Temkin's and universal relationships for activities in systems having complete miscibility in solid state*

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Liquidus and solidus curves in binary systems of the 2nd kind having complete miscibility in liquid and solid states are analyzed from the mathematic and thermodynamic points of view. The types T/K, K/T, T/T, U/K, K/U, U/U are discussed. (T, K or U denote Temkin's, classic or universal model for activity.) For each type the characteristic equation of liquidus or solidus curve (if the equation exists), and the equation for extremum are derived. The limit values of the tangents at the melting points of pure components are calculated. Thermodynamic conditions for the existence of a monotonic course of liquidus and solidus curves and for a course with common extremum on both curves are determined.

С математической и термодинамической точек зрения были анализированы кривые ликвидуса и солидуса в системах второго рода с неограниченной взаимной растворимостью компонентов как в жидком, так и в твердом состояниях. Были дискутированы типы T/K, K/T, T/T, U/K, K/U и U/U. (T, K и U обозначают модели Темкина, классический и универсальный.) Для каждого типа было выведено – пока вообще существует – характеристическое уравнение кривой ликвидуса или солидуса, а также уравнение для экстремума. Были рассчитаны предельные значения угловых коэффициентов касательных в точке плавления чистых компонентов. Были выведены термодинамические условия для существования монотонного хода кривых ликвидуса и солидуса и также для экстремума на обеих кривых.

The course of liquidus and solidus curves in binary ionic systems of the 2nd kind having complete miscibility in liquid and solid states has been discussed in [1, 2]. In

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the quoted papers a general functional relation between activity and composition was assumed.

In this work the theoretical relations derived in the cited papers are used for the detailed analysis of Temkin's and universal relations between activity and composition [3, 4]

$$a_i = \mathrm{Te}(x_i) \qquad i = 1, 2 \tag{1}$$

$$a_i = \mathrm{U}(x_i) \tag{2}$$

It holds

$$x_1 + x_2 = 1 \tag{3}$$

where both mole fractions are related to the same phase. The considerations are based on the thermodynamic relation

Table 1

System N_pA_q—N_rB_t with common ion, type T/K

a_1^l	a_2^l	a_1^s	a_2^s
$\left[\dfrac{qx_1^l}{t+x_1^l(q-t)}\right]^q$	$\left[\dfrac{t(1-x_1^l)}{t+x_1^l(q-t)}\right]^t$	x_1^s	$1-x_1^s$

Characteristic equation of liquidus curve

$$MQ - Q\left[\frac{qx_1^l}{t+x_1^l(q-t)}\right]^q - M\left[\frac{t(1-x_1^l)}{t+x_1^l(q-t)}\right]^t = 0$$

	$t>1$	$t=1$
$\lim\limits_{T\to T_1^f} dT/dx_1^l$	$\dfrac{t}{\Delta H_1^f}R(T_1^f)^2$	$\dfrac{qQ_0-1}{qQ_0\Delta H_1^f}R(T_1^f)^2$
	$q>1$	$q=1$
$\lim\limits_{T\to T_2^f} dT/dx_1^l$	$-\dfrac{q}{\Delta H_2^f}R(T_2^f)^2$	$\dfrac{1-tM_0}{tM_0\Delta H_2^f}R(T_2^f)^2$
	$t>1$	$t=1$
$\lim\limits_{T\to T_1^f} dT/dx_1^s$	∞	$qQ_0 \lim\limits_{T\to T_1^f} dT/dx_1^l$
	$q>1$	$q=1$
$\lim\limits_{T\to T_2^f} dT/dx_1^s$	$-\infty$	$tM_0 \lim\limits_{T\to T_2^f} dT/dx_1^l$

Equation for extremum

$$\left[\frac{t}{t+x(q-t)}\right]^t(1-x)^{t-1}\left\{\left[\frac{q}{t+x(q-t)}\right]^q x^{q-1}\right\}^{-\Delta H_2^f/\Delta H_1^f} - Q_0 = 0$$

$$\frac{a_i^{\mathrm{l}}}{a_i^{\mathrm{s}}}=\exp\left[\frac{\Delta H_i^{\mathrm{f}}}{R}\left(\frac{1}{T_i^{\mathrm{f}}}-\frac{1}{T}\right)\right] \tag{4}$$

The results of theoretical analysis are summarized in Tables 1—11 and possible shapes of liquidus and solidus curves are drawn in Figs. 1—5. If the functional relationship $a_i=\mathrm{f}(x_i)$ is the same for both liquid and solid solutions, the course of the liquidus and solidus curves in the corresponding phase diagram will be always

Table 2

System N_pA_q—N_rB_t with common ion, type K/T

a_1^{l}	a_2^{l}	a_1^{s}	a_2^{s}
x_1^{l}	$1-x_1^{\mathrm{l}}$	$\left[\frac{\mathrm{q}x_1^{\mathrm{s}}}{\mathrm{t}+x_1^{\mathrm{s}}(\mathrm{q}-\mathrm{t})}\right]^{\mathrm{q}}$	$\left[\frac{\mathrm{t}(1-x_1^{\mathrm{s}})}{\mathrm{t}+x_1^{\mathrm{s}}(\mathrm{q}-\mathrm{t})}\right]^{\mathrm{t}}$

Characteristic equation of solidus curve

$$Q[\mathrm{t}(1-x_1^{\mathrm{s}})]^{\mathrm{t}}-[\mathrm{t}+x_1^{\mathrm{s}}(\mathrm{q}-\mathrm{t})]^{\mathrm{t}}+M(\mathrm{q}x_1^{\mathrm{s}})^{\mathrm{q}}[\mathrm{t}+x_1^{\mathrm{s}}(\mathrm{q}-\mathrm{t})]^{\mathrm{t}-\mathrm{q}}=0$$

