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I. In two papers one of us has given an extensive description of heterogeneous equilibria in the system sulphuretted hydrogen-water 1). It has appeared in this investigation that through the appearance of a compound and through unmixing in the liquid state a four-phase equilibrium hydrate of sulphuretted hydrogen – two liquid layers – gas occurs in this system; the three-phase-lines which intersect in this quadruple point, were determined, and besides a number of analyses was carried out to get to know the composition of the hydrate. These analyses, however, yielded very different results; the number of molecules of water which is bound with one molecule of sulphuretted hydrogen varies between 5.1 and 5.5 according to these determinations. This result led to the conclusion that the formula of the hydrate would be $H_2S \cdot 5H_2O$, because for this substance, and for gas hydrates in general a phenomenon occurs that causes the water content on analysis to be found too high. When we consider that the two liquid layers consist almost of pure sulphuretted hydrogen, resp. pure water, and that therefore, the hydrate must be formed by cooperation of the two liquid layers, it is clear that this formation of hydrate gives rise to a separation of the layers on the boundary of the liquids. In analyses an excess of sulphuretted hydrogen was always used, which was pumped off after action of the liquid layers. It is clear that when this excess of sulphuretted hydrogen has been removed, water can be left behind in the solid substance, as this possesses hardly any tension at low temperature as ice; this is accordingly the reason that formerly always lower values were found for the water content as more care was devoted to the interaction of the layers. Chronologically arranged the analyses yielded water contents of 15 2), 12 3) and 7 4) molecules

1) These Proceedings. 13. 829 (1911) and 14. 195- (1911).
2) De Forcrand. C.r. 94. 967. (1882).
4) De Forcrand and Villard. C.r. 106. 1402. (1886).
of water per molecule of sulphuretted hydrogen. In the above-mentioned determinations this content had fallen to 5.1—5.5, and the conclusion was obvious that the true water content would be lower: \( \text{H}_2\text{S} \cdot \text{5H}_2\text{O} \) was therefore the most probable formula on the ground of these experiments.

2. As direct analysis yielded dubious results, and the formula \( \text{H}_2\text{S} \cdot \text{5H}_2\text{O} \) can only be considered probable on account of the observed disturbance — there were no indications pointing to a second disturbance in opposite sense — we have tried to find a method of analysis that yielded more certain results.

Indications to a definite formula that did not rest on direct analysis are the following:

a. \( \text{VILLARD} \) deems the formula \( \text{H}_2\text{S} \cdot \text{6H}_2\text{O} \) probable on account of the analogy with other gas hydrates, for which he has drawn up a formula \( \text{M} \cdot \text{6H}_2\text{O} \)). This analogy must certainly be supported by a closer proof, before it convinces us of the accuracy of the said composition.

b. \( \text{VILLARD} \) could see the two liquids at temperatures at which the hydrate can form, with the hydrate of \( \text{N}_2\text{O} \) and this leads him to the conclusion that the hydrate of sulphuretted hydrogen will possess the same water content \( \). This reason, too, makes him consider the formula \( \text{H}_2\text{S} \cdot \text{6H}_2\text{O} \) probable.

c. \( \text{DE FORCRAND} \) makes use of a rule holding for three-phase lines, which is analogous to that of \( \text{TOUTON} \) for liquid-gas equilibria \( \). This rule may be represented as follows. When the three-phase line of a dissociating compound, which splits up into solid-gas, reaches a vapour tension of one atmosphere, the quotient of the heat of transformation and the absolute temperature has the value 30. He gives some examples for this rule, and then applies it to determine the quantity of water in gas hydrates. That this rule is, however, dangerous appears already sufficiently from the fact that on application to the hydrate of sulphur dioxide the composition \( \text{SO}_2 \cdot \text{8H}_2\text{O} \) was found, whereas on the strength of \( \text{BAKHUIS ROOZEBOOM} \)'s and \( \text{VILLARD} \)'s analyses it could be concluded with great probability that this water-content is too high \( \). His rule, likewise, leads to \( \text{H}_2\text{S} \cdot \text{6H}_2\text{O} \).

