c. in the case of change of solubility and surface-tension through combining with salt- or sugar-solutions.

Divergencies are seen on either side. Some strong-smelling scents, moschus and scatol, set up a sensation even in dilutions, the electrifying power being next to none. With antipyretica on the contrary, the smell-intensity is all but inappreciable, the electrifying power very considerable. For an interpretation we must, in the present stage of our research, look to the five conditions, just mentioned, upon the fulfilment of which the properties depend. Maybe the study of the dielectric-constant will throw some more light on the subject in connection with A. Coehn's theory of contact-electricity, according to which the difference of potential, in the case of mutual contact of two substances is proportional to the difference of the dielectric constants [1]. The differences between the dielectric-constants of odorous substances and those of water are generally very great, so that likewise we may look for great charges on numberless droplets, when odorous molecules accumulate on their surfaces in virtue of the fall of the surface-tension. The rapid evaporation from the measureless area makes these differences all the more probable, especially when a slight rise of the temperature increases the evaporation and the sprayer is placed at the proper distance from the intercepting screen.

Chemistry. — "*The equilibrium solid-liquid-gas in binary systems which present mixed crystals*". (*Fourth communication*). By Prof. H. R. Kruyt. (Communicated by Prof. Ernst Cohen).

(Communicated in the meeting of September 30, 1916.)

1. In the former communication [2] has been communicated a research of Dr. W. D. Helderman and myself on the three-phase equilibrium solid-liquid-gas (S L G) in the system bromine-iodine. The three-phase line exhibited in its PT-projection two maxima and one minimum, a peculiarity which is closely connected with the appearance of the compound IBr. For the general knowledge of the binary systems it is not uninteresting to more closely consider these equilibria; all the more so because the appearance of two maxima and one minimum on the melting branch of a com-

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[1] A. Coehn u. U. Raydt. Göttinger Nachrichte 1909 p. 263.

[2] Proc. Royal Ac. A'dam, Meeting of June 1916.

pound is also possible when no formation of mixed-crystal takes place whatever. The mutual proportions, however, are very different there and, as we will notice below, the conditions for the appearance of these remarkable points are also different.

2. The general equation for the three-phase equilibrium in a binary system can, as is well-known [1]), be written as follows.

$$T \frac{dP}{dT} = \frac{(x_S - x_L) Q_{GS} - (x_S - x_G) Q_{LS}}{(x_S - x_L) V_{GS} - (x_S - x_G) V_{LS}} \quad \ldots \quad (1)$$

or

$$T \frac{dP}{dT} = \frac{Q_{GS} - \dfrac{x_S - x_G}{x_S - x_L} Q_{LS}}{V_{GS} - \dfrac{x_S - x_G}{x_S - x_L} V_{LS}} \quad \ldots \ldots \quad (2)$$

in which the symbols with a double phase-index indicate respectively the heat and the change in volume when one gram-molecule of one phase is dissolved in an infinitely large quantity of the other, the external conditions being kept constant. Q_{GS} has, therefore, the order of a sublimation heat, Q_{LS} that of a melting heat. Hence Q_{GS} is usually a few times greater than Q_{LS}. Likewise V_{GS} is always greater than V_{LS} and this in the order of 10^4 times greater.
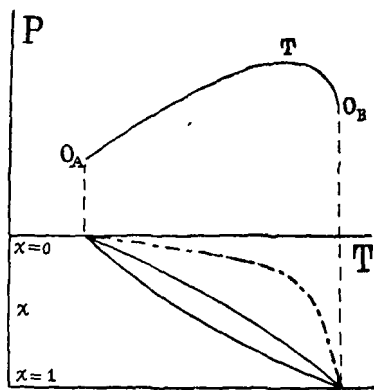

Fig. 1.

