O-353

J. Chem. Thermodynamics **1990**, 22, 327–333

Investigation of the equilibria of the reaction: $CH_3(CH_2)_4OH$ + $(CH_3)_2C:CH_2$ = $CH_3(CH_2)_4OC(CH_3)_3$

A. M. ROZHNOV, V. I. BARKOV, K. G. SHARONOV, and
V. S. TSVETKOV

Kuibyshev Polytechnical Institute,
Department of Chemical Technology,
Kuibyshev 443010, U.S.S.R.

(Received 25 July 1989; in final form 21 December 1989)

Equilibria have been studied of the reaction of synthesis of amyl *t*-butyl ether (ATBE) from *n*-pentan-1-ol and 2-methylpropene in the liquid (313 to 413 K) and gas (399 to 447 K) phases. It has been found that in the liquid phase (ATBE + *n*-pentan-1-ol + 2-methylpropane) is non-ideal. Its mole-fraction equilibrium product K_x depends on the composition of the reaction mixture at constant temperature. With $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \geqslant 2$ in the starting mixture, K_x is approximately constant. It has been shown that the values of K_x found for $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} = 4$ can be used for the establishment of the enthalpy of reaction without corrections for non-ideality of the mixture. An ebulliometric method was used to find the vapour pressure of ATBE. $\Delta_r H^\circ_m = -(67.09 \pm 4.94)\ kJ \cdot mol^{-1}$ and $\Delta_r S^\circ_m = -(173.1 \pm 11.6)\ J \cdot K^{-1} \cdot mol^{-1}$ were found for the reaction: $CH_3(CH_2)_4OH$ + $(CH_3)_2C:CH_2$ = $CH_3(CH_2)_4OC(CH_3)_3$ in the gas phase for $T = 423\ K$. The following values of thermodynamic quantities of ATBE have been found both from chemical equilibria and (p, T) results: $\Delta_f H^\circ_m(298.15\ K, g) = -(380.6 \pm 6.8)\ kJ \cdot mol^{-1}$; $\Delta_{vap} H_m(298.15\ K) = (46.89 \pm 0.99)\ kJ \cdot mol^{-1}$, and $\Delta_{vap} H_m = (39.1 \pm 3.1)\ kJ \cdot mol^{-1}$ at the normal boiling temperature, 419.156 K.

1. Introduction

Alkyl *t*-butyl ethers are widely used in industry as high octane additives to motor fuels. Mostly methyl and ethyl *t*-butyl ethers are involved, and their effectiveness has been shown in several papers.(1–3)

The basic method of producing alkyl *t*-butyl ethers is the interaction of the appropriate alkanol with 2-methylpropene in the liquid phase in the presence of "sulfocationite" catalyst. Despite the practical importance of this process, its thermodynamics has not been studied in detail. The literature(4–6) is limited to the reaction of methanol with 2-methylpropene. The results from those sources, as well as from the studies of the equilibria of the synthesis reactions of ethers made in our laboratory,(7–11) testify to the deviation from ideal behaviour of all those mixtures. This is demonstrated by the dependence of the mole-fraction equilibrium products at constant temperature upon the compositions of the initial and product mixtures. This does not permit the use of such mole-fraction equilibrium products for the

0021-9614/90/040327+07 $02.00/0

TABLE 1. Dependence of K_x and K_γ of reaction (1) in the liquid phase upon $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\}$ at 363 K; x denotes mole fraction in the equilibrium mixture; γ denotes activity coefficient

$\frac{n(C_5H_{11}OH)}{n\{(CH_3)_2C:CH_2\}}$	$K_x = \frac{x(ATBE)}{x(C_5H_{11}OH)x\{(CH_3)_2C:CH_2\}}$	$K_\gamma = \frac{\gamma(ATBE)}{\gamma(C_5H_{11}OH)\gamma\{(CH_3)_2C:CH_2\}}$
0.8	46.7	0.64
1.0	23.5	0.78
2.0	9.3	1.06
4.0	7.6	1.18
6.0	8.0	1.18
8.0	7.8	1.19

determination of thermodynamic quantities of reactions.

