

Phase Equilibria Relevant to Acid Gas Injection, Part 1—Non-Aqueous Phase Behaviour

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Abstract

The design of an acid gas injection scheme requires a significant amount of information regarding phase equilibria. The purpose of this paper is to review the literature for the available experimental data, and survey methods for calculations of the non-aqueous equilibria. This study will be limited to the following components: hydrogen sulfide, carbon dioxide, methane, ethane, propane, and, to some extent, water.

It is demonstrated that the widely available Peng-Robinson equation of state is adequate for predicting the non-aqueous phase equilibria in these mixtures. However, the design engineer should be cognizant of the capabilities of the model selected to perform the calculations. If uncertain, it is wise to verify the software package, and more importantly the chosen model, by comparing it with experimental data. Available data are compiled as a part of this paper.

Acid Gas Injection

Acid gas injection has become the environmentally friendly way to deal with the unwanted by-product of the sweetening of natural gas. In the future it may become a means of dealing with carbon dioxide from other sources as well.

In a basic acid gas injection scheme, the acid gas off the amine regenerator tower is compressed and transported via pipeline to an injection well. From there, it is injected into a suitable formation for disposal. The formation is selected based on geological criteria such as the size of the disposal reservoir, and the containment of the injected acid gas. In an acid gas injection scheme, pressures can range from near atmospheric up to 30 MPa or more; the upper limit dictated by the selected reservoir. The temperature can range from about 30° C up to as much as 200° C; again the upper limit is being the reservoir conditions.

The design of the injection scheme requires a thorough knowledge of the phase equilibria encountered in wet acid gas mixtures. This paper reviews the experimental investigations into the relevant systems. This study is limited to the following components: hydrogen sulfide, carbon dioxide, methane, ethane, propane, and water. Even so, an interesting variety of phase equilibria will be presented. The design engineer is advised to be aware of all of the various phenomena encountered in mixtures of these components, as they will have a significant effect on the design.

Experimental Investigations

In this section, experimental investigations important to acid

gas injection will be reviewed. Typically, in acid gas injection schemes, we are not concerned with hydrocarbons heavier than propane. So, for this study, only equilibrium between the acid gas components and methane, ethane, and propane will be considered.

Hydrogen Sulfide + Carbon Dioxide

The most important non-aqueous system involved in acid gas injection is the binary mixture hydrogen sulfide + carbon dioxide, since acid gas is composed almost exclusively of these components.

Two early studies of the phase equilibrium in the system hydrogen sulfide + carbon dioxide were Bierlein and Kay⁽¹⁾ and Sobocinski and Kurata⁽²⁾. Bierlein and Kay measured vapour-liquid equilibrium (VLE) in the range of temperature from 0° to 100° C and pressures to 9 MPa, and they established the critical locus for the binary mixture. For this binary system, the critical locus is continuous between the two pure component critical points. Sobocinski and Kurata confirmed much of the work of Bierlein and Kay and extended it to lower temperatures, down as low as -95° C, which is where solids are formed. Furthermore, liquid phase immiscibility was not observed in this system. Liquid H₂S and CO₂ are completely miscible.

Robinson and Bailey⁽³⁾ and Robinson et al.⁽⁴⁾ studied the VLE in the ternary mixtures of hydrogen sulfide + carbon dioxide + methane. These investigations also included a few points for the binary system H₂S + CO₂. The points for the binary mixtures were at temperatures between 4° and 71° C, and at pressures from 4 to 8 MPa.

Recently Kellerman et al.⁽⁵⁾ reported data for the thermodynamic properties, including VLE, for the system H₂S + CO₂. Their measurements of the phase boundary were for temperatures between -25° and 60° C and pressures up to 9 MPa.

Hydrogen Sulfide + Hydrocarbons

Experimental investigations into binary systems containing hydrogen sulfide and light hydrocarbons are summarized in Table 1.

