4

QUALITATIVE PHASE BEHAVIOR

In this book we are concerned primarily about the application of energy to achieve desired goals. The energy possessed by any substance depends on its phase. There are three different familiar phases ... solid, liquid and gas (vapor). You have learned to identify them by sight.

A solid possesses a definite shape and is hard to the touch. It is composed of molecules with very low energy that stay in one place even though they vibrate. There is space between these molecules so a solid is not impenetrable.

A liquid has a definite volume but no definite shape. It will assume the shape of the container in which it is placed but will not necessarily fill that container. The molecules of which the liquid is composed possess more energy than in a solid; enough energy to move from place to place. By virtue of this energy there is more space between molecules. So, a substance is less dense in the liquid form than in the solid form.

A vapor has no definite volume or shape and will fill a container in which it is placed. The molecules have more energy than in the liquid form. In fact, they are very active. Vapor density usually is low enough that one can see through a vapor. As might be expected, the density of a given substance is lower in the vapor phase than in the liquid phase.

Our primary concern is the difference in energy level between phases. If we wish to melt a solid to form liquid we must add energy. If enough additional energy is added, the liquid can be vaporized.

We must know the phase or phases that exist at given conditions of pressure, volume and temperature in order to ascertain the corresponding energy level. To do this, we separate substances into two classifications – *pure substances* (single component systems) and *mixtures* of substances (multi-component systems).

SINGLE COMPONENT SYSTEMS

The word component refers to the number of molecular or atomic species present in the substance. A single component system is composed entirely of one kind of atoms or molecules. We often use the word "pure" to describe a single component system.

Figure 4.1 is a typical phase diagram for a pure substance. It has three axes – P, V and T. It is composed of a series of plane surfaces, each of which represents a given phase or a mixture of phases. We are particularly interested in the two-phase planes:

> BDHG – solid plus liquid, FGIJ – solid plus vapor, and an irregular-shaped plane HCI for the liquid plus vapor. All of these planes are *perpendicular* to the temperature axis.

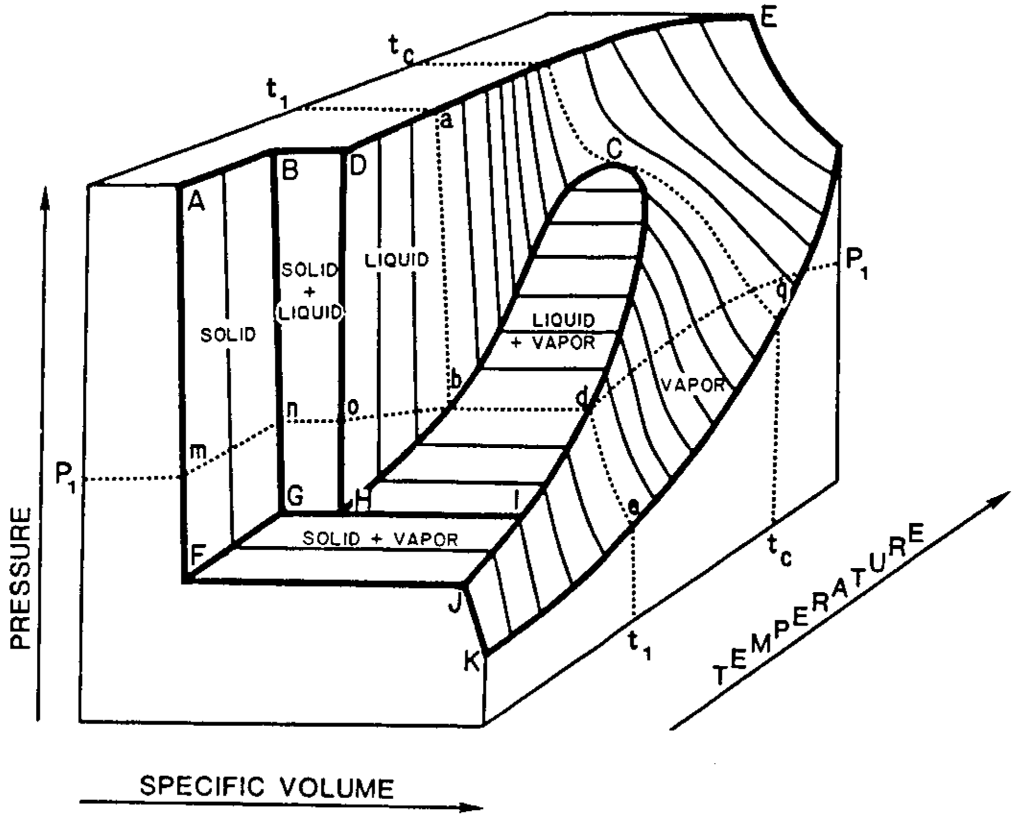


Figure 4.1 **P-V-T Diagram for a Single Component System**

The liquid-only plane is the "cliff" to the left of plane HCI and adjacent to plane BDHG. The vapor-only plane is the "slope" to the right of plane HCI.

Although all planes are of interest, we are primarily concerned with plane HCI, the vapor-liquid region of the phase diagram.

A three dimensional phase diagram like Figure 4.1 is awkward to use. So, we normally draw a projection of this diagram. Both P-T and P-V projections are important.

P-T Plot for a Pure Substance

Since all of the two-phase planes in Figure 4.1 are perpendicular to the T axis, they appear as single lines in a P-T projection like Figure 4.2.

Lines HD, HC, and FH are the equilibrium lines – combinations of pressure and temperature at which the adjoining phases are in equilibrium. At equilibrium one can change phase, at constant pressure and temperature, by simply adding or removing energy from the system. Point H, the triple point, is the only combination of pressure and temperature at which all three phases can exist together.

Along line FH no liquid phase is ever present and solid *sublimes* to vapor. The use of "dry ice" for cooling is an example of this. Line HD is the equilibrium line between solid and liquid. Ice water at 0°C [32°F] and atmospheric pressure occurs on this line. Line HD can have a positive or negative slope depending on whether the liquid expands or contracts on freezing. The energy change occurring along line HD is called the *heat of fusion*. At any P and T along this line the system can be all solid, all liquid or a mixture of the two depending on the energy level. This line could be called the solid-liquid saturation or solid-liquid equilibrium line.

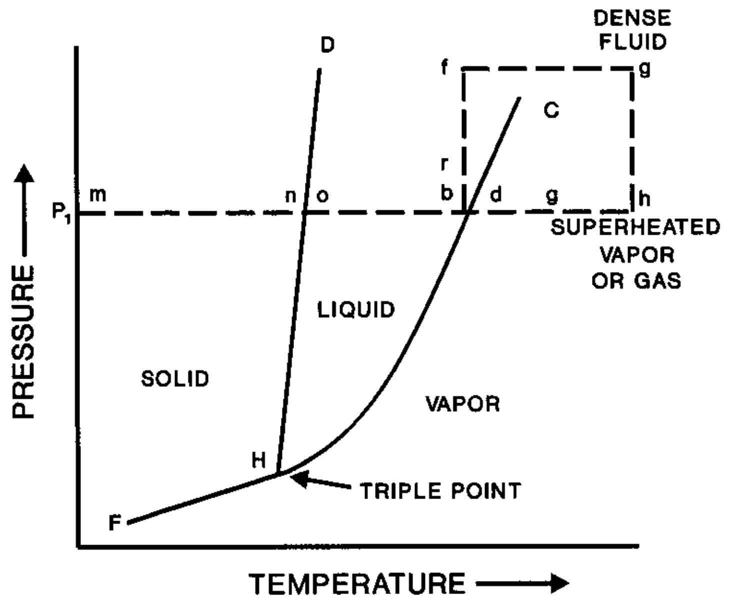


Figure 4.2 P-T Diagram for a Single Component System

Line HC is the saturation or equilibrium curve between vapor and liquid. It starts at the triple point and terminates at the critical point "C." The pressure and temperature conditions at this latter point are known as critical temperature (T_c) and critical pressure (P_c). At this point the properties of the liquid and vapor phases become identical. For a pure substance the critical point can be defined as that point above which liquid cannot exist as a unique separate phase. Above P_c and T_c the system is oftentimes referred to as a dense fluid to distinguish it from normal vapor and liquid.

Line HC is often referred to as the *vapor pressure curve.* Such vapor pressure curves are available from many sources. Line HC is also the bubblepoint and dewpoint curve for the pure substance (See Chapter 5).

In Figure 4.2, consider a process starting at pressure P_1, and proceeding at constant pressure. From "m" to "n" the system is entirely solid. The system is all liquid for the segment o-b. At "b" the system is a *saturated liquid* – any further addition of energy will cause vaporization at constant pressure and temperature. At "d," the system is in the *saturated vapor* state. At temperatures above "d," it is a *superheated vapor.*

Line HC is thus known by many names – equilibrium, saturated, bubblepoint, dewpoint and vapor pressure. For a pure substance these words all mean the same thing.

At the pressure and temperature represented by HC the system may be all saturated liquid, all saturated vapor or a mixture of vapor and liquid. The exact phase condition of the system depends on the energy level at the P and T involved.

The rectangle "bfghd" illustrates another important phase property that is confirmed experimentally. Suppose we place a liquid in a windowed cell at condition "b" and light it so it is easily visible. We then increase pressure at constant temperature (isothermally). As we proceed toward point "f" the color will begin to fade. At some point (as we blink our eyes) the color disappears completely. The cell now contains what looks like a vapor, but no bubble of vapor was ever seen to form.

At "f" (above the critical) the system is in a fourth phase that cannot be described by the senses. It is usually called *dense phase fluid,* or simply fluid. The word "fluid" refers to anything that will flow and applies equally well to gas and liquid.

This fluid at "f" looks like a gas but possesses different properties from regular gas found to the right of line HC and below the critical pressure. It is denser than regular gas but is more compressible than a regular liquid. Gas type correlations are used but must be modified to reflect the different behavior patterns of this dense phase fluid.

From "f" one can proceed at constant pressure (isobaric) to "g," reduce pressure isothermally to "h," and then proceed isobarically to "d." One has gone from saturated liquid to saturated vapor without encountering any discernible change of phase.

One could go from "b" and "d" directly by just adding energy to the liquid at constant pressure. In the cell you would observe bubbles of vapor forming and an interface would develop between gas and liquid. As energy input continued the liquid level would fail until the liquid phase disappeared. No temperature change would occur in going from "b" (saturated liquid) to "d" (saturated vapor).

Refer again to Figure 4.1. On the temperature axis you will note t_c. If you follow this line it will go through the critical point "c" and is tangent to the phase envelope HCI. The temperature lines between line HC and CI inside the phase envelope occur at constant pressure. This is a basic characteristic of all such diagrams for pure substances.

Figure 4.3 is a vapor pressure plot for light paraffin hydrocarbons. The lines shown are curve HC in Figure 4.2. They have been straightened artificially by using an odd scale on the abscissa. Figure 4.4 is a corresponding vapor pressure chart for paraffins based on their normal boiling point.$^{(4.1)}$

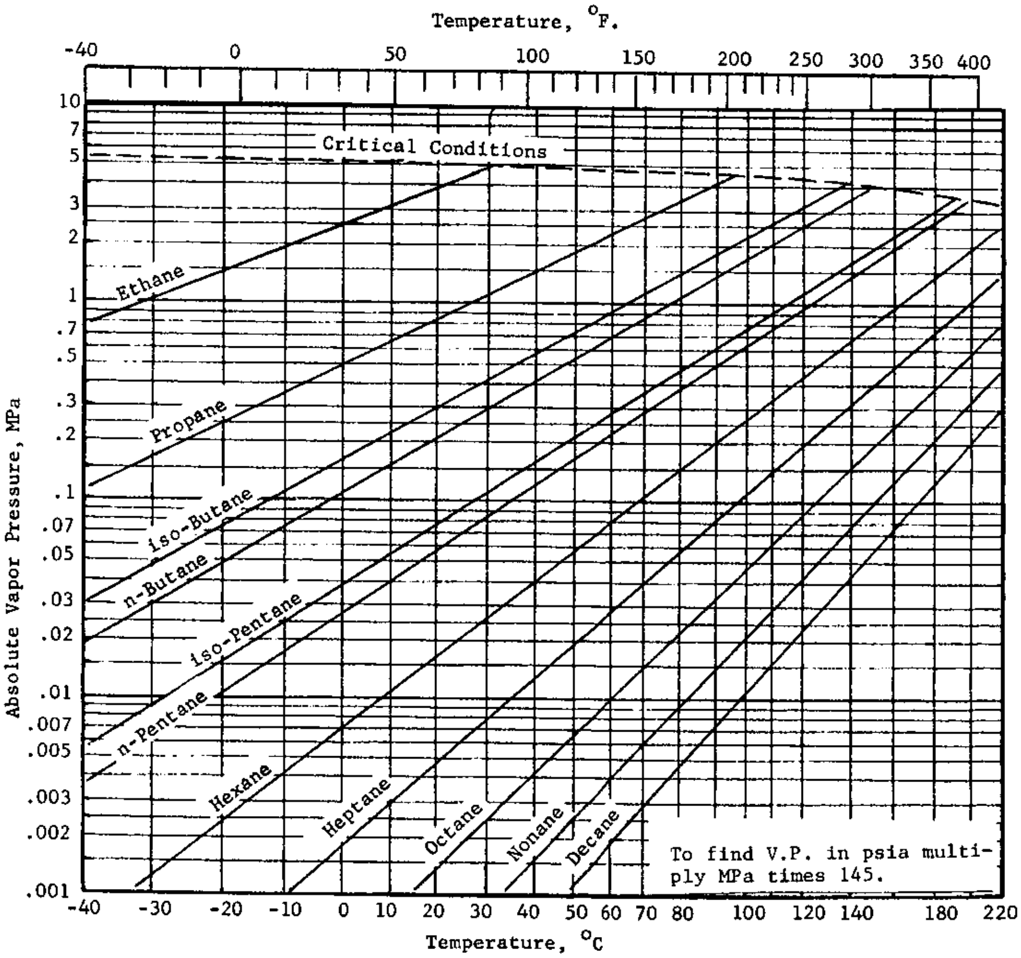


Figure 4.3 **Vapor Pressure Chart for Paraffin Hydrocarbons**

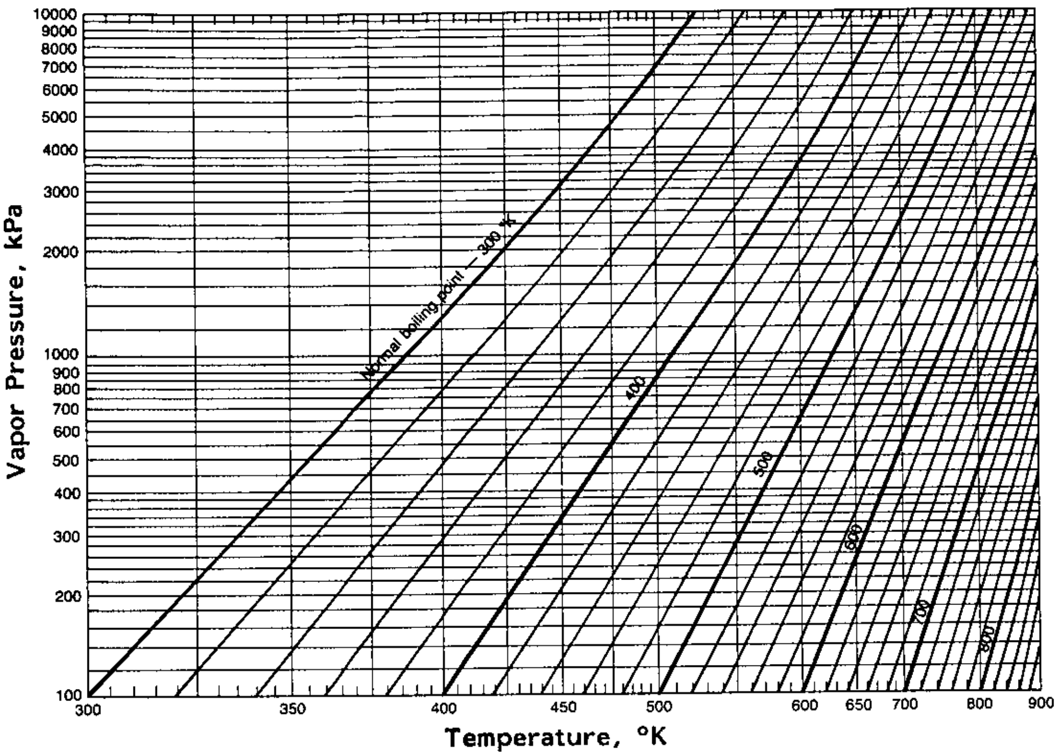


Figure 4.4 Vapor Pressure Chart for Normal Paraffin Hydrocarbons Based on Normal Boiling Point

Although the true vapor pressure curve of a pure component must terminate at its critical point, the line often is extrapolated above that point in the calculation of mixture properties. This pseudo value may be used to estimate the contribution of that molecular species to total mixture properties.

MULTI-COMPONENT SYSTEMS

For a multi-component system, another variable must be added to the phase diagram – composition. The location of the lines on a phase diagram depends on composition.

For a pure substance phase envelope HCI is a plane surface parallel to the temperature axis. For a multi-component mixture of substances this phase envelope is not a plane; it has thickness, somewhat like your tongue. Composition is the variable that reflects this thickness. If you replace specific volume in Figure 4.1 by composition and then make a pressure-temperature projection of the solid diagram, you obtain a figure like 4.5. The location of the lines in Figure 4.5 thus varies with composition. This figure is a projection showing only the liquid-vapor portion of the total phase diagram.

There are several terms used to define the location of various points on the phase envelope.

Cricondenbar – maximum pressure at which liquid and vapor may exist (Point N).

Cricondentherm – maximum temperature at which liquid and vapor may coexist in equilibrium (Point M).

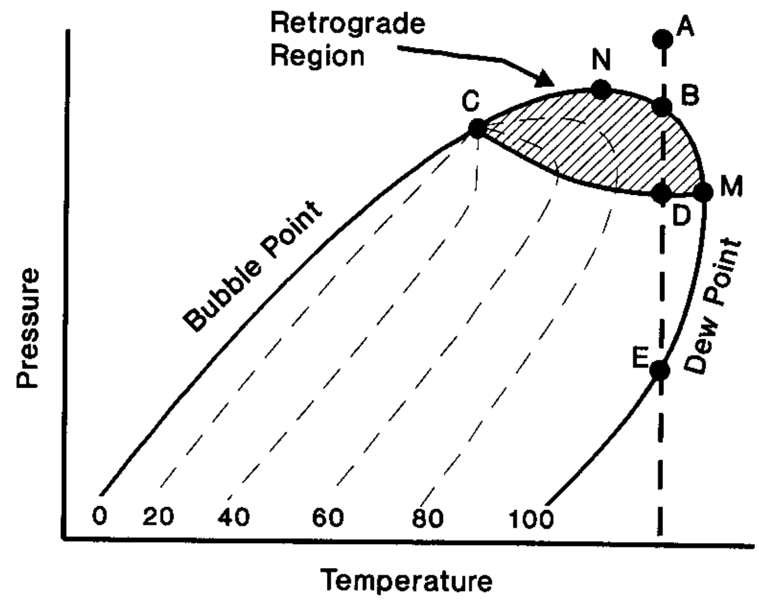


Figure 4.5 Typical Phase Diagram for a Multi-Component Mixture

Retrograde Region – that area inside phase envelope where condensation of liquid occurs by lowering pressure or increasing temperature (opposite of normal behavior).

Quality Lines – those lines showing constant percentages which intersect at the critical point (C) and are essentially parallel to the bubblepoint and dewpoint curves. The bubblepoint curve represents 0% vapor and the dewpoint curve 100% vapor.

Line ABDE represents a typical isothermal retrograde condensation process occurring in a condensate reservoir. Point A represents the single phase fluid outside the phase envelope. As pressure is lowered, Point B is reached where condensation begins. As pressure is lowered further, more liquid forms because of the change in the slope of the quality lines. The retrograde area is governed by the inflection points of such lines. As the process continues outside the retrograde area, less and less liquid forms until the dewpoint is reached (Point E). Below E no liquid forms.

In my experience the critical point has always occurred to the left of the cricondenbar for *naturally occurring* hydrocarbon gas mixtures. It is not, however, necessarily in the position shown. It may be further down on the phase curve or closer to the cricondenbar. Location of "C" is most important, for it fixes the shape of the quality lines which in turn governs the vapor-liquid ratio at a given temperature and pressure within the phase envelope.

As shown later in Figure 4.6, the critical point may occur to the right of the cricondenbar. If so, there will be two retrograde regions. But, Figure 4.5 is representative of most systems encountered in production/processing operations.

Note that the pseudocritical values calculated in Chapter 3 are not point "C" on Figure 4.5 except by coincidence. Calculation of the true critical values is discussed later in this chapter.

Effect of Composition

Figure 4.6 for the methane-propane binary system shows the effect of composition on the shape and location of the phase envelope. Two of the lines are the vapor pressure curves for methane and propane, which terminate at their critical point.

Three phase envelopes are shown for three different compositions of methane and propane. This illustrates the fact that the shape and location of the phase envelope depend on composition.

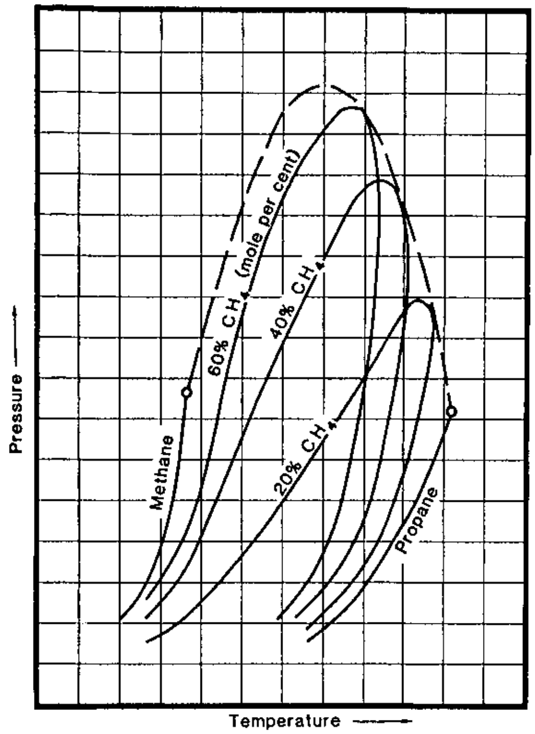


Figure 4.6 **Effect of Composition on Phase Envelope, Methane-Propane Binary**

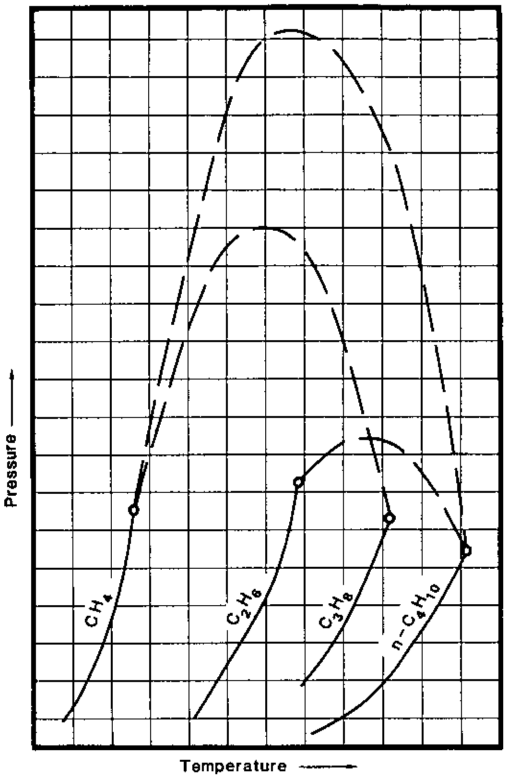


Figure 4.7 **Location of Critical Loci for Several Binary Systems**

The dashed line is the line drawn tangent to all possible phase envelopes or methane-propane binaries at the critical point on each curve. It is called the *critical locus*. It starts at the critical point of methane and ends at the critical point of propane. From the shape of this curve one can deduce that the critical point location on each phase envelope varies with composition.

Figure 4.7 shows the critical loci for a number of common binary mixtures. This behavior of binaries is the basis for the convergence pressure concept used for multi-component mixtures discussed in more detail in Chapter 5. For mixtures of over two components there is more than one critical locus. Thus, convergence pressure is merely a correlation device rather than an exact representation of phase behavior.

Figure 4.6 and 4.7 show that composition has a significant effect on shape and location of the phase envelope. This means that a reliable, representative analysis is important to obtain reliable phase behavior predictions. The accurate prediction of bubble and dewpoint conditions may be critical to design and/or operation. The accuracy of liquid recovery predictions depends on the corresponding quality of the phase data. Chapter 5 will clarify the calculations.

Effect of C_7+ Characterization

As previously discussed, the analysis and/or characterization of the C_6+ or C_7+ fraction in a natural gas mixture is not routine, yet has a significant effect on the shape of the phase envelope. This is illustrated for one gas in Figure 4.8.

Figure 4.8 presents phase envelopes for 4 different characterizations of the C_6+ fraction – C_7, C_9, C_{11} and full characterization based on a distillation analysis.

Special gas chromatographic techniques can identify individual components through about C_8-C_{10}. (See Chapter 1) This is called an extended analysis. If the phase behavior of the gas has a significant effect

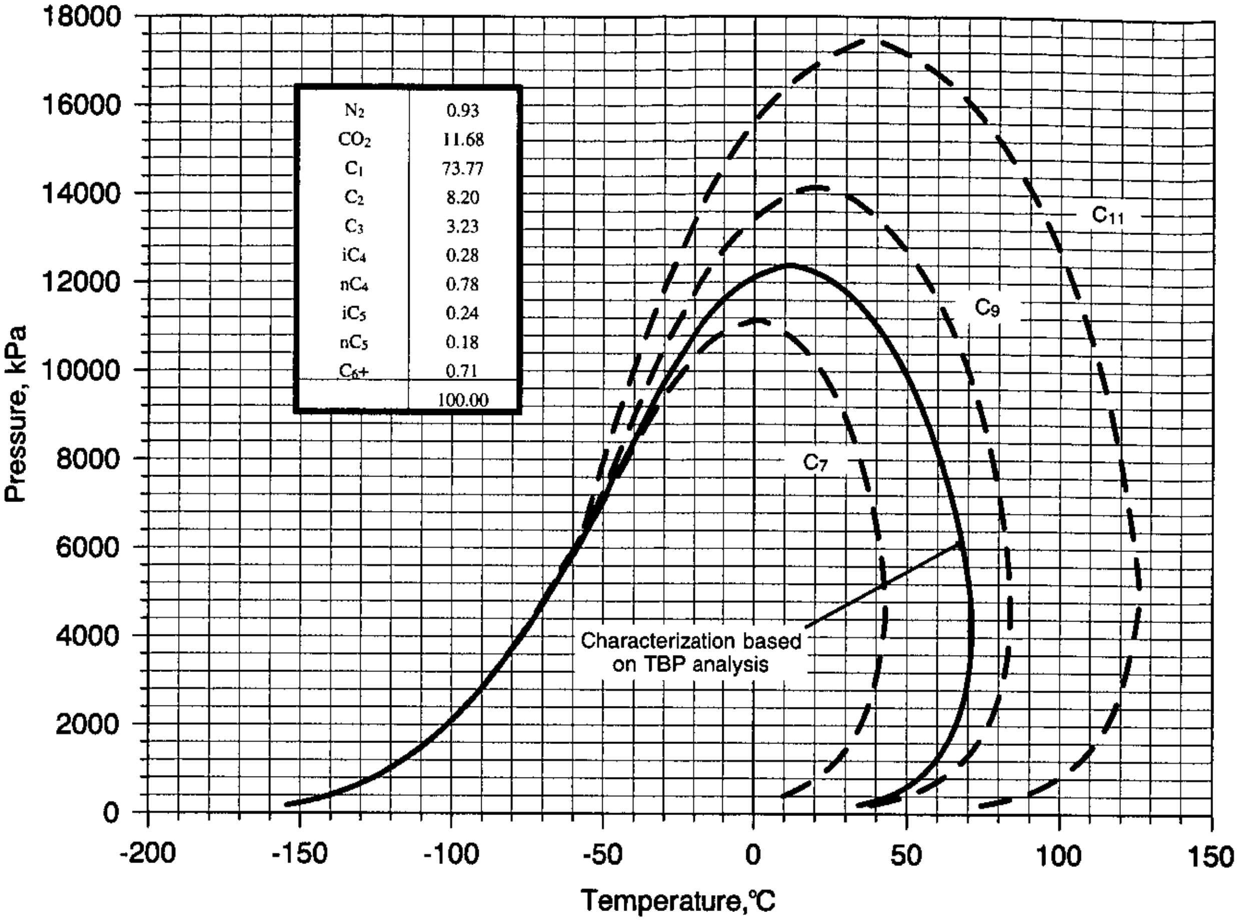


Figure 4.8 **Effect of C_6+ Characterization on Phase Envelope for Non-Associated Gas**

on the system design it is highly recommended that an extended analysis be performed. If an extended analysis is not available, predictive characterization techniques may be used . Several of these are summarized in Chapter 5.

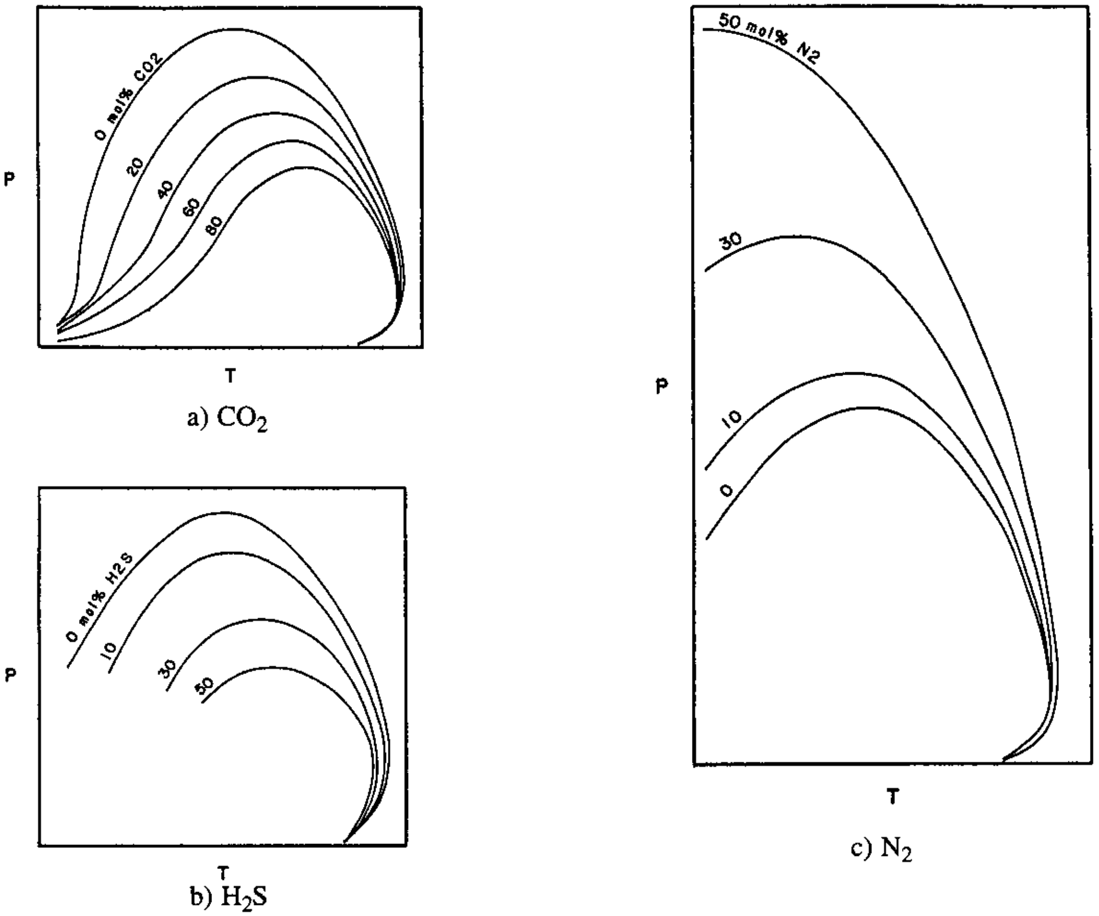
For lean natural gases the C_7+ characterization has a dramatic effect on the dewpoint line. The effect on the location of quality lines is much less significant.

Effect of Impurities

Hydrocarbons are frequently produced with non-hydrocarbon impurities. The most common include water, carbon dioxide, hydrogen sulfide and nitrogen. Since water has a low vapor pressure and is virtually immiscible in the hydrocarbon liquid phase, it does not have a significant effect on the shape of the hydrocarbon phase envelope except at high temperatures and low pressures.

The effect of CO_2, H_2S and N_2 is shown in Figure 4.9. Both CO_2 and H_2S lower the cricondenbar of the mixture. If sufficient quantities of the CO_2 and H_2S components are added to a reservoir fluid and the reservoir pressure is kept above the phase envelope, a single *dense fluid* phase exists. Although the actual mechanism is more complex, it is this solubility that is the primary driving force behind *miscible flood* enhanced oil recovery projects. NGL components such as ethane, propane and butane have a similar effect.

Nitrogen, on the other hand, raises the cricondenbar and decreases miscibility. It is typically used for pressure maintenance.



a) CO_2

b) H_2S

c) N_2

Figure 4.9 **Effect of CO_2, H_2S, and N_2 on Natural Gas Phase Envelope**

APPLICATION OF PHASE ENVELOPES

Proper analysis of many petroleum problems requires knowledge about at least a portion of the phase envelope. Several examples are summarized to illustrate some of these applications.

Reservoir Behavior

The reservoir is the "warehouse" from which we withdraw fluid for production and processing operations. Knowledge about the behavior of this fluid is critical if we are to proceed intelligently.

In Figure 4.10 four different kinds of reservoirs are shown. Points 1, 2, 3 and 4 represent the initial bottom hole pressure. The vertical line from these points represents reservoir pressure decline at constant temperature. The curved line represents pressure and temperature changes that occur in the wellbore. Point "w" represents wellhead conditions.

Reservoir (1) is called a *black oil reservoir.* Its temperature is less than the critical temperature. The reservoir, as shown, is undersaturated. No gas will form in the reservoir until the pressure reaches the bubblepoint, at which point it becomes saturated; as shown, gas would form in the wellbore, however.

Reservoir (2) is usually called a *volatile oil reservoir.* It also occurs to the left of the critical temperature. But, the gas-oil ratio is higher than for a black oil reservoir. The oil may be lighter in color but color is not a reliable indicator of the reservoir type. Once again, no gas forms in the reservoir until the bubblepoint pressure is attained, even though gas forms in the wellbore as shown.

