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and lies in the plane (F_2s_1'') . Both component parts are variable.

There are apparently five more systems equivalent to this, each determined by a pencil (σ^2) and a pencil (d).

The locus of the conics σ^2 is therefore also here of order *ten*.

The surface A appears to be of order *eight*; it has d_{12} as *quadruple straight line*, each of the *six* straight lines s as *nodal lines*. For if the complete intersection of two surfaces A is considered, it appears that the order x is to be found from the equation $x^2 - 3x - 40 = 0$; hence $x = 8$.

In a plane Φ a cubic involution possessing one singular point of order four and six singular points of order two is determined by this $[Q^3]$. It has been described in § 14 of my paper quoted above.

Chemistry. — “*Equilibria in Ternary Systems*” XVIII. By Prof. SCHREINEMAKERS.

In the previous communications here and there some equilibria between solid substances and vapour have been brought in discussion already; now we will consider some of these equilibria more in detail. We may distinguish several cases according as F and G are unary, binary or ternary phases.

I. The equilibrium $F + G$; F is a ternary compound, G a ternary vapour.

The equilibrium $F + G$ is monovariant (P and T constant), this means that the vapours, which can be in equilibrium with solid F , are represented by a curve. In order to find this curve we construct a cone, which touches the vapourleaf of the ζ -surface and which has its top in the point, representing the ζ of the solid substance F . The projection of the tangent curve is the curve sought for, viz. the saturationcurve (P and T constant) of the substance F . From this deduction it is apparent also, that this curve is circumphased and that we cannot construct from F a tangent to it.

The equilibrium $F + G$ is determined by:

$$Z_1 + (a-x_1) \frac{\partial Z_1}{\partial x_1} + (\beta-y_1) \frac{\partial Z_1}{\partial y_1} = \zeta \quad . \quad . \quad . \quad (1)$$

When we keep P and T constant in (1), it determines the vapour-saturationcurve (P, T) of F . When we assume that in the vapour the compound F is completely decomposed into its components and that the gas-laws are true, (1) passes into:

$$a \log x_1 + \beta \log y_1 + (1-a-\beta) \log (1-x_1-y_1) = C \quad . \quad . \quad (2)$$

or :

$$x_1^\alpha y_1^\beta (1-x_1-y_1)^{1-\alpha-\beta} = C_1 \dots \dots \dots (2a)$$

wherein C and C_1 are independent of P and T . When we introduce the partial vapour-tension :

$$P_A = x_1 P, \quad P_B = y_1 P \quad \text{and} \quad P_C = (1-x_1-y_1) P$$

then (2) passes into :

$$\alpha \log P_A + \beta \log P_B + (1-\alpha-\beta) \log P_C = C \dots \dots \dots (3)$$

or :

$$P_A^\alpha \cdot P_B^\beta P_C^{1-\alpha-\beta} = C_1 \dots \dots \dots (3a)$$

When we keep the temperature constant, it follows from (1)

$$\left. \begin{aligned} [(x_1-\alpha)r_1 + (y_1-\beta)s_1] dx_1 + [(x_1-\alpha)s_1 + (y_1-\beta)t_1] dy_1 = \\ = \left[V_1 - v + (\alpha-x_1) \frac{\partial V_1}{\partial x_1} + (\beta-y_1) \frac{\partial V_1}{\partial y_1} \right] dP \end{aligned} \right\} \dots \dots (4)$$

We call l the distance from F to a point (x_1, y_1) of the vapour-saturationcurve; we take dl positive in such a direction that l becomes larger. Then we have :

$$\frac{dl}{l} = \frac{dx_1}{x_1-\alpha} = \frac{dy_1}{y_1-\beta}$$

When we substitute these values of dx_1 and dy_1 in (4) and when we represent the coefficient of dP by ΔV_1 , we find :

$$dl = \frac{l \cdot \Delta V_1 \cdot dP}{(x_1-\alpha)^2 r_1 + 2(x_1-\alpha)(y_1-\beta)s_1 + (y_1-\beta)^2 t_1} \dots \dots (5)$$

Herein ΔV_1 is the increase of volume when 1 mol. solid F sublimates into such a large quantity of vapour that the composition does not change. It follows from (5) : each point of the vapoursaturationcurve moves on increase of pressure ($dP > 0$) away from F ($dl > 0$) and on decrease of pressure ($dP < 0$) towards F ($dl < 0$). We may express this also in the following way : on increase of pressure the vapoursaturationcurve extends itself, on decrease of pressure it contracts.

