

*Citation:*

H.R. Kruyt, The equilibrium solid-liquid-gas in binary system which present mixed crystals. (2nd communication), in:

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As the expression  $\Delta'S_m$  is homogeneous in  $\alpha$  and  $\beta$ , there must exist between the coefficients of  $S_m = 0$  resp.  $\frac{m^2}{4} - 1$  and  $\frac{m^2-1}{4} - 1$  relations, if this equation is to pass by means of *affine* transformation into the form  $\psi(\xi) + \psi(\eta) = 2k$ .

§ 6. If we consider the conic represented by  $S_2(x,y) = 0$  and the cubic curve represented by  $S_3(x,y) = 0$ , it is evident that these are symmetric with respect to the line  $y = x$ .

Whilst in § 5 we have found for the coordinates  $x$  and  $y$  of a point of a curve  $S_2(x,y) = 0$ , resp.  $S_3(x,y) = 0$  expressions, which were irrational with respect to the odd function  $\tau = \sigma \cdot \omega(\sigma^2)$ , we can also express the coordinates of the conic and of the *unicursal* cubic curve in *rational* functions of  $\tau$ .

For the conic we have only to put

$$x = \frac{p_2\tau^2 + p_1\tau + p_0}{q_2\tau^2 + q_0}, \quad y = \frac{p_2\tau^2 - p_1\tau + p_0}{q_2\tau^2 + q_0}. \quad (30)$$

and for the rational cubic curve

$$x = \frac{p_3\tau^3 + p_2\tau^2 + p_1\tau + p_0}{q_2\tau^2 + q_0}, \quad y = \frac{-p_3\tau^3 + p_2\tau^2 - p_1\tau + p_0}{q_2\tau^2 + q_0}. \quad (31)$$

Elimination of  $\tau$  out of the equations (30) furnishes

$$(p_0q_2 - p_2q_0)^2(x - y)^2 + p_1^2[q_0(x + y) - 2p_0][q_2(x + y) - 2p_2] = 0, \quad (32)$$

whilst after elimination of  $\tau$  out of the expressions (31) we arrive at

$$(p_0q_2 - p_2q_0)^2[q_2(x + y) - 2p_2](x - y)^2 + [q_0(x + y) - 2p_0][(p_1q_2 - p_3q_0)(x + y) - 2(p_1p_2 - p_0p_3)]^2 = 0. \quad (33)$$

The equations (32) and (33) can now very easily be identified with the standard forms  $S_2 = 0$  and  $S_3 = 0$ .

**Chemistry.** — “*The equilibrium solid-liquid-gas in binary systems which present mixed crystals.*” (2<sup>nd</sup> Communication). By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of May 28, 1910).

In a previous communication<sup>1)</sup> I showed what forms the line of the monovariant three-phase equilibrium solid-liquid-gas can assume in systems in which a continuous series of mixed crystals forms the solid phase. The appearance of the three possible forms (maximum,

<sup>1)</sup> Proc. Vol. XII, p. 537.

minimum or without max. and min.) proved to be dependent on the difference of the triple point pressures of the components and of the form of the melting diagram.

I have started the experimental investigation of this kind of equilibria with the system *paradichloro-* and *paradibromobenzene*, a system in which a complete series of solid-gas equilibria and the boiling point lines have already been determined by KÜSTER<sup>1)</sup>. That system had the great advantage that both its components could be determined analytically in a mixture.

The investigations have been carried out by means of an apparatus the principle of which is the same as that of KÜSTER's, but in which a number of technical improvements have been made in consultation with our mechanician Mr. DE GROOT, thus removing many difficulties. Full details of the experiments will not be given here, but later in the "Zeitschrift für physikalische Chemie". The Figures 1 and 2 will be understood sufficiently after a slight explanation.

In Fig. 1 is shown the section of a diving-bell which plunges into the thermostat *A* (also indicated in Fig. 2). Both the air and the partially fused substance contained in the small basin *I* are stirred by means of the stirrers (*G* and *F*) which are connected with the bell by metallic mercuryseals (*C* and *D*). If after a number of hours the saturated vapour has formed in the bell, some litres of this are drawn off through the tube *L*. In Fig. 2 it will then be seen that this gas passes through a tube placed in the furnace *m* and filled with calcium oxide which decomposes the  $p$   $C_6H_4Cl_2$  and  $p$   $C_6H_4Br_2$  and retains the halogens as  $CaCl_2$  and  $CaBr_2$ , which may be readily determined quantitatively. The amount of gas which has passed out of the bell is ascertained by measuring the water which has run from the aspirator flask *s*.

