3a corresponds to the dependence  $\sigma = \sigma(\alpha)$  for constants  $b$ ,  $c$ , and  $d$  at the temperature 70°C. From Fig. 3 it is evident that the optimum  $\alpha$  is in the interval 0.6–0.7. The values of the constants  $b$ ,  $c$ ,  $d$ ,  $\alpha$  and the corresponding deviations in  $y_{\text{THF}}$  for single experimental points are given in Table III and IV. As to the systems with high positive deviations from the Raoult law it is necessary to examine more closely the quantity  $G11$  whose value indicates the limited

miscibility. That is why, using the procedure described in the paper<sup>18</sup>, the dependences of  $G_{11}$  on composition were determined from smoothed experimental data  $P - x$  and  $y - x$ . These dependences are represented in Figs 4a and 5a. The agreement of found values is considered good (in the concentration range  $x_{\text{THF}} = 0.15 - 0.5$ , the maximum deviation in  $G_{11}$  is 0.05 and on the average the deviations keep within 0.03). The dependence of  $G_{11}$  on composition determined from Eq. (5) with the constants  $b, c, d, \alpha$  calculated by above-said (classic) method is represented by the curve 1 in Figs 5b and 6b. At the temperature 50°C  $(G_{11})_{\text{calc}} > 0$  in whole concentration range. At the temperature 70°C for the composition  $x_{\text{THF}} \in (0.1, 0.14)$ , however,  $(G_{11})_{\text{calc}} < 0$ , which corresponds to the separation of the homogeneous system into two phases. In both cases both the values and shape of the dependence of  $(G_{11})_{\text{calc}}$  on composition are inconsistent with  $G_{11} = G_{11}(x_{\text{THF}})$  determined from experimental data (Figs 5a, b). To remove these discrepancies we used the recently proposed

TABLE III  
Vapour-Liquid Equilibrium in the THF-Water System at 50°C

$x_{\text{THF}}$	$y_{\text{THF}}$	$P, \text{Torr}$	$\Delta y_{\text{THF}}^a$	$\Delta y_{\text{THF}}^b$
0.028	0.700	303.2	-0.0088	0.0289
0.038 <sub>5</sub>	0.745	359.8	0.0019	0.0295
0.046	0.767	383.4	0.0090	0.0310
0.075	0.781	420.5	-0.0039	0.0040
0.1165	0.797	440.4	0.0020	0.0004
0.183	0.800	445.4	0.0026	-0.0039
0.228	0.802	447.0	0.0036	-0.0027
0.264	0.800	447.8	0.0002	-0.0050
0.354	0.802	449.4	-0.0016	-0.0042
0.441	0.803	451.1	-0.0035	-0.0054
0.531	0.805	453.5	-0.0032	-0.0062
0.611	0.810	456.2	-0.0001	-0.0035
0.698	0.820	459.8	0.0047	-0.0007
0.765	0.832	463.4	0.0061	0.0021
0.798	0.840	464.8	0.0058	0.0029
0.868	0.865	465.4	0.0022	0.0027
0.888	0.870 <sub>5</sub>	464.3	-0.0043	-0.0027
0.922	0.901	462.1	-0.0003	-0.0034
0.956	0.936	456.4	-0.0004	0.0040
0.979	0.965	450.0	-0.0010	0.0016
		$\sigma =$	0.0033	0.0072

Values calculated with constants: <sup>a</sup>  $\alpha$  0.65,  $b$  0.9614,  $c$  0.2407,  $d$  0.2256 which were determined by classical method, <sup>b</sup>  $\alpha$  0.77,  $b$  0.9698,  $c$  0.1204,  $d$  0.1701 ( $x_0$  0.25,  $(G_{11})_{\text{min}}$  0.02).

method<sup>18</sup> consisting in the fact that at the point  $x_0$  at which  $G_{11}$  has the minimum value  $(G_{11})_{x_0}$ , the relations must be fulfilled

$$(G_{11})_{x=x_0} = (G_{11})_{x_0} \quad \text{and} \quad (G_{111})_{x=x_0} = 0.$$

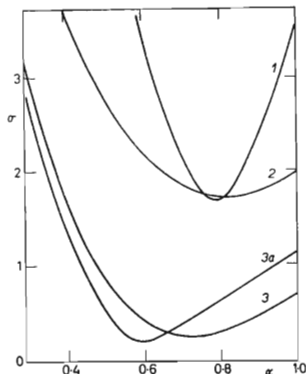


FIG. 3

Dependence of Mean Deviation  $\sigma$  (%) on Used  $\alpha$  with Various Number of Constants of the Modified Redlich-Kister Equation

1 Const.  $b$  ( $50^\circ\text{C}$ ), 2 const.  $b, c$  ( $50^\circ\text{C}$ ), 3 const.  $b, c, d$  ( $50^\circ\text{C}$ ), 3a const.  $b, c, d$  ( $70^\circ\text{C}$ ).