One of the interesting features of the system hydrogen sulfide + methane is liquid-phase immiscibility. The H₂S-rich and CH₄-rich liquids are immiscible. However, this occurs at temperatures well below those of interest in acid gas injection. However, unusual looking phase diagrams are often obtained for mixtures rich in H₂S and CH₄, because the algorithms typically are not designed for multiple liquid phases and they get "confused" (as does the design engineer generating them).

TABLE 1: Experimental investigations vapor-liquid equilibrium (non-aqueous) for mixtures containing hydrogen sulfide and light hydrocarbons.

Other Gas	Temperature (° C)	Pressure (MPa)	Reference
CH ₄	4 to 171	1.4 to 70	Reamer et al. ⁽¹⁵⁾
	-100 to 100	up to 13.8	Kohn and Kurata ⁽¹⁶⁾
C ₂ H ₆	-6 to 100	up to 8.9	Kay and Brice ⁽¹⁷⁾
	10	1.6 to 3.1	Robinson and Kalra ⁽¹⁸⁾
C ₃ H ₈ *	-73 to 10	0.06 to 3.1	Kalra et al. ⁽¹⁹⁾
	50 to 94	2.8 to 4.1	Gilliland and Scheeline ⁽²⁰⁾
	-30 to 15	0.2 to 1.7	Steckel ⁽²¹⁾
	-1 to 100	1.4 to 8.3	Kay and Rambosek ⁽²²⁾
	-56 to 71	0.1 to 2.8	Brewer et al. ⁽²³⁾
	25 to 100	up to 7 MPa	Jou et al. – azeotropy ⁽²⁴⁾

* see Reference (25) for a detailed review of the system propane + hydrogen sulfide, including a critical review of the works noted in the table.

TABLE 2: Experimental investigations vapor-liquid equilibrium (non-aqueous) for mixtures containing carbon dioxide and light hydrocarbons.

Other Gas	Temperature (° C)	Pressure (MPa)	Reference
CH ₄	-73 to 23	1.4 to 8.3	Donnelly and Katz ⁽²⁶⁾
	-176 to -61	up to 4.8	Davis et al. ⁽²⁷⁾
	-68 to -75	4 to 5.5	Sterner ⁽²⁸⁾
	-40 to 10	3.7 to 8.2	Kaminishi et al. ⁽²⁹⁾
	-87 to -53	2.7 to 6.9	Neumann and Walch ⁽³⁰⁾
	-20 to 15	2.6 to 8.6	Arai et al. ⁽³¹⁾
	-120 to -54	1.2 to 6.4	Hwang et al. ⁽³²⁾
	-43 to -23	0.9 to 8.5	Davalos et al. ⁽³³⁾
	-3	3.2 to 8.4	Somait and Kidnay ⁽³⁴⁾
	-120 to -54	0.6 to 4.7	Mraw et al. ⁽³⁵⁾
	-54 to -3	0.6 to 8.5	Al-Sahhaf et al. ⁽³⁶⁾
	15 and 20	5.1 to 8.15	Xu et al. ⁽³⁷⁾
	28	6.9 to 7.7	Bian et al. ⁽³⁸⁾
	-43 to -3	0.9 to 8.3	Wei et al. ⁽³⁹⁾
C ₂ H ₆	10 to 20	3.1 to 6.3	Khazanova and Lesnevshaya ⁽⁴⁰⁾
	-31 to 10	up to 5	Gugnoni et al. ⁽⁴¹⁾
	-31 to 10	up to 5	Gugnoni et al. ⁽⁴²⁾
	-20	1.4 to 2.3	Nagahama et al. ⁽⁴³⁾
	16	3.6 to 5.5	Robinson and Kalra ⁽¹⁸⁾
	-50 to 20	0.5 to 6.3	Fredenslund and Mollerup ⁽⁴⁴⁾
	-23	1.3 to 2.1	Davalos et al. ⁽³³⁾
	10 to 25	3 to 6.6	Ohgaki and Katayama ⁽⁴⁵⁾
	-33 to -3	1.5 to 3.6	Brown et al. ⁽⁴⁶⁾
	-33 to -3	0.3 to 3.3	Wei et al. ⁽³⁹⁾
C ₃ H ₈	17 to 93	up to 7	Poettmann and Katz ⁽⁴⁷⁾
	4 to 71	up to 7	Reamer et al. ⁽⁴⁸⁾
	-40 to 0	0.1 to 3.5	Akers et al. ⁽⁴⁹⁾
	32 to 88	5 to 7	Roof and Baron ⁽⁵⁰⁾ - critical
	-20 to 0	0.2 to 3.5	Nagahama et al. ⁽⁴³⁾
	-29 and -7	0.5 to 2.6	Hamam and Lu ⁽⁵¹⁾