As in our opinion the indirect methods have not yet yielded certain results, either concerning the composition of the hydrate, we have tried

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1) \( \text{VILLARD. Ann. chim. phys. (7). II. 289. (1897).} \)
2) \( \text{DE FORCRAND. C.R. 135. 999. (1902).} \)
3) \( \text{BAKHUIS ROOZEBOOM. Rec. 3. 29. (1884); VILLARD. Ann. chim. phys. (7). II. 289. (1897).} \)
to find another for a long time. We think we have found a method that enables us to find the composition of the gas-hydrates with great certainty, of which the description follows below.

3. In order to make the principle on which this analysis rests, as clear as possible, we will imagine a binary system, of which the first component (A) is gaseous in a definite temperature range, the second (B) is in the neighborhood of its melting-point under the same circumstances and not perceptibly volatile. On increase of pressure a solid compound can form from the gaseous first and the solid second component. In the melted second component the gas is soluble neither as such nor as compound. Then the P-T projection of the spacial figure is represented by figure 1. Hence the first component A appears in these equilibria in free state as a gas (G) and bound in the compound (S). The second component B occurs free as solid (SB) and liquid (L), bound to the first component in the compound (S).

The three-phase lines $S_B LG$ and $SS_B L$ coincide with the melting-point line of $B$. The transformation is namely indicated by $S_B \geq L$ on both three-phase lines, and is the same as on the melting-point line of pure $B$. The triple-point of $B$ (point $B$ in fig. 1) lies near the $T$-axis; the sublimation – and the boiling-point line of $B$ practically coincide with the $T$-axis.

When we indicate the compound by $AB_n$, the transformations on the two other three-phase lines are indicated by:

$$AB_n \rightleftharpoons A + nB - E_1 \quad \text{(on } SS_B G)$$

$$AB_n \rightleftharpoons A + nB - E_2 \quad \text{(on } S L G)$$

Hence the difference between the two transformation energies $E_1$
and $E_2$ amounts to the melting energy or melting heat of $n$ molecules $B$. When the heat of melting of one molecule $B$ is indicated by $Q$, we get:

$$E_2 - E_1 = nQ$$  \hspace{1cm} (1)

When we apply the equation of Clapeyron to the two three-phase equilibria, the indices 1 resp. 2 again referring to the equilibria $SSBG$ resp. $SLG$, the following relations follow:

$$T \frac{dP_1}{dT} = \frac{Q_1}{\Delta V_1}$$ and $$T \frac{dP_2}{dT} = \frac{Q_2}{\Delta V_2}$$  \hspace{1cm} (2)

in which $Q_1$ and $Q_2$ represent the heats of transformation.

When $V_S$ and $V_L$ are neglected with respect to $V_G$, which is allowed, when the density of the gas phase is small with respect to that of the other phases (pressure of the quadruple point $C$ smaller than or in the neighbourhood of one atmosphere) and when the law of Boyle is applied to the gas phase, we get:

$$T \frac{dP_1}{dT} = \frac{Q_1}{RT} P_1$$ and $$T \frac{dP_2}{dT} = \frac{Q_2}{RT} P_2$$  \hspace{1cm} (3)

From this follows on integration on the assumption that $Q_1$ and $Q_2$ are no functions of the temperature $^1$:

$^1$ This assumption indicates that the algebraic sum of the specific heats (that of the gas at constant pressure) of the substances participating in the transformation is zero. This is easily seen for the equilibrium liquid-gas on the following consideration. From the equation of Clausius $\frac{dQ}{dT} = h - H + \frac{Q}{T}$, in which $h$ and $H$ represent the specific heats of gas and liquid along the boundary line (Van der Waals-Kohnstamm. Thermodynamik. L. S 67) and from the equation $h = c_v + T \left( \frac{dP}{dT} \right)_v \left( \frac{dv}{dT} \right)_{gr}$ (Ibid. I. S. 34, Gl. IIa; the index $gr$ denotes that $\frac{dv}{dT}$ is measured along the boundary line) follows $\frac{dQ}{dT} = c_v - H + T \left( \frac{dP}{dT} \right)_v \left( \frac{dv}{dT} \right)_{gr} + \frac{Q}{T}$. If the law of Boyle holds good for the gas phase, the two last terms of the second member of this equation can be replaced by $R$ and we get $\frac{dQ}{dT} = c - H$.