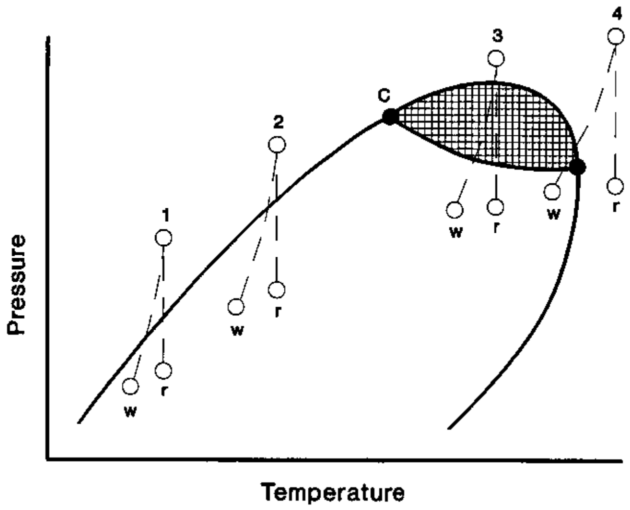


Figure 4.10 Use of Phase Envelopes in Reservoir Prediction

A reservoir whose temperature is between that of the critical and the cricondentherm is a *gas-condensate reservoir.* As it declines in pressure to the dewpoint, liquid forms in the reservoir. Said liquid will not flow to the wellbore until it reaches a critical saturation in the pore space. Most of this liquid will come from the heaviest ends in the dense phase fluid. At the dewpoint, the gas composition in the wellbore might change. The flow rate might also change if non-flowing liquid partially blocks gas flow.

As the pressure declines below the dewpoint, liquid formation increases so long as the pressure is in the retrograde region. Below this region some revaporization occurs.

Reservoir (4) is a true *gas reservoir.* It occurs at a temperature above the cricondentherm. No liquid can form in the reservoir at any pressure. If the wellhead conditions are inside the phase envelope, however, some liquid will form in the wellbore and appear at the surface. So ... once again ... you cannot tell what the reservoir is doing by what you observe at the surface.

In Figure 4.10 the one phase envelope has been used to describe several different types of reservoirs. In actual practice the phase envelopes for each reservoir are different. This is illustrated in Figure 4.11.

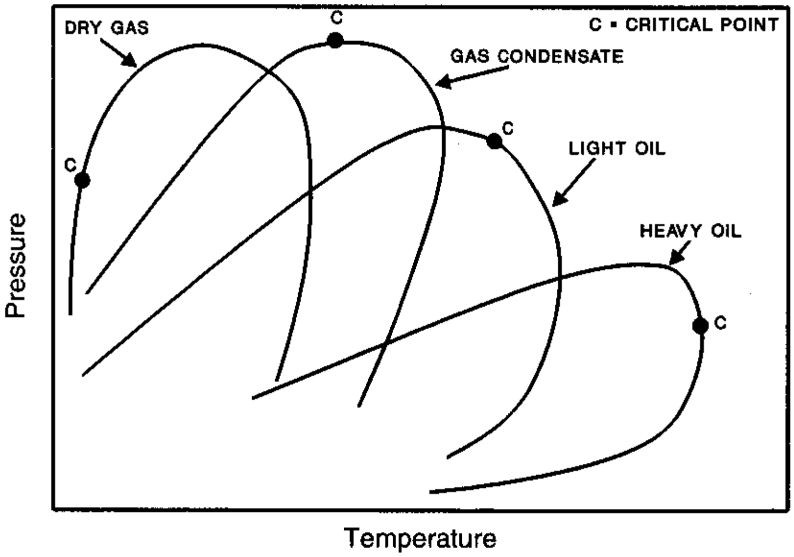


Figure 4.11 Characteristic Phase Envelopes for Four Reservoirs

For a black oil reservoir about all one needs is a section of the bubblepoint curve. For reservoirs that might be volatile oil, gas condensate or gas, what do you need? The upper section of the phase curve, the critical, the cricondenbar and cricondentherm may be necessary. One of the most common mistakes is failure to obtain good reservoir fluid samples and then determine the phase behavior characteristics of said sample. Such failure requires one to make a series of unnecessary "guesses" that may prove to be very expensive.

Pumping Liquids

We often pump commercially pure liquids like ethane and propane at their bubble point. It is important that no vapor form in the pump suction to prevent cavitation. Point A in Figure 4.12 represents the condition in the storage tank (saturated). Point B represents the pressure at the pump inlet due to the head of liquid in the suction piping. Point C represents the pressure inside the pump suction element.

Pressure drop B-C occurs in the pump suction. Point C must be above the saturation curve to prevent cavitation. If the head A-B is not greater than pressure drop B-C, cavitation will occur.

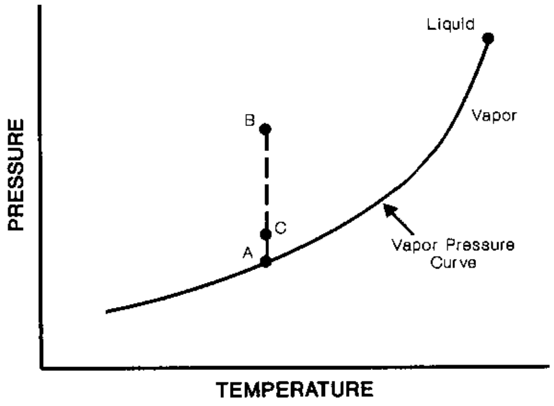


Figure 4.12 **Phase Diagrams and Pumping**

High Pressure Pipelines

At least a portion of the phase curve must be known in the pipelining of gas.

Consider Figure 4.13. Suppose the solid line represents the phase curve of the gas entering the pipeline and Points I and J represent the inlet and outlet conditions of that line. When line I-J crosses the dewpoint curve, liquid will begin to condense in the line. From that point on, two-phase flow exists.

Liquid can be prevented by removing enough of the heavy ends to change the shape and position of the phase curve. Suppose in our example that the composition is changed enough so that the dashed line results. No liquid will form in the pipeline because the dewpoint curve is not crossed. Any liquid present would be due to separator liquid carryover or a composition different from the one used to construct the phase curve.

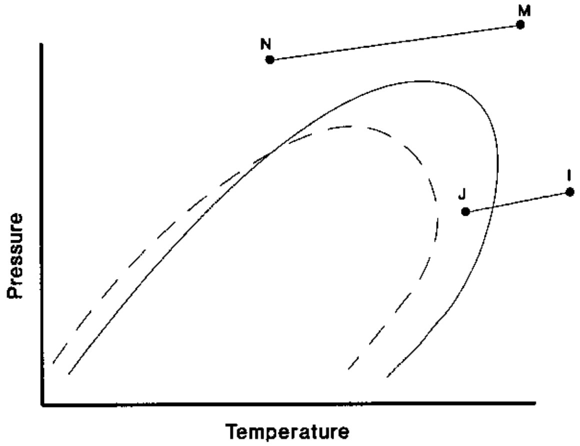


Figure 4.13 **High Pressure Pipelines**

Line M-N is a different situation. This represents operation of a pipeline in the *dense fluid* region. This is frequently done to avoid liquid condensation in the line and the associated problems of designing and operating a two-phase system. There are two very pertinent questions: (1) Will line M-N intersect the phase envelope and liquid form? (2) Will Point N end up below the cricondenbar, to the left of the phase curve, so that the line will have more nearly liquid characteristics than those of a dense phase fluid at its discharge end?

To answer these questions requires a good analysis and a reliable phase curve (preferably from a laboratory determination). If separation has occurred between the wellhead and the line, the analysis entering the line must be used to construct the phase curve. The phase curve is very sensitive to composition. One only has to look at Figure 4.8 to be reminded of this fact.

Refrigeration Processes

Refrigeration is frequently used to cool a gas in order to meet a hydrocarbon dewpoint specification. When the refrigeration takes place at high pressure, it is very important to have an accurate description of the phase behavior. Figure 4.14 shows the phase envelope for a lean gas typical of that found in the southern North Sea or Gulf of Mexico. The cricondentherm of this gas is 30°C [86°F] and occurs at a pressure of 3000 kPa [435 psia].

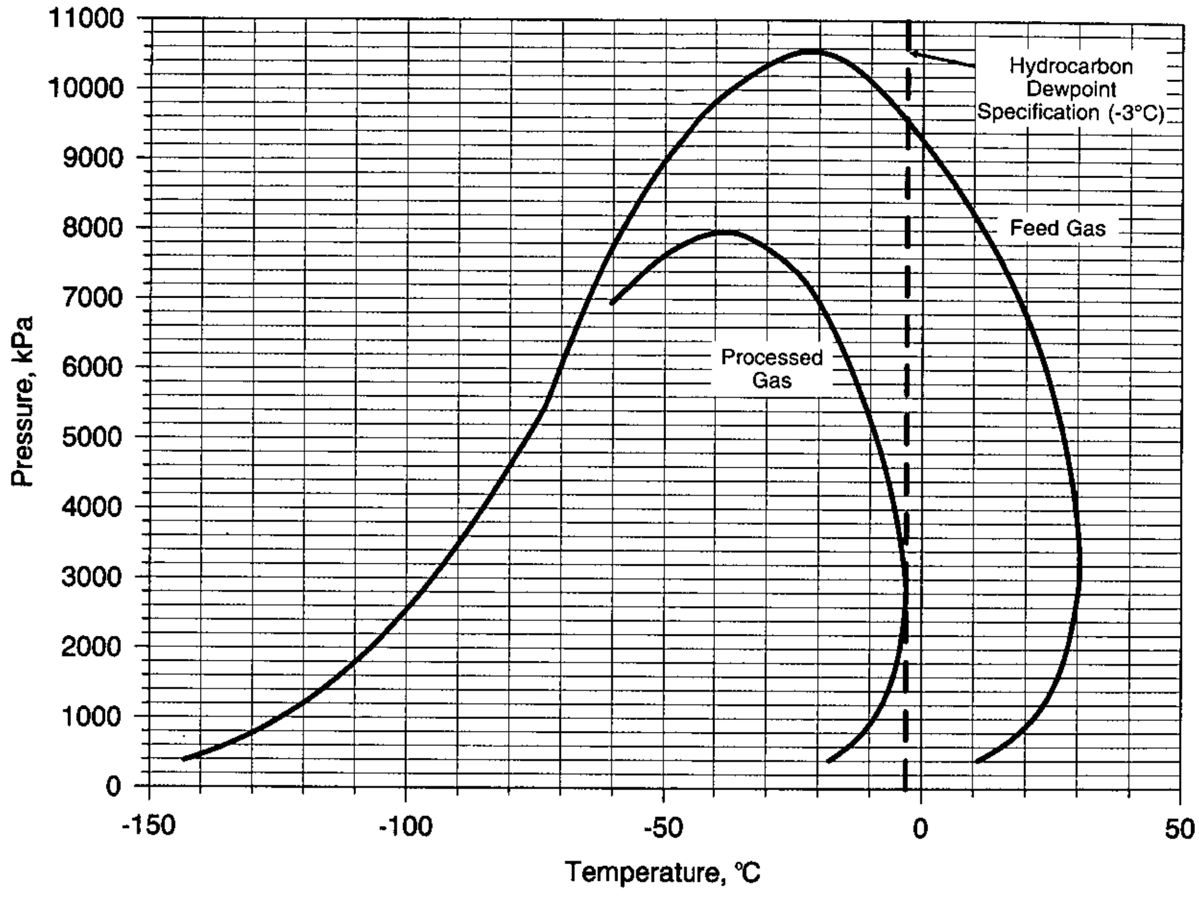


Figure 4.14 Effect of Pressure on Dewpoint Control Processing Temperatures

Assume that this gas is to be processed in a mechanical refrigeration plant to meet a hydrocarbon dewpoint specification of –3°C [27°F]. If the processing pressure is 3000 kPa [435 psia], the gas must be cooled to at least –3°C [27°F] to meet the dewpoint specification. However, if the processing pressure is 7500 kPa [1088 psia], the gas must now be cooled to –25°C [–13°F]. The following shows the processing temperature required to meet the dewpoint specification at various process temperatures.

P, kPa	T, °C
3000	-3.0
5000	-7.2
7000	-19.4
7500	-25.1
7900	-34.0

Above about 8000 kPa [1160 psia] this gas could not be processed in a mechanical refrigeration plant to meet the hydrocarbon dewpoint specification. In order to meet the specification an expansion process (valve or expander) or an adsorption process must be used.

Operation Near the Critical Region

In some cases, having an accurate phase envelope is not good enough; you also need a reliable, true critical point. The pseudocritical found from PVT models are seldom reliable. This may be illustrated by the quality lines discussed previously. If, in Figure 4.15, the critical is at C_1 the 20% and 80% quality lines might be as shown. Suppose, instead, that the true critical is at C_2. Notice the possible change in the location of the same quality lines. If the operating pressure is much less than C_2, the error in the amount of liquid predicted will be relatively small.

However, if the operating pressure falls between C_2 and C_1, the error can be significant – having a profound effect on system design and/or operation. In general, operation near the critical point should be avoided. Common sense dictates that if the system is difficult to model it will be difficulat to operate and control. If near-critical operation is unavoidable, the process design should reflect the uncretainties involved. the most common examples of potential near-critical operation are low temperature expander plants and de-ethanizers.

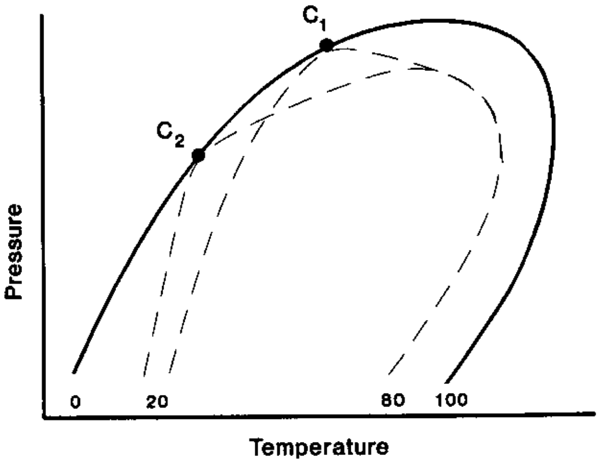


Figure 4.15 Refrigeration Processes

Practical Suggestions

The above are merely examples of typical problems that have arisen. One could cite many others. Failure to handle phase behavior in a workmanlike, professional manner has proven, and will continue to prove, very expensive for the petroleum industry. The cost of obtaining good data is usually trivial compared to the economic benefits obtained.

There are some good guidelines that should be followed:

1. Obtain good samples using experienced samplers.
2. Handle the samples carefully.
3. Analyze the samples in a proven laboratory.
4. Develop all, or that portion needed, of the phase curve. Above about 14 MPa [2000 psi] calculated points are suspect no matter how big the computer or how complex the program. The results should be regarded as estimates only. If an estimate is good enough, fine. If not, go to a reliable laboratory. In many cases a few laboratory points supplemented by calculations will suffice.

GIBBS PHASE RULE

One of the applications of phase behavior is to control the state of the system. In many applications the phase rule is useful. It is written:

$$F + P = C + 2 \tag{4.1}$$

Where:
F = number of degrees of freedom which a system possesses
P = number of phases in the system
C = number of components or chemical compounds in the system

The degrees of freedom refer to the variables necessary to fix the phase state of the system. One or more of the following variables are commonly used: pressure, temperature, volume, and total or partial composition of the one or more phases present.

Consider the single component system shown in Figure 4.2. The number of components equals one. Therefore, F + P = 3. Along line HC (Figure 4.2), if we have two phases in equilibrium, P = 2, and F = 1. Therefore, specification of either pressure or temperature would be sufficient to fix the system state. At point "h" only one phase is present (P = 1) and F = 2. Therefore, knowledge of both pressure and temperature would be necessary to fix the state of the system (exact location of point "h" on phase diagram).

At the triple point (pure component) there are three phases present, so P = 3. Since C = 1, F = 0 from Equation 4.1. This means that once you say "triple point" you have completely defined the system since there is only one triple point.

The number of phases present is not necessarily limited to three. There can be only one gas phase but there can be more than one liquid and solid phase.

Suppose you have a system containing gas, liquid hydrocarbon, liquid water, ice and hydrate. The two liquid phases are *immiscible* and possess different properties. Ice and hydrate are both solids and rather white in color, but they possess different physical characteristics and properties. So ... how many phases are present? Five!

A phase is any entity within the system that contains separately identifiable behavior and properties.

A miscible mixture is made up of molecules possessing different properties, but we cannot measure these separately in the mixture state. So ... this mixture is only one phase.

The number of components used in Equation 4.1 depends on how much we know about the system, or need to know, for the application involved. If we are dealing with an equation or correlation where composition is not important, we can handle any phase as one component; simply as gas, liquid or solid. If composition is important we can handle each component in the system as a phase rule component.

Example 4.1: Suppose we have a system for which nine components are analyzed ($C_1 - C_7+$); "C" in Equation 4.1 will be 9. Suppose further that we have a two phase system (liquid-vapor).

$$F + 2 = 9 + 2 \quad , \quad F = 9$$

We must fix nine variables to fix the state of the system. How many independent variables do we have to work with? We have eight independent component compositions (the ninth is fixed by difference and therefore is not independent), pressure and temperature, to name the obvious ones. If we fix any nine of these ten, the state of the system is fixed.

The Gibbs Phase Rule is a factor in the design of controls for systems. A common problem is excess control. When there are more controls than needed they fight each other and system stability suffers. Suppose one is using pure propane in a refrigeration chiller. Line HC in Figure 4.2 represents the P-T relationship. From Equation 4.1, F = 1. So, control of pressure fixes a point on line HC which in turn fixes temperature; fixing temperature through control likewise fixes pressure. Control of both P and T is not needed.

Degrees of freedom (F) will be some number greater than unity everywhere on a phase curve except along the phase boundary lines. Unless the control system is compatible with the phase behavior and Gibbs Phase Rule, it will not be entirely satisfactory.

PREDICTION OF PHASE ENVELOPE

The location of the bubblepoint and dewpoint lines may be calculated using the methods of Chapter 5. For most naturally occurring systems above about 14 MPa [2000 psia], the validity of the standard calculation becomes questionable. If the location of the curve at high pressure is very important – and if a reliable fluid sample is obtainable – a laboratory determination of at least selected parts of this curve is recommended.

However, there are circumstances where the calculation of all or part of the upper phase curve may be satisfactory. References 4.2 on, at the end of this chapter, provide further details.

Estimation of the critical, cricondentherm and cricondenbar points is particularly important.

Cricondentherm and Cricondenbar T and P

Grieves and Thodos have prepared correlations for these points based on 123 binary and 15 multi-component mixtures.(4.3,4.4) For the systems tested, the agreement between predicted and measured values was very satisfactory. The prediction of temperature is better than pressure. The maximum is less than 5%, whereas the maximum pressure deviation was around 13%.

These correlations are useful in conjunction with vapor-liquid equilibrium (VLE) calculations and critical point predictions. Usually in all of these it may be possible to construct a phase curve (or portion thereof) that is useful for at least planning purposes. This may be the case in the early stages of development when good fluid samples are not yet available. Sometimes the only samples are from drill–stem tests or nonproduced exploratory wells, which taints the validity of the laboratory results. Some calculated cricondentherm and cricondenbar numbers may prove helpful, for they denote the maximum T and P of any phase curve.

Critical Pressure and Temperature

The prediction of the location of the critical point is difficult. The most reliable way remains a laboratory study of a reliable sample. But, there are many circumstances where a calculated number may be suitable.

Based on an empirical fit of 25 natural gas systems possessing a molecular weight less than 30, the following equation has been developed.

$$T_c/T_c' = 1.0 + (0.03)(M\ \text{gas} - 16) \tag{4.2}$$

Where: T_c = actual critical temperature
T_c' = pseudocritical temperature from Kay's Rule (Chapter 3)

For the samples tested the error was less than plus or minus 5%.

A more accurate method(4.5) uses the equation

$$T_{c_{mix}} = \sum \varphi_i T_{c_i} \tag{4.3}$$

Where: $T_{c_{mix}}$ = critical temperature of mixture
T_{c_i} = critical temperature of each component
φ_i = critical volume fraction as defined in Equation 4.4

$$\varphi_i = \frac{y_i \nu_{c_i}}{\sum y_i \nu_{c_i}} \tag{4.4}$$

Where: y_i = mol fraction
ν_{c_i} = critical volume of each component

A similar method(4.6) has been proposed which employs third parameters and more complex mixing rules, but the increased accuracy is marginal.

No simple, satisfactory correlation has been found for critical pressure. References 4.6, 4.7, and 4.8 outline some methods available.

One problem is prediction of the critical values for the hydrocarbon fractions heavier than hexane shown in analyses. Correlations based on the mean boiling point of the fraction, as found from distillation test, have proven useful.(4.2, 4.9)

Simon and Yarborough(4.10) present a correlation for predicting critical pressure based on 14 gas-solvent reservoir systems using composition and the heptanes plus fraction molecular weight and characterization factor as parameters. A total of 37 other systems shown in the literature were tested. The average deviation was about 5%.

Whitson(4.11) has proposed a series of generalized equations for property prediction, including critical values for heavier fractions such as heptanes plus. The following equations were proposed that used earlier data.(4.12)

The value of T_b in Equations 4.5 and 4.6 may be found from a distillation analysis or from a mixing rule.

$$P_c = a(T_b)^b\,(\gamma)^c \tag{4.5}$$

		Metric	English
Where:	T_b = average boiling point	K	°R
	γ = relative density	–	–
	P_c = critical pressure	kPa	psia
	a = empirical constant	5.53×10^9	3.12×10^9
	b = empirical constant	–2.31	
	c = empirical constant	2.32	

Equation 4.5 applies for any liquid having a boiling point less than 472 K [850°R].

$$T_c = a(T_b)^b\,(\gamma)^c \tag{4.6}$$

		Metric	English
Where:	T_c = critical temperature	K	°R
	a = empirical constant	19.1	24.3
	b = empirical constant	0.59	
	c = empirical constant	0.36	
	γ = relative density	–	

It is recommended that references like those cited immediately above be used with caution and only by those very familiar with phase behavior. They are shown to illustrate the type of simple, manual correlations available.

Equations of state provide the most accurate and consistent methods of predicting critical properties. However, even these methods provide an approximation only.

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NOTES:

5

VAPOR-LIQUID EQUILIBRIUM BEHAVIOR

Many production/processing operations involve control of the phases present. Selected components must be vaporized or condensed to achieve specified goals. For a given mixture fluid composition the phase envelope defines the vapor, liquid and two-phase regions. Determination of the bubble and dewpoint curves fixes the extent of the two-phase region. Within this region it is necessary to predict vapor-liquid ratio and the composition of both phases. The latter involves the concept of equilibrium.

"Equilibrium" is the word commonly used to describe a state wherein the passage of further time will have no effect on system behavior. In a flow system, the rate is independent of time. In a phase behavior context, the composition of the vapor and liquid in contact will remain constant with time.

It takes time for two phases to reach equilibrium. In a typical hydrocarbon system up to several minutes of contact is required. Since a well-designed separator will have a vapor-liquid contact time of this magnitude it is assumed normally that a separator should be calculated as an equilibrium process.

In absorption and fractionation calculations no true equilibrium exists because the vapor and liquid are not in contact long enough to achieve it. The assumption of equilibrium (made for convenience) must be corrected by an efficiency factor.

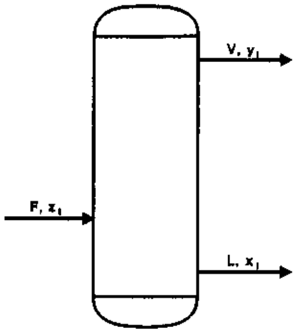
The concept of equilibrium in a two phase system does not mean that the system is static. There is still a continuous transfer of molecules between phases. The rate of vaporization and condensation of all molecular species is equal. Thus, no net change in composition occurs.

EQUILIBRIUM VAPORIZATION RATIO

It is convenient to represent equilibrium with an *equilibrium vaporization ratio*, K. This is defined by

$$K_i = \frac{y_i}{x_i}$$

Values of z_i, x_i and y_i are specified or found from sampling and the resultant analyses. Values of F, V and L are specified or measured (for an existing system). The detailed procedure for using this balance will be discussed in a later section.

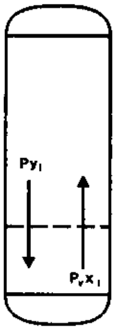


This K_i may be incorporated into a material balance around a separator, where:

z_i = mol fraction of any component in total feed stream to separation vessel
y_i = mol fraction of any component in the vapor phase
x_i = mol fraction of any component in the liquid phase
K_i = equilibrium vaporization ratio (equilibrium constant) = y_i/x_i
F = total mols of feed
V = total mols of vapor
L = total mols of liquid

Partial Pressure Concept

At pressures up to about 400 kPa [60 psia], where ideal gas concepts apply, vapor pressure may be used to find equilibrium behavior.



At equilibrium, the rate of vaporization of all components must equal the rate of condensation so that no change occurs in vapor or liquid composition. For this to occur, the driving force in both directions must be equal. This driving force may be represented by a partial pressure (pp).

$$\text{pp (vapor phase)} = P\,y_i$$
$$\text{pp (liquid phase)} = P_{v_i}\,x_i$$

Where: P_{v_i} = vapor pressure of any component at the P and T of separation

At equilibrium,

$$P\,y_i = P_{v_i}\,x_i\ , \quad \text{or} \quad K_i = \frac{P_{v_i}}{P} \qquad (5.1)$$

Equation 5.1 applies anywhere within the phase envelope. It does not apply for the liquid water phase in a hydrocarbon system since water is essentially immiscible with liquid hydrocarbons. (Chapter 6 will discuss this in detail.) Equilibrium calculations on the hydrocarbon portion of the system are not influenced to a measurable degree by the presence of water except at low pressures and high temperatures.

Equation 5.1 is also the best and most convenient way to find K at pressure approaching atmospheric. P_v may be found from vapor pressure data and simply divided by total absolute pressure P. Also, the values obtained are more reliable than other methods of obtaining K discussed in later sections, since these oftentimes fail to converge properly at low pressures.

Fugacity Derived K Values

The term fugacity (f) is a conceptual term related to free energy and other basic thermodynamic concepts. It has the units of pressure. Since it is one way to correct for nonideal behavior, and may be related to compressibility factor Z, it is sometimes referred to as a "corrected pressure." Some correlations are developed using fugacity coefficient (f/P), a convenient dimensionless term.

The partial pressure concept can be extended to about 3.5 MPa [500 psia] by using fugacity as a representation of driving force. At a given equilibrium pressure and temperature,

$$K_i = \frac{y_i}{x_i} = \frac{f^o_{i_L}}{f^o_{i_V}} \qquad (5.2)$$

Where: $f^o_{i_L}$ = fugacity of component "i" in the pure liquid state
$f^o_{i_V}$ = fugacity of component "i" in the pure vapor state

According to the law of ideal solutions (not to be confused with the ideal gas laws)

$$f_{i_L} = f^o_{i_L}\, x_i \quad \text{and} \quad f_{i_V} = f^o_{i_V}\, y_i \tag{5.3}$$

Where: $\hat{f}_{i_L}$ = fugacity of component "i" in the liquid mixture

$\hat{f}_{i_V}$ = fugacity of component "i" in the vapor mixture

At equilibrium, $f_{iV} = f_{iL}$, because of the necessary free energy relationship. From Equation 5.3, $f^o_{iL} x_i = f^o_{iV} y_i$, and $y_i/x_i = f^o_{iL}/f^o_{iV} = K_i$.

Computer Solutions for K

Today the majority of the calculations utilizing K are made on computers. In general, determination of K values follows one of the two methods below:

1. Equation of State Method

As previously indicated, fugacity is a thermodynamic property which is related mathematically to P, V & T. For convenience, fugacity coefficients, φ, are frequently used where $\varphi_i = f_i/y_iP$

@ equilibrium $$f_{i_V} = f_{i_L} \quad \text{so} \quad K_i = \frac{\varphi_{i_L}}{\varphi_{i_V}}$$

Fugacity coefficients can be calculated from Equation 5.4 where the P, V, T relationships are provided by an Equation of State (PR, SRK, BWRS, etc.).

$$\ln \varphi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\delta P}{\delta n} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln Z \tag{5.4}$$

This is the most common method of determining K values for hydrocarbon mixtures. Why don't different programs yield the same K values?

First of all, the calculation involves solving P-V-T equations of state, which in turn requires the use of combination rules. As with Z, H, S and other quantities, there is no one correlation that fits all systems equally well. A given approach is the result of fitting data for a specified system empirically.

So long as the molecules involved are similar, the problem of fitting is relatively routine. Predicted values for the normal paraffins ethane through decane are usually quite reliable. Methane poses a problem because of its high vapor pressure and unusual behavior in the liquid phase. Nitrogen poses a similar problem. One can likewise correlate values for the aromatics. Hydrogen sulfide, water and carbon dioxide act differently from hydrocarbons because of their polarity.

If one has a mixture containing many, or all, of the above components, the behavior is rather complex. As noted in Chapter 3 for other properties, special correlations or computer subroutines are necessary for some mixtures.

2. Activity Coefficients

Equation of state methods generally do a reasonably good job of determining vapor phase fugacities. The liquid phase is much more difficult, especially when the liquid contains dissimilar molecules. Polar molecules like H_2S, H_2O, alcohols and glycol are not easily handled. In situations like these the liquid phase fugacity is calculated from Equation 5.5.

$$f_{i_L} = f^o_{i_L} x_i \gamma_{i_L} \qquad (5.5)$$

where the activity coefficient, γ_i, is an empirically determined correction factor.

The activity coefficient (γ_{i_L}) approaches unity as the concentration of any component approaches 100%. It is expressible by the Margules, van Laar, Wilson or Renon type equations. Standard thermodynamics may be used to relate the effect of temperature and pressure on activity coefficient. The effect of composition is not so easy. The Hildebrand equations may be used to estimate activity coefficients with satisfactory accuracy for nonpolar mixtures. The K value is then determined from Equation 5.6.

$$K_i = \frac{y_i}{x_i} = \frac{f_{i_L} \gamma_i}{P \varphi_{i_V}} \qquad (5.6)$$

The Chao Seader method is an example of a K value correlation which utilizes activity coefficients.

Stated simply, there is no one, magic correlation or program that works equally well for all mixtures. The choice of program must be made by one who has experience with the use of a given calculation and knows the kind of fit to be expected so adjustments can be made. This is not an area for an "amateur" even though he knows how to use the computer and can obtain a printout. Most problems resulting from the use of K values result more from the persons developing and using them than from the weaknesses of the calculations themselves.

A K value is a function of pressure, temperature and composition. Of the two phases present, liquid composition is the most critical. One difference between correlations is the method chosen to find the coefficients used to characterize the liquid phase.

Those who specialize in the K value area generally have a favorite method (often theirs) which they promote with all the fervor of a religious zealot. The net result is a somewhat chaotic series of claims that might confuse more than help. There is only one true criterion for evaluating K values. How well do they check the performance of equipment designed from them? Once the equipment is operating, get some actual values. Compare them with the correlation used. Use this information to modify the correlation or to develop alternatives. A sound set of values used in this manner will produce useful, consistent results.

K Value Plots

The K value of any component depends on pressure, temperature and the composition of the total fluid involved. Traditionally, many plots of log K versus P and T have been proposed. The effect of composition may be ignored by making the plot for a specific group of components. Up to a pressure of about 6.9 MPa [1000 psia] the effect of composition on K usually is not critical although it may affect methane significantly.

Two sets of K values are summarized in two appendixes at the end of this chapter. Appendix 5A is a series of computer-generated charts using SRK equations. The values shown are useful particularly for the calculation of systems discussed in this book wherein liquid is being condensed from gas systems.(5.1)

Appendix 5B is based on data obtained from field tests and correlations on oil-gas separators.(5.2) The data set was based on over 3000 values. This correlation has been used often for oil separation calculations.

The values in Appendix 5A will be used in all examples in this book to achieve internal consistency. These values also are a printout of the K value program developed for use with this book.

Convergence Pressure Concept

Almost all current applications of K values involve calculations made on a programmable calculator or a computer. But, charts still are available which use convergence pressure (P_k) as a parameter to represent compositional effects. Thus, this brief summary of the concept involved.

Figure 4.7 contained a series of lines which were the loci of the critical points of all possible analyses of a given binary mixture. The location of these lines depended on the components making up this binary, since they were drawn between the critical points of said components. The concept of convergence pressure was based on this binary behavior. References 5.3-5.8 present methods for using the convergence pressure concept.

Figure 5.1 is a plot of log K vs. log P (at constant temperature) for four different mixtures where methane is the lightest component and normal decane the heaviest.$^{(5.3)}$ The curve shape is typical of K value plots. The curves for propane and heavier have a negative slope with increasing pressure until they reach an inflection point after which they have a steep positive slope.

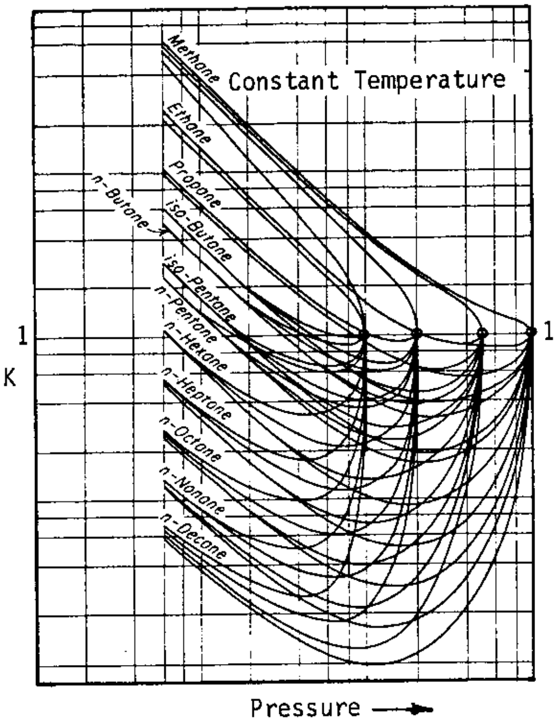


Figure 5.1 **Effect of Composition on K Values**

As shown, the position of the curves changes with composition. For any one composition the curves converge at K = 1.0. The pressure of this convergence is called *convergence pressure.* As shown in Figure 5.1, it varies with composition. If the temperature at which the curves were plotted was the critical temperature, the convergence point would be the critical pressure. At critical conditions K = 1.0 for all components. However, at any other temperature convergence pressure is not on the phase curve; it merely is a correlating number.

Figure 5.2 is a convenient way to estimate convergence pressure for a hydrocarbon mixture containing methane as the lightest component. It is included for the convenience of those readers who might have occasion to estimate such a number for a manual calculation.

Notice in Figure 5.1 that the slope of the K value curves is very steep to the right of the slope change inflection point. In this section it is difficult (if not impractical) to read accurate values of K. For this reason, this type of correlation should not be used where P is within about 7 MPa [1000 psi] of the convergence pressure. Above a P of about 14 MPa [2000 psi] such correlations have limited utility.