*defg* is a constant level arrangement and *l* a steam jacket to prevent condensation of the saturated vapour between the thermostat and the combustion tube; *c* is the appertaining boiler.

The extra pressure in the bell is finally read off on the water-filled manometer *O* (Fig. 1).

The water drawn from the aspirator gives us the volume of the gas drawn from the bell in the following manner:

Let us call  $V_1$  the volume wanted,  $V_2$  that of the water passed out;  $T_1$  and  $P_1$  the temperature and pressure in the bell,  $T_2$  and  $P_2$  that in the aspirator;  $\pi_1$  the saturated water vapour pressure at  $T_1^\circ$ ,  $\pi_2$  that at  $T_2^\circ$ , then we have:

<sup>1)</sup> Zeitschr. f. physik. Chem. 50, 65 and 51, 222 (1905).

$$V_1 = V_2 \frac{P_2 - \pi_2}{P_1 - \pi_1} \frac{T_1}{T_2}$$

But this  $V_1$  does not yet represent the exact volume. For during the passage through the tube the molecules of the substituted benzenes have been decomposed and have used the requisite amount of oxygen for their combustion <sup>1)</sup>. Therefore,  $V_1$  will have to be increased with

$$7\frac{1}{2} \times \frac{T_1}{273} \times \frac{760}{P_1} \times 22.43 \text{ c.c.m.}$$

for each millimol. which, according to the analysis, has been destroyed by the calcium oxide.

Now, if we know the volume drawn out and, from the analysis, the number of molecules of the compounds present therein we can calculate the pressure exercised by the saturated vapour in the bell. This indirect determination of small vapour pressures suffers, of course, from the defect that no notice is taken of any association of molecules. But this is of very little consequence in these experiments.

I refrain from giving, in this communication, full details as to the purification of the various materials, the preliminary experiments made to see whether my experiments were in accord with those of KÜSTER and the experiments made to find a simple analytical method for the determination of Br and Cl in presence of each other; also the results of blank experiments. I will only state that the melting points are:  $p\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $53^\circ.0$  and  $p\text{-C}_6\text{H}_4\text{Br}_2$ ,  $87^\circ.2$ . My preparations had, therefore, a higher m. p. than those of KÜSTER and were, therefore, presumably purer and in fact, on repeating one of KÜSTER's experiments I found a somewhat higher vapour pressure. The analytical method employed consisted in dissolving the calcium oxide in dilute  $\text{HNO}_3$  and adding an excess of  $\text{N}/10 \text{ AgNO}_3$ , the precipitate consisting of silver chloride and bromide was weighed in a Gooch crucible and the excess of silver in the filtrate was determined by VOLHARD's method. From these *data* the two halogens may be readily calculated.

The branches of the melting point line were determined in the usual manner. It should be observed here that the branch of the composition of the liquid may be determined very sharply (initial solidifying points) but, on the other hand the determination of the end solidifying points and the initial melting points is beset with

<sup>1)</sup> The  $\text{CO}_2$  formed is retained in a washbottle containing strong KOH (Fig. 2) and also by the liquid from the aspirator which has been rendered alkaline with KOH.

