ТЕОРЕТИЧЕСКИЕ ОСНОВЫ ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

544.344.016:544.344.2

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*: , , , ,
, .*

(-
) $L(x)$
- $\Delta h^E(x,T)$
, - $L(x,T)$.
-
[1]. -
, , -

[2ó4]. - $\Delta h^E(x,T)$ $L_i^0(T)$. -
-
, $\Delta h^E(x,T)$
, - [11ó
, - 14]. :

(. 1). - 1) $\left(\dfrac{\partial \Delta h^E(x)}{\partial T}\right)_P > 0$;

$L(x,T)$

[8, 9]. , - 2) $\left(\dfrac{\partial \Delta h^E(x)}{\partial T}\right)_P < 0$;

( ) -

[8, 10]. 3) $\left(\dfrac{\partial \Delta h^E(x)}{\partial T}\right)_P = 0$.

- , -
: -

$$L = \overline{L}_1 x_1 + \overline{L}_2 x_2 , \qquad (1)$$, . .

$$\overline{L}_i = L_i^0 + \overline{L}_i^E = L_i^0 - \overline{h}_i^E .$$ $\left(\partial \Delta h^E / \partial T\right)_{P,x} = \Delta c_P^E$. ,

0 1

-

$\Delta c_P^E(x) \; > = < 0$ $\Delta c_P^E(x) \; < = > 0$,

-

L_i^0 $\Delta c_P^E(x)$ [14, 15]. -

$\Delta h^E(x)$: 1) 2).

-

$$L = (L_1^0 x_1 + L_2^0 x_2) - \Delta h^E = L^a - \Delta h^E , \qquad (2)$$ [14],

$$\Delta h^E = \overline{h}_1^E x_1 + \overline{h}_2^E x_2$$ - ,

. $\Delta h^E(x)$ $\Delta c_P^E(x)$ (. 2)

L, Дж/моль

( )

L, Дж/моль

( )

