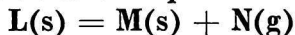


# The Effect of Admixtures in Solid Phases and of Geometrical Properties of Particles on Equilibrium of the Reaction



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Received February 14, 1969

When in the three-component equilibrium system  $M-M'-N$ , formed on thermal decomposition of solid solution  $L-L'$  according to the discussed equation, perfect solid solutions  $M-M'$  and  $L-L'$  coexist with pure ideal gas  $N$ , then the mole fractions of  $L'$  and  $M'$  can be calculated from equations similar to those of van Laar describing *e.g.* equilibrium between liquid and solid perfect solutions in binary systems.

The effect of dimensions of coexisting crystalline phases  $L$  and  $M$  on the equilibrium of the reaction  $L(s) = M(s) + N(g)$  can be expressed by the approximative equation

$$\ln \frac{f_{N;e}}{f_{N;e}^*} \doteq \frac{1}{RT} \left( V_L \cdot \frac{2\Phi_L}{h_L} - V_M \cdot \frac{2\Phi_M}{h_M} \right).$$

$f_{N;e}$  — equilibrium fugacity of  $N$  in the system under investigation

$f_{N;e}^*$  — equilibrium fugacity of  $N$  in a system in which the influence of surface area on reaction equilibrium can be neglected

$V_i$  — molar volume of the  $i$ -th substance

$\Phi_i$  — mean specific free surface enthalpy or „surface tension“ formally defined by Gibbs equation of the  $i$ -th substance

$h_i$  — perpendicular distance of the surface area from the origin of the Wulff's coordinate system in the  $i$ -th crystalline phase.

The unsatisfactory reproducibility of measurement of equilibrium temperature ( $t_e$ ) and of gas pressure  $N$  ( $p_{N;e}$ ) in systems formed by thermal decomposition



performed by different methods of measurement may be caused, apart from other circumstances, by the presence of impurities which occur in the form of solid solutions in both phases, and by different geometrical properties of the two solid phases. In the present paper the influence of these two factors on the equilibrium of the reaction (A) is discussed in details.

*The effect of impurities forming solid solutions in the two solid phases on the values  $t_e$  and  $p_{N;e}$*

In the subsequent considerations we assume that the substance  $L$  forms a solid solution with the „impurity“  $L'$ , which dissociates upon heating, similarly as the substance  $L$ , according to the equation

$$L'(s) = M'(s) + N(g) \quad (B)$$

and the substances  $M'$  and  $M$  form a solid solution too. The error of measurement of  $t_e$  and  $p_{N;e}$  (related to the two-component system  $M-N$ ), caused by the presence of solid solutions in both solid phases can be estimated on the basis of the study of equilibrium in the three-component system  $M-M'-N$ .

In Fig. 1 and 2 two extreme cases of equilibria in three-component system  $M-M'-N$  at an arbitrary constant pressure and at different temperatures of isothermal plane sections through the isobaric prism are shown. Phases constituted chiefly by the substances  $L$  and  $L'$  are designated by „ $\alpha$ “ and those constituted chiefly by the substances  $M$  and  $M'$  are designated by „ $\beta$ “.

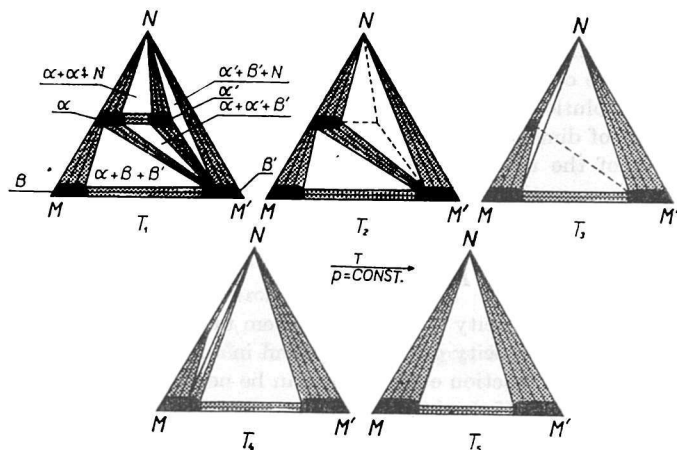


Fig. 1. Isothermic sections of the phase diagram of the system  $M-M'-N$ . The substances  $L$  and  $L'$  ( $M$  and  $M'$ ) are partly miscible in the phase  $\alpha$  ( $\beta$ ); the substances  $L$  and  $L'$  ( $M$  and  $M'$ ) are partly soluble in the phase  $\beta$  ( $\alpha$ ).

