Phase Equilibrium in the System Water–Hydrogen Sulphide: Hydrate-Forming Conditions

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Recently revealed problems with the fluid phase equilibria data for the system H_2S–H_2O as presented by Selleck et al. (1952) prompted this review of the hydrate-forming conditions. The smoothed tables of Selleck et al. (1952) along the three-phase loci are replaced with equations which are based on a critical review of all of the experimental data.

Les problèmes soulevés récemment à propos des données d'équilibre en phase liquide pour le système H_2S–H_2O telles qu'elles sont présentées par Selleck et al. (1952) nous ont incités à examiner les conditions de formation des hydrates. Les tableaux lissés de Selleck et al. (1952) ainsi que les loci des trois phases sont remplacés par des équations basées sur un examen critique de toutes les données expérimentales.

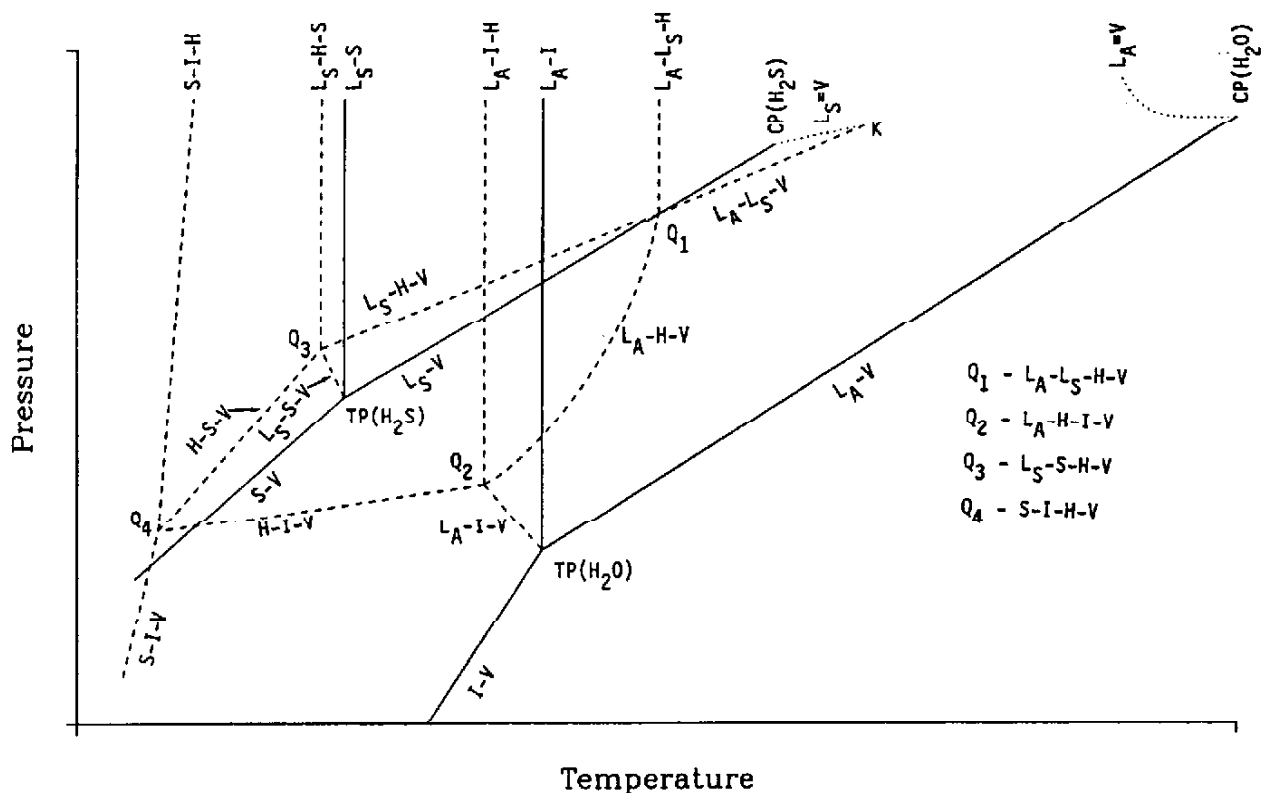Keywords: H_2S–H_2O, three-phase equilibria, hydrates.

Figure 1 — Schematic pressure-temperature diagram for the system water–hydrogen sulphide (not to scale).