L, Дж/моль

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L, Дж/моль

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. 1.   :
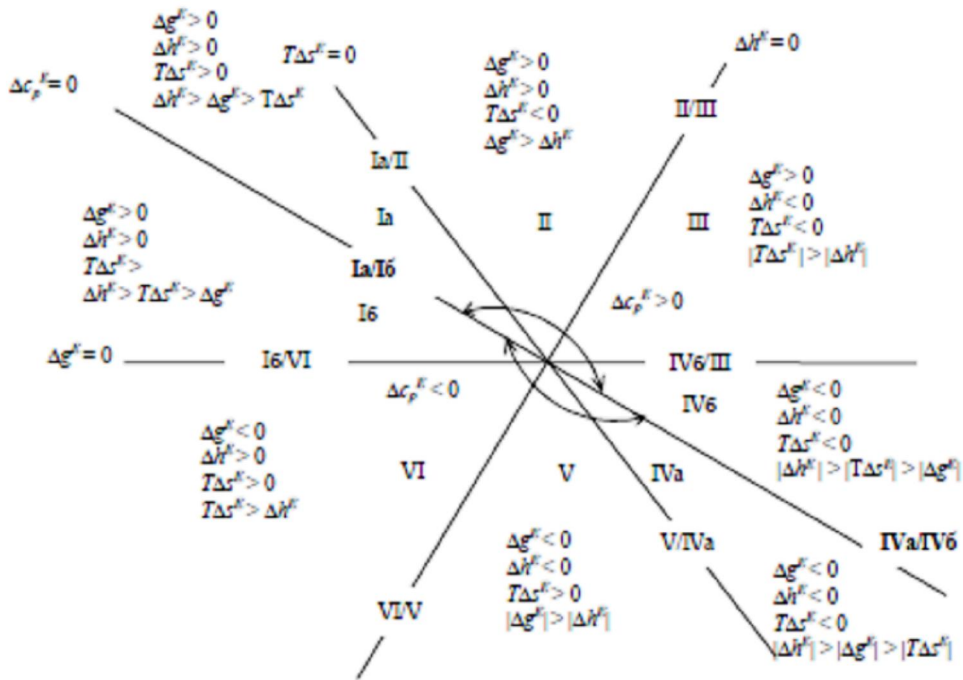) HF ( ) ó BrF$_3$ (1-) [5];   )   ( ) ó   (1-), 760   . . [6];
)   ( ) ó   (1-)   380,   570   ♦ ♦ ♦ 760   . . [6];
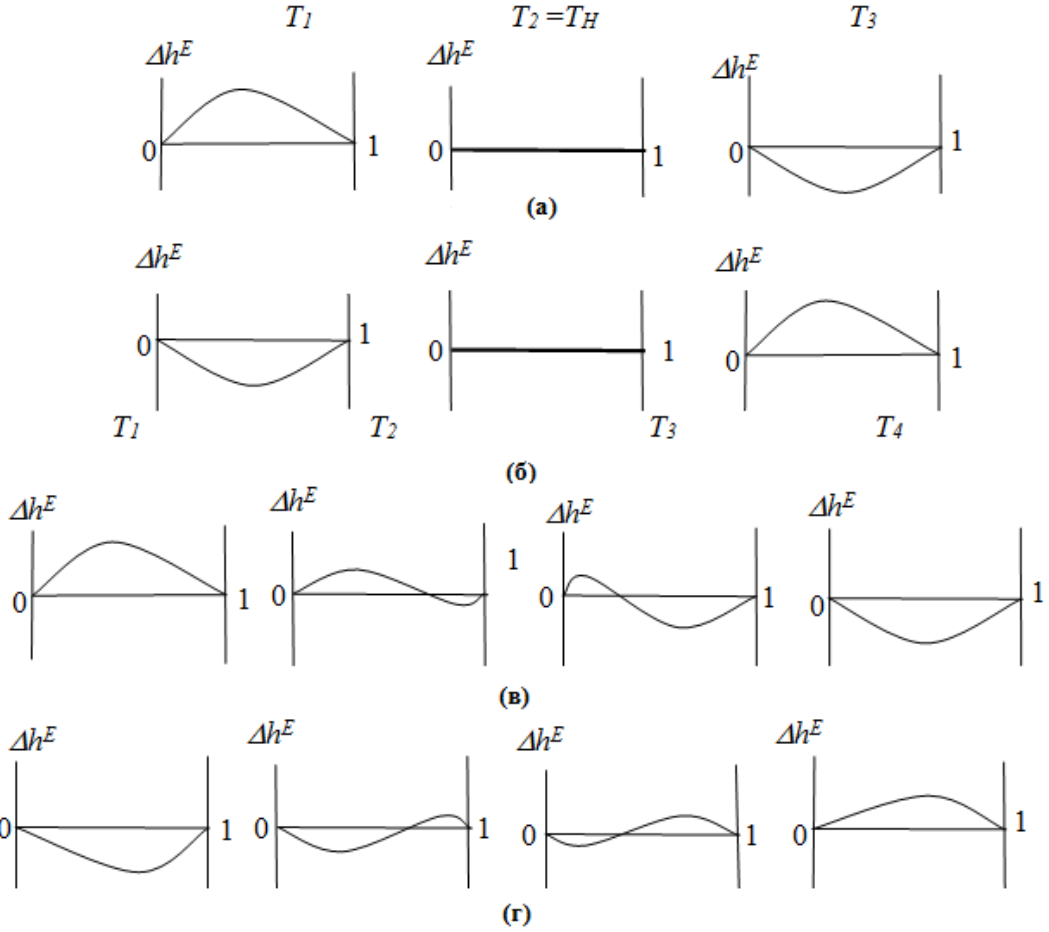)   ( ) ó   (1-)   298.15   [7].

$\Delta g^E > 0$
$\Delta h^E > 0$
$T\Delta s^E > 0$ $T\Delta s^E = 0$
$\Delta h^E > \Delta g^E > T\Delta s^E$

$\Delta c_p^E = 0$

$\Delta g^E > 0$
$\Delta h^E > 0$
$T\Delta s^E < 0$
$\Delta g^E > \Delta h^E$

$\Delta h^E = 0$

II/III

Ia/II

Ia   II   III

$\Delta g^E > 0$
$\Delta h^E < 0$
$T\Delta s^E < 0$
$|T\Delta s^E| > |\Delta h^E|$

$\Delta g^E > 0$
$\Delta h^E > 0$
$T\Delta s^E >$
$\Delta h^E > T\Delta s^E > \Delta g^E$

Ia/Iб

Iб

$\Delta c_p^E > 0$

$\Delta g^E = 0$

Iб/VI

IVб/III

$\Delta c_p^E < 0$

IVб

$\Delta g^E < 0$
$\Delta h^E < 0$
$T\Delta s^E < 0$
$|\Delta h^E| > |T\Delta s^E| > |\Delta g^E|$

$\Delta g^E < 0$
$\Delta h^E > 0$
$T\Delta s^E > 0$
$T\Delta s^E > \Delta h^E$

VI   V   IVa

$\Delta g^E < 0$
$\Delta h^E < 0$
$T\Delta s^E > 0$
$|\Delta g^E| > |\Delta h^E|$

V/IVa

VI/V

IVa/IVб

$\Delta g^E < 0$
$\Delta h^E < 0$
$T\Delta s^E < 0$
$|\Delta h^E| > |\Delta g^E| > |T\Delta s^E|$

. 2.   .