In a similar way we find : on increase of pressure the vapour-saturationcurve contracts, on decrease of pressure it extends.

When we keep the temperature constant and when we lower the pressure, then the vapoursaturationcurve shall, as it contracts, reduce itself under a definite pressure to the point F . The solid substance F is then in equilibrium with a vapour of the composition F or in other words : the solid substance F sublimates. To every temperature T consequently a definite pressure P belongs, under which F sublimates. When we draw in a P, T -diagram the temperatures and the

corresponding sublimation-pressures, we obtain the sublimationcurve of the substance F . [Confer for instance curve aK in fig. 3 (III)]. Previously we saw that this curve ends in the uppermost sublimationpoint K ; at higher temperatures viz. is formed solid F + liquid + vapour. When the formation of liquid fails to make its appearance, this curve may be extended of course.

II. The equilibrium $F + G$; F is a binary compound, G is a ternary vapour.

With the aid of the vapourleaf of the ζ -surface we find that the vapours, which can be in equilibrium with solid F , form again a curve. When F is a binary compound of B and C , this vapoursaturationcurve has two terminatingpoints on side BC ; the point F is always situated between these two terminatingpoints. Therefore we call this curve circumphased again. Consequently the binary compound can be in equilibrium with a series of ternary vapours and with two binary vapours, consisting of B and C . The equilibrium is determined by (1) when we put herein $\alpha = 0$. We find from this for the vapoursaturationcurve:

$$[x_1 r_1 + (y_1 - \beta) s_1] dx_1 + [x_1 s_1 + (y_1 - \beta) t_1] dy_1 = 0 \quad . \quad (6)$$

[We find this also from (4) by putting herein $\alpha = 0$ and $dP = 0$]. For a terminatingpoint of this curve on the side BC is $x_1 = 0$ and $\text{Lim } x_1 r_1 = RT$; the tangent in this terminatingpoint is consequently fixed by:

$$\left(\frac{dy_1}{dx_1}\right)_{x_1=0} = -\frac{RT + (y_1 - \beta) s_1}{(y_1 - \beta) t_1} = -\frac{y_1(1 - y_1) + y_1 - \beta}{y_1 - \beta} \quad . \quad (7)$$

The first expression is generally applicable; the second only when the gas-laws hold good.

The rules mentioned sub I apply to the movement of this curve on change of P or of T .

In a similar way as we have acted in I, we find also here, that at each temperature a definite pressure exists, under which the vapoursaturationcurve reduces itself to the point F ; this pressure is the sublimation-pressure of the binary compound F . Therefore we may draw in a P, T -diagram a sublimationcurve of F .

III. The equilibrium $F + G$; F is one of the components, G is a ternary vapour.

We find that the vapours, being in equilibrium with solid F , form again a curve. When F is the component B , this vapoursaturationcurve has two terminatingpoints, the one on side BA , the other on side BC . The component B can, therefore, be in equilibrium with

a series of ternary and with two binary vapours. The one binary vapour contains B and C , the other B and A . The equilibrium is determined by (1) when we put herein $\alpha = 0$ and $\beta = 0$. The rules mentioned above, apply again to the movement of this curve on change of P or of T . The same as in the case I applies to the disappearance of the vapour saturation curve in point B , to the sublimation-pressure and to the sublimation curve of B .

IV. The equilibrium $F + F' + G$; G is a ternary vapour.

We distinguish herewith two cases, according as the solid substances together contain the three components or not.

1. F and F' contain together the three components.

The line FF' consequently is situated within the triangle; of course this is always the case, when one of the substances or both are ternary compounds. It may however be also the case when both substances are binary compounds and even when one of those is one of the components.

The equilibrium $F + F' + G$ is, under a constant P and at a constant T , invariant; this means that at a given temperature and under a given pressure the vapour has a fixed composition. We may understand this also in the following way. We imagine under the given P and at the given T the vapour saturation curves of F and F' to be drawn. These may either intersect one another or not; they can touch one another as transition-case. When they do not intersect one another, no vapours exist; when they intersect one another, two vapours G_1 and G_2 exist, which may be in equilibrium with $F + F'$, both these vapours are situated on the two sides of the line FF' . The points F , F' and r may be situated with respect to one another in three ways:

A. The point r is situated between F and F' ; consequently the two curves touch one another outwardly in r . Consequently the reaction $F + F' \rightleftharpoons G$ may occur. When we bring F and F' into a space, a part of each of these substances evaporates in order to form the vapour G . We call this a congruent sublimation of $F + F'$.