In Fig. 1 five isothermal sections of the isobaric prism of the system are shown in which the substances  $L$  and  $L'$  ( $M$  and  $M'$ ) possess a limited miscibility in the phase  $\alpha$  ( $\beta$ ); the substances  $L$  and  $L'$  ( $M$  and  $M'$ ) are partly soluble in the phase  $\beta$  ( $\alpha$ ).

In Fig. 2 three equilibria states of the system are shown, wherein the substances  $L$  and  $L'$  in the phase  $\alpha$  and the substances  $M$  and  $M'$  in the phase  $\beta$  are perfectly miscible; substances  $L$  and  $L'$  ( $M$  and  $M'$ ) are insoluble in the phase  $\beta$  ( $\alpha$ ).

In both cases only the presence of the substance  $N$  is assumed in the gaseous phase.

If under the conditions of the experiment the gaseous substance  $N$  can be considered to be an ideal gas and if the change of chemical potentials of pure solids occurring upon the change of pressure can be neglected, then the equilibria states of the system  $M-M'-N$  can be, in the presence of the gaseous phase at the given temperature and at the chosen constant pressure  $p_{N;e}$ , quantitatively expressed by the equations ( $L$  ( $L'$ ) and  $M$  ( $M'$ ) do not form a solid solution):

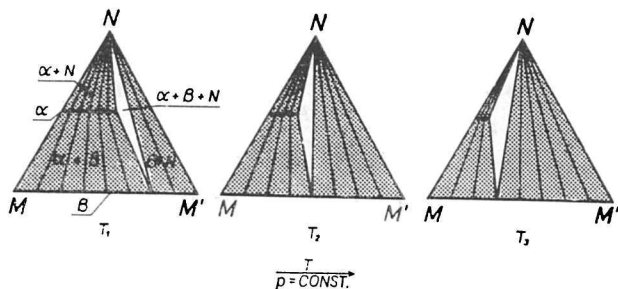


Fig. 2. Isothermic sections of the phase diagram of the system M—M'—N. The substances L and L' (M and M') are perfectly miscible in the phase  $\alpha$  ( $\beta$ ); substances L and L' (M and M') are insoluble in the phase  $\beta$  ( $\alpha$ ).

$$\ln p_{N;e} = - \frac{(\Delta G_A^0)_{p=760 \text{ torr}}}{RT} + \ln \frac{a_{L;e}}{a_{M;e}} = \ln p_{N;A;e} + \ln \frac{a_{L;e}}{a_{M;e}} \quad (1)$$

and

$$\ln p_{N;e} = - \frac{(\Delta G_B^0)_{p=760 \text{ torr}}}{RT} + \ln \frac{a_{L';e}}{a_{M';e}} = \ln p_{N;B;e} + \ln \frac{a_{L';e}}{a_{M';e}} \quad (2)$$

The indexes *A* and *B* designate magnitudes related to the respective reaction or the system which arise in this reaction; the state of pure substances at the pressure of 1 atm is considered to be standard. Rearranging the above equations we may write:

$$\frac{p_{N;e}}{p_{N;A;e}} = \frac{a_{L;e}}{a_{M;e}} \quad (3)$$

and

$$\frac{p_{N;e}}{p_{N;B;e}} = \frac{a_{L';e}}{a_{M';e}} \quad (4)$$

When the equilibrium activities  $a_{L;e}$  and  $a_{M;e}$  are known, it is possible to calculate from the equation (1) and (3), respectively, the error of determination of the value  $p_{N;A;e}$ .

The most simple is the numerical description of the equilibrium of the system in which phase  $\alpha$  ( $\beta$ ), is formed by perfect solutions of the substances L and L' (M and M') only. In this special case it is possible to insert into the equation (3) and (4) the relations:

$$\begin{aligned} a_{i;e} &= x_{i;e}, \\ x_{L;e} + x_{L';e} &= 1, \\ x_{M;e} + x_{M';e} &= 1 \end{aligned}$$

and from the equations thus obtained it is possible to express equilibrium molar fractions  $x_{i;e}$  of all solids as functions of  $p_{N;e}$  in the systems M—M'—N, M—N and M'—N:

$$x_{L;e} = \frac{p_{N;e} - p_{N;B;e}}{p_{N;A;e} - p_{N;B;e}}; \quad (5a)$$

$$x_{L';e} = \frac{p_{N;e} - p_{N;A;e}}{p_{N;B;e} - p_{N;A;e}}; \quad (5b)$$

$$x_{M;e} = \frac{p_{N;A;e}(p_{N;e} - p_{N;B;e})}{p_{N;e}(p_{N;A;e} - p_{N;B;e})}; \quad (5c)$$

$$x_{M';e} = \frac{p_{N;B;e}(p_{N;e} - p_{N;A;e})}{p_{N;e}(p_{N;B;e} - p_{N;A;e})}. \quad (5d)$$

Hence, at constant temperature the expression  $p_{N;e}$  is, in the given case, linear function of  $x_{L;e}$  and  $x_{L';e}$ , respectively.