[14ó16].

,

$\Delta h^E(x)$, (. 3 ,). , -

: , $\Delta h^E(x) = 0$

(H) с

(. 3 ,), .

« » , -

T_1 $T_2 = T_H$ T_3

(а)

T_1 T_2 T_3 T_4

(б)

(в)

(г)

. 3.

:

),) ;),) .

$T_1 < T_2 < T_3 < T_4$

- 4) $\left(\partial \Delta L_i^0 \middle/ \partial T\right)_P > 0; = 0; < 0 .$ $\left(\partial \Delta L_i^0 \middle/ \partial T\right)_P = 0$

[3]. -

-

$\Delta L_i^0(T) = L_1^0(T) - L_2^0(T)$, , -

;

- ,

: ó , . .

1) $\left(\partial \Delta L_i^0 \middle/ \partial T\right)_P > 0 ;$ $L_i^0 = const$ [2]. $L_1^0(T) = L_2^0(T)$ -

,

.

2) $\left(\partial \Delta L_i^0 \middle/ \partial T\right)_P < 0 ;$ (-

): ΔL_i^0 $\Delta h^E(x)$. -

T_H (3, 7, 15, 27, 31)

3) $\left(\partial \Delta L_i^0 \middle/ \partial T\right)_P < 0; = 0; > 0 ;$ T_L (37-48).

(39, 43).

$$\Delta L_i^0 \qquad \Delta h^E(x)$$

	$L_i^o(T)$	$\Delta h^E(x)$	$\Delta C_p^E(x)$			$L_i^o(T)$	$\Delta h^E(x)$	$\Delta C_p^E(x)$	
1	const	>0	>0	Ia, II	25	< 0	> 0	>0	Ia, II
2		< 0		III, IV	26		< 0		III, IV
3		=0		II/III	27		=0		II/III
4		< = > 0		II ó III	28		< = > 0		II ó III
5	const	>0	<0	I , VI	29	<0	> 0	<0	I , VI
6		< 0		V, IVa	30		< 0		V, IVa
7		=0		V/VI	31		=0		V/VI
8		> = < 0		V ó VI	32		> = < 0		V ó VI
9	const	>0	0	Ia /I	33	<0	>0	0	Ia /I
10		<0	0	IVa óIV	34		<0	0	IVa /IV
11		>0	< = > 0	Ia ó I	35		>0	< = > 0	Ia ó I
12		<0	< = > 0	IVa ó IV	36		<0	< = > 0	IVa ó IV
13	> 0	> 0	>0	Ia, II	37	< = > 0	> 0	>0	Ia, II
14		< 0		III, IV	38		<0		III, IV
15		=0		II/III	39		=0		II/III
16		< = > 0		II ó III	40		< = > 0		II ó III
17	> 0	>0	<0	I , VI	41	< = > 0	>0	<0	I , VI
18		< 0		V, IVa	42		< 0		V, IVa
19		=0		V/VI	43		=0		V/VI
20		> = < 0		V ó VI	44		> = < 0		V ó VI
21	>0	>0	0	Ia /I	45	< = > 0	>0	0	Ia /I
22		<0	0	IVa óIV	46		< 0	0	IVa /IV
23		>0	< = > 0	Ia ó I	47		>0	< = > 0	Ia ó I
24		<0	< = > 0	IVa ó IV	48		< 0	< = > 0	IVa ó IV

«   » $\Delta h^E(x)$
(4, 8, 16, 20, 28, 32, 40, 44)   -
                    $\Delta h^E = 0$
                    ,   ,
(2), $L = L^a$ (. 4 -).

. 4.
          ( ) ó   (1-):
) 298 ;) 323.15 ;) 348.15 ;) 373.15 .
          $\Delta h^E(x)$ Aspen Tech.

