

## 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)	$\omega$ (-)	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 <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
CO <sub>2</sub>	PR	0.0974	0.0000			
	SRK	0.0989	0.0000			
CH <sub>4</sub>	PR	0.0840	0.0919	0.0000		
	SRK	0.0849	0.0933	0.0000		
C <sub>2</sub> H <sub>6</sub>	PR	0.0833	0.1322	-0.0020	0.0000	
	SRK	0.0852	0.1363	-0.0078	0.0000	
C <sub>3</sub> H <sub>8</sub>	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<sub>2</sub>S + CH<sub>4</sub> 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  $\text{H}_2\text{S}+\text{CH}_4$  at  $4.4^\circ\text{C}$  ( $40^\circ\text{F}$ ),  $37.8^\circ\text{C}$  ( $100^\circ\text{F}$ ), and  $71.1^\circ\text{C}$  ( $160^\circ\text{F}$ ). Data from Kohn and Kurata (1958) Curves from the Peng-Robinson Equation of State
- Fig. B2 Pressure-Composition Diagram for the System  $\text{CO}_2+\text{CH}_4$  at  $-3^\circ\text{C}$  (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  $\text{H}_2\text{S}+\text{CO}_2+\text{CH}_4$  at  $4.4^\circ\text{C}$  ( $40^\circ\text{F}$ ) 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  $\text{H}_2\text{S}+\text{CO}_2+\text{CH}_4$  at  $-34.4^\circ\text{C}$  ( $-30^\circ\text{F}$ ) 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  $\text{CO}_2+\text{CH}_4$  at  $-20^\circ\text{C}$ ,  $0^\circ\text{C}$ , and  $10^\circ\text{C}$ . Data from Kaminishi et al. (1968) and Curves from Peng-Robinson Equation of State
- Fig. B6 Pressure-Composition Diagram for the System  $\text{CO}_2+\text{CH}_4$  at  $-13.3^\circ\text{C}$  ( $-25^\circ\text{F}$ ) and  $-1.7^\circ\text{C}$  ( $29^\circ\text{F}$ ). Data from Donnelly and Katz (1954) and Curves from the Peng-Robinson Equation of State
- Fig. B7 Pressure-Composition Diagram for the System  $\text{CO}_2+\text{C}_2\text{H}_6$  at  $-10^\circ\text{C}$  and  $+10^\circ\text{C}$ . Data from Fredenslund and Mollerup (1974) and Curves from the Peng-Robinson Equation of State
- Fig. B8 Pressure-Composition Diagram for the System  $\text{H}_2\text{S}+\text{C}_2\text{H}_6$  at  $-17.8^\circ\text{C}$  ( $0^\circ\text{F}$ ) and  $+10^\circ\text{C}$  ( $50^\circ\text{F}$ ). Data from Kalra et al. (1977) and Curves from the Peng-Robinson Equation of State