	$\mathrm{t}>1$	$\mathrm{t}=1$
$\lim\limits_{T\to T_1^{\mathrm{f}}} \mathrm{d}T/\mathrm{d}x_1^{\mathrm{l}}$	$-\infty$	$\frac{\mathrm{q}}{Q_0}\lim\limits_{T\to T_1^{\mathrm{f}}}\mathrm{d}T/\mathrm{d}x_1^{\mathrm{s}}$
	$\mathrm{q}>1$	$\mathrm{q}=1$
$\lim\limits_{T\to T_2^{\mathrm{f}}} \mathrm{d}T/\mathrm{d}x_1^{\mathrm{l}}$	∞	$\frac{\mathrm{t}}{M_0}\lim\limits_{T\to T_2^{\mathrm{f}}}\mathrm{d}T/\mathrm{d}x_1^{\mathrm{s}}$
	$\mathrm{t}>1$	$\mathrm{t}=1$
$\lim\limits_{T\to T_1^{\mathrm{f}}} \mathrm{d}T/\mathrm{d}x_1^{\mathrm{s}}$	$-\frac{\mathrm{t}}{\Delta H_1^{\mathrm{f}}}R(T_1^{\mathrm{f}})^2$	$\frac{Q_0-\mathrm{q}}{\mathrm{q}\,\Delta H_1^{\mathrm{f}}}R(T_1^{\mathrm{f}})^2$
	$\mathrm{q}>1$	$\mathrm{q}=1$
$\lim\limits_{T\to T_2^{\mathrm{f}}} \mathrm{d}T/\mathrm{d}x_1^{\mathrm{s}}$	$\frac{\mathrm{q}}{\Delta H_2^{\mathrm{f}}}R(T_2^{\mathrm{f}})^2$	$\frac{\mathrm{t}-M_0}{\mathrm{t}\,\Delta H_2^{\mathrm{f}}}R(T_2^{\mathrm{f}})^2$

Equation for extremum

$$\left[\frac{\mathrm{t}+x(\mathrm{q}-\mathrm{t})}{\mathrm{t}}\right]^{\mathrm{t}}\frac{1}{(1-x)^{\mathrm{t}-1}}\left\{\left[\frac{\mathrm{t}+x(\mathrm{q}-\mathrm{t})}{\mathrm{q}}\right]^{\mathrm{q}}\frac{1}{x^{\mathrm{q}-1}}\right\}^{-\Delta H_2^{\mathrm{f}}/\Delta H_1^{\mathrm{f}}}-Q_0=0$$

Table 3

System N_pA_q—N_rB_t with common ion, type T/T

a_1^{l}	a_2^{l}	a_1^{s}	a_2^{s}
$\left[\frac{qx_1^{l}}{t+x_1^{l}(q-t)}\right]^{q}$	$\left[\frac{t(1-x_1^{l})}{t+x_1^{l}(q-t)}\right]^{t}$	$\left[\frac{qx_1^{s}}{t+x_1^{s}(q-t)}\right]^{q}$	$\left[\frac{t(1-x_1^{s})}{t+x_1^{s}(q-t)}\right]^{t}$

Characteristic equation of liquidus curve

$$(Q^{-(1/t)}-1)t-x_1^{l}[t(Q^{-(1/t)}-1)+q(1-M^{-(1/q)})]=0$$

$\lim\limits_{T\to T_1^{f}} dT/dx_1^{l}$	$\frac{t(Q_0^{1/t}-1)}{Q_0^{1/t}\,\Delta H_1^{f}}R(T_1^{f})^2$
$\lim\limits_{T\to T_1^{f}} dT/dx_1^{s}$	$Q_0^{1/t}\lim\limits_{T\to T_1^{f}} dT/dx_1^{l}$
$\lim\limits_{T\to T_2^{f}} dT/dx_1^{l}$	$\frac{q(1-M_0^{1/q})}{M_0^{1/q}\,\Delta H_2^{f}}R(T_2^{f})^2$
$\lim\limits_{T\to T_2^{f}} dT/dx_1^{s}$	$M_0^{1/q}\lim\limits_{T\to T_2^{f}} dT/dx_1^{l}$

Table 4

System M_pA_q—N_rB_t without common ion, type T/K

a_1^{l}	a_2^{l}
$\left[\frac{px_1^{l}}{r+x_1^{l}(p-r)}\right]^{p}\left[\frac{qx_1^{l}}{t+x_1^{l}(q-t)}\right]^{q}$	$\left[\frac{r(1-x)}{r+x_1^{l}(p-r)}\right]^{r}\left[\frac{t(1-x_1^{l})}{t+x_1^{l}(q-t)}\right]^{t}$
a_1^{s}	a_2^{s}
x_1^{s}	$1-x_1^{s}$

Characteristic equation of liquidus curve

$$Q-\frac{Q}{M}\left[\frac{px_1^{l}}{r+x_1^{l}(p-r)}\right]^{p}\left[\frac{qx}{t+x_1^{l}(q-t)}\right]^{q}-\left[\frac{r(1-x_1^{l})}{r+x_1^{l}(p-r)}\right]^{r}\left[\frac{t(1-x_1^{l})}{t+x_1^{l}(q-t)}\right]^{t}=0$$

$\lim\limits_{T\to T_1^{f}} dT/dx_1^{l}$	$\frac{r+t}{\Delta H_1^{f}}R(T_1^{f})^2$
$\lim\limits_{T\to T_2^{f}} dT/dx_1^{l}$	$-\frac{p+q}{\Delta H_2^{f}}R(T_2^{f})^2$
$\lim\limits_{T\to T_1^{f}} dT/dx_1^{s}$	∞
$\lim\limits_{T\to T_2^{f}} dT/dx_1^{s}$	$-\infty$

Equation for extremum

$$\left[\frac{r^{r+1}pt^{t}(1-x)^{r+t-1}}{[r+x(p-r)]^{r+1}[t+x(q-t)]^{t}}+\frac{r^{r}t^{t+1}q(1-x)^{r+t-1}}{[r+x(p-r)]^{r}[t+x(q-t)]^{t+1}}\right]\cdot$$

$$\cdot\frac{1}{\dfrac{pr}{r+x(p-r)}+\dfrac{qt}{t+x(q-t)}}\left\{\frac{p^{p}q^{q}x^{p+q-1}}{[r+x(p-r)]^{p}[t+x(q-t)]^{q}}\right\}^{-\Delta H_2^f/\Delta H_1^f}=Q_0$$

Table 5

System M_pA_q—N_rB_t without common ion, type K/T

a_1^l	a_2^l
x_1^l	$1-x_1^l$
a_1^s	a_2^s
$\left[\dfrac{px_1^s}{r+x_1^s(p-r)}\right]^p\left[\dfrac{qx_1^s}{t+x_1^s(q-t)}\right]^q$	$\left[\dfrac{r(1-x_1^s)}{r+x_1^s(p-r)}\right]^r\left[\dfrac{t(1-x_1^s)}{t+x_1^s(q-t)}\right]^t$