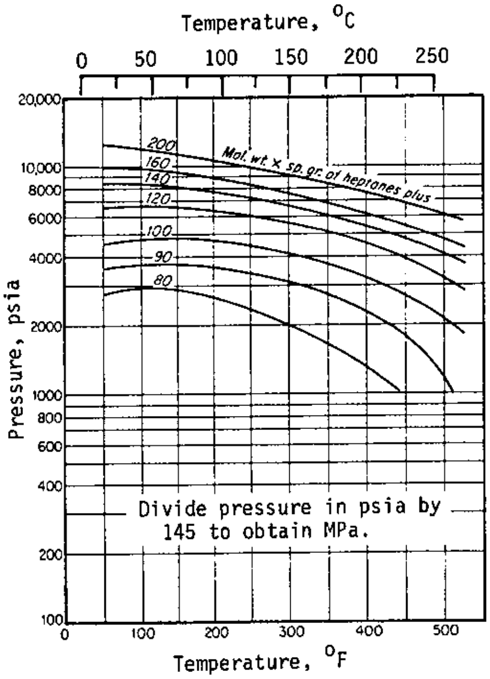


Figure 5.2 **Estimation of Convergence Pressure from Heptanes Plus**

K Values for Heaviest Fraction

When one is using a K value plot or table of values, an extrapolation may be necessary to find a K for the heaviest fraction. As shown in Appendix 5B, the mean average boiling point of the fraction may be used. This fraction may vary from pentanes plus to nonane plus depending on the system.

It usually is satisfactory to use the heptanes plus fraction for gases separated from crude oil at, or near, ambient temperatures. With the molecular weight and specific gravity of this fraction one can predict gas behavior very satisfactorily.

For gas condensate and crude oil systems, the nonanes plus fraction is very desirable for the heaviest fraction is usually a significant part of the total stream. In specifying the analysis of a sample from these streams, you should require an analysis through not less than nonanes plus and a boiling point curve on this heaviest fraction.

What do you do if you already have an analysis for a crude oil system and it goes only through heptanes plus? Several techniques have been proposed for creating a pseudo analysis of this fraction to better predict K values.(5.10-5.14) The simplest approach assumes a logarithmic probability distribution of heavy molecules and that nothing but normal paraffins are present.

For systems handling reservoir produced fluids, compounds other than paraffins are present. A normal chromatographic analysis does not reflect this fact. Most of the aromatics, napthenes and the like will be shown as n-hexane or heavier. So ... in many cases we also recommend more than an ordinary chromatographic analysis be run to identify the type and quantity of nonparaffins. This is important knowledge.

For many calculations it is sufficient to predict a single value of K for the heptanes plus fraction. The five approaches outlined are in the order of my personal preference.

1. **Log K vs. T_c^2**

   We have found that this plot is linear for all hydrocarbon K data studied to date. There are some semiscientific reasons to support this result. What is more important, this relationship serves two practical purposes: (1) checking K values for internal consistency and (2) extrapolating pure component K values to obtain the K of the heaviest fraction.(5.9)

   Figure 5.3 is an example of the chart we use. The abscissa is really T_c^2 but has been drawn to reflect the component and the molecular weight of the heaviest fraction. It is used as follows:

   a. Plot K values for each pure component at the P and T of the equilibrium.
   b. Draw the best straight line through the points for propane through hexane components.
   c. If any K value points are not on the line, use the line values for any calculation.
   d. Find the K value of the C_7+ fraction from its molecular weight and the straight line extrapolation.

   If the K values come from a computer program the values may be rectified into a straight line by regression analysis since the equation of the straight line is $\log K = a + bT_c^2$.

2. **Volatility Exponent**

   This is a correlation expressed by the equation

$$K\,(C_7+) = \frac{K_7}{(K_2/K_7)^b} \tag{5.7}$$

Where:
b = exponent found from Figure 5.4
K_2 = K of ethane
K_7 = K of heptane

Figure 5.4 requires a knowledge of the atmospheric boiling point of the heptanes plus fraction. If not known from other sources, use Figure 5.5 to find it. Values of K for ethane and heptane are those used in the calculation. This approach has been used for a long time and is reliable for most natural gas streams.

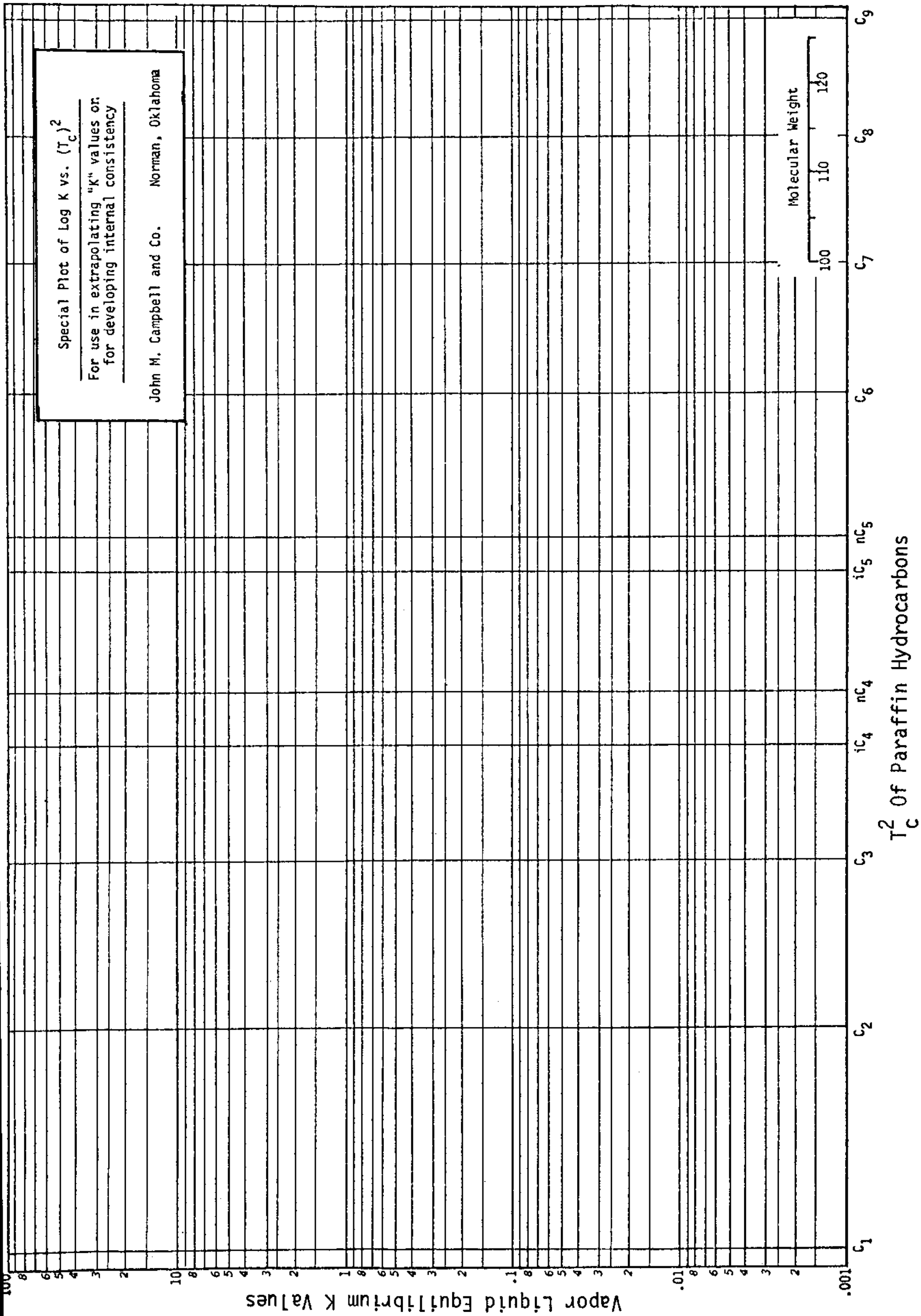


Figure 5.3 Plot of Log K vs. T_c^2

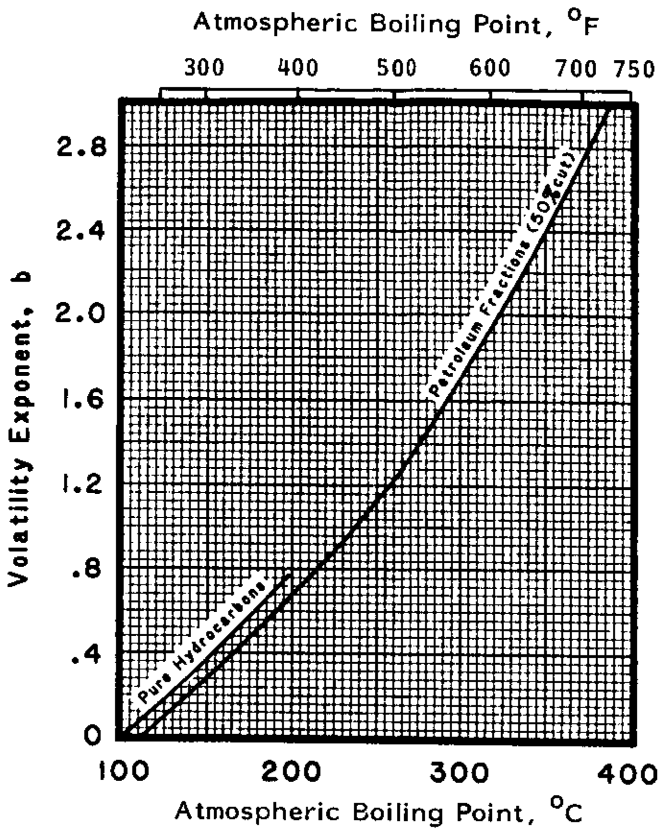


Figure 5.4 Volatility Exponent for Use in Finding the K of C_7+

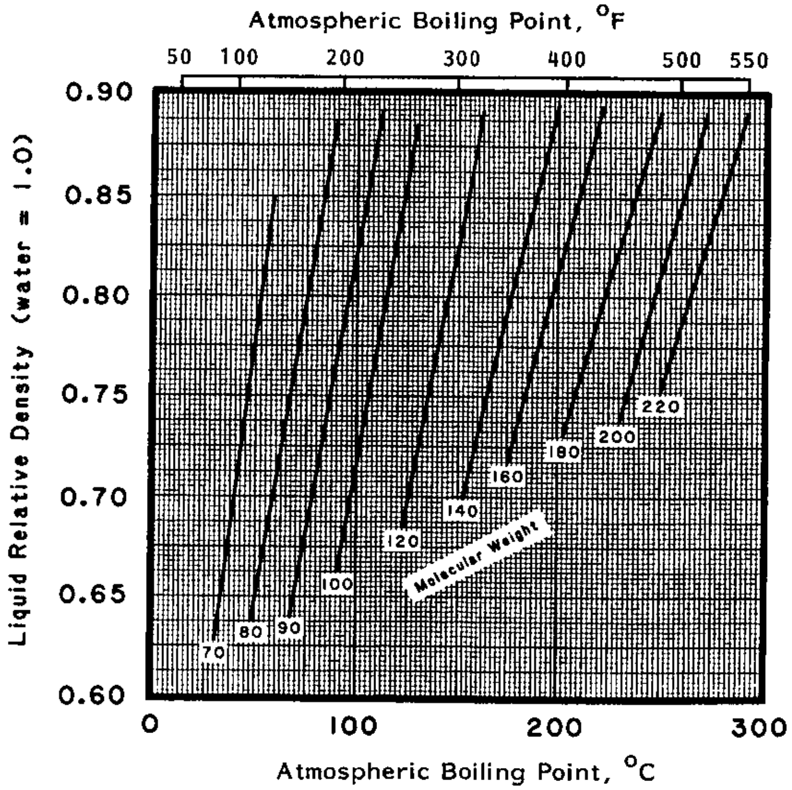


Figure 5.5 Another Correlation for Estimating Hydrocarbon Boiling Point

3. **Use of a KP Plot**

   This is a modification of Method 4. One plots log (KP) vs. $b[(1/T_b) - (1/T)]$ for the components for which K values are known. Extrapolate this straight line to obtain K for the fraction having a boiling point (T_b) in absolute units. This boiling point for a given fraction may be estimated from Figure 5.5. The value of "b" is found from the equation

$$b = \frac{A\,[\log P_c - \log B]}{(1/T_b) - (1/T_c)} \tag{5.8}$$

Where: B = 100 kPa [or 14.50 psia]
A = 1.8 when T is in K and B in kPa [1.0 when T is in °R and B in psia]

4. **Plot log K vs ($1/T_b$)**

   This is a straight line for the heavier components. It has been superseded for the most part by the first three methods. It also is extrapolated to the T_b of the heaviest fraction.

5. **Use Octane K Value**

   If the heaviest fraction is formed by condensation of liquid from a previously all vapor stream, one usually may approximate the heptanes plus fraction by using the K of octane (or the K of heptane for hexanes plus, etc.) or, as an alternative, using the component K value closest in molecular weight to that of the heaviest fraction.

APPLICATION OF K VALUES

Three different calculations are required for vapor-liquid phase behavior calculations: (1) a bubblepoint calculation to define that portion of the phase envelope, (2) a dewpoint calculation for the remaining portion, and (3) a flash calculation at any P and T inside the phase envelope.

In the discussion which follows, the K values from Appendix 5A will be used in all examples.

Bubblepoint Determination

The bubblepoint may be defined as that condition at which the system is all liquid with one (infinitesimally small) bubble of vapor present. The amount of vapor is specified as a matter of convenience so that the composition of the liquid is essentially equal to the composition of the total system. By definition, the sum of the mol fraction of all components must add up to unity in both vapor and liquid. It follows that

$$\sum K_i x_i = \sum y_i = 1.0 \tag{5.9}$$

Where: $K_i x_i$ = K value times "x" the mol fraction for each component in the mixture

The procedure is as follows for a system of known composition:

1. Assume a temperature for the known pressure (or assume pressure if temperature is known).
2. Find K_i at pressure and temperature known and assumed.
3. Multiply K_i from Step 2 by corresponding x (Eqn. 5.9).
4. If summation of values from Step 3 is 1.0, you assumed the right pressure or temperature. If not, repeat Steps 1-3 until $\Sigma K_i x_i = 1.0$, within accuracy limits prescribed.

Note: One can use mol percent instead of mol fraction for x_i, in which case Equation 5.9 sums up to 100 instead of unity.

Example 5.1: etermine the bubblepoint of the mixture shown at 4.0 MPa [580 psia] assuming that the C_7+ fraction has the properties of C_8. This is a trial-and-error solution. One must guess a temperature, find K_i, and calculate $\Sigma K_i x_i$. The right temperature has been assumed when $\Sigma K x_i = 1.0$ (or 100).

Comp.	x_i	K_i	$K_i x_i = y_i$
CO_2	1.25	1.50	1.88
H_2S	0.50	0.41	0.21
C_1	21.36	3.48	74.33
C_2	36.78	0.58	21.33
C_3	10.21	0.16	1.63
iC_4	6.38	0.063	0.40
nC_4	9.84	0.043	0.42
iC_5	2.63	0.017	0.04
nC_5	4.01	0.012	0.048
C_6	3.90	0.0036	0.014
C_{7+}	3.14	0.00033	0.001
			100.30

The solution above is the final try at T = −14°C [7°F]. Since percentages rather than mol fractions are used, the right-hand column should sum to 100.

Dewpoint Determination

The dewpoint is defined as an all vapor system except for one small droplet of liquid. In this case, the system composition, z_i, is equal to that of the vapor, y_i. So,

$$\sum (y_i/K_i) = \sum x_i = 1.0 \tag{5.10}$$

Example 5.2: Determine the dewpoint of the mixture shown at 4.0 MPa [580 psia], assuming the C_{7+} fraction has the properties of C_8.

Comp.	y_i	K_i	$y_i/K_i = x_i$
CO_2	1.25	4.83	0.26
H_2S	0.50	2.38	0.21
C_1	21.36	6.36	3.36
C_2	36.78	2.84	12.95
C_3	10.21	1.57	6.50
iC_4	6.38	1.02	6.25
nC_4	9.84	0.86	11.44
iC_5	2.63	0.55	4.78
nC_5	4.01	0.49	8.18
C_6	3.90	0.28	13.93
C_{7+}	3.14	0.097	32.37
			100.23

The results above are for an assumed temperature of 153°C. It is obtained after a series of trials. Previous trials were made at: 120, 139 and 150°C.

The system in question is a rich one. The percentage methane is low and there are a lot of heavy ends. Notice that in spite of this, methane is the biggest number in the bubblepoint K_ix_i column. If the percentage methane had been larger it would have had an even greater effect.

For the dewpoint, the heptanes plus had the largest single effect. This quantity is the least exact both from the viewpoint of analysis results and its properties. A dewpoint calculation is therefore inherently less exact than a bubblepoint calculation, particularly for lean gases containing only a trivial quantity of these heavy ends.

Many hydrocarbon dewpoint control plants are designed that use some type of refrigeration process. Theoretically, the gas leaving the gas-liquid separator is at its dewpoint (as with any equilibrium separation). In practice, this separator will be designed to operate 10-11°C [18-20°F] below the desired dewpoint temperature. Why? To account for potential error in the dewpoint calculation and for some degree of liquid entrainment which occurs inevitably, at least periodically. The liquid leaving an equilibrium vessel is at its bubblepoint.

Flash Calculation

The purpose of the flash calculation on a two-phase system is to establish the amounts of vapor and liquid, and the analysis of each. At the beginning of this chapter I showed a schematic view of an equilibrium separation.

Overall balance

$$F = V + L$$

For each component

$$F\,z_i = V\,y_i + L\,x_i \tag{5.11}$$

Where:
F = mols of total feed entering separation process
V = mols of gas leaving system for F mols of feed
L = mols of liquid leaving system for F mols of feed
z_i = mols of component "i" in feed stream per mol total feed
y_i = mol fraction of component "i" in gas stream (V)
x_i = mol fraction of component "i" in liquid stream (L)

For convenience, let F = 1 mol, then $z_i = y_iV + x_iL$, but by definition of the equilibrium constant, $y_i = Kx_i$. Substituting accordingly and rearranging the terms,

$$x_i = \frac{z_i}{L + V\,K_i} \quad , \quad y_i = \frac{z_i}{V + (L/K_i)}$$

Furthermore, the sum of all the mol fractions in any stream must equal 1. Therefore, algebraically,

$$\sum x_i = \sum \frac{z_i}{L + V\,K_i} = 1.0 \quad , \quad \sum y_i = \sum \frac{z_i}{V + (L/K_i)} = 1.0 \tag{5.12}$$

Therefore, a means of solution is offered, though it is trial and error. By assuming an L or V, one may solve iteratively the equations above. If $\Sigma\,x_i$ or $\Sigma\,y_i = 1.0$, a solution is obtained. Thus, the compositions of the streams as well as the quantities may be calculated.

Convergence is obtained in Equation 5.12 when $\Sigma\,x_i$ or $\Sigma\,y_i = 1.0$.

Another objective function is $(\Sigma\,y_i - \Sigma\,x_i) = 0$. This results in Equation 5.13.

$$\sum y_i - \sum x_i = \sum \frac{z_i\,(K_i - 1)}{V\,(K_i - 1) + 1} = 0 \tag{5.13}$$

Equation 5.13 is the most common objective function used in computer programs.

The basic calculation procedure for a flash is as follows:

1. Find K at the pressure and temperature of the two-phase system (separation conditions).
2. Assume V or L.
3. Solve flash equation (Equation 5.12 or 5.13, or equivalent).
4. If objective function is satisfied, calculation is complete. If not, repeat Steps 2-4.
5. Calculate x_i and y_i

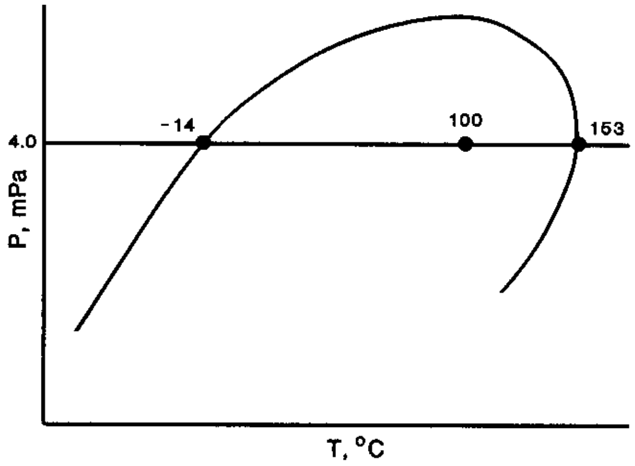
Example 5.3 illustrates the calculation details.

Example 5.3: Calculate the analyses and quantities of vapor and liquid for a flash at 4.0 MPa [580 psia] and 100°C [212°F]. Use the K values in Appendix 5A.

Comp.	z_i	K_i	$y_i - x_i$	x_i	y_i
CO_2	1.25	4.050	1.139	0.373	1.512
H_2S	0.50	1.740	0.236	0.319	0.554
C_1	21.36	5.950	21.974	4.439	26.413
C_2	36.78	2.160	22.535	19.427	41.962
C_3	10.21	1.030	0.299	9.979	10.279
iC_4	6.38	0.600	−3.688	9.220	5.532
nC_4	9.84	0.490	−8.264	16.203	7.940
iC_5	2.63	0.280	−4.250	5.903	1.653
nC_5	4.01	0.240	−7.348	9.668	2.320
C_6	3.90	0.120	−10.646	12.098	1.452
C_7+	3.14	0.031	−11.987	12.370	0.383
		Σ	0.000	100.000	100.000

The 1st step is to assume a V or L. The table reflects the end result of several trials for V = 0.770.

Computer Solutions. These solutions use the same material balance principles shown above. A wide variety of flash equations and convergence algorithms have been used. However, all are not reliable under all phase conditions and constraints imposed by the user. Computer-run dewpoint solutions have sometimes been inaccurate. Volume 3 of this book discusses the computer problem in detail.(5.15)



From the flash we have predicted the relative quantity and analysis of the system at the conditions specified. The vapor and liquid leaving are saturated – at their dewpoint and bubblepoint, respectively.

As we can see from the figure, the flash at 100°C is much closer to the dewpoint than the bubblepoint. Therefore, we would expect far more gas than liquid. If we remember the quality lines from Chapter 4, lowering the temperature would lower the relative quantity of vapor.

Determination of Phase

It often is necessary to determine whether the fluid in a line is all gas, all liquid or two-phase. If only this information is needed it is not necessary to make the above detailed calculations. One can set up a calculation for $\Sigma\, K_i\, z_i$ and $\Sigma\, (z_i/K_i)$ at the pressure and temperature of the system.

If: $\Sigma\, K_i\, z_i$ and $\Sigma\, (z_i/K_i)$ are both greater than 1.0 (or 100), a two-phase system exists.

$\Sigma\, K_i\, z_i$ is less than 1.0 (or 100), the system is all liquid.

$\Sigma\, (z_i/K_i)$ is less than 1.0 (or 100), the system is all vapor.

(Both $\Sigma\, K_i\, z_i$ and $\Sigma\, (z_i/K_i)$ cannot be less than 1.0).

If you do this manually, the following column headings are used: Component, z_i, K_i (at P and T), $K_i z_i$ and z_i/K_i. This not a trial-and-error solution.

Stage Separation

Several stages of separation are often used as shown below. This is called either two-stage or three-stage separation, depending on whether you call the stock tank a stage. Most systems consist of two-separator stages, but three or more may be used in selected instances.

The first-stage pressure is normally fixed by specification or economics. The stock tank pressure will be at, or near, atmospheric pressure. Intermediate stage pressures can be fixed arbitrarily to yield maximum stock tank recovery.

One can optimize these intermediate pressures by a series of flashes. The flash in Stage One fixes the analysis and quantity of liquid leaving, which is the feed to Stage Two. A corresponding flash on Stage Two gives stock tank feed.

A flash is normally performed on the stock tank even though the actual process is some combination of differential vaporization, weathering, "breathing" losses and flash vaporization. The result is good enough for planning purposes and the calculation is routine.

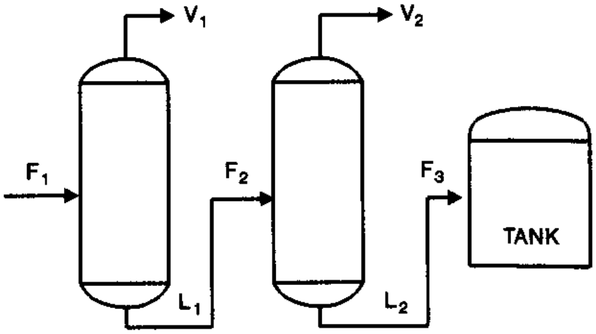
For a separation involving two separators, the optimum second stage pressure may be estimated by the Equations 5.14-5.15.

Pseudo-Relative Density of Feed > 1.0

$$P_2 = \alpha\, A\, (P_1)^{0.686} + C \qquad (5.14)$$

Pseudo-Relative Density of Feed < 1.0

$$P_2 = \alpha'\, A\, (P_1)^{0.765} + C' \qquad (5.15)$$



Where:

		Metric	English
P_1	= 1st stage pressure	kPa	psia
P_2	= 2nd stage pressure	kPa	psia
α	= constant	1.83	1.0
α'	= constant	1.57	1.0
C	= shifting constant	(A+0.057)/0.0034	(A+0.057)/0.0233
C′	= shifting constant	(A+0.028)/0.0017	(A+0.028)/0.012
A	= constant found from Fig. 5.6		

Example 5.4: Find the optimum second-stage pressure for the wellstream shown below for P_1 = 3.45 MPa [500 psia].

(1) Comp.	(2) mol fraction	(3) mol weight	(4) (2)x(3)
C_1	0.40	16.01	6.40
C_2	0.20	30.07	6.01
C_3	0.10	44.09	4.41
C_4	0.10	58.12	5.81
C_5	0.10	72.15	7.22
C_6	0.05	86.17	4.31
C_{7+} (C_8)	0.05	115.22	5.76
	1.00		39.92

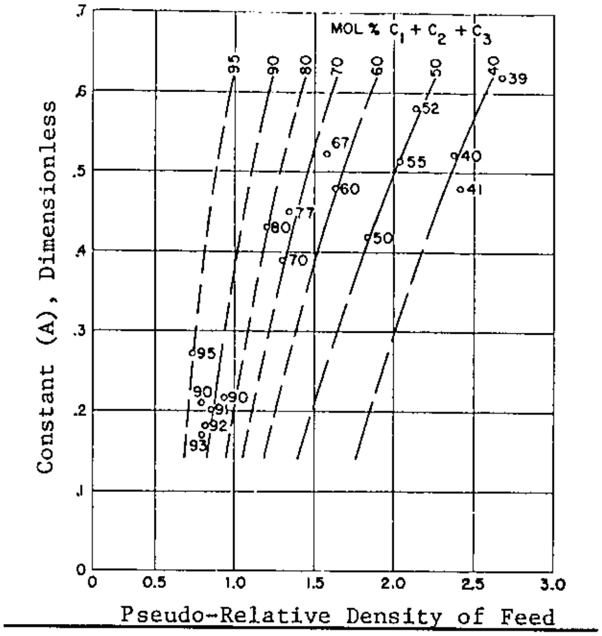


Figure 5.6 Constant "A" vs. Pseudo-Density of Feed at T=80°F

Relative Density = 39.92/28.96 = 1.38
$C_1 + C_2 + C_3$ = 70 percent

From Fig. 5.6, A = 0.42; hence, from Eq. 5.14

Metric: $C = \dfrac{(0.42 + 0.057)}{0.0034} = 140$

$P_2 = (1.83)(0.42)(3450)^{0.686} + 140 = \underline{345\text{ kPa}}$

English: $C = \dfrac{(0.42 + 0.057)}{0.0233} = 20.5$

$P_2 = (1.0)(0.42)(500)^{0.686} + 20.5 = \underline{50.4\text{ psia}}$

This approach is for estimation purposes only. The most rigorous approach is to optimize pressure using a series of stage separation calculations on a computer.

SOME CONVERSION CALCULATIONS

In making equilibrium calculations it often is necessary to convert or combine quantities to meet the need of that calculation. Summarized below are some convenient calculations often encountered.

Table 5.1 summarizes useful conversion factors for the paraffins through normal decane. In this table standard conditions are:

Metric: 15°C and 100 kPa **English:** 60°F and 14.7 psia

In the preparation of the quantities shown at these standard conditions, the following conversion factors are used:

379.3 scf/lb mol, 23.96 m^3/kmol

Density of water = 8.33 lbm/U.S. gal = 1000 kg/m^3

The values shown in Table 5.1 can be calculated for any hydrocarbon fraction if one knows the molecular weight and specific gravity of that fraction. Small deviations in some numbers result from round-off procedures.

TABLE 5.1
Properties of Paraffin Hydrocarbon Liquids - Metric Units

Component	Mol Wt.	std m^3 Gas per m^3 Liquid	m3/kmol	kmol/m^3	Normal BP °C	Relative Density Liquid
Methane	16	(442)	(0.05)	(20)	–162	(0.3)
Ethane	30	281	0.084	11.90	–89	0.356
Propane	44	272	0.087	11.49	–42	0.508
i-Butane	58	229	0.103	9.71	–12	0.563
n-Butane	58	238	0.099	10.10	–0.5	0.584
i-Pentane	72	205	0.116	8.62	28	0.624
n-Pentane	72	207	0.114	8.77	36	0.631
n-Hexane	86	182	0.130	7.69	69	0.664
n-Heptane	100	162	0.146	6.85	98	0.688
n-Octane	114	146	0.162	6.17	126	0.707
n-Nonane	128	133	0.177	5.64	151	0.722
n-Decane	142	122	0.193	5.17	174	0.734

Note: std m^3 @ 15°C, 100 kPa

TABLE 5.1(a)
Properties of Paraffin Hydrocarbon Liquids - English Units

Component	Mol Wt.	scf/U.S. gal	U.S. gal per lb-mol	lb-mol per U.S. gal	Normal BP °F	Relative Density Liquid
Methane	16	(59.1)	(6.40)	(0.1555)	–259	(0.3)
Ethane	30	37.5	10.12	0.0988	–127	0.356
Propane	44	36.4	10.42	0.0959	–44	0.508
i-Butane	58	30.7	12.38	0.0808	11	0.563
n-Butane	58	31.8	11.94	0.0836	31	0.584
i-Pentane	72	27.4	13.86	0.0722	82	0.624
n-Pentane	72	27.7	13.71	0.0729	97	0.631
n-Hexane	86	24.4	15.59	0.0641	156	0.664
n-Heptane	100	21.7	17.46	0.0573	209	0.688
n-Octane	114	19.6	19.38	0.0516	258	0.707
n-Nonane	128	17.8	21.28	0.0470	303	0.722
n-Decane	142	16.3	23.20	0.0431	345	0.734

Composition Expressed as Liquid, Mol or Weight %

Analyses are given normally in mol percent, but it is sometimes necessary to convert from one type to another. The procedure is illustrated below.

Comp.	(1) Mol %	(2) Mol Wt	(3) (3) = (1)x(2)	(4) Wt %	(5) γ_L	(6) (6) = (3)/(5)	(7) Liquid %
C_1	5.40	16	86.4	0.74	0.30	288	1.79
C_2	6.98	30	209.4	1.80	0.36	582	3.61
C_3	12.54	44	551.8	4.74	0.51	1082	6.72
iC_4	5.38	58	312.0	2.68	0.56	557	3.46
nC_4	6.42	58	372.4	3.20	0.58	642	3.98
C_5+*	63.18	160	10 108.8	86.84	0.78	12 960	80.44
	100.00		11 640.8	100.00		16 111	100.00

* MW = 160, $\gamma_L = 0.775$

Column (3) is the mass (in kg or lbm) corresponding to the mols in Column (1). Column (4) is simply each entry in Column (3) divided by the total of that column. Column (6) is each mass entry in Column (3) divided by relative density to find the equivalent volume. Each entry in Column (6) divided by its total gives the values shown in Column (7).

For a gas,

$$\text{mol \%} = \text{volume \%} = \text{partial pressure \%}$$

Composite Stream Analysis

The best way to sample a two-phase stream is to use a test separator. In this you sample and analyze the liquid and gas streams leaving, as well as measure their flow rates. These results may then be recombined to form a composite (or total) stream analysis.

To do this the flow rates must be expressed in mass units before they can be added. Since no chemical reaction is occurring, the mol is a convenient mass unit. The example following illustrates the procedure.

Example 5.5:

Gas flow rate: 67 800 std m^3/d Pressure: 6.9 MPa
Temperature: 46°C
Gas and liquid analysis: As shown below
Gas oil ratio: 2335 m^3 gas/m^3 oil
Mol wt separator liquid: 80.6 (from analysis); separator liquid, $\gamma_L = 0.7$

Metric Unit Solution: **(0.7) x 1000 kg/m^3** = 700 kg/m^3 oil (oil density)
700/80.6 = 8.685 kmol oil/m^3
Gas-oil ratio (from test) = 2335 m^3 gas/m^3 oil or 428 m^3 oil/10^6 std m^3
8.685 kmol/m^3 x 428 $m^3/10^6 m^3$ = 3717 kmol oil/10^6 std m^3

Note: 10^6 std m^3 = 41 740 kmol of gas

Example 5.5 (Cont'd.):

In tabular form:

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Comp.	Mol fr. Gas	$\frac{\text{kmol}}{10^6 \text{ std m}^3}$	Mol fr. Liq.	$\frac{\text{kmol}}{10^6 \text{ std m}^3}$	Well Stream kmol	Mol Fr. Well Stream
C_1	0.8946	37 341	0.2022	752	38 093	0.8380
C_2	0.0541	2 258	0.0656	244	2 502	0.0550
C_3	0.0310	1 294	0.1116	415	1 709	0.0376
iC_4	0.0055	229	0.0445	165	394	0.0087
nC_4	0.0078	326	0.0708	263	589	0.0130
iC_5	0.0022	92	0.0465	173	265	0.0058
nC_5	0.0012	50	0.0337	125	175	0.0038
C_6	0.0026	109	0.1033	384	493	0.0108
C_7	0.0010	42	0.3218	1196	1 238	0.0272
	1.0000		1.0000		45 458	1.0000

The above metric tabulation and the corresponding English unit tabulation are based on the same principle. Columns (2) and (4) are the gas and liquid analyses from sampling. Multiplying each number in Column (2) by 41 740 gives the number of mols of each component per million std cubic meters of gas shown in Column (3). Multiplying each number in Column (4) by 3717 kmol oil/million std cubic meters gives the numbers shown in Column (5).

Cols. (3) and (5) may now be added (for they are on the same basis) to obtain Col. (6). Dividing each entry in Col. (6) by its total gives the desired mol fraction analysis of the well stream.

Conversion of Flash Results for Actual Flow Rates

It is customary to make flash calculations on the basis of 1.0 or 100 mols of feed because it is convenient. Once V and L have been obtained on this basis, they must be adjusted to find the actual rate.