Fig. B1

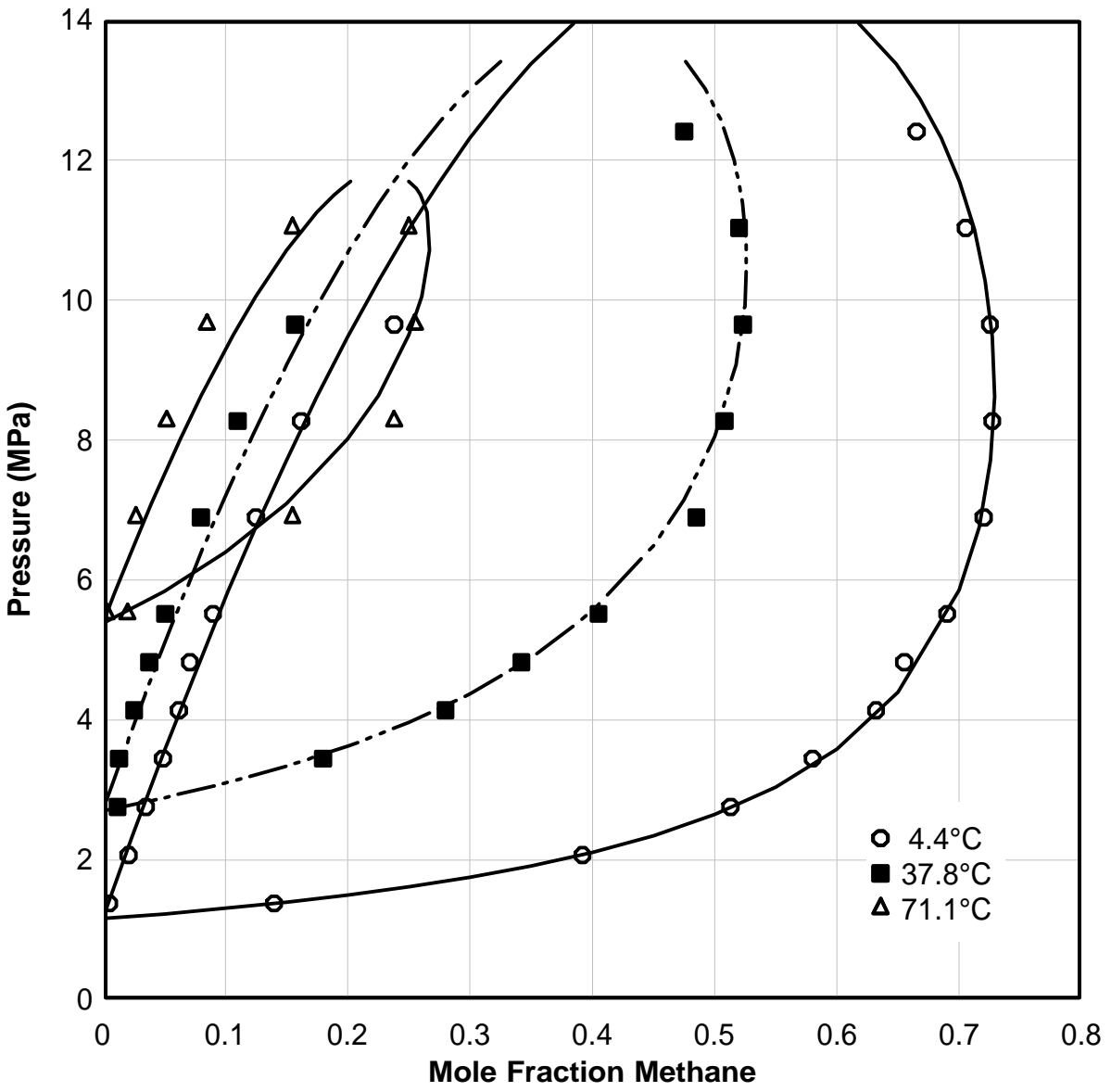


Fig. B2