The equations (5a)–(5d) can be rewritten as isobaric dependences of  $x_{i;e}$  on  $T_e$ . Thus, when the standard reaction enthalpy  $\Delta H_A^0$  and  $\Delta H_B^0$  does not change with temperature, the following relations are valid for the two-component systems M–N and M'–N':

$$\ln p_{N;A;e} = \ln p_{N;e} - \frac{\Delta H_A^0}{R} \left( \frac{1}{T_e} - \frac{1}{T_{A;p_{N;e}}} \right) = \ln p_{N;e} - \lambda_A$$

and

$$\ln p_{N;B;e} = \ln p_{N;e} - \frac{\Delta H_B^0}{R} \left( \frac{1}{T_e} - \frac{1}{T_{B;p_{N;e}}} \right) = \ln p_{N;e} + \lambda_B,$$

resp.

$$p_{N;A;e} = p_{N;e} \cdot e^{-\lambda_A}$$

and

$$p_{N;B;e} = p_{N;e} \cdot e^{+\lambda_B}.$$

$T_{i;p_{N;e}}$  are temperatures at which the gas pressure N in the equilibrium system, formed by the  $i$ -th reaction, reaches the chosen value  $p_{N;e}$ . Inserting into the equations (5b) and (5d) we get the isobaric relations:

$$x_{L';e} = \frac{e^{\lambda_A} - 1}{e^{\lambda_A + \lambda_B} - 1} \quad (5e)$$

and

$$x_{M';e} = \frac{e^{\lambda_A} - 1}{e^{\lambda_A} - e^{-\lambda_B}}, \quad (5f)$$

which agree with the van Laar equations [1], describing *e.g.* equilibrium between perfect liquid and solid solutions in binary systems.

From the isothermal relations (5a ÷ d) or from the isobaric dependences of  $x_{i;e}$  on  $T_e$  it is possible to estimate, on the basis of the properties of the systems M–N and M'–N, the extent of the error of determination of  $p_{N;A;e}$ , and  $T_{A;p_{N;e}}$ , respectively.

According to the properties of the substances L and L' it is possible to classify the investigated systems into two groups:

1. When in the system M—M'—N at the given temperature the inequalities are valid:

$$p_{N;e} \gg p_{N;B;e}$$

and

$$p_{N;A;e} \gg p_{N;B;e}$$

then ( $\delta a \div d$ ) will be transformed to approximative equations:

$$x_{L;e} \doteq \frac{p_{N;e}}{p_{N;A;e}}; \quad (6a)$$

$$x_{L';e} \doteq \frac{p_{N;A;e} - p_{N;e}}{p_{N;A;e}} = \frac{\varepsilon_p}{p_{N;A;e}}; \quad (6b)$$

$$x_{M;e} \doteq 1; \quad (6c)$$

$$x_{M';e} \doteq 0. \quad (6d)$$

2. When in the system M—M'—N at the given temperature the inequalities are valid

$$p_{N;B;e} \gg p_{N;e},$$

$$p_{N;B;e} \gg p_{N;A;e}$$

then the equations ( $\delta a \div d$ ) will be transformed to approximative relations:

$$x_{L;e} \doteq 1; \quad (7a)$$

$$x_{L';e} \doteq 0; \quad (7b)$$

$$x_{M;e} \doteq \frac{p_{N;A;e}}{p_{N;e}}; \quad (7c)$$

$$x_{M';e} \doteq \frac{p_{N;e} - p_{N;A;e}}{p_{N;e}} = \frac{-\varepsilon_p}{p_{N;e}}. \quad (7d)$$

$\varepsilon_p$  is the error of determination of  $p_{N;A;e}$  at the chosen temperature.

To exemplify the above said, with the aid of equations (5b) and (6b), taking for  $t_e = 882^\circ\text{C}$ , or with the aid of graphical functions (5e) and (5f) constructed for the constant pressure 760 torr, the values  $\varepsilon_p$  ( $\varepsilon_t$ ) for  $x_{L'} = 0.01$  mole % were determined in the systems CaO—SrO—CO<sub>2</sub> (Fig. 3) and CaO—MnO—CO<sub>2</sub> in which in the first approximation the formation of perfect solid solutions in the carbonate and oxide phase and an ideal behaviour of the gaseous phase (CO<sub>2</sub>) were assumed:

$$\varepsilon_{p;SrCO_3} \doteq 0.08 \text{ torr}; \quad \varepsilon_{p;MnCO_3} \doteq - 730 \text{ torr},$$

resp.

$$\varepsilon_{t;SrCO_3} \doteq - 0.03^\circ\text{C}; \quad \varepsilon_{t;MnCO_3} \doteq 54^\circ\text{C}.$$

For the calculation of  $p_{CO_2;i;e}$  extrapolated relations reported by [2, 3] or relations calculated on the basis of data reported by [4, 5] were taken.