If liquid is obtained from a separation, that liquid existed in the feed because none is formed in the separator. The amount of feed will be the quantity of liquid plus the quantity of gas produced. Sometimes this feed flow rate is expressed in gas volumetric units even though some liquid is present. If so, remember that this is a *pseudo* or *equivalent volume* and not the real volume of the two-phase stream. In reality, one normally should express the flow rate in a convenient mass unit to avoid the volume problem.

The traditional gas flow terminology originated in the U.S. The basic unit was the standard cubic foot; the volume of gas is measured at 60°F and a standard pressure which has varied from 14.4 psia to 15.025 psia in various situations. For process calculations it has been common to use 14.7 psia as the base or standard pressure.

In metric countries 0°C and 15°C have been used commonly as base temperatures. The base pressure has been expressed in atmospheres, mm or cm of mercury, kg/cm^2 or bar. With the advent of the SI System, 100 kPa (1 bar) is the logical base pressure and will be used throughout this book. Some have proposed using 101.325 kPa (1 atm) as a base, but it is an inconsistent ("bastard") number in a "powers of ten" system.

In this book we will use the standard cubic meter as the basic gas unit, with the base conditions being 100 kPa and 15°C. The standard SI prefixes will be used. So, one million cubic meters will be written as

10^6 or (E+06). To differentiate *standard* from *actual* cubic meters, the standard volume will be written as "std m^3." The subscript "sc" also will be used to denote standard conditions.

In English units a standard cubic foot will be measured at 60°F and 14.7 psia in the traditional manner. One million standard cubic feet will be written as 1 MMscf/d in this book. In some references you will find it written as MMSFD, MMscfD, MMcfD, etc. These all mean the same thing.

Note: The prefix M (mega) is one million in the metric system. In the English system it is the Roman numeral for 1000. This is a possible source of confusion. In this book, to prevent confusion, I *will not* use the metric prefix mega (M) to describe gas volumes.

The liquid volumes will be expressed in cubic meters whenever practical. For small volumes the liter will be used. It will be abbreviated L in this text.

In English units the term gallon (U.S. or Imperial) will be used seldom. The cubic foot is preferred. In some cases the API barrel (bbl) will be used because it is employed commonly around the world. It will, however, be related to cubic meters or cubic feet whenever practical.

Basic Conversion Factors

Metric Units

100 000 N/m^2 = 100 000 Pa = 1.02 kg/cm^2 = 100 kPa

Standard conditions: 15°C and 100 kPa

1 000 000 std m^3 = 10^6 std m^3 = 41 740 kmol

There are 23.96 std m^3/kmol and 41 740 kmol/10^6 std m^3

Density of air at 15°C and 100 kPa = 1.21 kg/m^3

Density of gas at 15°C and 100 kPa = $(\gamma_g)(1.21)$

1 m^3 = 1000 liters; 1 liter = 1000 cm^3

1 g/cm^3 = 1000 kg/m^3

English Units

Standard conditions: 60°F and 14.7 psia

1 000 000 std cu ft = 1 MMscf = 2636 lb mol

There are 379 std ft^3/lb mol at 60°F and 14.7 psia

Density of air at 60°F and 14.7 psia = 0.0764 lb/ft^3

1 ft^3 = 7.48 U.S. gal = 6.23 Imperial gal

1 bbl = 42 U.S. gal = 35 Imperial gal = 5.61 ft^3

Conversions between Units

1 std ft^3 (@ 60°F and 14.7 psia) = 0.0286 std m^3 (@ 15°C and 100 kPa)

1 std m^3 (@ 15°C and 100 kPa) = 34.92 std ft^3 (@ 14.7 psia and 60°F)

1 bbl = 159 L = 0.159 m^3

1 m^3 = 35.31 ft^3 = 264 U.S. gal = 200 Imperial gal = 6.29 bbl

1 L = 0.264 U.S. gal = 0.22 Imperial gal = 0.0353 ft^3

ACCURACY OF EQUILIBRIUM CALCULATIONS

The accuracy of the results of calculations involving K values depends on the reliability of the sampling, of the analysis of that sample, and on the K value correlation used. The importance of sampling and analysis have been discussed previously.

There is no single K value correlation that is superior for all mixtures encountered. A knowledgeable practitioner may have two or three different models or programs available. Generally, crude oil and NGL phase behavior is handled by different models.

All K values are sensitive to composition, particularly the very volatile components like nitrogen, methane and ethane. In correlations like those shown in Appendixes 5A and 5B, the potential error in K for nitrogen and methane may be very large. Notice how different the values are for methane (at the same conditions) in these two Appendixes.

For design purposes, several models may be used to determine a range of results. This range, rather than one set of "magic" numbers, is then used to specify equipment. The name of the game is flexibility. It is doubtful if one ever will encounter the analyses, flow rates and exact other conditions specified.

It is most important that the K values be internally consistent. One can use Figure 5.3 for this purpose or accomplish it mathematically. Establish the best straight line through the points for propane through hexanes. Extrapolate this line to find the K values for methane and ethane and for the heavier ends. Maintaining the proper relativity of the K values reduces the effective error of the results.

An experienced person usually can predict the *quantity* of a specified liquid within ±5-6% (for a specified analysis and conditions). The detailed analysis will be off more than this. This is important, for in many systems a series of VLE calculations is made; the output from one is the input to another. The errors thus cumulate. Many less than desirable systems result from failure to recognize this.

Table 5.2 shows the comparative results of a low temperature calculation by several K value programs. Other comparisons are shown in the literature.*(5.17)* Comparisons like these should be made for your specific systems.

PRODUCT SPECIFICATION

In a production system using stage separation, the final liquid product is fixed by the stock tank conditions. Although the VLE mechanism in this tank is more nearly differential vaporization rather than flash vaporization, the latter is most often used for calculation purposes.

Many liquid products have a vapor pressure specification which must be satisfied by separation or stabilization.

Reid Vapor Pressure

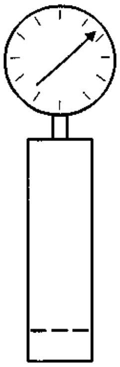
In order to measure true vapor pressure there can be nothing in the test cell except the liquid being tested. In practice this means that any air present at the beginning of the test must be removed (the cell evacuated) before introduction of the sample. This is inconvenient in a field or plant laboratory using operating personnel.

Reid vapor pressure (RVP) is the substitute specification used for some NGL liquids. If you see RVP after the vapor pressure it is the Reid vapor pressure; if RVP is not shown it is a true vapor pressure, by default.

TABLE 5.2
Comparison of Experimental and Predicted Liquefaction

	Weight % Total Fluid Condensed	Weight % Total Ethane Condensed	Weight % Total Propane Condensed
–55°F & 1000 psia			
Experimental	17.12	25.6	45.3
BWRS	18.16	28.0	47.4
Peng-Robinson	18.67	29.2	51.1
GPA SRK	19.01	29.9	52.04
–60°F & 900 psia			
Experimental	19.02	30.9	56.4
BWRS	19.57	32.3	56.5
Peng-Robinson	19.66	32.8	58.9
GPA SRK	19.83	33.3	60.2
–70°F & 1000 psia			
Experimental	33.8	44.6	57.1
BWRS	32.5	44.1	57.7
Peng-Robinson	31.0	44.7	62.2
GPA SRK	31.2	45.1	63.0
–100°F & 500 psia			
Experimental	23.23	52.1	85.4
BWRS	24.7	55.5	86.7
Peng-Robinson	24.9	56.6	87.9
GPA SRK	24.5	56.1	88.2

An RVP pressure must be determined in a *standard cell* to properly take care of the air partial pressure. The ratio of vapor space to sample space must be correct so the correction charts between Reid and true vapor pressure are applicable.



If RVP is known it may be corrected to an equivalent true vapor pressure. Figure 5.7 is convenient for this purpose, and accurate enough for most applications. True vapor pressure is read from the left-hand ordinate at the temperature of the sample.

Figure 5.8 is a nomograph for crude oils that has been modified from one issued by the API. It is used commonly for accepting crude oil shipments. Many purchasers have specifications on such a shipment to prevent loss of liquid in storage tanks. The procedure is simple. The temperature and RVP of the oil is measured at the transfer point. Figure 5.8 is then used to determine true vapor pressure to ascertain if that shipment fulfills contract specifications. Tanker imports of crude oil must often have an RVP limit of 10-11 psi.

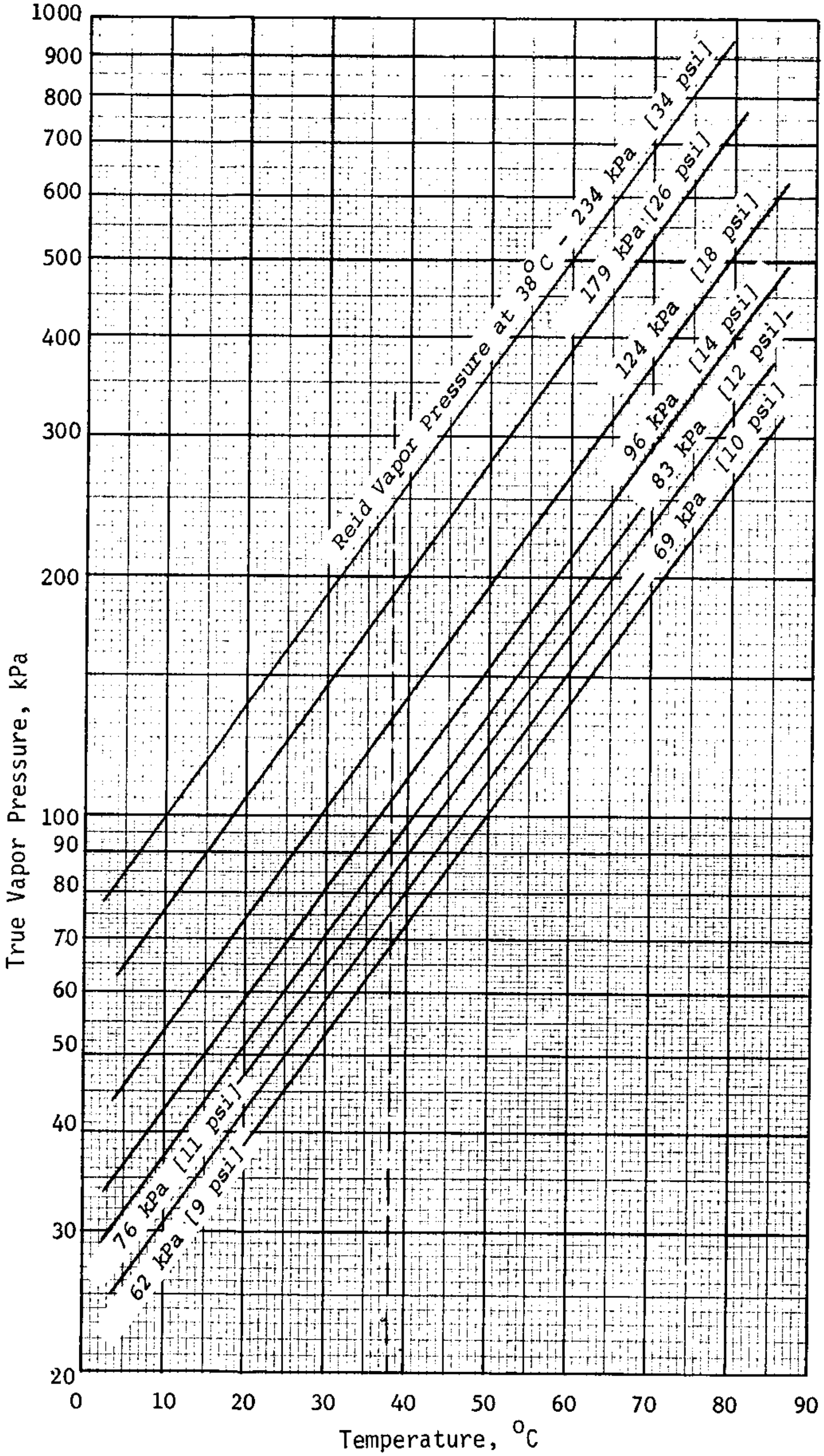


Figure 5.7 Reid Vapor Pressure vs. Temperature for Typical NGL Liquids

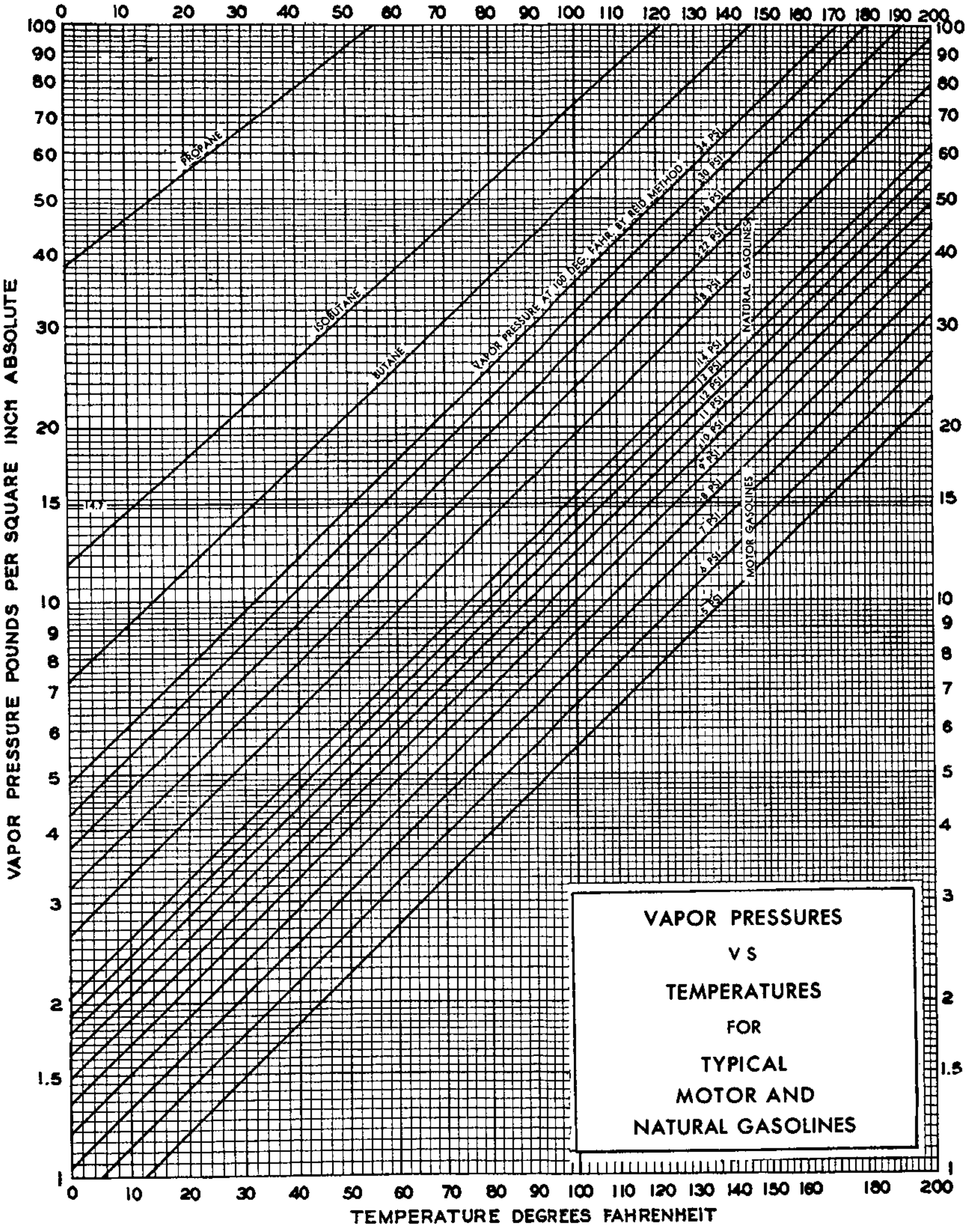


Figure 5.7a Vapor Pressures vs. Temperatures

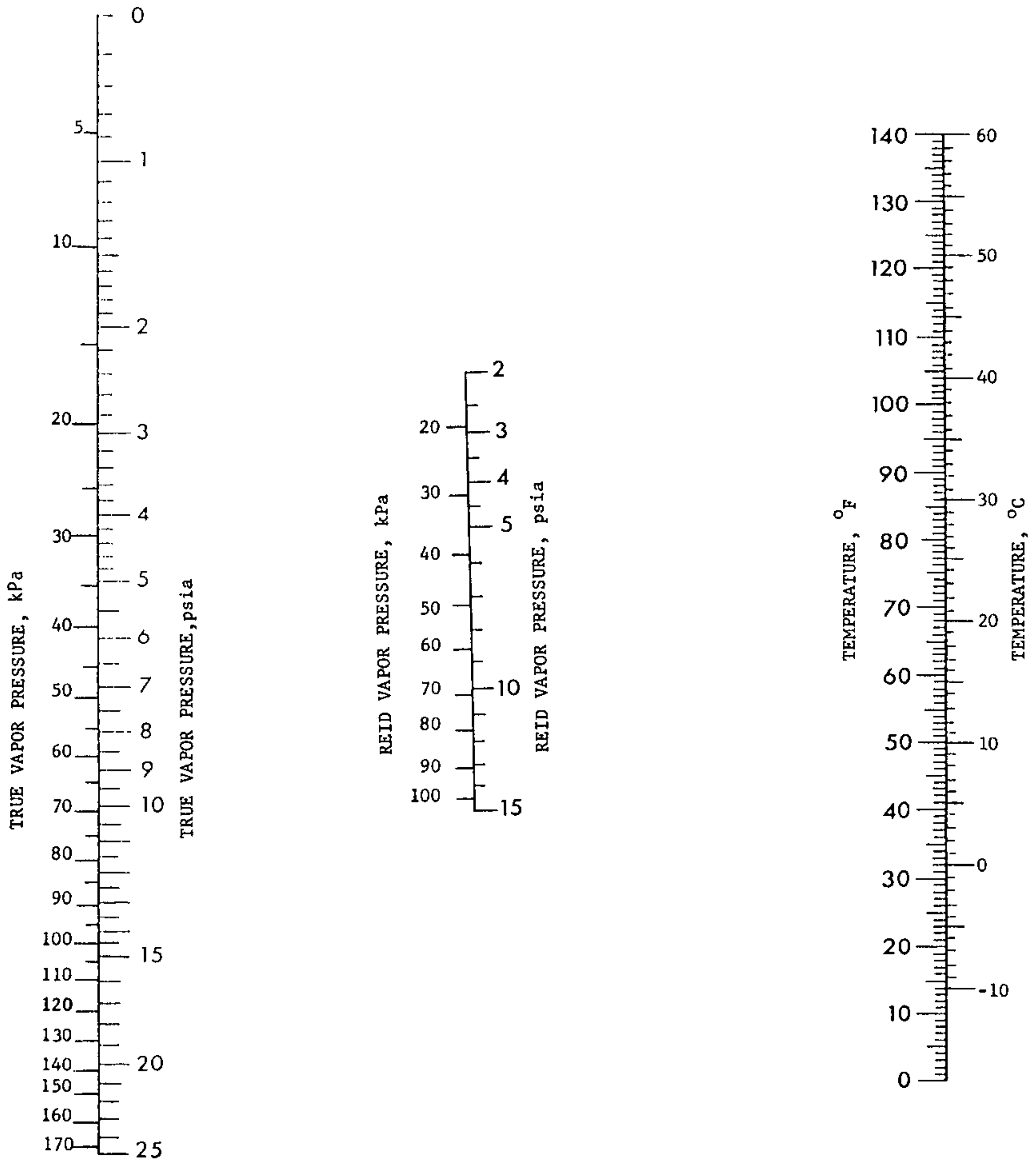


Figure 5.8 Reid Vapor Pressure vs. True Vapor Pressure for Crude Oils

PRELIMINARY PRODUCT SPLITS

Very early in the planning phase, before detailed calculations are made, it is necessary to establish the approximate quantity of the fluids to be produced. If one of the specifications is a vapor pressure the procedure which follows is useful approximation for planning and specification purposes.

The following general procedure is normally employed in making this preliminary split.

> *Natural Gasoline.* It is assumed that all components having a lower vapor pressure than that specified for the product will appear 100% in that product. For almost all natural gasolines this implies that all of the available pentanes plus entering the fractionation system will appear in the final product. One then adds the proper amount of butanes to give the desired vapor pressure. In the unusual case where all of the butanes won't do this, the necessary amount of propane is added.
>
> *Commercial Propane.* Simply calculate the volume of propane available from percent propane in the potential product stream. The actual product will have small percentages of ethane and butane, but these will have little effect on the quantity of product.
>
> *Commercial Butane.* Same as above except based on total availability of iso- and normal butane.

The vapor pressure is the primary property used to make this split. It is assumed that the mol fraction of each component times its vapor pressure represents the contribution of that component to the total mixture vapor pressure. The sum of this multiplication for each component is the total mixture vapor pressure (P_v).

$$P_v\,(\text{mixture}) = \sum x_i P_{vi} \qquad (5.16)$$

The normal fractionator can make a reasonably sharp separation between hydrocarbons with different molecular weight – butane from pentane, pentane from hexane, etc. However, a sharp separation between isomers possessing the same molecular weight is difficult – i-butane from n-butane and i-pentane from n-pentane. What separation that occurs will depend on the not yet available detailed design of the fractionator.

In the making of this preliminary split, Equation 5.17 will prove useful for predicting isomer behavior.

$$\frac{L'}{L} = A\left(\frac{x'}{x}\right) \qquad (5.17)$$

Where:
L = mol of the iso-paraffin in the final mixture
L' = mol of the normal paraffin in the final mixture
x' = mol fraction of normal paraffin in fractionator feed
x = mol fraction of iso-paraffin in fractionator feed
A = 1.25 for butanes and 1.12 for pentanes

The calculation is not truly trial-and-error but one does have to make some kind of guess about what the lightest component will be in desired mixture.

The amount of product produced can be found from the absolute feed rate. The above calculation predicts 61.94 mol of 124 kPa [18 psia RVP] product per 100 mol of feed. This ratio permits conversion of feed rate to product rate in the units of your choice.

This preliminary split will not check actual plant performance exactly but will be very adequate for planning purposes. In most cases the error should not exceed about 5%.

Example 5.6: Calculate the analysis of 124 kPa RVP [18 psi RVP] liquid product at 38°C [100°F]. From Figure 5.7 the true vapor pressure (TVP) is 133 kPa [19.5 psia]. The vapor pressures are from Chapter 3. The analysis of the feed is shown in Column 2 below.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Component	Mol %	Mols for Split	P_{v_i}	(3)x(4)	Mol Product	Mol %
Propane	33.09	–	1309	–		
i-Butane	8.52	L	498	498 L	5.66	9.14
n-Butane	12.70	1.87 L (= L′)	356	666 L	10.59	17.10
i-Pentane	5.63	5.63	141	794	5.63	9.09
n-Pentane	3.73	3.73	108	403	3.73	6.02
Hexane	10.43	10.43	34.2	357	10.43	16.84
Heptanes + (C_8)	25.90	25.90	3.7	96	25.90	41.81
	100.00	2.87 L + 45.69		1164 L + 1650	61.94	100.00

$$L' = 1.25\left(\frac{12.70}{8.52}\right)(L) = 1.87\text{ L for use in Column (3)}$$

$$\Sigma\, x_i\, P_{v_i} = \frac{\Sigma\,(\text{Mol Comp.})(P_{v_i})}{\text{Total Mol}} = \frac{\Sigma\,(\text{Mol Comp.})(P_{v_i})}{2.87\text{ L} + 45.69} = \frac{1164\text{ L} + 1650}{2.87\text{ L} + 45.69} = 133\ , \quad L = 5.66$$

$\Sigma\,(\text{Mol Comp.})(P_{v_i})$ is the total of Column (5).

In English units the results in Column (7) would be the same. The only difference would be the effect of using P_{v_i} values in Column (4) in psia which in turn would affect Column (5).

STORAGE OF LIQUIDS

Proper storage is of economic importance. The loss of potentially salable liquid is not large percentagewise but can represent a substantial amount of money on large systems.

LNG is normally stored at, or near, atmospheric pressure as noted in a later chapter. NGL liquids normally require pressure storage in a spherical or cylindrical tank. Liquid sold as crude oil is usually stored very near to atmospheric pressure.

Pressure Storage

The working pressure of the tank must be higher than the true vapor pressure of the liquid being stored. This tank is, in effect, a vapor pressure cell containing liquid and a vapor phase. The TVP must be calculated at the temperature of the liquid surface and in the vapor space, which will vary.

It also is important that the working pressure be high enough to prevent breathing losses. Thus, a further consideration is the pressure setting of the vacuum vent.

The following nomenclature is used in the storage pressure Equations 5.18 and 5.19 which follow:

			Metric	English
Where:	P_{st} =	required storage pressure	kPa(g)	psig
	P_{max} =	TVP at max. liquid temp.	kPa(a)	psia
	P_{min} =	TVP at min. liquid temp.	kPa(a)	psia
	P_v =	pressure at which vacuum vent opens	kPa(a)	psia
	T_{max} =	max. avg. temp. of vapor	K	°R
	T_{min} =	min. avg. temp. of vapor	K	°R
	A =	atmospheric pressure	kPa(a)	psia

For the condition where P_{min} is less than P_v,

$$P_{st} = P_{max} + \left[(P_v - P_{min}) \left(\frac{T_{max}}{T_{min}} \right) \right] - A \tag{5.18}$$

For the condition where P_{min} is greater than P_v,

$$P_{st} = P_{max} - A \tag{5.19}$$

With the situation represented by Equation 5.18, air or gas is admitted to the vapor space through the vacuum vent. Introduction of air can be a safety problem if an explosive mixture results. For this reason, a gas vent system may be employed. For the situation represented by Equation 5.19, air may be purged and kept out of the tank.

Crude Oil Storage

Oil may be stored in a fixed-roof tank of constant volume or a floating head (variable volume) tank. The latter is used to minimize breathing losses and those losses which occur by virtue of the filling method. If the fixed-volume tank is filled from the bottom, some stripping of the liquid already there occurs as gas "breaks out" of the entering oil. If the tank is filled at the top, some splashing or agitation may occur to cause excess liquid entrainment.

The cause of breathing is illustrated by Figure 5.9. A type of breathing also occurs when the tank is being emptied. Air or gas must be admitted to keep the tank from collapsing. Some of the oil must vaporize to maintain an equilibrium mixture.

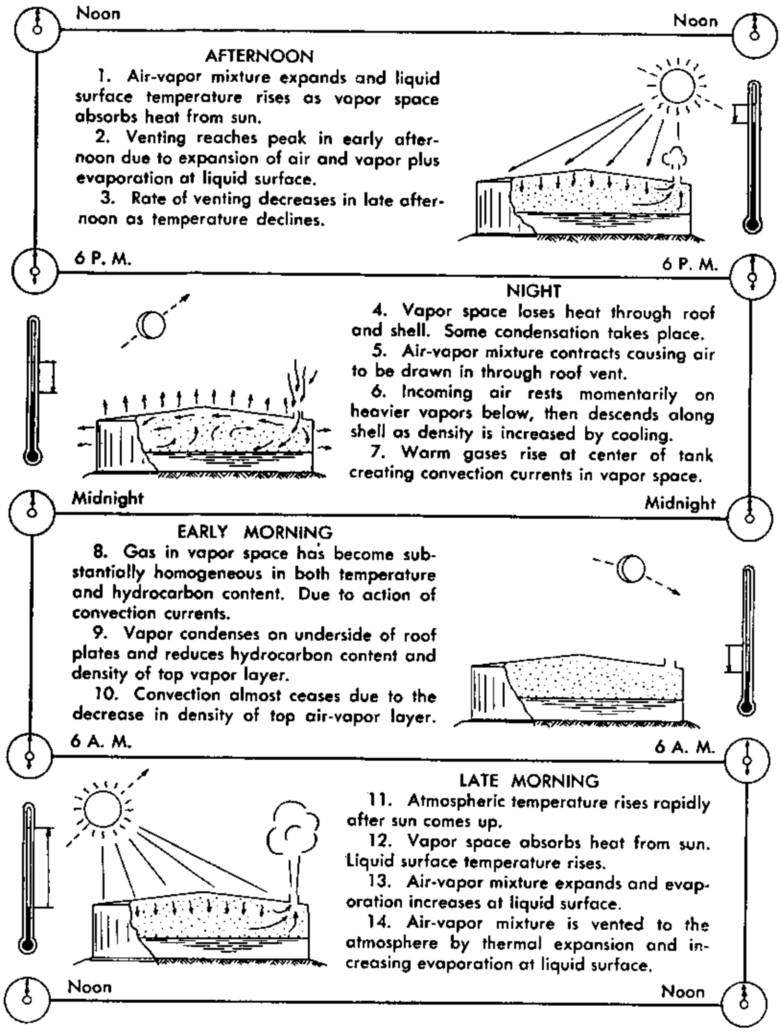
If this loss is too great, some alternative to a simple, fixed volume tank is indicated. One modification uses a layer of small spheres which float on the surface of the oil to form a barrier between the oil and gas. Another alternative is a vapor recovery system. (This usually is a refrigeration system operating on the very rich, effluent tank vapors.) A floating head tank is used for most large storage volumes.

The process of loss involves several mechanisms and thus use of vapor-liquid theory is limited to predict said loss. An API study committee has developed some empirical correlations for predicting oil tank losses from fixed-volume tanks. The key equations from their study are shown below.

The approximate volume loss is estimated from the equation

$$\text{Volume loss in \%} = (\text{m})(\text{Gravity loss in °API}) \tag{5.20}$$

Where: m = 4.45 for 15° API oil (0.97 g/cm^3)
m = 3.50 for 20° API oil (0.93 g/cm^3)
m = 2.72 for 25° API oil (0.90 g/cm^3)
m = 2.20 for 30° API oil (0.88 g/cm^3)
m = 1.76 for 35° API oil (0.85 g/cm^3)
m = 1.48 for 40° API oil (0.83 g/cm^3)



AFTERNOON

1. Air-vapor mixture expands and liquid surface temperature rises as vapor space absorbs heat from sun.
2. Venting reaches peak in early afternoon due to expansion of air and vapor plus evaporation at liquid surface.
3. Rate of venting decreases in late afternoon as temperature declines.

NIGHT

4. Vapor space loses heat through roof and shell. Some condensation takes place.
5. Air-vapor mixture contracts causing air to be drawn in through roof vent.
6. Incoming air rests momentarily on heavier vapors below, then descends along shell as density is increased by cooling.
7. Warm gases rise at center of tank creating convection currents in vapor space.

EARLY MORNING

8. Gas in vapor space has become substantially homogeneous in both temperature and hydrocarbon content. Due to action of convection currents.
9. Vapor condenses on underside of roof plates and reduces hydrocarbon content and density of top vapor layer.
10. Convection almost ceases due to the decrease in density of top air-vapor layer.

LATE MORNING

11. Atmospheric temperature rises rapidly after sun comes up.
12. Vapor space absorbs heat from sun. Liquid surface temperature rises.
13. Air-vapor mixture expands and evaporation increases at liquid surface.
14. Air-vapor mixture is vented to the atmosphere by thermal expansion and increasing evaporation at liquid surface.

Figure 5.9 Mechanism of Tank Breathing Loss

The actual loss will depend on prior conditioning of the oil, the method and rate of filling and the ratio of liquid surface area to liquid volume. The effects of all of the above losses are summarized in References 5.19 and 5.20. These references contain the same basic information.

The calculation of losses involves many factors, but the two equations which follow are useful approximations of the breathing loss and filling loss for fixed, cone roof tanks.

Breathing Loss. The basic equation is

$$B = \left[\frac{(P)(D)^{1.8}}{A}\right](F_o)(F_p) \qquad (5.21)$$

Where:			Metric	English
	B =	annual breathing loss	m^3	API bbl
	D =	tank diameter	meters	feet
	P =	TVP at average liquid temperature	kPa(g)	psig
	A =	unit factor	74	14.5

F_p = paint factor = 1.0 for aluminum; 0.75 for chalking white; 1.1 for light gray; 1.25 for black; no paint and tank needing repainting

F_o = outage factor based on the average distance to the top flange of the tank found from the following table

Outage		F_o	Outage		F_o
m	ft		m	ft	
0.31	1	0.39	9.15	30	1.23
1.53	5	0.55	10.68	35	1.33
3.05	10	0.72	12.20	40	1.43
4.58	15	0.87	13.73	45	1.53
6.10	20	1.00	15.25	50	1.62
7.63	25	1.12			

Equation 5.21 is based on a tank being about half full on the average, when storing a 65 kPa [9.5 psia] RVP product. Unfortunately, predicting breathing losses may show a 25% variation because of the many factors that cannot be accounted for in a quantitative manner.

Filling Losses. The filling loss prediction is more reliable than that for breathing loss. The basic cause of loss is the displacement of the air-vapor mixture by the incoming liquid. Once again, the experience varies with the company and the location. The recommended equation is

$$F = \left(\frac{PV}{A}\right)(K_f) \tag{5.22}$$

Where:		Metric	English
P	= true vapor pressure	kPa(g)	psig
V	= volume of liquid in	m^3	bbl
F	= filling loss	m^3	bbl
A	= conversion constant	22 740	3300

The value for K_f is found from the table below.

Tank Turnovers per Year	K_f	
	Refineries	Fields and Terminals
0-10	1.0	1.00
12	0.91	1.00
15	0.75	1.00
20	0.59	1.00
25	0.50	1.00
30	0.47	1.00
40	0.44	1.00
40-60		0.80
60-100		0.50

Conservation type (floating head) tanks are used to reduce losses. The Pan Type floating-head tank is primarily of historical interest. Of the two other common types, pontoon floating roof and double deck, each has its own particular advantages.

Filling losses are usually negligible. To estimate total losses, the following rule-of-thumb may be used.

3.8-4.6 m^3 per meter of diameter per bar of TVP per year

[0.5-0.6 API bbl per foot of diameter per psi of TVP per year]

Additional information on tank storage is available from the American Petroleum Institute.(5.21,5.22)

Automatic Custody Transfer (ACT)

When producing to a pipeline, a continuous monitoring system may be used instead of large tanks that are emptied periodically. Figure 5.10 shows the systems often used.

