PHASE EQUILIBRIA RELEVANT TO ACID GAS INJECTION

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The design of an acid gas injection scheme requires a significant amount of information regarding phase equilibria (Carroll and Maddocks, 1999; and Ng et al., 1999). This includes: (1) equilibrium involving the non-aqueous phases, (2) aqueous equilibrium including the water content of the non-aqueous phases and the solubility of the components in water, and (3) hydrate formation and inhibition.

The purpose of this paper is to review the literature for the available experimental data and survey methods for calculations of the various equilibria. This study will be limited to the following components: hydrogen sulfide, carbon dioxide, methane, ethane, propane, and water.

It is demonstrated that currently available calculation methods are adequate for predicting the various 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 chosen model (software package) by comparing it with experimental data. Available data are noted in this paper.

1. 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. Some countries have already imposed a carbon tax, a levy on the emission of carbon dioxide, making effusion of CO_2 an expensive proposition. It is not outside the realm of possibility that Canadians may face this prospect as well, in spite of claims from all levels of government.

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 criterion such as the size of the disposal reservoir and the containment of the injected acid gas.

The design of the injection scheme requires a thorough knowledge of the phase equilibrium encountered in wet acid gas mixtures. This paper reviews the experimental investigations into the relevant systems along with methods to make the required calculations.

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.

2. NON-AQUEOUS PHASE EQUILIBRIUM

The first aspect in the examination of the phase behavior is the equilibrium involving non-aqueous phases – the vapor and non-aqueous liquid. Phase equilibria involving an aqueous liquid and/or hydrates will be discussed in subsequent sections of this paper.

2.1 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.

2.1.1 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 (1953) and Sobocinski and Kurata (1959). Bierlein and Kay (1953) measured vapor-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 (1959) confirmed much of the work of Bierlein and Kay (1953) 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 H_2S and CO_2 are completely miscible.

Robinson and Bailey (1957) and Robinson et al. (1959) studied the VLE in the ternary mixtures of hydrogen sulfide+carbon dioxide+methane. These investigations also included a few points for the binary system H_2S+CO_2. 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. (1995) reported data for the thermodynamic properties, including VLE, for the system H_2S+CO_2. Their measurements of the phase boundary were for temperatures between -25° and 60°C and pressures up to 9 MPa.

2.1.2 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 H_2S-rich and CH_4-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 H_2S and CH_4 because the algorithms typically are not designed for multiple liquid phases and they get "confused" (as does the design engineer generating them).

2.1.3 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 CO_2 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.

2.1.4 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 H_2S+CO_2+CH_4 was performed by Ng et al. (1985). Although much of this study was at temperatures below those of interest in acid gas injection, they provide data useful for testing phase behavior 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.

2.2 Equations of State

To date it has largely been assumed that the calculation of the vapor-liquid equilibrium in acid gas systems can be performed using one of the popular equations of state (Soave, 1972; [SRK] and Peng and Robinson, 1976 [PR]). This assumption is put to the test in this paper.

In order to use an equation of state, requires several input parameters. 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 (for example see Reid et al., 1987). For more advanced equations of state, additional information may be required and the nature of that information 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 of 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 with the pure component and binary interaction parameters given in the appendix.[1]

2.2.1 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 H_2S+CO_2. The experimental data in the figure are from Bierlein and Kay (1953). Additional data from Bierlein and Kay (1953) are not shown for clarity, but the predictions are equivalent to those shown. The 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 recently reported by Kellerman et al. (1995). For clarity, one of their mixtures was omitted. In addition, 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 (1953) 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.

The next example is a little different. Figure 3 shows the pressure-composition diagram for carbon dioxide+ethane for two temperatures. The experimental data are bubble points from Gugnoni et al. (1973). This plot shows the azeotropic behavior of this system and that the equation of state approach can accurately model such behavior. Some are surprised that a simple model such as an equation of state can accurately model such highly non-ideal behavior.

As another illustration consider the ternary mixture H_2S+CO_2+CH_4. Figure 4 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 (1957).

Figure 4 requires a little explanation. At 4.137 MPa, the two-phase region is a trapezoid. The trapezoid extends from binary VLE between CO_2 and H_2S to binary VLE between H_2S and CH_4. To the left of this trapezoid, the fluid is a vapor. 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 vapor 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.

[1] The appendices have been omitted due to their size. Copies can be obtained by contacting the author directly.

For example, a mixture containing 30% H_2S, 30% CO_2, and 40% CH_4 would be a vapor at 37.8°C and 8.274 MPa. A mixture with an overall composition of 50% H_2S, 30% CO_2, and 20% CH_4 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% H_2S, 20% CO_2, and 5% CH_4 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).

As the next example, consider the ternary mixture CO_2+CH_4+C_2H_6. Figure 5 shows the ternary (triangular) phase diagram for this mixture at -23°C and 2.533 MPa. The data points on this plot are from Davalos et al. (1976).

In Figure 5 the region between the two curves is the two-phase region. The area to the left is a single-phase liquid whereas that to the right is the vapor. Therefore the curve on the right is the dew point locus and that on the left is the bubble point. At these conditions, if there is no methane in the mixture, then the fluid is single phase liquid, regardless of the ratio of ethane to carbon dioxide. On the other hand, binary mixtures of CH_4+C_2H_6 and CH_4+CO_2 exhibit phase splitting at these conditions. In both cases mixtures rich in methane will be gaseous and those lean in methane will be liquid. Note the curvature in the dew point curve is a vestige of the azeotropy in the CO_2+C_2H_6 mixture.

Figures 4 and 5 demonstrate that the PR equation is a good prediction of the ternary phase behavior. 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 6 shows the pressure-temperature diagram (phase envelope) for the mixture containing 40.23% H_2S, 9.88% CO_2, and 49.89% CH_4, which is the mixture studied by Ng et al. (1985). 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 behavior mentioned earlier manifests. Although very interesting, this phase behavior is not important to this study or to the design of acid gas injection. The reader is referred to the original work (Ng et al., 1985) for more discussion of this interesting phenomenon.

The curve and the data points shown in Figure 6 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.

A few additional phase diagrams are included in the appendix. These are provided for further evidence of the accuracy of the equation of state approach. No detailed explanation is provided for the figures given in the appendix.

2.2.2 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. (1978) in their study for the VLE and critical loci calculations for the similar mixtures (CO_2 or H_2S with hydrocarbons). The difference between this study and that of Huron et al. (1978) is that the predictions of Huron et al. (1978) were performed using the Soave (1972) 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. (1998). They concluded that the equations of state are inadequate for wet acid gas mixtures. A more detailed discussion of the work of Clark et al. (1998) is presented in the appendix.

2.3 Effect of Hydrocarbons

One of the problems encountered in both the design and operation 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 (Carroll and Lui, 1997), 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 7 shows a comparison between the phase envelope for an equimolar mixture of H_2S and CO_2 and for a similar mixture containing 2.5% CH_4. 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 H_2S and CO_2) 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 (1999), 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.

2.4 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 section of this paper. Calculations presented in this work for mixtures with water are calculated using *AQUAlibrium*,[2] 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 8 shows the non-aqueous phase envelope for a mixture containing 40% H_2S, 5% $C0_2$, 5% CH_4 and 50% water. The experimental data are from Huang et al. (1985). 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 9 is similar to Figure 7 in as much as it shows the phase envelopes for mixtures that are nominally equimolar in H_2S and CO_2. In Figure 9 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.

3. AQUEOUS PHASE EQUILIBRIUM

The topic of the phase equilibria involving acid and sour gases with water is a vast subject that requires a complete paper to do it justice. Therefore only an overview will be presented here. In addition, recent papers by Carroll (1998a,b) covered the nuances of the phase behavior in the binary system water+hydrogen sulfide in great detail.

3.1 Water Content

An important aspect of acid gas injection is the water content of the acid gas mixture. In addition, it is important to know the effect of the state (gas or liquid) of the acid gas on the water content of the mixture. Table 4 lists experimental investigations into the water content of mixtures containing hydrogen sulfide and/or carbon dioxide.

The study of Selleck et al. (1952) is considered the benchmark investigation of the system hydrogen sulfide+water. They published tables of smoothed data, which are commonly quoted. However, these tables are based on relatively few and scattered experimental data points. Carroll

[2] *AQUAlibrium* is copyright John Carroll. Additional information can be obtained by contacting him.

and Mather (1989a) re-evaluated the phase behavior in this system showing a clearer picture of the equilibria and accurately reflecting all of the available experimental data.

There have been many investigations of the water content of CO_2-rich fluids. In general there is reasonable agreement amongst the various sets of data in the low and moderate pressure regions. The benchmark investigation of the phase behavior in the system carbon dioxide+water was that of Wiebe and Gaddy (1939,1940,1941).

For many years there were two sets of conflicting data for the VLE in the system CO_2+H_2O at high pressure (up to 300 MPa). These were Tödeheide and Franck (1963) and Takenouchi and Kennedy (1964). Although these studies agreed qualitatively, they differed significantly quantitatively. Recent results by Mather and Franck (1992) indicate that the data of Tödeheide and Franck (1963) are the correct ones.

Finally, the author of this paper has performed thorough reviews of the literature and is unaware of any experimental data for the water content for binary mixtures of H_2S+CO_2 in the public domain. Such data, if available, would be very useful.

There have been several experimental investigations into the water content of hydrocarbons. Table 5 lists those of interest in this study. In this paper, we are not strictly interested in the water content of hydrocarbons, but in acid gas mixtures containing hydrocarbons. We require a model that accurately predicts the water content of hydrocarbons in order to have the confidence that it will work for the multicomponent mixtures. Those are the reasons why they are included here.

3.2 Solubility

The topic of the solubility of these gases in water is also an immense subject. Although it too is of some importance to the design of acid gas injection scheme, it will not be discussed here. Recent reviews of the solubility of carbon dioxide in water (Carroll et al., 1991; and Scharlin, 1996) and hydrogen sulfide in water (Fogg and Young, 1988; and Carroll and Mather, 1989b) are available to those interested in the subject.

3.3 Calculation Methods

Equations of state, which are widely used for petroleum systems as mentioned earlier, cannot be used for aqueous systems. As a first criterion for their application, an equation of state must accurately predict the vapor pressure of the pure components. Neither the original form of the SRK nor the PR accurately reproduces the vapor pressure of water. So one must resort to a modified form such as the one proposed by Stryjek and Vera (1986), the PRSV equation. However, there are other such modifications available.

The next problem with aqueous systems is that the simple mixing rules are inadequate. That is, the mixing rule based on the single interaction parameter does not work for aqueous phase equilibrium. This too can be overcome. Without being over-simplistic, this requires new mixing rules. Basically, the mixing rule must be phase specific. In order to be phase specific, the mixing rule must include a density effect, a composition effect, or both. Simply having a mixing rule

that is temperature-dependent will not work because the temperature of the phases is all the same. The same is true of the pressure. Wong and Sandler (1992) proposed a mixing rule that has become quite popular, but there are many others.

Having said that, a properly constructed equation of state can be used for calculating the multiphase equilibrium in systems containing acid gas+water systems. However, the design engineer would be wise to confirm that the modeling software that they are using is sufficiently accurate for their design. To verify the model the design engineer should compare the predictions with the experimental data discussed earlier.

An alternative to using equations of state is to use a two-fluid approach. For example, a Henry's law approach can be used for the aqueous phase and an equation of state for the non-aqueous phases. This method has been successfully implemented in *AQUAlibrium*, a commercially available software package. Results presented in this paper for equilibria involving water were calculated using *AQUAlibrium*.

The first series of calculations is intended to show the accuracy of *AQUAlibrium*. Similar accuracy can be anticipated from any well-constructed, thermodynamically consistent model. But, as mentioned earlier, the design engineer is well advised to confirm that the model chosen is indeed applicable for this purpose.

In general, the simple methods used for estimating the water content of sweet gas should not be used for acid gas. For example, the chart provided in GPSA Engineering Data Book (1998) is not accurate for acid gases, especially under pressure. As will be demonstrated, the water content of acid gases differs from that of sweet gases. There are corrections provided in the GPSA Engineering Data Book (1998) , but even they are insufficient for acid gases.

3.3.1 Hydrogen Sulfide

To begin, a single isotherm will be presented in order to reveal some of the detail of the phase behavior in mixtures of H_2S and water. Figure 10 shows the water content of H_2S at 37.8°C. Data from two sources are plotted along with the calculation from *AQUAlibrium*. This plot demonstrates the aforementioned problem with the data of Selleck et al. (1952). At this temperature they measured only three points for the water content of H_2S, only one of which is in the vapor region, whereas their smoothing has eleven points.

The calculations show three branches. The lower branch is the water content of the gas. This curve indicates that the water content of the gas is a strong function of pressure – as the pressure increases the water content decreases. The horizontal broken line is a three-phase point, the three phases being an aqueous liquid, an H_2S-rich liquid, and a vapor. The pressure of this point is estimated to be 2.64 MPa. The third branch, which is very steep, is the water content of liquid H_2S. A small region representing the non-aqueous vapor-liquid equilibrium for mixture of H_2S+H_2O, and lean in water, is not shown. This region would extend from the three-phase point to the vapor pressure of pure H_2S at the zero water-content axis. The vapor pressure of H_2S at this temperature is estimated to be 2.70 MPa, indicating how narrow this region is.

This diagram can be used as a map to indicate the nature of the phases present for a given overall water content. Water concentrations to the left of the curves (i.e., lean in water) are undersaturated – an aqueous phase does not form. On the other hand, for those to the right of the curve an aqueous phase will form. For example, a mixture with 0.25 mol% water at 2 MPa would be a single-phase vapor. A mixture with 1 mol% water at 10 MPa would be a single phase liquid. On the other hand, at 2.5 mol% water and 2 MPa an aqueous phase is present in addition to a gas. From the figure, at these conditions the composition of the gas is about 0.3 mol% water. Finally, at 2.5 mol% water and 10 MPa there are two phases: an aqueous liquid and an H_2S-rich liquid.

Figure 11 shows three more isotherms for mixtures of water and hydrogen sulfide. This figure is more difficult to interpret, but for each of the three isotherms there is a three-branched curve analogous to the one in the previous figure. All of these isotherms have a three-phase point, represented by the horizontal, broken line. This includes a three-phase point at 104.4°C, which Selleck et al. (1952) believed did not exist, probably because this temperature is greater than the critical point of pure H_2S (100°C). However, its existence was demonstrated by Carroll and Mather (1989a). Note the significant scatter in the experimental data and in particular the data of Selleck et al. (1952). This presents a different picture of the phase equilibrium than their often-quoted smoothed data.

Figure 12 depicts three additional isotherms for the system H_2S+H_2O. All of these are for temperatures where an H_2S-rich liquid does not exist. The prominent feature of these curves is the minimum in the water content. For these isotherms the minimum occurs between 10 and 15 MPa, but it is a function of the temperature. Again, note the significant scatter in the experimental data, particularly those of Selleck et al. (1952). For example, at 137.8°C there is a cluster of points from Selleck et al. (1952) between 7 and 15 MPa that appear to be randomly scattered between 6 and 8 mol% water. It is a little difficult to judge the adequacy of a model based on these data. Any model that passes through this cluster of points would probably be of sufficient accuracy. However, the model should be judged on its overall performance and not just on select regions.

Admittedly *AQUAlibrium* is not a perfect fit of the experimental data for the binary system H_2S+H_2O. However, it is a good compromise considering the scatter in the raw data available in the literature.

3.3.2 Carbon Dioxide

The phase behavior in the system CO_2+H_2O is qualitatively the same as H_2S+H_2O. Therefore a detailed discussion of the nature of the equilibria for this system will not be presented. One significant difference between the phase equilibria for the two systems is that a CO_2-rich liquid does not exist for temperatures greater than about 31°C, whereas for H_2S the non-aqueous liquid forms up to about 106°C.

Figure 13 shows the water content of carbon dioxide for five temperatures. Experimental data from five sources are also shown on this plot. Similar to the supercritical H_2S, the prominent feature on these plots is the minimum in the water content.

Figure 14 shows the water content of liquefied and supercritical CO_2 for five isotherms (the critical point of CO_2 is 31°C and 7.38 MPa). For the three lowest temperatures, the curves extend from the three-phase pressure. The other two curves are at temperatures where a CO_2-rich liquid does not form. These two isotherms do however exhibit the minimal behavior shown in the previous figure. This region has been omitted for clarity.

For the isotherms shown in the two figures, *AQUAlibrium* is a good fit of the experimental data, with the exception of a few points. This includes the critical region, which is notorious as a region where phase equilibrium calculations are difficult.

3.3.3 Hydrocarbons

Although we are not specifically interested in the water content of hydrocarbons in this study, they are presented for two reasons. The first of these is, as was mentioned earlier, to demonstrate the accuracy of the software. The second reason is to show how the behavior of hydrocarbons differs from that of the acid gas components.

Figure 15 shows three isotherms for the water content of methane. Note that for methane, the water content is a continually decreasing function of the pressure. This is what one would expect, but it differs from the behavior shown earlier for acid gas mixtures.

Figure 16 shows the water content of propane at three temperatures. Propane, unlike methane, is relatively easily liquefied. Much of the data shown is for the water content of liquid propane. The interesting point that this plot demonstrates is that the water content of liquid hydrocarbon is less than that of the gas. Again this differs from acid gas, where the water is more soluble in the liquid than it is in the gas.

3.3.4 Additional Calculations

A few additional calculations for the water content of gas mixtures are included in the appendix. These are provided for additional support of the accuracy of *AQUAlibrium*, but no detailed explanation is provided.

4. HYDRATES

Hydrates are ice-like solids that form in the presence of water and a relatively small molecule. The water molecules form a hydrogen-bonded lattice that is stabilized by the presence of the "guest" molecule. Hydrates form at temperatures greater than the freezing point of water and therefore a solid phase can form where one would not expect. Hydrates are notorious in the natural gas business for plugging flow line and process equipment.

Of the components commonly found in natural gas, none forms a hydrate more easily than hydrogen sulfide. The hydrate of H_2S forms at the lowest pressure and persists to the highest temperature. Carbon dioxide is also a hydrate former. Thus acid gas mixtures are notorious for forming hydrates.

The literature for the formation of hydrates in the system H_2S has been thoroughly reviewed by Carroll and Mather (1991). This review covers all investigations back to the middle of the 19th century. A good review of the carbon dioxide hydrate was presented by Bakker et al. (1996). For studies of hydrates in other systems, the reader is referred to the tome of Sloan (1998).

4.1 Inhibition

In the natural gas industry there are three common approaches to combating hydrates: (1) dehydration, (2) the use of heat, and (3) inhibition with chemicals, usually methanol. The philosophy behind dehydration is that if there is insufficient water present, then a hydrate cannot form. Essentially, heat is used to keep the fluid at a temperature above that at which a hydrate can form. Chemicals can be used to depress the temperature at which a hydrate forms. The mechanism is similar to using salt to remove the ice from an icy sidewalk in the winter or the use of glycol to de-ice airplanes.

Ng and Robinson (1994) presented some data for the hydrate forming conditions of H_2S+CO_2+ CH_4 in the presence of methanol. In addition to the inhibiting effect of methanol, they observed another interesting phenomenon. Since H_2S and CO_2 have significant solubilities, the methanol affected the composition of the gas. The gas was leaner in these components than the feed gas. Since the acid gas components are significant contributors to the hydrate formation, their removal from the non-aqueous phases can magnify the inhibiting effect.