Carbon Dioxide + Hydrocarbons

Experimental investigations into binary systems containing carbon dioxide and light hydrocarbons are summarized in Table 2.

Among the interesting equilibria observed in these systems is that ethane and carbon dioxide exhibit azeotropy. This makes separation of these two components by binary distillation impossible. Another fascinating feature of systems containing CO₂ is that solids (dry ice) may form at temperatures encountered in cryogenic processing. Although these temperatures are not of interest

in acid gas injection, the design engineer should be aware of them for other applications.

Multicomponent Mixtures

Table 3 summarizes the experimental investigations into multicomponent systems containing hydrogen sulfide and/or carbon dioxide with light hydrocarbons.

An interesting investigation of the ternary mixture H₂S + CO₂

TABLE 3: Experimental investigations vapor-liquid equilibrium (non-aqueous) for mixtures containing hydrogen sulfide and/or carbon dioxide and light hydrocarbons.

Gas	Temperature (°C)	Pressure (MPa)	Reference
H ₂ S + CO ₂ +	38	4.1 to 12.4	Robinson and Bailey ⁽³⁾
CH ₄	4 and 71	6.9 to 12.4	Robinson et al. ⁽⁴⁾
	-34 to -51	2.1 to 4.8	Hensel and Massoth ⁽⁵²⁾
	-83 to 29	1 to 13	Ng et al. ⁽⁶⁾
CO ₂ + CH ₄ +	-23	2.1 to 3.0	Davalos et al. ⁽³³⁾
C ₂ H ₆	-43	1.1 to 6.6	Wei et al. ⁽³⁹⁾
H ₂ S + CO ₂ +	6 to 37	4.0 to 8.5	Clark et al. ^{(11)*}
CH ₄ + H ₂ O			

* these measurements contained a small amount of water in a mixture of H₂S+CO₂+ CH₄, but are not water-content measurements

+ CH₄ was performed by Ng et al.⁽⁶⁾ Although much of this study was at temperatures below those of interest in acid gas injection, they provide data useful for testing phase behaviour prediction models. The multiphase equilibrium they observed for this mixture, including multiple critical points for a mixture of fixed composition, should be of interest to all engineers working with such mixtures. It demonstrates that the equilibria can be complex, even for relatively simple systems.

Equations of State

To date, it has largely been assumed that the calculation of the vapour-liquid equilibrium in acid gas systems can be performed using one of the popular equations of state [Soave (SRK)⁽⁷⁾ and Peng and Robinson, (PR)⁽⁸⁾]. This assumption is put to the test in this paper.

In order to use an equation of state, several input parameters are required. For pure component inputs, these equations require: the critical temperature, critical pressure, and acentric factor; and for enthalpy and entropy calculations, the ideal gas heat capacities. For all of the components in acid gas injection, these quantities are well known⁽⁹⁾. For more advanced equations of state, additional information may be required, and the nature of that infor-

mation depends on the equation under consideration.

To use these equations for mixtures requires mixing rules. Typically these mixing rules require binary interaction parameters, which are usually obtained from experimental phase equilibrium data. Mixing rules account for binary interaction and higher order interactions are ignored.