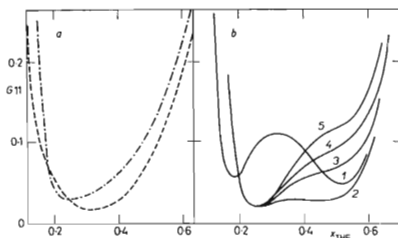


FIG. 4

Dependence of  $G_{11}$  on Composition at  $50^\circ\text{C}$

a Determined from experimental data, ----- from  $P-x$  curve, -.-.-.- from  $y-x$  curve; b calculated 1 by classical method ( $\sigma$  0.3%), 2-5  $x_0 = 0.25$ ,  $(G_{11})_{\min} 0.02$ ; 2  $\alpha$  0.7, ( $\sigma$  0.5%), 3  $\alpha$  0.75, ( $\sigma$  0.7%), 4  $\alpha$  0.77, ( $\sigma$  0.72%), 5  $\alpha$  0.8, ( $\sigma$  0.8%).

The corrected method of calculations was programmed so that during optimization of constants it was possible to choose besides  $x_0$  and  $(G11)_{x_0}$  the quantity  $\alpha$ , too.

When correlating the equilibrium data along the 50°C isotherm, the values of  $x_0 = 0.25$  and  $(G11)_{x_0} = 0.02$  were chosen. In Fig. 5b the calculated dependences of  $(G11)_{\text{calc}}$  on composition for several values of  $\alpha$  are given. The best approximation

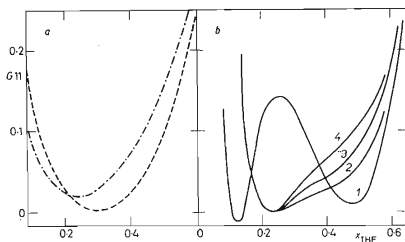


FIG. 5

Dependence of  $G11$  on Composition at 70°C

*a* Determined from experimental data, - - - - - from  $P-x$  curve, - · - · - from  $y-x$  curve; *b* calculated 1 by classical method ( $\sigma$  0.3%), 2—4  $x_0 = 0.23$ ,  $(G11)_{\text{min}} = 0.002$ ; 2  $\alpha$  0.65, ( $\sigma$  0.6%), 3  $\alpha$  0.67, ( $\sigma$  0.7%), 4  $\alpha$  0.7, ( $\sigma$  0.7%).

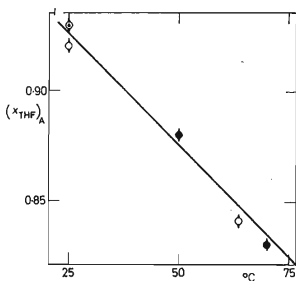


FIG. 6

Dependence of Composition of Azeotrope  $(x_{\text{THF}})_A$  on Temperature

● Our data, ○ ref.<sup>3</sup>, ○ ref.<sup>1</sup>.

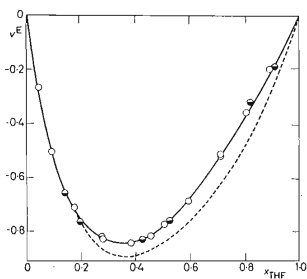


FIG. 7

Dependence of Excess Molar Volume  $V^E$  ( $\text{cm}^3 \text{mol}^{-1}$ ) on Composition

● Our data, ○ ref.<sup>7</sup>, - - - - - ref.<sup>1</sup>.



to the values of  $G_{11}$  shows the curve with  $\alpha = 0.77$ . The computation with corresponding constants  $b$ ,  $c$ ,  $d$  yields a mean deviation of 0.72% in the composition of the equilibrium vapour phase. For the analogous computations of the 70°C isotherm which is in the immediate proximity of the lower critical solution point ( $x_{LCST} = 0.228$ ), the values of  $x_0 = 0.23$  and  $(G_{11})_{x_0} = 0.002$  were chosen. From Fig. 5b it is evident that the optimum agreement of  $G_{11}$  and  $(G_{11})_{calc}$  sets in for  $\alpha = 0.67$ . The results of the correlation of equilibrium data in the system THF-water obtained with optimum constants  $b$ ,  $c$ ,  $d$ ,  $\alpha$  are presented in Tables III and IV.

#### Dependence of the Composition of Azeotrope on Temperature

The composition of azeotrope was read off from the  $y - x$  diagram at 50°C ( $x_{THF} = 0.88 \pm 0.002$ ) and at 70°C ( $x_{THF} = 0.83 \pm 0.002$ ). The composition of azeotrope is strongly dependent on temperature, which is evident from Fig. 6 in which further data from the literature<sup>1,3</sup> are given as well. This fact enables to separate fully the components by rectification at two different pressures.