4.2 Calculation Methods

A commonly employed method for doing rapid hydrate calculations is the Katz K-factor charts (GPSA Engineering Data Book, 1998). When applied to the pure acid gas components, these charts are surprisingly accurate from the lower quadruple point to the upper quadruple point. However, they should not be used outside this range. Their accuracy is reduced considerably when applied to mixtures of acid gases. In general their use for such mixtures is not recommended.

Computer methods are based on the theory of van der Waals and Platteeuw (1959). Essentially these use a statistical thermodynamic model to estimate the conditions at which a hydryte will form. Most modern calculation packages are based on the theory of van der Waals and Platteeuw (1959), although modification have been included to account for the pressures and phases of interest to natural gas industry. Two notable examples are the models of Parrish and Prausnitz (1972) and Ng and Robinson (1977).

These models, and the software packages developed from them, can successfully model the hydrate forming conditions in acid gas mixtures.

5. 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 also demonstrated that currently available calculations tools are quite accurate for predicting the complex phase equilibria exhibited by these systems. This includes such non-ideal behavior as liquid phase immiscibility and azeotropy.

6. REFERENCES

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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. (1951a)
	-100 to 100	up to 13.8	Kohn and Kurata (1958)
C_2H_6	-6 to 100	up to 8.9	Kay and Brice (1953)
	10	1.6 to 3.1	Robinson and Kalra (1974)
	-73 to 10	0.06 to 3.1	Kalra et al. (1977)
C_3H_8†	50 to 94	2.8 to 4.1	Gilliland and Scheeline (1940)
	-30 to 15	0.2 to 1.7	Steckel (1945)
	-1 to 100	1.4 to 8.3	Kay and Rambosek (1953)
	-56 to 71	0.1 to 2.8	Brewer et al. (1953)
	25 to 100	up to 7 MPa	Jou et al. (1995) – azeotropy

† - see Carroll and Mather (1992) 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 (1954)
	-176 to -61	up to 4.8	Davis et al. (1962)
	-68 to -75	4 to 5.5	Sterner (1961)
	-40 to 10	3.7 to 8.2	Kaminishi et al. (1968)
	-87 to -53	2.7 to 6.9	Neumann and Walch (1968)
	-20 to 15	2.6 to 8.6	Arai et al. (1971).
	-120 to -54	1.2 to 6.4	Hwang et al. (1976)
	-43 to -23	0.9 to 8.5	Davalos et al. (1976)
	-3	3.2 to 8.4	Somait and Kidnay (1978)
	-120 to -54	0.6 to 4.7	Mraw et al. (1978)
	-54 to -3	0.6 to 8.5	Al-Sahhaf et al. (1983)
	15 and 20	5.1 to 8.15	Xu et al. (1992)
	28	6.9 to 7.7	Bian et al. (1993)
	-43 to -3	0.9 to 8.3	Wei et al. (1995)
C_2H_6	10 to 20	3.1 to 6.3	Khazanova and Lesnevshaya (1966)
	-31 to 10	up to 5	Gugnoni et al. (1973)
	-31 to 10	up to 5	Gugnoni et al. (1974)
	-20	1.4 to 2.3	Nagahama et al. (1974)
	16	3.6 to 5.5	Robinson and Kalra (1974)
	-50 to 20	0.5 to 6.3	Fredenslund and Mollerup (1974)
	-23	1.3 to 2.1	Davalos et al. (1976)
	10 to 25	3 to 6.6	Ohgaki and Katayama (1977)
	-33 to -3	1.5 to 3.6	Brown et al. (1988)
	-33 to -3	0.3 to 3.3	Wei et al. (1995)
C_3H_8	17 to 93	up to 7	Poettmann and Katz (1945)
	4 to 71	up to 7	Reamer et al. (1951b)
	-40 to 0	0.1 to 3.5	Akers et al. (1954)
	32 to 88	5 to 7	Roof and Baron (1967) - critical
	-20 to 0	0.2 to 3.5	Nagahama et al. (1974)
	-29 and -7	0.5 to 2.6	Hamam and Lu (1976)

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
$H_2S+CO_2+CH_4$	38	4.1 to 12.4	Robinson and Bailey (1957)
	4 and 71	6.9 to 12.4	Robinson et al. (1959)
	-34 to -51	2.1 to 4.8	Hensel and Massoth (1964)
	-83 to 29	1 to 13	Ng et al. (1985)
$CO_2+CH_4+C_2H_6$	-23	2.1 to 3.0	Davalos et al. (1976)
	-43	1.1 to 6.6	Wei et al. (1995)
$H_2S+CO_2+CH_4+H_2O$	6 to 37	4.0 to 8.5	Clark et al. (1998)†

† - these measurements contained a small amount of water in a mixture of $H_2S+CO_2+CH_4$ but are not water-content measurements

Table 4 Experimental Investigations of the Water Content of Mixtures Containing Hydrogen Sulfide and Carbon Dioxide

Gas	Temperature (°C)	Pressure (MPa)	Reference
H_2S	5 to 60	up to 0.50	Wright and Maass (1932)
	37 to 171	2.7 to 35	Selleck et al. (1952)
	90 to 150	1.5 to 3.5	Lee and Mather (1977)
	37 to 315	up to 10	Gillespie et al. (1984)
CO_2	25 to 75	0.1 to 71.0	Wiebe and Gaddy (1941)
	25 to 100	1.7 to 5.1	Coan and King (1971)
	100 to 200	0.2 to 5.0	Zawisza and Malesinska (1981)
	16 to 260	0.7 to 13.8	Gillespie et al. (1984)
	-28 to 25	0.7 to 13.8	Song and Kobayashi (1987)
	100 to 200	0.3 to 8.1	Müller et al. (1988)
	15 to 40	5.2 to 20.3	King et al. (1992)
H_2S+CH_4	70	1.3 to 10.3	Lukacs and Robinson (1963)
	54 and 71	6.9 to 10.3	Maddox et al. (1988)
CO_2+CH_4	37 and 71	6.9 and 13.8	Maddox et al. (1988)
	15 to50	5.7 to 13.8	Song and Kobayashi (1989)
H_2S+CO_2 $+CH_4$	37 to 177	4.8 to 18.2	Huang et al. (1985)
	37	7.6 and 13.1	Maddox et al. (1988)
H_2S+CO_2+ $CH_4+C_3H_8$	49 and 93	1.4 to 69	Ng et al. (1999)

Table 5 Experimental Investigations of the Water Content of Mixtures Containing Light Hydrocarbons

Gas	Temperature (°C)	Pressure (MPa)	Reference
CH_4	37 to 240	up to 70	Olds et al. (1942)
	70	1.2 to 10.3	Lukacs and Robinson (1963)
	25 to 100	2.2 to 10	Rigby and Prausnitz (1968)
C_2H_6	37 to 240	up to 70	Reamer et al. (1943)
	25 to 100	2.2 to 5.1	Coan and King (1971)
	-30 to 30	?†	Parrish et al. (1982)
	-33 to 32	2.5 to 4.8	Song and Kobayashi (1994)
C_3H_8	37 to 150	up to 20	Kobayashi and Katz (1953)
	312 to 387	up to 200	de Loos et al. (1980)
	-30 to 30	?†	Parrish et al. (1982)
	-37 to 27	0.6 to 1.1	Song and Kobayashi (1994)
CH_4+C_2H_6	32 to 60	4 to 20	Villarreal et al. (1954)
C_2H_6+C_3H_8	-30 to 30	?†	Parrish et al. (1982)
	-17 to 24	4.1	Song and Kobayashi (1994)

† - the pressure of these measurements is not stated, but they indicate that they are at the "vapor pressure" of the hydrocarbon

FIGURE CAPTIONS

Fig. 1 Phase Envelopes for Mixtures of H_2S+CO_2. Data from Bierlein and Kay (1953) and Curves from Peng-Robinson Equation of State

Fig. 2 Phase Envelopes for Mixtures of H_2S+CO_2. Data from Kellerman et al. (1995) and Curve from Peng-Robinson Equation of State

Fig. 3 Pressure-Composition Diagram for CO_2+C_2H_6. Data from Gugnoni et al. (1975) and Curve from Peng-Robinson Equation of State

Fig. 4 Phase Envelopes for Mixtures of H_2S+CO_2+CH_4 at 37.8°C (100°F) and 4.137 MPa (600 psi) and 8.274 MPa (1200 psi). Data from Robinson and Bailey (1957) and Curves from Peng-Robinson Equation of State

Fig. 5 Phase Envelopes for Mixtures of CO_2+CH_4+C_2H_6. at -23.15°C (250 K) and 2.533 MPa Data from Davalos et al. (1976) Curves from Peng-Robinson Equation of State

Fig. 6 Pressure-Temperature Phase Diagram for the Mixture 40.23% H_2S, 9.88% CO_2, and 49.89% CH_4. Data from Ng et al. (1985) and Curves from Peng-Robinson Equation of State

Fig. 7 Phase Envelope for the Mixtures 50% H_2S + 50% CO_2 and 48.75% H_2S + 48.75% CO_2 + 2.50% CH_4 Calculated Using the Peng-Robinson Equation of State

Fig. 8 Pressure-Temperature Phase Diagram for the Mixture 40% H_2S, 5% CO_2, 5% CH_4. and 50% H_2O. Data from Huang et al. (1985) and Curves from *AQUAlibrium*

Fig. 9 Phase Envelope for the Mixtures 50% H_2S + 50% CO_2 (Water-free Basis) and Saturated with Water Calculated with *AQUAlibrium*.

Fig. 10 Water Content of Hydrogen Sulfide at 37.8°C (100°F). Data from Selleck et al. (1952) and Gillespie et al. (1984) and Curves from *AQUAlibrium*

Fig. 11 Water Content of Hydrogen Sulfide at 71.1°C (160°F), 93.3°C (200°F), and 104.4°C (220°F). Data from Selleck et al. (1952) [solid points] and Gillespie et al. (1984) [open points] and Curves from *AQUAlibrium*

Fig. 12 Water Content of Hydrogen Sulfide at 137.8°C (280°F), 148.9°C (300°F), and 171.1°C (340°F). Data from Selleck et al. (1952) [solid points] and Gillespie et al. (1984) [open points] and Curves from *AQUAlibrium*

Fig. 13 Water Content of Carbon Dioxide at 50°C, 75°C, 100°C, and 125°C. Data from Weibe and Gaddy (1941) [●, O], Coan and King (1971) [Δ,▼, ∇], Zawisza and Malesinska (1981) [■], Gillespie et al. (1984) [◊], and Müller et al. (1988) [▼] and Curves from *AQUAlibrium*

Fig. 14 Water Content of Carbon Dioxide at 15°C, 20°C, 25°C, 35°C, and 40°C. Data from King et al. (1992) and Curves from *AQUAlibrium*

Fig. 15 Water Content of Methane at 37.8°C (100°F), 71.1°C (160°F), and 104.4°C (220°F). Data from Olds et al. (1942) and Curves from *AQUAlibrium*

Fig. 16 Water Content of Propane at 37.8°C (100°F), 65.5°C (150°F), and 87.8°C (190°F). Data from Kobayashi and Katz (1953) and Curves from *AQUAlibrium*

Fig. 1

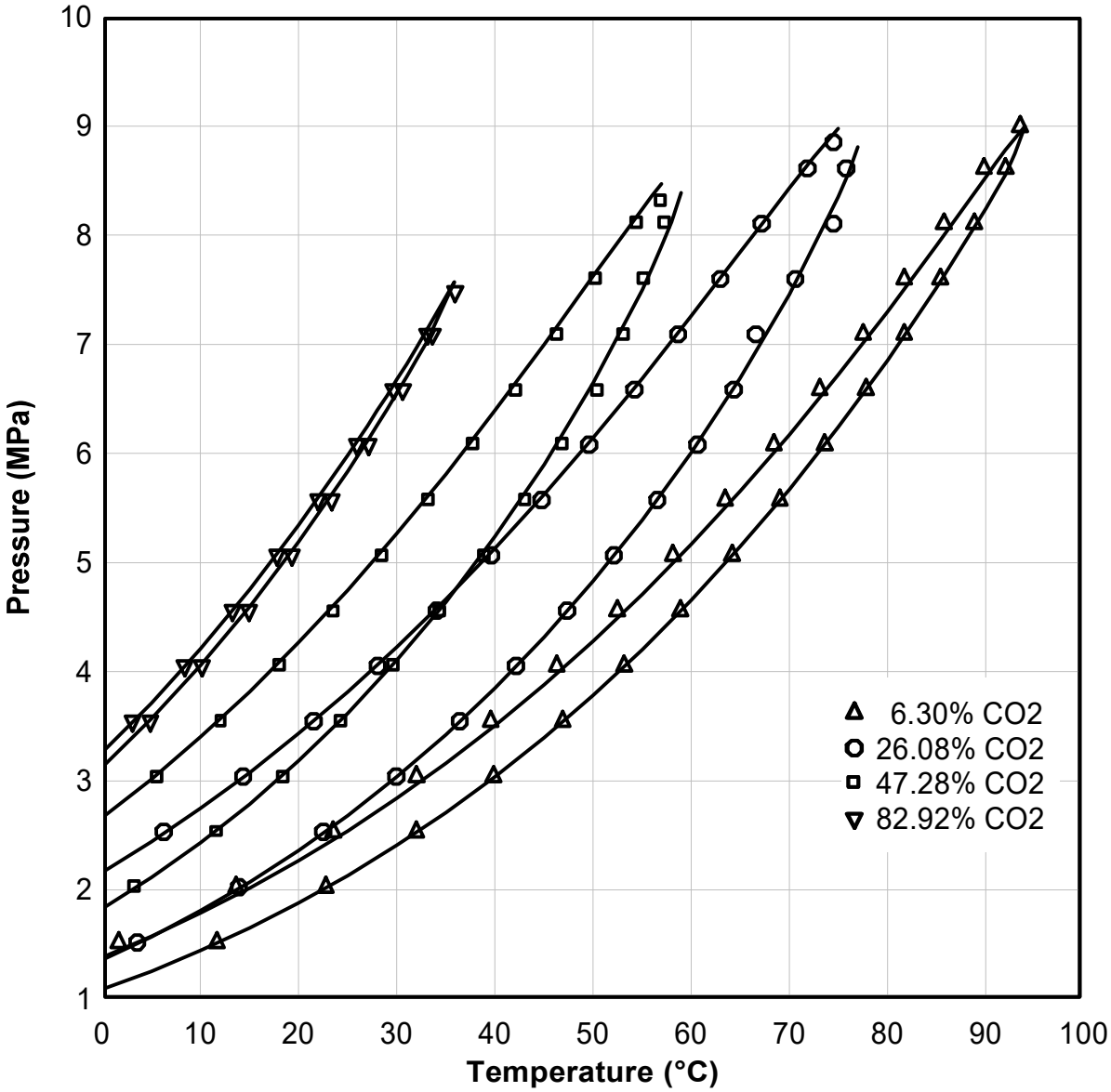

Pressure (MPa)
Temperature (°C)
6.30% CO2
26.08% CO2
47.28% CO2
82.92% CO2

Fig. 2

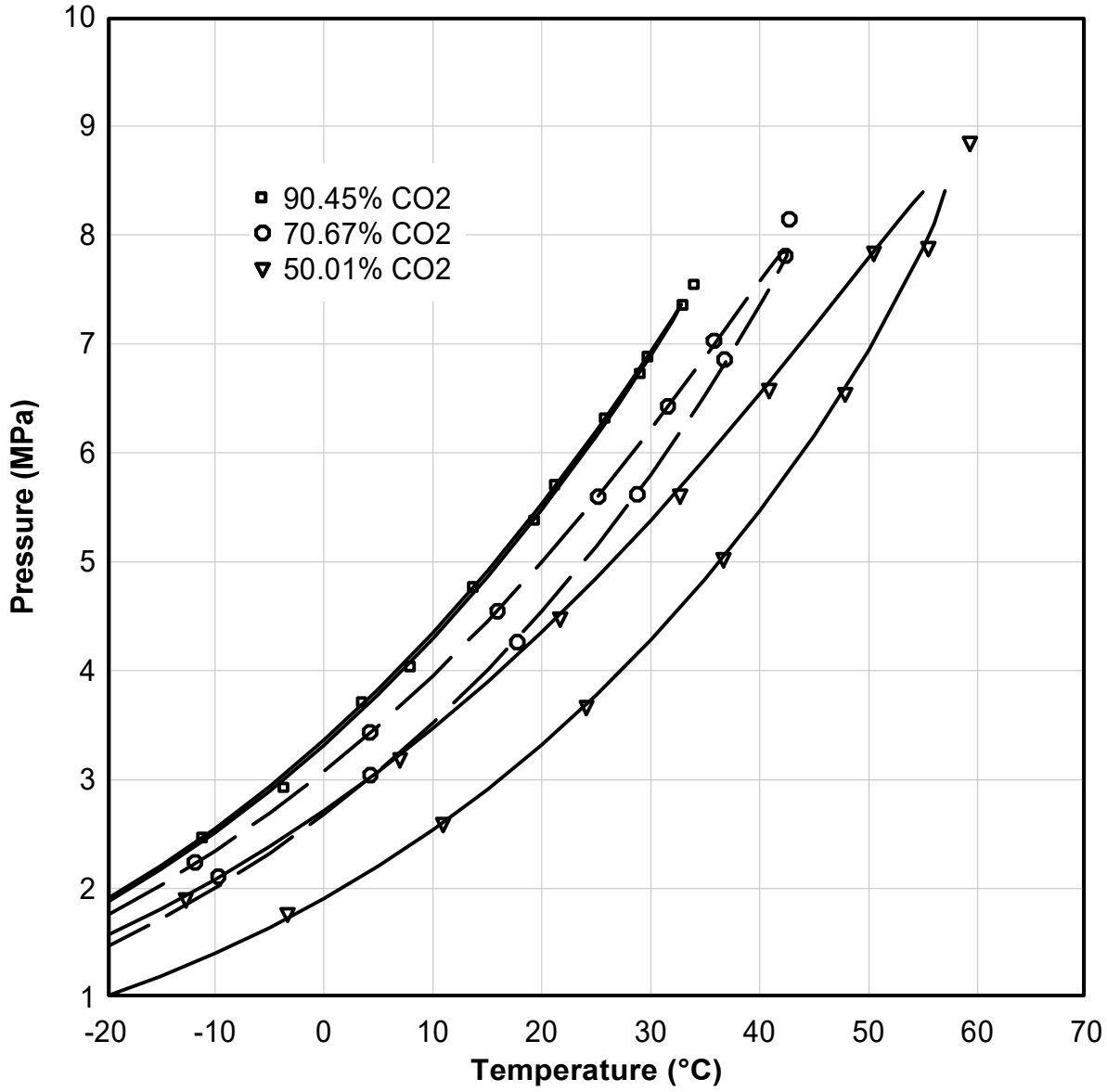

90.45% CO2
70.67% CO2
50.01% CO2
Pressure (MPa)
Temperature (°C)
10
9
8
7
6
5
4
3
2
1
-20
-10
0
10
20
30
40
50
60
70

