

IMPACT OF THERMOPHYSICAL PROPERTIES RESEARCH ON ACID GAS INJECTION PROCESS DESIGN

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Abstract

Stricter regulations and increased environmental concerns are making the previously common practice of flaring acid gas less attractive. Producers are being forced to find alternative methods to deal with this unwanted by-product. Acid gas injection has quickly become the method of choice for disposal, especially for small producers.

Presented in this paper is a brief overview of the acid gas injection process. Included in this discussion is a description of what physical property and phase equilibria data are required and why.

In addition, some new experimental data for the water content and density of sour gas mixtures are presented. These data are useful for checking the validity of the correlations used in the design of an acid gas injection scheme. In addition, such data are useful for optimizing the interaction parameters in the thermodynamic models employed to calculate such properties.

1.0 ACID GAS INJECTION

Acid gas injection occurs in three basic steps: (1) compression, (2) transportation by pipeline, and (3) injection. The acid gas injection process has been reviewed previously (Wichert and Royan, 1997; Carroll and Maddocks, 1999) so it will only be discussed here briefly.

Acid gas, the top product off the amine regenerator column, is at low pressure, typically 35 to 50 kPa[g] (5 to 7 psig). The acid gas is made up largely of hydrogen sulfide and carbon dioxide, but it also contains small amounts of light hydrocarbons and possibly nitrogen. Because of the nature of the stripping process, the acid gas is saturated with water at these conditions.

In order to get it through the pipeline and into the injection well, the acid gas has to be compressed. The compression takes place in a multi-stage compressor with interstage cooling and liquids knock-out. The interstage exchangers are typically aerial coolers and are designed to cool the acid gas to 49°C (120°F). At this temperature, an aqueous phase is likely to form and is removed using interstage knock-out scrubbers.

Next the acid gas is transported to an injection well in a pipeline. Based on safety considerations, the pipeline is generally kept as short as possible. On the other hand, the injection well may be an existing well converted for injection purposes. Then the length of the pipeline is dictated by the distance from the plant to the well of choice. Regardless, when in operation, the line is filled with acid gas and a leak would release a large volume of the deadly gas. By keeping the line short as possible, the amount of gas released can be kept to a minimum.

The design of the pipeline follows the standard procedures for pipeline design. However, depending upon the circumstances the line may carry a gas, a liquid, or a mixture of both. Therefore, the procedure used to design the pipeline must be able to handle these multiphase cases.

Finally, the fluid enters the injection well where it eventually enters a deep formation for the ultimate disposal. The calculation of the injection profiles, and hence the injection pressures, was a topic covered in previous papers: Carroll, and Lui (1997) and Carroll and Maddocks (1999). However, it is worth repeating – the accurate calculation of the injection pressure is only possible with accurate fluid density estimates.

2.0 PHASE EQUILIBRIA AND PHYSICAL PROPERTIES

There are several important physical property and phase equilibria to be considered in the design of an acid gas injection scheme. These include, but are not limited to: (1) non-aqueous phase behavior, (2) water content of the acid gas and the possible formation of an aqueous liquid, (3) hydrate formation, and (4) the density and viscosity of the acid gas.

Perhaps the most significant problem with the calculations for acid gas injection is that much of the process occurs at conditions that are near the critical point of the mixture. Typically the range of temperature is $0.75 < T_R < 1.25$, where T_R is the reduced temperature, the ratio of the temperature to the critical temperature. The vicinity of the critical point is a region where it is difficult to accurately calculate the physical properties. Not only do the property estimations tend to be poor, but in addition, the properties are strong functions of the temperature and the pressure. In this region, small changes in pressure or temperature can have a dramatic effect on the physical properties.

This means that properties are required for gas, liquid, and supercritical fluid states. In addition, the calculations must make a smooth transition between the various states. As demonstrated by Carroll and Lui (1997), not all models make this smooth transition.