The equilibrium of the liquid-phase reaction of the synthesis of methyl cumyl ether from methanol and α-methylstyrene has been investigated,(7) and it has been shown that by diluting the mixture with methanol (the component most strongly influencing the deviation of the mixture from the ideal) the mole-fraction products found can be used with little error for the calculation of $\Delta_r H^\circ_m$ and $\Delta_r S^\circ_m$. To support this conclusion and accumulate values on the thermodynamics of the process of synthesis of alkyl *t*-butyl ethers, we investigated the equilibria of the interaction of *n*-pentan-1-ol with 2-methylpropene in the liquid and gas phases and found the vapour pressure of amyl *t*-butyl ether (ATBE).

2. Experimental

The equilibrium of the reaction:

$$CH_3(CH_2)_4OH + CH_2:C(CH_3)_2 = CH_3(CH_2)_4OC(CH_3)_3, \qquad (1)$$

was investigated in the liquid and gas phases. The experiments in the liquid phase were made in sealed glass ampoules in the presence of "sulfocationite KU-23" as a catalyst at 343 to 393 K. The investigation in the gas phase was made in a glass flow reactor with a fixed bed of catalyst at 400 to 447 K. The reactor was heated by the vapours of the boiling liquids.

2-Methylpropene (99.8 mass per cent), *n*-pentan-1-ol (99.5 mass per cent), and ATBE (98.5 mass per cent) were used for the investigation. ATBE was produced in the laboratory through the interaction of 2-methylpropene and *n*-pentan-1-ol followed by distillation. A sample of ATBE with a purity of 99.9 mass per cent was produced to find the vapour pressure. The analysis of the reaction products was made by g.l.c. with the help of a "Chrom-4" apparatus with a flame-ionization detector and programmable temperature on a packed column 6 m long, filled with 15 mass per cent of PEG 20M on AW-HMDS Chromatone.

Papers(4, 6) on the investigation of the equilibrium reaction of the synthesis of methyl *t*-butyl ether from methanol and 2-methylpropene showed that the mole-

TABLE 2. Results for reaction (1) in the liquid phase in the presence of "sulfocationite KU-23": w, mass fraction of catalyst; τ, time of the experiment; n, number of experiments; x, mole fraction in equilibrium mixture; $\langle K \rangle$, mean value of the mole-fraction equilibrium product K_x

T/K	$10^2 w$	τ/h	n^a	$x(C_5H_{11}OH)$	$x(ATBE)$	$x\{(CH_3)_2C:CH_2\}$	$\langle K_x \rangle$
343	5 to 15	2 to 10	16 (10)	0.7544	0.2278	0.0177	17.06 ± 0.24
363	1 to 10	1.5 to 6	10 (10)	0.7581	0.2093	0.0326	8.47 ± 0.31
378	1 to 5	1.5 to 3	10 (5)	0.7616	0.1921	0.0463	5.45 ± 0.41
393	1 to 5	1.5 to 3	11 (12)	0.7659	0.1705	0.0636	3.50 ± 0.34
413	1 to 5	0.5 to 1.5	7 (5)	0.7722	0.1388	0.0890	2.02 ± 0.17

[a] For reaction or, in parentheses, the reverse of the reaction.

fraction equilibrium product K_x did not correspond to the equilibrium constant K° because of the deviation of the mixture from ideal behaviour. The value of K_x for the same temperature depends on the composition of the equilibrium mixture. Table 1 shows the dependence of K_x and K_γ on $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\}$ at 363 K for reaction (1). Here $K_\gamma = \gamma(ATBE)/[\gamma(C_5H_{11}OH)\gamma\{(CH_3)_2C:CH_2\}]$ where the γs are activity coefficients. The latter were calculated by the UNIFAC method[12] on the basis of quantitative results for the molecular fragments given in reference 13.

The results in table 1 show that at $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \geqslant 2$, K_x does not depend on the composition of the mixture. At the same time, $K_\gamma \neq 1$ at such ratios though a trend analogous to K_x is observed in the change of K_γ with the change of the relation of the reacting components, bringing K_x to a constant value at $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \geqslant 4$. Taking these results into account, the liquid-phase-reaction equilibrium (1) was investigated for $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} = 4$.

The criterion of equilibrium was the constancy of K_x with the change of the starting product (direct or reverse reaction), the quantity of the catalyst, and the time of reaction. Table 2 shows the results of the investigation.