Characteristic equation of solidus curve

$$Q\left[\frac{r(1-x_1^s)}{r+x_1^s(p-r)}\right]^r\left[\frac{t(1-x_1^s)}{t+x_1^s(q-t)}\right]^t+M\left[\frac{px_1^s}{r+x_1^s(p-r)}\right]^p\left[\frac{qx_1^s}{t+x_1^s(q-t)}\right]^q-1=0$$

$\lim\limits_{T\to T_1^f} dT/dx_1^l$	$-\infty$
$\lim\limits_{T\to T_2^f} dT/dx_1^l$	$+\infty$
$\lim\limits_{T\to T_1^f} dT/dx_1^s$	$-\dfrac{r+t}{\Delta H_1^f}R(T_1^f)^2$
$\lim\limits_{T\to T_2^f} dT/dx_1^s$	$\dfrac{p+q}{\Delta H_2^f}R(T_2^f)^2$

Equation for extremum

$$\frac{[r+x(p-r)]^{r}[t+x(q-t)]^{t}}{r^{r}t^{t}(1-x)^{r+t-1}}\cdot\left\{\frac{[r+x(p-r)]^{p}[t+x(q-t)]^{q}}{p^{p}q^{q}x^{p+q-1}}\right\}^{-\Delta H_2^f/\Delta H_1^f}-Q_0=0$$

Table 6

System $M_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ without common ion, type T/T

a_1^l	a_2^l
$\left[\dfrac{px_1^l}{r+x_1^l(p-r)}\right]^p\left[\dfrac{qx_1^l}{t+x_1^l(q-t)}\right]^q$	$\left[\dfrac{r(1-x_1^l)}{r+x_1^l(p-r)}\right]^r\left[\dfrac{t(1-x_1^l)}{t+x_1^l(q-t)}\right]^t$
a_1^s	a_2^s
$\left[\dfrac{px_1^s}{r+x_1^s(p-r)}\right]^p\left[\dfrac{qx_1^s}{t+x_1^s(q-t)}\right]^q$	$\left[\dfrac{r(1-x_1^s)}{r+x_1^s(p-r)}\right]^r\left[\dfrac{t(1-x_1^s)}{t+x_1^s(q-t)}\right]^t$

Characteristic equation cannot be given because it is not possible to eliminate either x_1^l or x_1^s

$$M=\left(\frac{x_1^l}{x_1^s}\right)^{p+q}\left[\frac{r+x_1^s(p-r)}{r+x_1^l(p-r)}\right]^p\left[\frac{t+x_1^s(q-t)}{t+x_1^l(q-t)}\right]^q$$

$$Q=\left(\frac{1-x_1^l}{1-x_1^s}\right)^{r+t}\left[\frac{r+x_1^s(p-r)}{r+x_1^l(p-r)}\right]^r\left[\frac{t+x_1^s(q-t)}{t+x_1^l(q-t)}\right]^t$$

$\lim\limits_{T\to T_1^f} \mathrm{d}T/\mathrm{d}x_1^l$	$\dfrac{(r+t)(Q_0^{1/(r+t)}-1)}{Q_0^{1/(r+t)}}R(T_1^f)^2/\Delta H_1^f$
$\lim\limits_{T\to T_2^f} \mathrm{d}T/\mathrm{d}x_1^l$	$\dfrac{(p+q)(1-M_0^{1/(p+q)})}{M_0^{1/(p+q)}}R(T_2^f)^2/\Delta H_2^f$
$\lim\limits_{T\to T_1^f} \mathrm{d}T/\mathrm{d}x_1^s$	$Q_0^{1/(r+t)}\lim\limits_{T\to T_1^f} \mathrm{d}T/\mathrm{d}x_1^l$
$\lim\limits_{T\to T_2^f} \mathrm{d}T/\mathrm{d}x_1^s$	$M_0^{1/(p+q)}\lim\limits_{T\to T_2^f} \mathrm{d}T/\mathrm{d}x_1^l$

Table 7

System $M_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ without common ion, type U/K

a_1^l	a_2^l	a_1^s	a_2^s
$(x_1^l)^{r+t}$	$(1-x_1^l)^{p+q}$	x_1^s	$1-x_1^s$

Characteristic equation of liquidus curve

$$Q(x_1^l)^{r+t}+M(1-x_1^l)^{p+q}-MQ=0$$
$$(p+q>1)\wedge(r+t>1)\wedge(p+q=r+t)$$

$\lim_{T \to T_1^f} dT/dx_1^l$	$\frac{r+t}{\Delta H_1^f} R(T_1^f)^2$
$\lim_{T \to T_2^f} dT/dx_1^l$	$-\frac{p+q}{\Delta H_2^f} R(T_2^f)^2$
$\lim_{T \to T_1^f} dT/dx_1^s$	∞
$\lim_{T \to T_2^f} dT/dx_1^s$	$-\infty$

Table 8

System $N_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ with common ion, type U/K

$$p = r = 0$$

a_1^l	a_2^l	a_1^s	a_2^s
$(x_1^l)^t$	$(1-x_1^l)^q$	x_1^s	$1-x_1^s$

Characteristic equation of liquidus curve

$$Q(x_1^l)^t + M(1-x_1^l)^q - MQ = 0$$

	t = 1 q > 1	t > 1 q = 1	t = 1 q = 1
$\lim_{T \to T_1^f} dT/dx_1^l$	$\frac{1}{\Delta H_1^f} R(T_1^f)^2$	$\frac{tQ_0-1}{Q_0 \Delta H_1^f} R(T_1^f)^2$	$\frac{Q_0-1}{Q_0 \Delta H_2^f} R(T_1^f)^2$
$\lim_{T \to T_2^f} dT/dx_1^l$	$\frac{1-M_0 q}{M_0 \Delta H_2^f} R(T_2^f)^2$	$\frac{1}{\Delta H_2^f} R(T_2^f)^2$	$\frac{1-M_0}{M_0 \Delta H_2^f} R(T_2^f)^2$
$\lim_{T \to T_1^f} dT/dx_1^s$	$+\infty$	$Q_0 \lim_{T \to T_1^f} dT/dx_1^l$	$Q_0 \lim_{T \to T_1^f} dT/dx_1^l$
$\lim_{T \to T_2^f} dT/dx_1^s$	$M_0 \lim_{T \to T_2^f} dT/dx_1^l$	$-\infty$	$M_0 \lim_{T \to T_2^f} dT/dx_1^l$