R. KRUYT. "The equilibrium solid-liquid-gas in binary systems which present mixed crystals."  
2nd Communication.

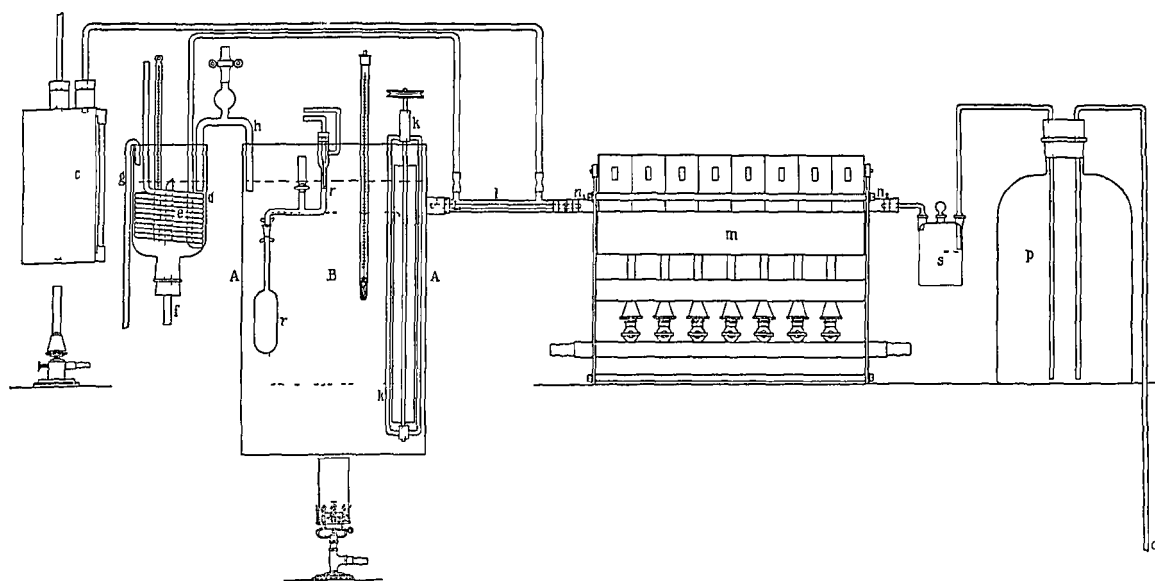


Fig. 2.

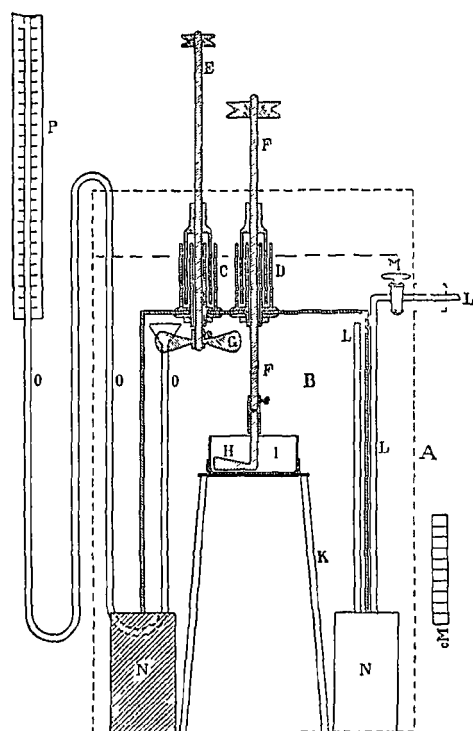


Fig. 1.

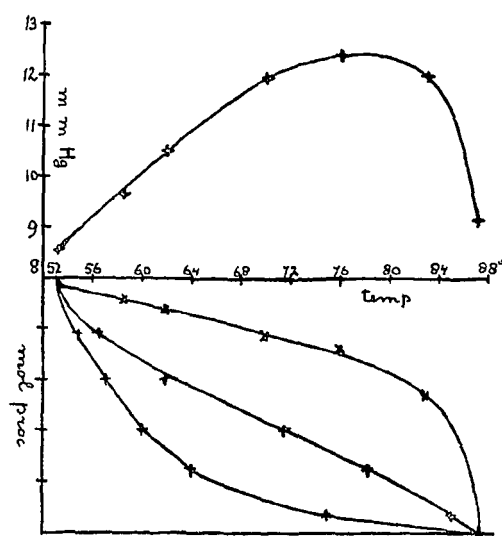


Fig. 3

great difficulties so that the accuracy of the figures for those branches is not so great. In table I are found the results of the respective determinations.

In table II are given the results of the determination of the two triple point pressures. From this we notice that they differ but very little and that one of the conditions for a course with a maximum or minimum in the three-phase line has, therefore, been complied with.

Finally, we find in table III the results of the three-phase tension and gas-composition for mixtures. In Fig. 3, a combined  $pt$  and  $tx$  projection, all the results have been united.

From this graphic representation it is shown that we are dealing here with a case which, in my previous paper, I have called case IIa.