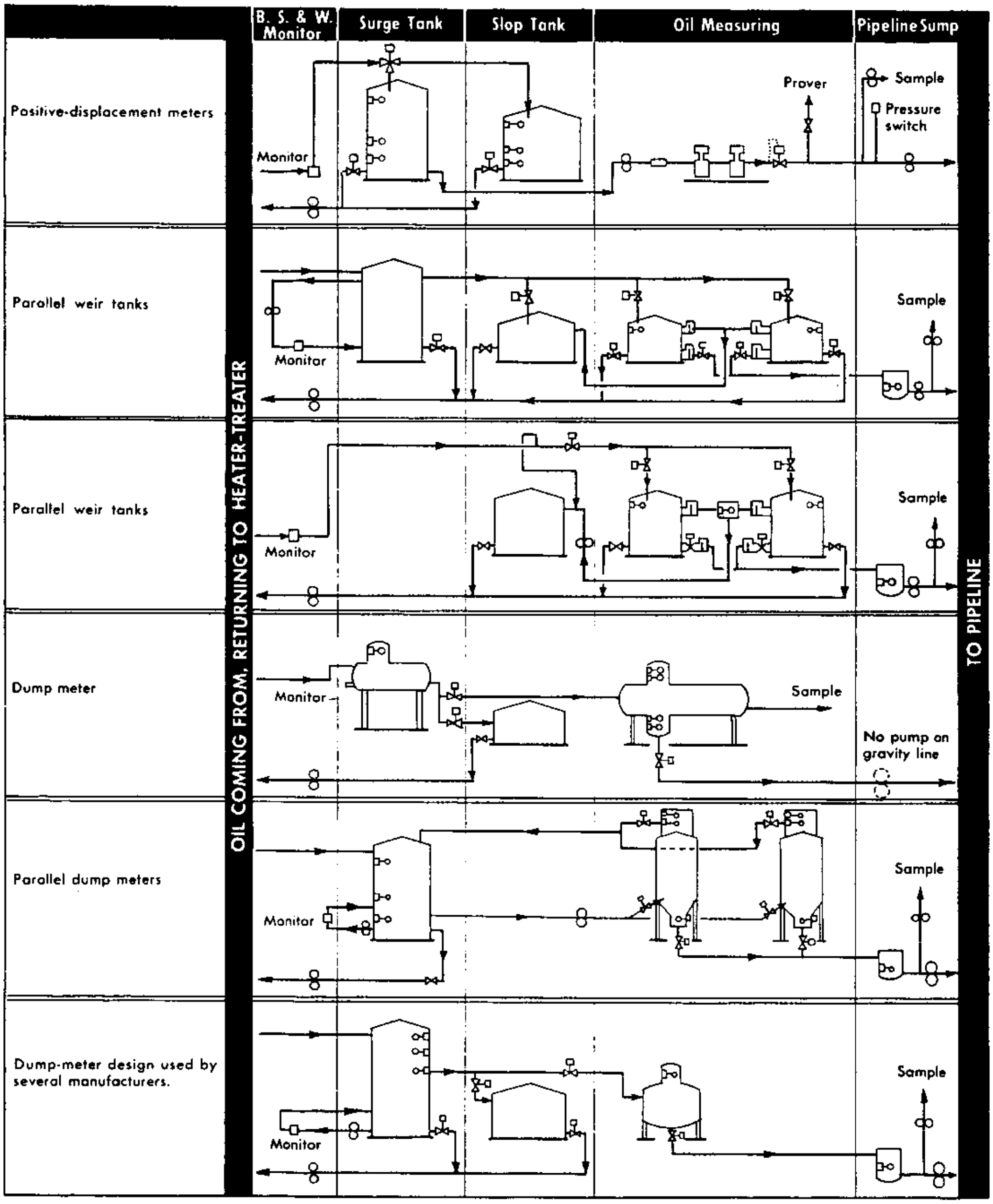


Figure 5.10 Various Types of ACT Systems

The monitor for B.S. & W. (basic sediment and water) rejects any oil not meeting specifications and sends it to the slop tank for retreatment. A surge tank may, or may not, be used depending on circumstances.

The most common method of oil metering is the positive displacement (p.d.) meter. A weir tank is used, particularly if tanks are already on site. Weirs are added, top and bottom, to control the volume passed on each fill and emptying cycle. The dump (metering) tank is like any metering vessel using level controls.

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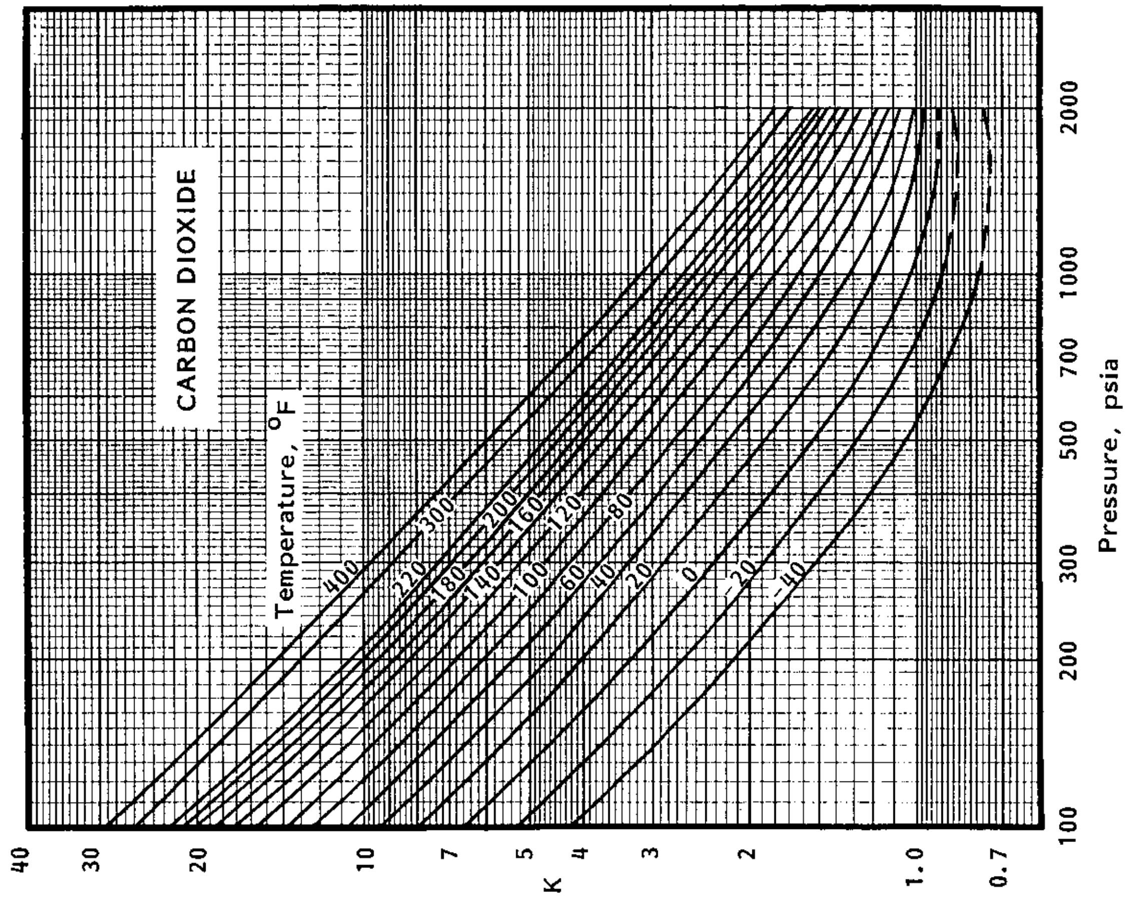
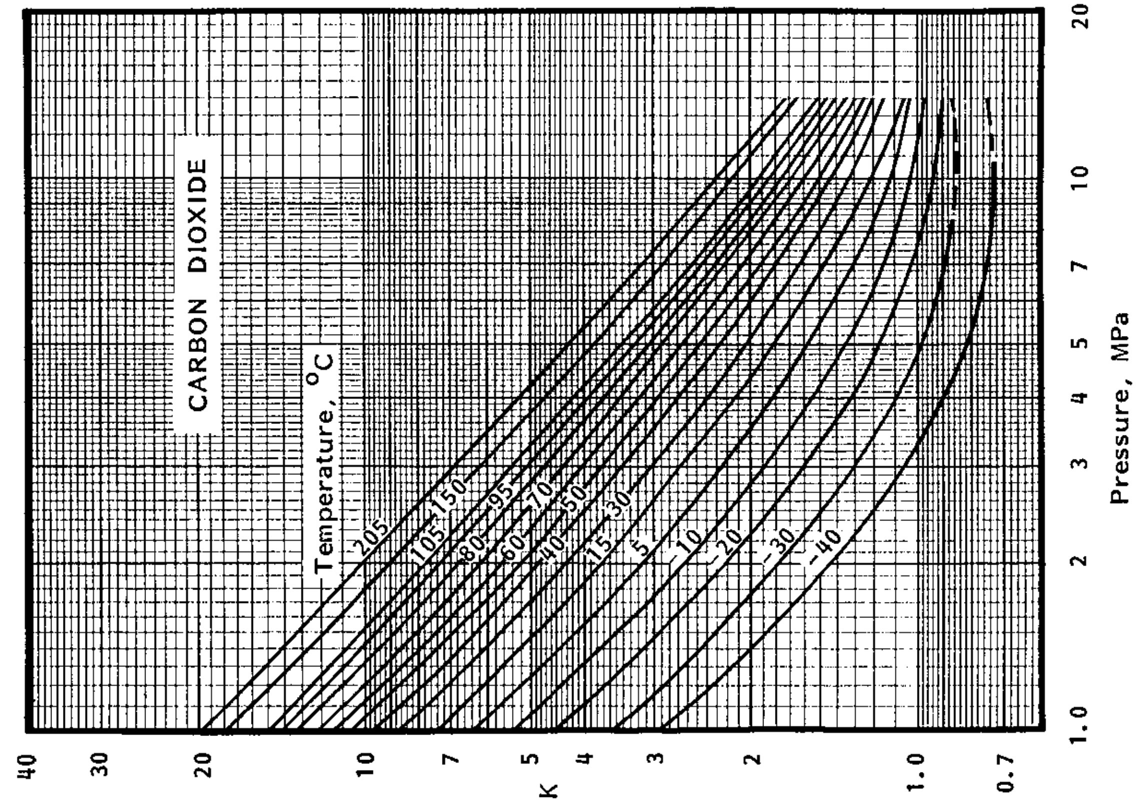
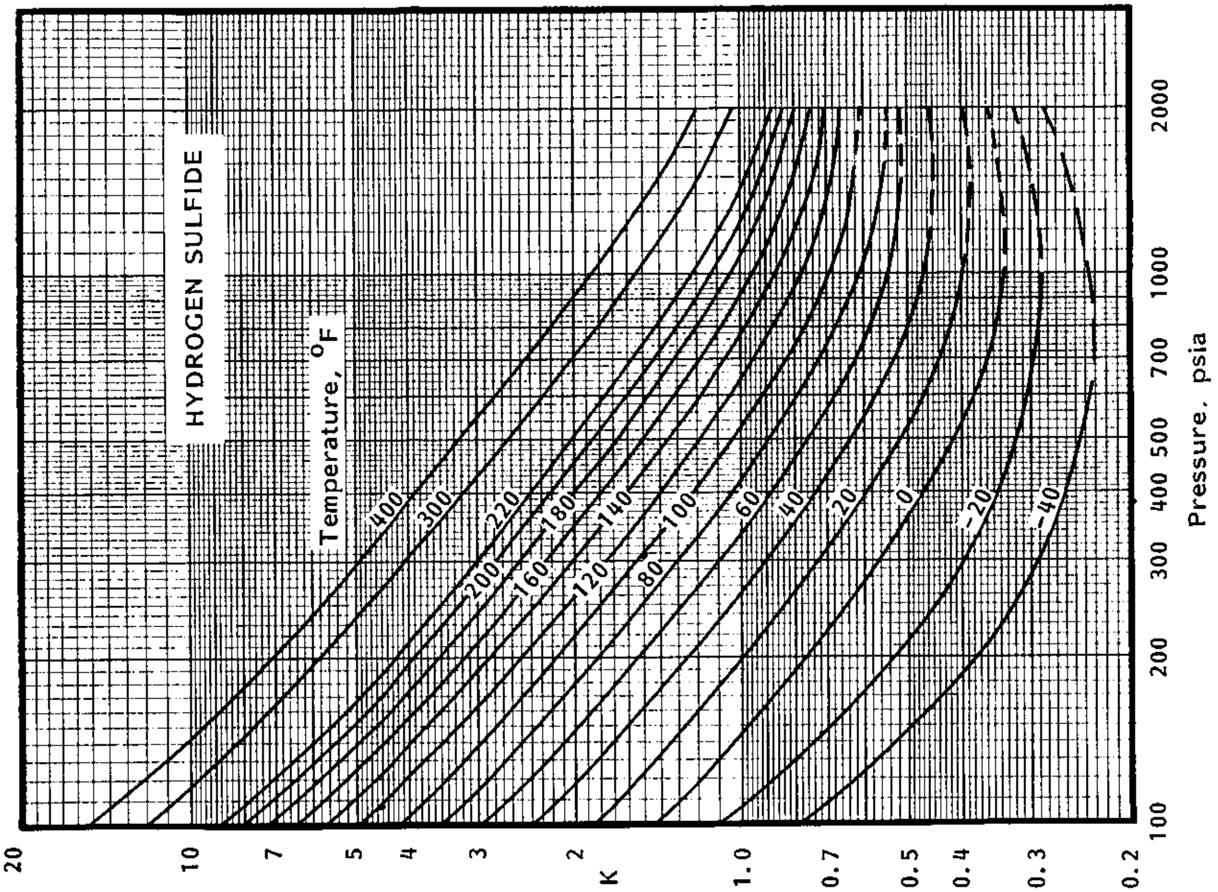
APPENDIX 5A

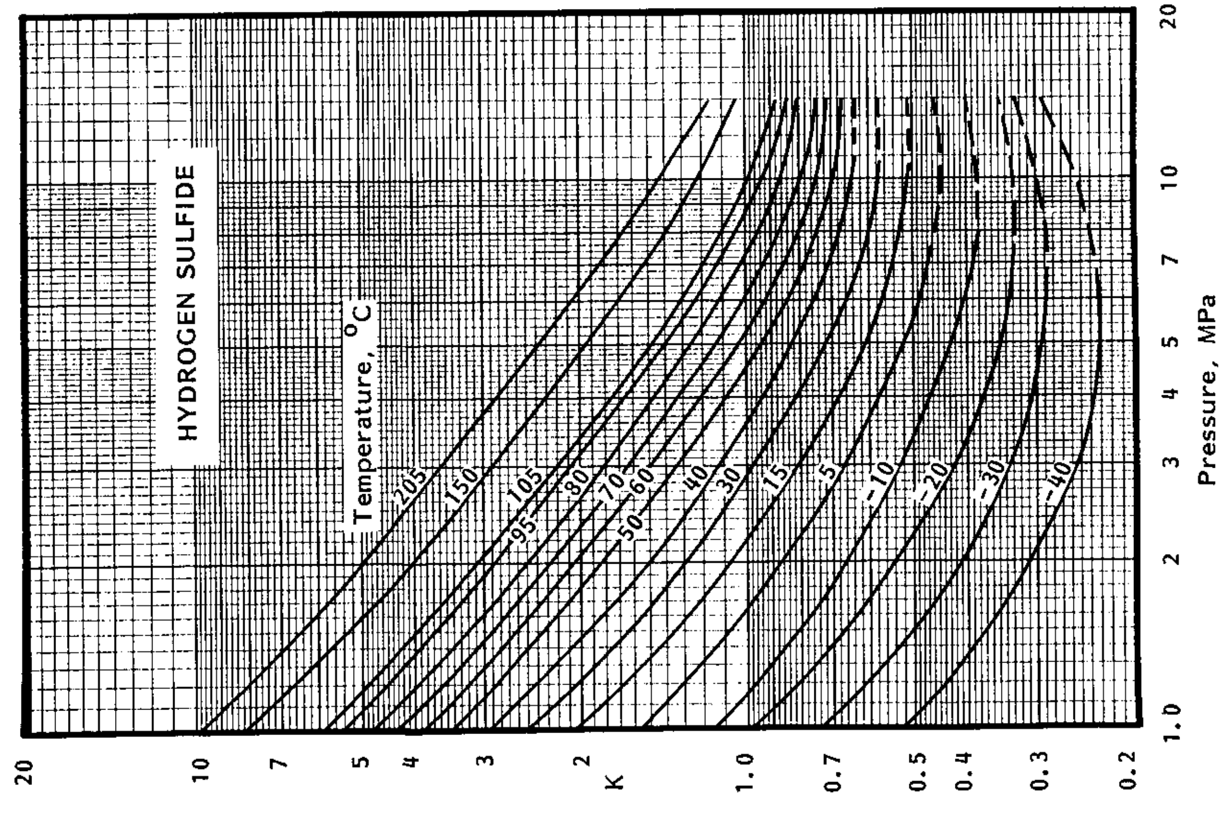
This appendix contains K value charts for Carbon Dioxide, Hydrogen Sulfide, Nitrogen and the paraffin hydrocarbons methane through decane. Both metric and English unit charts are included.

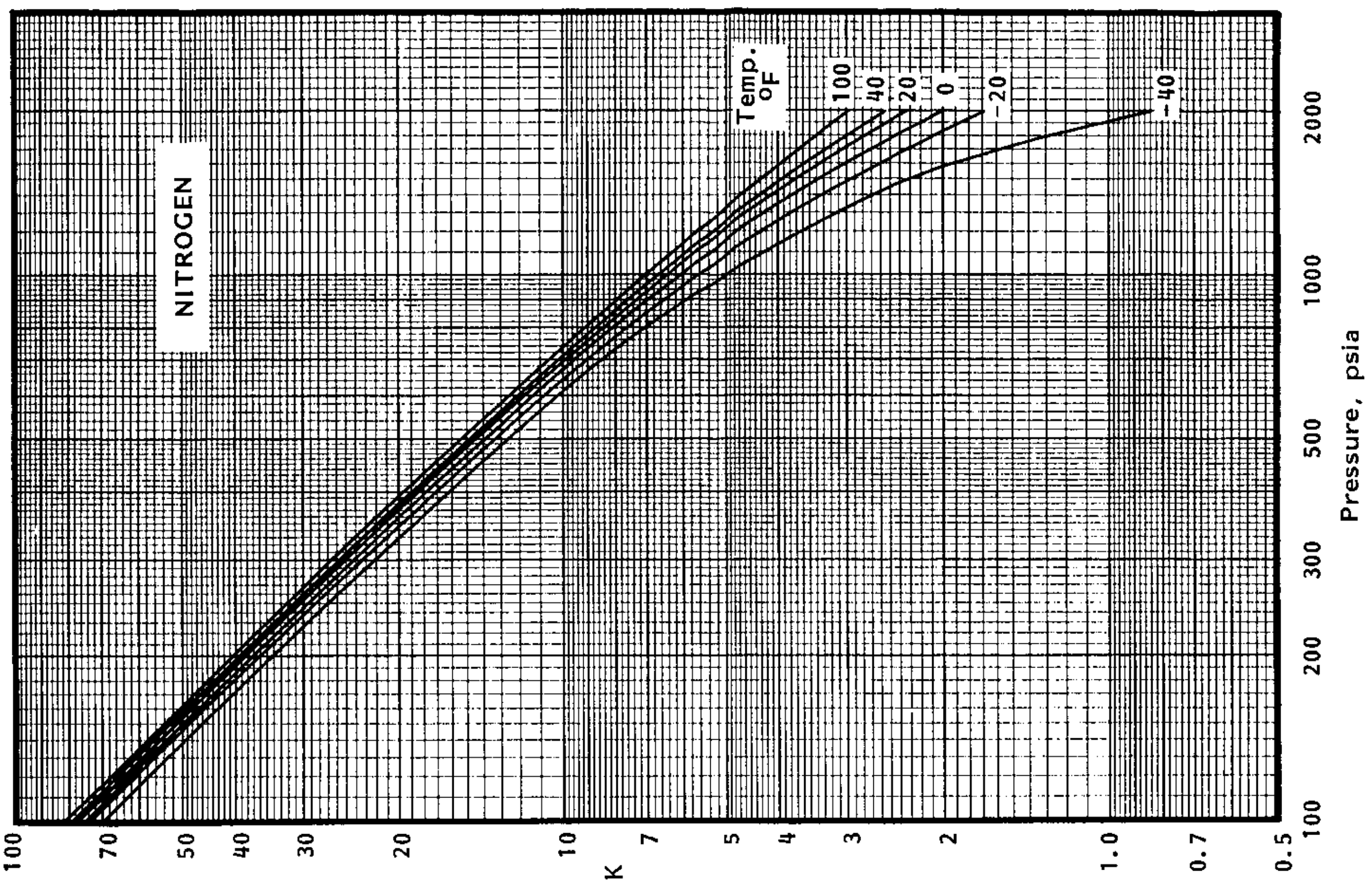
They are used in all examples involving K values. They also are compatible with the computer programs that go with this book.

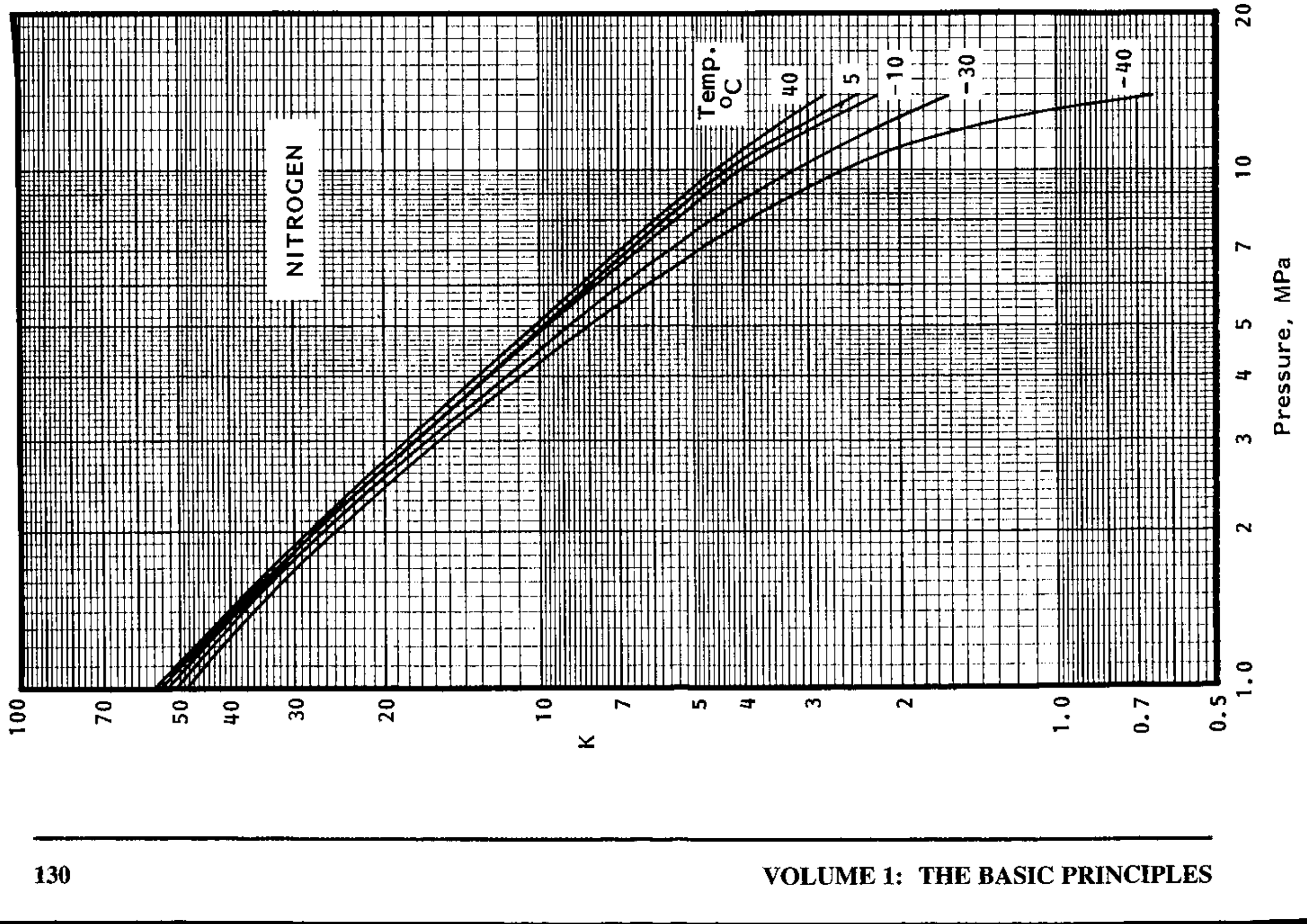

CARBON DIOXIDE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
40
30
20
10
7
5
4
3
2
1.0
0.7
Pressure, psia
100
200
300
500
700
1000
2000

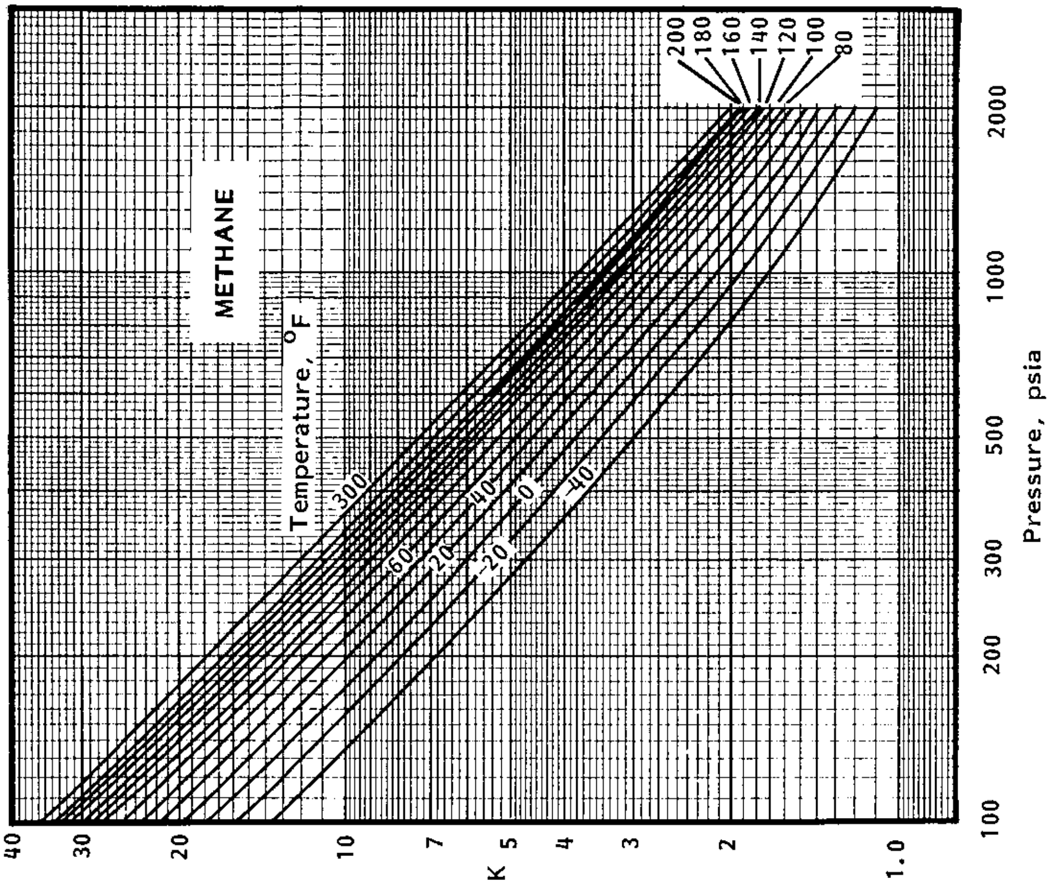

CARBON DIOXIDE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
40
30
20
10
7
5
4
3
2
1.0
0.7
Pressure, MPa
1.0
2
3
4
5
7
10
20

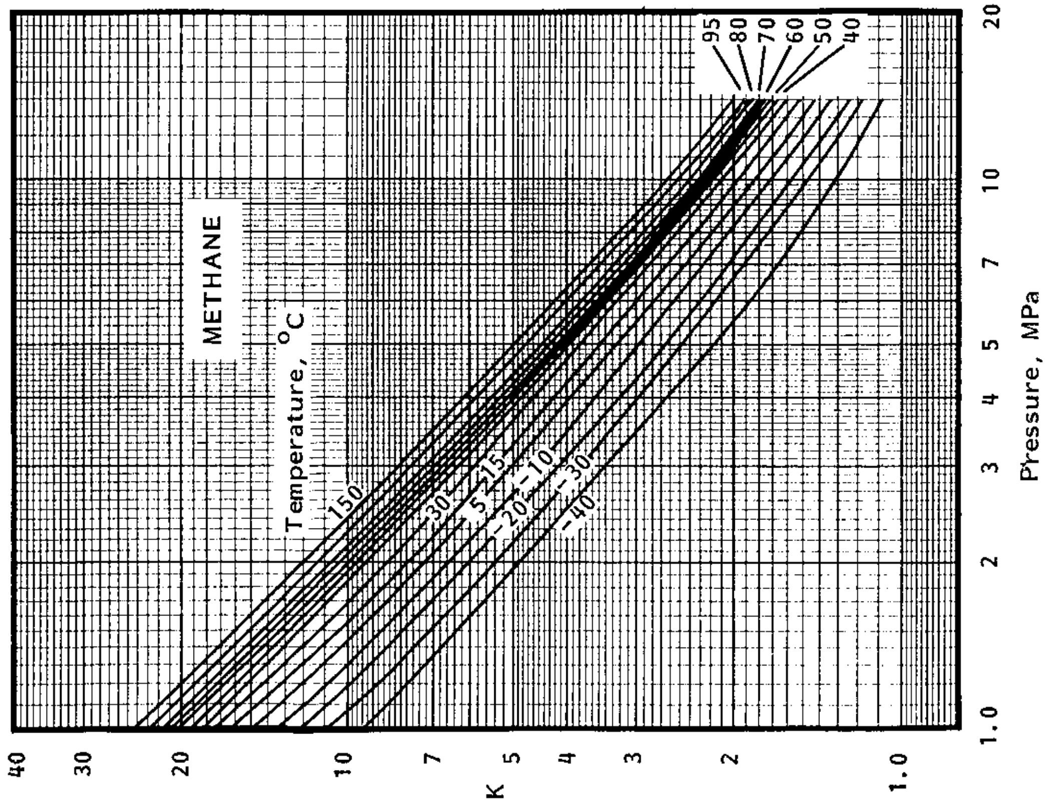

HYDROGEN SULFIDE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
20
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
Pressure, psia
100
200
300
400
500
700
1000
2000


HYDROGEN SULFIDE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
20
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
Pressure, MPa
1.0
2
3
4
5
7
10
20


NITROGEN
Temp. °F
100
40
20
0
-20
-40
K
100
70
50
40
30
20
10
7
5
4
3
2
1.0
0.7
0.5
Pressure, psia
100
200
300
500
1000
2000


NITROGEN
Temp. °C
40
5
-10
-30
-40
K
100
70
50
40
30
20
10
7
5
4
3
2
1.0
0.7
0.5
Pressure, MPa
1.0
2
3
4
5
7
10
20


METHANE
Temperature, °F
300
60
40
20
0
-20
-40
200
180
160
140
120
100
80
K
40
30
20
10
7
5
4
3
2
1.0
Pressure, psia
100
200
300
500
1000
2000