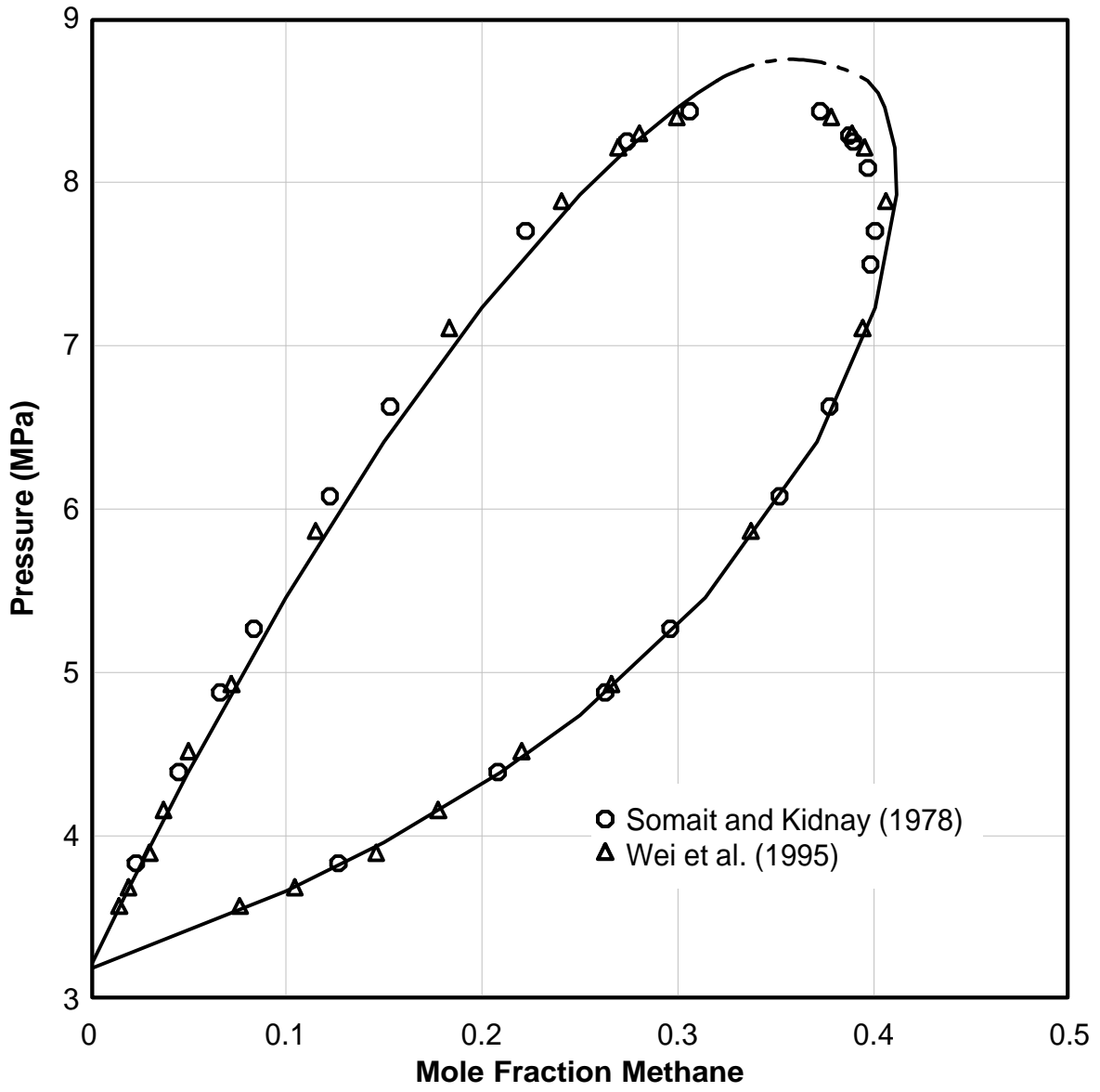


Fig. B3

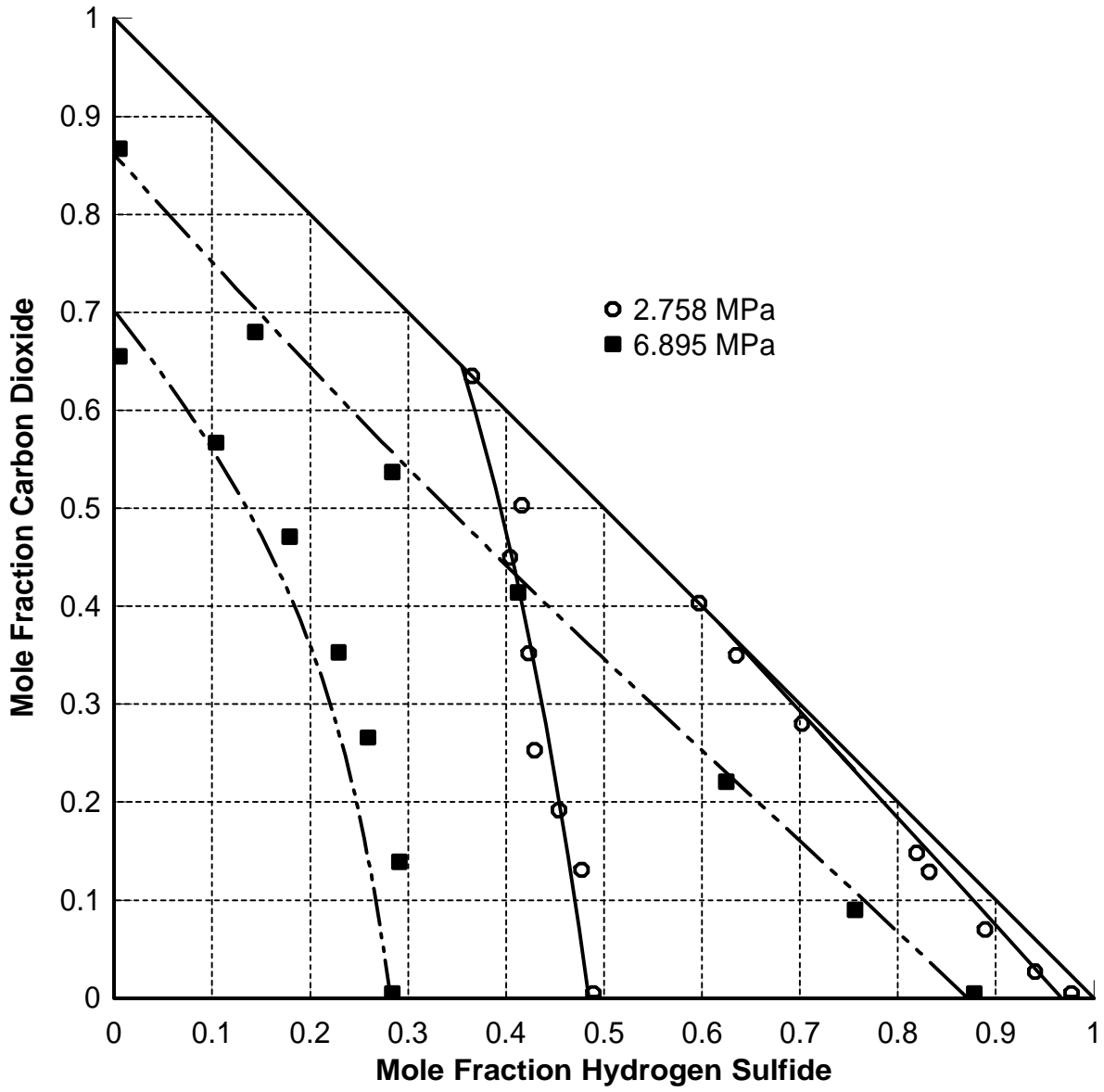


Fig. B4