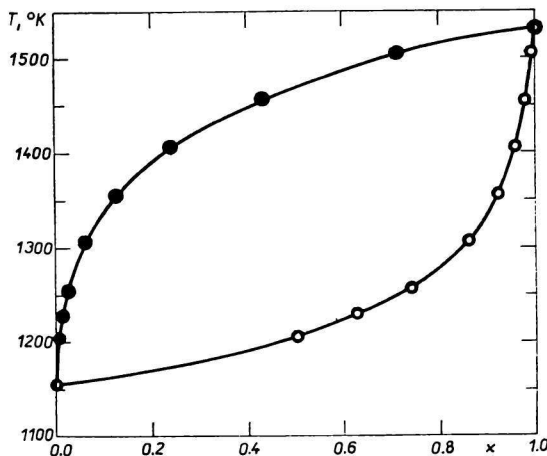


Fig. 3. Temperature dependences of the equilibrium mole fraction ( $x$ )  $\text{SrCO}_3$  in the carbonate phase ( $\circ$ ) and  $\text{SrO}$  in the oxide phase ( $\bullet$ ) in the system in which perfect solid solutions  $(\text{Ca},\text{Sr})\text{CO}_3$  and  $(\text{Ca},\text{Sr})\text{O}$  coexist with  $\text{CO}_2$  ( $p_{\text{CO}_2} = 760$  torr) which behaves as an ideal gas.

From Fig. 3 it can be seen that the absolute value of the actual error of determination of  $t_{A;e}$  ( $|\varepsilon_i|$ ) depends, at the chosen gas pressure  $N$  in the system  $M-N$ , on the amount and kind of the „impurity“  $L'$  in the phase „ $\alpha$ “. The content of  $L'$  in „ $\alpha$ “ being identical,  $\varepsilon_i$  is great (small) if  $p_{N;B;e} \gg p_{N;e}$  ( $p_{N;B;e} \ll p_{N;e}$ ).

If the value of  $p_{N;A;e}$  is known and when the above inequalities are valid it is possible, on the basis of the measured value of  $p_{N;e}$ , to use the relations (6) and (7) for the approximative calculation of  $x_{i;e}$ .

*The influence of geometrical properties of particles of both crystalline phases on the values of  $t_e$  and  $p_{N;e}$  in two-component system formed by the reaction (A)*

Reaction equilibrium of closed system which comprises also crystalline substances is affected by some properties of these substances. Basically, the following types of these equilibria can be discerned:

1. The increase of free enthalpy of crystalline phases, wherein only the isotropic pressure of the surrounding gaseous phase acts [ $p_v = p_g$  (pressure in the vapour phase)  $\doteq p_N$ ] and in which the difference between the values of chemical potential  $\mu$  of elementary particles on the surface and in the bulk of these phases does not decrease is, at constant temperature and at constant pressure, defined in most cases by the relation

$$\begin{aligned}
 dg = & \sum_{X,v} \sum \mu_{X;v;1} dn_{X;v} + \sum_{X,v} \sum_{s,i} \sum \sum (\mu_{X;v;s;i} - \mu_{X;v;1}) dn_{X;v;s;i} + \\
 & + \sum_{X,v} \sum_{d} \sum (\mu_{X;v;d} - \mu_{X;v;1}) dn_{X;v;d},
 \end{aligned} \quad (8)$$

in which

$$dn_{X;v} = dn_{X;v;1} + \sum_{s,i} dn_{X;v;s;i} + \sum_{d} dn_{X;v;d},$$

where:

X — kind of elementary particles forming crystalline phases

v — kind of crystalline phase

l — position of elementary particles in the defectless lattice

s — the part of surface in which the elementary particles are placed

i — certain area of the s-th part of surface (e.g. dislocation)

d — kind of lattice defects inside the crystalline phase (e.g. vacancy).

The equation for the equilibrium condition of the reaction (A) will be simplified when the following conditions are satisfied:

a) The number of all defects inside the solid phases does not change in the course of the equilibrium reaction or an equilibrium between these defects and their surroundings is maintained.

b) Number of corners on the crystalline particles is constant in the course of the equilibrium reaction.

c) No adsorption of the gas N on the surface of solid phases takes place in the course of the equilibrium reaction.

d) Substances L and M do not form solid solutions.

e) Only surface areas of the crystalline phases take part in the equilibrium reaction.