Equilibrium in the gas phase was investigated at a total pressure of 0.1 MPa in the presence of aluminosilicate catalyst. The equilibrium here was reached both for the direct and reverse reactions. In the first case, the mixture of 2-methylpropene with *n*-pentan-1-ol was used as the starting crude; in the second case, pure ATBE, or its mixture with $C_5H_{11}OH$. The products leaving the reactor were collected in the traps with toluene cooled to 273 K in order to avoid the loss of 2-methylpropene. The contents of the traps were then analysed with the help of g.l.c. The starting mixture was diluted with hexane at low temperatures with the aim of lowering the partial pressures of ether and alcohol. Table 3 shows the results of the experiments in the gas phase.

The dependence of the vapour pressure of ATBE upon temperature was found ebulliometrically with an apparatus previously described.[13] The errors in the measurements were 0.003 K in temperature and 13 Pa in pressure. The measurements were made from 319 to 365 K. ATBE boiled in this temperature range without decomposition. Table 4 shows the (p, T) results found.

TABLE 3. Results for reaction (1) in the gas phase in the presence of aluminosilicate catalyst: v, velocity of liquid mixture; n, number of the experiments; x, mole fraction in equilibrium mixture; $\langle K \rangle$, mean value of the equilibrium product

T/K	Starting mixture	$\frac{10\,v}{\mathrm{cm^3 \cdot s^{-1} \cdot g^{-1}}}$	n	$x(C_6H_{14})$	$x(C_5H_{14})$	x(ATBE)	$x\{(CH_3)_2C:CH_2\}$	$\langle K \rangle$
399	A	0.8 to 2.5	12	0.6370	0.2399	0.0143	0.1088	0.548 ± 0.048
	B	0.8 to 2.5	6	0.4929	0.3325	0.0269	0.1477	
412	C	1.7 to 4.2	12	0.6330	0.2447	0.0079	0.1144	0.282 ± 0.024
	D	1.7 to 4.2	6	0.6603	0.2072	0.0074	0.1251	
423	A	1.7 to 4.2	12	0.6313	0.2467	0.0052	0.1168	0.180 ± 0.06
	B	1.7 to 4.2	6	0.4848	0.3435	0.0100	0.1617	
433	E	0.8 to 2.5	14		0.9333	0.0601	0.0067	0.119 ± 0.007
	F	0.8 to 2.5	7		0.6411	0.3335	0.0254	
447	G	0.8 to 5.0	15		0.6675	0.0128	0.3197	0.060 ± 0.007
	F	0.8 to 5.0	7		0.6454	0.0132	0.6454	

Mole percentages of starting mixtures

	A	B	C	D	E	F	G
C_6H_{14}	71.5	48.0	69.4	65.5			
$C_5H_{11}OH$	14.7	35.0	15.1	21.3	92.9	65.5	51.1
ATBE	13.8		15.5		7.1		48.9
$(CH_3)_2C:CH_2$		17.0		13.2		35.0	

3. Results and discussion

Noting that the liquid phase (alcohol + ether + 2-methylpropene) shows deviation from the ideal, let us analyse the possibility of applying the mole-fraction equilibrium products to finding thermodynamic quantities of reactions. The activity of a component is $a_i = x_i \gamma_i$. Then, for the thermodynamic equilibrium constant K° we have

$$K^\circ = K_x K_\gamma. \tag{2}$$

As

$$\ln K^\circ = \Delta_r G^\circ_m / RT = -(\Delta_r H^\circ_m - T\Delta_r S^\circ_m)/RT, \tag{3}$$

then

$$\begin{aligned} \ln K^\circ &= \ln K_x + \ln K_\gamma = -\{\Delta_r G^\circ_m(K_x)/RT + \Delta_r G^\circ_m(K_\gamma)/RT\} \\ &= -\{\Delta_r H^\circ_m(K_x) - T\Delta_r S^\circ_m(K_x)\}/RT + \{\Delta_r H^\circ_m(K_\gamma) - T\Delta_r S^\circ_m(K_\gamma)\}/RT. \end{aligned} \tag{4}$$

TABLE 4. Dependence of the vapour pressure of ATBE upon temperature

T/K	p/Pa	T/K	p/Pa
319.14	2220	352.98	10738
333.03	4452	358.87	13608
343.70	7245	364.68	17049