We derive in an analogous way that a similar formula also holds for the three-phase equilibria described in the text.

When the algebraic sum of the specific heats differs from zero, the integrated equation 4 may only be used for a small range of temperature; then the heat of transformation at the quadruple point must be calculated from the found value of $Q$. A similar calculation follows in the discussion of the quantitative data. We may point out in conclusion that if $Q$ is no temperature function, the energy of transformation, which is $RT$ smaller, does depend on the temperature. The variation in $E$, caused by this correction is generally small with respect to the values of $Q$ and $E$. (See tables with the quantitative data in the following paper).
\[
\ln P_1 = -\frac{Q_1}{RT} + C_1 \quad \text{and} \quad \ln P_2 = -\frac{Q_2}{RT} + C_2 \quad (4)
\]

From a graphical representation \(\ln P_i = f_i(T^{-1})\) and \(\ln P_2 = f_2(T^{-1})\) the slopes of the two straight lines can then be determined. Then the tangent of the angle of inclination amounts to \(-\frac{Q_1}{R}\) resp. \(-\frac{Q_2}{R}\).

The difference multiplied by \(R\) yields the heat of melting \(Q_2 - Q_1\), which is equal here to the energy of melting \(E_2 - E_1\), and from this follows by the aid of equation (1) the value of \(n\) and with it the composition of the hydrate.

Accordingly for the application of this method of analysis the three-phase lines \(SS_BG\) and \(SLG\) must be experimentally determined.

4. The system sulphurated hydrogen-water presents great analogy with the ideal system of § 3. As was demonstrated in the above-mentioned papers by one of us, a quadruple point \(SL_LG\) appears in this system, indicated in fig. 2 by \(D\). The stable part of the three-phase line \(SL_LG\), a number of points of which was already determined before \(^1\), terminates in the quadruple point \(SS_BLG\); indicated in

\(^1\) It appears from the transformations given in § 3 that \(Q_1 = E_1 + RT\) and \(Q_2 = E_2 + RT\), as one gramme molecule of gas is formed in both conversions. It follows from this that \(Q_2 - Q_1 = E_2 - E_1\). The volumes of solid and liquid are neglected by the side of these of gas, and the expansion at melting does not cause an appreciable difference between melting energy and heat.

\(^2\) These Proceedings: 18., 829 (1911).
fig. 2 by C. Through this quadruple point passes also the threephase line \( SS_E G \), and we shall now show that the determination of the said three-phase lines \( SS_E G \) and \( SL_G \) is again sufficient for the calculation of the composition of the hydrate; the sole difference with the case of § 3 consists in this that a few corrections must be applied, which, however, can be calculated for the system sulphurated hydrogen-water with sufficient accuracy from the data of the literature. The required corrections will be mentioned separately for each of the two three-phase lines.

5. The three-phase line \( SS_E G \).

Now the transformation on this three-phase line is not as in § 3 expressed by

\[
AB_s \xrightarrow{(solid)} A + nB \rightarrow (gas) E,
\]

because the gas does not consist of the pure first component \((A = H_2S)\), but ice \((\text{solid } B)\) has always some, though little, vapour tension. Hence a modification only occurs in the gas phase. When from the observed pressures \( P \) we now subtract the tension of ice of the same temperature, we find the values \( P(\text{corr}) \), which accordingly denote the partial pressures of the sulphurated hydrogen in the gas phase\(^1\). When we now determine \( \log P(\text{corr}) \) and the corresponding \( T^{-1} \) values, the graphical representation yields a curve which only little departs from a straight line. For this curve, the following equation holds:

\[
T \frac{dP(\text{corr})}{dT} = \frac{Q_1}{RT} P(\text{corr})
\]

or, integrated, over a small range of temperature, where \( Q_1 \) may be considered as constant:

\[
\ln P(\text{corr}) = \frac{Q_1}{RT} + C_1.
\]

If the curve does not differ perceptibly from a straight line, this expression may be directly applied to the whole line and \( Q_1 \) can be calculated from the inclination.