METHANE
Temperature, °C
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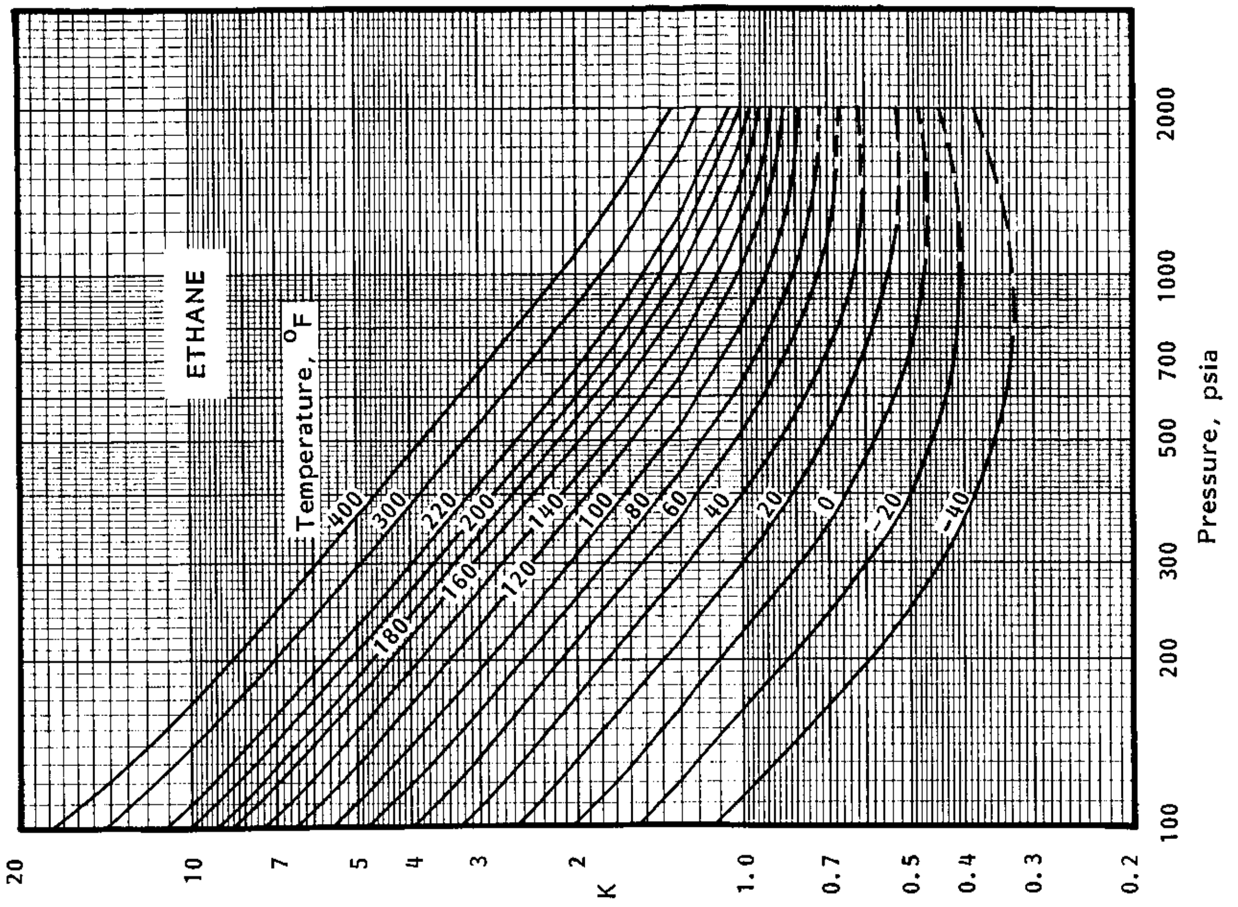
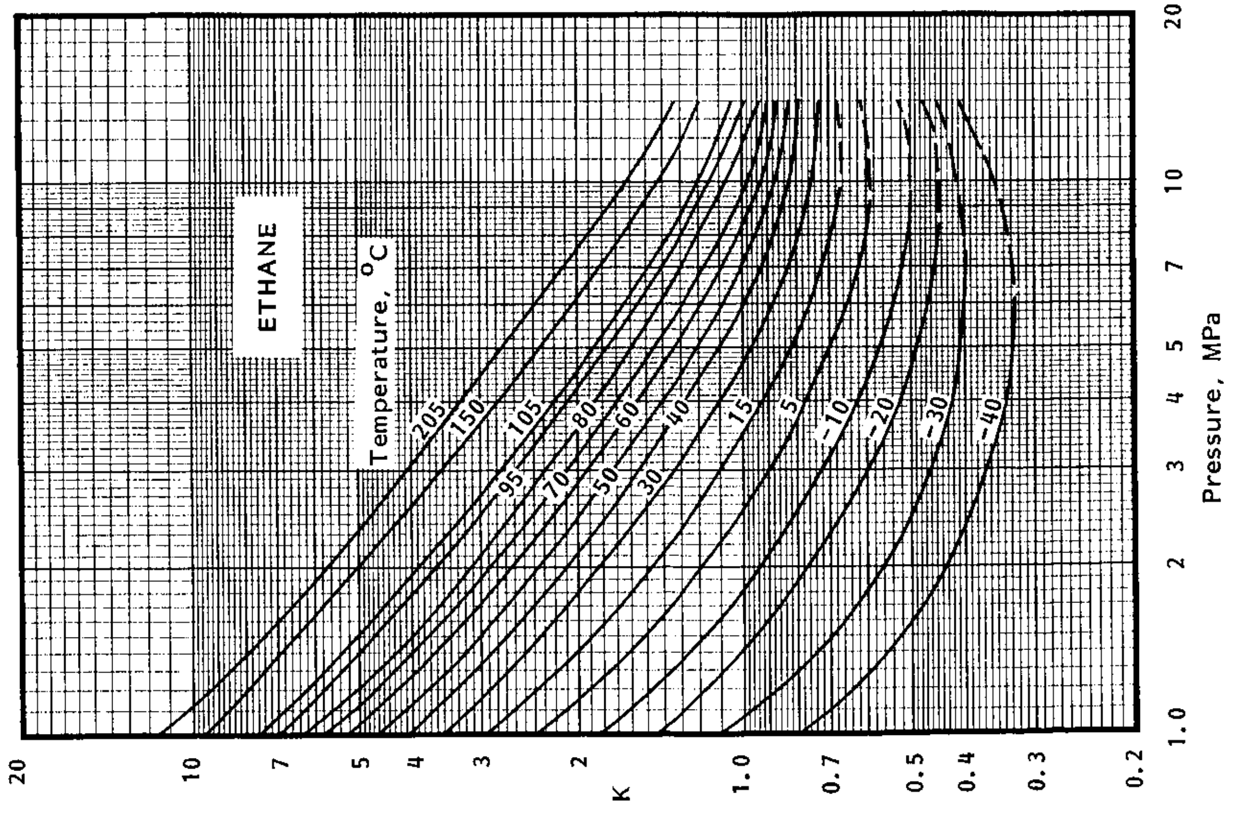
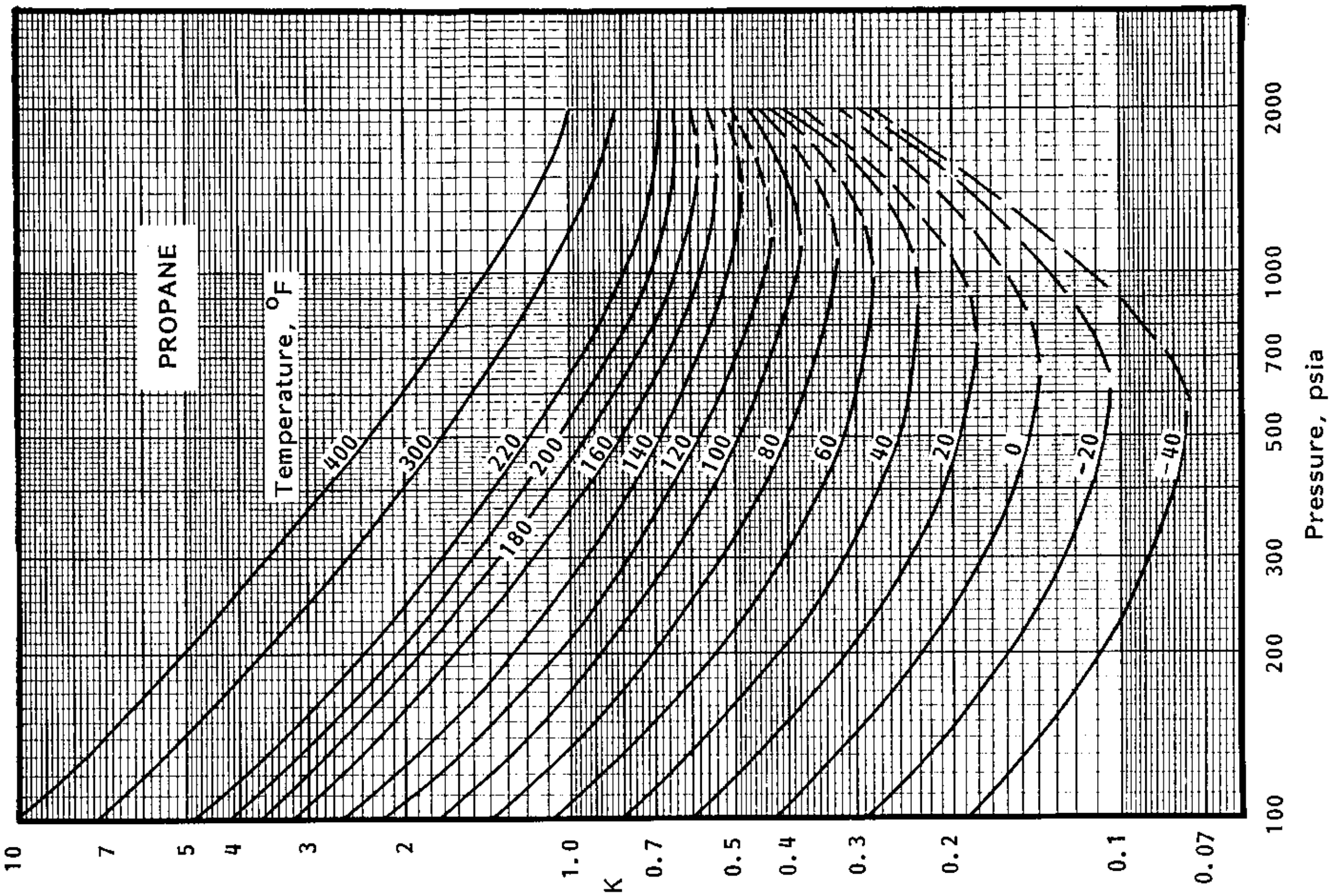
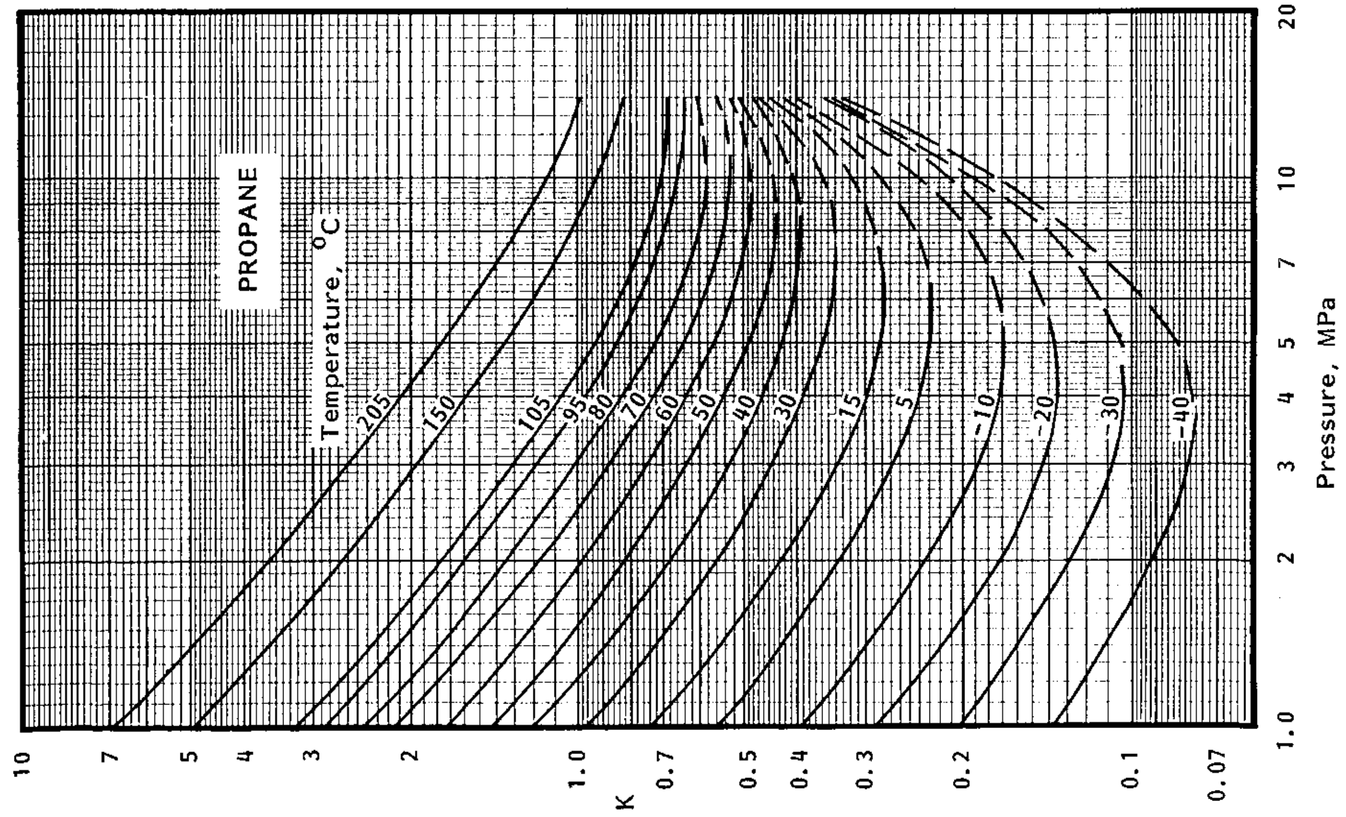
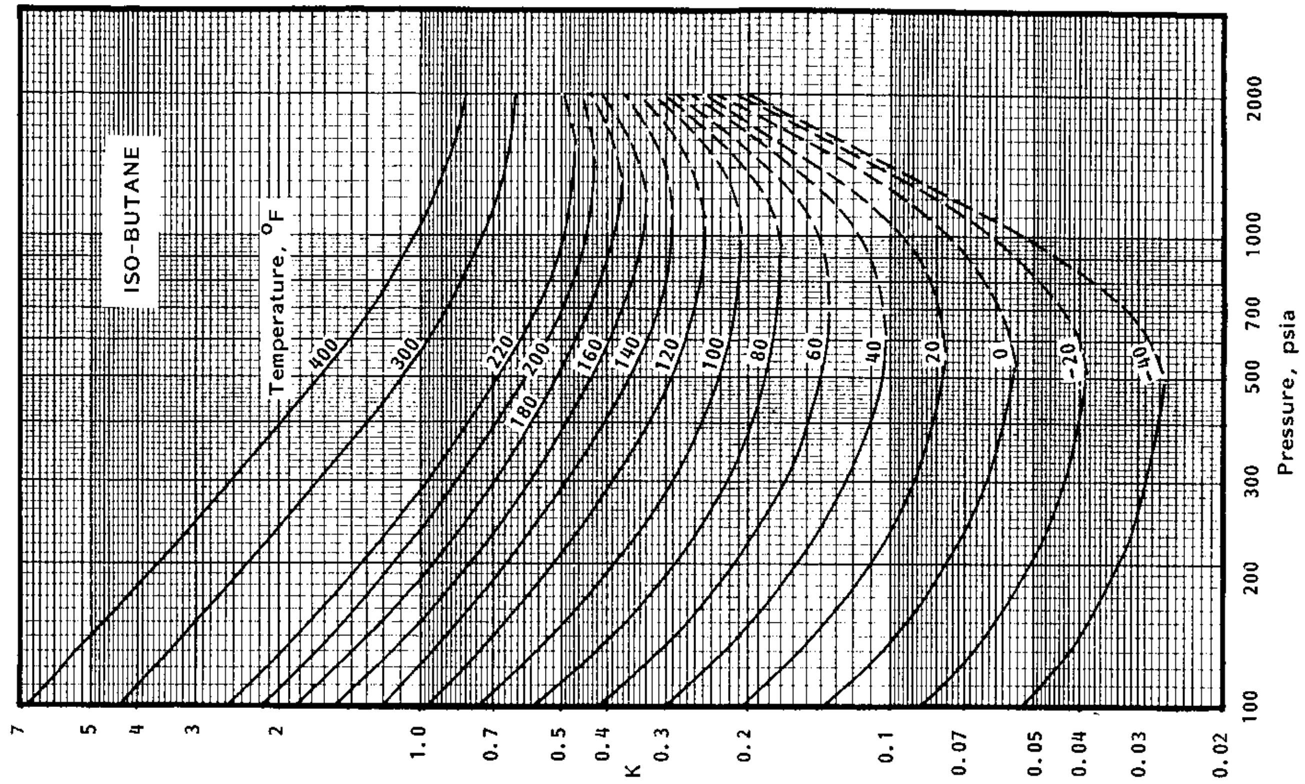
30
15
5
-10
-20
-30
-40
95
80
70
60
50
40
K
40
30
20
10
7
5
4
3
2
1.0
Pressure, MPa
1.0
2
3
4
5
7
10
20

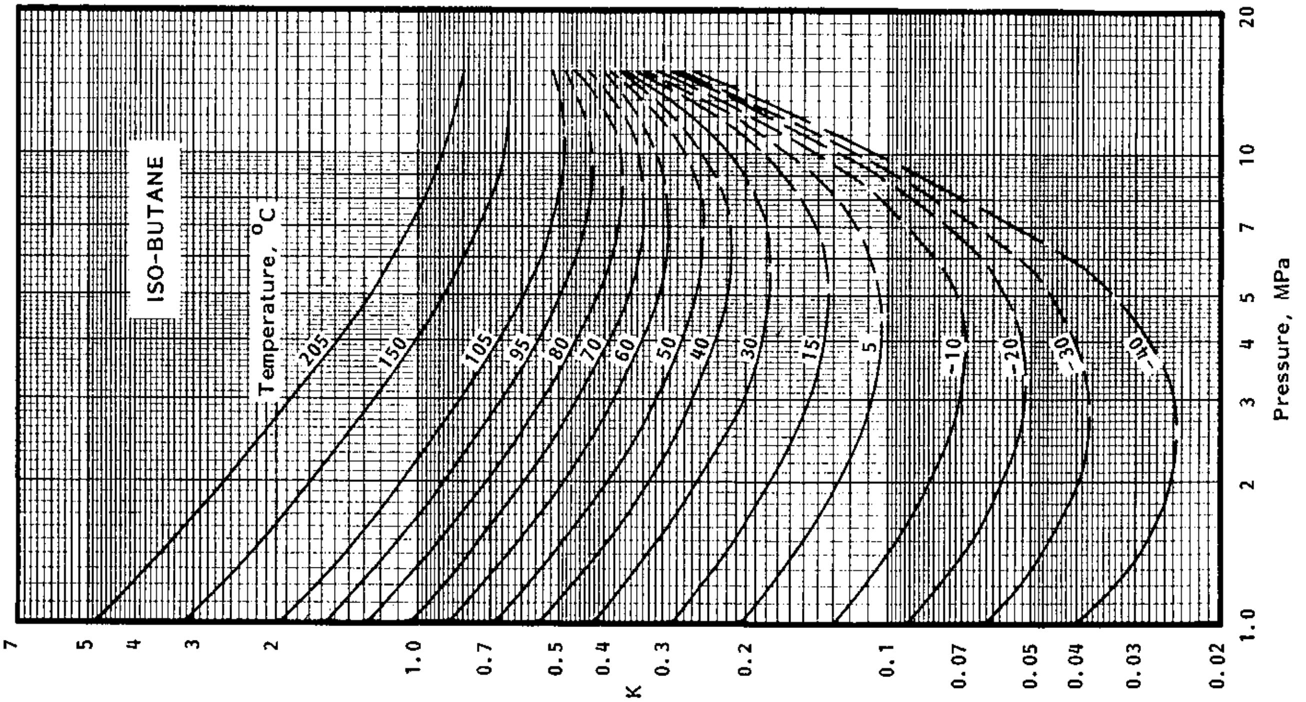

ETHANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
20
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
Pressure, psia
100
200
300
500
700
1000
2000

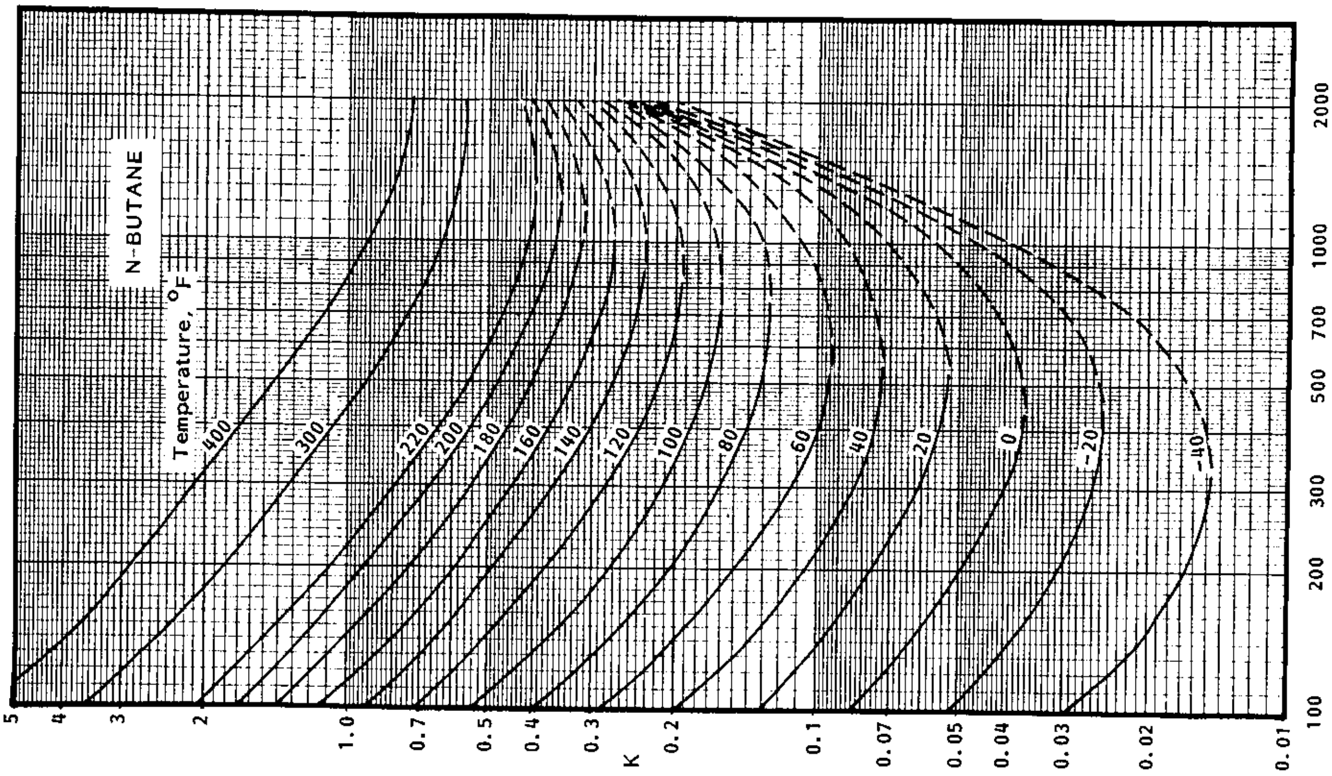

ETHANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
20
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
Pressure, MPa
1.0
2
3
4
5
7
10
20

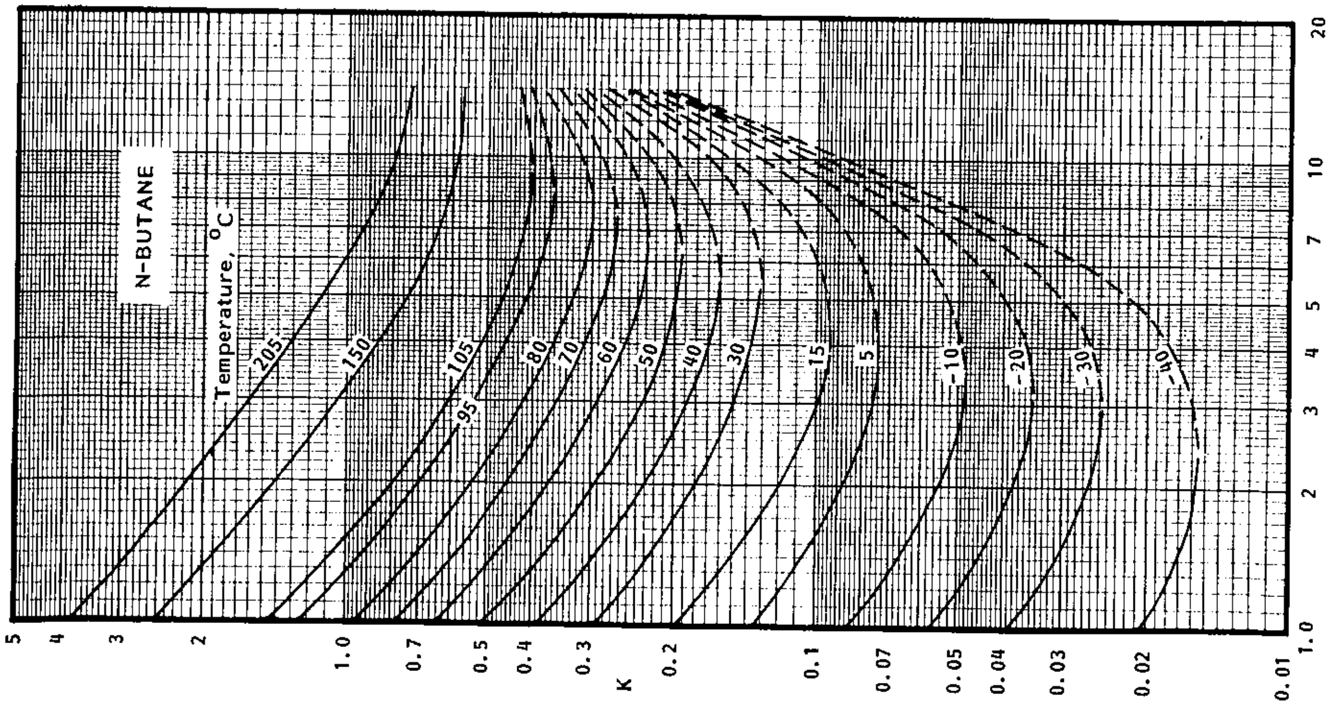

PROPANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
Pressure, psia
100
200
300
500
700
1000
2000

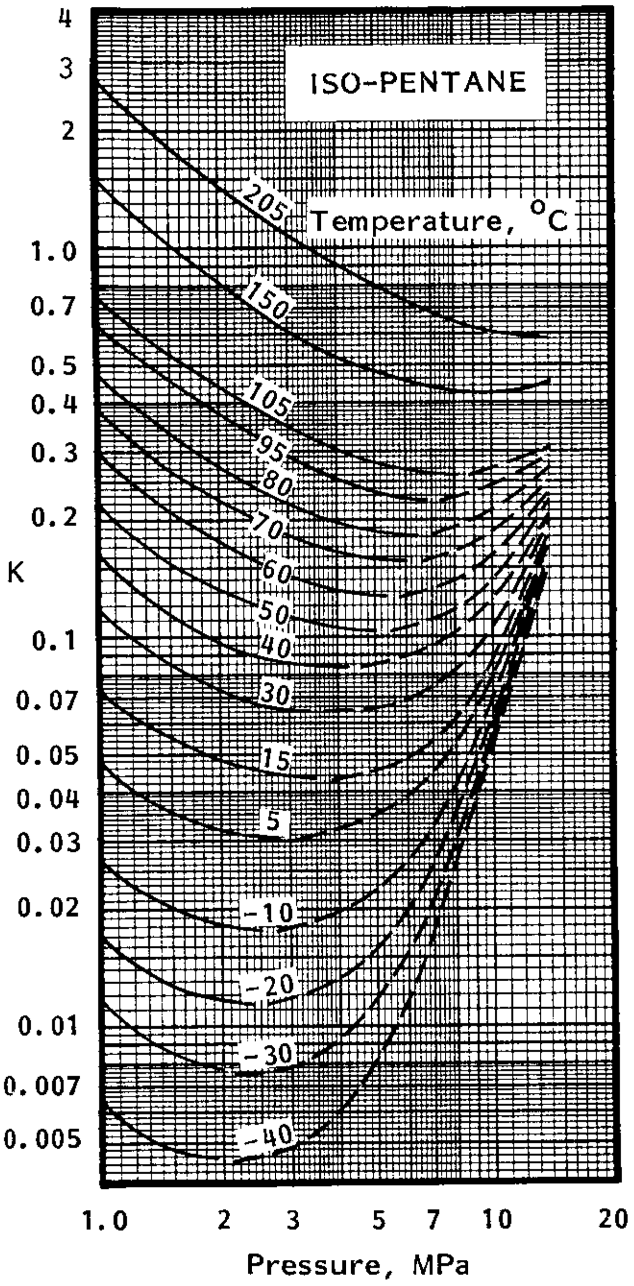

PROPANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
10
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
Pressure, MPa
1.0
2
3
4
5
7
10
20

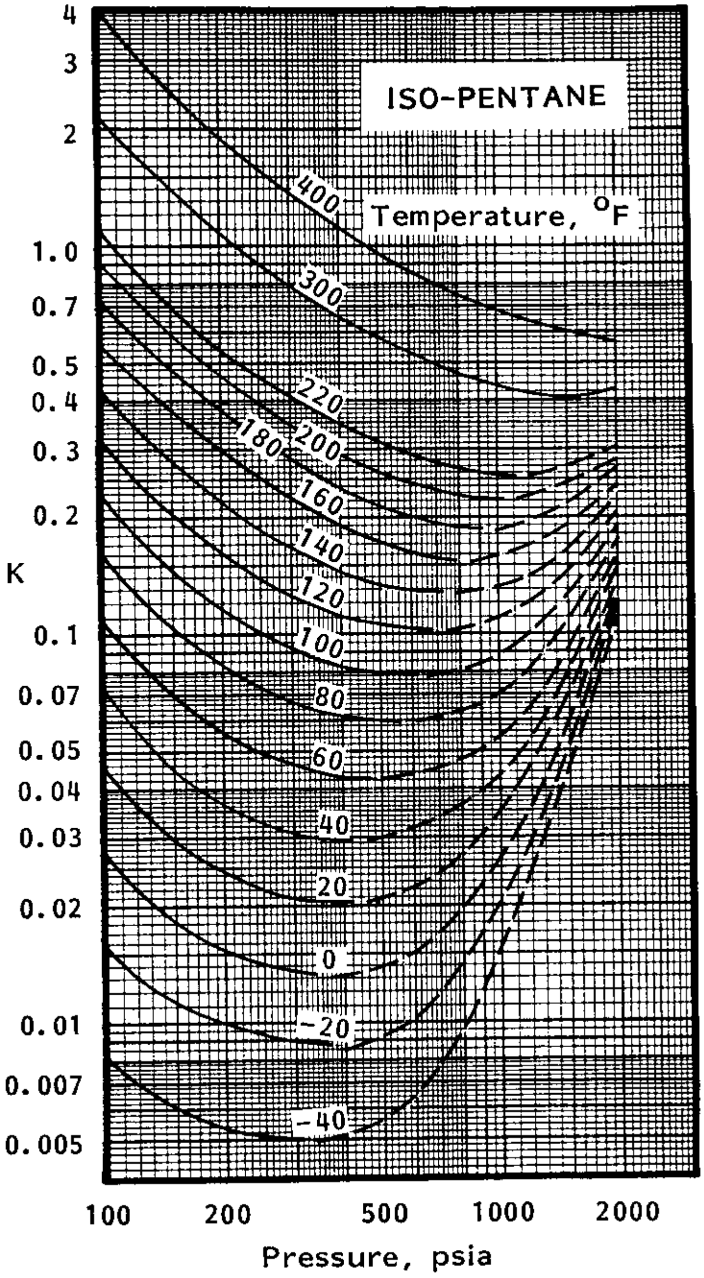

ISO-BUTANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
Pressure, psia
100
200
300
500
700
1000
2000

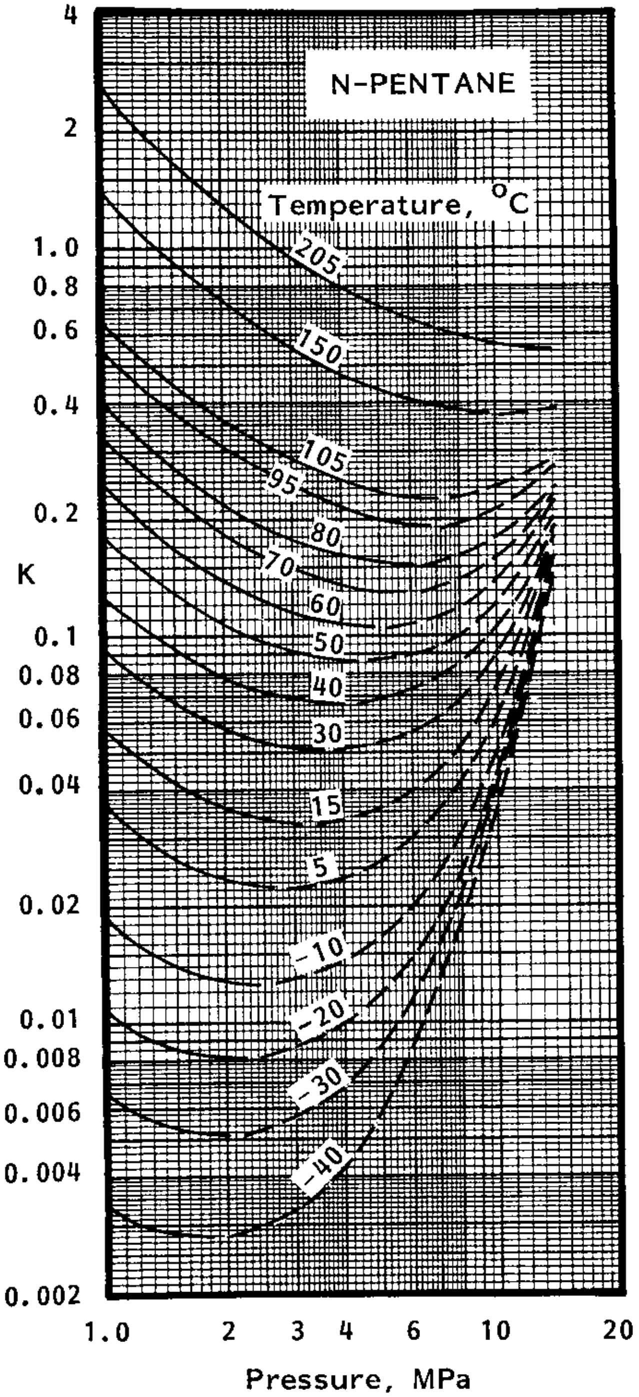

ISO-BUTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
7
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
Pressure, MPa
1.0
2
3
4
5
7
10
20

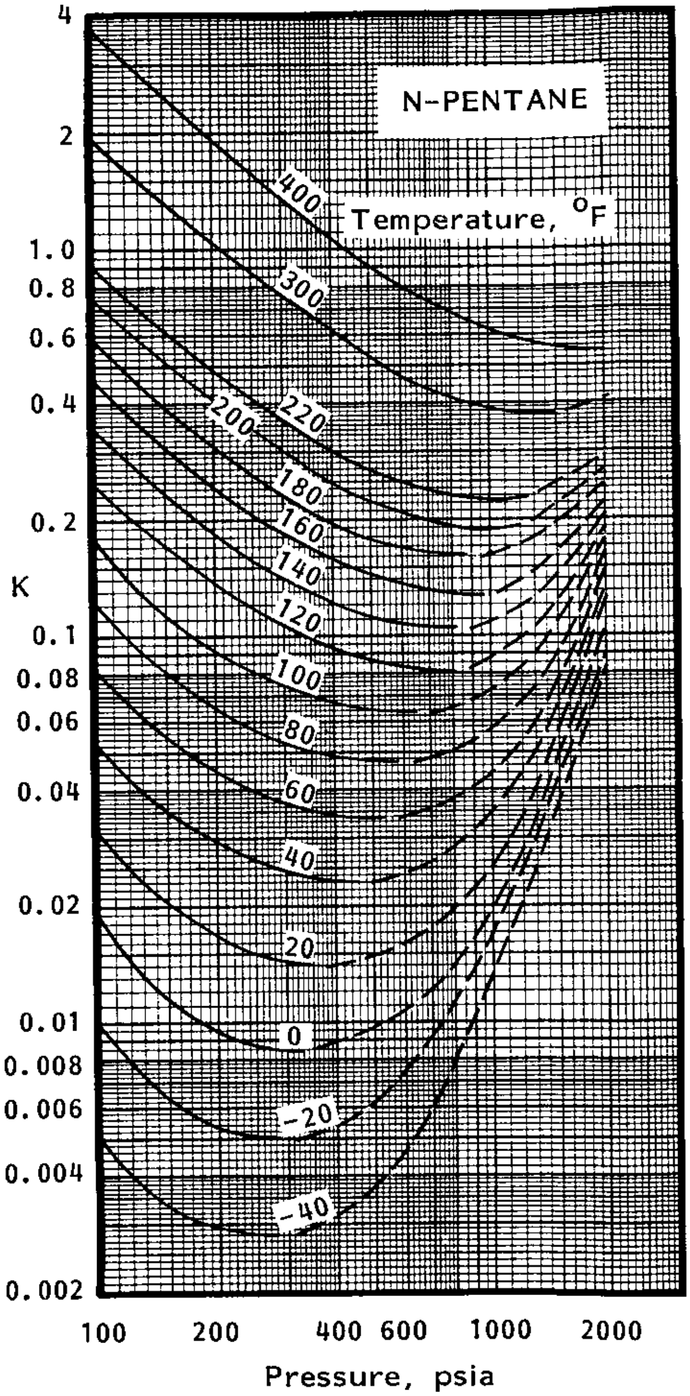

N-BUTANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
0.01
Pressure, psia
100
200
300
500
700
1000
2000