It is clear that $\Delta_r H^\circ_m(K_x)$ and $\Delta_r S^\circ_m(K_x)$ in expression (4) show the change of enthalpy and entropy of the reaction for a standard condition, found by the dependence of K_x upon temperature. $\Delta_r H^\circ_m(K_y)$ and $\Delta_r S^\circ_m(K_y)$ found by the dependence of K_y upon temperature correspond to the values of the deviation of $\Delta_r H^\circ_m$ and $\Delta_r S^\circ_m$:

$$\Delta_r H^\circ_m(K_y) = \Delta_r H^\circ_m - \Delta_r H^\circ_m(K_x), \tag{5}$$

$$\Delta_r S^\circ_m(K_y) = \Delta_r S^\circ_m - \Delta_r S^\circ_m(K_x). \tag{6}$$

The activity coefficients depend(12) on the composition of the mixture and but little on temperature. We may assume that K_y will depend little on temperature for the compositions of mixtures which correspond to $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \geqslant 3$, where K_x and K_y are practically constant. Calculations of K_y by the UNIFAC method for reaction (1) show the same effect. The following values of K_y: 1.18 at 343 K, 1.18 at 363 K, 1.19 at 378 K, 1.19 at 393 K, and 1.19 at 413 K were found for $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} = 4$. Consequently we can accept $\Delta_r H^\circ_m(K_y) = 0$. Then

$$\begin{aligned}\ln K^\circ &= -\{\Delta_r H^\circ_m(K_x) - T\Delta_r S^\circ_m(K_x)\}/RT - T\Delta_r S^\circ_m(K_y)/RT \\ &= -\Delta_r H^\circ_m(K_x)/RT + \{T\Delta_r S^\circ_m(K_x) + T\Delta_r S^\circ_m(K_y)\}/RT. \end{aligned} \tag{7}$$

Equation (7) shows that $\Delta_r H^\circ_m(K_x)$ corresponds to $\Delta_r H^\circ_m$ of the reaction in the range $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \geqslant 3$. The change in molar entropy differs from the true value by

$$\Delta\Delta_r S^\circ_m = \Delta_r S^\circ_m(K_y) = R \cdot \ln k_y. \tag{8}$$

The values of the equilibrium products of the liquid-phase reaction shown in table 2 are described by

$$\lg K_x = -4.20 + 1863(\mathrm{K}/T). \tag{9}$$

For the average temperature of the experiment, 368 K, the following values of the thermodynamic quantities of reaction (1) in the liquid phase were obtained: $\Delta_r H^\circ_m = -(35.66 \pm 1.96)\,\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_r S^\circ_m = -(80.35 \pm 5.68)\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

The values of the equilibrium products for the gas-phase reaction are given by the equation:

$$\lg K_{p/p^\circ} = -9.04 + 3504(\mathrm{K}/T), \tag{10}$$

where $p^\circ = 0.1$ MPa.

For the average temperature, 422.7 K, the following values of the thermodynamic quantities were obtained: $\Delta_r H^\circ_m = -(67.09 \pm 4.94)\,\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_r S^\circ_m = -(173.1 \pm 11.6)\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The results of the vapour-pressure measurements on ATBE (table 4) were processed by the Antoine, Rankine, and Cragoe equations, as well as by the four-parameter equation:

$$\lg(p/\mathrm{Pa}) = a + b(\mathrm{K}/T) + c \cdot \lg(T/\mathrm{K}) + d(T/\mathrm{K}). \tag{11}$$

The last equation describes best the experimental results for ATBE, where $a =$

TABLE 5. Basic thermodynamic values for the vaporization of ATBE for equilibrium condition (normal boiling temperature: 419.156 K)

$T = 419.156$ K
$\Delta Z = 0.9376$; $\Delta_{\text{vap}}H_{\text{m}} = (39.1 \pm 3.1)\ \text{kJ} \cdot \text{mol}^{-1}$; $\Delta_{\text{vap}}S_{\text{m}} = (93.2 \pm 7.8)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $(\text{d}p/\text{d}T) = 2890.2\ \text{Pa} \cdot \text{K}^{-1}$
$T = 298.15$ K
$\Delta Z = 0.9989$; $\Delta_{\text{vap}}H_{\text{m}} = (46.89 \pm 0.99)\ \text{kJ} \cdot \text{mol}^{-1}$; $\Delta_{\text{vap}}S_{\text{m}} = (115.4 \pm 3.2)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $(\text{d}p/\text{d}T) = 41.7\ \text{Pa} \cdot \text{K}^{-1}$