Fig. 3

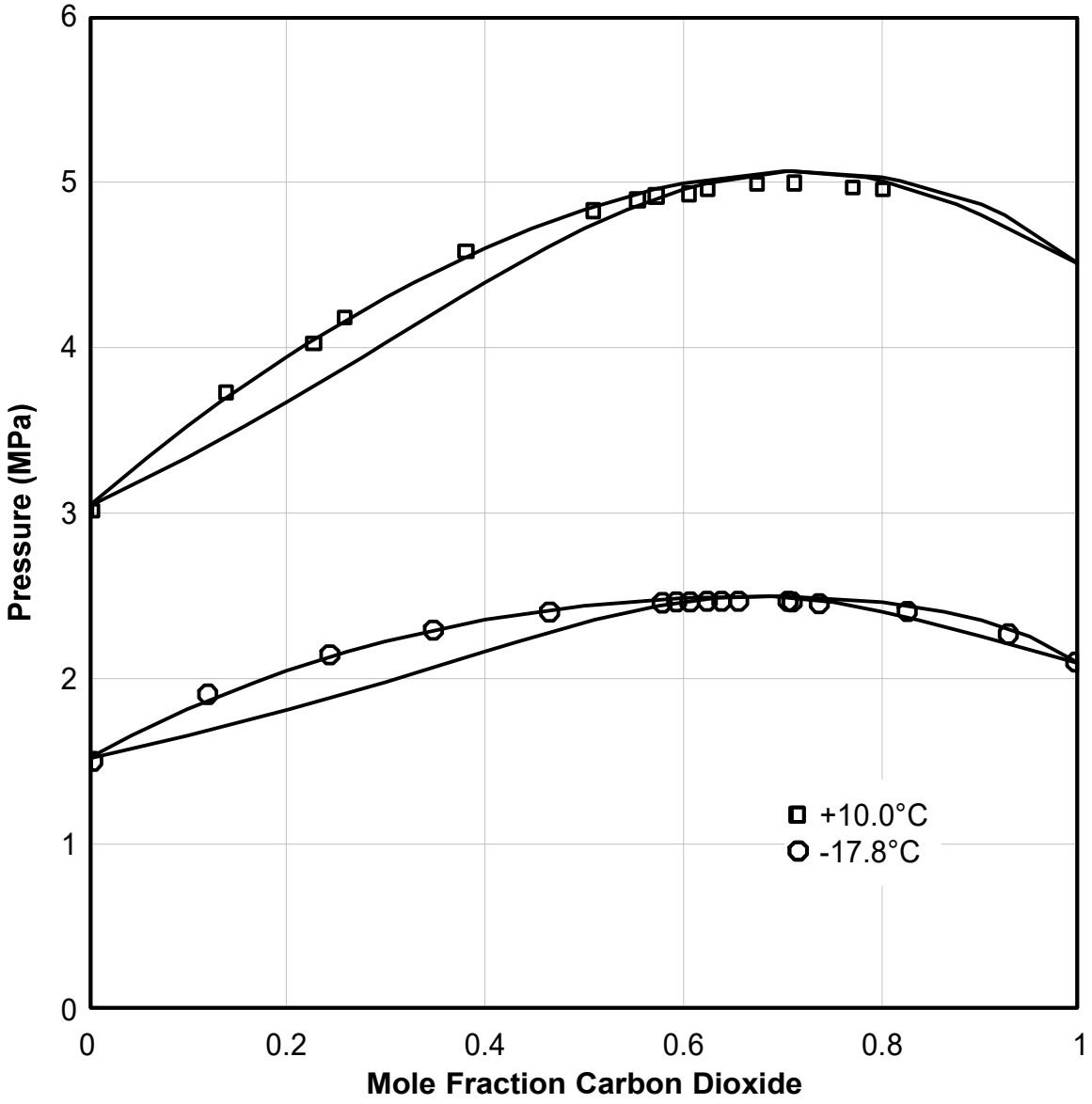

Pressure (MPa)
Mole Fraction Carbon Dioxide
0
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1
+10.0°C
-17.8°C

Fig. 4

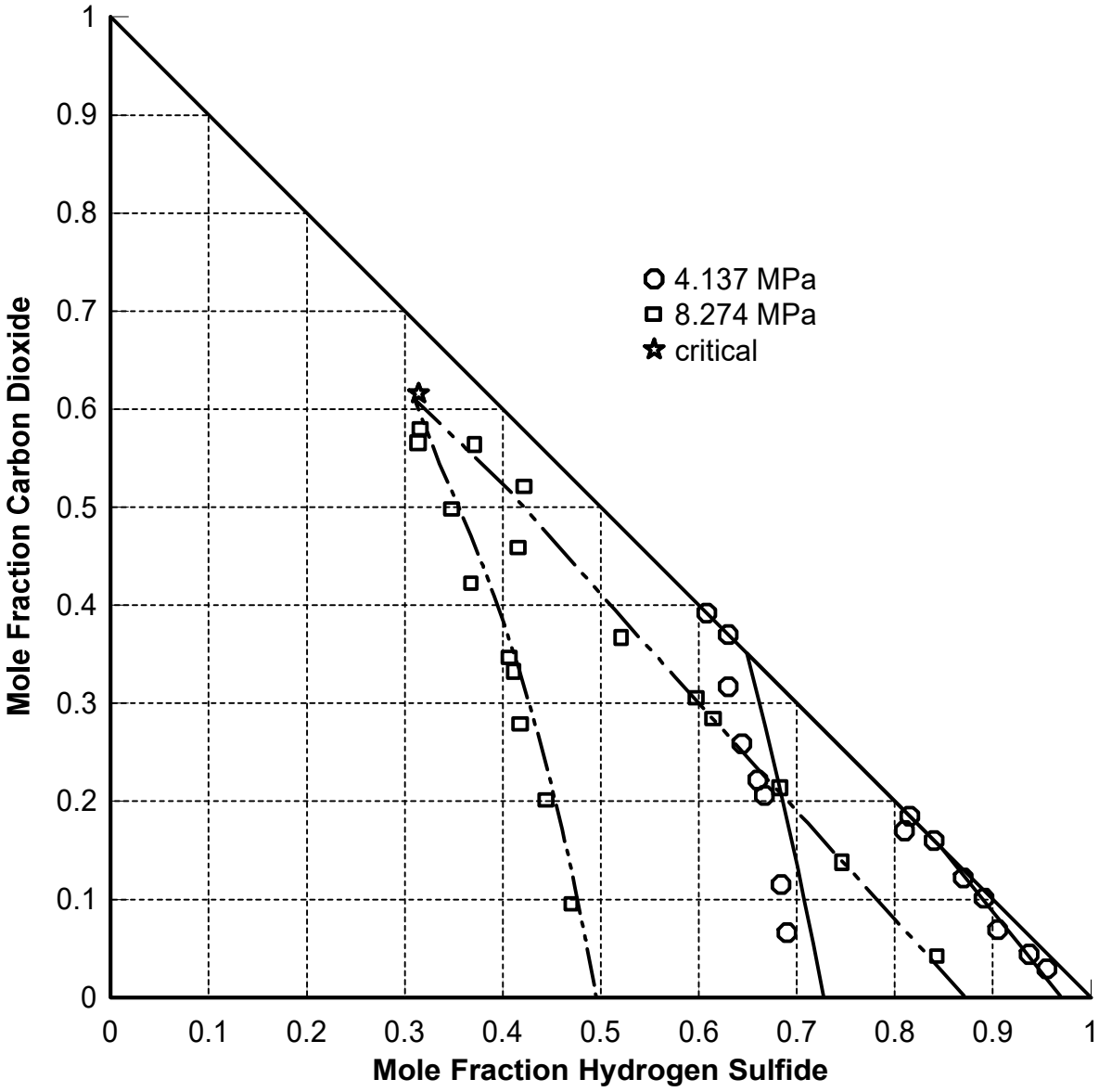

Mole Fraction Carbon Dioxide
Mole Fraction Hydrogen Sulfide
4.137 MPa
8.274 MPa
critical
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Fig. 5

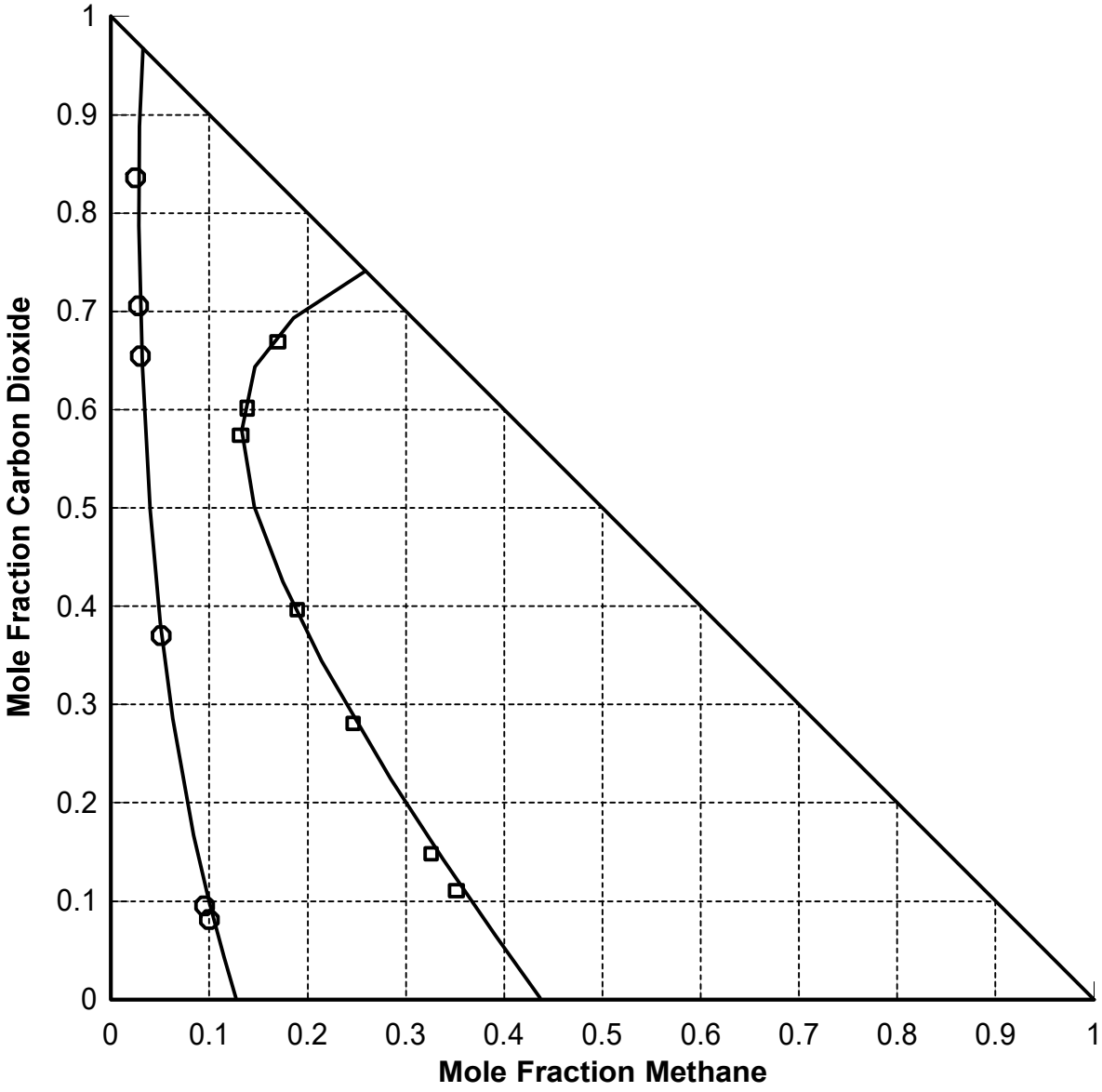

Mole Fraction Carbon Dioxide
Mole Fraction Methane
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Fig. 6

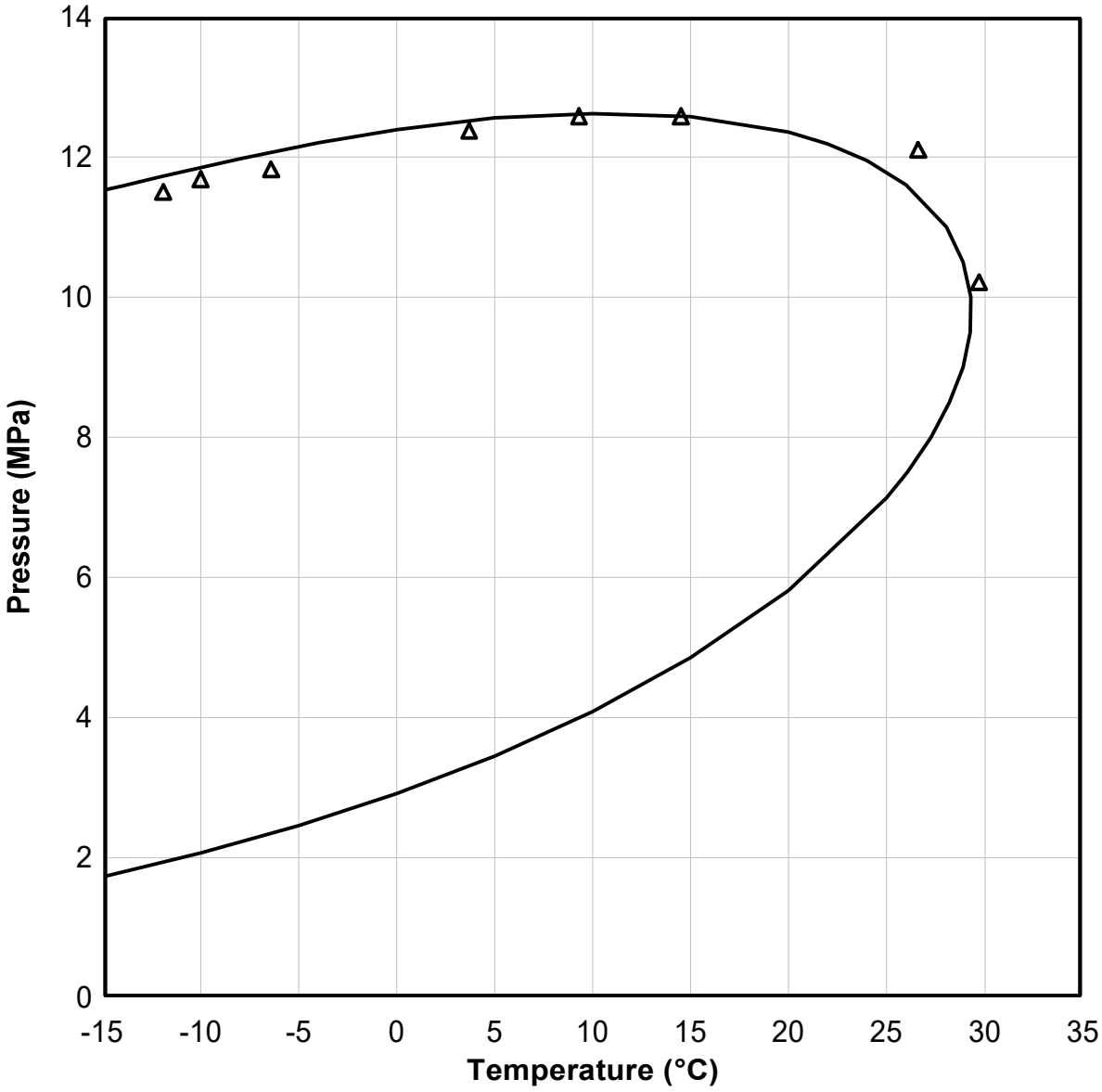

14
12
10
8
6
4
2
0
Pressure (MPa)
-15
-10
-5
0
5
10
15
20
25
30
35
Temperature (°C)

Fig. 7

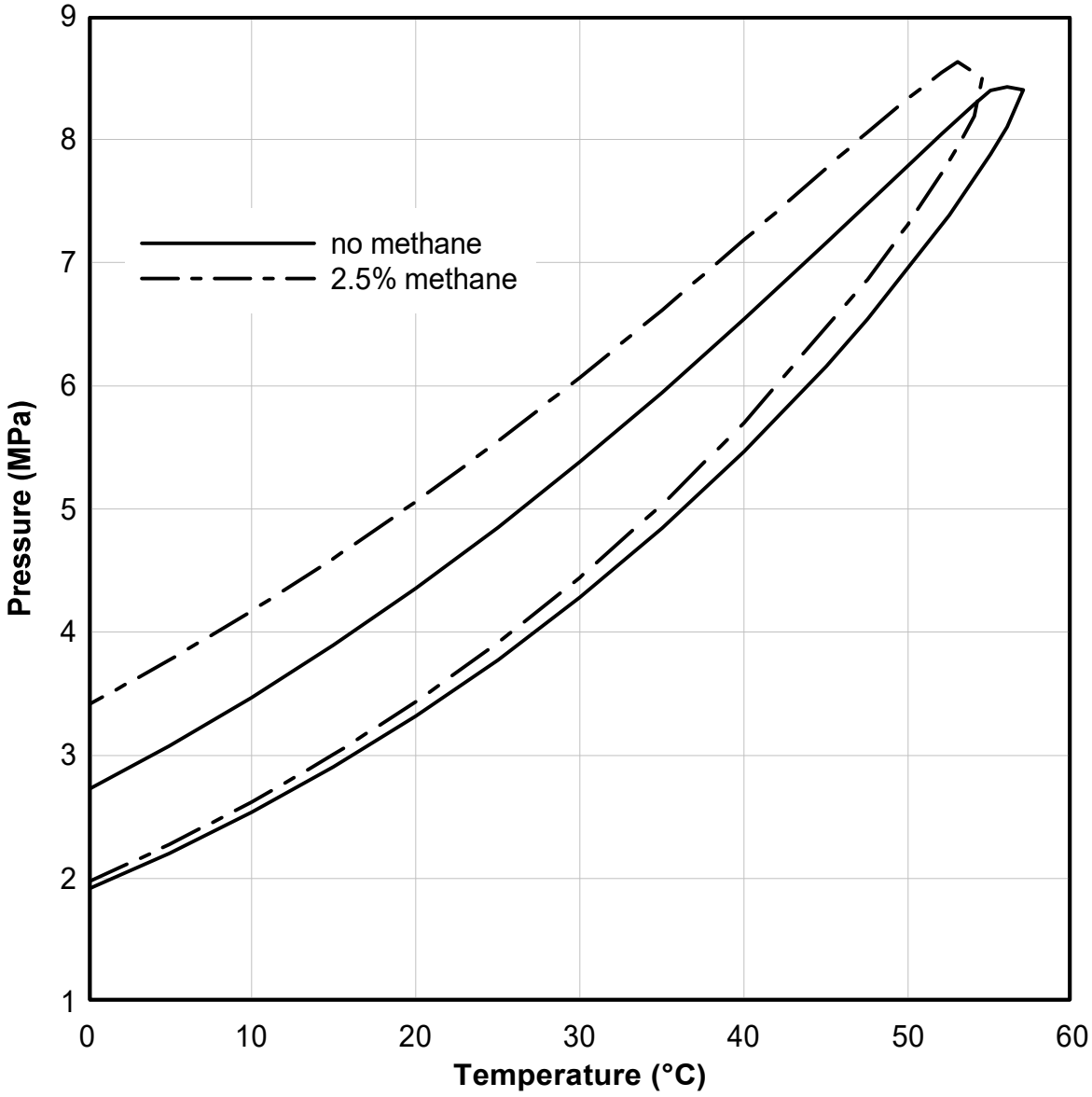

9
8
7
6
5
4
3
2
1
Pressure (MPa)
no methane
2.5% methane
0
10
20
30
40
50
60
Temperature (°C)