Let us now consider first a system with a continuous series of mixed crystals such as the system $p \, Cl_2C_6H_4$ $-p \, Br_2C_6H_4$ [2]), in which the three-phase line has a form as in fig. 1 when sketched as PT- and Tx-projection. We remember that for a maximum (or minimum) it is necessary that the numerator in the equation (2) should become zero and that for this it is required that

$$\frac{x_S - x_G}{x_S - x_L} = \frac{Q_{GS}}{Q_{LS}} \quad \ldots \ldots \ldots \quad (3)$$

[1]) Compare VAN DER WAALS-KOHNSTAMM, Lehrbuch der Thermodynamik II p. 521 et seq. (Leipzig 1912).

[2]) Comp. my communications I and II in these Proc. 1909, 537 and 1910, 206 also Zeitschr. f. physik Chem. 79, 657 (1912).

Now it will be evident how the formula describes the course taken by the three-phaseline. For in the Tx-projection we notice that in O_A $x_S = x_L = x_G$, and that starting from O_A, the fraction $\dfrac{x_S - x_G}{x_S - x_L}$ gradually increases and thus the possibility exists that it attains to a value equal to $\dfrac{Q_{GS}}{Q_{LS}}$.

Then $\dfrac{dP}{dT} = 0$, the maximum is attained ; $\dfrac{dP}{dT}$ then becomes negative and the line on the PT-projection falls to O_B[1]).

The question whether indeed a maximum occurs thus depends on the concentration ratios of the coexisting phases and those of the heat values. By means of another method we previously arrived at a similar result (see our first communication).

The three-phase line proceeds without a maximum or minimum if the component A which at each temperature has the highest vapour pressure, has a higher triplepoint temperature than B. $x_S—x_L$ is then continuously negative. which prevents the numerator from becoming zero. The impossibility of a maximum is moreover directly evident by looking at the spacial figure for that case.

3. In Fig. 2 the diagram (PT and Tx) is drawn for a system in which occurs a compound [2]) 'on the melting branch' of which in succession $x_S = x_L$, $x_S = x_G$ and $x_L = x_G$ is realised. In such case that branch exhibits also two maxima and one minimum. A further remarkable fact is the occurrence of a point towards $\dfrac{dP}{dT} = \infty$, and moreover the maximum point of sublimation and the

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[1]) In the system p $Cl_2C_6H_4 — p$ $Br_2C_6H_4$ the maximum lies at about 76°. If by interpolation we calculate the composition of the coexisting phases at that temperature we find approximately

$$x_S = 0.94$$
$$x_L = 0.76$$
$$x_G = 0.27$$

from which follows

$$\frac{x_S - x_G}{x_S - x_L} = \frac{Q_{GS}}{Q_{LS}} = 3,7$$

which is a rather low value for that ratio.

[2]) For a detailed description of this class of three-phase lines compare v. d. WAALS-KOHNSTAMM l c ; H. W. BAKHUIS ROOZEBOOM, These Proceedings 1905 ; G. II. LEOPOLD, Dissertation. Amsterdam 1906 ; A. SMITS, Zeitschr. f. physik. Chem. **78**, 708 (1912).

Fig. 2.

minimum melting point in which points the lines for the quasi-unary two-phase equilibrium compound $+ L$ and compound $+ G$ meet the three-phase line, respectively.

The connexion between this graphic representation of the three-phase equilibrium and the analytical expression used in § 2 has been worked out in the papers cited. On CTF the concentration fraction $\dfrac{x_S - x_G}{x_S - x_L}$ grows steadily greater (compare th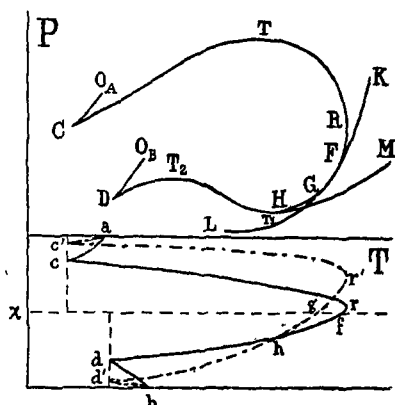e Tx-projection). The value for the maximum T is soon attained, then the numerator of equation 2 becomes negative. Just before x_S becomes $= x_L$ (comp. equation 1)

$$(x_S - x_L) \Gamma_{GS} \text{ will become } = (x_S - x_G) V_{LS}$$

and, therefore $\dfrac{dP}{dT} = \infty$ (point R) for the concentration fraction approaches ∞ (when $x_S = x_L$) and so a value of about 10^4 is once attained.