B. The point F' is situated between F and r ; both the curves touch one another in r , consequently externally; the vapour saturation curve of F surrounds that of F' . Consequently the reaction $F' \rightleftharpoons F + G$ may occur. When we bring F and F' into a space, then, in order to form the vapour G , only a part of F' shall evaporate, while at the same time solid F is separated. In order to obtain the equilibrium $F + F' + G$, consequently we have only to

bring a sufficient quantity of F' into a space. We call this an incongruent sublimation of $F + F'$.

C. The point F is situated between F' and r . This case is exactly analogous with the previous.

D. As transition case between A and B (or C) point r coincides with F' (or F). We shall refer to this later.

When we lower the pressure below P_r , the points of intersection disappear. In the case, mentioned sub A , then the two curves are situated outside one another; the equilibria $F + G$ and $F' + G$ then both occur in stable condition. On further decrease of P these curves disappear; that of F under the sublimation pressure of F , that of F' at the sublimation pressure of F' .

In the case B the two curves touch one another internally in r ; further the curve of F' is surrounded by that of F . On decrease of P both the curves contract and then two cases are imaginable. When in the vicinity of r curve F contracts more rapidly than curve F' , two points of intersection arise; when, however, curve F' contracts more rapidly than curve F , curve F' happens to fall completely within curve F . In order to show that only this latter is the case, we apply (5) to the point of contact r of the two curves. When we represent Fr by l , formula (5) is true for curve F . When we represent $F'r$ by l' , then for curve F' a formula (5) is true, in which l , α and β are replaced by l' , α' and β' . As the value of ΔV_1 is very approximately the same in both the formulae, the relation $dl : dl' = l' : l$ follows. This means: on change of P the velocities of the two curves in the vicinity of their point of contact are in inverse ratio to one another, as the distances from r to F and F' . In the case, now under consideration, ($l > l'$) curve F' consequently moves in the vicinity of the point r more rapidly than curve F . On increase of P consequently two points of intersection arise; on decrease of P these points of intersection disappear and curve F' is completely surrounded by curve F . The equilibrium $F + G$ occurs, therefore, in stable condition; the equilibrium $F' + G$ can occur only in metastable condition.

When we lower the pressure still further, firstly curve F' disappears and afterwards curve F ; consequently the sublimation-point of the substance F' is metastable. In the case A , F and F' may both sublime without decomposition; in the case B only F sublimes without decomposition, while F' converts itself into $F + G$.

As to the case B analogous considerations apply to the case C .

From the previous considerations among others the following can be deduced: To each temperature T belongs a definite congruent or

incongruent sublimation pressure of $F + F'$. This sublimation pressure is higher than that of each of the substances F and F' separately, independent of whether both or only one of them has a stable sublimation pressure.

When we draw in a P, T -diagram the temperatures and the corresponding sublimation pressures of F , F' and $F + F'$, we obtain three curves. In fig. 1 (VII) aK is the sublimation curve of F , $a'K'$ that of F' and $a''D$ that of $F + F'$. According to the previous curve $a''D$ must of course be situated higher than the curves aK and $a'K'$. Formerly we saw that these curves terminate in K , K' and D ; when the formation of liquid fails to come, we can pursue them further.

In the case A the curves aK , $a'K'$ and $a''D$ can be realised in stable condition; for this we must bring into a space solid F , or F' or $F + F'$ and we must take care that the solid substances are not evaporated completely. In fig. 1 (VII) $a'K'$ is situated above aK , the reverse can of course be the case also.

In the case B only the curves aK and $a''D$ may be realised in stable condition, for this purpose we must bring into a vacuum F or $F + F'$. When, however, we bring F' into a space, then solid $F' +$ vapour F' is not formed, but in more stable condition $F + F' +$ vapour. Consequently we do not determine the sublimation curve $a'K'$ of F' , but that of $F + F'$, therefore, curve $a''D$. We would be able to determine the curve $a'K'$, only when the reaction $F' \rightarrow F + G$ failed to come. Further it is apparent that curve $a'K'$ must be situated higher than aK .

Analogous considerations apply to the case C as in the preceding case B .