In addition to the demand for about equal triple point pressures, it is also necessary to comply with the demand that, at the side of  $p\text{-C}_6\text{H}_4\text{Cl}_2$ , the branches of the melting point line shall diverge widely. Now, this is not exactly what takes place here and at the beginning of this research, after finding that the triple point pressures were nearly the same, I fully expected to find case IIb (minimum), because from the line of the initial solidifying points, as found by KÜSTER a closed figure at the side of the dichloro-component was to be expected. Nevertheless, the remark on pg. 544 of my first communication explains these results; because in the expression

$$(1-x_L) P_{T_1} e^{\int \frac{RT_1}{q} (x_S - x_L)} + p_B < P_{T_1},$$

the term  $x_S - x_L$  occurs as an exponential, even a very small value of that term will cause an increase of the pressure proceeding from the triple point along the three-phase line.

The three-phase line with a maximum is therefore remarkably enough, the normal case in the systems with mixed crystals, as well as in those with pure crystallised components. I may add (and indeed this will be readily noticed) that such is also the case for systems with a limited miscibility in the solid phase; the study of the spacial

TABLE I.  
Melting point line branches.

gr. $p\text{-C}_6\text{H}_4\text{Cl}_2$	gr. $p\text{-C}_6\text{H}_4\text{Br}_2$	mol. % $\text{C}_6\text{H}_4\text{Br}_2$	Initial solidifying point	Initial melting point
33.493	3.054	4.8	53°.2	53°.0 à 53°.1
23.633	11.502	21.7	56°.3	55°
15.392	15.973	39.3	62°.6	57°
9.041	21.360	59.5	71°.7	60°
5.679	27.669	75.7	78°.3	64°
1.502	31.826	93.0	84°.8	75°

diagrams of those systems, also of the peculiar properties of the three-phase line, has engaged my attention for a considerable time. I hope to refer to this later.

TABLE II.  
Triple point pressures of the components.

Component.	Temp.	Duration of the experiment	Mols in 100.000 L		Pressure in mm. of Hg.
			found	mean	
$\text{pC}_6\text{H}_4\text{Cl}_2$ }	53°.0	3 hours	41.7	{ 41.9	8.53
	53°.0	6 "	42.1		
$\text{pC}_6\text{H}_4\text{Br}_2$ ,	87°.2	4 hours	39.5	{ 40.5	9.10
	87°.2	4 "	41.5		

TABLE III.  
Tension on the three-phase line and composition of the gas.

No.	Experiment temp.	Duration of the experiment in hours	mol. % of $\text{pC}_6\text{H}_4\text{Br}_2$ in the mixture used	mols in 100.000 L		Pressure in mm. of mercury	Composition of gas-phase in mol. % $\text{pC}_6\text{H}_4\text{Br}_2$	
				found	mean		found	mean
1	58.5°	10½	{ 26.1	46.9	{ 46.6	9.64	7.8	{ 8.5
2	58.5°	12½		46.3			9.2	
3	62.0°	7½	42.0	50.5	{ 50.3	10.52	12.6	{ 12.2
4	62.0°	7	41.9	50.1			11.8	
5	69.8°	10	{ 39.5	55.5	{ 55.9	11.96	23.6	{ 23.7
6	69.8°	12		56.4			23.8	
7	76.0°	10	{ 75.2	57.1	{ 57.0	12.39	26.7	{ 26.8
8	76.0°	25		56.9			26.8	
9	83.0°	21	{ 93.0	53.6	{ 54.0	12.00	45.8	{ 46.0
10	83.0°	23		54.3			46.2	

Utrecht, VAN 'T HOFF-laboratory. May 1910.

**Chemistry.** — "On the alkaloid content in the leaves of the *Cinchonas*." By P. VAN LEERSUM.

(Communicated in the meeting of May 28, 1910).

#### Historical review.

In his report as to the alkaloid content of the bark and the leaves of the cinchona trees cultivated in Java (Jan. 1, 1864), JENGHOUN states that according to the Calcutta Gazette Supplement (Aug. 15, 1863) Dr. TH. ANDERSON had prescribed successfully decoctions of the fallen leaves of *C. Succirubra* for fever in the hospital at Darjeeling.