In this case substituting in (8)

$$\sum_X \sum_i (\mu_{X;v;s_1;i} - \mu_{X;v;l}) dn_{X;v;s_1;i} = \bar{\varphi}_{v;s_1} \cdot do_{v;s_1}$$

and

$$\sum_X \sum_i (\mu_{X;v;s_2;i} - \mu_{X;v;l}) dn_{X;v;s_2;i} = \bar{\varphi}_{v;s_2} \cdot do_{v;s_2}$$

we can express the equilibrium of the reaction (A) at the given temperature and at the pertinent gas pressure N with the aid of the equation

$$dG_A = \mu_{L;l} \cdot dn_L + \mu_{M;l} \cdot dn_M + \mu_N \cdot dn_N + \sum_v \sum_{s_1} \bar{\varphi}_{v;s_1} \cdot do_{v;s_1} + \sum_v \sum_{s_2} \bar{\varphi}_{v;s_2} \cdot do_{v;s_2} = 0. \quad (10)$$

*Definition of symbols used:* Index  $s_1$  and  $s_2$ , designate areas and their intersections on the surface of the crystalline phases, respectively. The magnitude of these surfaces and of their intersections is designated by the symbol  $o$ .

$\bar{\varphi}_{v;s_1}$  and  $\bar{\varphi}_{v;s_2}$  are mean specific surface free enthalpies of surface areas and of their intersections, respectively.

From the equation (A) it follows:

$$-dn_L = dn_M = dn_N = dn. \quad (11)$$

Further the following relations are valid:

$$dn = -\frac{dv_L}{V_{L;s}} = \frac{dv_M}{V_{M;s}} \quad (12)$$

and

$$\mu_N = \mu_N^0 + RT \ln f_N. \quad (13)$$

$V_{L;s}$  and  $V_{M;s}$  are molar volumes of the substance L and M in the surface area of their crystalline phases and  $f_N$  is fugacity of the gaseous substance N.

Inserting from the equations (11), (12) and (13) into (10), dividing this equation by  $(-dn)$  and rearranging we get:

$$\ln f_{N:e} = \frac{1}{RT} \left[ \mu_{L;1} - \mu_{M;1} - \mu_N^0 + \frac{V_{L;s}}{dv_L} \left( \sum_{s_1} \bar{\varphi}_{L;s_1} \cdot do_{L;s_1} + \sum_{s_2} \bar{\varphi}_{L;s_2} \cdot do_{L;s_2} \right) - \frac{V_{M;s}}{dv_M} \left( \sum_{s_1} \bar{\varphi}_{M;s_1} \cdot do_{M;s_1} + \sum_{s_2} \bar{\varphi}_{M;s_2} \cdot do_{M;s_2} \right) \right] \quad (14)$$

The value of the equilibrium fugacity of the gaseous substance N in the system arising by the reaction (A), in which the influence of the surface of the crystalline phases (designation\*) on the reaction equilibrium may be neglected, is given by the relation:

$$\ln f^* = \frac{1}{RT} (\mu_{L;1}^* - \mu_{M;1}^* - \mu_N^0), \quad (15)$$

where, putting  $p_g \doteq p_{N:e}$  and  $p_g^* \doteq p_{N:e}^*$ :

$$\mu_{v;1}^* \doteq \mu_{v;1} - V_{v;1} (p_{N:e} - p_{N:e}^*). \quad (16)$$

Subtracting (15) from (14) and substituting from (16) we get:

$$\ln \frac{f_{N:e}}{f_{N:e}^*} \doteq \frac{1}{RT} \left[ (V_{L;1} - V_{M;1}) (p_{N:e} - p_{N:e}^*) + \frac{V_{L;s}}{dv_L} \left( \sum_{s_1} \bar{\varphi}_{L;s_1} \cdot do_{L;s_1} + \sum_{s_2} \bar{\varphi}_{L;s_2} \cdot do_{L;s_2} \right) - \frac{V_{M;s}}{dv_M} \left( \sum_{s_1} \bar{\varphi}_{M;s_1} \cdot do_{M;s_1} + \sum_{s_2} \bar{\varphi}_{M;s_2} \cdot do_{M;s_2} \right) \right] \quad (17)$$

In the systems, in which the influence of the intersection of surface areas on the equilibrium of the reaction (A) could be neglected, the surfaces of the individual phases L and M are in the thermodynamical equilibrium if the Wullf's condition is satisfied [6]:

$$\frac{\bar{\varphi}_{v;s_1}}{h_{v;s_1}} = \text{const.}, \quad (18)$$

in which  $h_{v;s_1}$  is the perpendicular distance of the area  $s_1$  from the origin of the Wullf's coordinate system in the crystalline phases  $v$ .