148.26532, $b = -6753.122$, $c = -53.11944$, and $d = 2.898852 \times 10^{-2}$. Noting that the Antoine equation $\{\lg(p/\text{Pa}) = A - B/\{C + (T/\text{K})\}$ is widely used to describe (p, T) results, below are shown coefficients of this equation: $A = 9.13151$, $B = 1458.445$, and $C = -67.04$. The enthalpy and entropy of vaporization were calculated(15) from the coefficients of equation (11). The calculation was made by taking into account differences ΔZ in the compression factors of vapour and liquid.(16) The critical quantities were found by the Lydersen method.(12)

The thermodynamic values for the vaporization process are shown in table 5. For the molar enthalpy of vaporization at 298.15 K, $\Delta_{\text{vap}}H_{\text{m}}^{\circ}$ was equal to $(46.89 \pm 0.99)\ \text{kJ} \cdot \text{mol}^{-1}$. Ambrose *et al.*(17) give the molar enthalpies of vaporization of methyl ethers. In the series of dimethyl to methyl decyl ethers, those results show an increment of the molar enthalpy of vaporization of $4.84\ \text{kJ} \cdot \text{mol}^{-1}$ for the $-\text{CH}_2-$ group.

An estimate of the molar enthalpy of vaporization of ATBE, $47.1\ \text{kJ} \cdot \text{mol}^{-1}$, was found from $\Delta_{\text{vap}}H_{\text{m}}^{\circ}$(ethyl *t*-butyl ether, 298.15 K) $= 32.6\ \text{kJ} \cdot \text{mol}^{-1}$,(17) and from the $-\text{CH}_2-$group increment of $4.84\ \text{kJ} \cdot \text{mol}^{-1}$. That value corresponds closely to $46.89\ \text{kJ} \cdot \text{mol}^{-1}$ found by us.

Let us discuss thermodynamic quantities of the liquid-phase reaction. The value of $-35.66\ \text{kJ} \cdot \text{mol}^{-1}$ found for $\Delta_{\text{r}}H_{\text{m}}^{\circ}$ is lower than that obtained(8) earlier for this reaction. However, we consider it more valid as it has been found over a wider temperature range from more values of the equilibrium constants. A value of $-39.8\ \text{kJ} \cdot \text{mol}^{-1}$, close to the above, was found calorimetrically for $\Delta_{\text{r}}H_{\text{m}}^{\circ}$ of the synthesis reaction of methyl *t*-butyl ether.(18)

The experimental values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}$ can be taken to refer to 298.15 K without large error, when taking into account an insignificant value of $\Delta C_{p,\text{m}}$ of reaction (1) (approximately $3\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ according to the results for the gas-phase synthesis reactions of methyl *t*-butyl ether from methanol and 2-methylpropene, as well as diethyl ether from ethanol and ethene). The difference of the molar enthalpies of vaporization for the compounds of reaction (1) gives: $\Delta\Delta_{\text{vap}}H_{\text{m}}^{\circ} = \Delta_{\text{vap}}H_{\text{m}}^{\circ}(\text{ATBE}) - \Delta_{\text{vap}}H_{\text{m}}^{\circ}\{(\text{CH}_3)_2\text{C} : \text{CH}_2\} - \Delta_{\text{vap}}H_{\text{m}}^{\circ}(\text{C}_5\text{H}_{11}\text{OH}) = (46.89 - 56.94 - 20.59)\ \text{kJ} \cdot \text{mol}^{-1} = -30.64\ \text{kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpy of vaporization of ATBE $(\Delta_{\text{vap}}H_{\text{m}}^{\circ})$ at 298.15 K was accepted equal to the equilibrium value $(\Delta_{\text{vap}}H_{\text{m}})$ because $\Delta Z \approx 1$. The results for *n*-pentan-1-ol and 2-methylpropene were taken from reference 19. The recalculation of $\Delta_{\text{r}}H_{\text{m}}^{\circ}$ with the value found for $\Delta\Delta_{\text{vap}}H_{\text{m}}^{\circ}$ gives $\Delta_{\text{r}}H_{\text{m}}^{\circ}(298.15\ \text{K}) = -36.45\ \text{kJ} \cdot \text{mol}^{-1}$. This value is close to the experimental one $(-35.66\ \text{kJ} \cdot \text{mol}^{-1})$, found from the equilibrium constants of the liquid-phase reaction. The coincidence of the values of $\Delta_{\text{r}}H_{\text{m}}^{\circ}$ suggests that the mole-fraction equilibrium products K_x, found when one of the reacting components is in excess, could be used for the calculation of the enthalpy of reaction in the liquid non-ideal mixture.