Gas hydrates are a solid, ice-like phase. They belong to a class of compounds called inclusion compounds or clathrates. A guest molecule fits into a chamber formed by hydrogen-bonded water molecules. Hydrates can form two structures called type I and II. Hydrogen sulphide forms a type I hydrate. In a type I hydrate 46 water molecules form eight polyhedra: two dodecahedra (12 faces, all regular pentagons) and six tetrakaidecahedra (14 faces, two regular hexagons and twelve regular pentagons). Hydrogen sulphide is of a size that it can occupy both kinds of cages. This structure results in a theoretical formula of 8 H_2S · 46 H_2O or H_2S · 5.75 H_2O; however hydrates are non-stoichiometric. A stable phase forms without a guest molecule in all of the cages. The degree of saturation is a function of temperature and pressure.

The phase equilibria in the system H_2S–H_2O is quite complex. Figure 1 shows the pressure-temperature diagram for this system. Note, this plot is not to scale. The pure component two-phase loci are the solid lines, the three-phase loci are the broken lines and the binary critical loci are dotted. The pure component two-phase loci are well known [see Goodwin (1983) for hydrogen sulphide and Keenan et al. (1978) for water]. The L_4-L_5-V locus and the three-phase critical end point (point K on Figure 1) were determined by Carroll and Mather (1989a). It is the purpose of this paper to establish the location of the L_4-H-V, L_5-H-V, L_4-L_5-H and H-I-V loci by critically reviewing the data in the literature. The remaining three phase loci have not been studied. Their location on Figure 1 is speculation on the part of the authors and are included for completeness. From this

diagram the location of the three-phase loci, with respect to each other, can be ascertained.

At the points where four three-phase loci intersect there is a quadruple point. Two quadruple points for the system water–hydrogen sulphide are well established. These are the H-I-V-L_A point at $-0.4°C$ and 93.1 kPa and the L_S-L_A-H-V point at 29.4°C and 2.24 MPa. Two other quadruple points are believed to exist, H-I-S-V and H-S-L_S-V, but they have not been measured.

Hydrates are a significant problem in the production, transportation and processing of natural gas. Of the components commonly found in natural gas, the hydrate of H_2S forms at the lowest pressure and persists to the highest temperature. It is not, however, the purpose of this paper to review hydrates. The reader is referred to Sloan (1990) for an excellent and thorough review.

Literature review

The first report of the hydrate of hydrogen sulphide was by Wöhler (1840). However, the first detailed investigation of the H_2S hydrate was that by de Forcrand and co-workers (de Forcrand, 1882a; de Forcrand, 1882b; de Forcrand, 1883; de Forcrand and Villard, 1888a; de Forcrand and Villard, 1888b; de Forcrand and Villard, 1888c; Villard, 1897; de Forcrand, 1902a and de Forcrand, 1902b). These studies included measurements of the L_A-H-V locus for hydrogen sulphide, the study of several double hydrates with hydrogen sulphide as one of the components, and the compositions of the hydrates. Although in their earlier work de Forcrand and co-workers estimated that the formula for the hydrate was $H_2S \cdot 12H_2O$ or $H_2S \cdot 16\ H_2O$, in 1902 he calculated that it was $H_2S \cdot 5.96\ H_2O$. But, assuming that the ratio should be an integer he rounded it off to 6. Cailletet and Bordet (1882) also reported values for the pressure and temperature along the L_A-H-V locus for hydrogen sulphide–water.

A thorough investigation of the phase behavior in the system water–hydrogen sulphide was conducted by Scheffer and co-workers (Scheffer, 1911a; Scheffer, 1911b; Scheffer, 1913; Scheffer and Meyer, 1919a; Scheffer and Meyer, 1919b; Korvezee and Scheffer, 1931). They included measurements of the three-phase loci in the region near the L_A-L_S-H-V quadruple point. Korvezee and Scheffer (1931) reported measurements along the H-I-V and L_A-H-V loci. They concluded that the composition of the hydrate at the L_A-H-I-V quadruple point was 6.06 ± 0.13 molecules of water per molecule of hydrogen sulphide. However, they too believed that the value should be an integer and thus rounded it to 6.

Wright and Maass (1932), in a study of the solubility of hydrogen sulphide, obtained a few pressure–temperature measurements along the L_A-H-V locus. The solubility data of Wright and Maass (1932) are among the best available for H_2S in water. However, as will be shown in this paper, their measurements of the L_A-H-V locus are not of high quality.