Table 9

System $M_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ without common ion, type K/U

a_1^l	a_2^l	a_1^s	a_2^s
x_1^l	$1-x_1^l$	$(x_1^s)^{r+t}$	$(1-x_1^s)^{p+q}$

Characteristic equation of solidus curve

$$Q(1-x_1^s)^{p+q}-M(x_1^s)^{r+t}-1=0$$
$$(p+q>1)\wedge(r+t>1)\wedge(p+q=r+t)$$

$\lim\limits_{T\to T_1^f} dT/dx_1^l$	$-\infty$
$\lim\limits_{T\to T_2^f} dT/dx_1^l$	$+\infty$
$\lim\limits_{T\to T_1^f} dT/dx_1^s$	$-\dfrac{r+t}{\Delta H_1^f}R(T_1^f)^2$
$\lim\limits_{T\to T_2^f} dT/dx_1^s$	$\dfrac{p+q}{\Delta H_2^f}R(T_2^f)^2$

Table 10

System $N_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ with common ion, type K/U

$$p=r=0$$

a_1^l	a_2^l	a_1^s	a_2^s
x_1^l	$1-x_1^l$	$(x_1^s)^t$	$(1-x_1^s)^q$

Characteristic equation of solidus curve

$$Q(1-x_1^s)^q-M(x_1^s)^t-1=0$$

	t = 1, q > 1	t > 1, q = 1	t = 1, q = 1
$\lim\limits_{T\to T_1^f} dT/dx_1^l$	$-\infty$	$\dfrac{Q_0-t}{Q_0\Delta H_1^f}R(T_1^f)^2$	$\dfrac{Q_0-1}{Q_0\Delta H_1^f}R(T_1^f)^2$
$\lim\limits_{T\to T_2^f} dT/dx_1^l$	$\dfrac{q-M_0}{M_0\Delta H_2^f}R(T_2^f)^2$	∞	$\dfrac{1-M_0}{M_0\Delta H_2^f}R(T_2^f)^2$
$\lim\limits_{T\to T_1^f} dT/dx_1^s$	$\dfrac{1}{\Delta H_1^f}R(T_1^f)^2$	$Q_0\lim\limits_{T\to T_1^f} dT/dx_1^l$	$Q_0\lim\limits_{T\to T_1^f} dT/dx_1^l$
$\lim\limits_{T\to T_2^f} dT/dx_1^s$	$M_0\lim\limits_{T\to T_2^f} dT/dx_1^l$	$\dfrac{1}{\Delta H_2^f}R(T_2^f)^2$	$M_0\lim\limits_{T\to T_2^f} dT/dx_1^l$

Table 11

System $M_{p^*}A_{q^*}$—$N_{r^*}B_{t^*}$ with and without common ion, type U/U

a_1^l	a_2^l	a_1^s	a_2^s
$(x_1^l)^{r+t}$	$(1-x_1^l)^{p+q}$	$(x_1^s)^{r+t}$	$(1-x_1^s)^{p+q}$

Characteristic equation of liquidus curve

$$x_1^l = \frac{M^{1(r+t)}(1-Q^{1(p+q)})}{M^{1/(r+t)}-Q^{1/(p+q)}}$$

$\lim\limits_{T\to T_1^f} dT/dx_1^l$	$\dfrac{(Q_0^{1/(p+q)}-1)(r+t)}{Q_0^{1/(p+q)}\Delta H_1^f}R(T_1^f)^2$
$\lim\limits_{T\to T_2^f} dT/dx_1^l$	$\dfrac{(1-M_0^{1/(r+t)})(p+q)}{M_0^{1/(r+t)}\Delta H_2^f}R(T_2^f)^2$
$\lim\limits_{T\to T_1^f} dT/dx_1^s$	$Q_0^{1/(p+q)}\lim\limits_{T\to T_1^f} dT/dx_1^l$
$\lim\limits_{T\to T_2^f} dT/dx_1^s$	$M_0^{1/(r+t)}\lim\limits_{T\to T_2^f} dT/dx_1^l$

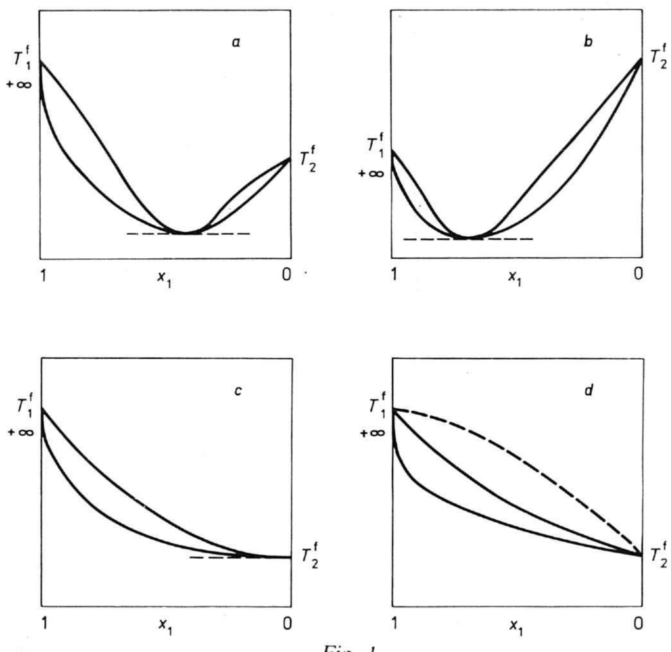

Fig. 1

Fig. 1. Solutions with common ion.

a) Type T/K; $t > 1 \wedge q = 1$; $\Delta H_1^f < R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t$.

b) Type T/K; $t > 1 \wedge q = 1$ in all cases.

c) Type T/K; $t > 1 \wedge q = 1$; $\Delta H_1^f = R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t$.

d) Either the type T/K; $t > 1 \wedge q = 1$; $\Delta H_1^f > R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t$;

or the type U/K; $t^* = 1 \wedge q^* > 1$; $\Delta H_1^f > R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln q^*$.