If the curve has a perceptible curvature the value \( Q_1 \) can be calculated for the small range of temperature in question from every time two observations for temperatures that differ little (indices \( a \) and \( b \)) by the aid of

\( Q_1 \) In this we therefore assume that the compound does not exist in gaseous state. If it occurs for a small amount in gaseous state, its influence will certainly remain within the errors of observation, the tension of water vapour being already small itself.

\( ^1 \)
\[
\ln P_a (\text{corr}) - \ln P_b (\text{corr}) = - \frac{Q_1}{R} (T_a^{-1} - T_b^{-1})
\]

This value \(Q_1\) is, therefore, the heat which would be required for transformation, if ice had no vapour tension, and agrees, therefore, in significance with the homonymous heat of § 3. It is the heat that we want for the calculation; it is a function of the temperature, but only a feeble one, the change of the heat of transformation with the temperature is namedly expressed by the algebraic sum of the specific heats of hydrate, \(n\) molecules of ice, and one molecule of sulphuretted hydrogen at constant pressure (see § 3). If the law of Kopp is valid, this sum of specific heats will be indicated by the difference between that of one molecule of solid \(H_2S\) and one molecule of gaseous \(H_2S\) (at constant pressure). As now the specific heat of solid \(H_2S\) amounts to about \(10\), that of gaseous \(H_2S\) to about \(8.5\), and the difference is therefore \(1.5\), it is clear that this correction for a range of temperature of about \(20^\circ\) to a heat effect of about \(5000\) calories (see later) constitutes a correction of about \(6.9\%\), which is negligible for our purpose.

Hence the above calculation gives us the heat of the transformation:

\[
H_2S \cdot n H_2O \xrightarrow{(\text{solid})} H_2S + n H_2O - E_1 
\]

The change of energy \(E_1\) may be found from \(Q_1\) by deduction of the external work \(RT\). (In the transformation evaporates one mol. of gas).

6. The three-phase line \(SL_4G\).

In the transformation \(S \xrightarrow{\text{solid}} L_4 + G - E_{SL_4G}\) an appreciable deviation from the corresponding case of § 3 occurs. For not only does sulphuretted hydrogen dissolve in the aqueous liquid, but water has also a definite not to be neglected vapour tension. The transformation at this equilibrium may be split up into:

\[
H_2S \cdot n H_2O \xrightarrow{(\text{solid})} H_2S + n H_2O - E_1, 
\]

1) See NERNST. Theor. Chem. Gesetz von DULONG und PETIT.

2) In the same way as this has been done for the line hydrate-liquid-gas (see further on) the value of \(E_1\) may also be calculated from \(T \frac{dP}{dT} = \frac{Q}{V}\), in which \(V\) represents the volume gas formed by decomposition of one gramme molecule of hydrate (sulphuretted hydrogen + water vapour); then the heat \(Q\) must be corrected for the heat of sublimation of a small quantity of ice in order to find \(Q_1\) and \(E_1\) with it.
\[ \begin{align*}
&\quad \text{and} \\
&\quad sH_2O + \text{much water} \xrightarrow{\text{(gas)}} \text{solution} + sE_0 \quad . \quad . \quad . \quad (8)
\end{align*} \]

Then the total change of energy at the transformation becomes:

\[ E_{SLaG} = E_2 + rE_0 - sE_o. \]

When we introduce the quantities of heat instead of the changes of energy, we get:

\[ \begin{align*}
E_{SLaG} + (1 + r - s)RT &= E_2 + rE_0 + rRT - sE_o - sRT \\
\text{or} \\
Q_{SLaG} &= Q_2 + rQ_o - sQ_o,
\end{align*} \]

in which \( Q_2 \) represents the heat required for the calculation, and has a meaning analogous to that of the homonymous heat in \( \S \, 3 \), \( Q_o \) indicates the heat of evaporation of one molecule of water, \( Q_e \) the heat of solution of one mol. of \( H_2S \).