Bond and Russell (1949) investigated the L_A-H-V locus and the effect of several "antifreeze agents" (NaCl, CaCl$_2$, methanol, ethanol, ethylene glycol, diethylene glycol, dextrose and sucrose). All of these chemicals were found to reduce the temperature at which the hydrate would form at a given pressure. Ng and Robinson (1985) performed a similar experiment to study the effect of methanol on the hydrate formation of several gases including hydrogen sulphide.

The investigation of Selleck et al. (1951, 1952) is considered to be the benchmark study for the system water–hydrogen sulphide. Data in the 1952 paper were smoothed and extrapolated from the raw data which were presented in the 1951 supplementary publication. It also incorporated work from some previous investigations, especially the work of Scheffer and co-workers. It is the smoothed data that are often-quoted. However, some problems with the smoothed data for the fluid phase equilibria were demonstrated by Carroll and Mather (1989b). A thorough review and re-interpretation of the raw data of Selleck et al. (1951) is given by Carroll (1990). The values along the three-phase locus obtained by Carroll (1990) from the data of Selleck et al. (1951) will be used in this investigation.

There are few direct measurements of the compositions of hydrates reported in the literature. One such study was that of Cady (1981). Cady (1981) made measurements of the hydrate compositions for hydrogen sulphide in water at 0°C at pressures ranging from 164 to 349 kPa.

Carroll (1990), in conjunction with the measurement of the L_A-L_S-V locus (see Carroll and Mather, 1989a), made some measurements of the L_A-H-V and L_S-H-V loci. These data were obtained with an apparatus designed for fluid phase equilibrium and thus are not of high quality. The loci measured by Carroll (1990) and those of Selleck et al. (1951) as interpreted by Carroll (1990) are listed in the Appendix.

The L_A-H-V locus

In order to compare the experimental values, all of the data were correlated using a Clausius–Clapeyron-type equation.

$$\ln P = A + B/T \qquad\qquad (1)$$

Table 1 lists the constants for the individual sets of data and these values are for P in kPa and T in K. The stated ranges are the 95% confidence intervals. From this table and plots of pressure versus temperature (see Figures 2 and 3) it is concluded that the data of the Forcrand and Villard (1888), Scheffer (1913) and Scheffer and Meyer (1919a,b) are the best; they have the narrowest confidence intervals. Note, these data were selected in spite of their age. Over a narrow range of temperature the Clausius–Clapeyron-type equation provides an adequate fit of the data, especially for comparison purposes. Unfortunately, the Clausius–Clapeyron equation is not the best for correlating these data over the entire range of temperature. The following equation was significantly better:

$$\ln P = -26.8952 + 0.15139\ T + 2788.88/T$$
$$- 3.5786 \ln T \qquad\qquad (2)$$

where P is in kPa and T in K.

In their review of hydrates, van der Waals and Platteuw (1959) misquote Selleck et al. (1952) by stating that the dissociation pressure of the H_2S hydrate at 0°C was 93.1 kPa (698 mm Hg). This is actually the pressure at $-0.4°C$, the H-I-V-L_A quadruple point. At 0°C, Selleck et al. give 97.5 kPa (731 mm Hg), whereas Equation (2) gives 98.6 kPa (739 mm Hg). de Forcrand and Villard (1888) measured a value of 97.5 kPa (731 mm Hg) at 0°C. Also, from Equation (2), the dissociation temperature at 101.325 kPa (1 atm) is 0.3°C.

TABLE 1
Correlation of the L_A-H-V Locus for the System Water-Hydrogen Sulphide From Several Sources
Via a Clausius-Clapeyron-Type Equation [Equation (1)]. For Use with P in kPa and T in K

Ref	NP	t_{min} (°C)	t_{max} (°C)	Slope B	Intercept A	r^2
1	12	0.5	29.0	-8071 ± 614	34.18 ± 2.13	0.9885
2	10	1.0	25.0	-7281 ± 903	31.68 ± 3.16	0.9774
3	16	0.0	5.2	-7790 ± 116	33.10 ± 0.42	0.9993
4	11	16.3	29.5	-9436 ± 324	38.86 ± 1.09	0.9979
5	4	1.0	7.1	-7776 ± 127	33.07 ± 0.46	1.0000
6	5	2.2	10.5	-8008 ± 1863	33.74 ± 6.64	0.9842
7	3	10.0	26.5	-8093 ± 3264	34.33 ± 11.22	0.9990
8	5	11.7	24.4	-8608 ± 633	36.07 ± 2.18	0.9984
9	13	25.5	27.7	-8659 ± 1591	36.37 ± 5.31	0.9288

