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Components and composants.

In our considerations we have represented the composition, the thermodynamical potential etc. of the different phases with the aid of the quantities of the components; we may, however, also represent them in another way.

For example we take a quaternary system with the components X Y Z and U. The composition of an arbitrary phase may be represented by:

$$F = x\,X + y\,Y + z\,Z + (1 - x - y - z)\,U \quad . \quad . \quad . \quad (1)$$

wherein xX, yY etc. represent x quantities of X, y quantities of Y, etc. In a system of coördinates with the axes x y z the component U is situated, therefore, in the origin of the coordinates; we call U the fundamental-component.

We now take in the quaternary system under consideration, four arbitrary phases M N P and Q; we may represent the composition of the phase F by:

$$F = m\,M + n\,N + p\,P + (1 - m - n - p)\,Q \quad . \quad . \quad . \quad (2)$$

As definite values of m n and p belong to each composition of F, we may, therefore, also consider the composition of F as a function of m n and p.

We call the phases M, N, P and Q, in which we express the composition of a phase F, the *composants* of the system; we shall call Q the *fundamental composant.*

When we represent the composition of a phase F by (1), consequently expressed in its components, then its thermodynamical potential, its free energy etc. a function of x y and z; when we represent the composition by (2), consequently expressed in composants, then we may represent its thermodynamical potential, its free energy etc. also as functions of m n and p. Of course there exist relations between those two way of representations; we shall deduce them further.

We now consider the equilibrium between a variable (f.i. liquid) phase L and a constant (f.i. solid) phase F. The composition of L may be x, y, z and $1-x-y-z$ expressed in the components, the composition of F: a, b, c and $1-a-b-c$.

When we deduce in some way the condition of equilibrium for this system $F+L$, then we find:

$$\zeta-(x-a)\frac{\partial \zeta}{\partial x}-(y-b)\frac{\partial \zeta}{\partial y}-(z-c)\frac{\partial \zeta}{dz}=\zeta_1 \quad . \quad . \quad . \quad (3)$$

wherein ζ represents the thermodynamical potential of L and ζ_1 that of F.

We now express the composition of L and F in the composants M, N, P and Q. Let be the composition of L: m, n, p and $1-m-n-p$; that of F: α, β, γ and $1-\alpha-\beta-\gamma$. In a similar way as we may deduce (3) we then find:

$$\zeta-(m-\alpha)\frac{\partial \zeta}{\partial m}-(n-\beta)\frac{\partial \zeta}{dn}-(p-\gamma)\frac{\partial \zeta}{\partial p}=\zeta_1 \quad . \quad . \quad . \quad (4)$$

Let us take two variable phases L and L_1 (f.i. two liquids or vapour + liquid or mixed crystals + liquid etc.). We express the composition of those phases with the aid of the components viz. $x\ y\ z$ and $x_1\ y_1\ z_1$, with the aid of the composants viz. $m\ n\ p$ and $m_1\ n_1\ p_1$. In the first case we find as conditions for equilibrium:

$$\left.\begin{array}{l} \zeta-x\dfrac{\partial \zeta}{dx}-y\dfrac{\partial \zeta}{\partial y}-z\dfrac{\partial \zeta}{\partial z}=\zeta_1-x_1\dfrac{\partial \zeta_1}{\partial x_1}-y_1\dfrac{\partial \zeta_1}{\partial y_1}-z_1\dfrac{\partial \zeta_1}{\partial z_1} \\[2ex] \dfrac{\partial \zeta}{\partial x}=\dfrac{\partial \zeta_1}{dx_1} \qquad \dfrac{\partial \zeta}{\partial y}=\dfrac{\partial \zeta_1}{\partial y_1} \qquad \dfrac{\partial \zeta}{\partial z}=\dfrac{\partial \zeta_1}{\partial z_1} \end{array}\right\} \quad . \quad (5)$$

When expressed in the composants, we find:

$$\left.\begin{array}{l} \zeta-m\dfrac{\partial \zeta}{\partial m}-n\dfrac{\partial \zeta}{\partial n}-p\dfrac{\partial \zeta}{\partial p}=\zeta_1-m_1\dfrac{\partial \zeta_1}{\partial m_1}-n_1\dfrac{\partial \zeta^1}{\partial n_1}-p_1\dfrac{\partial \zeta_1}{\partial p_1} \\[2ex] \dfrac{\partial \zeta}{\partial m}=\dfrac{\partial \zeta_1}{\partial m_1} \qquad \dfrac{\partial \zeta}{\partial n}=\dfrac{\partial \zeta_1}{\partial n_1} \qquad \dfrac{\partial \zeta}{\partial p}=\dfrac{\partial \zeta_1}{\partial p_1} \end{array}\right\} \quad . \quad (6)$$

Generally we may say that the equations for equilibrium have a same form, independent on the fact whether they are expressed in components or in composants.