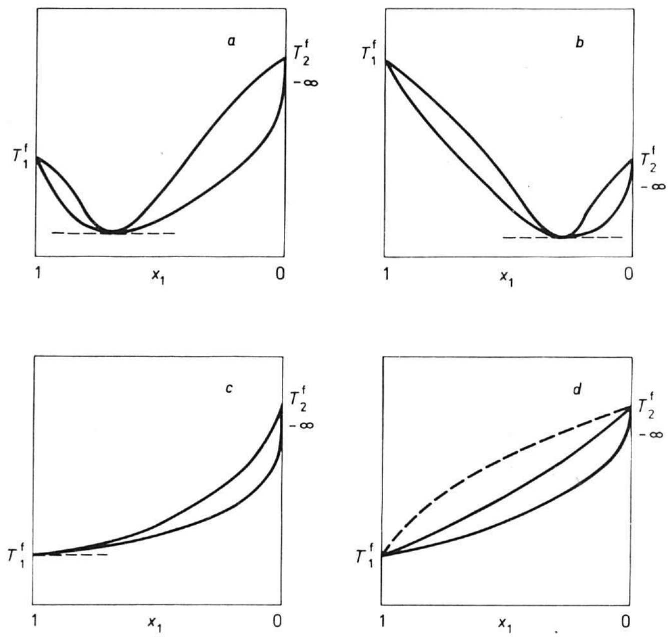

Fig. 2. Solutions with common ion.

a) Type T/K; $t = 1 \wedge q > 1$; $\Delta H_2^f < R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln q$.

b) Type T/K; $t = 1 \wedge q > 1$ in all cases.

c) Type T/K; $t = 1 \wedge q > 1$; $\Delta H_2^f = R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln q$.

d) Either the type T/K; $t = 1 \wedge q > 1$; $\Delta H_2^f > R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln q$;

or the type U/K; $t^* > 1 \wedge q^* = 1$; $\Delta H_2^f > R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t^*$.

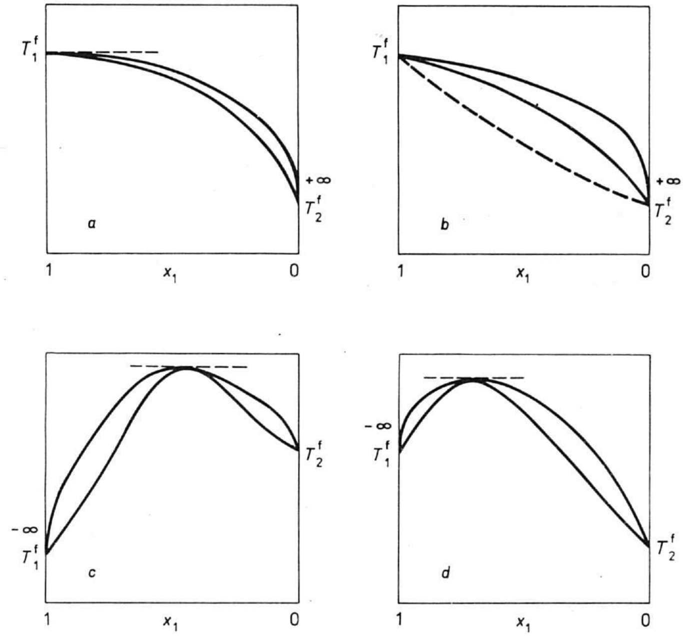

Fig. 3. Solutions with common ion.

a) Type K/T; $t = 1 \wedge q > 1$; $\Delta H_2^f = R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln q$.

b) Either the type K/T; $t = 1 \wedge q > 1$; $\Delta H_2^f > R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln q$;

or the type K/U; $t^* > 1 \wedge q^* = 1$; $\Delta H_2^f > R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t^*$.

c) Type K/T; $t > 1 \wedge q = 1$; $\Delta H_1^f < R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t$.

d) Type K/T; $t > 1 \wedge q = 1$ in all cases.

monotonic [2]. The numerical calculations (see Figs. 6—9) were carried out using computer Siemens 4004 (Calculating Centre of Universities, Mlynská dolina, Bratislava). The characteristic equation of liquidus curve (higher than of the second degree) and nonalgebraic equation of extremum were solved using the iterative method of division the interval into halves [5]. The roots were calculated with relative error smaller or equal to 5×10^{-5}.

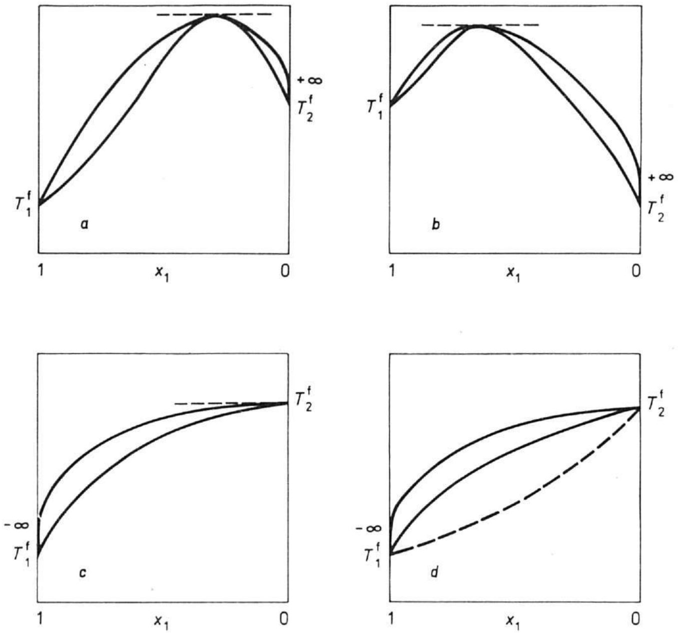

Fig. 4. Solutions with common ion.

a) Type K/T; $t>1 \wedge q=1$; $\Delta H_1^f = R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t$.

b) Either the type K/T; $t>1 \wedge q=1$; $\Delta H_1^f > R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t$;

or the type K/U; $t^* = 1 \wedge q^* > 1$; $\Delta H_1^f > R \dfrac{T_1^f T_2^f}{T_2^f - T_1^f} \ln q^*$.

c) Type K/T in all cases.

d) Type K/T; $t=1 \wedge q>1$; $\Delta H_2^f < R \dfrac{T_1^f T_2^f}{T_1^f - T_2^f} \ln q$.