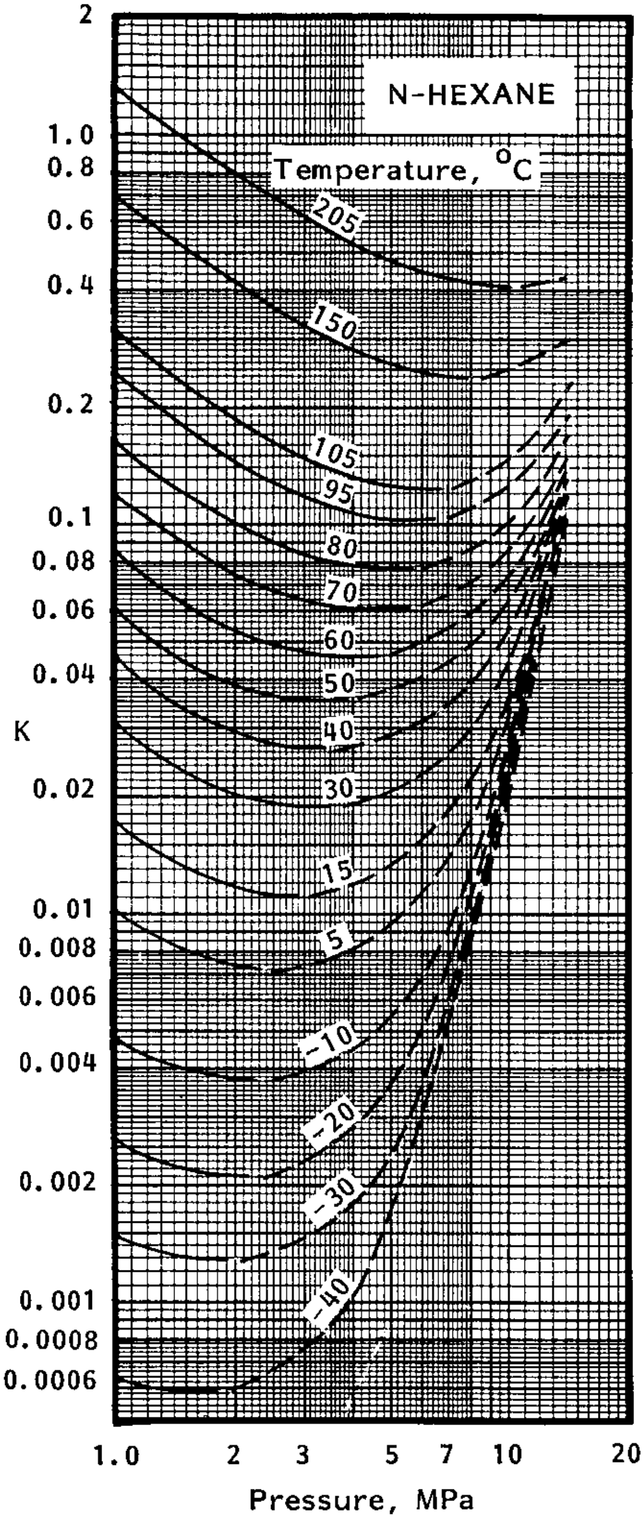

N-BUTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
5
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
0.01
Pressure, MPa
1.0
2
3
4
5
7
10
20

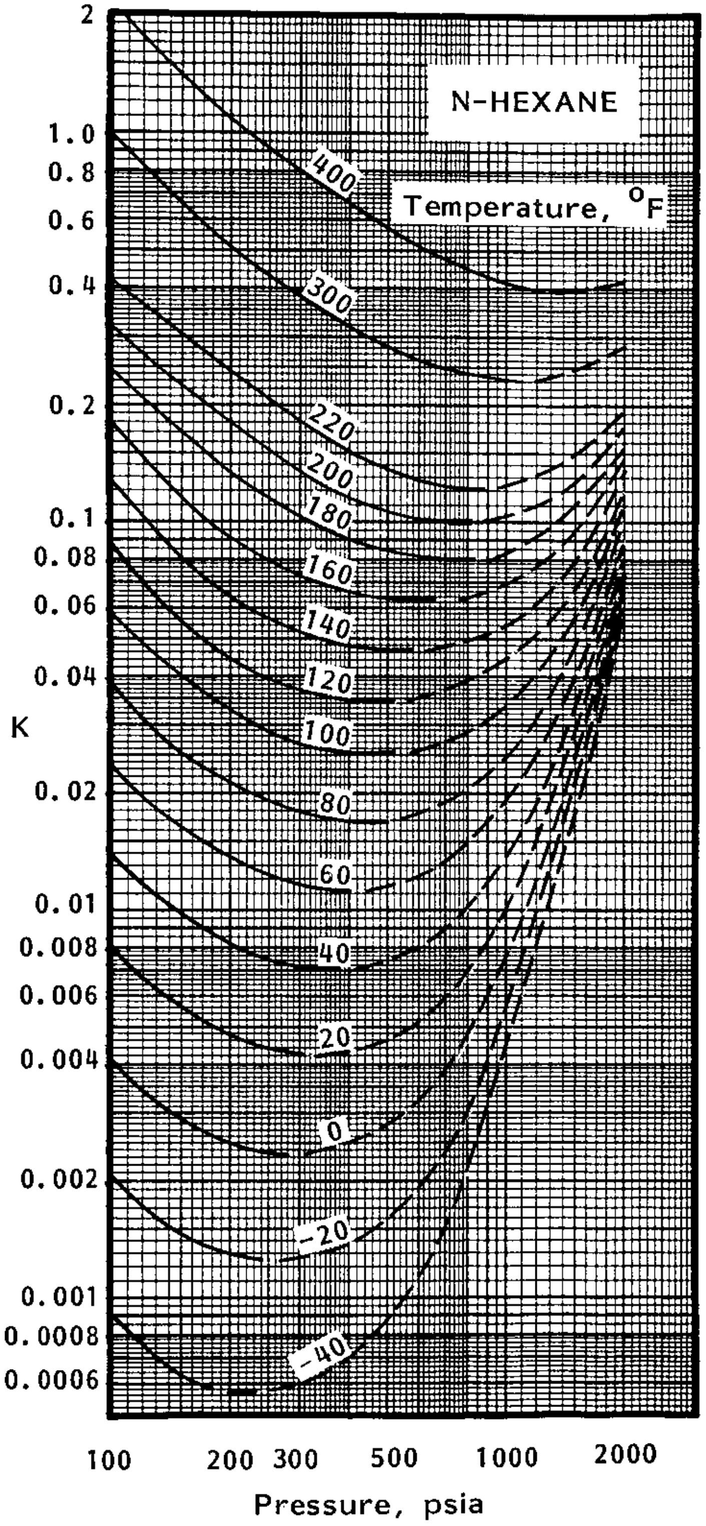

ISO-PENTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
0.01
0.007
0.005
1.0
2
3
5
7
10
20
Pressure, MPa

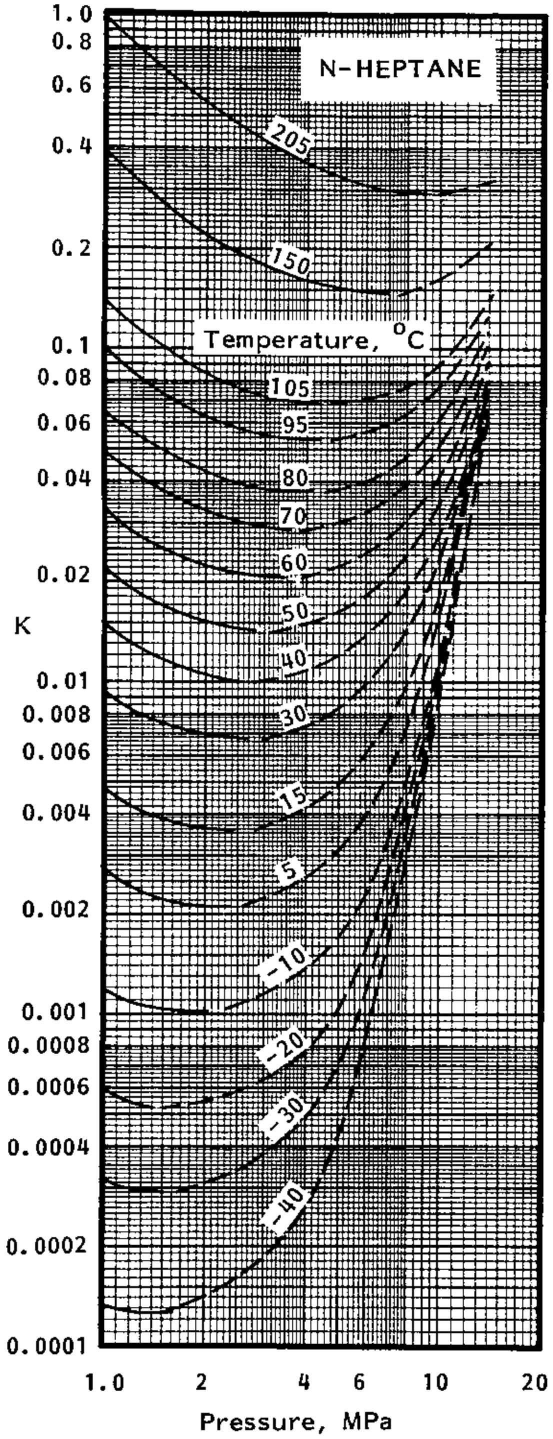

ISO-PENTANE
Temperature, °F
400
300
220
180
200
160
140
120
100
80
60
40
20
0
-20
-40
K
4
3
2
1.0
0.7
0.5
0.4
0.3
0.2
0.1
0.07
0.05
0.04
0.03
0.02
0.01
0.007
0.005
100
200
500
1000
2000
Pressure, psia

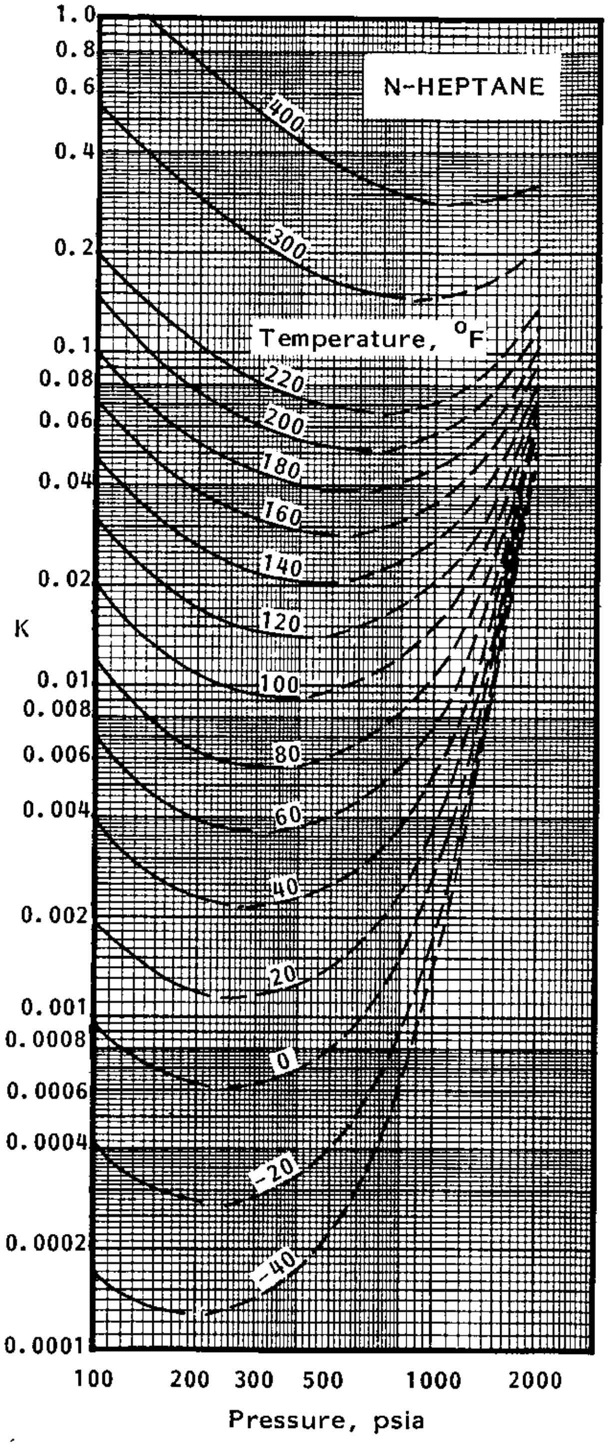

N-PENTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
4
2
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
1.0
2
3
4
6
10
20
Pressure, MPa

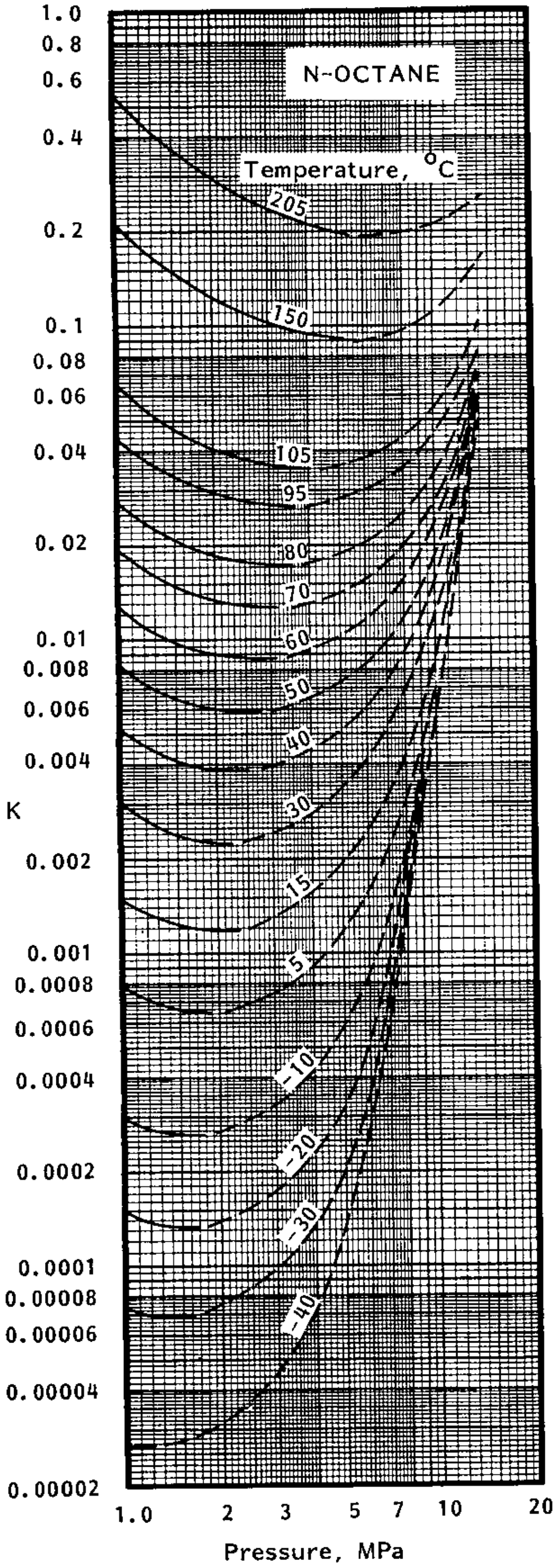

N-PENTANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
4
2
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
100
200
400
600
1000
2000
Pressure, psia

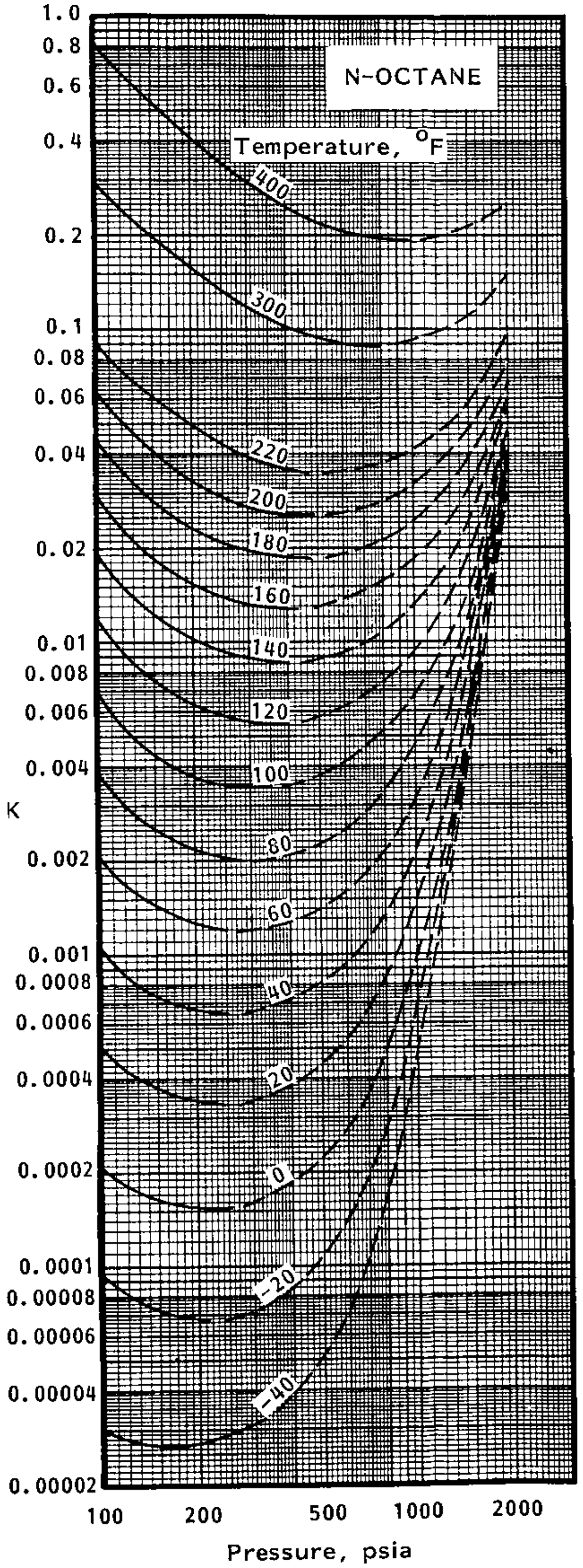

2
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
K
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
N-HEXANE
Temperature, $^{\circ}$C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
1.0
2
3
5
7
10
20
Pressure, MPa

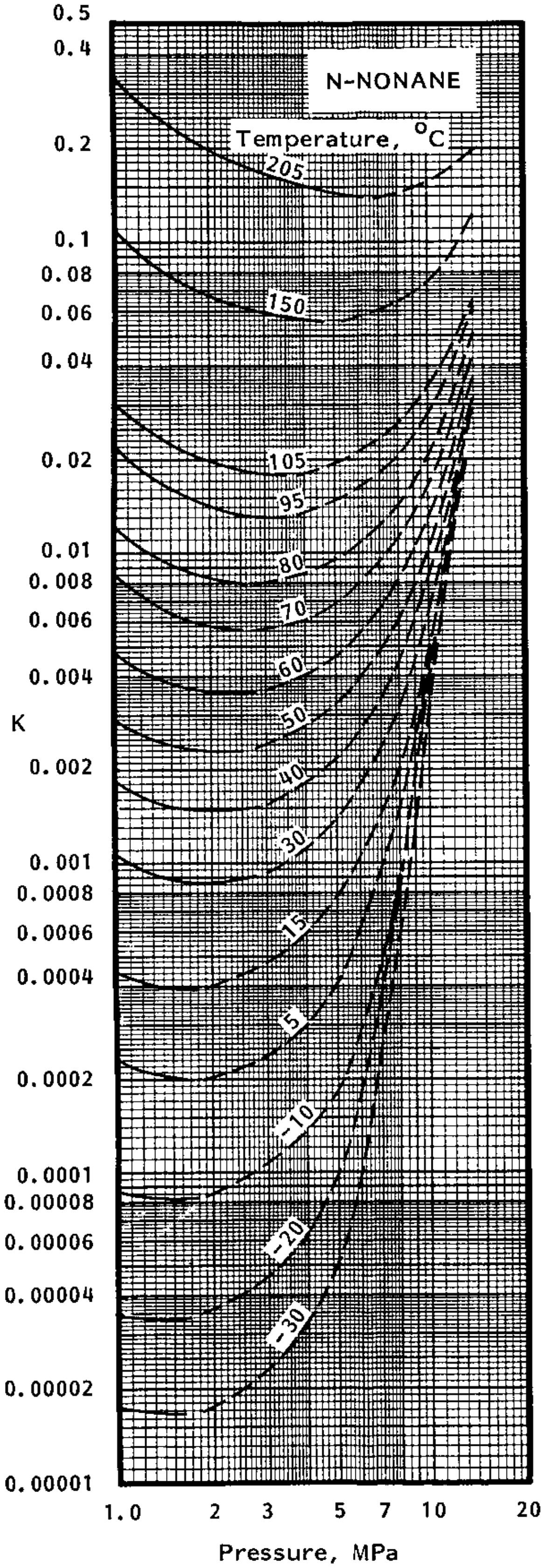

2
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
K
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
N-HEXANE
Temperature, $^{\circ}$F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
100
200
300
500
1000
2000
Pressure, psia

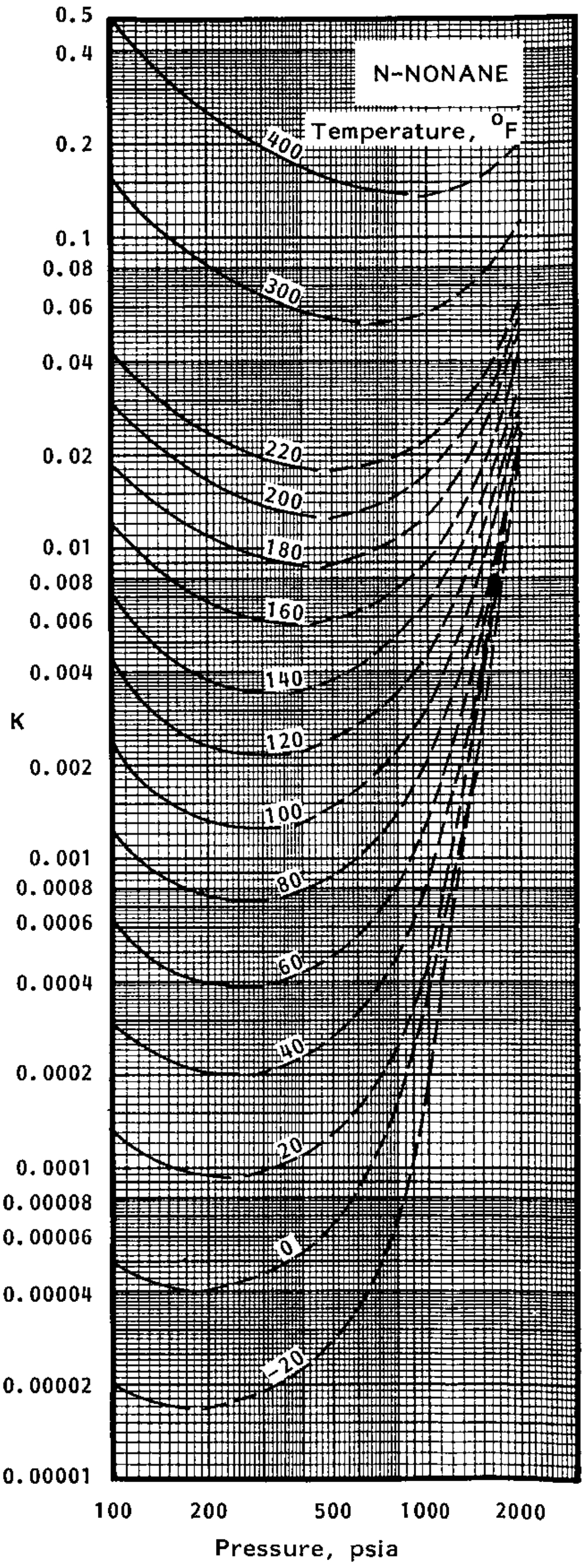

N-HEPTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
1.0
2
4
6
10
20
Pressure, MPa

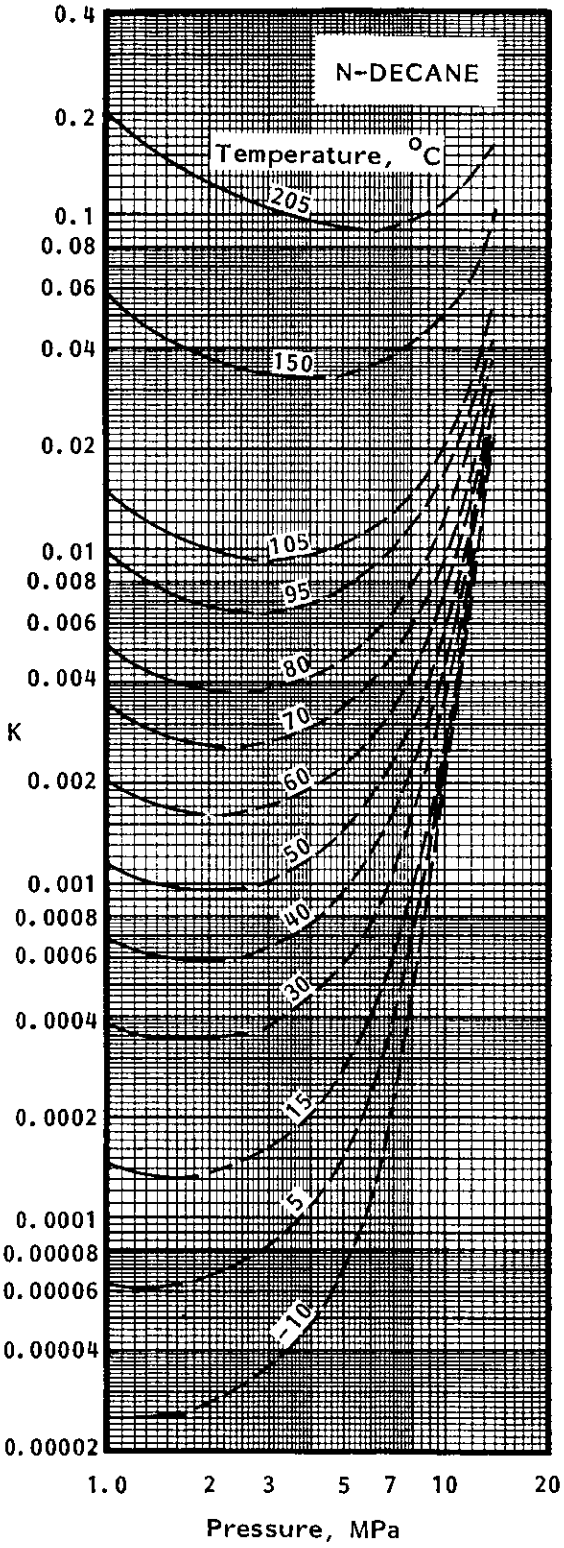

N-HEPTANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
100
200
300
500
1000
2000
Pressure, psia

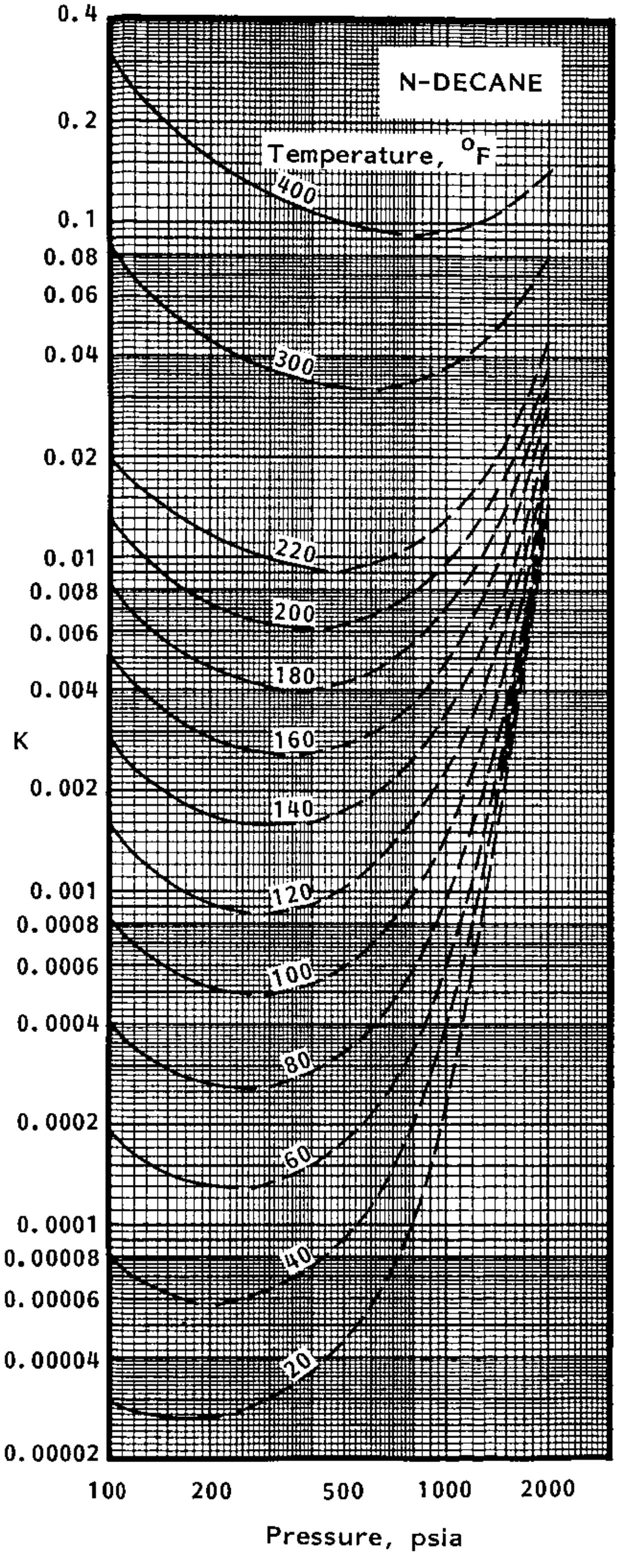

N-OCTANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
-40
K
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
1.0
2
3
5
7
10
20
Pressure, MPa


N-OCTANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
K
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
100
200
500
1000
2000
Pressure, psia


N-NONANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
-20
-30
K
0.5
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
0.00001
1.0
2
3
5
7
10
20
Pressure, MPa


N-NONANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
0
-20
K
0.5
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
0.00001
100
200
500
1000
2000
Pressure, psia


N-DECANE
Temperature, °C
205
150
105
95
80
70
60
50
40
30
15
5
-10
K
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
1.0
2
3
5
7
10
20
Pressure, MPa


N-DECANE
Temperature, °F
400
300
220
200
180
160
140
120
100
80
60
40
20
K
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
0.0008
0.0006
0.0004
0.0002
0.0001
0.00008
0.00006
0.00004
0.00002
100
200
500
1000
2000
Pressure, psia

APPENDIX 5B

The composite charts are based on the work of Latham and Campbell. (Reference 5.2) They are designed primarily for use with crude oils; whereas, Appendix 5A is based on natural gas liquids.