We now shall consider more in detail the relations between components and composants. For this we take again the composants $M\ N\ P$ and Q. We represent, expressed in components, the composition:

of	M	by	$\alpha_1\ \beta_1\ \gamma_1$	and $1-\alpha_1-\beta_1-\gamma_1$
,,	N	,,	$\alpha_2\ \beta_2\ \gamma_2$	,, $1-\alpha_2-\beta_2-\gamma_2$
,,	P	,,	$\alpha_3\ \beta_3\ \gamma_3$	,, $1-\alpha_3-\beta_3-\gamma_3$
,,	Q	,,	$\alpha_4\ \beta_4\ \gamma_4$	,, $1-\alpha_4-\beta_4-\gamma_4$

In order to express the composition of a phase

$$F = x\,X + y\,Y + z\,Z + (1 - x - y - z)\,U \quad . \quad . \quad . \quad . \quad (7)$$

in the four composants, we put:

$$F = m\,M + n\,N + p\,P + (1 - m - n - p)\,Q \quad . \quad . \quad . \quad (8)$$

so that Q is the fundamental composant. As (7) and (8) represent the same phase F, it follows:

$$\left.\begin{array}{l} m\,(\alpha_1 - \alpha_4) + n\,(\alpha_2 - \alpha_4) + p\,(\alpha_3 - \alpha_4) = x - \alpha_4 \\ m\,(\beta_1 - \beta_4) + n\,(\beta_2 - \beta_4) + p\,(\beta_3 - \beta_4) = y - \beta_4 \\ m\,(\gamma_1 - \gamma_4) + n\,(\gamma_2 - \gamma_4) + p\,(\gamma_3 - \gamma_4) = z - \gamma_4 \end{array}\right\} \quad . \quad (9)$$

so that $m\,n$ and p are defined.

In order to define, however, $m\,n$ and p from (9) the determinant, formed by the coefficients of $m\;n$ and p may not be zero. Consequently in general we have the following:

in a system of n components we may choose n arbitrary phases like composants, notwithstanding their determinant is not zero.

For a ternary system this means: we may choose three arbitrary phases as composants notwithstanding those are not situated on a straight line. In a quaternary system we may take 4 arbitrary phases as composants notwithstanding those are not situated in a flat plane.

When we represent the composition of a phase F as in (8) with the aid of composants, then we may consider the thermodynamical potential ζ of this phase also as a function of $m\;n$ and p. Hence it follows:

$$\frac{\partial\zeta}{\partial m} = \frac{\partial\zeta}{\partial x}\cdot\frac{dx}{dm} + \frac{\partial\zeta}{\partial y}\,\frac{dy}{dm} + \frac{\partial\zeta}{\partial z}\cdot\frac{dz}{dm} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and still 2 similar relations, which we obtain by substituting in (10) m by n and p. With the aid of (9) we now find:

$$\left.\begin{array}{l} \dfrac{\partial\zeta}{\partial m} = (\alpha_1 - \alpha_4)\dfrac{\partial\zeta}{\partial z} + (\beta_1 - \beta_4)\dfrac{\partial\zeta}{\partial y} + (\gamma_1 - \gamma_4)\dfrac{\partial\zeta}{\partial z} \\[2ex] \dfrac{\partial\zeta}{\partial n} = (\alpha_2 - \alpha_4)\dfrac{\partial\zeta}{\partial x} + (\beta_2 - \beta_4)\dfrac{\partial\zeta}{\partial y} + (\gamma_2 - \gamma_4)\dfrac{\partial\zeta}{\partial z} \\[2ex] \dfrac{\partial\zeta}{dp} = (\alpha_3 - \alpha_4)\dfrac{\partial\zeta}{\partial x} + (\beta_3 - \beta_4)\dfrac{\partial\zeta}{\partial y} + (\gamma_3 - \gamma_4)\dfrac{\partial\zeta}{\partial x} \end{array}\right\} \quad . \quad . \quad (11)$$

From those equations it follows also, with the aid of (9)

$$m\frac{\partial\zeta}{\partial m} + n\frac{\partial\zeta}{\partial n} + p\frac{\partial\zeta}{\partial p} = (x - \alpha_4)\frac{\partial\zeta}{\partial x} + (y - \beta_4)\frac{\partial\zeta}{\partial y} + (z - \gamma_4)\frac{\partial\zeta}{\partial z} \quad . \quad (12)$$