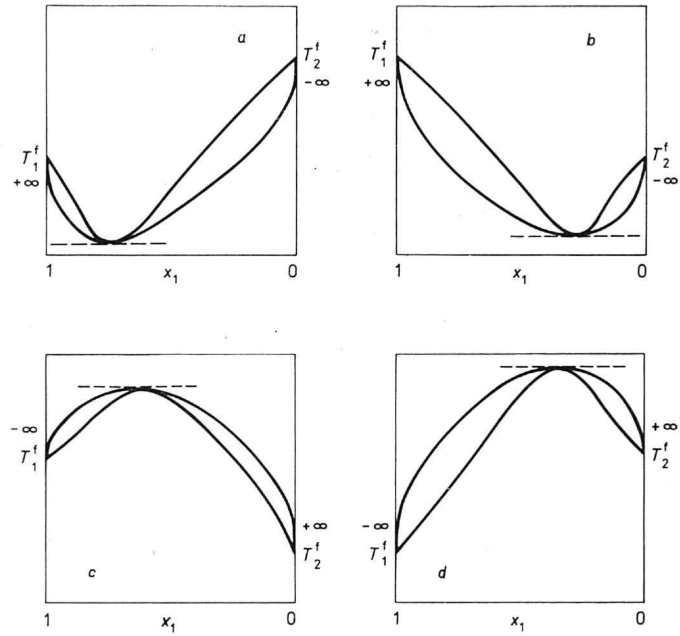

Fig. 5. Solutions either with or without common ion.
a) With common ion.
Type T/K, if $t > 1 \wedge q > 1$; type U/K, if $t^* > 1 \wedge q^* > 1 \wedge t^* = q^*$.
Without common ion.
Type T/K in all cases; type U/K, if $p^* + q^* = r^* + t^*$.
b) With common ion.
Type T/K, if $t > 1 \wedge q > 1$; type U/K, if $t^* > 1 \wedge q^* > 1 \wedge t^* = q^*$.
Without common ion.
Type T/K in all cases; type U/K, if $p^* + q^* = r^* + t^*$.
c) With common ion.
Type K/T, if $t > 1 \wedge q > 1$; type K/U, if $t^* > 1 \wedge q^* > 1 \wedge t^* = q^*$.
Without common ion.
Type K/T in all cases; type K/U, if $p^* + q^* = r^* + t^*$.
d) With common ion.
Type K/T, if $t > 1 \wedge q > 1$; type K/U, if $t^* > 1 \wedge q^* > 1 \wedge t^* = q^*$.
Without common ion.
Type K/T in all cases; type K/U, if $p^* + q^* = r^* + t^*$.

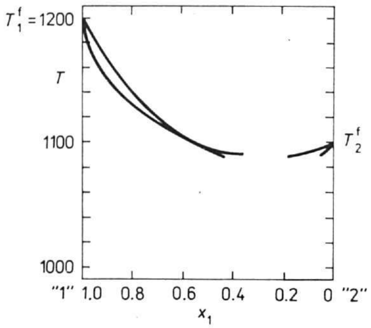

Fig. 6

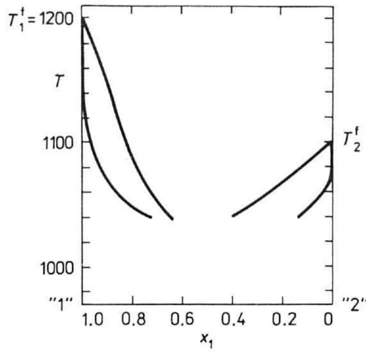

Fig. 7

Fig. 6. Phase diagram of the binary system $NA—NB_2$ of the type U/K having common ion with the following parameters:

$T_1^f = 1200$ K; $T_2^f = 1100$ K; $\Delta H_1^f = 6.2802 \times 10^4$ J mol^{-1}; $\Delta H_2^f = 12.5604 \times 10^4$ J mol^{-1}.

Fig. 7. Phase diagram of the binary system $NA_2—NB_3$ of the type U/K having common ion with the following parameters:

$T_1^f = 1200$ K; $T_2^f = 1100$ K; $\Delta H_1^f = 6.2802 \times 10^4$ J mol^{-1}; $\Delta H_2^f = 12.5604 \times 10^4$ J mol^{-1}.

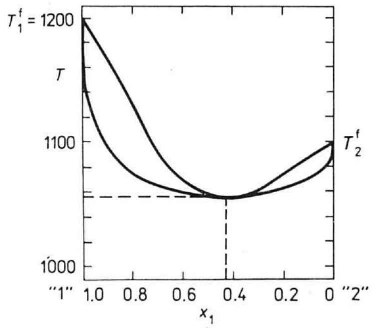

Fig. 8

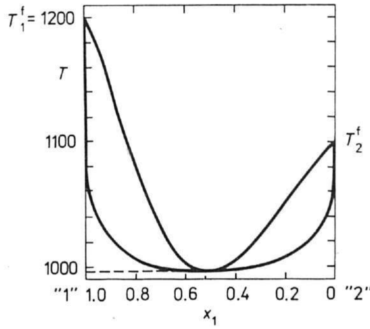

Fig. 9

Fig. 8. Phase diagram of the binary system $NA_2—NB_2$ of the type T/K≡U/K having common ion with the following parameters:

$T_1^f = 1200$ K; $T_2^f = 1100$ K; $\Delta H_1^f = 6.2802 \times 10^4$ J mol^{-1}; $\Delta H_2^f = 12.5604 \times 10^4$ J mol^{-1}; $x_{ex} = 0.427$; $T_{ex} = 1057$ K.

Fig. 9. Phase diagram of the binary system $NA_3—NB_3$ of the type T/K≡U/K having common ion with the following parameters:

$T_1^f = 1200$ K; $T_2^f = 1100$ K; $\Delta H_1^f = 6.2802 \times 10^4$ J mol^{-1}; $\Delta H_2^f = 12.5604 \times 10^4$ J mol^{-1}; $x_{ex} = 0.52$; $T_{ex} = 994$ K.

The systems of the type U/K

The character of universal functional relationship between activity and composition (see [4]) does not need in the analysis to distinguish between systems with and without common ion. However, it is necessary to distinguish between the numbers denoting the amount of new particles brought into solution with a given substance and the values of stoichiometric coefficients. Therefore, the stoichiometric coefficients will be denoted by symbols p^*, q^*, r^*, t^*. The numbers indicating the amount of foreign ions will be denoted according to the following agreement:

p = the amount of foreign cations brought into solution by substance "1".
q = the amount of foreign anions brought into solution by substance "1".
r = the amount of foreign cations brought into solution by substance "2".
t = the amount of foreign anions brought into solution by substance "2".

