

centre; in fact in Sankulirang the deposits become more and more pelagic, as the sediments lie more eastward, and point to an old marine territory in Macassar Strait (L. RUTTEN, l.c. 1916). It does not seem probable, though, that also the western geosyncline was bounded in the N.W. by a deep sea. First of all there are factors pointing to the smaller significance of this geosynclinal territory than that of the East. The strike of the western geosyncline almost coincided with the northwest coast of the island as is shown on the map of C. SCHMIDT (l.c.). In its south-western elongation nothing is known of a continuation of the subsided area; we find ourselves there in the old landmasses of Sambas<sup>1)</sup> and the Natuna-Islands<sup>2)</sup>. One is impressed with the idea that the subsided region, which most likely extended from the Philippines as far as the northwest coast of Borneo, terminated here. There is still something else. In 1914 I obtained from Dr. NIETHAMMER a fragment of limestone from a territory far removed from the Borneo-coast viz. the islet of Mangalum (see sketchmap). It is an Operculina limestone, which, it is true, includes only Operculina complanata Defr., and which on that account may be quaternary as well as tertiary, but it bears a close resemblance to a Lepidocyclina-bearing Operculina-limestone from Pulu Labuansklambu near the northwestern point of Borneo. It cannot be doubted, therefore, but that the the limestone from Mangalum is still met with in litoral facies so far from the coast, so that it seems highly improbable that the Northwestern geosyncline should have been bounded in the North-West by a deep sea. It may be deemed more probable that here lay a subsided area, which at one time was alternately shallow sea, delta-territory or low land; that it was bounded on the one side by the old land-centre of Borneo, on the other by an old continent now transgressed by the Chinese Sea, and formerly perhaps connected with Indo-China, which is also an old continental region. According to this view both J. MOTLEY and MOLENGRAAFF would be right, the former in referring the source of the material of the tertiary formations of Northwest Borneo to the Northwest, the latter in looking for it in the South-east. Moreover this view would also favour the conclusion that the central landmass of Borneo, which had already to contribute so much detritus towards the East and the South-East, was somewhat disburdened as to its contribution towards the Northwest.

Utrecht, 2 Febr 1921.

<sup>1)</sup> N. WING EASTON. Versl. Geol. Sectie. Geol. Mijnbk. Gen. I. 1914. p. 179—189.

<sup>2)</sup> P. G. KRAUSE. Samml. Geol. Reichsmus. Leiden. (1) V. 1898. p. 221—236.

Chemistry. — "In-, mono- and divariant equilibria". XXI. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 26, 1921).

*Equilibria of n components in n phases, in which the quantity of one of the components approaches to zero. The influence of a new substance on an invariant (P or T) equilibrium. (Continuation).*

In communication XX we have examined the influence of a new substance on the invariant (P or T) equilibrium:

$$E = L_1 + L_2 + \dots + F_1 + F_2 + \dots \quad (1)$$

With this we have assumed that  $L_1, L_2, \dots$  are liquids and  $F_1, F_2, \dots$  solid substances of unvariable composition. The general form of this equilibrium  $E$  is:

$$E = G + L_1 + L_2 + \dots + M_1 + M_2 + \dots + F_1 + F_2 + \dots \quad (2)$$

in which  $G$  is a gas and  $M_1, M_2, \dots$  are mixed crystals, which may contain all components or not.

When we know the reaction, occurring in this invariant (P or T) equilibrium, then we may deduce again with the aid of (12) and (15) (XX) which influence has the addition of a new substance. Now we shall consider some special cases of this equilibrium.

We take the unary equilibrium  $G + L_1$  viz. an unary liquid in equilibrium with the vapour; this equilibrium is invariant (P or T). As the reaction is  $L_1 \rightleftharpoons G$ , it follows:

$$\sum (\lambda x) = x - x_1 \quad \sum (\lambda H) = H - H_1 \quad \sum (\lambda V) = V - V_1$$

in which  $x, H$  and  $V$  relate to the vapour  $G$ .