$L(x)$ $L(x,T)$:

(3)

.

$\Delta h^E(x)$ $\overline{L}_1 - \overline{L}_2$ -

(2). ΔL_i^0 -

Microsoft

Exsel, $L_i^0(T)$ $(L = L^a)$

=const

ChemCad.   [16].

$L(x,T)$ -   -

ΔL_i^0 $\Delta h^E(x)$.

-   :

$L(x,T)$ $$\frac{dx_1^{Az}}{dT} = x_1 x_2 \frac{L_1^0 - L_2^0}{RT^2} .$$ (4)

(. 5).   -

$L(x,T)$

(- $L(x)$ -

)   (. 4).   .

. 6:

$0 < x_I < x$ (. 6) $x < x_I < 1$

L, Дж/моль

35546

35504   298.15 K
         Xextr = 0.87

(. 6), $\Delta \overline{L}_i$ ΔL_i^0

,

34555

34494   313.15 K
         Xextr = 0.85

x_{II}

33533

33439   328.15 K
         Xextr = 0.80

(3)

.

32485

32332   343.15 K
         Xextr = 0.77

( )

. 5.

( ) б   (1-).
$\Delta h^E(x)$ [12].

,

б

[8]:
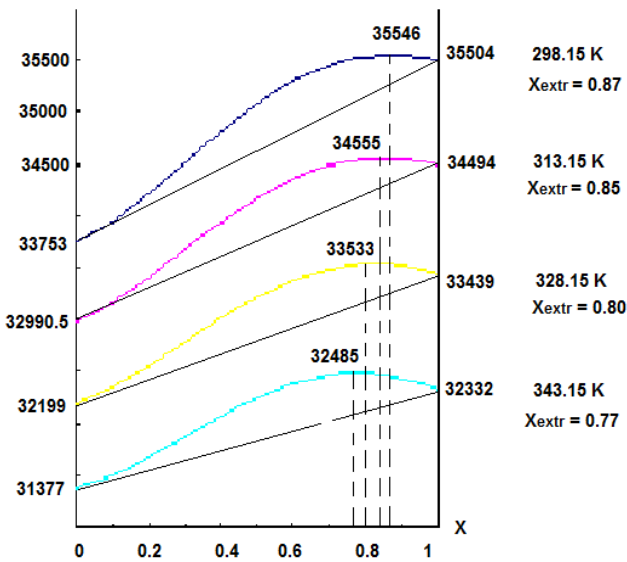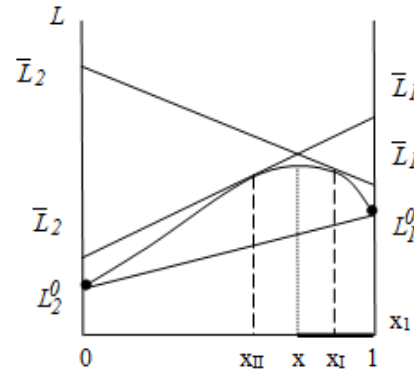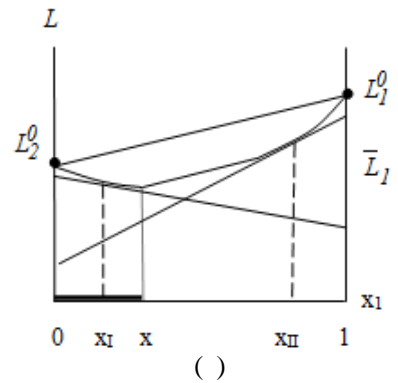
$$\frac{dx_1^{Az}}{dT} = \frac{x_1 x_2}{1 - \dfrac{\partial y_1}{\partial x_1}} \left[\frac{\overline{L}_1 - \overline{L}_2}{RT^2} \right] .$$ (3)

( )

. 6.

:   ) $\Delta h^E(x) > 0$;

) $\Delta h^E(x) < 0$.

,   -
.   -

(1)   -

$$L = L^a$$

-

$$x^{Az}(T)$$

$$\Delta h^E(x) \neq 0 \ .$$

-

[9, 16].

$$L = L^a$$

-

.

,

(3),

.

L_D

$L(x)$ P=const (
) T_D =const.

$$Q = D(R+1)L_D \ ,$$ (5)

D ó   , R ó
, L_D ó

T_D.

ó

, $L_D \approx L_i^0$.   -

,   '

Q   '

Δh^E ,   (2),

$L \approx L^{ad}$.   . 7.