2.1 Non-Aqueous Phase Behavior

Knowledge of the vapor-liquid equilibrium in the non-aqueous phases is important throughout the design of the acid gas injection. For example, it is important in the design of the compressor to know under what conditions the acid gas will liquefy. We do not want liquids forming in the compressor, nor do we want non-aqueous liquids forming in the interstage knock-outs.

Here we are basically concerned with the vapor-liquid equilibrium in the acid gas mixture. We are also concerned to some extent with the effect of water on this equilibrium. The traditional tools, notably the Soave (1972) and Peng-Robinson (1976) equations of state or their more recent modifications, can be applied to these mixtures. It is well known that even these commonly employed tools require at least a single binary interaction parameter to obtain accurate results. The desired method of obtaining these interaction parameters is by fitting experimental data.

2.2 Water Content

The water content of acid gas is also a significant consideration in the design of an acid gas injection scheme. Sour water is highly corrosive and can cause other processing problems.

Unlike sweet gas where the water content is a continually decreasing function of the pressure (i.e., the higher the pressure the less water the sweet gas holds), acid gases and their mixtures have a minimum water content. We can take advantage of this minimum in the water holding-capacity and eliminate the need for a dehydration unit. Only if the water-holding capacity of the acid is well established and predictable can we exploit this property. For this reason, accurate experimental data are highly valuable.

The estimation of the water content of both sour and acid gases is more difficult than those for sweet gas. The short-cut methods (such as the McKetta chart) are simple to use and provide reasonably accurate results for sweet gas. The suggested correction methods for sour gas make these methods more difficult to use and the results are much less accurate. In general they cannot be employed for acid gas mixtures.

Ng et al. (1983, 1985, 1995) presented water content data for systems containing both sour and acid gases in GPA-sponsored research program (Research Report RR-66, RR-87 and RR-149).

Another significant problem in the calculation of the water content of acid gases is the fact that they are relatively simple to liquefy (per the earlier discussion). The liquefied acid gas can hold more water than in the gaseous state. Again, the design engineer should attempt to take advantage of this property.

2.3 Hydrate Formation

Gas hydrates are ice-like solids that form at conditions where a solid probably would not otherwise be expected to form. Hydrates are well-known in the natural gas processing business and are notorious for plugging pipelines and process equipment. Therefore the conditions where hydrates may form is an important consideration in process design. It is equally important to have a strategy to deal with hydrates when they do form during normal operation, as well as start-up, shut-down, and during process upsets.

Of the components commonly present in natural gas, none forms a hydrate more easily than hydrogen sulfide. The hydrate of H₂S forms at the lowest pressures and persists to the highest temperatures. For a thorough review of the hydrate forming condition for hydrogen sulfide see Carroll and Mather (1991). Carbon dioxide also readily forms a hydrate. A brief review of the hydrate forming conditions for CO₂ is given by Chun et al. (1996). Ng et al. (1983, 1985, 1986, 1987) presented hydrate and hydrate inhibition data for systems containing acid gas mixtures as part of GPA-sponsored research program (Research Report RR-66, RR-87, RR-92 and RR-106).

Thorough reviews of gas hydrates are also available. Perhaps the most significant of these is the book by Sloan (1998). He also summarizes the experimental work on gas hydrates up to that time.

In acid gas injection, one of the methods for combating hydrate formation is the use of methanol or other hydrate inhibitor. The design engineer should carefully consider the amount of methanol to use. Over injection results in wasted methanol, and hence wasted money. Insufficient methanol use risks the formation of an equipment-plugging hydrate and potentially an unwanted shut-down to deal with the problem.

2.4 Density and Viscosity

The density and viscosity are also required for the design of an acid gas injection scheme.

The design of the pipeline follows traditional methods for pipeline design. Therefore, in order to calculate pressure drops in the lines the Reynolds number, which is a function of the density and the viscosity, is required.

In addition, as demonstrated by Carroll and Lui (1997) and Carroll and Maddocks (1999), the density is the key parameter in the calculation of the injection profiles for the injection wells.