Fig. 8

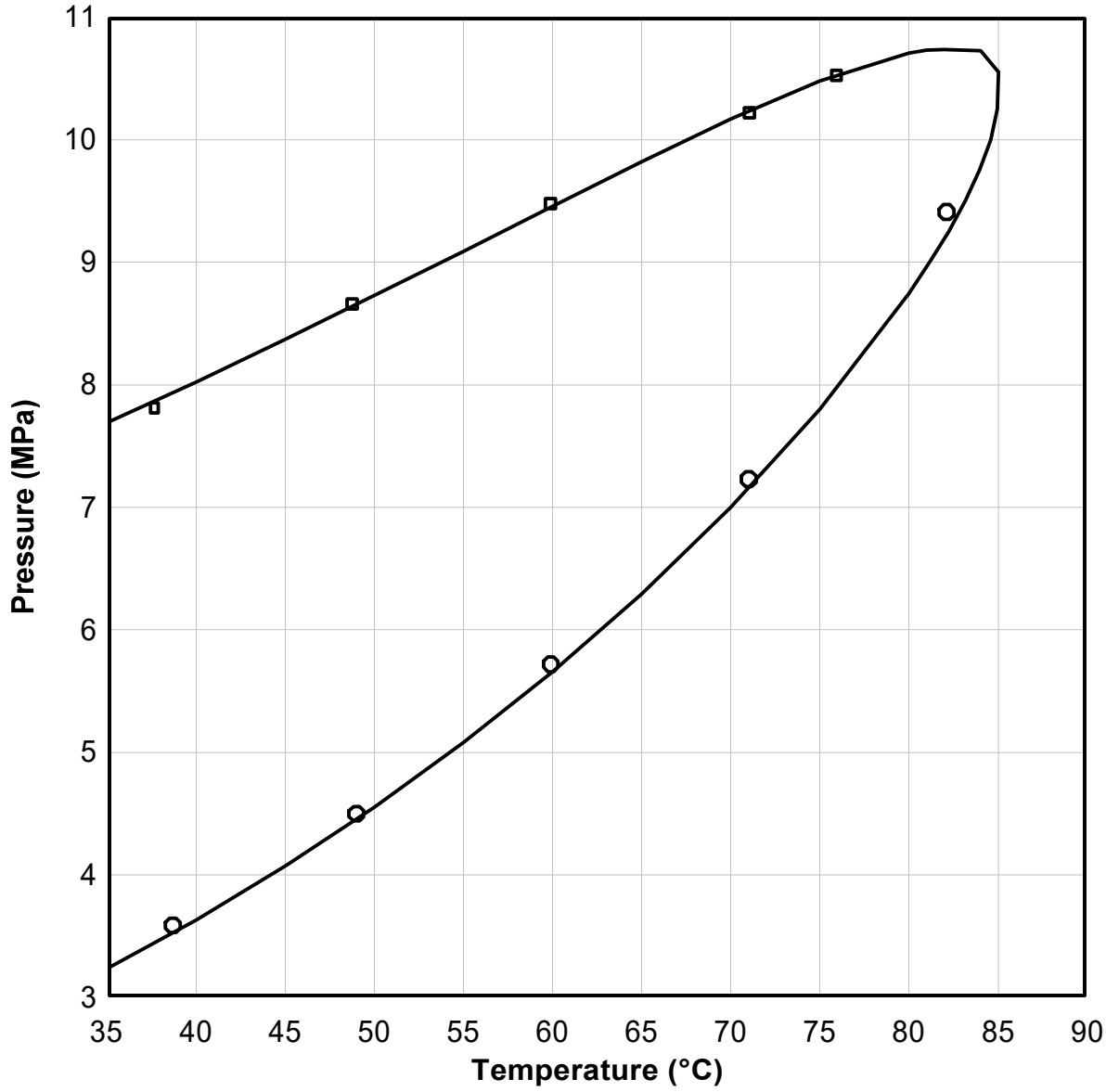

Pressure (MPa)
11
10
9
8
7
6
5
4
3
35
40
45
50
55
60
65
70
75
80
85
90
Temperature (°C)

Fig. 9

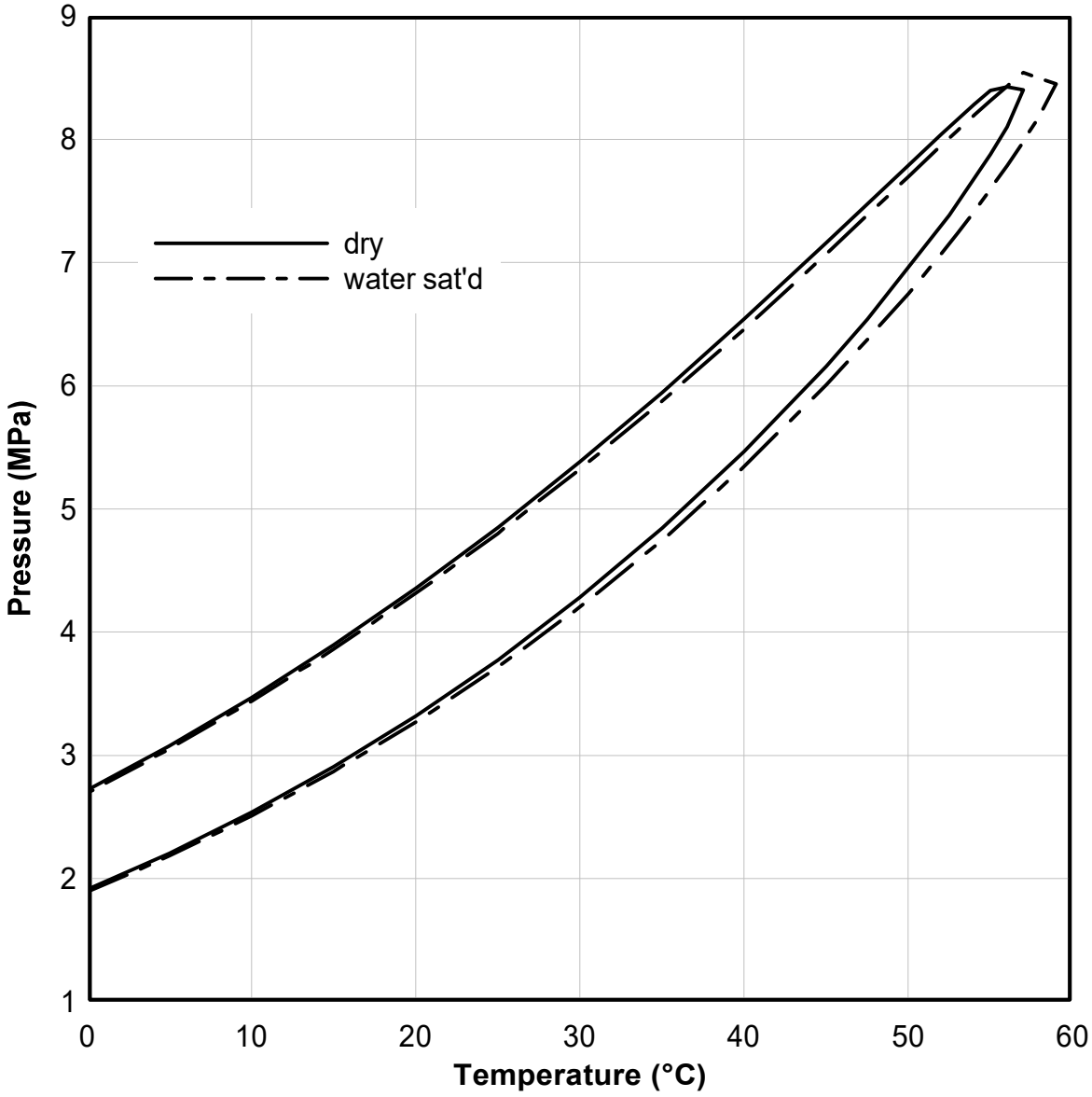

dry
water sat'd
Pressure (MPa)
Temperature (°C)
1
2
3
4
5
6
7
8
9
0
10
20
30
40
50
60

Fig. 10

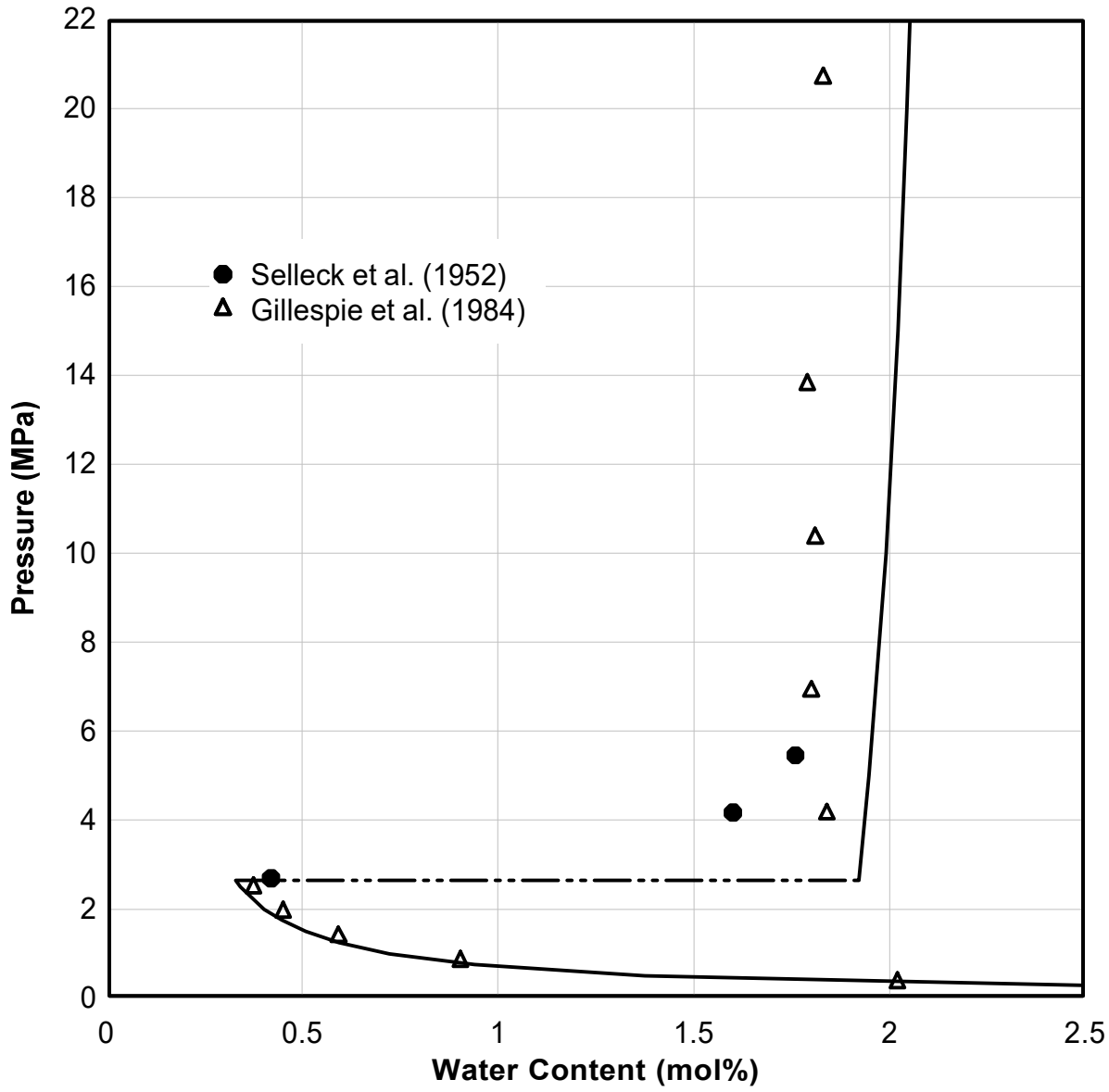

Selleck et al. (1952)
Gillespie et al. (1984)
Pressure (MPa)
Water Content (mol%)
0
2
4
6
8
10
12
14
16
18
20
22
0
0.5
1
1.5
2
2.5

Fig. 11

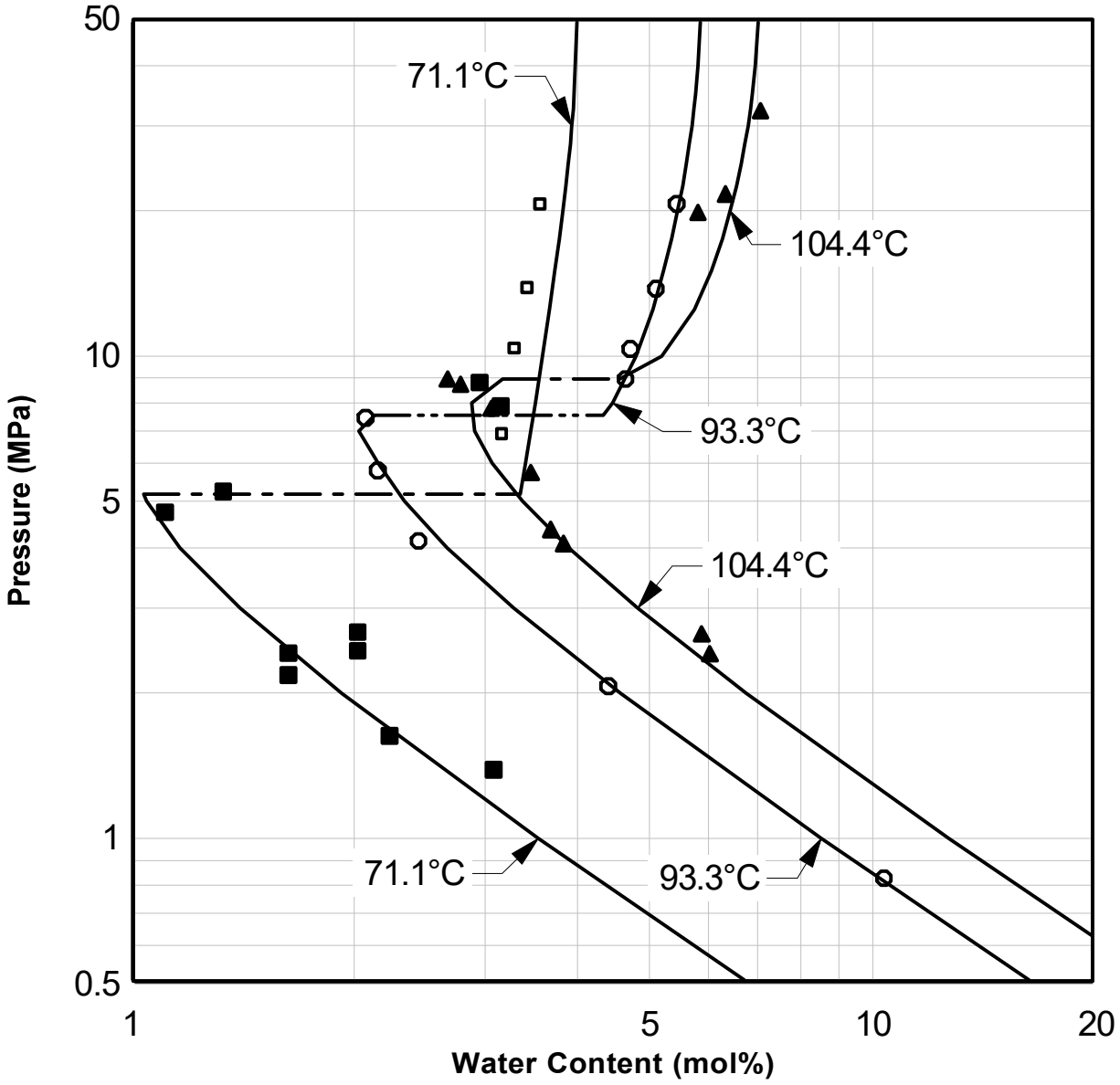

50
10
5
1
0.5
Pressure (MPa)
71.1°C
104.4°C
93.3°C
104.4°C
71.1°C
93.3°C
1
5
10
20
Water Content (mol%)