In the transition case D we assume that r coincides with F . While the cases A , B , and C may occur at a series of temperatures, D occurs at a definite temperature only. In order to understand this, we imagine the vapour saturation curves of F and F' , which touch one another in a point r on the line FF' . When we change the temperature, we must also change the pressure, in order to let the two curves touch one another again; their point of contact r however, shall also get another place on the line FF' . Consequently on change of T not only the sublimation-pressure of $F + F'$, but also the composition of the vapour r changes. As, therefore, the point r shifts on change of temperature along the line FF' , it may coincide at a definite temperature with F' . The vapour saturation-curve of F' is reduced in this case to the point F' and that of F goes through the point F' . The pressure corresponding with this

temperature is consequently the sublimation pressure of F' . Therefore we find: r can coincide with F' ; the equilibrium $F + F' + G$ passes then into $F + F' + \text{vapour } F'$. This can only be the case at a definite temperature and under a corresponding pressure; this pressure is the sublimation-pressure of F' .

In the P, T -diagram the sublimation-curves of $F + F'$ and of F' have, therefore, a point in common with one another, as the first curve is situated generally above the second, the two curves touch consequently one another in this point. We may express this also in the following way: when in the concentration diagram the common point of contact of two vapour saturation curves goes through F' , then in the P, T -diagram the sublimation curves of $F + F'$ and F' touch one another.

This point of contact divides both the curves into two parts. At the one side of this point on the curve of $F + F'$ congruent sublimation takes place and the curve of F' is stable; at the other side of this point on the curve of $F + F'$ incongruent sublimation takes place and the curve of F' is metastable.

2. F and F' contain together two components only.

The line FF' coincides, therefore, with one side of the triangle. This is always the case when both the substances are components; it may yet also be the case when one of them or both substances are binary compounds. The previous considerations sub IV. 1. apply still also now, with slight changes however, which we shall indicate briefly. Firstly we take (at T constant) a pressure, under which the two vapour saturation curves intersect one another. The two curves have, however, one point of intersection now, so that only one equilibrium $F + F' + G$ occurs. When we assume, for fixing the ideas, that F and F' contain together the components B and C , this point of intersection moves on decrease of pressure towards the side BC , in order to fall on the side BC under a definite pressure P_r . As r is now a binary vapour, the equilibrium $F + F' + G_r$ is binary; P_r is the sublimation pressure of $F + F'$.

Although F , F' and r are situated on a straight line, yet the two curves do not touch one another in this point r in this case; this is, as we have seen above, indeed the case when r is situated within the triangle. The cases A , B and C of IV. 1. apply to the position of the points F , F' and r with respect to one another.

On further decrease of pressure the two curves contract, the same as is described in IV. 1 applies to their position with respect to one another, the considerations given there about the sublimation-curves remain also valid here.

It follows immediately from the direction of the tangent which is determined by (7) that, as has been said above, the two curves do not touch one another in the point r on side BC . As this direction depends not only on y_1 , but also on β , and as β is different for F and F' , the two tangents do not coincide.

V. The equilibrium $F + F' + F'' + G$; G is a ternary vapour.

We may also distinguish here two cases, according as the solid substances contain together the three components or not.

1. F , F' and F'' are not situated on a straight line.

As the three components occur in four phases, the equilibrium is monovariant, consequently at each temperature it exists under a definite P only and also the vapour has a definite composition. We can understand this also in the following way. We imagine the vapour saturationcurves of F , F' and F'' to be drawn for any T and P ; it is evident that as a maximum six points of intersection can occur. Now we change the pressure, while the temperature remains constant; a definite pressure P_u will occur, under which the three curves go through one and the same point u . Consequently the equilibrium $F + F' + F'' + G$ occurs under a definite pressure P_u and the vapour G has then the composition u . As each curve intersects each of the two other curves in two points, P_u is higher than the sublimationpressure of the three pairs of liquids: $F + F'$, $F + F''$ and $F' + F''$. Consequently we find: the sublimationpressure of $F + F' + F''$ is larger than that of $F + F'$, $F + F''$ and $F' + F''$ and, therefore, also larger than that of F , F' , and F'' .

Now we can distinguish three cases, according to the position of u with respect to the solid substances.

A. The reaction $F + F' + F'' \rightleftharpoons G$ occurs. When we bring, therefore, the three substances into a space, a part of each of these substances evaporates in order to form the vapour G . Consequently we have a congruent sublimation of $F + F' + F''$.

B. The reaction $F + F' \rightleftharpoons F'' + G$ occurs. When we bring F , F' and F'' into a space, consequently, in order to form G , only a part of F and F' will evaporate, while at the same time solid F'' is deposited. In order to obtain the equilibrium $F + F' + F'' + G$, we have, therefore, only to bring a sufficient quantity of $F + F'$ into a space. Consequently we have an incongruent sublimation of $F + F' + F''$.