The traditional cubic equations of state (Soave, 1972; and Peng and Robinson, 1976) are basically correlations of the molar volume (and hence the density) as functions of the temperature, pressure and, through the mixing rules, the composition. However, they are notoriously poor at predicting the density of the liquid phase. Many attempts have been made over the years to improve the accuracy of these equations in this

regard. These modifications rely on accurate experimental data to obtain the required parameters. The design engineer must be aware of this limitation. Failure to do so will result in improperly sized equipment and lines.

A further complicating factor is that typical viscosity correlations use the density as an intrinsic parameter. Therefore accurate estimation of the density is important for accurate prediction of the viscosity.

2.5 Other Properties

The design of an acid gas injection scheme requires other physical property information. Properties such as: enthalpy, entropy, and heat capacity tend to play a less significant role – or at least a less visible role. However, they are required in the design of the compressor and heat exchange equipment. These other thermodynamic properties are usually obtained in the traditional manner (typically using an equation of state). This also requires the ideal gas heat capacities, which, for the components of interest in acid gas injection, are readily available.

In the design of heat transfer equipment and heat loss calculations, the thermal conductivity of the process fluids is also required. However, the design engineer can often get away with poor estimates of the thermal conductivity, since it usually does not have a significant effect on the design.

3.0 PROCESS SIMULATION

One of the most important advances in the field of process engineering has been the advent of the general-purpose process simulators. The power that these software packages put on the desktop of the modern engineer was unheard-of thirty years ago. The downside of these tools is that they have made the process engineer a little lazy. Users are often so overwhelmed by these tools that they blindly believe the results they supply. The design engineer should be aware of the old adage – garbage in, gospel out. Always question the results obtained in these simulations.

These observations are no less true in the emerging application of acid gas injection. The tools provided in the general purpose process simulators are of great help in the design of an acid gas injection scheme. However, the phase equilibria and physical properties encountered in acid gas systems require the design engineer to be more wary of these results. In addition, as noted earlier, the design engineer should be aware of the limitations of the models used when working in the near-critical region.

The models used in the simulation software require high accuracy experimental data to obtain the required adjustable parameters. Without the data the models can be in error and often significantly so. But the design engineer is usually oblivious to this limitation, rarely questioning what models are being used, never mind whether or not the required parameters have been optimized.

4.0 EXPERIMENTAL DETAILS

As outlined in this paper physical properties and phase equilibria are keys to the economic design of an acid gas injection scheme. Presented in this paper are some preliminary results. These should be very useful for testing and tuning the models available to the design engineer.

4.1 Experimental Equipment

The experimental measurements were carried out in a variable-volume, visual phase behavior cell as shown in Fig. 1.

The main body of the cell consisted of a Pyrex glass cylinder 20.3 cm (8.0 in) long with an internal diameter of 3.2 cm (1.25 in) and a 1.26 cm (0.5 in) wall. The effective working volume was about 110 cm³ (6.7 in³). This cylinder was housed inside a sturdy outer steel shell. Vertical opposing tempered flat glass plates mounted in this outer shell permitted visual observation over the entire working range of the cell. The cell was equipped with a floating piston so that the fluid being studied could be isolated from mercury, the hydraulic fluid. The volume, and hence the pressure of the fluids under investigation, were controlled by a positive displacement pump connected through mercury to the cell contents. A second transparent fluid, connected through the same hydraulic system and confined between the steel shell and the cylinder, was used to balance pressures across the Pyrex cylinder.

The entire cell assembly was mounted on a rocking mechanism inside a temperature controlled air oven. Temperatures were measured with a Resistance Temperature Device (RTD). The RTD for the cell contents was inserted into the bottom of the cell and protruded into the mercury. The signals were read out on a digital temperature indicator and were reliable to within $\pm 0.2^\circ\text{F}$ ($\pm 0.1^\circ\text{C}$). Pressures were measured using a calibrated Heise pressure gauge.