Fig. 12

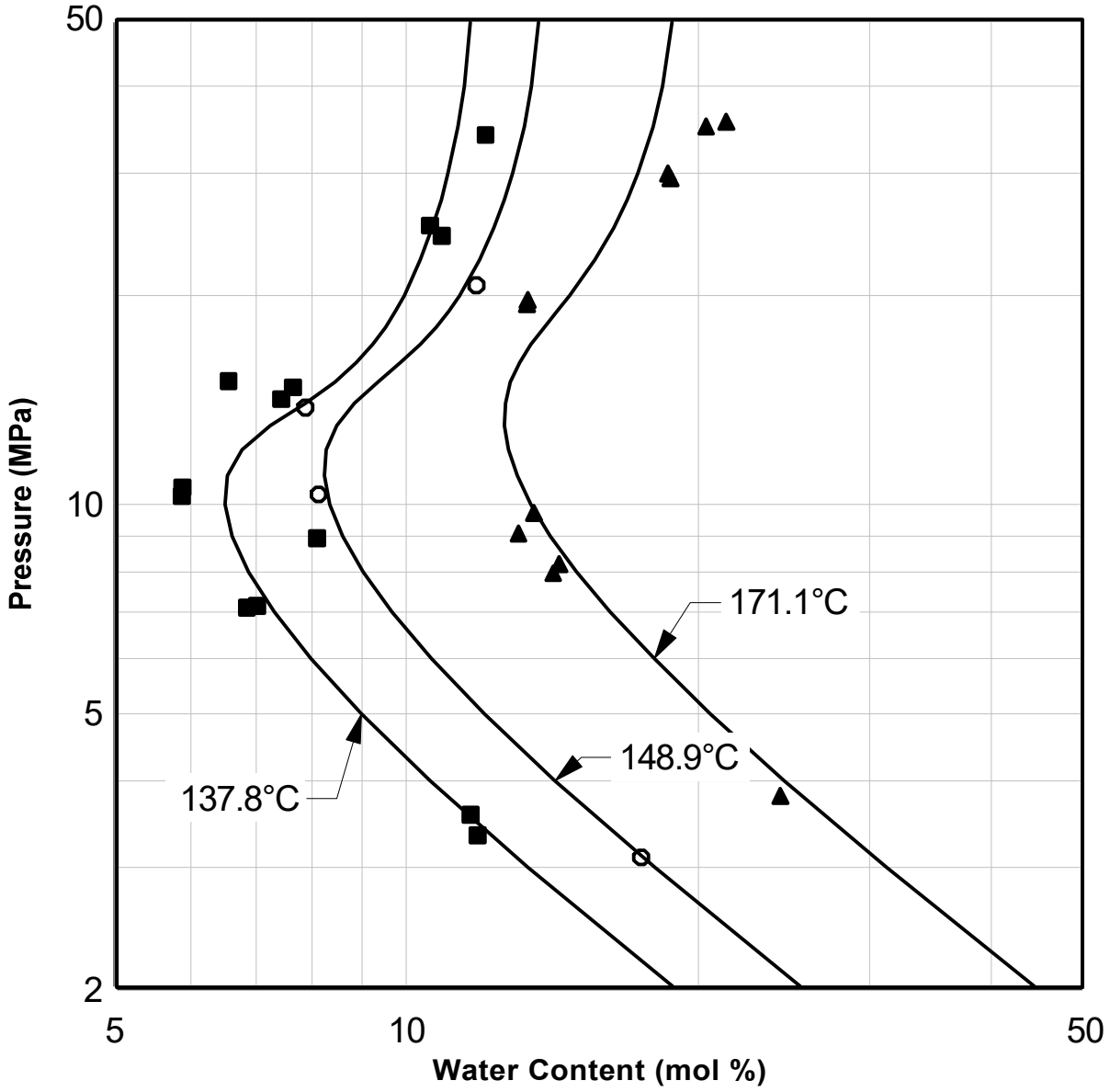

50
10
5
2
Pressure (MPa)
5
10
50
Water Content (mol %)
171.1°C
148.9°C
137.8°C

Fig. 13

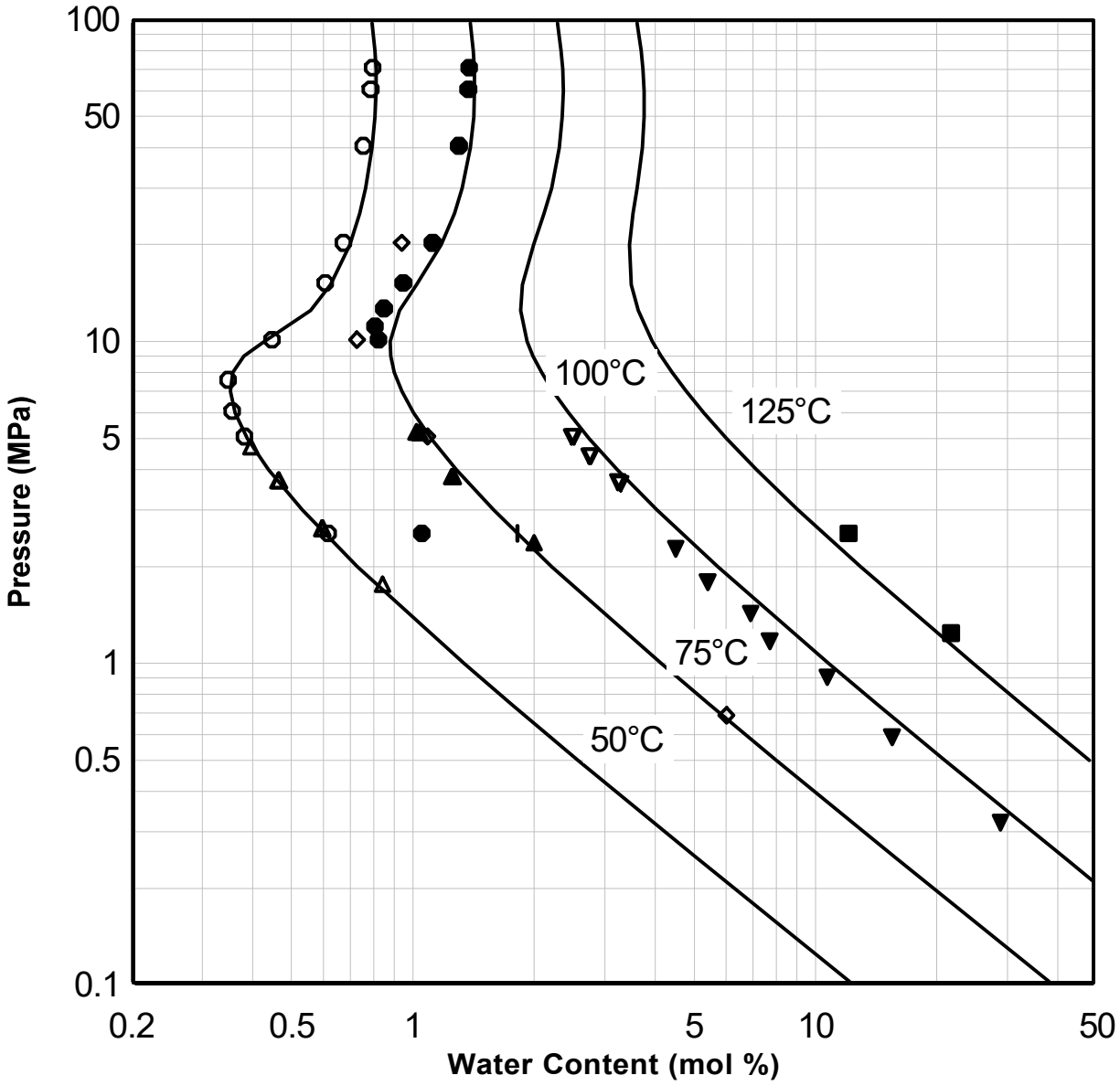

100
50
10
5
1
0.5
0.1
Pressure (MPa)
0.2
0.5
1
5
10
50
Water Content (mol %)
100°C
125°C
75°C
50°C

Fig. 14

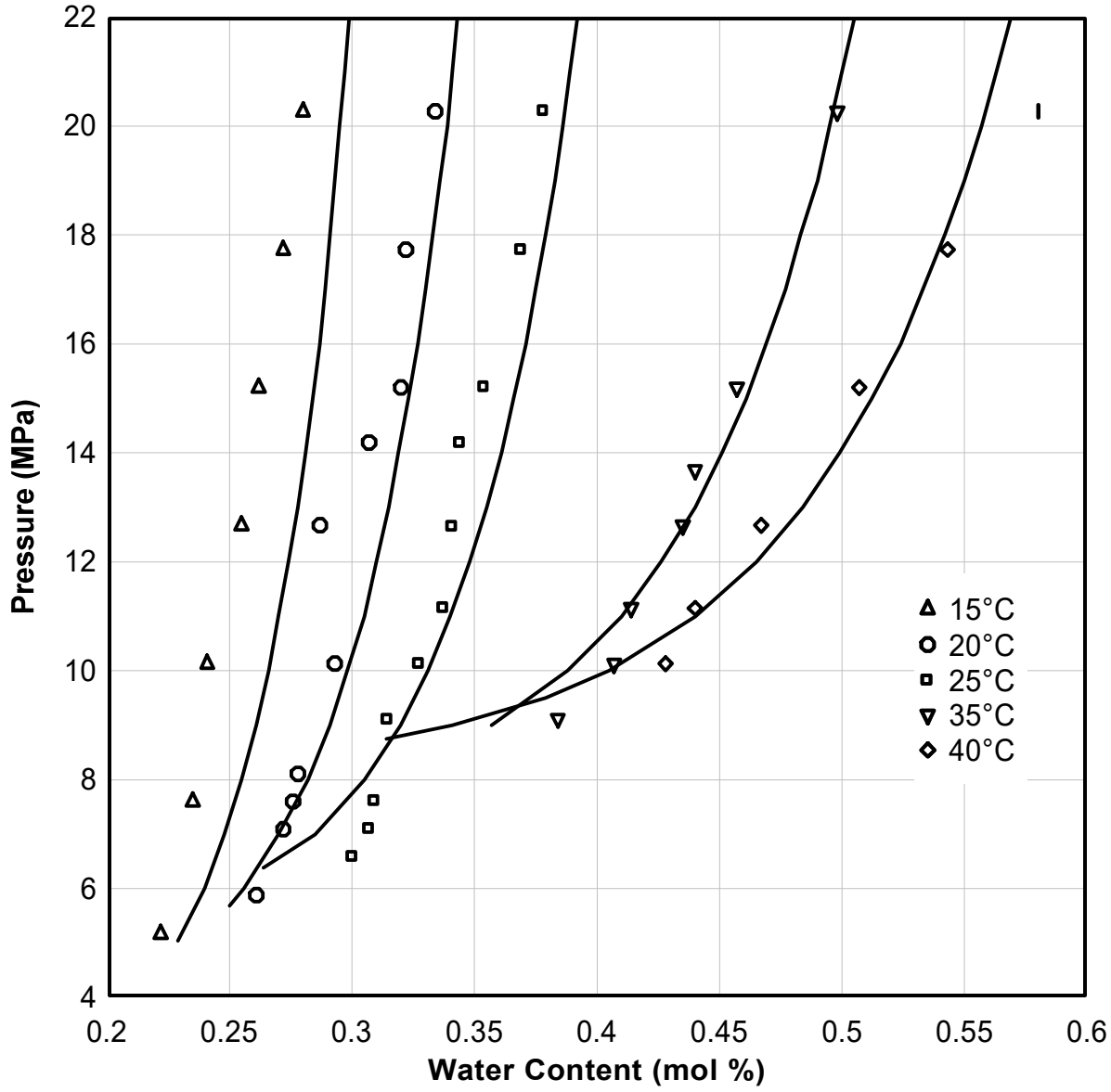

Pressure (MPa)
Water Content (mol %)
22
20
18
16
14
12
10
8
6
4
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
15°C
20°C
25°C
35°C
40°C

Fig. 15

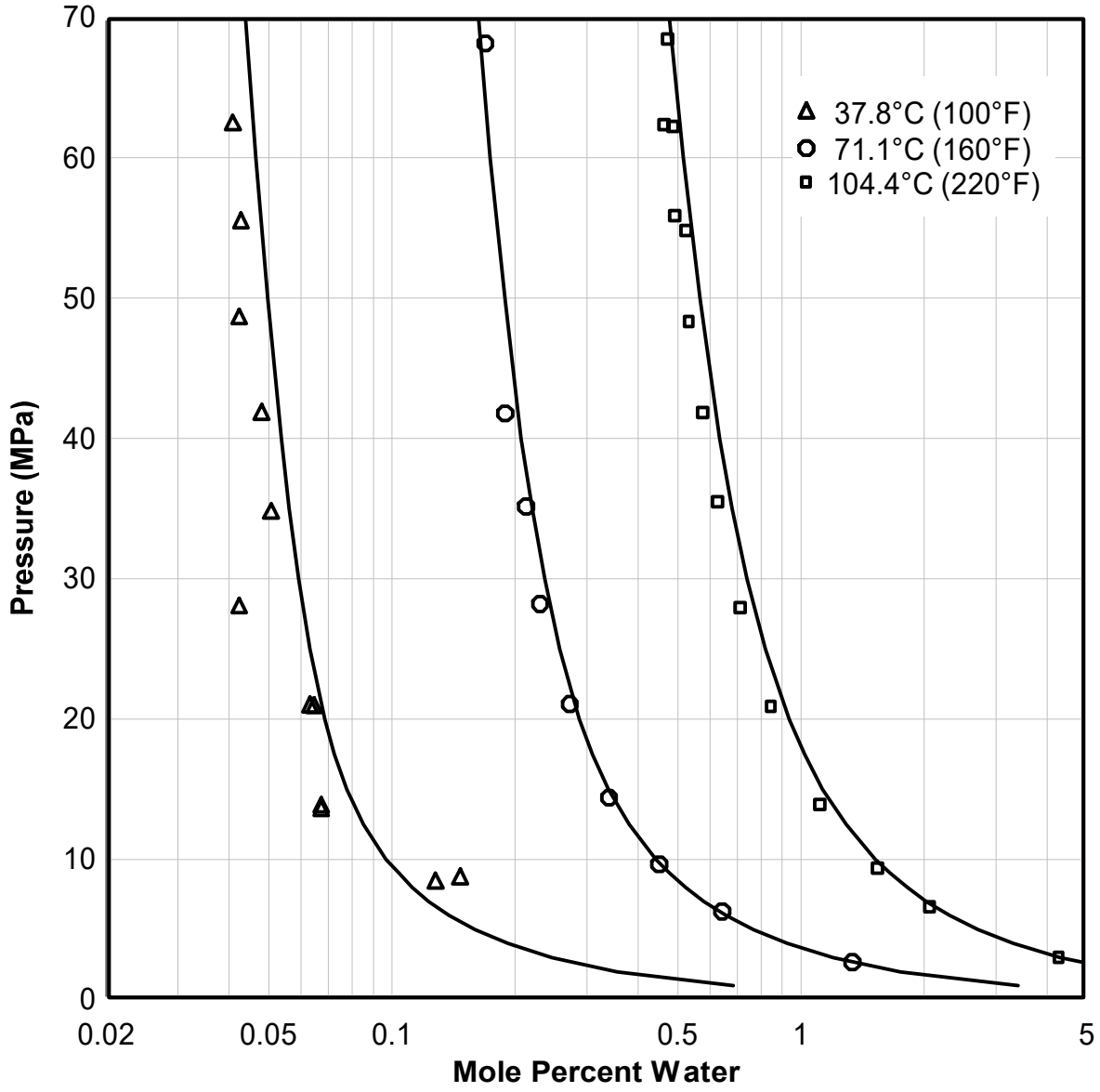
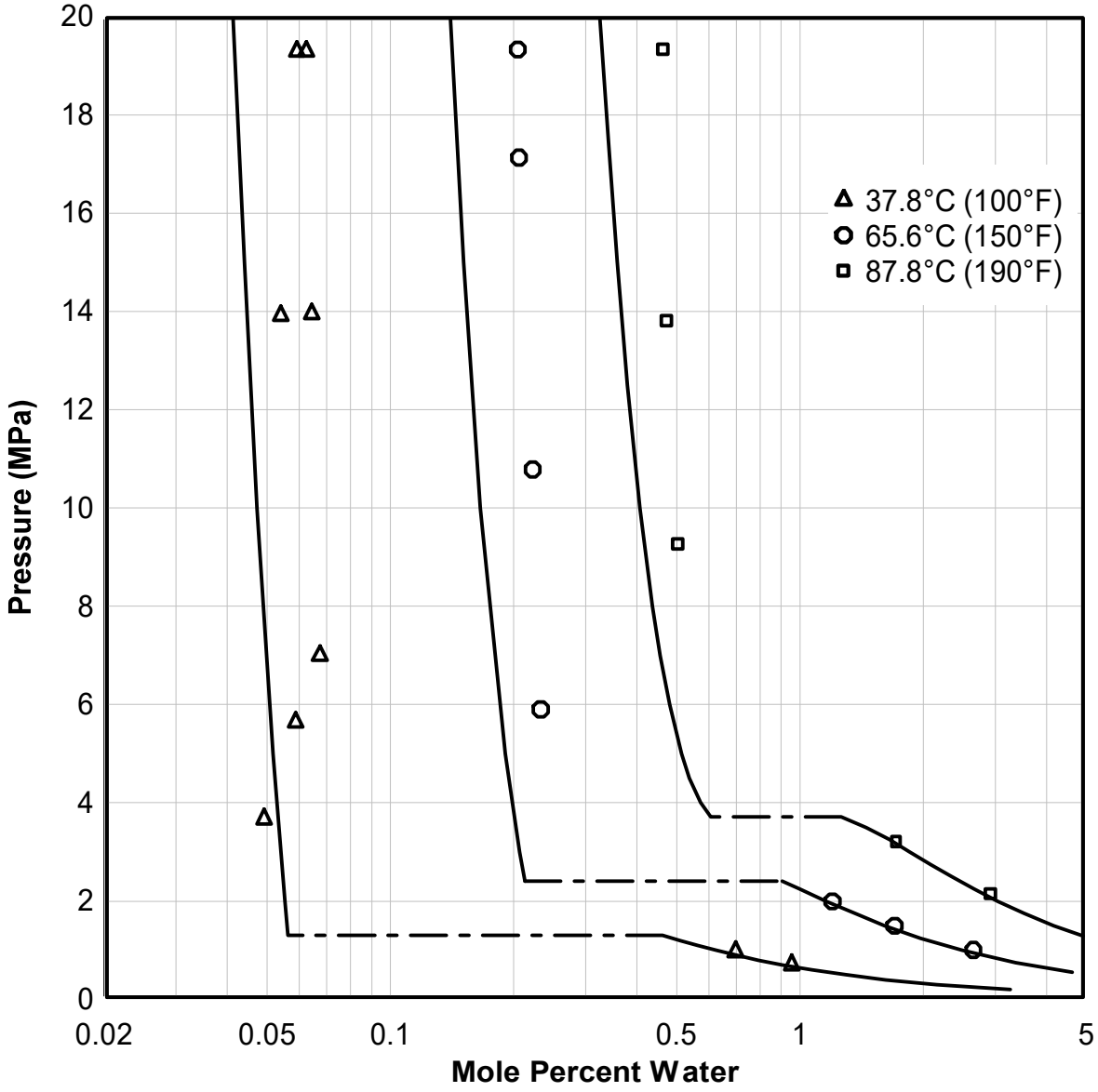

70
60
50
40
30
20
10
0
Pressure (MPa)
0.02
0.05
0.1
0.5
1
5
Mole Percent Water
37.8°C (100°F)
71.1°C (160°F)
104.4°C (220°F)

Fig. 16


Pressure (MPa)
20
18
16
14
12
10
8
6
4
2
0
0.02
0.05
0.1
0.5
1
5
Mole Percent Water
37.8°C (100°F)
65.6°C (150°F)
87.8°C (190°F)

APPENDIX A Equation of State Parameters

The following tables summarize the parameters used for the Peng-Robinson calculations presented in this paper. The pure component properties could also be used for Soave-Redlich-Kwong calculations. Binary interaction parameters are given for both equations.

Table A1 Pure Component Parameters for Equation of State Calculations

	T_C (K)	P_C (kPa)	ω (-)	MW (g/mol)
hydrogen sulfide	373.2	8960	0.100	34.080
carbon dioxide	304.2	7376	0.225	44.010
methane	190.6	4600	0.008	16.043
ethane	305.4	4880	0.099	30.070
propane	369.8	4250	0.153	44.094

Table A2 Binary Interaction Parameters for Acid Gas Components for the PR and SRK Equations

		H_2S	CO_2	CH_4	C_2H_6	C_3H_8
CO_2	PR	0.0974	0.0000			
	SRK	0.0989	0.0000			
CH_4	PR	0.0840	0.0919	0.0000		
	SRK	0.0849	0.0933	0.0000		
C_2H_6	PR	0.0833	0.1322	-0.0020	0.0000	
	SRK	0.0852	0.1363	-0.0078	0.0000	
C_3H_8	PR	0.0878	0.1241	0.0330	-0.0067	0.0000
	SRK	0.0855	0.1289	0.0289	-0.0100	0.0000

From Knapp et al. (1982) except for $H_2S + CH_4$ which are from this work.

APPENDIX B Additional Phase Equilibrium Calculations for Non-Aqueous Equilibria

The following additional phase diagrams are presented to demonstrate the accuracy of the Peng-Robinson equation of state for the calculation for the non-aqueous phase equilibrium. No detailed description of the figures will be provided.