The following calculations assume such an arrangement of equilibrium system which allows application of differential calculus for calculation of equilibrium. In this case the following is valid [7]:

$$do_{v;s_1} = \frac{2dv_{v;s_1}}{h_{v;s_1}}. \quad (19)$$



In the above equations it may be substituted for

$$dv_v = \sum_{s_1} dv_{v;s_1}. \quad (19a)$$

Substituting from (18), (19), (19a) into (17) and rearranging we get ( $\sum_{s_2} \bar{\varphi}_{v;s_2} \cdot d\sigma_{v;s_2} \doteq 0$ ):

$$\ln \frac{f_{N;e}}{f_{N^*;e}} \doteq \frac{1}{RT} \left[ (V_{L;1} - V_{M;1}) (p_{N;e} - p_{N^*;e}) + V_{L;s} \frac{2\bar{\varphi}_{L;s_1}}{h_{L;s_1}} - V_{M;s} \frac{2\bar{\varphi}_{M;s_1}}{h_{M;s_1}} \right]. \quad (20)$$

If the first member in the square brackets on the right hand side of (20) has a low value, then instead of the above equation the following approximative relation may be written:

$$\ln \frac{f_{N;e}}{f_{N^*;e}} \doteq \frac{1}{RT} \left( V_{L;s} \frac{2\bar{\varphi}_{L;s_1}}{h_{L;s_1}} - V_{M;s} \frac{2\bar{\varphi}_{M;s_1}}{h_{M;s_1}} \right). \quad (21)$$

2. Inside the crystalline phases of the substances L and M the isotropic pressure acts when the difference ( $\mu_{v;s} - \mu_{v;1}$ ) is zero, *e.g.*, as consequence of the diffusion of vacancies to the surface of these phases taking place simultaneously with the reaction (A). If the influence of the intersections of surface areas on the equilibrium of the reaction (A) can be neglected, then, according to [8] (p. 302), the magnitude of this pressure in equilibrium is given by the relation ( $p_g \doteq p_N$ ):

$$p_v \doteq p_N + \frac{2\sigma_{v;s_1}}{h_{v;s_1}}. \quad (22)$$

$h_{v;s_1}$  has the same meaning as in paragraph 1 and  $\sigma_{v;s_1}$  is the „surface tension“, defined by the Gibbs equation, of the  $s_1$ -area on the surface of the  $v$ -th crystalline phase. For sufficiently large crystals or for grains of the substances L and M wherein the influence of surface on properties is negligible, the equation (22) is transformed into the approximative relation

$$p_v^* \doteq p_N^* \quad (23)$$

as in the paragraph 1. To (16) the following equation corresponds:

$$\mu_v^* \doteq \mu_v - V_v \left( p_{N;e} - p_{N^*;e} + \frac{2\sigma_{v;s_1}}{h_{v;s_1}} \right). \quad (24)$$

By a procedure similar to that of the paragraph 1, we get the following expression

$$\ln \frac{f_{N;e}}{f_{N^*;e}} \doteq \frac{1}{RT} \left[ (V_L - V_M) (p_{N;e} - p_{N^*;e}) + \frac{2}{h_{L;s_1}} V_L \cdot \sigma_{L;s_1} - \frac{2}{h_{M;s_1}} V_M \cdot \sigma_{M;s_1} \right]. \quad (25)$$

When the first member in the square brackets can be neglected, the expression (25) attains a form similar to the equation (21):

$$\ln \frac{f_{N:e}}{f_{N:e}^*} \doteq \frac{1}{RT} \left( V_L \frac{2\sigma_{L:s_1}}{h_{L:s_1}} - V_M \frac{2\sigma_{M:s_1}}{h_{M:s_1}} \right). \quad (26)$$

3. When the substances L and M are in the state of anisotropic tension, then  $\mu_{v;s}$  and  $\mu_{v;l}$ , cannot be defined unequivocally [8] (p. 290) and consequently the values  $f_{N:e}$  and  $f_{N:e}^*$ , in this system cannot be determined with the aid of these magnitudes. In the equilibrium state, however, the crystalline phases of the substances L and M are in equilibrium with the gas phase. A closed system originating by the reaction (A) is then in equilibrium when the following relation is valid:

$$\Delta G_A = \mu_{M(g)} + \mu_{N(g)} - \mu_{L(g)} = 0. \quad (27)$$

$\mu_{L(g)}$  and  $\mu_{M(g)}$ , respectively, are chemical potentials of saturated vapours of substances L and M in the gas phase of the given system at the given temperature.