A specially designed header mounted on top of the cell provided for charging and sampling. The volume of each phase in the cell was determined using a cathetometer readable to the nearest 0.01 mm. A volume vs. height calibration for the cell, obtained by observing the change in elevation of the piston in the cell corresponding to a known change in volume, was used to transform the height measurements of the vapor-liquid interface.

4.2 Experimental Procedures and Methods

The experimental acid gas mixtures were prepared gravimetrically from pure components and stored at elevated pressures in the single-phase condition in stainless steel pipettes. At the start of a run, the cell was connected to a mercury pump and evacuated. An appropriate amount of water was then added to the cell, followed by a suitable amount of the prepared acid gas mixture.

Following the charging process, the pressure and temperature of the cell was adjusted to the required values and equilibration commenced. The vapor and aqueous liquid phases were present at each condition.

The most difficult part of the study was the sampling and analysis of each of the two phases. This was because of the very low concentration of water in the vapor phase, and limited solubility of hydrocarbon in the aqueous phase. For the vapor, one sample was taken for the CO₂, H₂S, and hydrocarbon component determination, and a large second sample was taken for determining the water content in the vapor phase. In this second large sample, a solvent with an internal standard was used to extract water from the vapor phase. The resulting liquid solutions were injected directly into a gas chromatograph to determine the water content.

For the aqueous liquid phase, a large sample was collected and flashed to atmospheric pressure and the released gases were analyzed by chromatography.

5.0 EXPERIMENTAL ACCURACY

5.1 Pressure

Pressures were measured using a 10,000 psi (69 MPa) calibrated Heise digital gauge. Pressures are thought to be known within ± 3 psi (± 20 kPa).

5.2 Temperature

The temperatures were measured using resistance temperature devices. They are believed known to within $\pm 0.2^\circ\text{F}$ ($\pm 0.1^\circ\text{C}$).

5.3 Materials

The source and purity of the raw material used for the experimental work is shown in the following table.

Material	Min. Purity	Supplier
Methane	99.95	Matheson of Canada
Propane	99.0	Praxair, Edmonton
Carbon Dioxide	99.8	Praxair, Edmonton
Hydrogen Sulfide	99.8*	Matheson of Canada
Water	Distilled	Serra Feinbiochemical GmbH & Co., N.Y.

* - This material was distilled once before using, improving the purity as received from 99.5 to 99.8 mole percent.

5.4 Composition

An HP5890 chromatograph with a combination of TCD and FID detectors was used for the compositional analyses. The concentration of major components determined by chromatography is thought to be known to within ± 0.003 mole fraction. The minor components such as hydrocarbon and sour components in the aqueous phase are known to be within $\pm 10\%$ of the reported value. The water concentration in the vapor phase is thought to be known to within 25 ppm.

6.0 EXPERIMENTAL RESULTS

Some preliminary results from an on-going, GPA-sponsored research program are presented here. These new data are for multicomponent mixtures containing CO₂, H₂S, methane, propane, and water. These include measurements of the vapor-liquid equilibrium between the sour gas and an aqueous liquid and the densities of the two phases.

Table 1 presents the data for a mixture containing 75% methane-propane (95/5 mole ratio) and 25% H₂S-CO₂ (1/3 mole ratio) plus water for four pressures at 48.9°C (120°F). The K-factors for these mixtures are given in Fig. 2. Table 2 presents the data for similar mixtures at 93.3°C (200°F). The K-factors for the data in Table 2 are given graphically in Fig. 3.

Even though the data presented in this work are not directly applicable to the acid gas injection process (the mixtures studied contain more hydrocarbon than encountered in a typical acid gas injection scheme), they provide a severe test of the available thermodynamic models. And in that sense they are highly valuable.

7.0 DISCUSSION

Acid gas injection is quickly becoming the method of choice for dealing with unwanted acid gas. Although the design of an acid gas injection scheme follows relatively conventional procedures, the engineer is dealing with fluids for which there is a relative paucity of experimental data. Therefore, accurate experimental data, such as those presented in this paper are required to validate and tune the existing models.