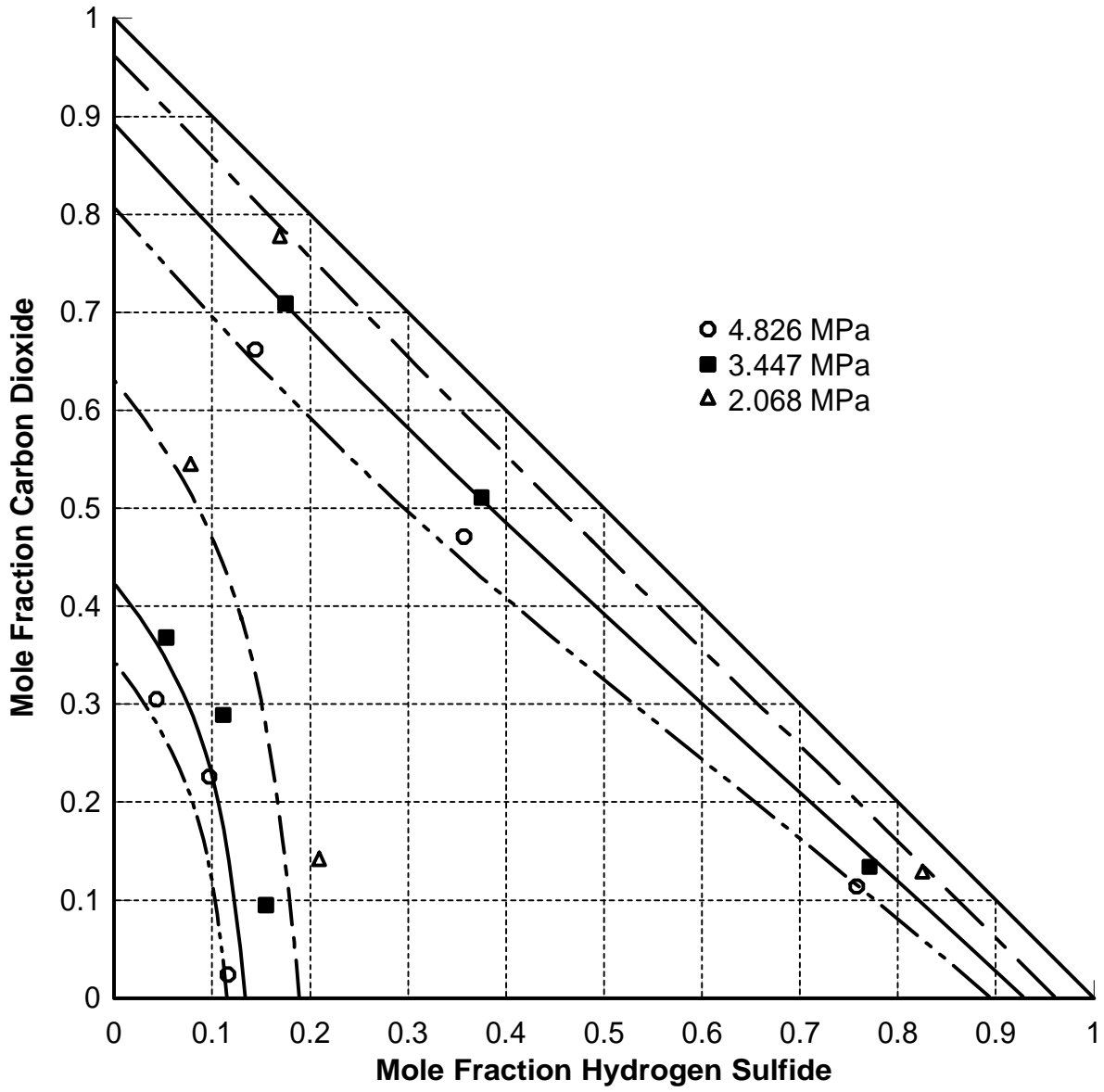


Fig. B5

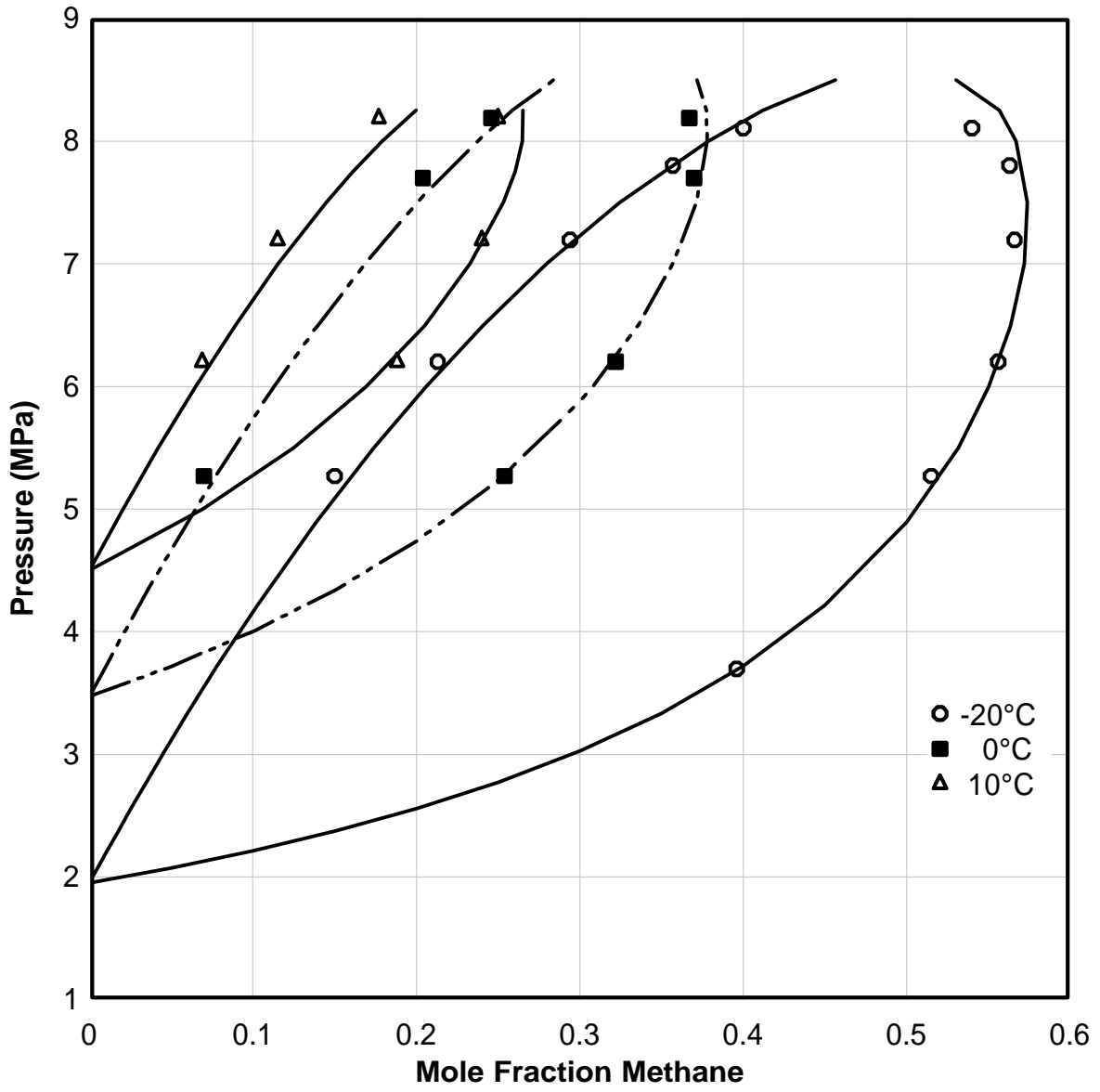