C. The reaction $F \rightleftharpoons F' + F'' + G$ occurs. When we bring the three solid substances into a space, then, in order to form the vapour G , only a part of F will evaporate, while at the same

time solid $F' + F''$ is deposited. In order to obtain the equilibrium $F + F' + F'' + G$, consequently we have only to bring a sufficient quantity of F into a space. We have, therefore, again a congruent sublimation.

D. The vapour G is represented by a point, which is situated with two of the solid substances on a straight line. We shall refer to this later.

When we change the temperature, then also the sublimation-pressure of $F + F' + F''$ changes, consequently in a P, T -diagram a sublimationcurve of $F + F' + F''$ may be drawn. Herein the sublimationcurve of $F + F' + F''$ is situated higher than that of $F + F'$, $F + F''$ and $F' + F''$, that of $F + F'$ higher than that of F and F' , that of $F + F''$ higher than that of F and F'' and that of $F' + F''$ higher than that of F' and F'' . Of these seven curves, several may represent metastable conditions. To each of these sublimationcurves applies:

$$T \frac{dP}{dT} = \frac{\Delta W}{\Delta V} \dots \dots \dots (8)$$

Herein ΔW is the heat, which must be added, ΔV the change of volume, when a reaction occurs under a constant P and at a constant T between the phases, which are in equilibrium. When the gas-laws are valid (8) can also be written in another form.

We can represent the sublimationcurve of $F + F' + F''$ also in the concentration-diagram. At change of T we change viz. not only the sublimationpressure, but also the composition of the vapour G (point u). The point u consequently traces a curve in the concentration diagram, the sublimationcurve, of $F + F' + F''$. With each point of this curve a definite T and P correspond.

When this curve intersects one of the sides (or its prolongation) of the threephase-triangle $FF'F''$, the transitioncase mentioned sub D occurs. We assume that this point of intersection u is situated on the line FF' . Consequently a definite temperature T_u and a definite pressure P_u belong to this point u . When we imagine the vapoursaturation-curves of F , F' and F'' to be drawn, it is apparent that those of F and F' touch one another in the point u . Consequently the pressure P_u is the congruent or incongruent sublimation-pressure of $F + F'$ belonging to the temperature T_u . In the P, T -diagram the sublimation-curves of $F + F' + F''$ and $F + F'$ will therefore, touch one another at the temperature T_u . Consequently we find: when in the concentration-diagram the sublimationcurve of $F + F' + F''$ intersects the line FF' , then in the P, T -diagram the sublimationcurves of $F + F' + F''$ and $F + F'$ touch one another in the P, T -diagram.

We may also imagine the case that the sublimationcurve of $F + F' + F''$ goes casually through the point F . We see easily that then in the P, T -diagram the sublimationcurves of $F + F' + F''$, $F + F'$, $F + F''$ and F touch one another.

The sublimationcurve of $F + F' + F''$ ends when a new phase X occurs; X can be a solid substance or a liquid. This equilibrium $F + F' + F'' + X + G$ is invariant; it exists, therefore, only at a definite T and under a definite P . In the P, T -diagram it is consequently represented by a point, the quintuple point. Five quadruplecurves proceed from this quintuplepoint, the position of these curves and of the threephase regions with respect to one another is fixed by definite rules and is dependent on the position of the five phases in the concentration-diagram.¹⁾

2. F, F' and F'' are situated in a straight line.

We distinguish, with respect to the position of this line $FF'F''$ two cases.

A. The substances together contain the three components, the line $FF'F''$ is, therefore, situated within the components-triangle. In order to find the vapour, which is in equilibrium with $F + F' + F''$, we may act in the following way. We represent the ζ 's of the solid substances F, F' and F'' by F_1, F_1' and F_1'' . As F, F' and F'' are situated on a straight line, F_1, F_1' and F_1'' are situated in a vertical plane, but generally not on a straight line. Consequently the equilibrium $F + F' + F''$ cannot occur and of the equilibria $F + F', F + F''$ and $F' + F''$ two (one) are stable and, therefore, one (two) are metastable. Now we take a definite P and T ; we keep the temperature constant and we change the pressure; under a definite pressure the points F_1, F_1' and F_1'' fall then in a straight line, so that the equilibrium $F + F' + F''$ occurs.