When applied to hydrocarbon mixtures, the SRK and PR equations provide good results, even when it is assumed that the binary interaction parameters are zero. Such is not the case when the non-hydrocarbons are present—interaction parameters must be included. All calculations given in this paper were performed using the PR equation.

Calculations

To demonstrate the accuracy one can expect when using a cubic equation of state for acid and sour gas systems, several examples will be presented. Although the results shown here are for the PR equation, equivalent results can be expected if the SRK equation were used, if proper interaction parameters are used.

Figure 1 shows the phase envelopes for four mixtures of H₂S + CO₂. The experimental data in the figure are from Bierlein and Kay⁽¹⁾. Additional data from Bierlein and Kay are not shown for clarity, but the predictions are equivalent to those shown. The

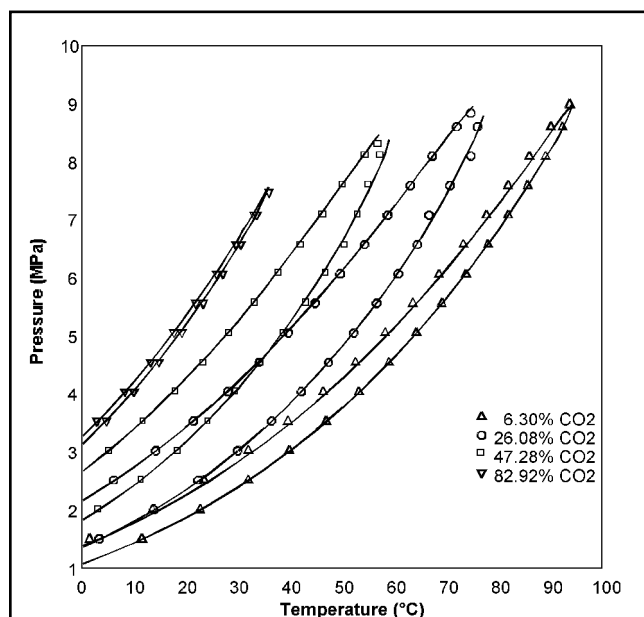


FIGURE 1: Phase Envelopes for Mixtures of H₂S + CO₂. Data from Bierlein and Kay⁽¹⁾ and Curves from Peng-Robinson Equation of State.

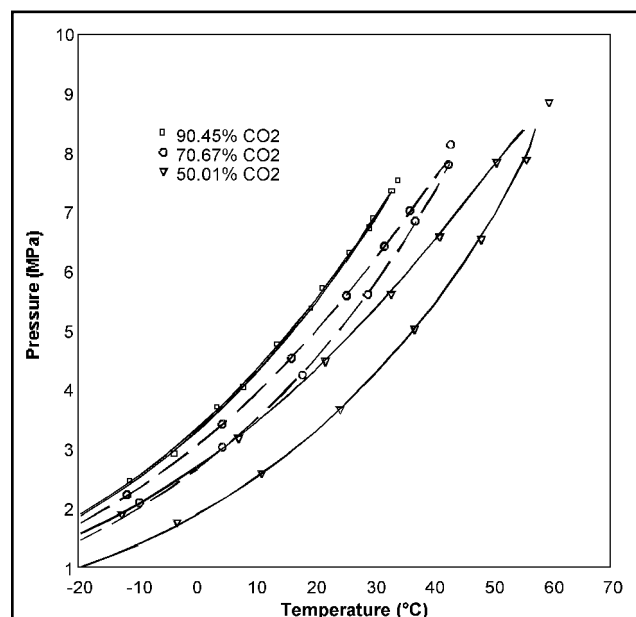
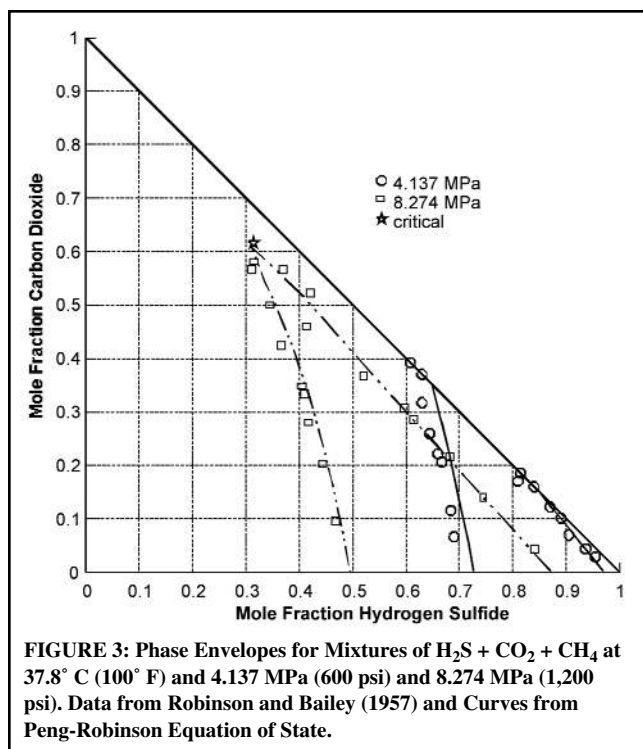