1. de Forcrand (1882,a,b)
2. Cailletet and Bordet (1882)
3. de Forcrand and Villard (1888)
4. Scheffer (1913)
5. Scheffer and Meyer (1919a,b)
6. Wright and Maass (1932)
7. Bond and Russell (1949)
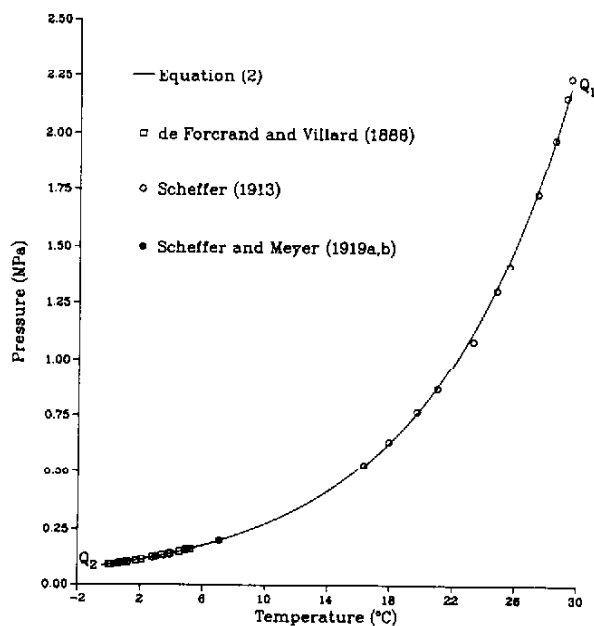8. Selleck et al. (1951)
9. Carroll (1990)

Figure 2 — The aqueous liquid-hydrate-vapour locus for the system water-hydrogen sulphide (best data).

Figure 3 — The aqueous liquid-hydrate-vapour locus for the system water-hydrogen sulphide (other data).

The L_A-H-V locus is plotted on Figure 2. This graph shows Equation (2) along with the data of de Forcrand and Villard (1888), Scheffer (1913), and Scheffer and Meyer (1919a,b). Figure 3 shows the above correlation along with the remaining experimental data. Note the large amount of scatter on this plot. These figures reinforce the selection of the three sets of data shown on Figure 2 as the best.

Even in the nineteenth century it was possible to measure the temperature to a fraction of a degree. Pressures below about 300 kPa could easily be measured to within 0.13 kPa (1 mm Hg) using a mercury manometer. Higher pressures could have been measured to ±1% (or better) using a bourdon tube gauge. Thus, the reason for the error is probably not due to the temperature or pressure measurements. The most likely reason for the errors is impurities in the
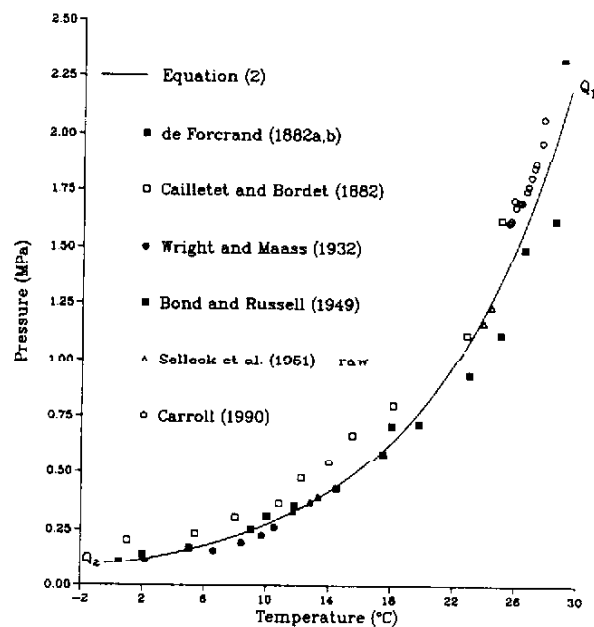
samples. Impurities can cause both increases and decreases in the hydrate formation temperature. Bond and Russell (1949) observed the effect of several antifreeze agents. Ng and Robinson (1985) investigated the effect of methanol on the H_2S hydrate. In both of these investigations, the hydrate pressure at a given temperature was increased by the antifreeze. Noaker and Katz (1954) studied the hydrate for H_2S-CH_4 mixtures. They observed that the presence of CH_4 increased the hydrate forming pressure. Also, some impurities decrease the pressure at which the hydrate forms. For example, mixtures of $H_2S-CH_2Cl_2$, H_2S-CH_3Cl and H_2S-CCl_4 all form hydrates at lower pressures than pure H_2S (Stackelberg and Frühbuss, 1954). This may explain why some values are at lower pressures than expected. Of course, there is also experimental error. Some problems with the data