When this line is situated below the vapourleaf of the ζ -surface, then the equilibrium $F + F' + F''$ is stable; we can construct then through this line two tangentialplanes to the vapourleaf; we call u and v the projections of the two points of contact. These points u and v are situated on either side of the line $FF'F''$. At the assumed temperature consequently a pressure $P_u = P_v$ exists, under which occur the equilibria: $F + F' + F''$, $F + F' + F'' + G_u$ and $F + F' + F'' + G_v$.

Generally the vapoursaturationcurves of F, F' and F'' intersect one another in six points; it is apparent from the previous that

¹⁾ F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOOM, III¹, 218—248.

they intersect one another under the pressure $P_u = P_v$ only in two points, viz. u and v . It follows from the intersection of these curves that the pressure $P_u = P_v$ is greater than the sublimation pressure of $F + F'$, $F + F''$ and $F' + F''$.

We have seen above that at each temperature a pressure $P_u = P_v$ exists, under which the points F_1 , F_1' and F_1'' , fall in a straight line. When this line is situated below the vapourleaf of the ζ -surface, the equilibria: $F + F' + F''$, $F + F' + F'' + G_u$ and $F + F' + F'' + G_v$ occur in stable condition. When this line is situated above the vapourleaf or when it intersects the vapourleaf, then the equilibrium $F + F' + F''$ is metastable and the equilibria $F + F' + F'' + G$ are impossible. As transition-case this line touches the vapourleaf at a definite temperature T_r and under a corresponding pressure P_r ; the projection r of the point of contact is situated on the line $FF'F''$. The vapour saturation curves of F , F' and F'' touch one another at this temperature and under this pressure consequently in the point r . In this transition case the vapour pressure is P_r , therefore, not larger but equal to the sublimation pressure of $F + F'$, $F + F''$ and $F' + F''$.

When we bring the three substances at a given temperature into a space, then vapour is formed, the composition of which is represented by a point of the line $FF'F''$. It is apparent from this that the equilibrium $F + F' + F'' + G_u$ (or G_v) cannot arise in this way, unless casually the temperature T_r was chosen. Therefore, we shall not call the pressure $P_u = P_v$ the sublimation pressure, but the equilibrium pressure of $F + F' + F''$. When we bring together the three solid phases into a space, generally, therefore, one of them will disappear; then one of the equilibria $F + F' + G$, $F + F'' + G$ or $F' + F'' + G$ is formed. Then the pressure becomes also not the equilibrium pressure $P_u = P_v$, but one of the lower sublimation pressures.

We may draw the equilibrium $F + F' + F'' + G$ as well in the P, T , as in the concentration diagram. When we draw the compositions of the vapours G_u and G_v in the concentration diagram, the points u and v trace a curve on change of T . Definite T and P correspond with each point of this curve. At the temperature T_r the points u and v coincide in the point r of the line $FF'F''$. This point r divides the curve into two parts; with each point u of the one branch viz. a point v of the other branch corresponds and in this way, that a same T and P belong to these points. Hence it follows that along this curve in the point r , T and P (consequently T_r and P_r) are maximum or minimum.

In order to examine this more in detail, we take the conditions of equilibrium for $F + F' + F'' + G$; they are:

$$Z_1 + (\alpha - x_1) \frac{\partial Z_1}{\partial x_1} + (\beta - y_1) \frac{\partial Z_1}{\partial y_1} - \zeta = 0. \quad (9)$$

and still two of such equations wherein the magnitudes, which relate to the solid substance F , have been replaced by those of F' and F'' . With the aid of (9) we may write them also in this way:

$$(\alpha - \alpha') \frac{\partial Z_1}{\partial x_1} + (\beta - \beta') \frac{\partial Z_1}{\partial y_1} + \zeta' - \zeta = 0 \quad (10)$$

and

$$(\alpha - \alpha'') \frac{\partial Z_1}{\partial x_1} + (\beta - \beta'') \frac{\partial Z_1}{\partial y_1} + \zeta'' - \zeta = 0 \quad (11)$$

The conditions (9), (10) and (11) are generally valid, when F , F' and F'' are situated on a straight line, we have

$$(\beta - \beta') : (\alpha - \alpha') = (\beta - \beta'') : (\alpha - \alpha'') = \mu \quad (12)$$

It follows from (10) and (11) with the aid of (12) that:

$$(\alpha'' - \alpha') \zeta + (\alpha - \alpha'') \zeta' + (\alpha' - \alpha) \zeta'' = 0. \quad (13)$$