FIGURE 2: Phase Envelopes for Mixtures of H₂S + CO₂. Data from Kellerman et al.⁽⁵⁾ and Curve from Peng-Robinson Equation of State.



banana-shaped phase envelopes are characteristic of acid gas mixtures. Another thing that is typical is that the equation of state method has difficulty in the region near a critical point. However, in general, from this plot it can be concluded that the PR equation is a good fit of the experimental data.

Figure 2 shows some of the data reported by Kellerman et al.⁽⁵⁾ For clarity, the temperature for this plot was limited to -15° C, and thus a few of their data points are not shown. As with the calculations shown for the Bierlein and Kay data, the equation of state represents a good fit of the experimental data. In addition to showing that the PR equation is an adequate model for the phase equilibrium, it indirectly demonstrates good agreement between the two sets of experimental data.

As another illustration consider the ternary mixture H₂S + CO₂ + CH₄. Figure 3 shows the triangular diagram for this ternary mixture at 37.8° C at two pressures: 4.137 and 8.274 MPa. The calculation from the PR equation is shown along with experimental data from Robinson and Bailey⁽³⁾.

Figure 3 requires a little explanation. At 4.137 MPa, the two-phase region is a trapezoid. The trapezoid extends from binary VLE between CO₂ and H₂S to binary VLE between H₂S and CH₄. To the left of this trapezoid, the fluid is a vapour. These fluids would be rich in methane. To the right of the trapezoid the mixture is a liquid. At the higher pressure, the two-phase region is the space bounded by the triangle (one apex of the triangle being a critical point). As before, to the left of this triangle, the fluid exists as a vapour and to the right the mixture is a liquid. For a given temperature and pressure the overall composition dictates the nature of the phase equilibrium. For example, a mixture containing 30% H₂S, 30% CO₂, and 40% CH₄ would be a vapour at 37.8° C and 8.274 MPa. A mixture with an overall composition of 50% H₂S, 30% CO₂, and 20% CH₄ would be two-phase at 37.8° C and 8.274 MPa. The composition of the equilibrium phases is given by a tie-line, which is not shown. Therefore, the compositions of the phases are not obvious from the given figure. Finally, a mixture 75% H₂S, 20% CO₂, and 5% CH₄ would be a liquid at 37.8° C and 8.274 MPa. If the pressure of this mixture was reduced to 4.137 MPa, then it would be in the two-phase region (inside the trapezoidal region).

Figure 3 demonstrates that the PR equation is a good prediction of the ternary phase behaviour. This is noteworthy because the model only includes binary parameters. No additional tuning was performed to do the ternary predictions.