Now it follows from (12) and (15) (XX):

$$(dT)_P = -\frac{RT(x-x_1)}{H-H_1} = \frac{RT^2(x_1-x)}{\Delta W} \quad (3)$$

$$(dP)_T = \frac{RT(x-x_1)}{V-V_1} = P(x-x_1) \quad (4)$$

Herein  $\Delta W$  is the heat of evaporation of a molecular quantity of liquid and  $V - V_1$  the increase of volume at the evaporation of this quantity of liquid. Consequently we re-find in (3) and (4) the known formula's. We find, therefore, the rule well-known:

When, at addition of a new substance the concentration of this

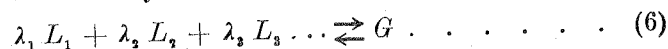
substance in the vapour (viz.  $x$ ) is larger (smaller) than in the liquid (viz.  $x_1$ ) then the boiling-point under constant pressure is lowered (raised) and the vapour-tension at constant  $T$  is raised (lowered);

when the new substance is not volatile (consequently  $x = 0$ ) then the boiling-point under constant  $P$  is raised and the vapour-tension at constant  $T$  is lowered.

We consider the invariant ( $P$  or  $T$ ) equilibrium

$$E = G + L_1 + L_2 + L_3 + \dots \quad (5)$$

viz. a complex of liquids in equilibrium with their vapour  $G$ . We write the reaction which may occur in  $E$ :



When all reaction-coefficients  $\lambda_1, \lambda_2, \dots$  are positive, then all liquids take part in the formation of vapour in the ratio  $\lambda_1 : \lambda_2 : \lambda_3 \dots$ , then we shall say that the vapour has a "average" composition. When, however, in (6) one or more of the reaction-coefficients are negative, then also one or more liquids arise at a time with the vapour; the vapour has then a "non-average" composition.

When we represent by  $\Delta W$  the heat, wanted to form one quantity of vapour, and the corresponding increase of volume by  $\Delta V$ , then  $\Delta W$  and  $\Delta V$  are positive, unless in very special cases.

Now we may write for (12) and (15) (XX):

$$(dT)_P = -\frac{RT^2 \sum (\lambda x)}{\Delta W} \quad \text{and} \quad (dP)_T = \frac{RT \sum (\lambda x)}{\Delta V} \quad (7)$$

Herein is:

$$\sum (\lambda x) = x - (\lambda_1 x_1 + \lambda_2 x_2 + \lambda_3 x_3 + \dots) \quad (8)$$

Now we take a mixture of the liquids  $L_1, L_2, \dots$  in such a ratio that it has the same composition as the vapour  $G$ . We call this mixture or complex of phases the "reduced mixture". As appears from (6) this mixture has the composition:

$$\lambda_1 L_1 + \lambda_2 L_2 + \lambda_3 L_3 + \dots \quad (9)$$

in which one or more of the coefficients may also be negative. When the vapour has an average composition, then all coefficients in (9) are positive; when the vapour, however, has a non-average composition, then one or more of the coefficients in (9) are negative. When we put now:

$$\lambda_1 x_1 + \lambda_2 x_2 + \lambda_3 x_3 + \dots = c \quad (10)$$

consequently  $c$  is the concentration of the new substance  $X$  in the reduced mixture. Instead of (7) we may write now:

$$(dT)_P = \frac{RT^2 (c-x)}{\Delta W} \quad \text{and} \quad (dP)_T = \frac{RT (x-c)}{\Delta V} \quad (11)$$

Hence follows the rule<sup>1)</sup>:

when, on addition of a new substance the concentration of this substance in the vapour (viz.  $x$ ) is larger (smaller) than in the reduced mixture (viz.  $c$ ) then the boiling-point under constant pressure is lowered (raised) and the vapour-tension is raised (lowered) at constant temperature.

Applying those and the following rules and formula (11) we have to consider to following.

When the vapour has an average composition, then  $c$  is positive when, however, the vapour has a non-average composition, then  $c$  may be as well positive as negative;  $x-c$  is then always positive when  $c$  is negative.

When we substitute in the rule above "reduced mixture" by "liquid" then we re-find the rule, which is true for the addition of a new substance to the unary equilibrium  $L + G$ .