TABLE IV  
Vapour-Liquid Equilibrium in the THF-Water System at 70°C

$x_{THF}$	$y_{THF}$	$P$ , Torr	$\Delta y_{THF}^a$	$\Delta y_{THF}^b$
0.032	0.697	765.4	-0.0016	0.0460
0.0715	0.745	904.5	0.0049	0.0146
0.0141	0.749	920.4	0.0055	-0.0040
0.241	0.750	920.0	0.0028	-0.0049
0.335	0.751	922.6	-0.0014	-0.0046
0.429	0.754	925.2	-0.0006	-0.0032
0.558	0.758	932.5	0.0023	-0.0034
0.625	0.768	939.5	-0.0012	0.0019
0.754	0.790	946.7	0.0071	0.0028
0.800	0.805	948.4	0.0044	0.0014
0.854	0.830	945.5	-0.0007	-0.0005
0.886	0.855	939.5	0.0001	0.0033
0.928	0.893	925.5	-0.0027	0.0012
0.966	0.945	900.8	0.0007	0.0044
		$\sigma =$	0.0026	0.0068

<sup>a</sup>  $\alpha = 0.55$ ,  $b = 0.9317$ ,  $c = 0.3323$ ,  $d = 0.2620$  which were determined by classical method. <sup>b</sup>  $\alpha = 0.67$ ,  $b = 0.9466$ ,  $c = 0.1892$ ,  $d = 0.1700$  ( $x_0 = 0.23$ ,  $(G_{11})_{min} = 0.002$ ).

### Dependence of Excess Volume on Composition

The values of  $V^E$  represented in Fig. 7 were calculated from the measured values of density, *i.e.* from the dependence of density on composition. The found values are in good agreement with the data of Morcom and Smith<sup>7</sup> in whole concentration range and with the data of Signer and coworkers<sup>1</sup> up to  $x_{\text{THF}} = 0.2$ . Considering that  $V^E$  is negative in whole concentration range, the region of limited miscibility of the system should diminish with an increase in pressure<sup>19</sup>.

### CONCLUSION

The system THF–water has great positive deviations from Raoult's law which increase with increasing temperature to such degree that the system shows limited miscibility<sup>8</sup>. The region of limited miscibility is closed and bounded by the mass fraction  $w_{\text{THF}} \in (0.28, 0.72)$  and by temperature  $t \in (71.8, 137.1)$  °C. The temperature and concentration dependence of excess functions ( $H^E, G^E$ ) is similar to that in system alcohols–water<sup>4,20</sup>. Unlike the systems alcohol–water<sup>21,22</sup> the activity coefficient of water in the system THF–water has a value higher than one even at low temperatures and low concentrations of THF. This was proved by a cryoscopic measurement<sup>23</sup> whose results will be reported in next paper. As it is seen from Fig. 8 the excess Gibbs function increases slowly with an increase in temperature whereas enthalpy increases quickly<sup>5</sup> with increasing temperature. Thus, the excess molar entropy increases with increasing temperature, which is the consequence of the increasing disarrangement caused probably by the degradation of water clusters and

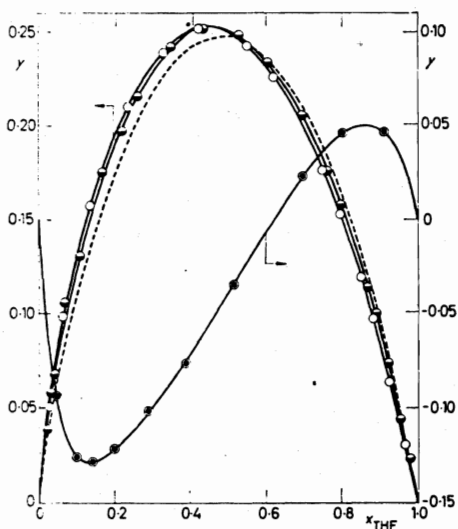


FIG. 8

Dependence of Excess Molar Gibbs Function and Enthalpy on Composition

○ 70°C and ● 50°C (our data), ---- 25°C (ref.<sup>1</sup>), ⊙ 25°C (ref.<sup>6</sup>).  $Y = H^E/2.303 RT$  for the curve with ⊙ points,  $Y = G^E/2.303 RT$  for the other curves.

by breaking the relatively weak hydrogen bonds between molecules of water and tetrahydrofuran. With respect to the great deviations from the ideal behaviour in the liquid phase and the unsymmetrical dependence of  $\gamma_1/\gamma_2$  on composition (expressed in mole fraction), the correlation of the data is difficult. Often an undesirable phenomenon occurs that the constants of correlation relationships correspond already to the limited miscibility, (i.e.  $\partial^2 G/\partial x_1^2 < 0$ ), though the system under given conditions is homogeneous. Authors either interpret obtained results incorrectly<sup>2</sup> or do not correlate such data<sup>1,3</sup>. By using the procedure presented in this paper, we obtained the constants of the modified Redlich–Kister equation which have physical meaning. The method is to be applied to advantage to the treatment of equilibrium data of strongly non-ideal systems.

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