As a final case, Figure 4 shows the pressure-temperature diagram (phase envelope) for the mixture containing 40.23% H₂S, 9.88% CO₂, and 49.89% CH₄, which is the mixture studied by Ng et al.⁽⁶⁾ The data points on the plot are their data.

Again, this figure requires some explanation. Only the region greater than -15° C is shown. This limit was imposed for two reasons. First this is the region of interest to acid gas injection. Second, at lower temperatures, some of the unusual phase behaviour mentioned earlier manifests. Although very interesting, this phase behaviour is not important to this study or to the design of acid gas injection. The reader is referred to the original work for more discussion of this interesting phenomenon.

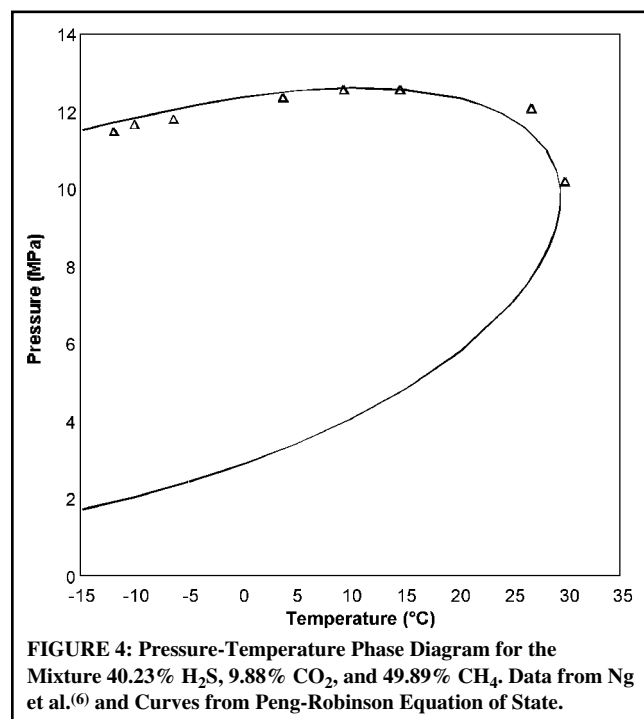
The curve and the data points shown in Figure 4 are all dew points, incipient liquid formation. The experimental critical temperature for this mixture is -16.9° C. Therefore, the plot presents the large retrograde region for this mixture. From the PR calculations, the cricondentherm is estimated to be 29° C. In this mixture, liquid can form at a temperature almost 45 Celsius degrees higher than the critical temperature. The cricondenbar is estimated to be 12.5 MPa. It is difficult to confirm the location of either the cricondenbar or the cricondentherm with the available experimental data. However, the PR is a good fit of the data, and thus it can be concluded that the estimation of these points is quite accurate as well.