When the added new substance is not volatile, then  $x = 0$ ; (11) passes then into:

$$(dT)_P = \frac{RT^2 c}{\Delta W} \quad \text{and} \quad (dP)_T = -\frac{RTc}{\Delta V} \quad (12)$$

When we keep in mind that  $c$  may be as well positive as negative, then we find the rule:

when the vapour has an average composition, then, on addition of a new substance, the boiling-point under constant pressure shall be raised and the vapour-tension at constant temperature shall be lowered;

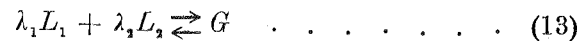
when the vapour has a non-average composition, then for  $c > 0$  this rule is true also; for  $c < 0$  however an opposite rule is true.

We may for some cases also represent the above results geometrically. Let us firstly consider the addition of a new substance to the binary equilibrium  $E = L_1 + L_2 + G$ . In figs 1-4 the sides  $ZX$  and  $ZY$  of the ternary concentration-diagram are partly drawn.  $a_1, a_2$  and  $a$  represent the two liquids and the vapour  $G$  of this equilibrium  $E$ . In figs 1 and 3 this vapour  $a$  has an average, in figs 2 and 4 a non-average composition. When, at constant  $T$  or  $P$ , we add a new substance, then the liquids  $L_1$  and  $L_2$  trace the curves  $a_1 b_1 c_1$  and  $a_2 b_2 c_2$ ; the vapour traces curve  $abc$ . Each of the

<sup>1)</sup> This rule is deduced already formerly for a definite case, viz. the addition of a new substance to the binary equilibrium  $L_1 + L_2 + G$ . F. A. H. SCHREINEMAKERS. Zeitschr. f. Phys. Chem. 38 (1901) 252.

phases on the ternary equilibrium traces, therefore, a three-phases-curve. Now we assume that on addition of very little of the new substance the two liquids and the vapour are represented by the points  $b_1, b_2$  and  $b$ ; consequently these points are situated in the immediate vicinity of  $a_1, a_2$  and  $a$ ; for sake of clearness they are drawn however in the figures on greater distance. Relating to the situation of the vapour-point  $b$  with respect to the line  $b_1, b_2$ , we shall say that the three-phases-triangle  $b_1, b_2, b$  turns his vapour-point in figs 1 and 2 away from the side  $YZ$  of the components-triangle and in figs 3 and 4 towards this side.

When we represent the reaction by



then is:

$$\Sigma(\lambda x) = x - \lambda_1 x_1 - \lambda_2 x_2 \quad \dots \quad (14)$$

in wich  $\lambda_1$  and  $\lambda_2$  are defined by

$$\lambda_1 + \lambda_2 = 1 \quad \text{and} \quad \lambda_1 y_1 + \lambda_2 y_2 = y \quad \dots \quad (15)$$

so that  $\lambda_1$  and  $\lambda_2$  are linear functions of  $y$ . When we consider  $x$  and  $y$  in (14) as running coördinates, then  $\Sigma(\lambda x) = 0$  represents

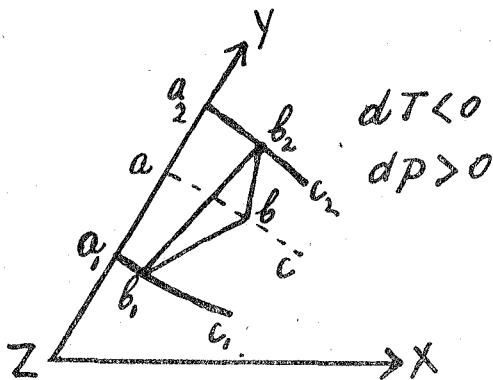


Fig. 1.

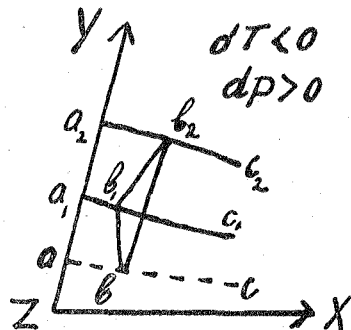


Fig. 2.

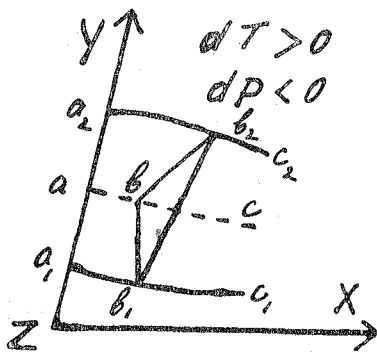


Fig. 3.