Combination of the value of $\Delta_r H_m^\circ = -67.09\ \mathrm{kJ \cdot mol^{-1}}$ for the gas-phase reaction as well as $\Delta_f H_m^\circ(298.15\ \mathrm{K})$ values for 2-methylpropene and *n*-pentan-1-ol equal, respectively, to $-(17.82 \pm 1.09)$ and $-(295.64 \pm 0.75)\ \mathrm{kJ \cdot mol^{-1}}$, gives $\Delta_f H_m^\circ(\mathrm{ATBE}, 298.15\ \mathrm{K}) = -(380.6 \pm 6.8)\ \mathrm{kJ \cdot mol^{-1}}$.

REFERENCES

1. Noreiko, L. M.; Feigin, S. N.; Radchenko, E. D.; Agafonov, A. V.; Klishina, G. P. *Khim. Techn. Topl. Masel* **1979,** 5, 26.
2. McCallum, P. W.; Timbario, T. J. *Chem. Eng. Progr.* **1982,** 8, 52.
3. Lastovkin, G. A.; Petrov, A. N. *Neftepererab. neftekhim.* **1981,** 3, 5.
4. Colombo, F.; Cori, L.; Dalloro, L.; Delogu, P. *Ind. Eng. Chem.* **1983,** 22, 219.
5. Gicquel, A.; Torck, B. *J. Catal.* **1983,** 83, 9.
6. Safronov, V. V.; Sharonov, K. G.; Rozhnov, A. M.; Alenin, V. I. *Khim. Prom.* **1988,** 10, 14.
7. Rozhnov, A. M.; Safronov, V. V.; Alenin, V. I.; Sharonov, K. G. *Zh. Fiz. Khim.* **1988,** 62, 2902.
8. Sharonov, K. G.; Rozhnov, A. M.; Barkov, V. I.; Tsvetkov, V. S.; Saveljeva, E. A. *V. Vsesojusnaja konferentsija po termodinamike organich. soedinenii; tesisi dokladov.* Kuibyshev. **1987,** p. 64.
9. Safronov, V. V.; Sharonov, K. G.; Rozhnov, A. M.; Alenin, B. I.; Sidorov, S. A. *V Vsesojusnaja konferentsija po termodinamike organich. soedinenii; tesisi dokladov.* Kuibyshev. **1987,** p. 103.
10. Sharonov, K. G.; Rozhnov, A. M.; Safronov, V. V.; Alenin, V. I.; Mishentseva, Y. B. *12 Vsesojusnaja konf. po khim. termodinamike i kalorimetrii. Tez. dokl.* Gorky. **1988,** pp. 1, 69.
11. Safronov, V. V.; Sharonov, K. G.; Rozhnov, A. M.; Alenin, V. I.; Sidorov, S. A. *Zh. Prikl. Khim.* **1989,** 62, 824.
12. Read, R.; Prausnitz, J.; Sherwood, T. *Svoistva gasov i jidkostei.* Leningrad. Khim. **1982,** p. 313.
13. Fredenslung, A.; Gmeling, J.; Michelsen, M. L. *Ind. Eng. Chem. Process Des. Dev.* **1977,** 16, 450.
14. Tsvetkov, V. S.; Nazmutdinov, A. G.; Karaseva, S. Y. *Dep. ONITECHIM.* Cherkassi **1984,** N 143 kp-D84.
15. Drujinina, A. I.; Varuschenko, R. M. *Zh. Fiz. Khim.* **1978,** 52, 1927.
16. Haggenmacher, T. E. *J. Am. Chem. Soc.* **1946,** 68, 1633.
17. Ambrose, D.; Ellender, J. H.; Sprak, C. H. S. *J. Chem. Thermodynamics* **1976,** 8, 165.
18. Arntz, H.; Gottlib, K. *J. Chem. Thermodynamics* **1985,** 17, 967.
19. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organo-metallic Compounds.* Academic Press: London. **1970.**