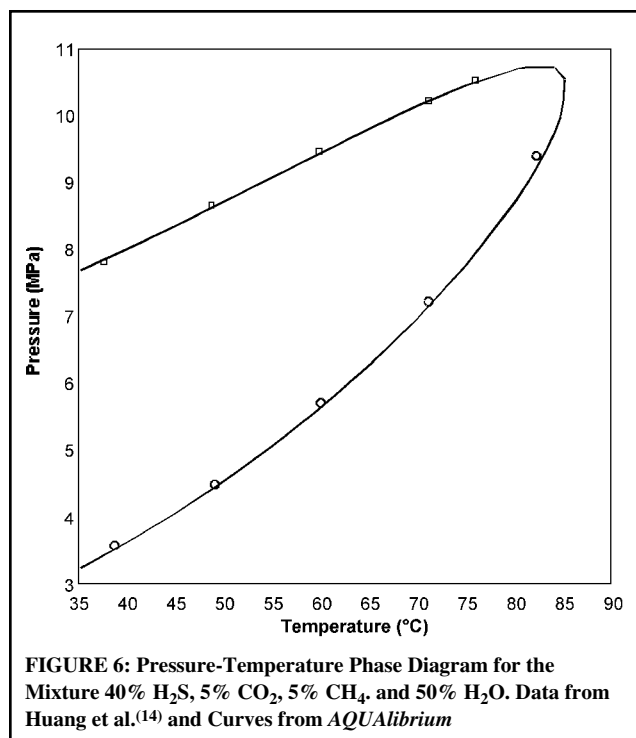
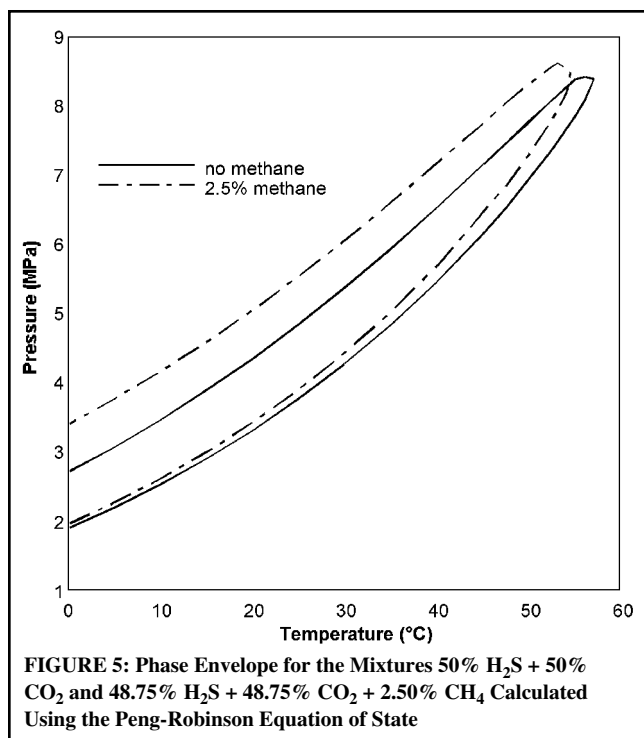
Synopsis

The results presented here are neither rigorous nor complete. However, they are exemplary. From these phase diagrams, we should have a fairly high level of confidence that the PR equation can adequately model the VLE in these acid and sour gas mixtures, provided we have a good set of input parameters.

The conclusion reached in this paper is the same as that obtained by Huron et al.⁽¹⁰⁾ in their study for the VLE and critical loci calculations for the similar mixtures (CO₂ or H₂S with hydrocarbons). The difference between this study and that of Huron et al. is that the predictions of Huron et al. were performed using the SRK equation. But, as was stated earlier, the VLE predictions of the PR and SRK equation are essentially equivalent.

On the other hand, this is contrary to the conclusion drawn by Clark et al.⁽¹¹⁾ They concluded that the equations of state are inadequate for wet acid gas mixtures. A review of their work indicates that their conclusion may be in error.





Effect of Hydrocarbons

One of the problems encountered in both the design and operation of acid gas injection schemes is the presence of hydrocarbons in the acid gas stream. The problems regarding the effect on the density have already been discussed⁽¹²⁾, so here we will focus on their effect on the phase equilibria.

In the comparison between experimental data and the PR equation, our calculation tool, some examples of the presence of hydrocarbons were shown. In this section, hydrocarbon concentrations will be limited to those normally observed in acid gas injection (i.e., a few mole percent).

Figure 5 shows a comparison between the phase envelope for an equimolar mixture of H₂S and CO₂ and for a similar mixture containing 2.5% CH₄. The presence of the methane has only a relatively small effect on the dew point (except near the critical point). This is because the less volatile components (the H₂S and CO₂) have a greater effect on the dew point. On the other hand, the bubble point has been increased significantly. In essence it requires more pressure to liquefy the more volatile hydrocarbon. The overall effect of the presence of the methane is to broaden the phase envelope.