Without accurate data, which lead to accurate models, the acid gas injection schemes will be over-designed. The problem with such over-design is the increase in cost that must result from such a practice.

8.0 REFERENCES

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Table 1 Equilibrium Phase Properties for Systems Containing 75% Methane-Propane (95/5 mole ratio) and 25% Hydrogen Sulfide-Carbon Dioxide (1/3 mole ratio) in the Presence of Water at 48.9°C (120°F)

COMPONENT	FEED	CONCENTRATION, MOLE %		K1
		LIQUID 1	VAPOR	
P = 200 psia = 1.379 MPa				
CH4	1.8600	0.0206	73.7208	3.58E+03
CO2	0.4901	0.0803	16.3903	2.04E+02
H2S	0.1634	0.0695	4.8633	6.99E+01
C3H8	0.0984	0.0008	3.9171	4.85E+03
H2O	97.3881	99.8288	1.1086	1.11E-02
VOL %		28.5	71.5	
Density(g/cm ³)		0.987	0.013	
P = 1500 psia = 10.342 MPa				
CH4	7.6613	0.1214	74.3182	6.12E+02
CO2	2.0196	0.3832	16.4459	4.29E+01
H2S	0.6720	0.3226	5.0497	1.57E+01
C3H8	0.4029	0.0024	3.9636	1.67E+03
H2O	89.2442	99.1704	0.2225	2.24E-03
VOL %		42.9	57.1	
Density(g/cm ³)		0.995	0.108	
P = 4000 psia = 27.579 MPa				
CH4	18.2695	0.2253	72.5156	3.22E+02
CO2	4.8153	0.5901	17.5582	2.98E+01
H2S	1.6031	0.3942	5.8814	1.49E+01
C3H8	0.9614	0.0030	3.8595	1.27E+03
H2O	74.3508	98.7874	0.1852	1.88E-03
VOL %		39.9	60.1	
Density(g/cm ³)		1.002	0.287	
P = 10000 psia = 68.947 MPa				
CH4	20.8731	0.3723	71.3409	1.92E+02
CO2	5.6663	0.6886	17.9201	2.60E+01
H2S	2.1092	0.3366	6.4730	1.92E+01
C3H8	1.1966	0.0019	4.1379	2.23E+03
H2O	70.1547	98.6007	0.1281	1.30E-03
VOL %		44.9	55.1	
Density(g/cm ³)		1.017	0.431	

Table 2 Equilibrium Phase Properties for Systems Containing 75% Methane-Propane (95/5 mole ratio) and 25% Hydrogen Sulfide-Carbon Dioxide (1/3 mole ratio) in the Presence of Water at 93.3°C (200°F)

COMPONENT	FEED	CONCENTRATION, MOLE %		K1
		LIQUID 1	VAPOR	
P = 200 psia = 1.379 MPa				
CH4	1.0989	0.0164	69.3268	4.24E+03
CO2	0.2896	0.0427	16.3005	3.81E+02
H2S	0.0960	0.0286	4.7116	1.65E+02
C3H8	0.0578	0.0006	3.7313	6.63E+03
H2O	98.4577	99.9117	5.9298	5.94E-02
VOL %		34.5	65.5	
Density(g/cm ³)		0.963	0.011	
P = 1500 psia = 10.342 MPa				
CH4	9.5455	0.1057	72.5179	6.86E+02
CO2	2.5188	0.2593	17.7578	6.85E+01
H2S	0.8388	0.1857	4.7363	2.55E+01
C3H8	0.5025	0.0023	3.8701	1.66E+03
H2O	86.5944	99.4469	1.1179	1.12E-02
VOL %		32.4	67.6	
Density(g/cm ³)		0.960	0.089	
P = 4000 psia = 27.579 MPa				
CH4	15.3273	0.2337	71.9676	3.08E+02
CO2	4.0455	0.4453	17.4255	3.91E+01
H2S	1.3475	0.3463	6.2095	1.79E+01
C3H8	0.8062	0.0036	3.7309	1.03E+03
H2O	78.4735	98.9712	0.6666	6.74E-03
VOL %		40.7	59.3	
Density(g/cm ³)		0.973	0.227	
P = 10000 psia = 68.947 MPa				
CH4	21.3049	0.3605	69.3699	1.92E+02
CO2	6.3600	0.6073	19.5619	3.22E+01
H2S	2.1732	0.3549	6.3461	1.79E+01
C3H8	1.2663	0.0024	4.1667	1.73E+03
H2O	68.8956	98.6749	0.5553	5.63E-03
VOL %		41.7	58.3	
Density(g/cm ³)		0.973	0.396	