Fig. B1 Pressure-Composition Diagram for the System H_2S+CH_4 at 4.4°C (40°F), 37.8°C (100°F), and 71.1°C (160°F). Data from Kohn and Kurata (1958) Curves from the Peng-Robinson Equation of State

Fig. B2 Pressure-Composition Diagram for the System CO_2+CH_4 at -3°C (270 K). Data from Somait and Kidnay (1978) and Wei et al. (1995) and Curves from the Peng-Robinson Equation of State

Fig. B3 Phase Envelopes for Mixtures of H_2S+CO_2+CH_4 at 4.4°C (40°F) and 2.758 MPa (400 psi) and 6.895 MPa (1000 psi) Data from Robinson et al. (1959) and Curves from Peng-Robinson Equation of State

Fig. B4 Phase Envelopes for Mixtures of H_2S+CO_2+CH_4 at -34.4°C (-30°F) and 2.068 MPa (300 psi), 3.447 MPa (50 psi), and 4.826 MPa (700 psi) Data from Hensel and Massoth (1964) and Curves from Peng-Robinson Equation of State

Fig. B5 Pressure-Composition Diagram for the System CO_2+CH_4 at -20°C, 0°C, and 10°C. Data from Kaminishi et al. (1968) and Curves from Peng-Robinson Equation of State

Fig. B6 Pressure-Composition Diagram for the System CO_2+CH_4 at -13.3°C (-25°F) and -1.7°C (29°F). Data from Donnelly and Katz (1954) and Curves from the Peng-Robinson Equation of State

Fig. B7 Pressure-Composition Diagram for the System CO_2+C_2H_6 at -10°C and +10°C. Data from Fredenslund and Mollerup (1974) and Curves from the Peng-Robinson Equation of State

Fig. B8 Pressure-Composition Diagram for the System H_2S+C_2H_6 at -17.8°C (0°F) and +10°C (50°F). Data from Kalra et al. (1977) and Curves from the Peng-Robinson Equation of State

Fig. B1

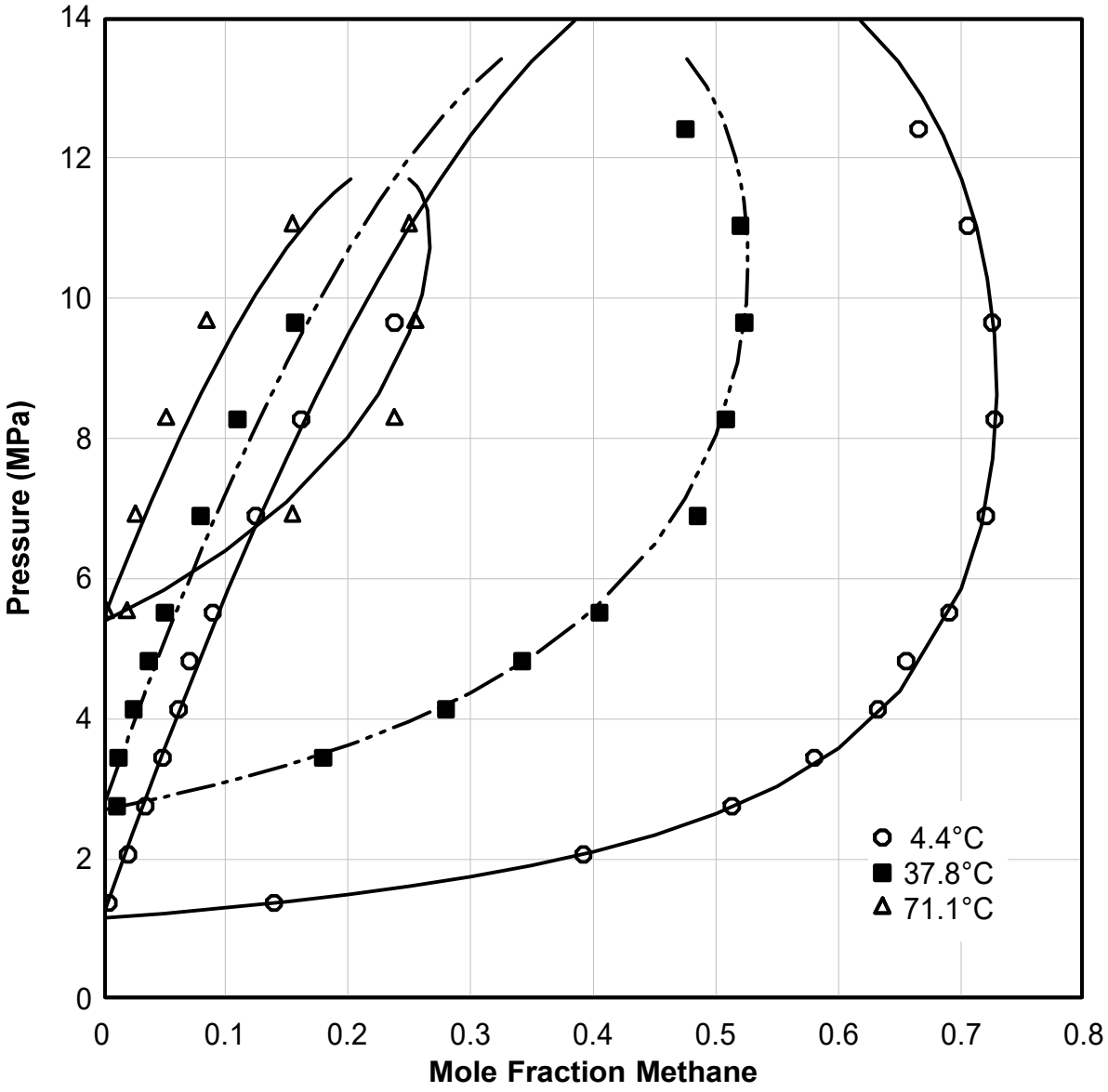

Pressure (MPa)
Mole Fraction Methane
0
2
4
6
8
10
12
14
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
4.4°C
37.8°C
71.1°C

Fig. B2

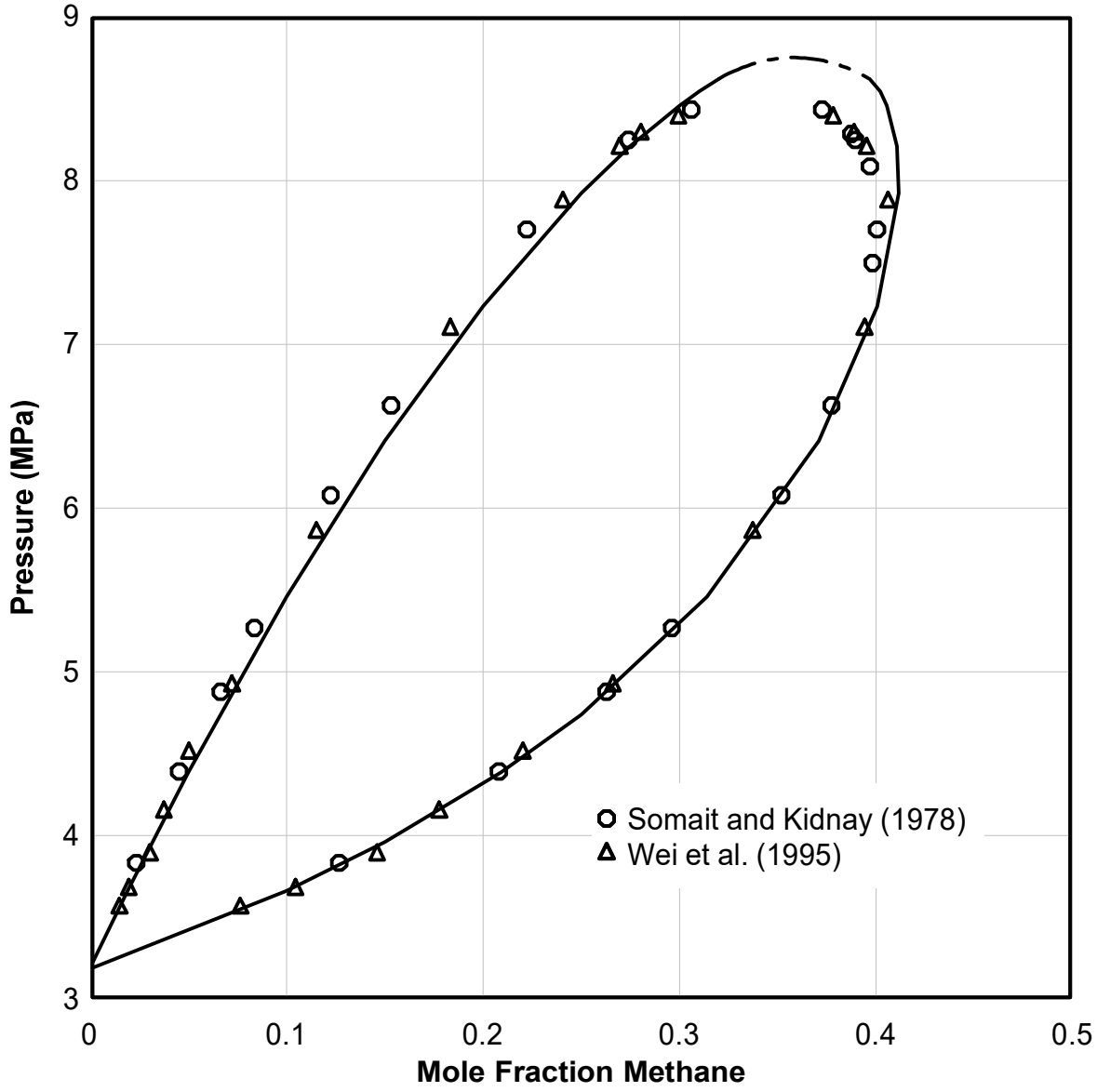

Pressure (MPa)
Mole Fraction Methane
9
8
7
6
5
4
3
0
0.1
0.2
0.3
0.4
0.5
Somait and Kidnay (1978)
Wei et al. (1995)

Fig. B3

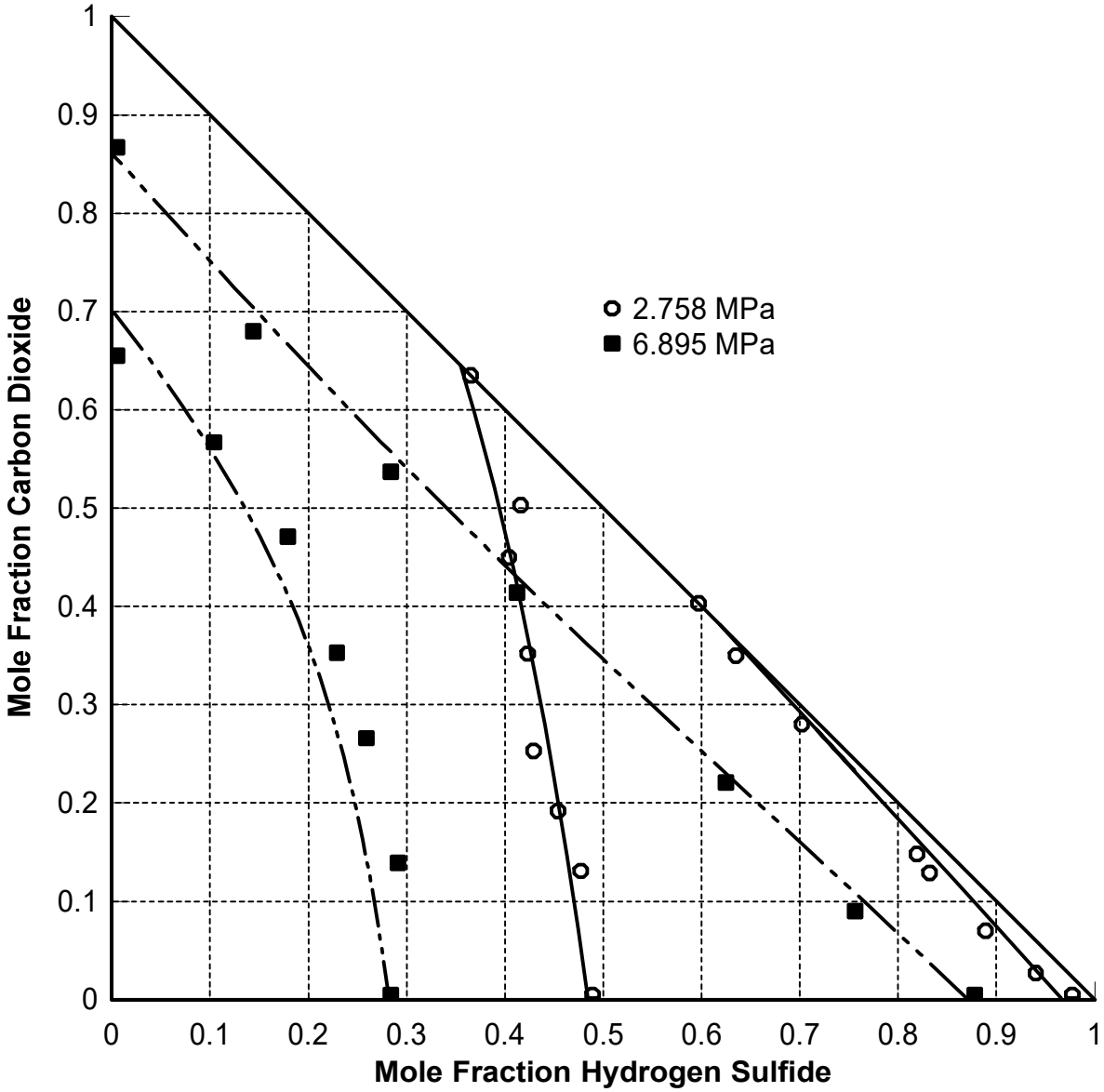

Mole Fraction Carbon Dioxide
Mole Fraction Hydrogen Sulfide
2.758 MPa
6.895 MPa
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Fig. B4

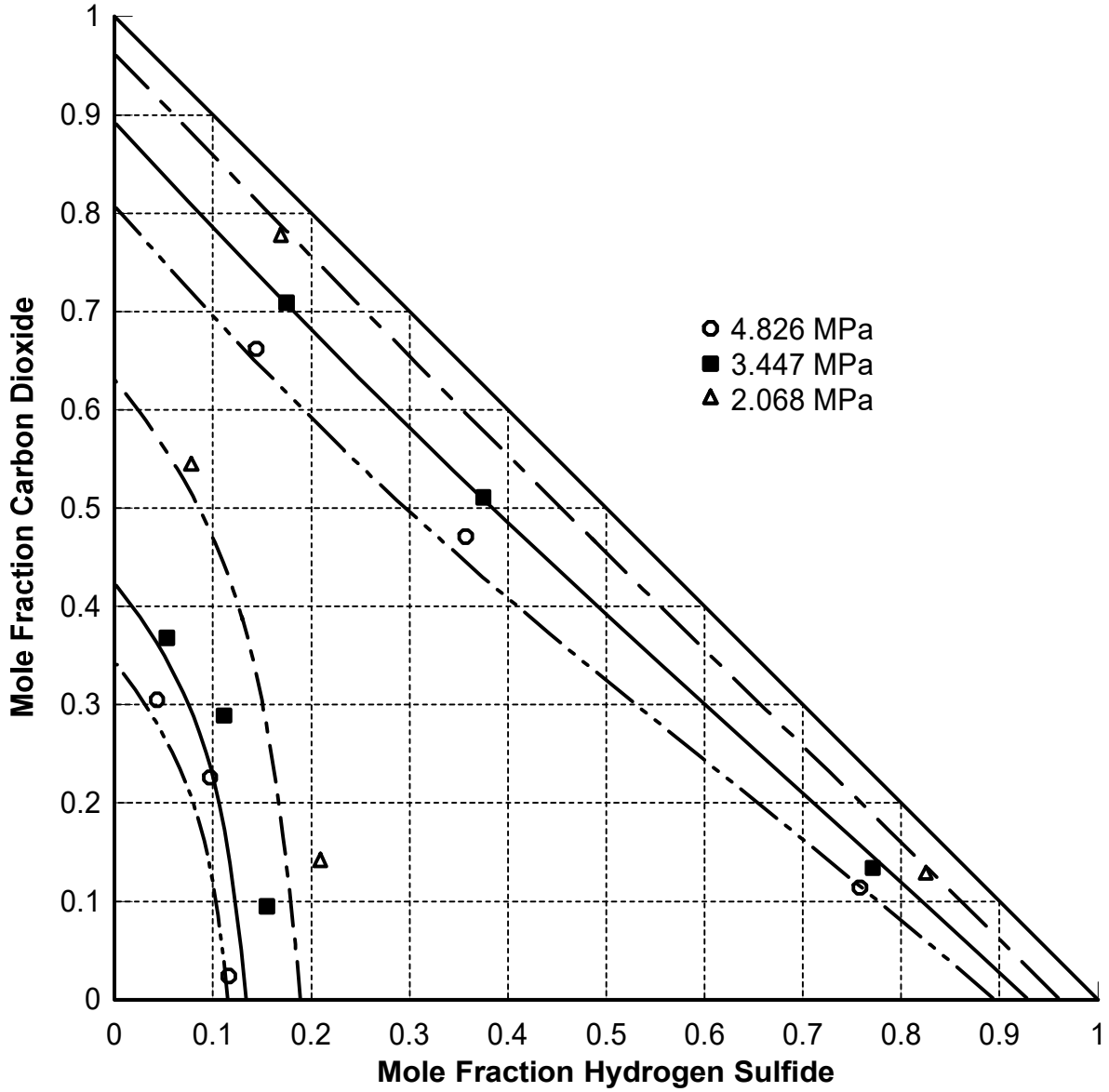

Mole Fraction Carbon Dioxide
Mole Fraction Hydrogen Sulfide
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
4.826 MPa
3.447 MPa
2.068 MPa

Fig. B5

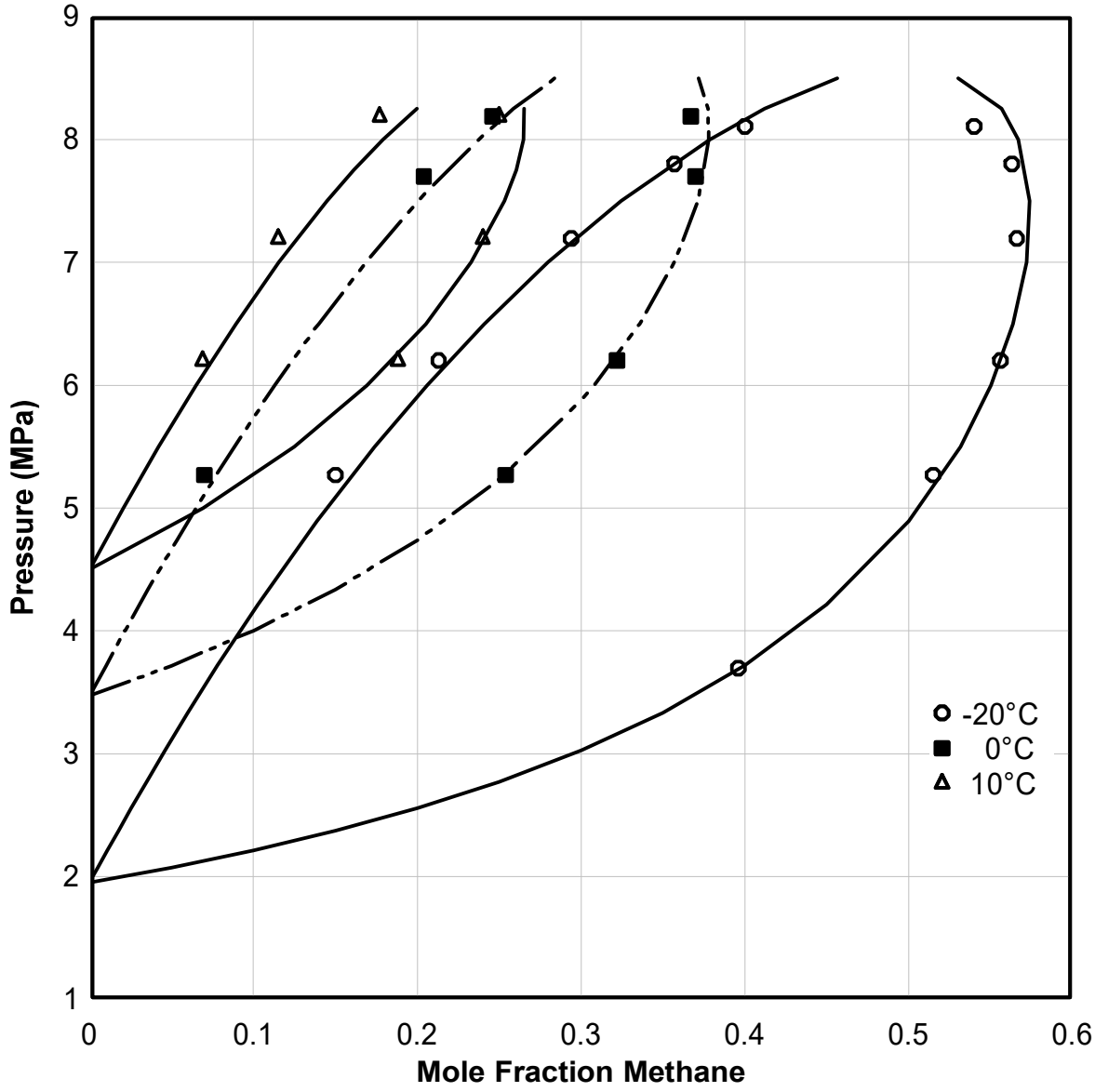

Pressure (MPa)
Mole Fraction Methane
-20°C
0°C
10°C
1
2
3
4
5
6
7
8
9
0
0.1
0.2
0.3
0.4
0.5
0.6