The numerator then has a great negative value, the denominator starts from R, also negative; hence $\dfrac{dP}{dT}$ positive. In F $x_L = x_S$; the concentration fraction in equation (2) which before F is very largely positive, becomes very largely negative beyond F. This negative value declines until in G it has become 0, as in that point $x_G = x_S$. The concentration fraction now again assumes a rising positive value and in H it becomes 1 as in that point $x_G = x_L$ and it will thus soon again attain a value causing

$$\frac{x_S - x_G}{x_S - x_L} = \frac{Q_{GS}}{Q_{LS}} \quad \ldots \ldots \ldots \quad (3)$$

we then are in the minimum T. For if now we examine the Tx figure between h and d we readily notice that after the crossing of the G- and L-branch in h $x_S - x_G$ increases much quicker in (negative) value than $x_S - x_L$; hence, the concentration fraction thus continues to rise at first, but in dd', x_L and x_G do not usually differ much [1]) as both are situated very close to the B-axis. Consequently the value of the concentration fraction has again begun to fall and once again the relation (3) has been satisfied, so causing the maximum T to appear. For the appearance of the minimum T_1 and the

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[1]) Much less than drawn in Fig. 2.

second maximum T_2 the crossing at H and the appearance of a minimum pressure in the Px-sections of the system is, therefore, a necessity.[1]

4. Now in the system Br-I also appear two maxima and one minimum, but in this system neither x_S becomes $= x_L$, nor $x_S = x_G$, nor $x_L - x_G$ at any temperature, as has been proved by the determinations of the melting and boiling curves by MEERUM TERWOGT[2]. Only, the 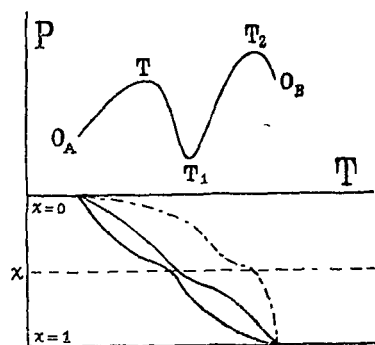differences $x_S - x_G$ and $x_S - x_L$ show and approach to 0 and this is sufficient to cause the appearance of the three marked points. For this we have only to examine Fig. 3, which indicates sketchily the proportions in the system Br-I in PT and Tx figure.

Starting in O_A the value of the concentration fraction $\dfrac{x_S - x_G}{x_S - x_L}$ will at first again increase and the value may become

Fig. 3.

equal to $\dfrac{Q_{GS}}{Q_{LS}}$, thus causing the maximum T to appear. As the numerator in equation (2) here becomes negative, the three-phase line will fall. This fall will be very pronounced, for the denominator of the concentration fraction decreases very strongly. For at about $x = 0.5$ the narrowing on the melting curve is very strong; it is, however, conceivable that the denominator in the second member of equation (2) will not turn to zero, for then the concentration fraction should assume the value 10000.

Meanwhile, not only the denominator of the concentration fraction assumes a small value, but the numerator will also decline particularly after the temperature has been passed at which the narrowing on the melting curve occurs. It is well known that vapour pressure[3] or boilingdiagrams of systems with a compound present a narrowing all the stronger when the dissociation is less. The boiling diagram[4] of the system Br—I also exhibits such a narrowing, even at a temperature about $100°$ above that of the three-phase line. This narrowing

[1] It is meanwhile evident that this relation is not necessarily decisive. For beyond H the concentration fraction must also attaintheratio of the caloric values (Consult the papers cited).