When the influence of the intersection of surface areas on the equilibrium of the reaction (A) can be neglected, then, according to [8] (p. 300); the values  $\mu_{L(g)}$  and  $\mu_{M(g)}$  are determined by the equations:

$$\mu_{L(g)} \doteq \mu_{L(g)}^* + V_L \frac{2\sigma_{L:s_1}}{h_{L:s_1}} + V_L (p_g - p_g^*)$$

or

$$\mu_{M(g)} \doteq \mu_{M(g)}^* + V_M \frac{2\sigma_{M:s_1}}{h_{M:s_1}} + V_M (p_g - p_g^*).$$

Substituting these equations into (27) and neglecting the last members of their right hand sides we get (26).

The equation (26) holds even when gas is adsorbed on the surface of the crystalline phase and when solid solutions of the substances L and M are formed.

In any of the three above equilibrium states the arrangement of the system created on the reaction (A) usually approaches one, or simultaneously several of the four models:

1. If the important dimension of the coexisting crystalline phases of the substances L and M are sufficiently large, then the values of the right hand sides of the equations (17), (20), (21) and (26) decrease to such an extent that the influence of the surface on the equilibrium magnitudes is overlapped by errors which occurred in the course of measurement of these magnitudes. After rearranging the above equations attain the form

$$f_{N:e} \doteq f_{N:e}^*. \quad (28)$$

2. The equation (28) is also satisfied when the right hand sides of the equations (17), (20), (21) and (26) equal zero. Thus, *e.g.*, when

$$\bar{\varphi}_{v;s_1} = \bar{\varphi}_{v;l} = \text{const.}$$

and

$$\bar{\varphi}_{v;s_2} = \bar{\varphi}_{v;2} = \text{const.} \quad (29)$$

we get — neglecting the influence of the dependence  $\mu_v$  on the pressure of the phase — from the equation (17):

$$V_{L;s} \left( \bar{\varphi}_{L;1} \frac{d\sigma_{L;1}}{dv_{L;1}} + \bar{\varphi}_{L;2} \frac{d\sigma_{L;2}}{dv_{L;2}} \right) = V_{M;s} \left( \bar{\varphi}_{M;1} \frac{d\sigma_{M;1}}{dv_{M;1}} + \bar{\varphi}_{M;2} \frac{d\sigma_{M;2}}{dv_{M;2}} \right). \quad (30)$$

$d\sigma_{v;1}$  and  $d\sigma_{v;2}$  is the sum of the increase of the surface area and of their intersections, respectively. When the influence of the intersections of the surface areas can be neglected, then the equation (30) will be of the form:

$$V_{L;s} \cdot \bar{\varphi}_{L;1} \frac{d\sigma_{L;1}}{dv_{L;1}} \doteq V_{M;s} \cdot \bar{\varphi}_{M;1} \frac{d\sigma_{M;1}}{dv_{M;1}}. \quad (31)$$

From the equations (30) and (31) the value of the ratio ( $\kappa$ ) of the important dimensions of the coexisting crystals or grains of the substances L and M in the equilibrium system, in which  $f_{N;e}$  equals  $f_{N;e}^*$  can be calculated.

Similarly for

$$\kappa_h = \frac{h_{L;s_1}}{h_{M;s_1}}$$

we get from the equation (21):

$$\kappa_h \doteq \frac{V_{L;s} \cdot \bar{\varphi}_{L;s_1}}{V_{M;s} \cdot \bar{\varphi}_{M;s_1}}. \quad (32)$$

Similar relation can be deduced from equation (26).

The values  $\Delta H_A$  and  $\Delta H_A^*$  may differ even in the case when the dimensions of the crystals L and M satisfy the equations (30), (31) and (32) [8] (p. 235).

When we assume, *e.g.* in the equilibrium system formed upon the thermic dissociation of calcite, the coexistence of cleavable rhombohedrons of  $\text{CaCO}_3$  ( $\alpha = 101^\circ 56'$ ,  $\bar{\varphi}_{\text{CaCO}_3;\{10\bar{1}\}} = 78 \text{ erg cm}^{-2}$  [9] and of cubes of CaO ( $\bar{\varphi}_{\text{CaO};\{100\}} = 820 \text{ erg cm}^{-2}$  [10]), we get, neglecting the influence of the crystal dimensions on the values  $\bar{\varphi}_{v;1}$ , on inserting the pertinent values into (31) ( $V_{v;s} \doteq V_{v;1} \doteq V_v$ ):

$$\kappa_{(31)} = \frac{b_{\text{CaCO}_3}}{b_{\text{CaO}}} \doteq \frac{V_{\text{CaCO}_3} \cdot \bar{\varphi}_{\text{CaCO}_3;\{10\bar{1}\}}}{V_{\text{CaO}} \cdot \bar{\varphi}_{\text{CaO};\{100\}}} \cdot \frac{\sin \alpha}{\sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}} \doteq 0.22.$$

$b_v$  is the length of the edge of the rhombohedron of  $\text{CaCO}_3$  or of the cube of CaO. With regard to relatively serious error in determination of the values  $\bar{\varphi}_{v;1}$  as reported yet [11], only the approximative value of  $\kappa$  can be calculated from this expression. For the same reason the difference between  $V_{v;s}$  and  $V_{v;1}$  was also neglected [12].  $\kappa$  can be calculated by the above method only when the crystals  $\text{CaCO}_3$  and CaO, though changing their volume, keep their shape.