In the following considerations we shall analyze the solutions of the type

$$M_{p^*}A_{q^*}—N_{r^*}B_{t^*}, \qquad N_{p^*}A_{q^*}—N_{r^*}B_{t^*}$$

In the case of solutions without common ions

$$p = p^* \qquad q = q^* \qquad r = r^* \qquad t = t^*$$

In the case of solutions having common cations

$$p = r = 0 \qquad q = q^* \qquad t = t^*$$

The functional relations between activity and composition can be expressed

$$a_1^l = \varphi_1(x_1^l) = (x_1^l)^{r+t} \qquad a_1^s = \psi_1(x_1^s) = x_1^s$$

$$a_2^l = \varphi_2(x_1^l) = (1 - x_1^l)^{p+q} \qquad a_2^s = \psi_2(x_1^s) = (1 - x_1^s)$$

The other relations (see [1, 2]) are

$$M = \frac{(x_1^l)^{r+t}}{x_1^s} \qquad Q = \frac{(1 - x_1^l)^{p+q}}{1 - x_1^s}$$

$$x_1^s = \Phi(M, x_1^l) = \frac{1}{M}(x_1^l)^{r+t}$$

The characteristic equation

$$Q(x_1^l)^{r+t} + M(1 - x_1^l)^{p+q} - MQ = 0$$

$$\frac{\partial F}{\partial x_1^l} = (r+t)Q(x_1^l)^{r+t-1} - M(p+q)(1 - x_1^l)^{p+q-1}$$

$$\frac{\partial F}{\partial T} = Q\frac{\Delta H_2^f}{RT^2}(x_1^l)^{r+t} + M\frac{\Delta H_1^f}{RT^2}(1 - x_1^l)^{p+q} - MQ\frac{\Delta H_1^f}{RT^2} - MQ\frac{\Delta H_2^f}{RT^2}$$

Calculating the limit values of partial derivative with respect to x_1^l we have to distinguish the case when $r+t-1=0$ (or $p+q-1=0$) from the case when $r+t-1 \neq 0$ (or $p+q-1 \neq 0$).

$p+q>1$:

$$\lim_{T \to T_1^f} dT/dx_1^l = \frac{r+t}{\Delta H_1^f} R(T_1^f)^2$$

$p+q=1$:

Because the parameters p, q, r, t are integers the equality $p+q=1$ can be fulfilled only if one of the parameters equals zero and the other equals unit. It means, however, that substance "1" brings into solution no new cations or anions. Therefore the system in question must have a common ion. Without detriment of generality we shall denote this system as

$$N_{p^*}A_{q^*}—N_{r^*}B_{t^*}$$

If $p=0$, then also $r=0$.

In this case

$$\lim_{T \to T_1^f} dT/dx_1^l = \frac{tQ_0-1}{Q_0 \Delta H_1^f} R(T_1^f)^2$$

$r+t>1$:

$$\lim_{T \to T_2^f} dT/dx_1^l = -\frac{p+q}{\Delta H_2^f} R(T_2^f)^2$$

$r+t=1$:

If $p=0$, then also $r=0$

$$\lim_{T \to T_2^f} dT/dx_1^l = \frac{1-M_{0q}}{M_0 \Delta H_2^f} R(T_2^f)^2$$

In a similar way we can calculate also the limit values of the slopes of tangents to the curves of solidus. The results are presented in Tables 7 and 8.

Let us investigate the existence of a monotonic course of liquidus and solidus curves.

a) For solutions having no common ion it always holds $(p+q>1) \wedge (r+t>1)$. In this case the signs of limit values of the slopes of tangents at the edge points of the interval $\langle 0, 1 \rangle$ are always opposite and, therefore, the monotonic course of the curves of liquidus and solidus cannot exist.

b) For solutions having common ion $p=r=0$. If $q>1$, then

$$\lim_{T \to T_1^f} dT/dx_1^l > 0$$

If the course of liquidus curves is to be monotonic it must be also fulfilled

$$\lim_{T \to T_2^f} dT/dx_1^l > 0$$

However, it is possible only if t = 1 and $1 - M_0 q > 0$. Hence it follows

$$\frac{\Delta H_1^f}{R} \frac{T_2^f - T_1^f}{T_1^f T_2^f} < -\ln q$$

If $T_1^f > T_2^f$

$$\Delta H_1^f > R \frac{T_1^f T_2^f}{T_1^f - T_2^f} \ln q \tag{5}$$

At q > 1 and t = 1 a monotonic course occurs if $T_1^f > T_2^f$ and the unequality (*5*) is fulfilled.

If $T_1^f < T_2^f$

$$\Delta H_1^f < -R \frac{T_1^f T_2^f}{T_2^f - T_1^f} \ln q$$

Because q > 1, ln q > 0 and, therefore, ΔH_1^f should be less than a negative number, which has no physical meaning. A monotonic course cannot therefore exist.

If q = 1, it holds

$$\lim_{T \to T_1^f} dT/dx_1^l = \frac{tQ_0 - 1}{Q_0 \Delta H_1^f} R(T_1^f)^2$$

If also t = 1, then $a_1^l = x_1^l$, $a_2^l = 1 - x_1^l$, *i.e.*, for liquidus and solidus curves the same functional relations are valid. From the principle of monotonousness (see [2]) it follows that the course of curves can be only monotonic.

If t > 1, then $\lim_{T \to T_2^f} dT/dx_1^l < 0$.

If the liquidus curve should be monotonic it must hold

$$tQ_0 - 1 < 0$$

$$\frac{\Delta H_2^f}{R} \frac{T_1^f - T_2^f}{T_1^f T_2^f} < -\ln t \quad .$$

For $T_1^f > T_2^f$

$$\Delta H_2^f < -R \frac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t$$

which is again physically impossible.

For $T_1^f < T_2^f$

$$\Delta H_2^f > R\,\frac{T_1^f T_2^f}{T_2^f - T_1^f}\ln t \tag{6}$$

At $q=1$ and $t>1$, a monotonic course can be expected if $T_1^f < T_2^f$ and the inequality (6) is fulfilled.