Fig. B6

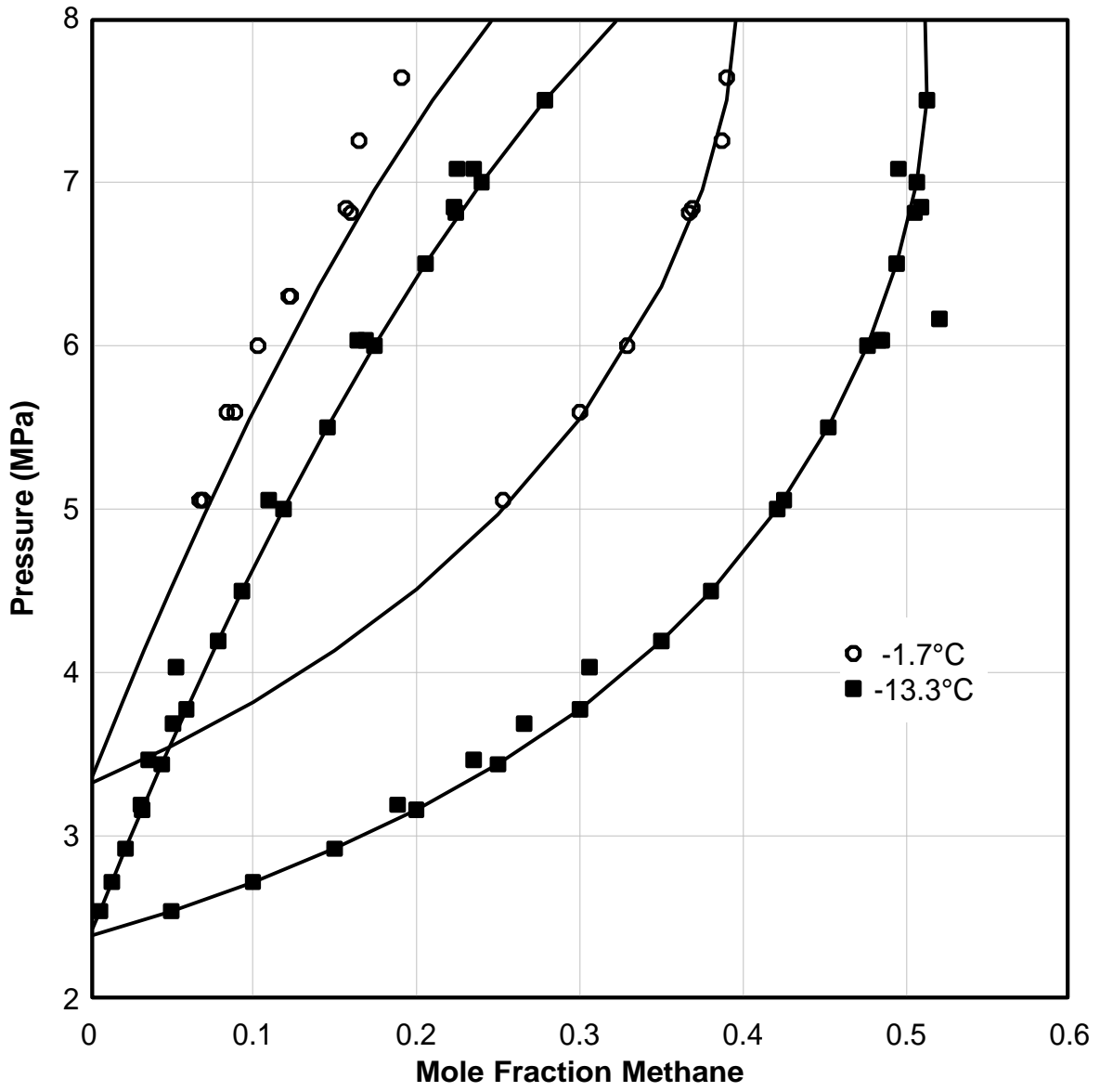


Fig. B7