Figure 1 Schematic of Phase Behavior System

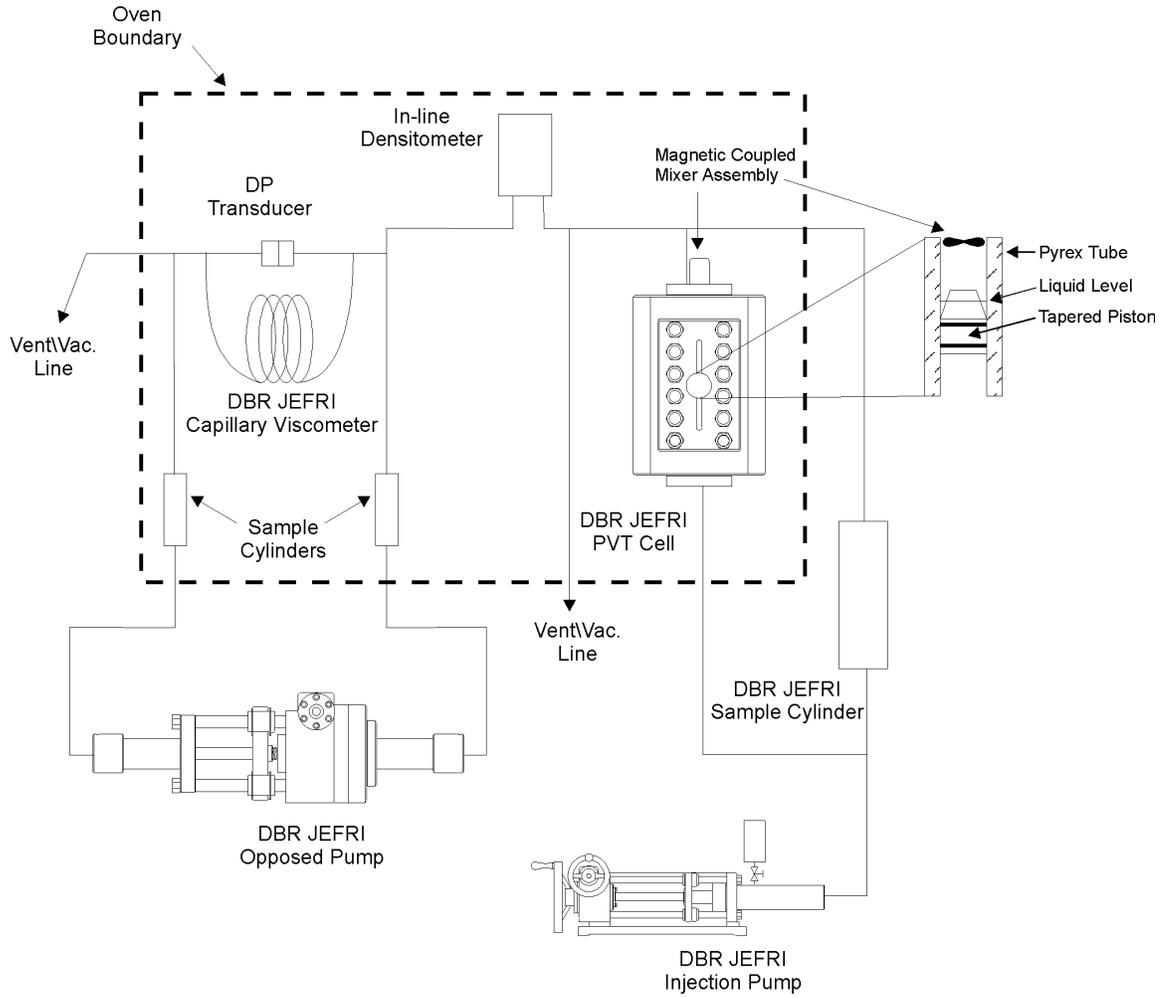


Figure 2 Equilibrium Ratio for Methane-Propane-Hydrogen Sulfide-Carbon Dioxide-Water System (75HC-25AC1) at 120°F (48.9°C)