Above we have seen that for an equilibrium $F + L$ as well equation (3) as (4) is valid; we are able also to prove this by converting equation (3) into (4) with the aid of the above relations. We write (3) in the form:

$$\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} - z\frac{\partial \zeta}{\partial z} = \zeta_1 - a\frac{\partial \zeta}{\partial x} - b\frac{\partial \zeta}{\partial y} - c\frac{\partial \zeta}{\partial z}$$

With the aid of (12) we may write:

$$\zeta - m\frac{\partial \zeta}{\partial m} - n\frac{\partial \zeta}{\partial n} - p\frac{\partial \zeta}{\partial p} = \zeta_1 - (a-\alpha_4)\frac{\partial \zeta}{\partial x} - (b-\beta_4)\frac{\partial \zeta}{\partial y} - (c-\gamma_4)\frac{\partial \zeta}{\partial x} \quad . \quad (13)$$

The composition of the phase in components is represented by a, b and c; α β and γ represent the composition of this same phase in composants. In accordance with (9) the following relations are valid:

$$\alpha(\alpha_1-\alpha_4) + \beta(\alpha_2-\alpha_4) + \gamma(\alpha_3-\alpha_4) = a-\alpha_4$$
$$\alpha(\beta_1-\beta_4) + \beta(\beta_2-\beta_4) + \gamma(\beta_3-\beta_4) = b-\beta_4$$
$$\alpha(\gamma_1-\gamma_4) + \beta(\gamma_2-\gamma_4) + \gamma(\gamma_3-\gamma_4) = c-\gamma_4$$

When we add those three equations to one another, after having multiplied the first one with $\frac{\partial \zeta}{\partial x}$, the second one with $\frac{\partial \zeta}{\partial y}$ and the third one with $\frac{\partial \zeta}{\partial z}$, then we find, with the aid of (11)

$$\alpha\frac{\partial \zeta}{\partial m} + \beta\frac{\partial \zeta}{\partial n} + \gamma\frac{\partial \zeta}{\partial p} = (a-\alpha_4)\frac{\partial \zeta}{\partial x} + (b-\beta_4)\frac{\partial \zeta}{\partial y} + (c-\gamma_4)\frac{\partial \zeta}{\partial z}$$

With the aid of this (13) now passes into:

$$\zeta - m\frac{\partial \zeta}{\partial m} - n\frac{\partial \zeta}{\partial n} - p\frac{\partial \zeta}{\partial p} = \zeta_1 - \alpha\frac{\partial \zeta}{\partial m} - \beta\frac{\partial \zeta}{\partial n} - \gamma\frac{\partial \zeta}{\partial p}$$

which is in accordance with (4).

We may also write the four equations (5) in the form (6). For the first one of the equations (5) we may viz. write:

$$\left.\begin{array}{l}\zeta - (x-\alpha_4)\dfrac{\partial \zeta}{\partial x} - (y-\beta_4)\dfrac{\partial \zeta}{\partial y} - (x-\gamma_4)\dfrac{\partial \zeta}{\partial z} \\ = \zeta_1 - (x_1-\alpha_4)\dfrac{\partial \zeta_1}{\partial x_1} - (y_1-\beta_4)\dfrac{\partial \zeta_1}{\partial y_1} - (z_1-\gamma_4)\dfrac{\partial \zeta_1}{\partial z_1}\end{array}\right\} \quad . \; . \quad (14)$$

With the aid of (12) (14) passes into the first one of the equations (6).

The three equations (11) excepted, which are valid for the phase without index, we have still also three similar equations, which we obtain from (11) by giving to all variables and to ζ also, the index 1.

We call those three equations 11^a. As, however, in accordance with (5) $\frac{\partial \xi}{\partial x} = \frac{\partial \zeta_1}{\partial x_1}$ etc., it follows from (11) and (11^a) also $\frac{\partial \zeta}{\partial m} = \frac{\partial \zeta_1}{\partial m_1}$ etc.

For a ternary system with the composants F_1 F_2 and F_0 we have, when we choose F_0 as fundamental component:

$$F = m F_1 + n F_2 + (1 - m - n) F_0 \quad . \quad . \quad . \quad . \quad (15)$$

When we represent the compositions of the components by α and β with the corresponding index, then the equations (9) pass into:

$$\left.\begin{array}{l} m(\alpha_1 - \alpha_0) + n(\alpha_2 - \alpha_0) = x - \alpha_0 \\ m(\beta_1 - \beta_0) + n(\beta_2 - \beta_0) = y - \beta_0 \end{array}\right\} \quad . \quad . \quad . \quad . \quad (16)$$

We now shall deduce those equations also in another way, by which at the same time the meaning of m and n in the graphical representation becomes clear.