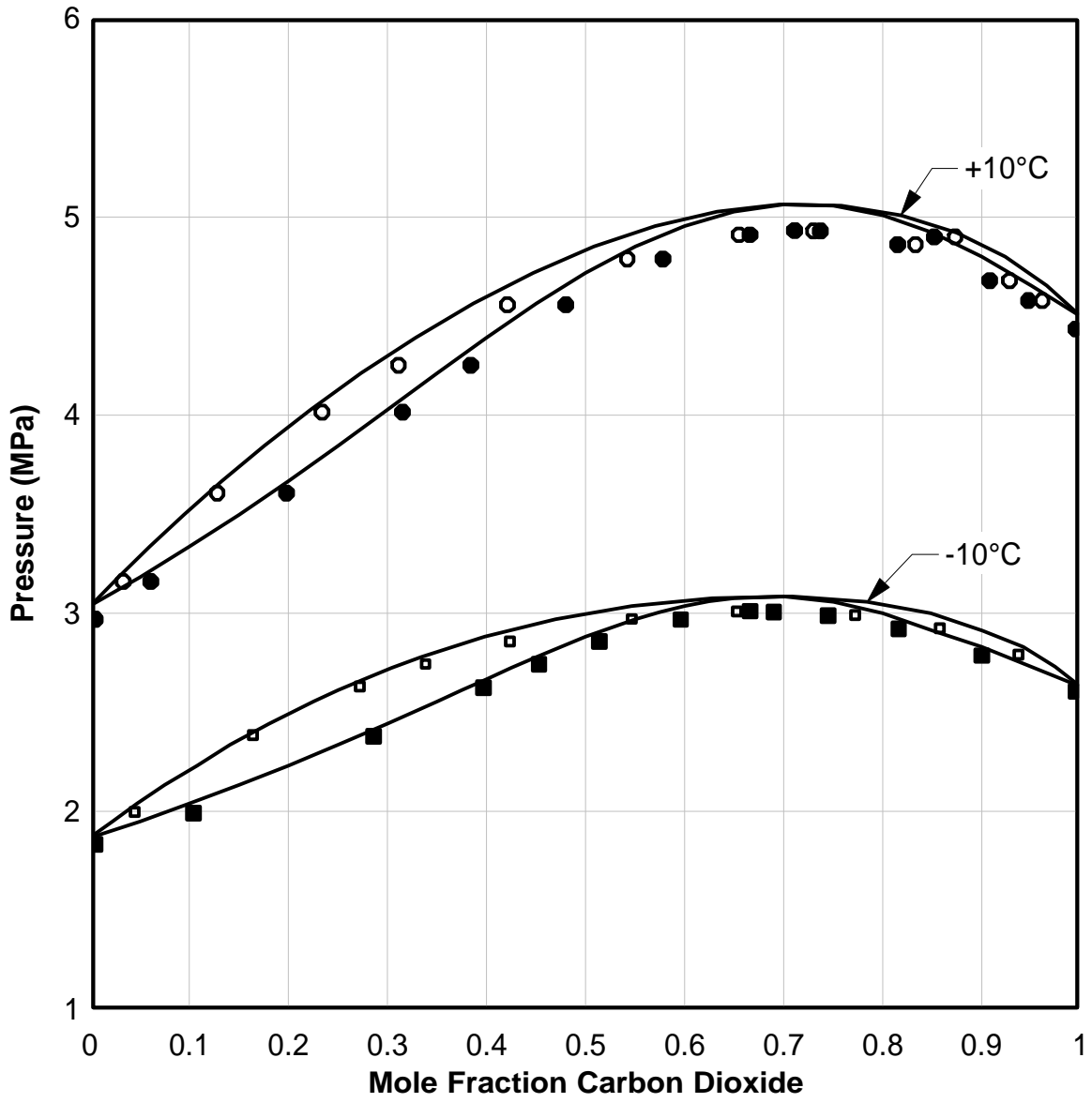
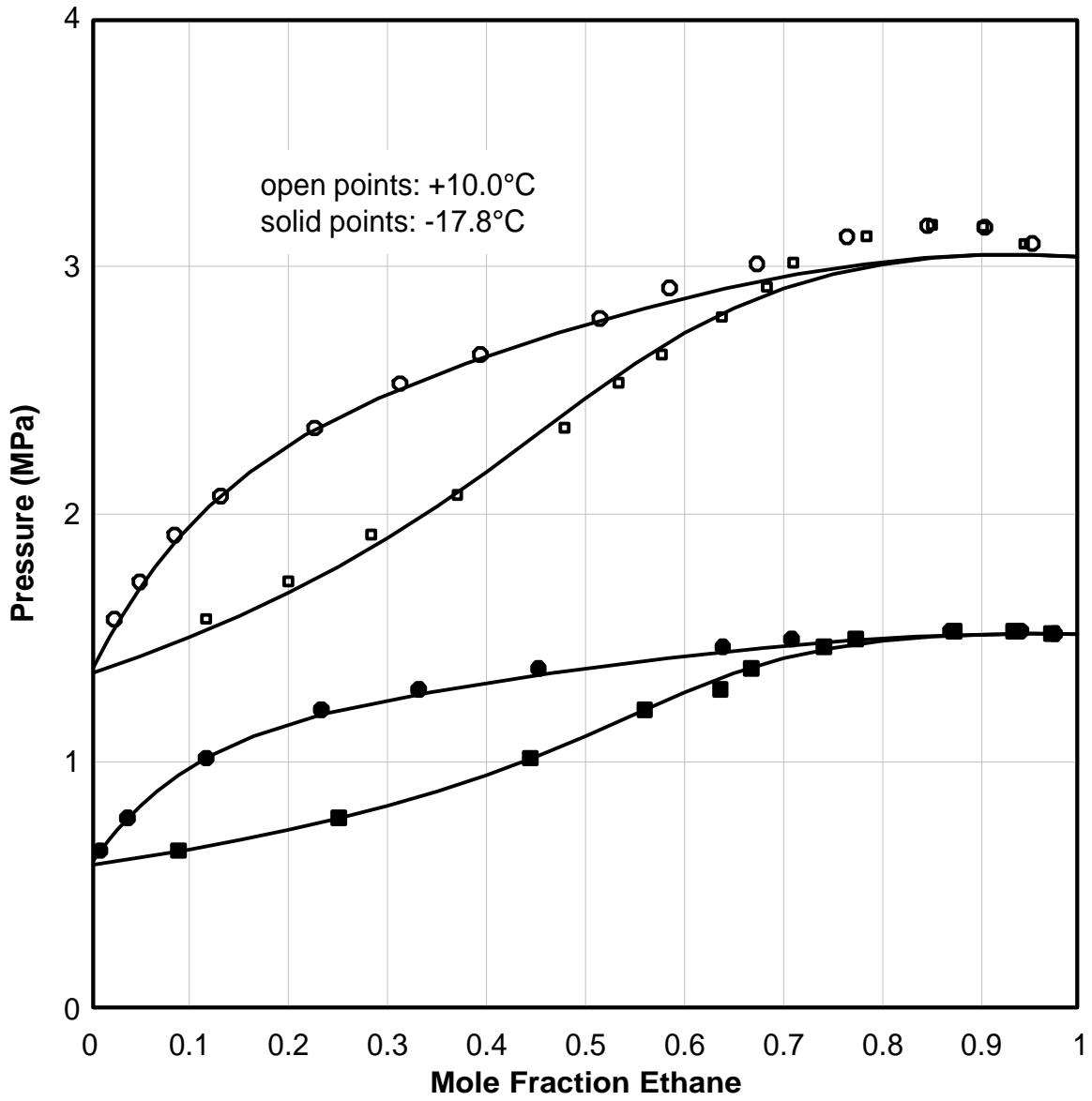