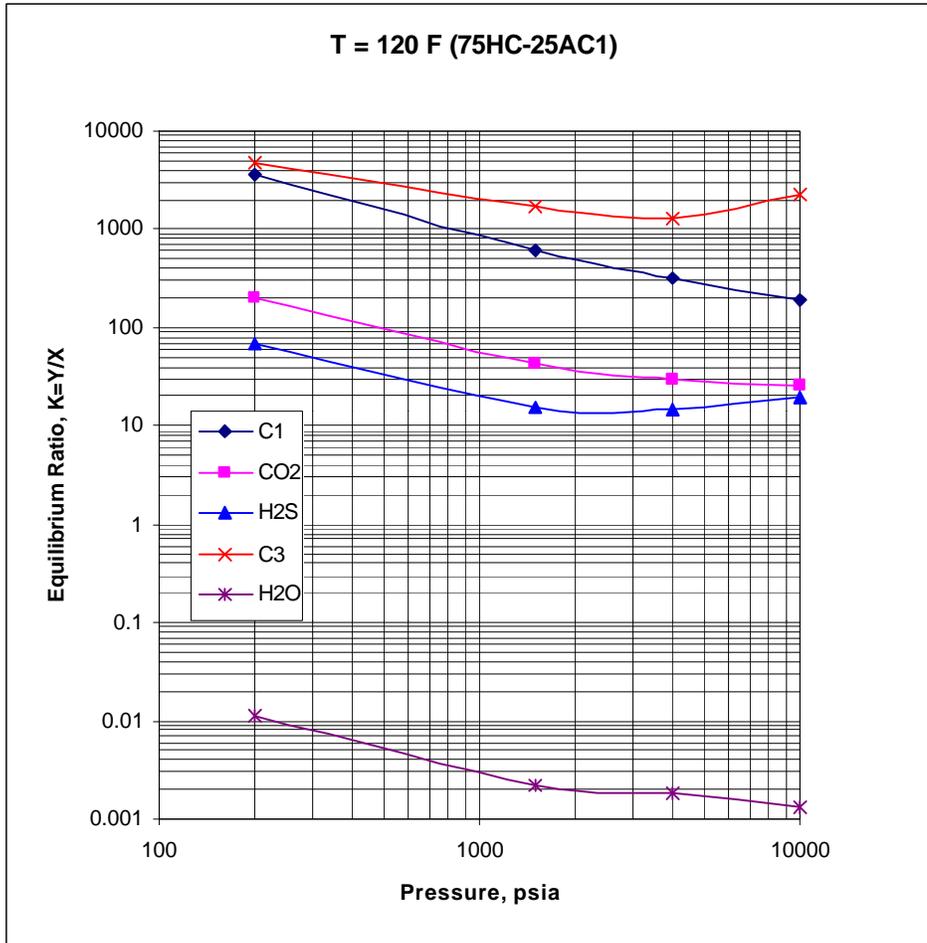


Figure 3 Equilibrium Ratio for Methane-Propane-Hydrogen Sulfide-Carbon Dioxide-Water System (75HC-25AC1) at 200°F (93.3°C)