Fig. B6

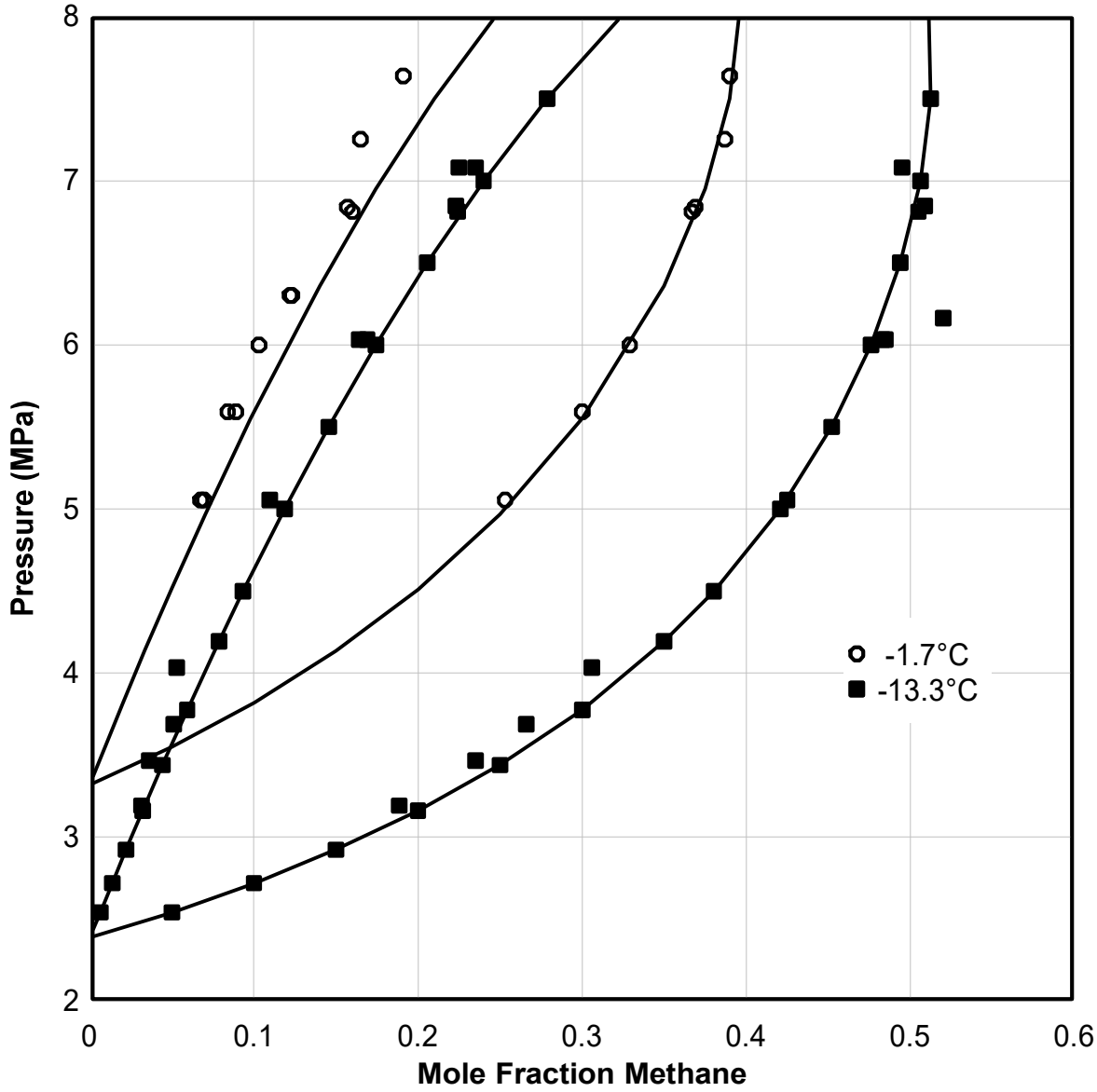

Pressure (MPa)
Mole Fraction Methane
-1.7°C
-13.3°C
8
7
6
5
4
3
2
0
0.1
0.2
0.3
0.4
0.5
0.6

Fig. B7

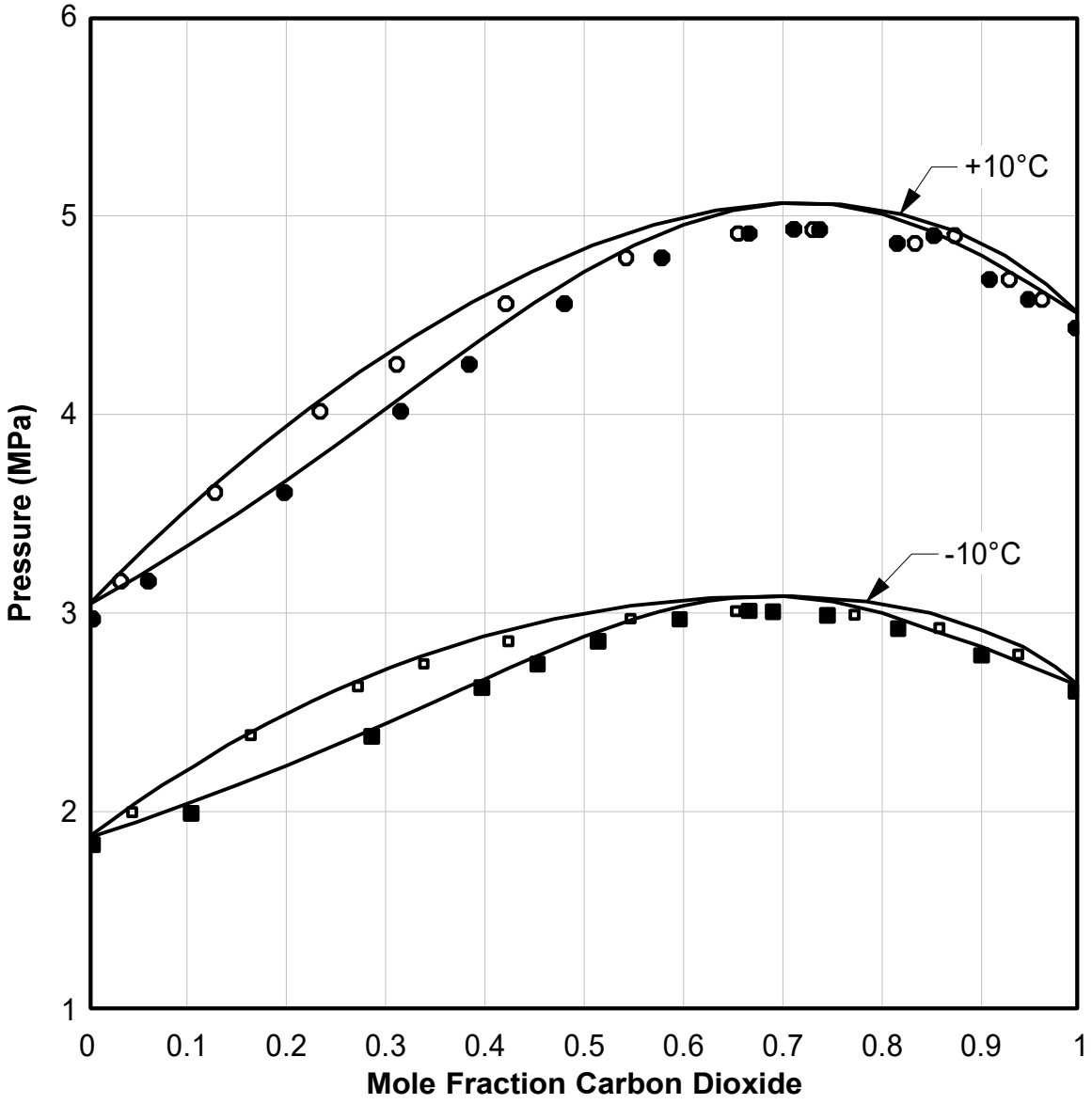
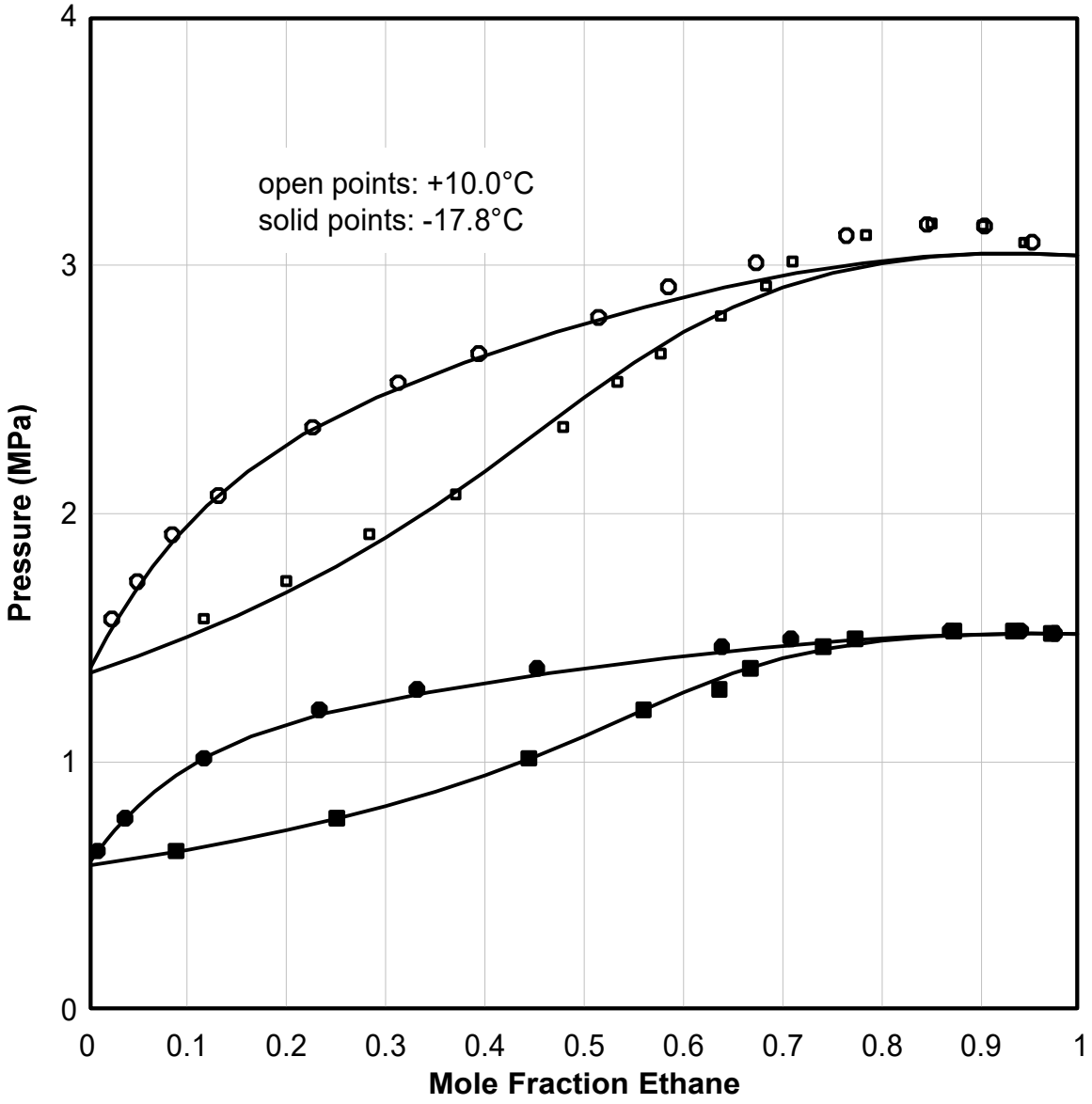

6
5
4
3
2
1
Pressure (MPa)
+10°C
-10°C
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Mole Fraction Carbon Dioxide

Fig. B8


open points: +10.0°C
solid points: -17.8°C
Pressure (MPa)
Mole Fraction Ethane
0
1
2
3
4
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

APPENDIX C Additional Phase Equilibrium Calculations for Aqueous Equilibria

The following additional phase diagrams are presented to demonstrate the accuracy of AQUAlibrium for the calculation of the water content of mixtures of interest to acid gas injection. No detailed description of the figures will be provided.

Fig. C1 Water Content of H_2S at Low Pressure. Data from Wright and Maass (1932) and Curves from *AQUAlibrium* (broken line is the hydrate curve)

Fig, C2 Water Content of CO_2 at 25°C. Data as Noted on the Figure and Curves from *AQUAlibrium*.

Fig. C3 Water Content of Ethane. Data from Reamer et al. (1943) and Curves from *AQUAlibrium*

Fig. C4 Water Content of Methane. Data from Gillespie et al. (1984) and Curves from *AQUAlibrium*

Fig. C1

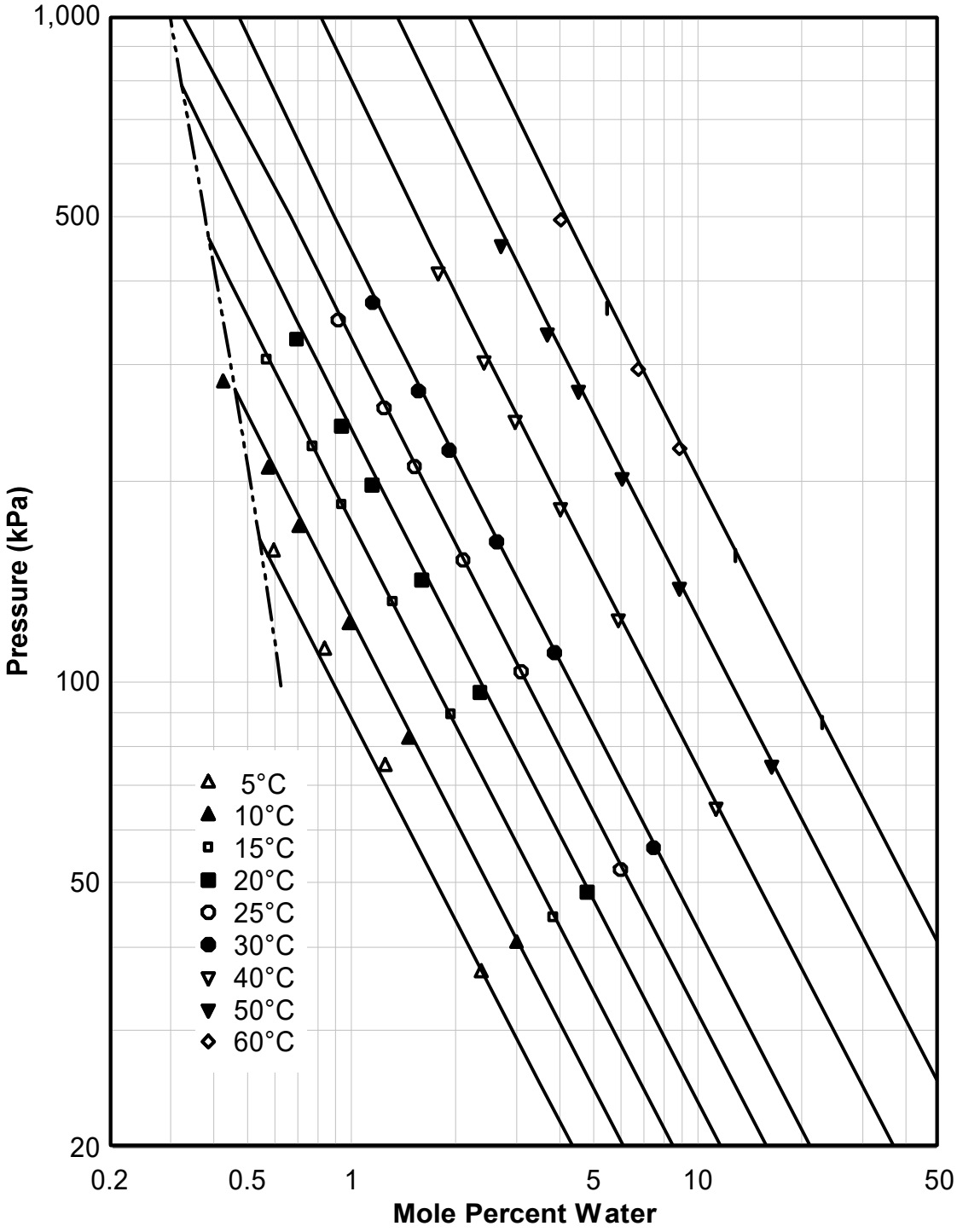

1,000
500
100
50
20
Pressure (kPa)
0.2
0.5
1
5
10
50
Mole Percent Water
5°C
10°C
15°C
20°C
25°C
30°C
40°C
50°C
60°C