TABLE 2

Compositions of the Co-Existing Phases Along the L_4-H-V
Locus for the System Water-Hydrogen Sulphide

Temp (°C)	Pressure[1] (kPa)	Mole Per Cent Hydrogen Sulphide		
		Aqueous[2]	Hydrate[3]	Vapour[2]
0	98.6	0.366	14.3	99.373
5	163.9	0.511	14.4	99.458
10	274.7	0.725	14.5	99.539
15	463.6	1.053	14.6	99.613
20	787.9	1.525	14.6	99.676

(1) — from Equation (2)

(2) — from the model of Carroll and Mather (1989c)

(3) — from a modified van der Waals-Platteeuw (1959) model
using the parameters from Munck et al. (1989) and the
hypothesis of Cady (1981)
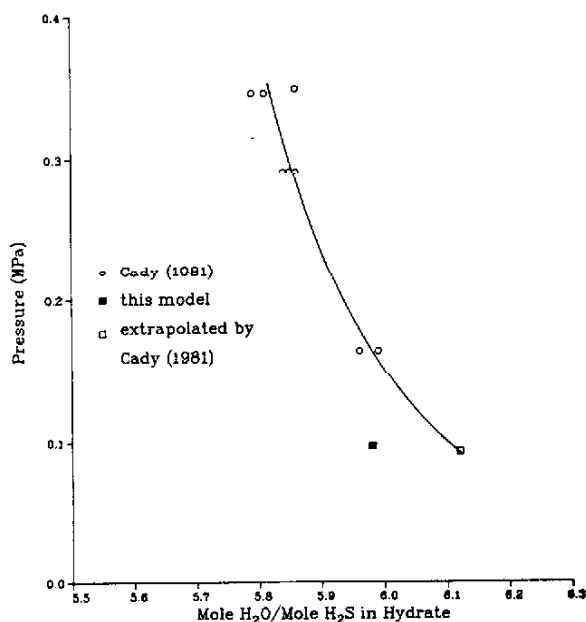
Figure 4 — Composition of the hydrogen sulphide hydrate at 0°C
[————— Model of Cady (1981)].

of Selleck et al. (1951) were demonstrated in Carroll (1990).
Also, as noted earlier, the data from Carroll (1990) are not
of high quality because of the apparatus used. It is interesting to note that although the solubility data of Wright and
Maass (1932) are considered to be among the most reliable
(see Carroll and Mather, 1989c), their hydrate data are at
significantly lower pressures than the other data and are concluded to be in error.

Composition of the hydrate

As noted earlier, the theoretical formula for the hydrate
is $H_2S \cdot 5.75\ H_2O$. There have been many attempts to
determine the composition of the H_2S hydrate. Most were
incorrect. Cady (1983) discusses the history and problems
associated with experimental measurements of hydrate
compositions.

A modification of the method van der Waals and Platteeuw
(1959) was used to estimate the composition of the hydrate
along the L_4-H-V locus. The procedure of Munck et al.
(1988) was used with some modification discussed here.
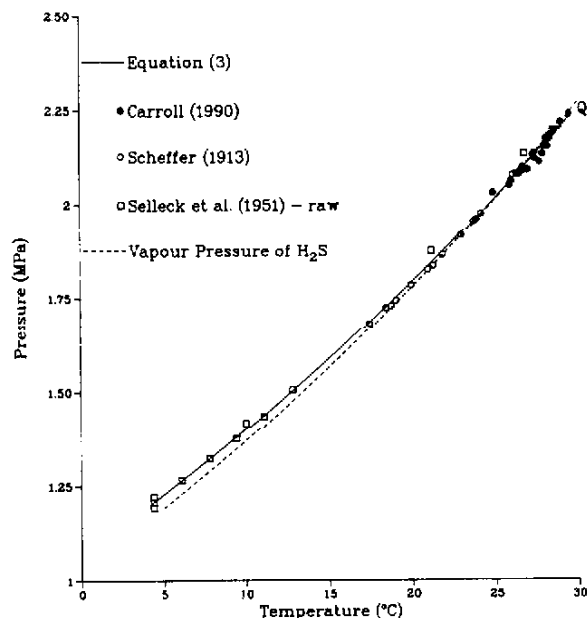Their model included the effect of the solubility of the