We take a system of coordinates with the axes OX and OY (Fig. 1) in which we represent the composition of the phases,

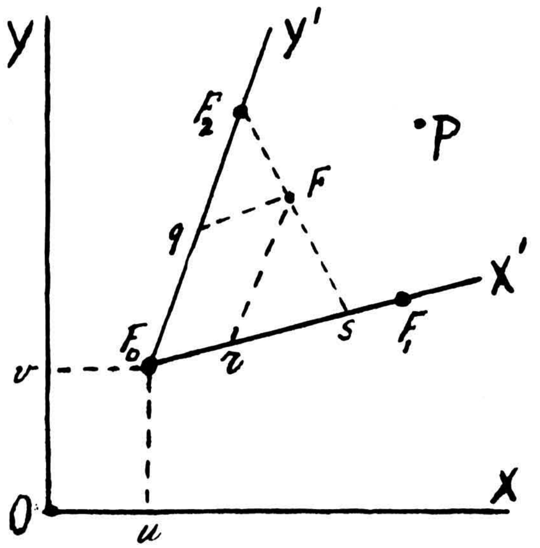

Fig. 1.

expressed in the components. We imagine the three composants F_0 F_1 and F_2 and the arbitrary phase F to be represented by the points F_0 F_1 F_2 and F. Consequently in the figure is $F_0v = \alpha_0$, $F_0u = \beta_0$ etc. Now we take F_0F_1 as new X-axis and F_0F_2 as new Y-axis; then the new coordinates of the point F are Fq and Fr; we put $Fq = x'$ and $Fr = y'$. When we call the angles, which the new axes F_0F_1 and F_0F_2 are making with the original X-axis φ_1 and φ_2 then it follows from the figure:

$$\left.\begin{array}{l} x = \alpha_0 + x' \cos \varphi_1 + y' \cos \varphi_2 \\ y = \beta_0 + x' \sin \varphi_1 + y' \sin \varphi_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

When we represent the length of F_0F_1 and F_0F_2 by l_1 and l_2, then we may write for (17)

$$\left.\begin{array}{l} x - \alpha_0 = \dfrac{x'(\alpha_1 - \alpha_0)}{l_1} + \dfrac{y'(\alpha_2 - \alpha_0)}{l_2} \\ y - \beta_0 = \dfrac{x'(\beta_1 - \beta_0)}{l_1} + \dfrac{y'(\beta_2 - \beta_0)}{l_2} \end{array}\right| \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Now we shall express the composition of the phase F in that of the three composants: F_0 F_1 and F_2. We find:

$$\text{quantity of } F_2 : \text{quantity of } (F_0 + F_1) = Fs : FF_2$$

$$\text{or: quantity of } F_2 : \text{quantity of } (F_0 + F_1 + F_2) = Fs : F_2s$$

When we put the total quantity of $F = F_0 + F_1 + F_2$ equal to zero, and when we bear in mind that:

$$Fs : F_2s = Fr : F_2F_0 = y' : l_2$$

then follows: quantity of $F_2 = \dfrac{y'}{l_2}$.

In a similar way we find: quantity of $F_1 = \dfrac{x'}{l_1}$.

Consequently there are wanted for forming the unit of quantity of the phase F: $\dfrac{x'}{l_1}$ quant. of F_1 and $\dfrac{y'}{l_2}$ quant. of F_2 and consequently also $1 - \dfrac{x'}{l_1} - \dfrac{y'}{l_2}$ quantities of F_0. We may write, therefore;

$$F = \frac{x'}{l_1} F_1 + \frac{y'}{l_2} F_2 + \left(1 - \frac{x'}{l_1} - \frac{y'}{l_2}\right) F_0 \quad . \quad . \quad . \quad . \quad (19)$$

When we put $\dfrac{x'}{l_1} = m$ and $\dfrac{y'}{l_2} = n$ then (18) and (19) pass into (15) en (16).

Hence it appears a.o. that m and n do not represent the coordinates x' and y' of the phase F, but they are functions of them; when m and n are known, then also x' and y' are known and reversally. For this reason we may call m and n yet also coordinates.