From a process perspective, this broadening of the phase envelope causes a few problems. As was discussed by Carroll and Maddocks⁽¹³⁾, condensation of the acid gas on the interstage of compression is to be avoided. The wider phase envelope makes this more difficult in the design stage.

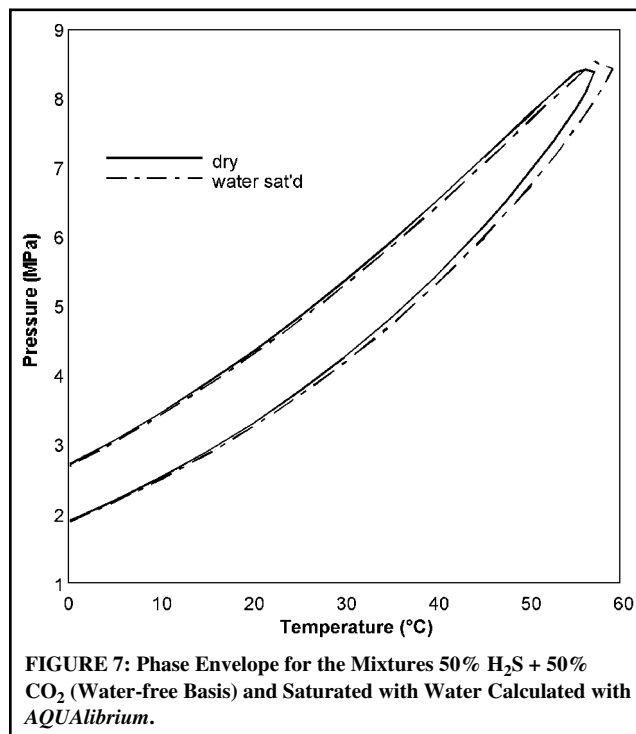
Effect of Water

Here what will be examined is the effect of water on the non-aqueous equilibrium. The aqueous phase equilibrium will be discussed in a subsequent paper. Calculations presented in this work for mixtures with water are calculated using *AQUAlibrium*, which is not strictly an equation of state method. However, the comparisons made between predictions presented earlier and those in this section are valid. *AQUAlibrium* uses the PR equation for the non-aqueous phases.

As a brief demonstration of the accuracy of the calculations, Figure 6 shows the non-aqueous phase envelope for a mixture containing 40% H₂S, 5% CO₂, 5% CH₄ and 50% water. The experimental data are from Huang et al.⁽¹⁴⁾ Not obvious from this figure is the presence of a third phase (aqueous liquid). What is shown in

the figure is the non-aqueous equilibria. This mixture has both bubble and dew points in the range of temperatures shown in the plot (unlike the one shown in Figure 6). The three-phase critical point for this mixture is estimated to be approximately 85° C and 10.6 MPa. From this figure we can conclude that the model is an accurate representation of the experimental data.

Figure 7 is similar to Figure 5 in as much as it shows the phase envelopes for mixtures that are nominally equimolar in H₂S and CO₂. For the dashed curve in Figure 7, the mixture is saturated in water. That means that for every point on the water-saturated curve, the water content of the mixture is different. As the temperature increases, so does the water content of the acid gas phases. At low temperature, the effect of water, is quite small. This is because, at low temperatures, the water is less volatile, and thus there is only a small amount of water in the non-aqueous phases.



As the temperature increases, so does the volatility of water and there is more water present in the non-aqueous phases. Thus water has an increased effect at higher temperatures.

Concluding Remarks

In the design of an acid gas injection scheme, the design engineer must consider a wide range of phase equilibria. They must be prepared to handle these calculations with the proper set of calculation tools that have been constructed using the best available experimental data

It was demonstrated that currently available calculations tools are quite accurate for predicting the complex phase equilibria exhibited by these systems. This includes such non-ideal behaviour as azeotropy.

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