(\( Q_o = 10780 - 11.3 t^1 \), \( Q_e = 4560 t^2 \))

When we now represent the number of molecules of \( H_2S \) that dissolves in one mol of \( H_2O \) under three-phase pressure by \( q \), the partial pressures of water and sulphuretted hydrogen by \( P_{H_2O} \) and \( P_{H_2S} \), we have:

\[ \frac{s}{n-r} = q \quad \text{and} \quad \frac{r}{1-s} = \frac{P_{H_2O}}{P_{H_2S}} \quad . \quad . \quad . \quad (9a \text{ and } b) \]

These equations may be transformed into:

\[ \begin{align*}
s &= \frac{n - P_{H_2O}}{P_{H_2S}} \\
r &= \frac{1 - nq}{1 - q} \frac{P_{H_2O}}{P_{H_2S}} \\
or in approximation into:
\end{align*} \]

\[ \begin{align*}
s &= nq \\
r &= (1 - nq) \frac{P_{H_2O}}{P_{H_2S}} \\
(10a \text{ and } b)
\end{align*} \]

That this approximation is allowable, will appear from the data. (See the tables in the following paper).

Now follows from 10a and b:

\[ \begin{align*}
1 + r - s &= (1 - nq) \left( 1 + \frac{P_{H_2O}}{P_{H_2S}} \right) \quad . \quad . \quad . \quad (11)
\end{align*} \]

When we apply the equation of Clausius to the three-phase equilibrium in question, we find:

1) LANDOLT-BÖRNSTEIN-ROTH. Tables.
2) THOMSEN. Thermochem. Unters.
\[ T \left( \frac{dP}{dT} \right)_{SL,G} = \frac{Q_{SL,G}}{\Delta V_{SL,G}} = \frac{Q_0 + r Q_v - s Q_o}{(1 + r - s) RT} P_{SL,G}, \quad (12) \]

in which the volumes of solid and liquid are neglected by the side of gas, and Boyle's law has been applied to the gas phase.

Transformation of (12) finally yields the required heat \( Q_2 \):

\[ \left( \frac{d \ln P}{dT} \right) = -\frac{1}{T^n} \left( \frac{d \ln P}{dT-1} \right), \]

\[ Q_2 = -r Q_v + s Q_o - (1 + r - s) R \left( \frac{d \ln P}{dT-1} \right)_{SL,G}. \quad (13) \]

As now \( Q_v \) (heat of evaporation of one molecule of water) and \( Q_o \) (heat of solution of one molecule \( H_2S \)) are known, \( r \) and \( s \) can be calculated from 10a and b (see also (11)), if an arbitrarily chosen value is substituted for \( n \), \( Q_2 \) can be calculated if the temperatures are chosen close to each other, so that the differential quotient in (13) can be replaced by the quotient of differences. Thus every time from two observations at temperatures differing little a value of \( Q_2 \) is found for that small range of temperature. This value \( Q_2 \), therefore, represents the heat of transformation on the three-phase line \( SL,G \), corrected for the phenomenon of solution and evaporation at the conversion. It is the heat belonging to the conversion:

\[ H S, n H_2O \rightleftharpoons H_2S + n H_2O - E_2 \quad \text{(solid)} \rightleftharpoons \text{(gas)} \rightleftharpoons \text{(liquid)} \quad (6) \]

The heat \( Q_2 \) (and the change of energy \( E_2 \)) will again be functions of the temperature. The algebraic sum of the specific heats is greater here than on the three-phase line \( SSB,G \) (§ 5); it may not be neglected. Hence the heat at transformation on \( SL,G \) in the immediate neighbourhood of the quadruple point must be found by extrapolation. The correction required for this is, however, small enough to allow linear extrapolation, in other words to enable us to consider the specific heats as independent of the temperature.

Now the value of \( n \) follows simply from the equations (5) and (6) in a way analogous to that in § 3.

\( \text{(To be continued).} \)

\[ 1) \text{As } r \text{ and } s \text{ themselves represent corrections, a change of } n \text{ brings about a modification in the correction which is already small. Whether 5 or 6 is chosen for } n \text{ gives only a slight variation in the result of the calculations. We shall come back to this point later on.} \]