Fig. C2

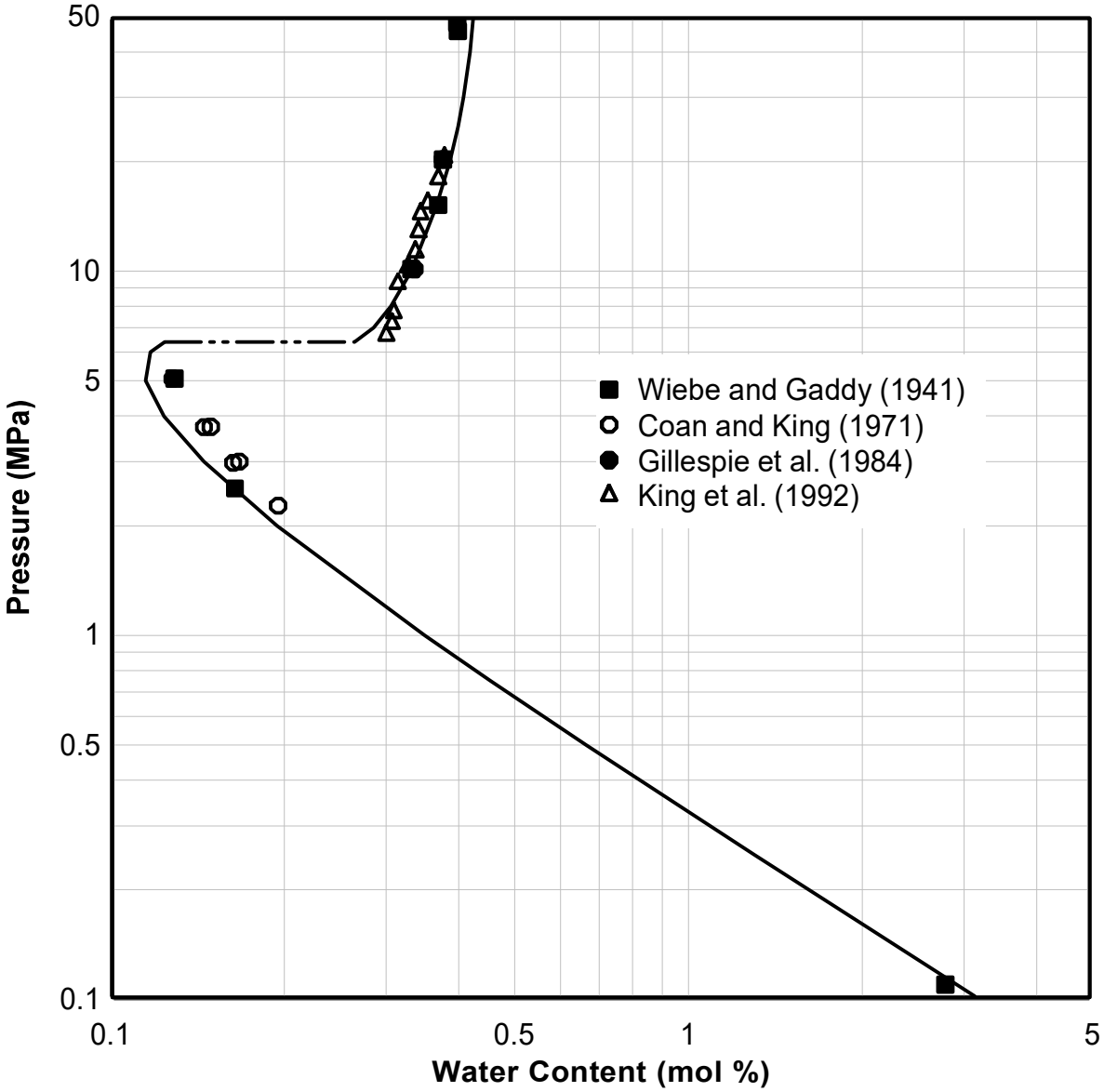

50
10
5
1
0.5
0.1
Pressure (MPa)
0.1
0.5
1
5
Water Content (mol %)
Wiebe and Gaddy (1941)
Coan and King (1971)
Gillespie et al. (1984)
King et al. (1992)

Fig. C3

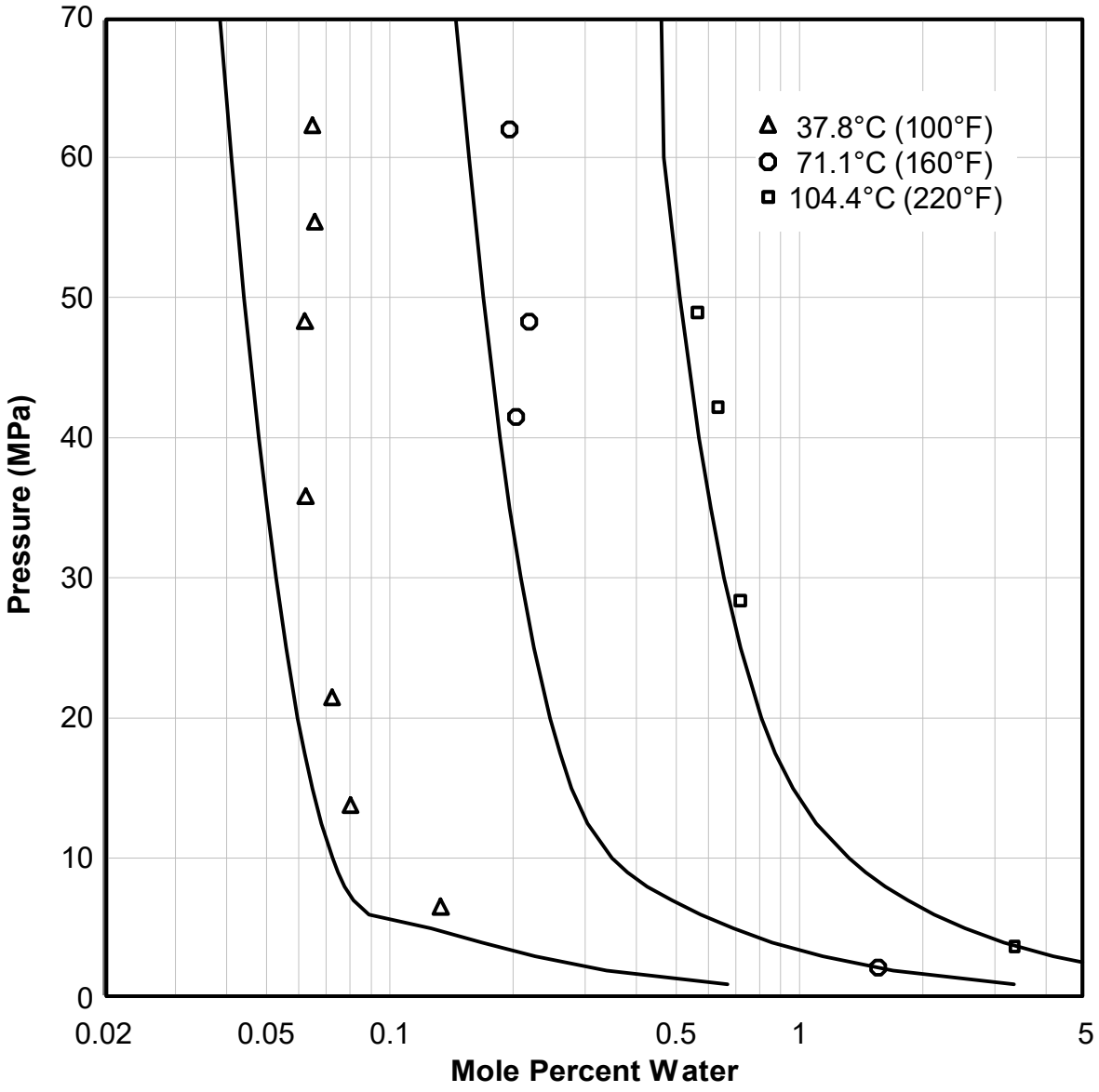
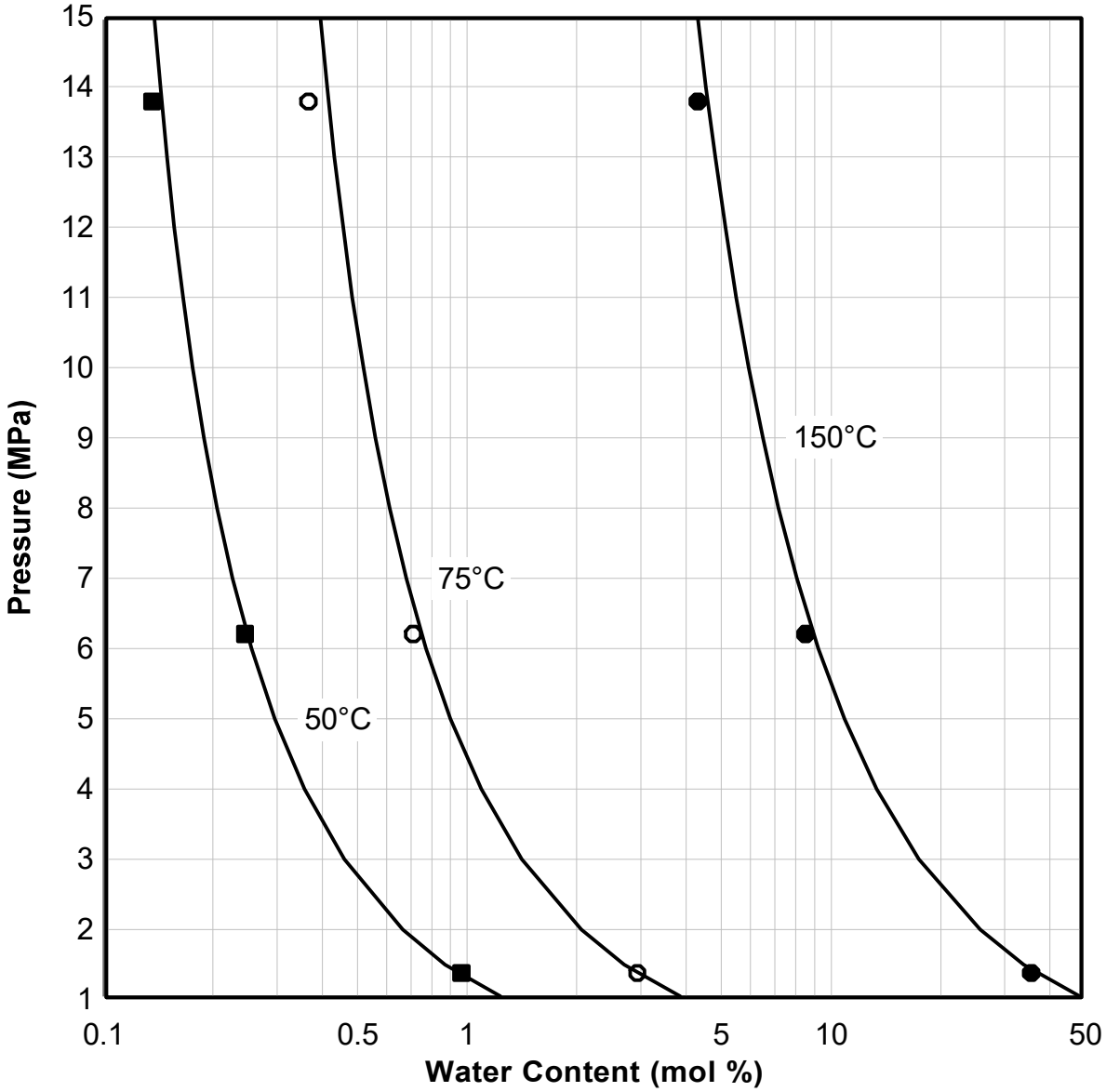

70
60
50
40
30
20
10
0
Pressure (MPa)
0.02
0.05
0.1
0.5
1
5
Mole Percent Water
37.8°C (100°F)
71.1°C (160°F)
104.4°C (220°F)

Fig. C4


Pressure (MPa)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0.1
0.5
1
5
10
50
Water Content (mol %)
150°C
75°C
50°C

APPENDIX D A Comment on the Work of Clark et al. (1998)

The work of Clark et al. (1998) requires additional comment because they arrive at a contradictory conclusion from the one reached in this work. They claim that the current models are not sufficiently accurate for acid gas systems.

The conclusion of Clark et al. (1998) appears to have been based solely on their own data and not on a more complete review of the literature such as that presented here. On the other hand, it is not the conclusion of this work that experimental data are unimportant. The correlations used in this work are constructed from experimental data. Furthermore, additional data provide farther tests of the correlations.

Fig. D1 shows the data of Clark et al. (1998) plotted along with some data from Kellerman et al. (1995). The two mixtures have similar compositions. The predictions from the Peng-Robinson equation are also plotted. As was discussed earlier, the Peng-Robinson is a good fit of the data of Kellerman et al. (1995). This plot demonstrates that there is significant difference between the two data sets.

It might be easy to assume that the differences between the two data sets are due to the presence of water in the mixture studied by Clark et al. (1998). But this is not the case. As was demonstrated in this paper, at the temperatures Clark et al. (1998) took their data, water is expected to have a small affect on the vapor-liquid equilibrium. This is true even if the acid gas is saturated with water, and the data of Clark et al. (1998) are undersaturated. Thus the effect of water on their phase envelope should be even smaller than that for the saturated case.

It seems logical that the addition of methane should reduce the critical temperature of a mixture of H_2S and CO_2. None of the binary mixtures that make up the ternary exhibit azeotropy, which could cause an unexpected increase in the critical temperature. However, the critical temperature of the mixture investigated by Clark et al. (1998) is reported to increase due to the presence of the methane. This may not be erroneous, but it certainly is surprising. Robinson and Bailey (1957), Robinson et al. (1959), and Ng et al. (1985) all indicate that the presence of methane decreases the critical temperature. Critical points of some mixtures are listed in Table D1.

An alternative conclusion is that the data of Clark et al. (1998) are in error. The temperature and pressure in their apparatus seemed to have been monitored with sufficient accuracy. Visual observation was made of the phase transitions in addition to the pressure-volume measurements. So the location of the phase transitions also appears to be accurate. This leaves the composition of the fluid. Is the composition of the mixture accurate?

One potential problem with their experimental procedure is that wet acid gases are in contact with mercury, which was used as a pressure transmission fluid. Clark (personal communication, 1999) contends that mercury is relatively inert and will not react with the hydrogen sulfide. It is the experience of this author that hydrogen sulfide and mercury do react. The wet acid gas will react with the mercury affecting the composition of the mixture.

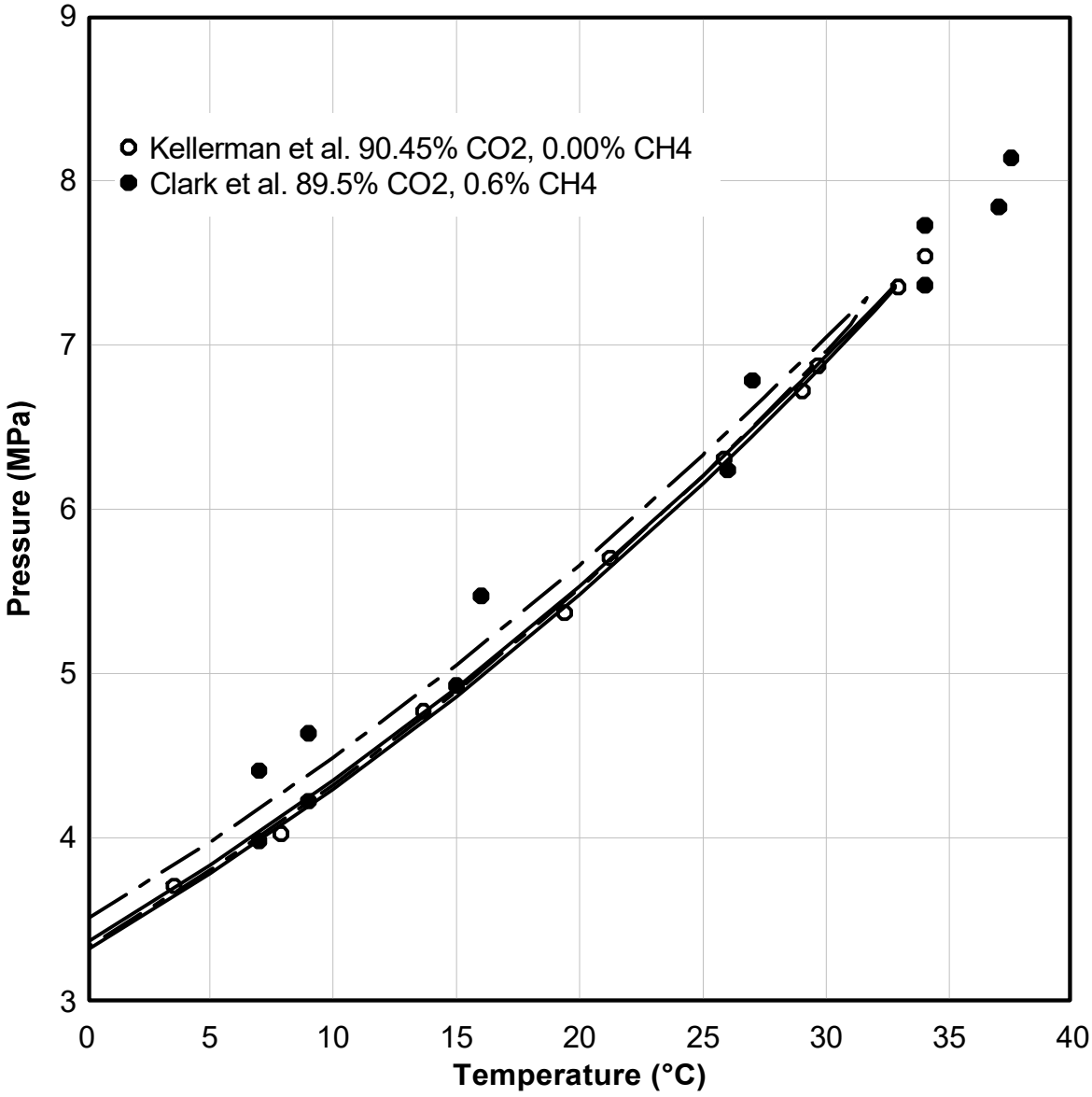
A small error was noted in the data of Clark et al. (1998), but this did not significantly effect either of our conclusions. Clarke (personal communication, 1999) indicated that the reported dew and bubble point pressures we in error by 0.117 MPa (17 psi). It is the corrected values that are plotted in Figure D1. This improves the agreement between their dew point data and those of Kellerman et al. (1995), but there remains a significant difference in the bubble points.

It should be pointed out that there is no definitive proof that the data of Clark et al. (1998) are indeed in error. This includes all of the arguments presented in this appendix. Clark (personal communication, 1999) continues to claim that the data are accurate. That claim is respected and at this point we agree to disagree.

Table D1 Critical Points for Mixtures of Hydrogen Sulfide, Carbon Dioxide and Methane

Composition (mol%)			T_c	P_c	Reference
H_2S	CO_2	CH_4	(°C)	(MPa)	
100.00	0.00	0.00	100.38	9.005	Bierlein and Kay (1953)
93.70	6.30	0.00	93.50	8.997	Bierlein and Kay (1953)
83.86	16.14	0.00	84.16	8.977	Bierlein and Kay (1953)
75.5	5.1	19.4	71.11	11.032	Robinson et al. (1957)
73.92	26.08	0.00	74.48	8.852	Bierlein and Kay (1953)
62.41	37.59	0.00	64.74	8.586	Bierlein and Kay (1953)
52.72	47.28	0.00	56.98	8.321	Bierlein and Kay (1953)
40	10	50	-16.9	11.03	Ng et al. (1985)
38.8	17.5	43.7	4.44	11.032	Robinson et al. (1957)
33.41	66.59	0.00	43.72	7.785	Bierlein and Kay (1953)
31.4	61.6	7.0	37.8	8.273	Robinson and Bailey (1957)
17.08	82.92	0.00	35.96	7.483	Bierlein and Kay (1953)
9.91	90.09	0.00	33.53	7.416	Bierlein and Kay (1953)
0.00	100.00	0.00	31.10	7.392	Bierlein and Kay (1953)

Fig. D1


Kellerman et al. 90.45% CO2, 0.00% CH4
Clark et al. 89.5% CO2, 0.6% CH4
Pressure (MPa)
Temperature (°C)
9
8
7
6
5
4
3
0
5
10
15
20
25
30
35
40