3. When in the equilibrium system formed by the reaction (A) small crystals (grains) of one substance coexist with very large crystals (grains) of the second

substance, then it is possible to neglect the pertinent member of the binomial in the right hand side brackets of the approximations (21) and (26). From (21) we get

$$\ln \frac{f_{N;e}}{f_{N^*;e}} \doteq \pm \frac{2V_{v;s} \cdot \bar{\varphi}_{v;s_1}}{RT \cdot h_{v;s_1}} \quad (33)$$

Signs + (−) are related to the substance L (M).

In this case we get similar relation also from equation (26).

Examples of calculated values  $f_{N;e}/f_{N^*;e}$  ( $\doteq p_{N;e}/p_{N^*;e}$ ) for systems formed by the reaction  $\text{MeCO}_3 = \text{MeO} + \text{CO}_2$  at temperature at which  $p_{N^*;e} \doteq 760$  torr ( $V_{v;s} \doteq V_{v;l}$ ) are listed in Table 1.

Table 1

Values of  $p_{N;e}/p_{N^*;e}$  for systems arising by the reaction  $\text{MeCO}_3 = \text{MeO} + \text{CO}_2$  at a temperature where at  $p_{N^*;e} \doteq 760$  torr

| M   | $\bar{\varphi}_{M;\{100\}}$<br>[erg cm <sup>-2</sup> ] | T [°K]   | $p_{N;e}/p_{N^*;e}$ for $2h_{M;\{100\}}$ [cm] |                    |
|-----|--|----------|---|--------------------|
|     |  |          | $1 \times 10^{-5}$                            | $5 \times 10^{-7}$ |
| MgO | 1200 [13]  | 596 [14] | 0.90  | 0.11               |
| CaO | 820 [10]   | 1155 [3] | 0.95  | 0.32               |

As to the accuracy of the calculated values of  $f_{N;e}/f_{N^*;e}$ , the same applies here what has been said on the calculation of  $\alpha$  in the previous paragraph.

4. In systems under consideration at sufficiently high temperatures, simultaneously with the reaction (A) or immediately after, sintering and grain growth of substances L and M can take place. When these two processes are considerably

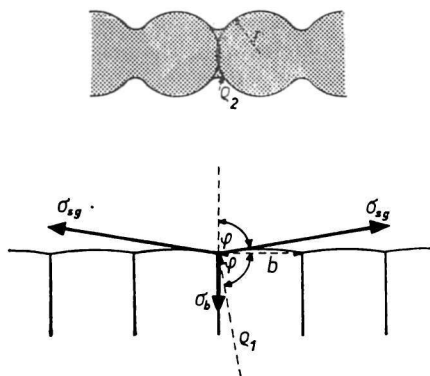


Fig. 4. A simplified model of geometrical arrangement of particles of coexisting substances L and M in the system wherein simultaneously with the reaction (A), or immediately after, the sintering and growth of particles take place ( $b$  is the designation of the dimension of a surface grain).

slower with regard to the establishment of the equilibrium of the reaction (A), then the system will pass through a series of metastable equilibrium states; the corresponding values of  $f_{N;e;m}$  will depend in this case — at the chosen temperature — on the curvature of both the surface and individual grains and the curvature of the surface of necks formed during the sintering.

With regard to low values of  $\sigma_{ss}$  ( $\sigma_{ss} \doteq 1/3 \sigma_{sg}$  [15]) the curvature of surface grains is, at the equilibrium between individual  $\sigma_{ij}$  (Fig. 4), relatively small; nevertheless its influence can be increased by thermal etching of grain surface near the grain boundary necks.

The curvature of the surface of the individual grains (usually of substance formed by the reaction) and especially the curvature of the surface of necks between the grains can be considerable. This is then responsible not only for the diffusion of vacancies in the crystalline phase [16] and for the change of its vapour tension, but also for the disturbance of the equilibrium of the reaction (A) in the immediate neighbourhood of these curved surfaces.

The equations (21) and (26) attain then in simple cases of the coexistence of crystal phases limited by curved surface areas, a form resembling the Kelvin equation; here, instead of the Wulff parameters the curvature radii —  $\rho_1$ ,  $\rho_2$  and  $r$  (Fig. 4) of the prevailing kind of surfaces, are taken.

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Translated by V. Šašková