,

, Δh^E L   -

. 8.

[4]

,

,

,

,   .   -

$\Delta h^E(x,T)$

$L(x,T)$

.

L, Дж/моль

( )

L, Дж/моль

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L, Дж/моль

( )

L, Дж/моль

( )

L, Дж/моль

( )

. 7.   ,
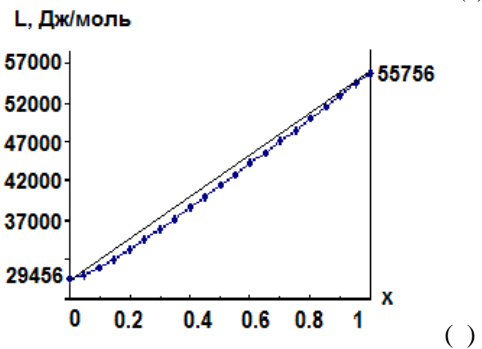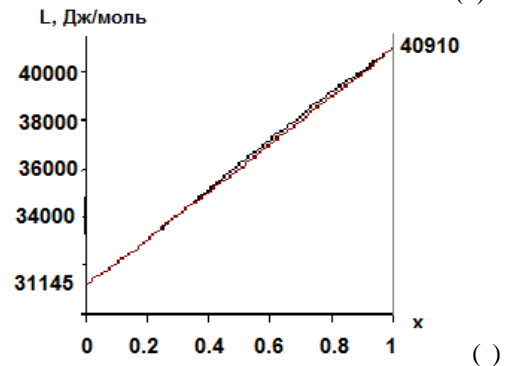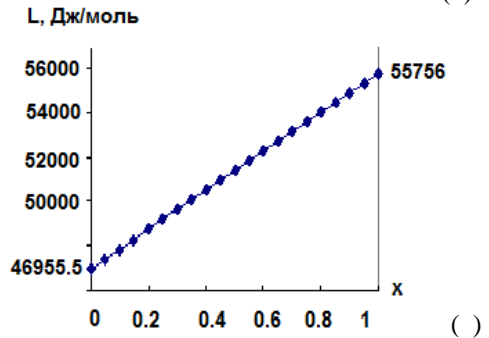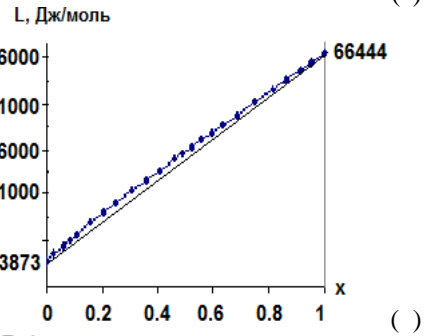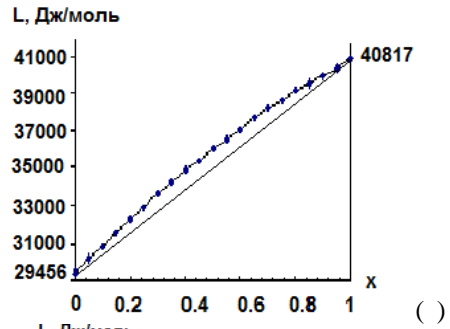
, 298.15   :
а)   ( ) ó   (1-) [17];
)   ( ) ó   (1-) [12];)   ( ) ó
ó 2-   (1-) [18];)   ( ) ó
(1-) [12];) 2-   ( ) ó   (1-) [17].

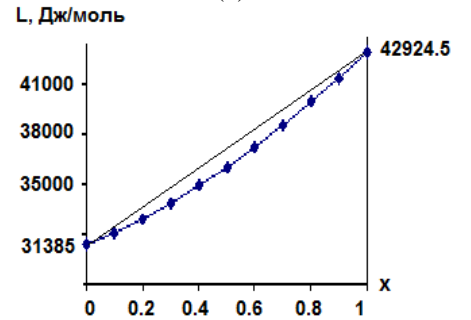( )　　　　　　　　　　　　( )　　　　　　　　　　　　( )