Fig. B8



## 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<sub>2</sub>S 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<sub>2</sub> 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

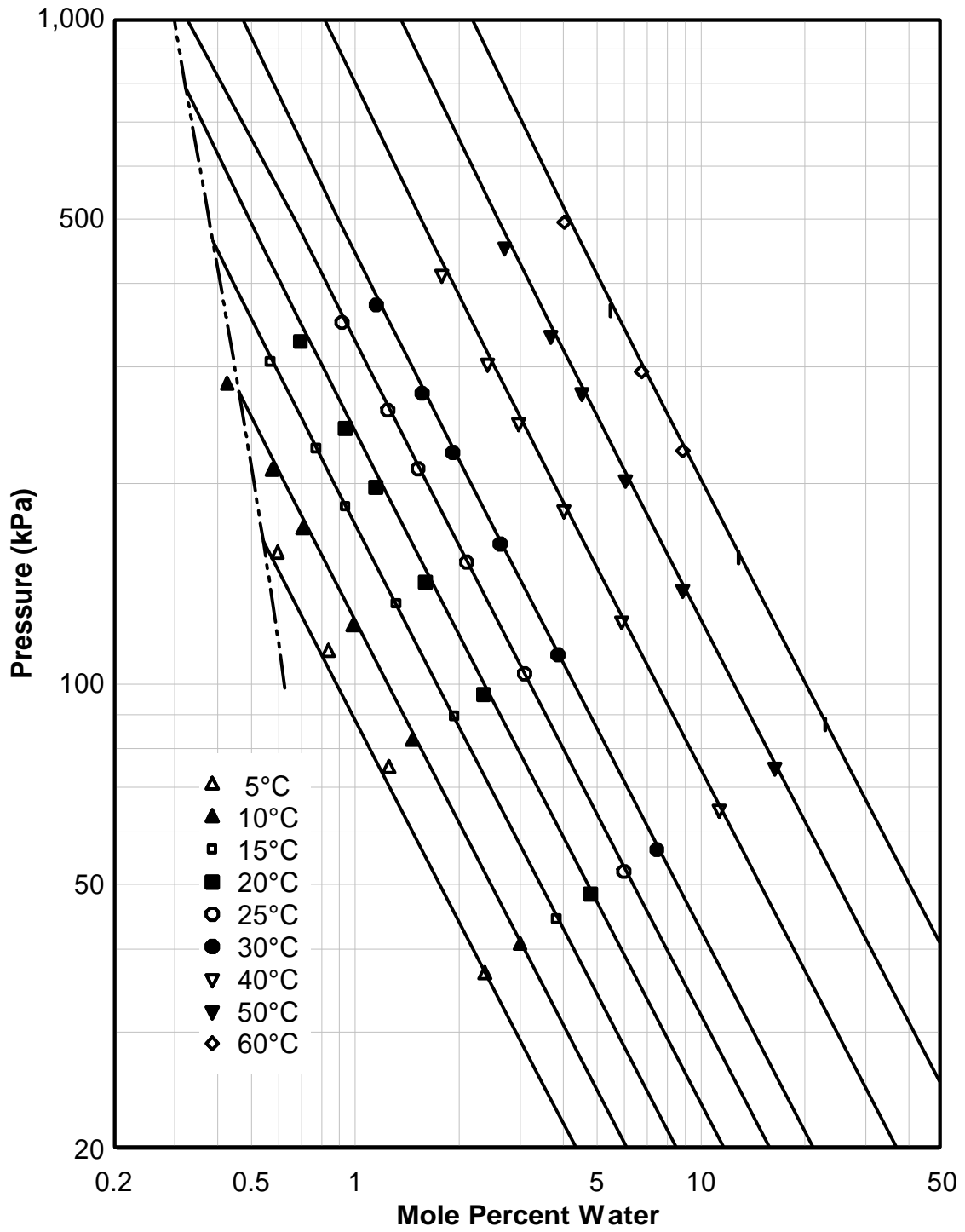


Fig. C2

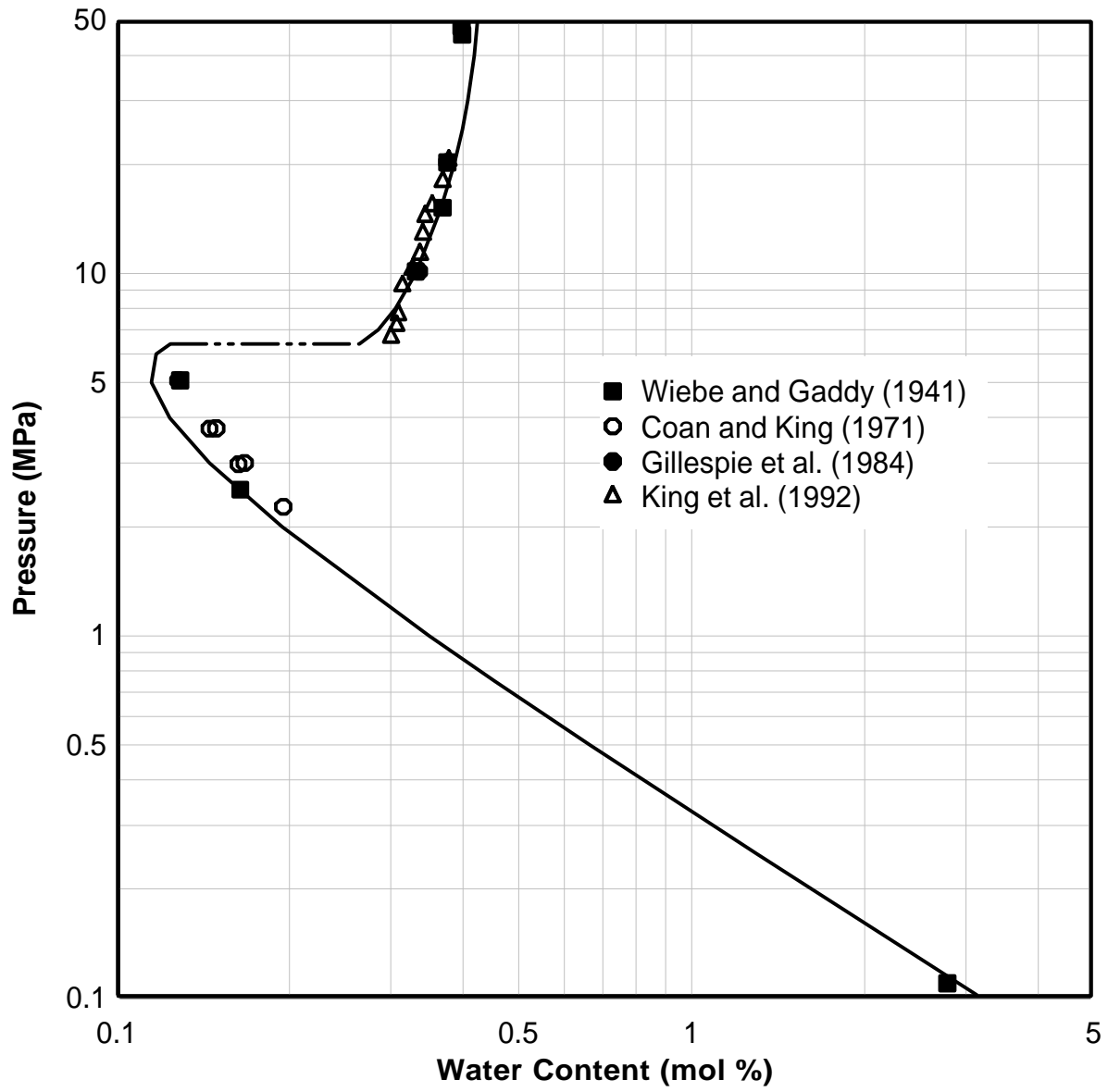


Fig. C3

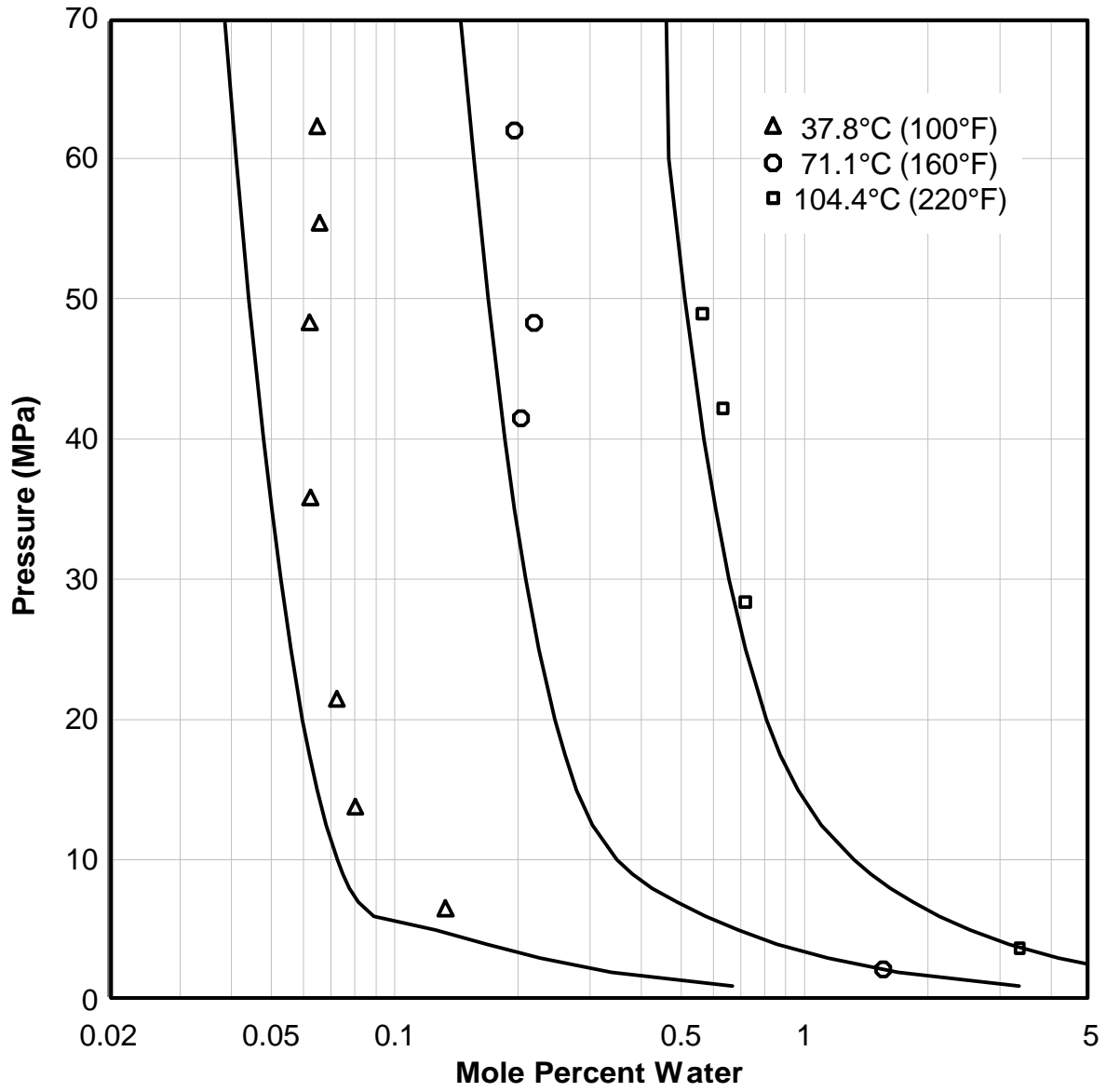