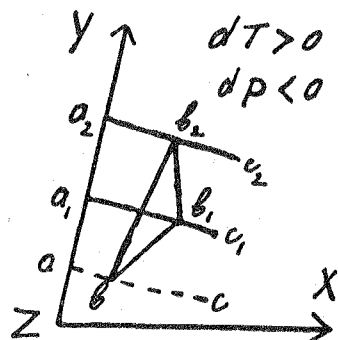


Fig. 4.

the equation of the straight line  $b_1, b_2$ . When we put viz.  $x = x_1$  and  $y = y_1$ , then follows from (15)  $\lambda_1 = 1$  and  $\lambda_2 = 0$  so that  $\Sigma(\lambda x) = 0$ ; consequently the line goes through the point  $b_1$ . In the same way it is apparent that this line goes through the point  $b_2$ . When the point  $xy$  is not situated on the line  $b_1, b_2$ , then  $\Sigma(\lambda x)$  is not zero, but positive or negative, in accordance to the situation of this point on the one or on the other side of this line. Now we imagine in the figs 1—4 a horizontal line drawn through  $a$ ; as  $b$  is situated in the immediate vicinity of  $a$ , this line goes also, by approximation, through  $b$ ; we call  $r$  the point of intersection of this line with the line  $b_1, b_2$ . On this horizontal line in  $r$  consequently  $\Sigma(\lambda x) = 0$ , at the right of  $r$   $\Sigma(\lambda x)$  is  $> 0$  at the left of  $r$   $\Sigma(\lambda x)$  is  $< 0$ . Consequently when we trace the line  $b_1, b_2$  in the direction from  $b_1$  towards  $b_2$ , then  $\Sigma(\lambda x)$  is at the right of this line positive and negative at the left of this line.

As in figs 1 and 2 the vapour point  $b$  is situated at the right of the line  $b_1, b_2$ , consequently  $\Sigma(\lambda x)$  is positive. Therefore, follows from (7):

$$(dT)_P < 0 \quad \text{en} \quad (dP)_T > 0 \quad \dots \quad (16)$$

which is also indicated in those figures. Hence follows: when we trace the three phases-curves (viz.  $abc, a_1 b_1 c_1$  and  $a_2 b_2 c_2$ ) beginning at their binary terminating-points (viz.  $a, a_1$  and  $a_2$ ) then the temperature decreases under constant pressure and the pressure increases at constant temperature.

In figs 3 and 4 the vapour-point is situated at the left of the line  $b_1, b_2$ , so that  $\Sigma(\lambda x)$  is negative. Now it follows from (7):

$$(dT)_P > 0 \quad \text{en} \quad (dP)_T < 0 \quad \dots \quad (17)$$

which is also indicated in the figs 3 and 4. Hence it follows, therefore: when we trace the 3 three-phases-curves, beginning at their binary terminating-points, then the temperature increases under constant pressure and the pressure decreases at constant temperature.

We may summarise those results in the following way:

When we trace the three-phases-curves of the ternary equilibrium  $L_1 + L_2 + G$  beginning at their binary terminating-points.

then under constant  $P$  the temperature decreases and at constant  $T$  the pressure increases, when the three-phases-triangle turns its vapour-point away from the side (with the binary terminating-points) (figs. 1 and 2)

and under constant  $P$  the temperature increases and at constant  $T$  the pressure decreases, when the three-phases-triangle turns its vapour-point towards the side (with the binary terminating-points) (figs. 3 and 4).



the pressure increases, when the four-phases-tetrahedron turns its vapour-point away from the side (with the ternary terminating-points) and under constant  $P$  the temperature increases and at constant  $T$  the pressure decreases, when the four-phases-tetrahedron turns its vapour-point towards the side (with the ternary terminating-points).

We now take an invariant ( $P$  or  $T$ ) equilibrium, in which occur, besides a liquid  $L$  yet also the mixed-crystals  $M_1, M_2, \dots$ ; we represent this equilibrium by



and the occurring reaction by:



Of course one or more of the reaction-coefficients may be negative. When all coefficients are positive, so that the liquid has a mediate composition, then (21) represents a congruent melting of the mixed-crystals; when one or more of the coefficients are negative, so that the liquid has a not-mediate composition then (21) represents a conversion of the one of mixed-crystals in the other, with formation of liquid, consequently an incongruent melting.