[2] Diss. A'dam 1904 and Zeitschr. f. anorgan. Chem. **47**, 203 (1905).

[3] In this connexion see J. J. VAN LAAR, Zeitschr f. physik Chem. **47**, 129 (1904).

[4] P. C. E. MEERUM TERWOGT, loc. cit.

in the Px-diagrams is strongest in the part of the figure at the side of the component with the smaller vapour tension [1]), hence at the iodine side. Whereas the numerator of the concentration fraction is now declining, its denominator gets larger when we have passed the narrowing in the melting diagram, favourable cooperation for allowing the value of the concentration fraction to rapidly fall again to that of $\dfrac{Q_{GS}}{Q_{LS}}$. The point T_1 will, therefore, be rapidly attained. Indeed it appeared in the research of Dr. HELDERMAN and myself that this point is attained at a temperature about 4° above the melting interval of the mixture $x_S = 0.50$ namely at $x_S =$ about 0.54. From the Tx side of figure 3 we can now readily read that the concentration fraction still continues to decrease but afterwards gradually rises again in consequence of the fact that $x_S - x_L$ decreases more rapidly than $x_S - x_G$. Hence, the possibility of a second maximum T_2 is created.

We will not discuss here any possible intermediate cases where a degeneration of maximum and minimum to points of inflection may take place. If will be quite evident now, that, where the narrowings are decisive for the appearance of the minimum, the above mentioned configuration occurs the more decidedly when the compound is less dissociated.

5. We will now call attention to the difference in behaviour between a compound as explained by Fig. 2 and Fig. 3, that is to say between a dissociating compound and one miscible with its dissociation products in the solid condition. If such a compound without formation of mixed crystals is heated to fusion at a constant pressure the equilibrium will be quasi-unary [2]), the compound has a sharp melting point. With the compound which forms mixed crystals such is not the case, for such a compound has a melting interval. In connexion therewith the equilibria at their own vapour tension, as read off from the PT-diagram are also more complicated.

First of all let us remember that in the point F of figure 2 $x_L = x_S$ and that consequently in equation (2) becomes $T\dfrac{dP}{dT} = \dfrac{Q_{LS}}{V_{LS}}$.

This, however, is the equation for the melting line of the compound;

[1]) VAN LAAR, loc. cit.

[2]) The expression *quasi unary*, *quasi binary* etc seems very appropriate for characterising the condition in which a system behaves as if it possesses one variable (or two, three etc.) less than indicated by the phase rule. (As to these equilibria see BAKHUIS ROOZEBOOM, Heterogene Gleichgewichte I pg. 34 and following).

that line is tangent therefore in F to the three-phase line and F is justly called the minimum melting point. Also in G $x_G = x_S$, hence

$$T \frac{dP}{dT} = \frac{Q_{GS}}{V_{GS}}$$ and the sublimation curve of the compound is tangent

here to the three-phase line. And in H $x_L = x_G$, hence

$$T \frac{dP}{dT} = \frac{Q_{GS} - Q_{LS}}{V_{GS} - V_{LS}} = \frac{V_{GL}}{Q_{GL}}$$

which involves the meeting of the three-phase line and the "line of the minima on the GL surface".

By these tangential contacts the PT-section at the composition of the compound gets the simple form of fig. 4[1]) $LGFK$ is a continuous curve
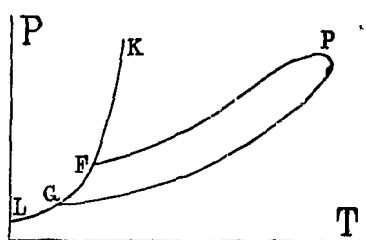

Fig. 4.

although LG is the quasi-unary sublimation curve, GF part of the three-phase line, and FK the quasi-unary melting line of the compound. FP and GP are demarcations for the complete condensation and evaporation, respectively. From a purely unary diagram, this figure is distinguished only by the fact that the triplepoint has grown to a range GF and the phenomena of the condensation and evaporation take place not at a single limit value, but also over an interval.