Calculation of the parameters of extremum

$$\varphi_2'(x_1^l) = -(p+q)(1-x_1^l)^{p+q-1}$$

$$\psi_2'(x_1^l) = -1$$

$$\frac{\partial \Phi}{\partial x_1^l} = \frac{1}{M}(r+t)(x_1^l)^{r+t-1}$$

$$\left[\frac{\partial \Phi}{\partial x_1^l}\right]_{x_1^l=x} = \frac{x}{x^{r+t}}(r+t)x^{r+t-1} = r+t$$

In the paper [2] the checking identity has been derived

$$\frac{\varphi_2'(x_{ex})}{\psi_2'(x_{ex})}\,\frac{1}{\Phi'(x_{ex})} \equiv \frac{\varphi_2(x_{ex})}{\psi_2(x_{ex})}$$

which in this case acquires the form

$$(p+q)(1-x)^{p+q-1} \equiv (r+t)(1-x)^{p+q-1}$$

Then the left side can be equal to the right side only if

$$p+q = r+t \tag{7}$$

An extremum can occur only if the condition (7) is fulfilled. Besides, the criterion of existence (see [2]) is to be fulfilled as well

$$(x^{r+t-1} < 1) \wedge ((1-x)^{p+q-1} < 1) \tag{8}$$

a) *Solution without common ion*

For this solution it always holds $(r+t-1>0) \wedge (p+q-1>0)$. Therefore, the inequality (8) has solution in the interval $\langle 0, 1 \rangle$. Then the necessary condition for the existence of common extremum on liquidus and solidus curves is the validity of the condition (7). The following systems can be given as an example of solutions of this type: MA_3—N_2B_2, M_2A—NB_2, MA_2—NB_2.

b) *Solution with common ion*

In this case $p=r=0$, and, therefore, in order to fulfil the relation (7)

$$q = t$$

The existence criterion can be written

$$(x^{q-1}<1)\wedge((1-x)^{q-1}<1)$$

If $q=t=1$, then $(x^{q-1}=1)\wedge((1-x)^{q-1}=1)$ and, therefore, the extremum cannot exist. In this case the solution is classically ideal and the curves have monotonic course.

The extremum occurs only if $q=t$ and simultaneously $q>1$. Then the universal functional relationship is identical with Temkin's one.

It should be stressed that the characteristic equation for solutions without common ion is identical with the characteristic equation of solutions having common ion if

$$q_1=p+q \qquad t_1=r+t$$

Universal functional relationship attributes to the solutions without common ion of the type M_pA_q—N_rB_t the same course of liquidus and solidus curves as to the solutions with common ion of the type $N_{p_1}A_{(p+q)}$—$N_{r_1}B_{(r+t)}$.

Physically interpretated can be only the case

$$p+q=r+t \quad \textit{i.e.} \quad q_1=t_1$$

In this case the universal relationship is identical with Temkin's one. *E.g.* for the solutions MA_3—NB_3, MA_3—N_3B, MA_3—N_2B_2, M_2A_2—N_2B_2 we found the same course of curves as for the solution $N_{p_1}A_4$—$N_{r_1}B_4$. Simultaneously

$$a_1^{\rm l}=(x_1^{\rm l})^4 \qquad a_2^{\rm l}=(1-x_1^{\rm l})^4$$

Conclusion

a) The analysis shows that solutions having no common ion cannot have a monotonic course of curves. Throughout the interval $\langle 0, 1\rangle$ it can be described by the universal functional relationship only if $p+q=r+t$. If this condition is not fulfilled, the equation $F(x, T)=0$ does not determine the implicit function $T=f(x)$ in each point of the interval $\langle 0, 1\rangle$.

b) Solutions having common ion show extremum if $(q=t)\wedge(q>1)\wedge(t>1)$. In this case the universal and Temkin's relations are identical.

If $(q\neq t)\wedge(q>1)\wedge(t>1)$, a monotonic course cannot exist as a consequence of opposite signs of limit values of the slopes of tangents at the edge points of the interval $\langle 0, 1\rangle$. In this case, however, there is also no extremum. It means that the characteristic equation does not determine the implicit function $T=f(x)$ in the whole interval. A disjunction appears at the point where the extremum should occur. At this point the function is not defined because the condition $q=t$ is not fulfilled. This condition would ensure that the point in which the derivative

$\partial F/\partial x=0$ lies on the curve of liquidus which is described implicitly by the equation $F(x, T)=0$ (see Fig. 7).

If $(q \neq t) \wedge (q=1 \vee t=1)$ and simultaneously the enthalpies of fusion ΔH_1^f, or ΔH_2^f do not obey the conditions (*5*) and (*6*) for monotonic course the function $F(x, T)=0$ does not determine the implicit function $T=f(x)$ in the whole interval $\langle 0, 1 \rangle$. Consequently for $T<\mathrm{Min}(T_1^f, T_2^f)$ the curve of liquidus should decrease towards minimum, however, the equation $F(x, T)=0$ has no solution in the interval $\langle 0, 1 \rangle$. The curve of solidus goes in this case even over the curve of liquidus (see Fig. 6).

The condition for extremum in the case of solutions of the type U/K can be stated also in the following way:

The solutions of the type U/K can show common extremum on liquidus and solidus curves only if their characteristic equation is identical with the characteristic equation of the adequate type T/K. Therefore, the equation of extremum for the type U/K has not been specially constructed because (in this case) it is identical with the equation of extremum for corresponding Temkin's functional relation.

Symbols

T/K	in liquid phase Temkin's functional relationship between activity and composition and in solid phase classic ideal behaviour ($a_i^s=x_i^s$) are assumed to be valid
K/T	in liquid phase classic ideal behaviour and in solid phase Temkin's functional relationship are assumed
T/T	in both liquid and solid phases Temkin's functional relationship is assumed to be valid
U/K	in liquid phase universal functional relationship and in solid phase classic ideal behaviour are assumed
K/U	in liquid phase classic ideal behaviour and in solid phase universal functional relationship are assumed
U/U	in both liquid and solid phases universal functional relationship is assumed to be valid
p, q, r, t	stoichiometric coefficients
a_i	activity of the i-th component
a_i^l, a_i^s	activity of the i-th component in liquid or in solid state
ΔH_i^f	change in molar enthalpy of pure i-th component at the temperature of fusion T_i^f at transition from solid to liquid phase
M_0	$\exp[(\Delta H_1^f/R)(1/T_1^f - 1/T_2^f)]$
Q_0	$\exp[(\Delta H_2^f/R)(1/T_2^f - 1/T_1^f)]$
R	gas constant
T	thermodynamic temperature, K
T_i^f	temperature of fusion of the i-th component
x_i^l, x_i^s	mole fraction of the i-th component in liquid or in solid state

l_i, s_i	corresponding liquidus and solidus curves
$Te(x_i)$	Temkin's relationship
$U(x_i)$	universal relationship

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