We shall call a mixture of the mixed-crystals  $M_1, M_2, \dots$  taken in such ratio, that it has the same composition as the liquid, the "reduced complex of mixed-crystals". Now we have:

$$\sum (\lambda x) = x - \lambda_1 x_1 - \lambda_2 x_2 - \lambda_3 x_3 - \dots = x - c \quad (22)$$

in which, therefore,  $c$  represents the concentration of the new substance  $X$  in the reduced complex of mixed crystals; consequently  $c$  may be as well positive as negative.

Therefore, we obtain again formula (11) in which  $\Delta W$  is the heat, which is necessary for the congruent or incongruent melting, and  $\Delta V$  the change in volume, occurring with this. We may assume again that in general  $\Delta W$  is positive;  $\Delta V$  may be, however, positive or negative.

When we only consider the change of the congruent or incongruent melting-point under constant pressure consequently, then follows the rule:

when, on addition of a new substance, the concentration of that substance in the liquid (*viz*  $x$ ) is greater (smaller) than in the reduced complex of mixed crystals (*viz*  $c$ ) than the (congruent or incongruent) melting-point of the mixed crystals under constant pressure decreases (increases).

When the new substance, which is added, does not occur in the mixed-crystals, then, as  $x_1, x_2, x_3, \dots$  are zero, also  $c = 0$ . (11) then passes into:

$$(dT)_P = \frac{-RT^2x}{\Delta W} \quad \text{and} \quad (dP)_T = \frac{RTx}{\Delta V} \quad (23)$$

Hence it follows:

on addition of a new substance, which does not occur in the mixed crystals, the (congruent or incongruent) melting-point of the mixed-crystals under constant pressure is lowered.

We shall briefly consider more in detail the case that a new substance is added to the binary invariant ( $P$  or  $T$ ) equilibrium;  $E = M_1 + M_2 + L$ . For this we imagine that in the figs 1—4 the points  $a_1, a_2$  and  $a$  represent the two mixed-crystals  $M_1$  and  $M_2$  and the liquid  $L$ . In the figs 1 and 3 then a congruent melting takes place and in the figs 2 and 4 an incongruent melting.

When we add at constant  $T$  or  $P$  a new substance, which occurs also in the mixed-crystals, so that ternary mixed-crystals occur, then  $M_1$  and  $M_2$  trace the three-phases-curves  $a_1 b_1 c_1$  and  $a_2 b_2 c_2$ ; the liquid  $L$  traces the three-phases-curves  $a b c$ . In figs 1 and 2 the three-phases-triangle  $b_1 b_2 b$  turns its liquid-point  $b$  away from the side  $YZ$  of the components-triangle, in figs 3 and 4 towards this side.

In a similar-way as with the equilibrium  $L_1 + L_2 + G$  we now find that also for the equilibrium  $M_1 + M_2 + L$  the sign of  $(dT)_P$  must be the same as is indicated in the figs 1—4; this is also valid for  $(dP)_T$  when  $\Delta V$  is  $> 0$ ; for  $\Delta V < 0$  we must take, however the opposite sign for  $(dP)_T$ .

Consequently we find the rule:

when we trace the three-phases-curves of the equilibrium  $M_1 + M_2 + L$  starting from their binary terminating-points,

then under constant  $P$  the temperature decreases, when the three-phases-triangle turns its liquid-point away from the side (with the binary terminating points) (figs 1 and 2),

and under constant  $P$  the temperature increases, when the three-phases-triangle turns its liquid-point towards the side (with the binary terminating-points) (figs 3 and 4).

The reader himself may easily find the rule for the change of pressure at constant  $T$ .

When the added new substance does not occur in the mixed-crystals, so that those rest binary ones, then in the figs 1—4 the curves  $a, b, c_1$  and  $a_2, b_2, c_2$  must coincide with the side  $YZ$ . The three-phases-triangle  $b_1, b_2, b$  is then always situated with the angle-points  $b_1$  and  $b_2$  on the side  $YZ$ , while the liquid-point  $b$  is situated within the concentration-diagram. Therefore, we imagine in the figs

1 and 2 the points  $b_1$  and  $b_2$  on  $YZ$  in the vicinity of  $a_1$  and  $a_2$ .