Figure 5 — The H_2S-rich liquid-hydrate-vapour locus for the
system water-hydrogen sulphide.

hydrate-forming gas in the aqueous phase. Although they
included this effect for CO_2, they state that it was negligible
for H_2S. However, the solubility of H_2S in water is larger
than that of CO_2. The solubility of H_2S was not neglected
in this application. The solubility of H_2S and the vapour
compositions were calculated using the model from Carroll
and Mather (1989c). The pressures were calculated using
Equation (2). According to Cady (1981), it is a good assumption that the saturation for the two different cavities are equal.
That is, there is an equal probability of there being an H_2S
molecule in the small voids as there is in the large voids.
(This was only true for H_2S and not for any other material).
This assumption was not made by Munck et al. (1988). With
this assumption, the values in Table 2 were calculated. At
0°C and 98.6 kPa, this method gives a ratio of H_2O to H_2S
in the hydrate of 5.98. Although Cady (1981) extrapolates
his data to get 6.12 at his point, the value of 5.98 is in good
agreement with the experimental data of Cady (1981). The
composition of the hydrate at 0°C is plotted on Figure 4.
Korvezee and Scheffer (1931) estimated the composition at
the lower quadruple point, approximately the same conditions, to be 6.06.

The L_S-H-V locus

Scheffer (1913), Selleck et al. (1951) and Carroll (1990)
report values for pressures and temperatures along the
L_S-H-V locus. The L_S-H-V lies very close to the vapour
pressure of H_2S. The agreement among the three sets of
data is quite good. All of the data were correlated with a
Clausius-Clapeyron-type equation. A least squares regression yields

$$\ln P = 14.5229 - 2061.05/T \qquad\qquad (3)$$

where P is in kPa and T in K. Figure 5 shows the experimental data from the three sources and Equation (3). Also
shown on this plot is the vapour pressure of H_2S taken from
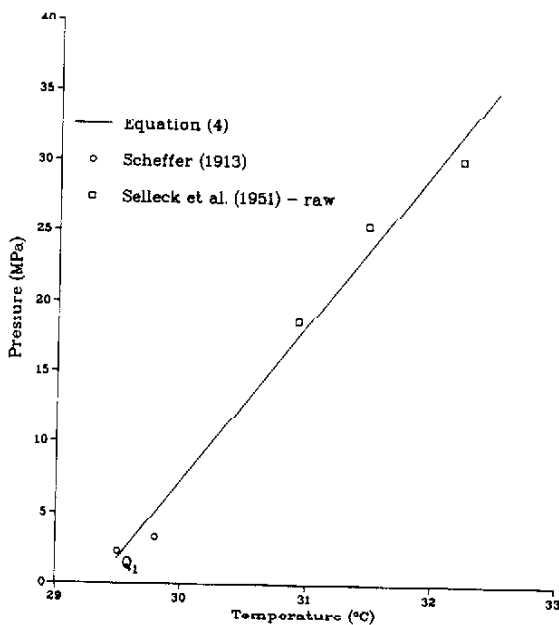the correlation of Goodwin (1982). At low temperatures, the