With a system of the type Br-I the difference with unary behaviour is much greater still. Because two phases nowhere attain the same composition, we miss the tangents at the three-phase line, in
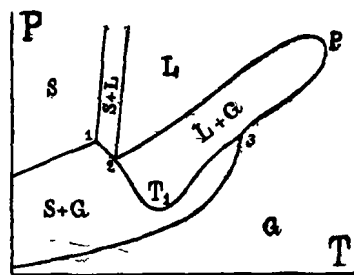
Fig. 5.

fact all lines for quasi-unary equilibrium get doubled to two streak limits. In Fig. 5 we notice the PT-section for $x = 0.50$. Fig. 5 therefore indicates the PT-condition diagram for the compound IBr and it may be readily deduced from the spacial figure (compare Fig. 5 of the third communication) or from our Fig. 3. It is only *one possible* configuration; at the deduction it will be noticed that the mutual relations of the concentrations of coexisting phases decide the form of a figure such as Fig. 5.

When following the section up from lower temperature we intersect first the region $S + G$. In point 1 the section for the first time meets the three-phase region, namely in the line indicating the composition ·of the mixed crystals. In point 2 the liquid branch

[1]) WUITE, Disseit Amsterdam 1909 p. 19.

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is reached; the vapour branch is, of course, only attained at a much higher temperature (point 3) when on the threephase line, $x_G = 0.50$; the three-phase line is then almost sure to have passed the minimum T_1.

From this figure it is readily observed how little the behaviour of the mixture $x = 0.50$ conveys the idea of a single substance. For it is evident from this figure how not only all the sharp demarcations have vanished but how peculiar *retrograde phenomena* (between T_1 and 3) complicate the behaviour. Direct stoechiometric criteria no longer exist for such a compound; it is only recognisable from the general connexion of the phenomena[1]).

6. It is not our intention to discuss the course of the three-phase line in all possible systems with formation of mixed crystal, but it is still of importance to devote some attention to the case that 'a maximum or a minimum appears in the sections of the spacial figure.

In Fig. 6 is drawn the case where in the Tx-sections appears a maximum for the equilibrium S—L, not, however, for the equilibrium L—G. Such a maximum often gives rise to doubt: does it indicate a compound or not? A further discussion of this question will be postponed to a future communication, but here it is important to know the three-phase line of this type of system.

Fig. 6.

In Fig. 6 we notice how, starting in O_A, the three-phase line rises, for the concentration fraction in (2) has a positive value, this rises and can attain the value where equation (3) is satisfied; the maximum T then appears. The numerator of equation (2) now obtains a negative value. As presently x_L will become $= x_S$ the concentration fraction increases very strongly and before x_L becomes $= x_S$ the denominator in equation (2) becomes zero,

so that $\dfrac{dP}{dT}$ becomes $= \infty$ (point R); $\dfrac{dP}{dT}$ then again becomes positive.

Soon x_L now becomes $= x_S$ as represented by point F. This point

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1) Vgl. H. R. KRUYT, Algemeene Theorie en bizondere Ervaring (Amsterdam 1916).

F is in many respects comparable with point F in Fig. 2, also here a line FK for quasi-unary melting phenomena will appear ("line of the maxima" in the melting diagrams at different pressure values), hence we might call point F the "minimum quasi unary melting point" of the system. As starting from F $x_S - x_L$ has a negative value whereas $x_S - x_G$ remains positive; both numerator and denominator in equation (1) will also be negative; a further appearance of a maximum or a minimum is, therefore, excluded (compare § 2 last lines). Only when equalisation of phases takes place, (which involves a minimum in the Px-figure from $S - G$ or $G - L$ equilibria) further remarkable points would be possible, such as a "maximum quasi-unary sublimation point" a minimum and a maximum on the three-phase line etc.