Then from fig. 1 a diagram arises, such as is drawn in fig. 6.

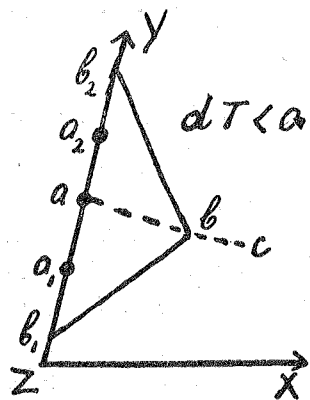


Fig. 6.

As the three-phases-triangle now turns always its liquid point away from the side  $YZ$ , the temperature must, according to the previous rule, decrease under constant  $P$ , viz. when we trace the curves starting from their binary terminating-points. This is in accordance also with the first formula (23).

In the previous communication XX we have deduced the relation:

$$(dP)_T : (dT)_P = - \left( \frac{dP}{dT} \right)_{x=0} \dots \dots \dots (24)$$

Hence appears: when in the invariant ( $P$  or  $T$ ) equilibrium (which consequently is monovariant) the pressure increases at increase of  $T$ , then  $(dP)_T$  and  $(dT)_P$  have opposite signs; when, however, the pressure decreases at increase of  $T$ , then  $(dP)_T$  and  $(dT)_P$  have the same sign. We now may express this in the following way:

we add a new substance to an invariant ( $P$  or  $T$ ) equilibrium;

when in this equilibrium the pressure increases at increase of temperature, then the influence on the pressure at constant  $T$  is opposite to the influence on the temperature under constant  $P$ ;

when in this equilibrium the pressure decreases at increase of temperature, then the influence on the pressure at constant  $T$  is the same as the influence on the temperature under constant  $P$ .

It is evident that "influence" means here the sign of the change of pressure of temperature.

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(To be continued).

**Physiology.** — "On the serological specificity of haemoglobin in different species of animals". By K. LANDSTEINER. (Communicated by Prof. C. H. H. SPRONCK).

(Communicated at the meeting of January 29, 1921).

The knowledge of species-specificity is based principally on morphological facts, on the phenomena of inheritance and transplantation, and on serological reactions. The first allow the direct inference that species-specificity is a property of all the constituents of the body; serological data, on the other hand — as far as animal organisms are concerned — bear first of all on the proteins of the blood serum.

Concerning these latter there exist numerous results of precipitin tests, of which the greater part were carried out by NUTTALL<sup>1)</sup>, and which may be summarised, that serological relationship in general corresponds to the zoological classification and that the difference of the precipitin reactions increase in a measure corresponding to the difference in the scale of animal classification.

For the other constituents of the body an analogous relationship is probable, and is often accepted as a matter of fact; this subject, however has been far less thoroughly investigated than the properties of the bloodserum.

Some proteins differ in a greater degree (protein of the eye-lens<sup>2)</sup> and the horny substance<sup>3)</sup>) and others (casein<sup>4)</sup>) in a smaller degree from the specificity type mentioned i. e. their specificity is more or less independant of the animal species. In these cases we cannot exclude the possibility that the species-specific structure although present is concealed by other structures.

Whether the haemagglutinating immune-sera with regard to their group reactions correspond as well to the zoological classification, as the before mentioned precipitins, is indeed still doubtful<sup>5)</sup>.

<sup>1)</sup> NUTTALL. Bloodimmunity and bloodrelationship, Cambridge (1904).

<sup>2)</sup> UHLENHUTH. Festschr. f. Rob. Koch.

<sup>3)</sup> KRUSIUS. Arch. f. Augenheilk. 67. (1910).

<sup>4)</sup> VERSELL. Zeitschr. f. Immunitätsf. 24. 267. (1915).

<sup>5)</sup> Cf. LANDSTEINER u. REICH. Zeitschr. f. Hyg. 58. 227. (1907).

BROCKMANN. Zeitschr. f. Immunitätsf. 9. 114 (1911).