This equation (13) is at the same time the condition for the occurrence of the equilibrium $F' + F'' + F$. It is apparent from this, therefore, as has already been found above, that the equilibria $F + F' + F''$ and $F + F' + F'' + G$ occur at the same T and under the same P . From (13) follows:

$$\frac{dH}{dT} = \frac{(\alpha'' - \alpha')\eta + (\alpha - \alpha'')\eta' + (\alpha' - \alpha)\eta''}{(\alpha'' - \alpha')v + (\alpha - \alpha'')v' + (\alpha' - \alpha)v''} = \frac{\Delta H}{\Delta V} = \frac{\Delta W}{T\Delta V} \quad (14)$$

which is true as well for the equilibrium $F + F' + F''$ as for $F + F' + F'' + G$. The meaning of ΔH , ΔW and ΔV is easily seen. When we choose the reaction in such a way that ΔW is positive, then ΔV may be ≥ 0 . The equilibrium $F + F' + F'' + G$ is fixed by (9), (10) and (14). Now we shall consider it in the point r : the point of intersection of the equilibrium-curve with the line $FF'F''$. In this point:

$$(\beta - \beta') : (\alpha - \alpha') = (\beta - y_1) : (\alpha - x_1) = \mu \quad (14)$$

when we develop (9) into a series, we find:

$$\left. \begin{aligned} (r_1 + \mu s_1) dx_1 + (s_1 + \mu t_1) dy_1 + \left(\frac{V_1 - v}{\alpha - x_1} + A \right) dP - \left(\frac{H_1 - \eta}{\alpha - x_1} + B \right) dT + \\ + \frac{1}{2} \left(-\frac{r_1}{\alpha - x_1} + C \right) dx_1^2 + \left(-\frac{s_1}{\alpha - x_1} + D \right) dx_1 dy_1 + \\ + \frac{1}{2} \left(-\frac{t_1}{\alpha - x_1} + E \right) dy_1^2 + \frac{R}{\alpha - x_1} = 0. \end{aligned} \right\} \quad (15)$$

It follows from (10) that:

$$\left. \begin{aligned} (r_1 + \mu s_1) dx_1 + (s_1 + \mu t_1) dy_1 + \left(\frac{v' - v}{\alpha - \alpha'} + A \right) dP - \left(\frac{\eta' - \eta}{\alpha - \alpha'} + B \right) dT + \\ + \frac{1}{2} C dx_1^2 + D dx_1 dy_1 + \frac{1}{2} E dy_1^2 + \frac{R'}{\alpha - \alpha'} = 0 \end{aligned} \right\} \quad (16)$$

We may easily calculate what is represented in (15) and (16) by A , B , C , D and E . R and R' contain only terms which are infinitely small with respect to those, which have been written down already. When we subtract (15) from (16) and when we put for the sake of abbreviation:

$$\frac{1}{2} r_1 dx_1^2 + s_1 dx_1 dy_1 + \frac{1}{2} t_1 dy_1^2 = K \quad (17)$$

then we find:

$$\left(\frac{V_1 - v}{\alpha - \alpha_1} - \frac{v' - v}{\alpha - \alpha'} \right) dP - \left(\frac{H_1 - \eta}{\alpha - \alpha_1} - \frac{\eta' - \eta}{\alpha - \alpha'} \right) dT - \frac{K}{\alpha - \alpha_1} = R'' \quad (18)$$

Herein R'' contains only terms which are infinitely small with respect to dP , dT , dx_1^2 , $dx_1 dy_1$ and dy_1^2 . Now between the phases F , F' and G we imagine a reaction to take place, at which the unity of quantity of vapour is generated. Let ΔV_1 be the increase of volume, ΔH_1 the increase of entropy at this reaction. When we put as first approximation in (18) $R'' = 0$, then follows:

$$\Delta V_1 \cdot dP - \Delta H_1 \cdot dT = K \quad (19)$$

Hence follows with the aid of (14):

$$\left(\Delta V_1 - \frac{\Delta H_1}{\Delta H} \cdot \Delta V \right) dP = K \quad (20)$$

ΔV_1 is a thousand times larger than ΔV ; consequently the coefficient of dP is generally positive; it is apparent from (17) that K is also positive. Therefore we find $dP > 0$ or: the pressure is a minimum in r . As $dT = \frac{\Delta V}{\Delta H} \cdot dP$, dT is ≥ 0 ; consequently the temperature is in r maximum or minimum.