The coordinates of the composant

F_0 are	$x' = 0$	$y' = 0$	consequently	$m = 0$	and	$n = 0$
F_1 ,,	$x' = l_1$	$y' = 0$	,,	$m = 1$	,,	$n = 0$
F_2 ,,	$x' = 0$	$y' = l_2$	,,	$m = 0$	,,	$n = 1$

Of course this is also in accordance with (15); when herein we put f.i. $m=1$ and $n=0$ then phase F represents the composant F_1.

When we express the composition of a phase in its components, consequently in x and y, then x and y are positive and $x+y \leqq 1$. When, however, we express its composition in composants, then m and n may also be negative and also $m+n>1$. The latter is the case f.i. for a phase, represented by the point P. In (15) m and n are then positive and $1-m-n$ is negative.

When we have a quaternary system then similar relations exist between the coordinates viz.

$$x' = m\,l_1 \qquad y' = n\,l_2 \qquad z' = p\,l_3$$

Till now we have assumed that each of the n composants of a system of n components contains also those n components. It is apparent, however, that we may choose the composants also in such a way that one or more or even all composants contain less than n components. Of course the n composants together must contain the n components. We may consider the representation with the aid of components as a special case of the representation with the aid of composants; each of the côomposants then contains a single component only. We shall, however, continue by calling this a representation with the aid of components. When, however, there is at least one composant, which contains more than one component, then we shall speak of a representation with the aid of composants.

As it is known, the deduced functions of the thermodynamical potential become infinitely large when the quantities of one or more of the components approach to zero. In a quaternary system f.i. $\frac{\partial \zeta}{\partial x}$ becomes infinitely large when x or $1-x-y-z$ approaches to zero; $\frac{\partial \zeta}{\partial y}$ when y or $1-x-y-z$ and $\frac{\partial \zeta}{\partial z}$ when z or $1-x-y-z$ approaches to zero.

Using composants this is otherwise, however. It follows viz. from (11) that $\frac{\partial \zeta}{\partial m}$, $\frac{\partial \zeta}{\partial n}$ and $\frac{\partial \zeta}{\partial p}$ become infinitely large, only then when one or more of the functions $\frac{\partial \zeta}{\partial x}$, $\frac{\partial \zeta}{\partial y}$ and $\frac{\partial \zeta}{\partial z}$ are infinitely large and this may take place, as we have seen above, only when one or more of the conditions:

$$x=0 \qquad y=0 \qquad z=0 \qquad 1-x-y-z=0 \quad . \quad (20)$$

is satisfied. In general $\frac{\partial \zeta}{\partial m}$, $\frac{\partial \zeta}{\partial n}$ or $\frac{\partial \zeta}{\partial p}$ become, therefore, infinitely large when we give such values to m, n and p, that one or more of the conditions (20) are satisfied. It is apparent that this may be casually only for $m=0$ or $n=0$ or $p=0$ or $1-m-n-p=0$.

At the same time the following is apparent. When we give to m, n and p such values that f.i. x becomes $=0$, then in (11) $\frac{\partial \zeta}{\partial x}$ becomes infinitely large, so that $\frac{\partial \zeta}{\partial m}$, $\frac{\partial \zeta}{\partial n}$ and $\frac{\partial \zeta}{\partial p}$ become infinitely large at the same time. When, however, we have chosen the composants in such a way that $\alpha_1 = \alpha_4$ then only $\frac{\partial \zeta}{\partial n}$ and $\frac{\partial \zeta}{\partial p}$ become infinitely large, while $\frac{\partial \zeta}{\partial m}$ remains finite.

When a liquid has the composition:

$$L = xX + yY + zZ + \dots$$

wherein X, Y etc. represent components, then the stability requires that for all values of dx, dy etc.

$$\left(\frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy + \dots\right)^{(2)} > 0 \qquad \dots\dots \quad (21)$$

When we imagine L to be divided into

$$L = \varkappa\, L_1 + (1-\varkappa)\, L_2$$

wherein:

$$L_1 = (x + dx_1)\, X + (y + dy_1)\, Y + \dots.$$
$$L_2 = (x + dx_2)\, X + (y + dy_2)\, Y + \dots$$

then must

$$\zeta < \varkappa\, \zeta_1 + (1-\varkappa)\, \zeta_2$$

from which (21) is following. When we now express the composition of L in composants viz.:

$$L = m\, M + n\, N + p\, P + \dots.$$

then it follows in the same way that

$$\left(\frac{\partial \zeta}{\partial m} dm + \frac{\partial \zeta}{dn} dn + \dots.\right)^{(2)} > 0$$

must be true for all values of dm, dn etc.

(*To be continued*)

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