The progressive change of these lines strongly reminds us of that of a compound without formation of mixed crystals but the configuration of Fig. 6 does not give us, however, an indication for the existence of a compound. On the contrary, an eventual decrease of the value $x_G - x_L$ which had such important consequences in § 4 does not affect any peculiarity on the three-phase line, not even a reduction of $x_G - x_L$ to zero in a maximum pressure would have that effect; only $x_G - x_L$ in a minimum would modify the line, but even then the doubt would remain whether we had to do with a chemical compound or not.

7. We must still refer in a few words to a system of the type d and l-carvoxim discussed in the previous communication. After the statement in § 6 it will be evident that the investigation of the three-phase line does not lead to a decision when the compound melts at a higher temperature than that of the components. But there is still another complication in a system of optic antipodes. It happens there that $x_G - x_L$ is *zero* at *all concentrations*. This is the case in the system d- and l α-pipecolin[1]) albeit there occurs undoubtedly a solid racemic compound [2]) in that system [3]).

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[1]). A. Ladenburg, Ber. deutsch. chem. Ges. **44**. 676 (1911); H. R. Kruyt, ibidem pg. 995.

[2]) A. Ladenburg and Sobecki, ibidem **43**, 2374 (1910).

[3]) The fact that, in such a system, all G-L equilibria are quasi-unary is connected with the peculiar small differences of the components; a_1 is there undoubtedly $= a_2$, also $b_1 = b_2$; also a_{12} is evidently equal to a, for then $\dfrac{da_x}{dx} = 0$

and also $\dfrac{db_x}{dx} = 0$ and for

$$\left(\frac{\partial \psi}{\partial x}_{VT}\right)_G = \left(\frac{\partial \psi}{\partial x}_{VT}\right)_L$$

we can simply write then

In the system of the carvoxims it is sure to be the same case and then the equation of the three-phase line becomes

$$T \frac{dP}{dT} = \frac{Q_{GS} - Q_{LS}}{V_{GS} - V_{LS}} = \frac{Q_{GL}}{V_{GL}}$$

The three-phase line simply coincides with the vapour tension line for liquid carvoxim (whether d, l, r or a mixture) between the melting temperature of the components and that of the pseudo-racemic mixed crystal. This curve is then a double line and in a certain sense we might then say that it has one maximum which of course, is plainly noticed in the Px-projection.

But as to the decision between racemic compounds and pseudo-racemic mixed crystals this course of the three-phase line yields no criterion. Only, VAN LAAR [1]) has pleaded for the conception that the form of the melting line of the carvoxims solely points to a compound, whereas TAMMANN [2]) on account of caloric values exactly arrives at the opposite result.

Utrecht, August 1916.   VAN 'T HOFF-*Laboratory*.

Chemistry. — "*On Nitro-derivatives of Alkyltoluidines and the relation between their molecular refractions and those of similar compounds*". By Dr. J. D. JANSEN. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of June 24, 1916).

Some years ago appeared a communication from HANTZSCH [3]) on chromoisomerism and homochromoisomerism of nitroanilines. In the conclusion of this remarkable publication, HANTZSCH says that yellow and orange di- and tri-nitroanilines, when their molecular refractions are abnormal, probably contain chromophores of different constitution. The *yellow* 3.4. dinitro-dimethyl-aniline and the *orange* 3.4. dinitro-diethyl-aniline, according to his opinion, are not *real-*, but *pseudo-* homologues, which manifested itself in the molecular refractions,

$$mRTl \frac{x_G}{1 - x_G} = mRTl \frac{x_L}{1 - x_L}$$

or

$$x_G = x_L$$

The fact that $a_{12} = a_1$ certainly points out that in the liquid and vapour occur no (or at least *very* few) racemic molecules.

[1]) Zeitschr. f. physik. Chem. **64**, 289 (1908).
[2]) Göttinger Nachrichten 1913.
[3]) B **43**, 1662, (1910).