Now we consider the P, T -diagram. The equilibrium $F + F' + F''$ is represented by a curve; as on this curve the conversion of one of the solid substances takes place into the two others, or reversally, we call this curve the conversion-curve. It follows from (14) that on increase of T the pressure can as well increase as decrease. The equilibrium-curve $F + F' + F'' + G$ coincides with the conversion-curve; it covers this curve, however, only partly. As the pressure is a minimum in its terminatingpoint r , it proceeds starting from r towards higher pressures. Through this point r moreover go the

sublimation-curves of $F + F'$, $F + F''$ and $F' + F''$. It is apparent from (8) that these three curves do not touch one another in r , but they intersect one another. According to our previous considerations, these curves, except in the point r , are always situated below the equilibrium-curve $F + F' + F'' + G$. Further it appears that at the one side of the point r two of these curves represent stable conditions, on the other side one of these curves.

Consequently we find: in the point r five curves come together, the conversion-curve ($F + F' + F''$) and the equilibrium-curve ($F + F' + F'' + G$) of which coincide. This last curve ends in r ; the four other curves go through this point; the point r divides these curves into two parts, the one of which represents stable conditions and the other metastable conditions.

We find these results also in the following way. We may consider the equilibrium $F + F' + F'' + G$, when G is represented by a point of $F'F''$, consequently it is invariant and it can be represented in the P, T -diagram by a point r . Therefore, through r four triple-curves must go, viz. the conversion-curve ($F + F' + F''$) and the sublimation-curves of $F + F'$, $F + F''$ and $F' + F''$. When we consider stable conditions only, we may say that these curves start all from r or that they end in r . The situation of these four curves with respect to one another is fixed by a definite rule.¹⁾ We may determine the direction of these curves with the aid of the isovolumetric and the isentropic reaction, which can occur between these 4 phases.²⁾ Let the isentropical reaction be:



wherein one or two of the coefficients n , n' and n'' can be negative; in the ordinary manner we must write the phases relating to that in the right part of the equation. As the volume of the vapour G is very large with respect to that of the solid substances, the reaction will take place from the right to the left with decrease of volume. The equilibria, which are formed at this reaction (from the right to the left) occur consequently under higher pressures. As we, in order to get the equilibrium $F + F' + F''$, must cause the reaction to take place from the right to the left, the conversion-curve ($F + F' + F''$) will go consequently always starting from r towards higher pressures. This is in accordance with our previous considerations,

¹⁾ F. A. H. SCHREINEMAKERS, Z. f. Phys. Chem. 82 59 (1913).

F. E. C. SCHEFFER, These Proceedings 21 446 (1912).

²⁾ F. A. H. SCHREINEMAKERS, Die heterogenen Gleichg. von BAKHUIS ROOZEBOOM, III^e, 219—220.

We may also represent the isovolumetric reaction by (21), then the coefficients will have another value. As at the reaction from right to left heat can as well be given out as absorbed, the equilibrium $F + F' + F''$ can, therefore, starting from r go as well towards higher as towards lower temperatures.

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(To be continued).

Chemistry. -- "Action of Sunlight on the Cinnamic Acids". By Dr. A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of March 27, 1915).

Some time ago ¹⁾ I communicated that *allo*-cinnamic acid is converted in sunlight into α -, β -truxillic acid and normal cinnamic acid.

In a communication as to this photo-action in the Recueil ²⁾ I drew, in connexion with the progressive change of the transformation and also because the addition of normal cinnamic to the *allo*-acid increased the quantity of β -truxillic acid, the conclusion that β -truxillic acid was formed by the combination of one molecule of *allo*-acid with one molecule of normal acid.

For a further study of β -truxillic acid it was of great importance to possess larger quantities of the same.

The preparation may take place from the split off coca acids, or from the *allo*-cinnamic acid that has been affected by sunlight.

The first process is tedious and, from a comparatively large quantity of split off acids, it yields but a small amount of β -truxillic acid.

In connexion herewith, attention may be called to the fact that commercial cinnamic acid may often contain not unappreciable quantities of β -truxillic acid which very likely has got into it in the preparation of the cinnamic acid from the above coca acids (both acids possess calcium salts sparingly soluble in water). For instance, a product called Ac. cinnamylicum puriss. D. Ap. V. contained 1.8% and another labelled Ac. cinnamylicum synth. puriss 3% of β -truxillic acid, whilst in the Ac. cinnamylicum purum of the same works occurred a trace. The β -truxillic acid, being the stronger acid, may be readily separated from the cinnamic acid by dilute aqueous sodium hydroxide.

¹⁾ Proc. 14, 100 (1911).

²⁾ R. 31, 258 (1912).