( )　　　　　　　　　　　　( )　　　　　　　　　　　　( )
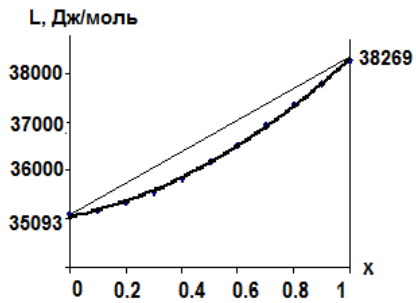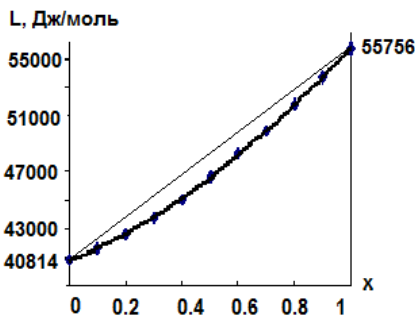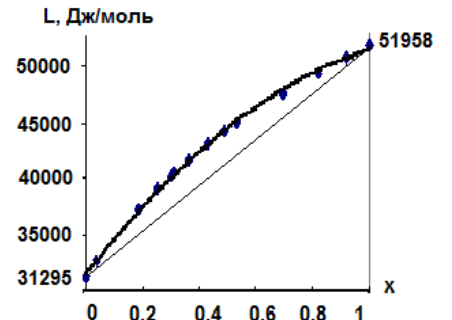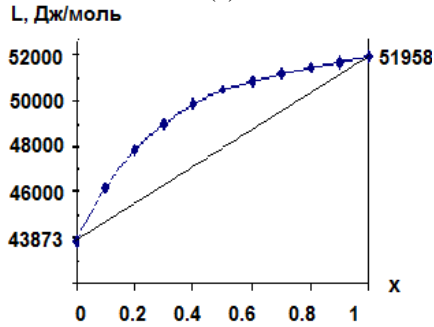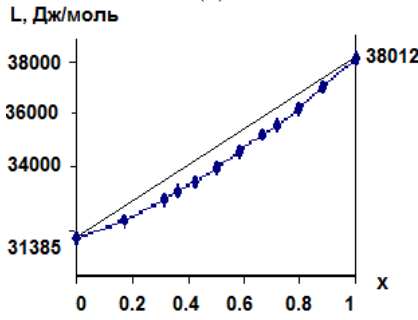
. 8. $L(x)$, 298.15 :
) ( ) ó (1-) [19];) 2- ( ) ó (1-) [17];
) ( ) ó (1-) [12];) ( ) ó (1-) [12];
) ( ) ó (1-) [12];) ( ) ó (1-) [12].

$L(x)$

L ó ; / , ó , . .; ó , ; T_H ó
, ; T_L ó , ; ó
, . .; extr ó , . .; Δh^E ó , / ; $\overline{h_i^E}$ ó
, / ; $\overline{L_i^E}$ ó
, / .

ó ; Az ó ; D ó ; $i, 1, 2$ ó ; 0 ó
.

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1. . ., . ., . .
// . . . 2011. . 45. 6.
. 634ó640.
2. ., ., . : . . / . . .
. ó .: , 1982. 592 .
3. . . . ó .: , 1975. 583 .
4. .
: . . í . . . ó ., 2011. 28 .

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         . .,   . .,   . .   ó   /
 . . .   . ó .:   , 1989. 344 .

9.   . .,   . .,   . .
                        //   .   .   . 1996. . 30.   1. . 27ó33.

10.   . .   . ó . - .:   , 1953. 336 .

11.   . ., ... ó .:
 , 1970. 320 .

12.   . .,   . .,   . .
            .   . ó .:   , 1981. 264 .

13.   . .,   . .   . ó .:
 , 1983. 266 .

14.   . .,   . .,   . .
                                                    //   .   .   .
1996. .30.   6. . 611ó617.

15.   . .,   . .
                        //   . 2009. . 4.   4. . 31ó39.

16.   . .
        :   . í   .   .   . ó .:   , 1998. 168 .

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 . 29ó36.

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methyl isobutyrate + toluene) and (propionitrile + methyl isobutyrate + ethylbenzene) at 298.15   // J.
Thermal Analysis & Calorimetry. 2000. V. 61.   2. . 377ó388.

VAPORIZATION HEAT OF BINARY MIXTURES

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The concentration dependences of integral vaporization heats of binary mixtures were calculated for atmospheric pressure with the use of experimental data. The character of changes of these dependencies under the influence of varying temperature was analyzed.

Key words: *binary mixture, azeotrope, heat of mixing, heat of vaporization of a substance, integral molar latent heat of vaporization, energy consumption for separation.*