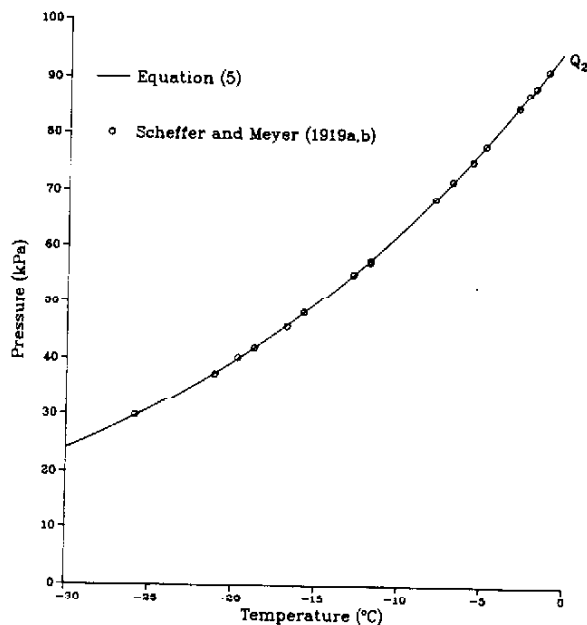Figure 6 — The H₂S-rich liquid-aqueous liquid-hydrate locus for the system water–hydrogen sulphide.

Figure 7 — The hydrate-ice-vapour locus for the system water–hydrogen sulphide.

L_S-H-V locus is at slightly higher pressures than the H_2S vapour pressure. As the L_A-L_S-H-V quadruple point is approached the difference becomes smaller. At the quadruple point the L_S-H-V and the vapour pressure are essentially the same.

The L_A-L_S-H locus

Scheffer (1913) and Selleck et al. (1951) both report points on the L_A-L_S-H locus. The total data set consists of only five points, two from Scheffer (1913) and three from Selleck et al. (1951). The data of the two sources were combined and correlated. The following equation was obtained.

$$P = 11.083\ T - 3352.515 \dots \dots \dots \dots \dots \dots (4)$$

where P is in MPa and T in K. Figure 6 shows the L_S-L_A-H locus. This correlation looks deceptively poor because of the temperature scale used. Unlike the other correlations, this equation uses P and not ln P.

The H-I-V locus

Although Selleck et al. (1952) report smoothed values along the H-I-V locus, the only experimental values in this region are those of Scheffer and Meyer (1919a,b). These data were fit with a Clausius–Clapeyron-type equation.

$$\ln P = 15.8059 - 3070.13/T \dots \dots \dots \dots \dots (5)$$

where P is in kPa and T in K. Figure 7 shows the experimental data and the correlation.

Conclusions

A thorough review of the literature was undertaken to obtain all of the data on the hydrate-forming conditions for hydrogen sulphide. These data were critically examined and correlations of the best data were obtained.

APPENDIX

For convenience the data of Carroll (1990) for the L_S-H-V and L_A-H-V loci are listed in Tables A1 and A2. Because of the proximity of the vapour pressure of H_2S and the L_S-H-V loci the vapor pressure is also listed in Table A1. For details of the experimental work see Carroll (1990).

The raw data of Selleck et al. (1951) are somewhat difficult to interpret. Carroll (1990) analyzed the data of Selleck et al. (1951) to obtain the pressure and temperature along the various three phase loci. The values obtained are listed in Tables A3 through A5. Also included in these tables are values interpolated from the smoothed values of Selleck et al. (1952).

TABLE A1

The L_S-H-V for the System Water–Hydrogen Sulphide Locus From Carroll (1990)

Temp (°C)	Three-Phase Pressure (MPa)	Vapour Pressure of H₂S* (MPa)
24.8	2.03	2.01
25.8	2.05	2.06
25.9	2.06	2.06
26.2	2.08	2.08
26.4	2.08	2.09
26.5	2.09	2.09
26.6	2.09	2.10
26.9	2.09	2.11
27.3	2.12	2.13
27.6	2.11	2.15
27.8	2.13	2.16
27.9	2.15	2.16
28.0	2.17	2.17
28.1	2.15	2.17
28.2	2.17	2.18
28.3	2.18	2.18
28.4	2.20	2.19
28.5	2.22	2.22
29.4	2.24	2.24

* — from Goodwin (1983)

Nomenclature

A = intercept of Clausius-Clapeyron-type equation [Equation (1)]

B = slope of Clausius-Clapeyron-type equation [Equation (1)]

CP = pure component critical point

H = hydrate

I = ice

K = three-phase critical end point

L_A = aqueous liquid

L_S = H_2S-rich liquid

NP = number of points

P = pressure. kPa or MPa

Q = quadruple point

r^2 = correlation coefficient

S = solid H_2S

t = Celsius temperature. °C

T = absolute temperature. K

TP = pure component triple point

V = vapour

Subscripts

max = maximum

min = minimum

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