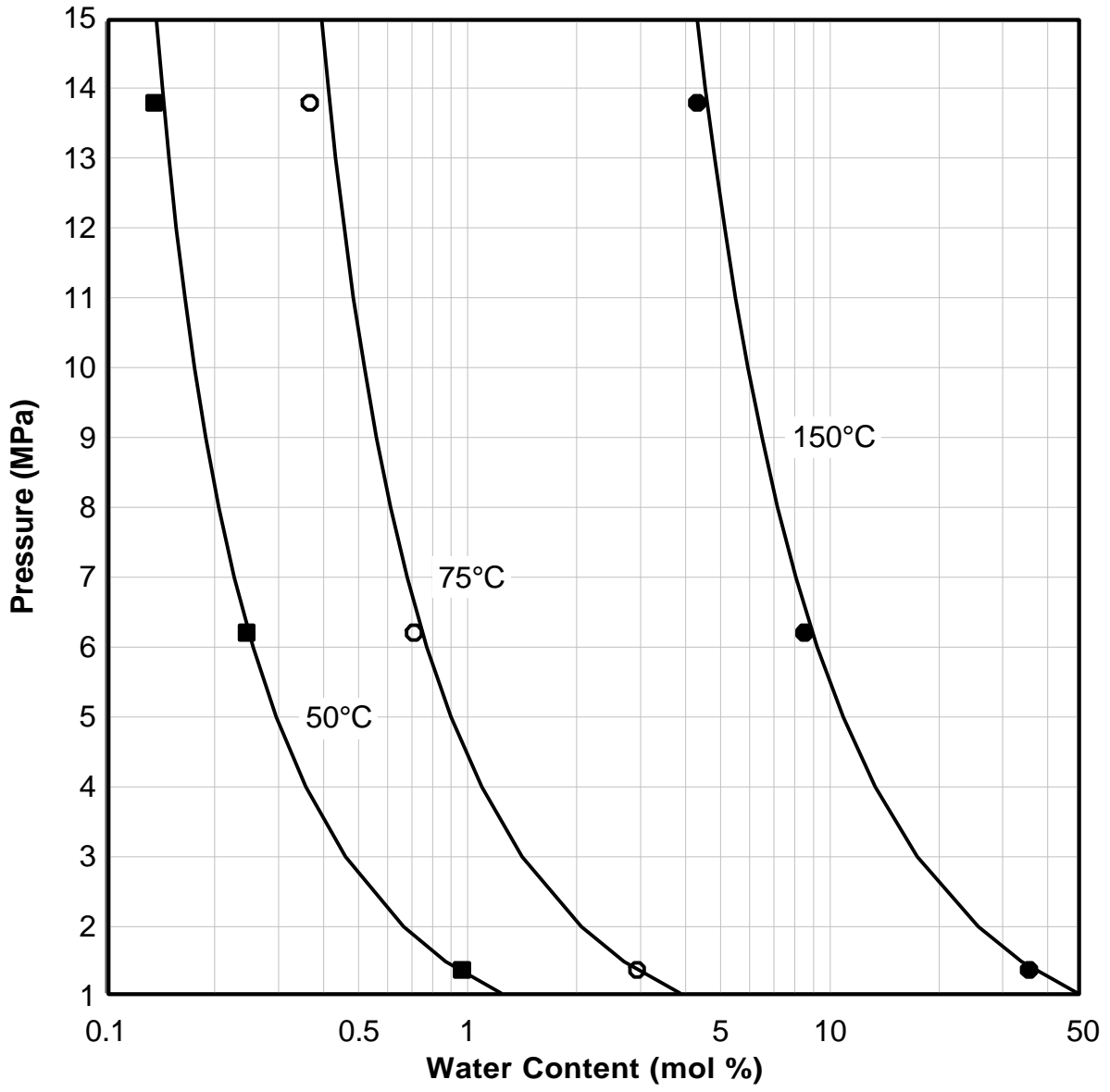


Fig. C4



## 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<sub>2</sub>S and CO<sub>2</sub>. 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 <sub>c</sub> (°C)	P <sub>c</sub> (MPa)	Reference
H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>			
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