COMPOSITE K VALUES FOR RESERVOIR FLUIDS

COMPONENT	TEMP., °F	PRESSURE, psia									
		100	200	300	400	500	600	700	800	900	1000
METHANE	−20	16.0	8.08	5.50	4.23	3.55	3.09	2.75	2.50	2.32	2.19
	0	17.8	9.06	6.18	4.72	3.89	3.34	2.95	2.68	2.44	2.28
	20	20.3	10.6	7.28	5.59	4.59	3.90	3.43	3.19	2.81	2.58
	40	23.1	11.8	7.95	6.16	5.04	4.30	3.70	3.30	3.00	2.72
	60	25.0	12.8	8.7	6.62	5.42	4.60	4.03	3.60	3.28	2.99
	80	26.9	14.3	9.9	7.78	6.44	5.50	4.81	4.38	3.90	3.65
	100	28.7	14.5	10.0	7.90	6.60	5.60	4.90	4.40	4.00	3.70
	120	33.0	16.5	11.5	8.95	7.30	6.15	5.25	4.90	4.50	4.10
ETHANE	−20	1.31	.708	.519	.438	.391	.366	.354	.345	.343	.347
	0	1.95	1.05	.755	.610	.538	.492	.466	.448	.439	.439
	20	2.50	1.32	.939	.768	.657	.590	.560	.539	.522	.518
	40	3.25	1.75	1.28	1.01	.890	.800	.740	.690	.668	.665
	60	3.95	2.12	1.52	1.21	1.05	.940	.862	.808	.770	.750
	80	4.60	2.48	1.78	1.41	1.20	1.08	.985	.918	.863	.821
	100	5.82	3.04	2.19	1.68	1.41	1.24	1.12	1.05	.980	.930
	120	6.40	3.32	2.31	1.81	1.52	1.36	1.22	1.14	1.08	1.01
PROPANE	−20	.269	.149	.111	.093	.083	.077	.076	.076	.079	.082
	0	.443	.244	.178	.144	.128	.116	.112	.112	.114	.119
	20	.600	.328	.245	.204	.179	.166	.159	.157	.157	.159
	40	.840	.458	.342	.289	.258	.241	.230	.223	.220	.220
	60	1.09	.596	.440	.370	.328	.305	.293	.285	.278	.277
	80	1.33	.730	.530	.430	.375	.345	.326	.312	.305	.300
	100	1.75	.930	.670	.550	.480	.430	.408	.385	.373	.365
	120	2.18	1.15	.810	.660	.575	.520	.489	.455	.438	.410
i-BUTANE	−20	.097	.058	.046	.039	.036	.034	.034	.033	.034	.035
	0	.145	.085	.067	.058	.054	.052	.051	.051	.052	.054
	20	.238	.124	.094	.081	.074	.071	.070	.070	.071	.074
	40	.298	.170	.133	.117	.108	.102	.100	.100	.100	.104
	60	.419	.242	.186	.159	.144	.136	.132	.130	.130	.135
	80	.561	.338	.248	.200	.180	.169	.161	.158	.155	.156
	100	.79	.441	.325	.270	.239	.218	.206	.195	.190	.189
	120	.990	.550	.386	.319	.282	.256	.242	.231	.227	.222
n-BUTANE	−20	.058	.035	.028	.024	.022	.021	.021	.022	.024	.026
	0	.090	.053	.041	.036	.033	.032	.032	.033	.034	.037
	20	.145	.082	.064	.054	.049	.046	.045	.046	.047	.050
	40	.203	.125	.097	.086	.079	.076	.074	.074	.074	.076
	60	.295	.171	.132	.116	.107	.101	.097	.096	.096	.098
	80	.418	.233	.178	.149	.136	.129	.125	.121	.120	.120
	100	.55	.311	.261	.194	.176	.162	.155	.150	.148	.148
	120	.750	.415	.305	.249	.221	.203	.189	.182	.180	.178
i-PENTANE	−20	.017	.010	.0079	.0068	.0062	.0060	.0061	.0065	.0073	.0085
	0	.030	.018	.015	.013	.012	.012	.012	.013	.014	.015
	20	.049	.030	.024	.021	.020	.019	.019	.020	.022	.024
	40	.076	.046	.038	.034	.032	.032	.032	.032	.034	.036
	60	.122	.072	.056	.049	.046	.045	.045	.046	.047	.049
	80	.168	.098	.077	.066	.061	.058	.057	.056	.057	.058
	100	.238	.135	.104	.090	.081	.076	.073	.072	.072	.074
	120	.334	.187	.139	.128	.106	.099	.096	.094	.092	.093
n-PENTANE	−20	.013	.0079	.0062	.0053	.0049	.0047	.0048	.0051	.0056	.0065
	0	.021	.013	.011	.010	.0096	.0095	.0099	.011	.011	.012
	20	.037	.023	.020	.017	.016	.016	.016	.016	.017	.019
	40	.056	.035	.029	.026	.024	.025	.025	.026	.028	.029
	60	.088	.055	.044	.039	.037	.035	.035	.035	.036	.037
	80	.126	.075	.060	.052	.048	.046	.045	.043	.046	.046
	100	.182	.105	.081	.071	.064	.060	.058	.058	.058	.059
	120	.255	.145	.110	.094	.084	.079	.077	.075	.075	.076
HEXANE	−20	.0027	.0020	.0019	.0019	.0020	.0022	.0024	.0027	.0030	.0034
	0	.0056	.0037	.0034	.0034	.0036	.0039	.0041	.0046	.0052	.0058
	20	.011	.0068	.0054	.0047	.0044	.0042	.0045	.0048	.0054	.0062
	40	.016	.011	.0087	.0081	.0080	.0080	.0083	.0086	.0091	.0098
	60	.027	.017	.013	.012	.012	.012	.012	.012	.013	.013
	80	.041	.025	.020	.018	.017	.016	.016	.017	.017	.018
	100	.066	.038	.029	.026	.024	.023	.023	.023	.024	.025
	120	.096	.055	.042	.036	.033	.030	.030	.030	.031	.032

APPENDIX 5B (Continued)

COMPOSITE K VALUES FOR RESERVOIR FLIUDS (CONT'D)

Temperature, °F	Pressure, psia									
	100	200	300	400	500	600	700	800	900	1000
240°F, MBP										
–20	.00028	.00033	.00035	.00039	.00041	.00047	.00050	.00060	.00074	.00078
0	.00096	.0007	.00061	.00069	.00080	.00089	.0010	.0011	.0014	.0016
20	.0023	.0014	.0012	.0010	.00096	.00098	.0011	.0012	.0015	.0017
40	.0036	.0024	.0021	.0020	.0020	.0021	.0022	.0024	.0027	.0029
60	.0060	.0039	.0031	.0026	.0027	.0032	.0037	.0042	.0044	.0046
80	.010	.0061	.0052	.0046	.0045	.0048	.0050	.0053	.0054	.0056
100	.016	.010	.0085	.0074	.0072	.0074	.0076	.0080	.0086	.0088
120	.030	.017	.013	.012	.010	.010	.010	.011	.011	.012
260°F, MBP										
–20	.00018	.00022	.00024	.00027	.00029	.00034	.00035	.00044	.00054	.00058
0	.00064	.00047	.00043	.00049	.00056	.00064	.00072	.00084	.0010	.0012
20	.0016	.00096	.00086	.00072	.00068	.00070	.00078	.00086	.0011	.0013
40	.0025	.0017	.0015	.0015	.0015	.0015	.0016	.0018	.0021	.0021
60	.0043	.0028	.0022	.0019	.0020	.0024	.0028	.0031	.0033	.0036
80	.0072	.044	.0039	.0034	.0033	.0035	.0037	.0040	.0041	.0043
100	.012	.0076	.0063	.0056	.0055	.0056	.0058	.0061	.0066	.0069
120	.022	.013	.0010	.0088	.0079	.080	.0081	.0040	.0092	.0097
280°F, MBP										
–20	.00011	.00015	.00016	.00018	.00020	.00024	.00025	.00032	.00040	.00042
0	.00044	.00032	.00030	.00033	.00040	.00046	.00052	.00060	.00074	.00090
20	.0011	.00067	.00060	.00051	.00048	.00050	.00056	.00077	.00079	.00096
40	.0017	.0012	.0010	.0010	.0011	.0011	.0012	.0013	.0015	.0016
60	.0030	.0020	.0016	.0014	.0014	.0017	.0021	.0024	.0025	.0028
80	.0053	.0032	.0029	.0025	.0025	.0026	.0027	.0031	.0033	.0034
100	.0089	.0055	.0047	.0041	.0042	.0042	.0043	.0047	.0052	.0054
120	.0017	.0095	.0075	.0068	.0060	.0062	.0064	.0070	.0072	.0075
300°F, MBP										
–20	.000070	.000097	.00011	.00013	.00014	.00017	.00018	.00023	.00028	.00030
0	.00028	.00022	.00020	.00024	.00029	.00033	.00037	.00044	.00054	.00066
20	.00076	.00046	.00043	.00036	.00034	.00036	.00041	.00057	.00060	.00072
40	.0012	.00081	.00074	.00074	.00078	.00082	.00090	.00095	.0011	.0012
60	.0021	.0014	.0011	.00099	.0010	.0013	.0015	.0017	.0019	.0021
80	.0038	.0024	.0021	.0019	.0018	.0020	.0021	.0023	.0024	.0025
100	.0066	.0041	.0034	.0031	.0032	.0032	.0034	.0035	.0040	.0042
120	.013	.0072	.0057	.0051	.0045	.0047	.0049	.0054	.0056	.0060

6

WATER-HYDROCARBON PHASE BEHAVIOR

Water and hydrocarbons are natural companions. Hydrocarbons are formed in a water environment and are in equilibrium with water at reservoir conditions.

Liquid water and hydrocarbons are essentially immiscible in each other. Their slight mutual solubility is important for hydrate prediction but has no measurable effect on their vapor-liquid equilibrium behavior. At 25°C and atmospheric pressure the mol fraction of a paraffin like n-pentane in water is about 10^{-5}. Volume 3 discusses solubility parameters in significant detail.(6.1)

If both liquid water and hydrocarbons - and gas - are present in a system there will be two liquid phases. The amount of water vapor in the gas will be governed by gas composition and the vapor pressure of the liquid water phase.

Two calculations are primary to the water-hydrocarbon system: calculation of the water content of the gas and prediction of the conditions under which hydrates will form. Prevention of hydrates by dehydration or inhibition is important in petroleum operations.

WATER CONTENT OF GASES

The water content of a gas depends on system pressure and temperature and the composition of the water containing gas. The published record in this area goes back to the work of Poynting in 1881. Current methods of calculation include the use of:

1. Partial pressure and partial fugacity relationships.
2. Empirical plots of water content versus P and T.
3. Corrections to (2) for the presence of contaminants like hydrogen sulfide, carbon dioxide and nitrogen.
4. PVT equations of state.

Partial Pressure and Fugacity

If Raoult's Law (discussed in Chapter 5) is applied to water, it is written

$$P\, y_w = P_v\, x_w \tag{6.1}$$

Where: P = absolute system pressure
y_w = mol fraction water in the vapor phase
P_v = vapor pressure of water at system temperature
x_w = mol fraction water in the liquid water phase (= 1.0)

The liquid mol fraction can be taken as unity because of the immiscibility of the liquid phases. Thus, for a known pressure and water vapor pressure the mol fraction water in the vapor phase is found from Equation 6.1.

However, this equation is valid only at low pressure where the ideal gas law is valid. Equation 6.1 is recommended for system pressures up to about 400 kPa [60 psia].

Empirical Plots

Until the early 1950's most of the commercial natural gas had been processed in NGL units for its heavier components and most of its contaminants. For this *lean, sweet natural gas* the log of water content (W) was plotted versus P and T. It was found that a plot of log W versus 1/T approximated a straight line at a given pressure: most plots use log W versus T.

Figures 6.1 and 6.1(a) are this type of plot. They are a composite based on all earlier charts and other data available to the author.(6.2-6.4) The water content shown is the maximum gas can hold at the P and T shown. It is fully saturated; the relative humidity is 100% or, stated another way, the temperature is the water dewpoint temperature of the gas at the concentration and pressure shown.

The concentrations in mass per unit standard volume are related to mol fraction, y, as follows:

$$\text{kg water}/10^6 \text{ std m}^3 = (y_w)(18)(41\,740) = 751\,320\, y_w$$

$$\text{lbm water/MMscf} = (y_w)(18)(2636) = 47\,448\, y_w$$

Where: 18 = mol wt of water
41 740 = kmol gas/10^6 std m^3 (@ 15°C and 100 kPa)
2636 = lb-mol gas/MMscf (@ 60°F and 14.7 psia)

Comparison of the water content at various points in the system serves many purposes. One is to determine the water loading for dehydration. Another is to establish how much water has been condensed as liquid in the line.

Suppose at one point in a system the water content (from a correlation) is 200 kg/million std m^3. At some point downstream the same correlation gives a maximum water content of 100 kg/million std m^3. What is the conclusion? If no water has been withdrawn, there is 100 kg of liquid water in the line per million std m^3 of gas flowing. This water is available to form hydrates unless it is removed or inhibited. It also is a primary source of corrosion-erosion problems. The purpose of dehydration is to prevent such water condensation.

Figures 6.1 and 6.1(a) are satisfactory for most applications involving lean, sweet natural gas. The likely error of 6-10% probably is more accurate than the data the correlation is being applied toward. However, as the amounts of carbon dioxide and hydrogen sulfide increase the accuracy becomes poorer. It is good practice to make a correction for these contaminants even though it may be small when concentrations and pressures are low.

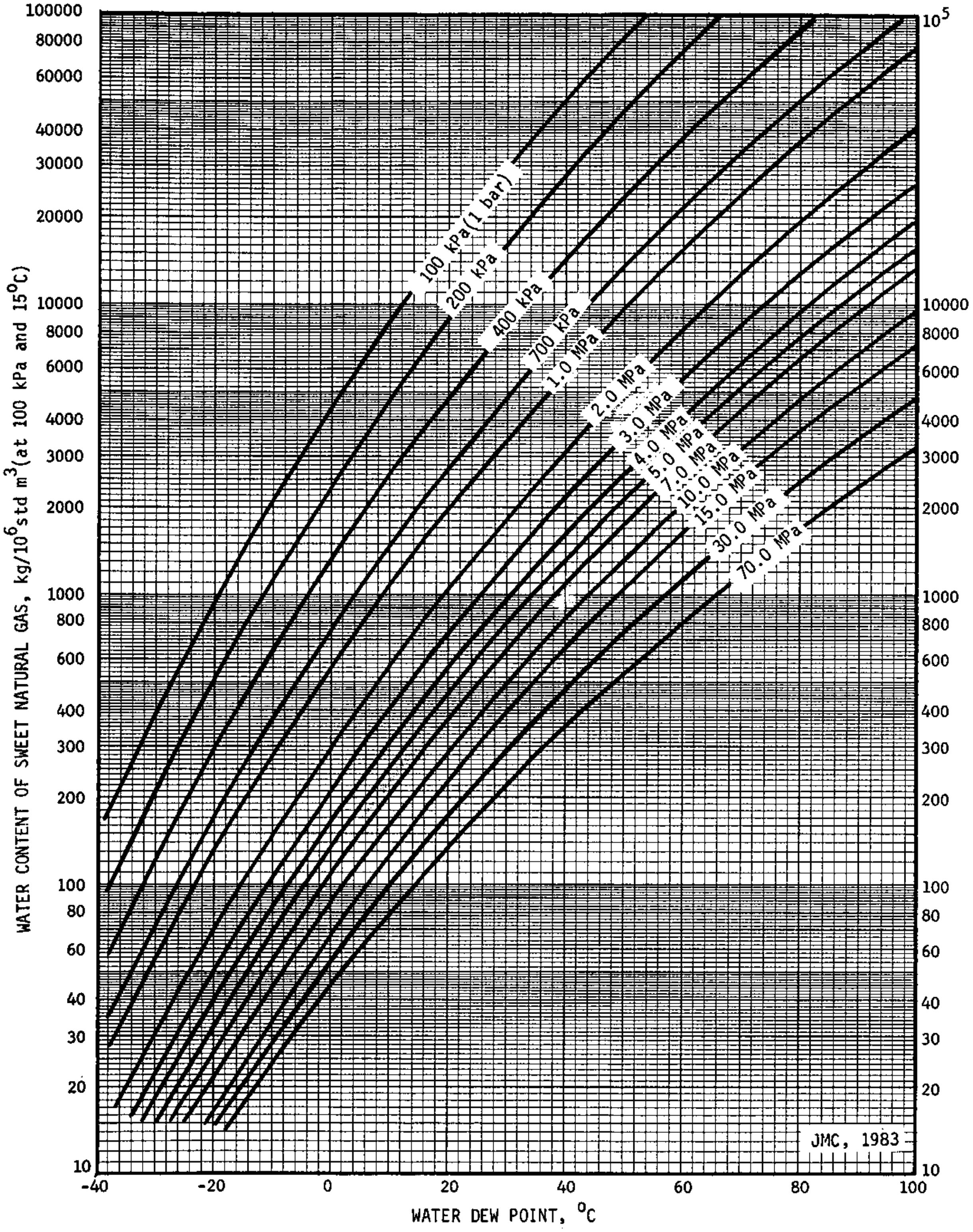


Figure 6.1 Water Content of Sweet, Lean Natural Gas

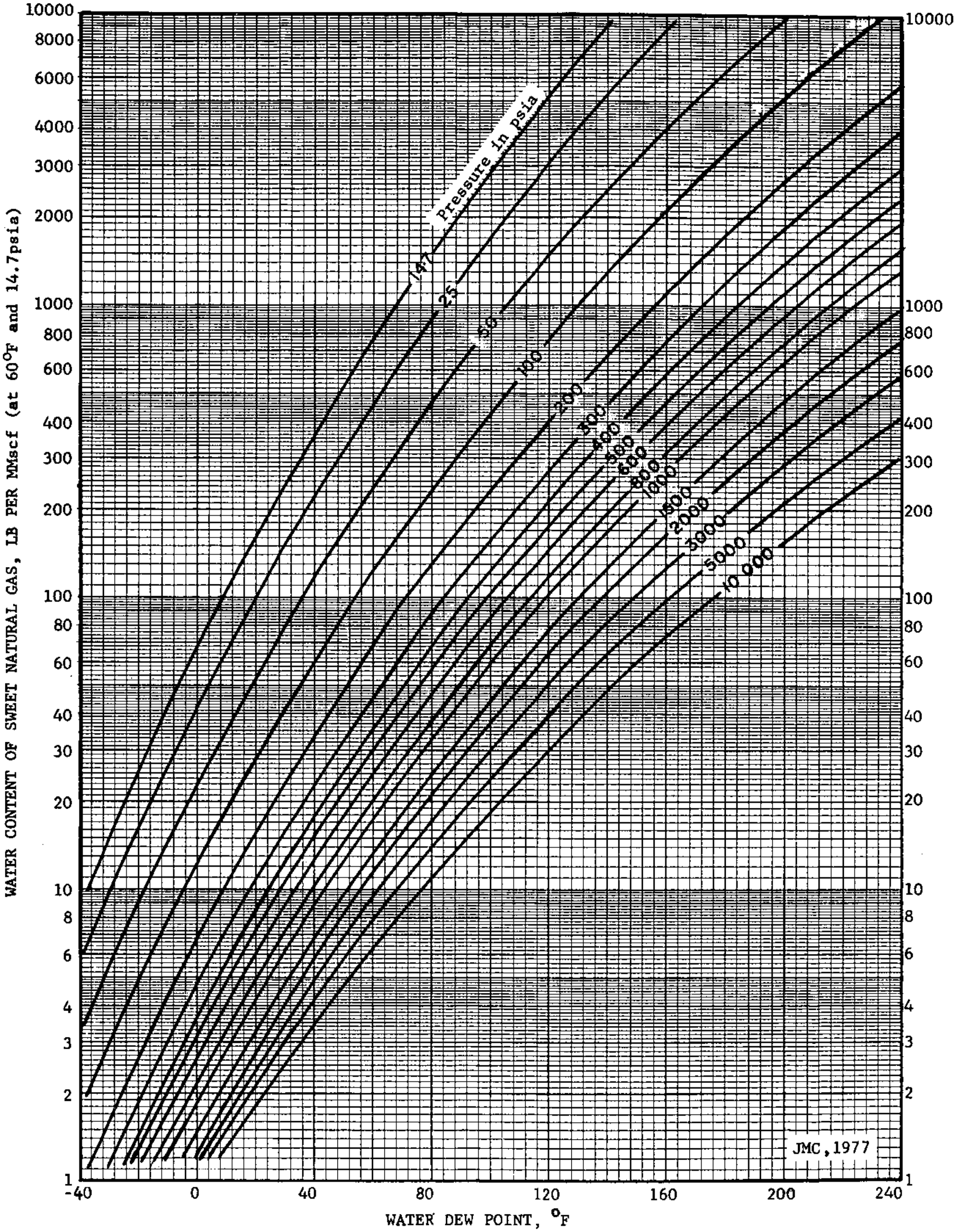


Figure 6.1(a) Water Content of Sweet, Lean Natural Gas

WATER CONTENT OF SOUR GASES

There are several available methods for determining the water content of gases containing H_2S and CO_2. Two of these use Equation 6.2 by multiplying the water content of the pure sour component by its mol fraction in the mixture. Figures 6.2 and 6.3 show what is called the "effective water content." These curves were based on the pure sour component data but were adjusted so that Equation 6.2 matched measured data on high pressure streams containing more than 20% H_2S.

As we have compared the results of this method with others we find that it is consistently high. It is the maximum possible value that can occur within a range of possible values.

$$W = y\,W_{hc} + y_1\,W_1 + y_2\,W_2 \tag{6.2}$$

Where:
W = water content of gas
W_{hc} = water content of hydrocarbon part of gas from Figure 6.1
W_1 = water content of CO_2 from Figure 6.2 or 6.4
W_2 = water content of H_2S from Figure 6.2 or 6.5
$y = 1 - y_1 - y_2$,
y_1 = mol fraction of CO_2,
y_2 = mol fraction of H_2S

A second correlation using Equation 6.2 is based on the data of Sharma discussed on the following pages. Figures 6.4 and 6.5 were obtained by cross-plotting and smoothing Sharma's binary data for methane, CO_2, and H_2S.*(6.5)*

SRK Sour Gas Correlation

Figure 6.6 is another correlation for estimating sour gas water content.*(6.6)* The charts shown were calculated from the SRK equation of state assuming that the hydrocarbon portion of the gas was methane. It was assumed also that CO_2 had 75% of the water content of H_2S at the same conditions. One thus multiplies the percent CO_2 by 0.75 and adds the result to the percent H_2S to use the charts. The water content shown in API bbl/MMscf can be converted as follows:

$$\text{lbm/MMscf} = (350)(\text{bbl/MMscf})$$

$$\text{kg}/10^6\ \text{std m}^3 = (5543)(\text{bbl/MMscf})$$

Figure 6.6 is a quick way to estimate sour gas water content. As shown, however, it also is limited somewhat by its reliance on binary data.

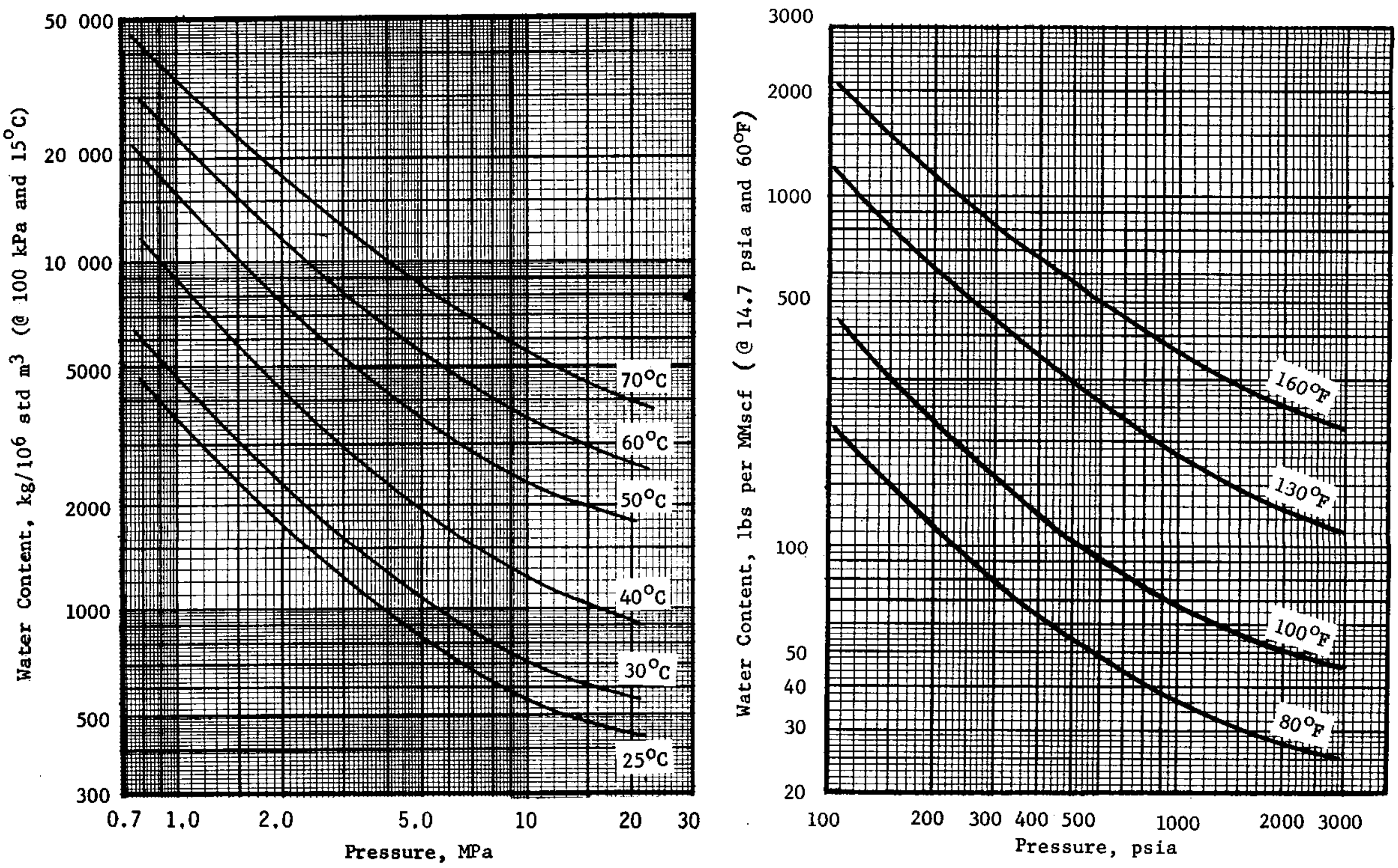


Figure 6.2 Effective Water Content of CO_2 in Saturated Natural Gas Mixtures

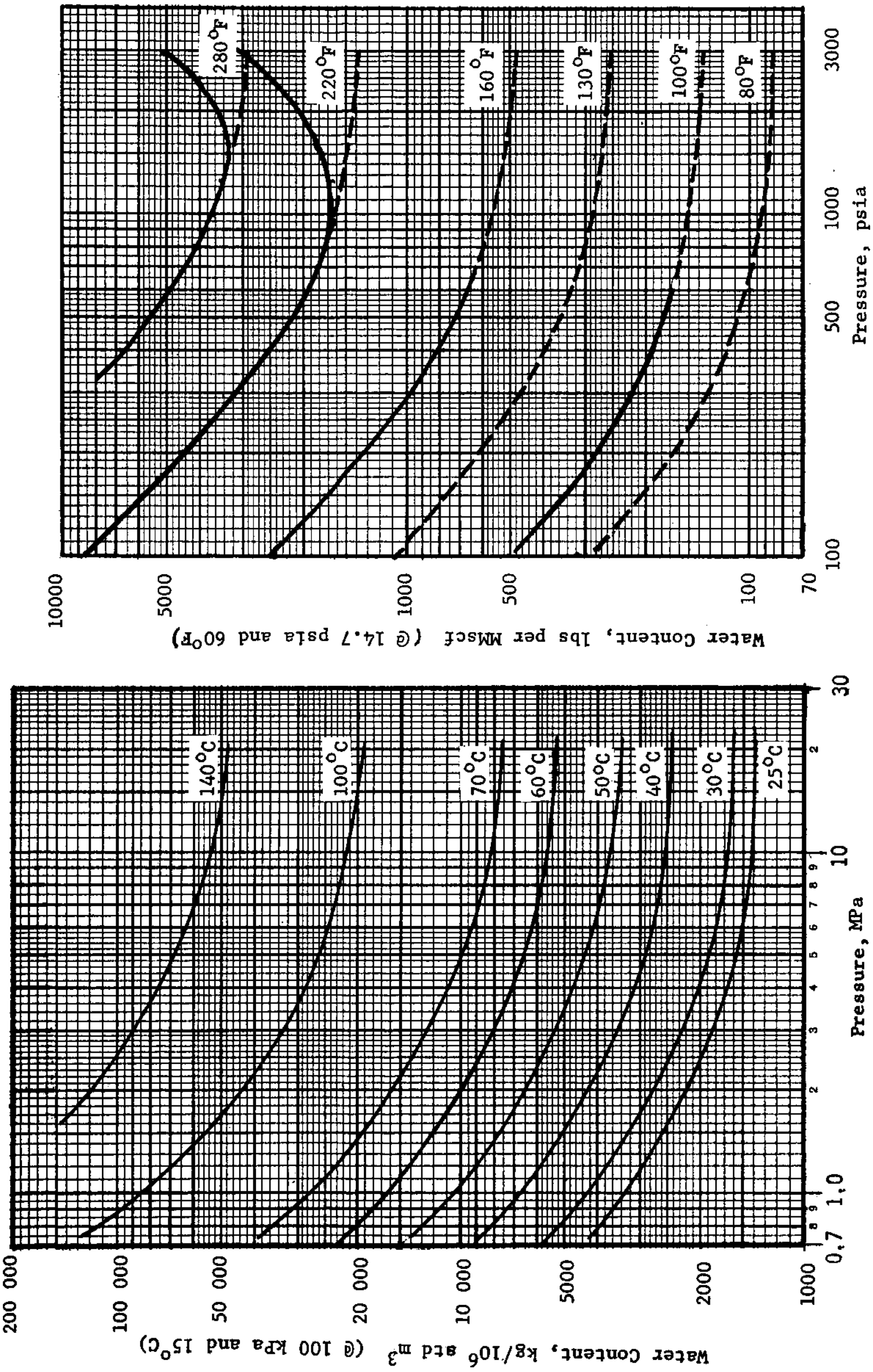


Figure 6.3 Effective Water Content of H_2S in Saturated Natural Gas Mixtures

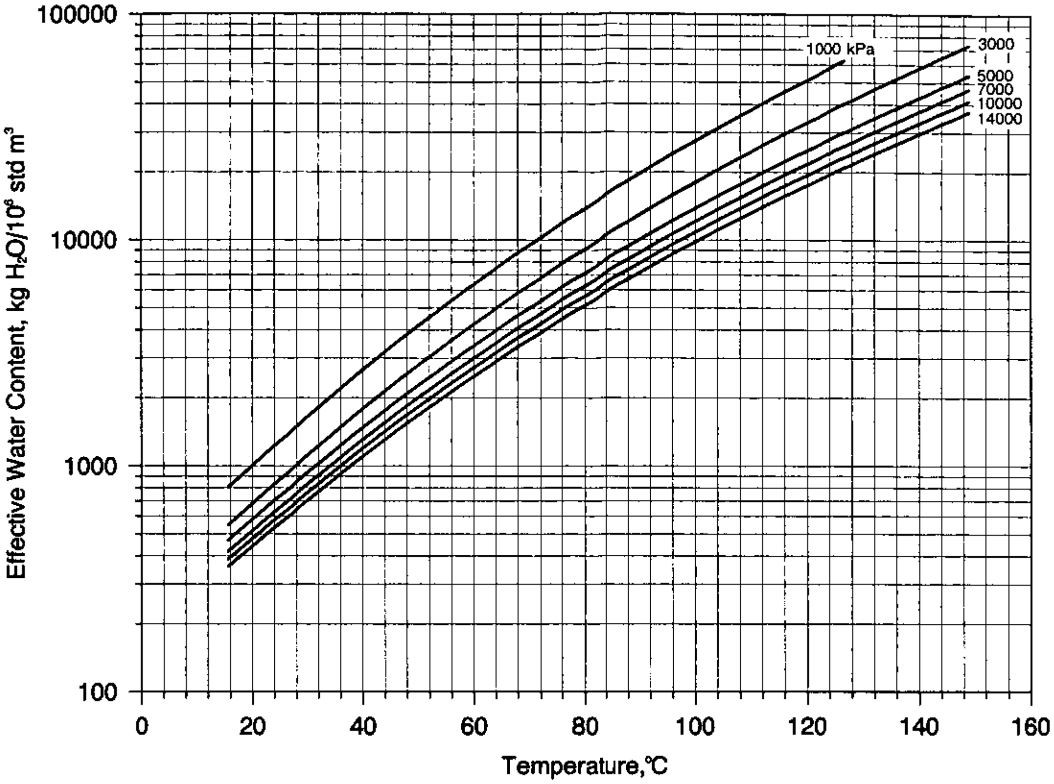


Figure 6.4 Water Content Contribution of CO_2

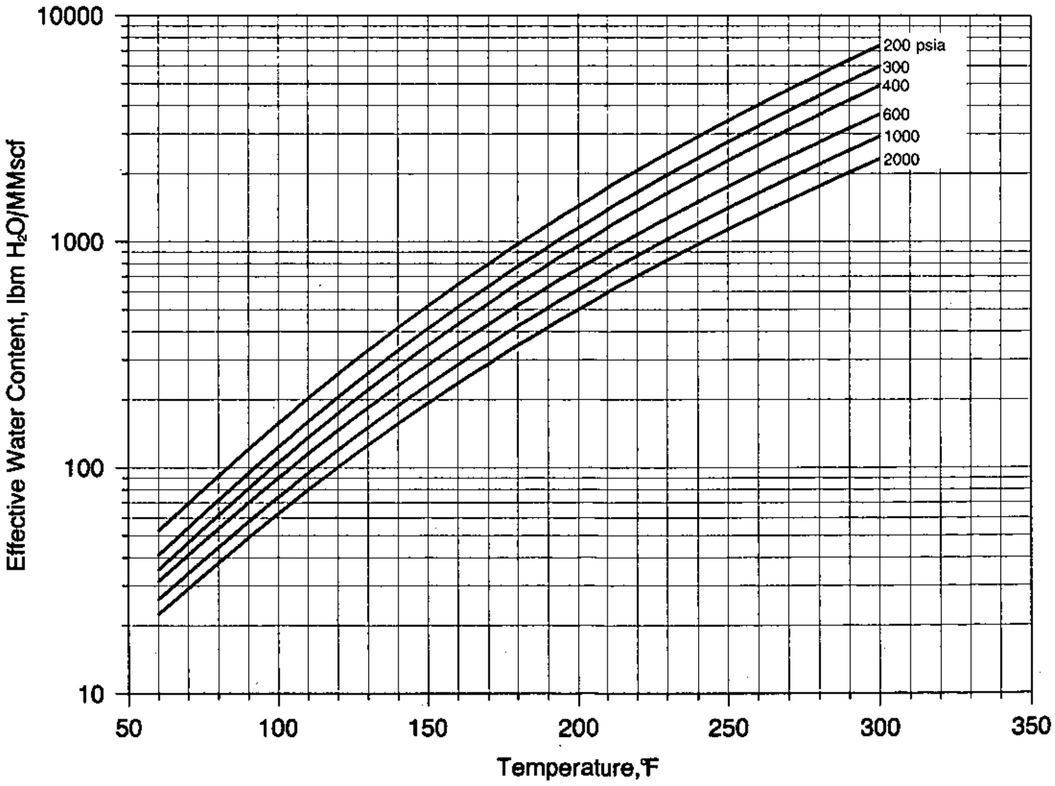


Figure 6.4(a) Water Content Contribution of CO_2

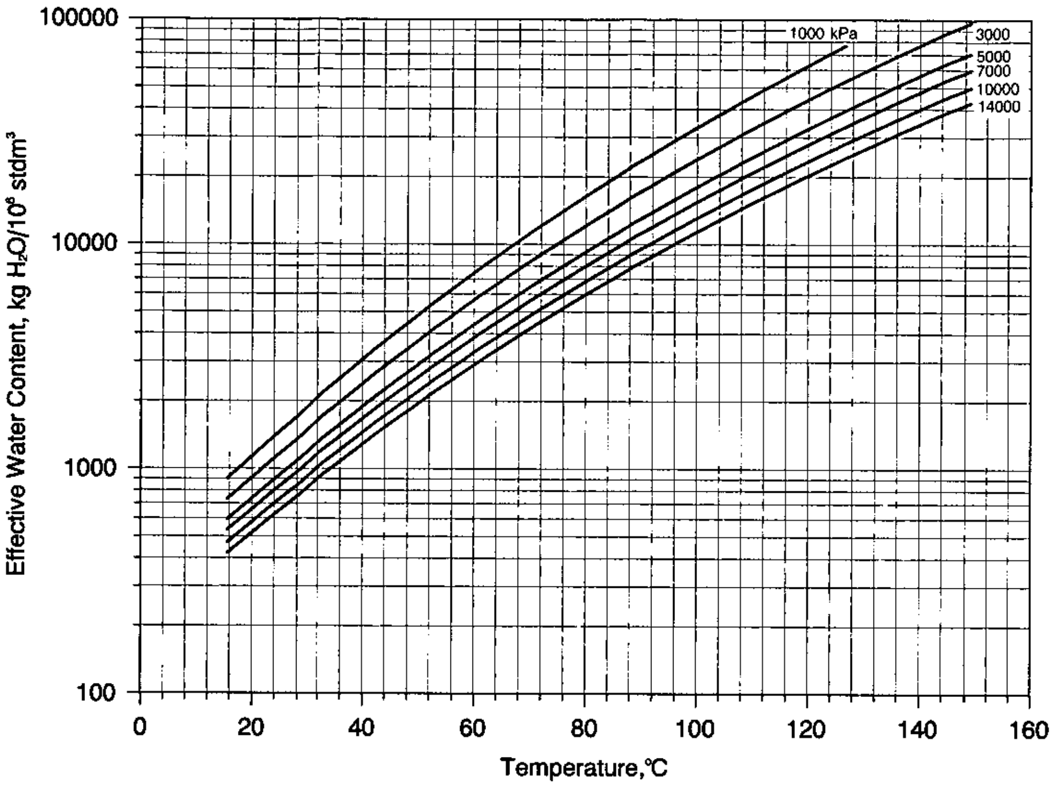


Figure 6.5 Water Content Contribution of H_2S

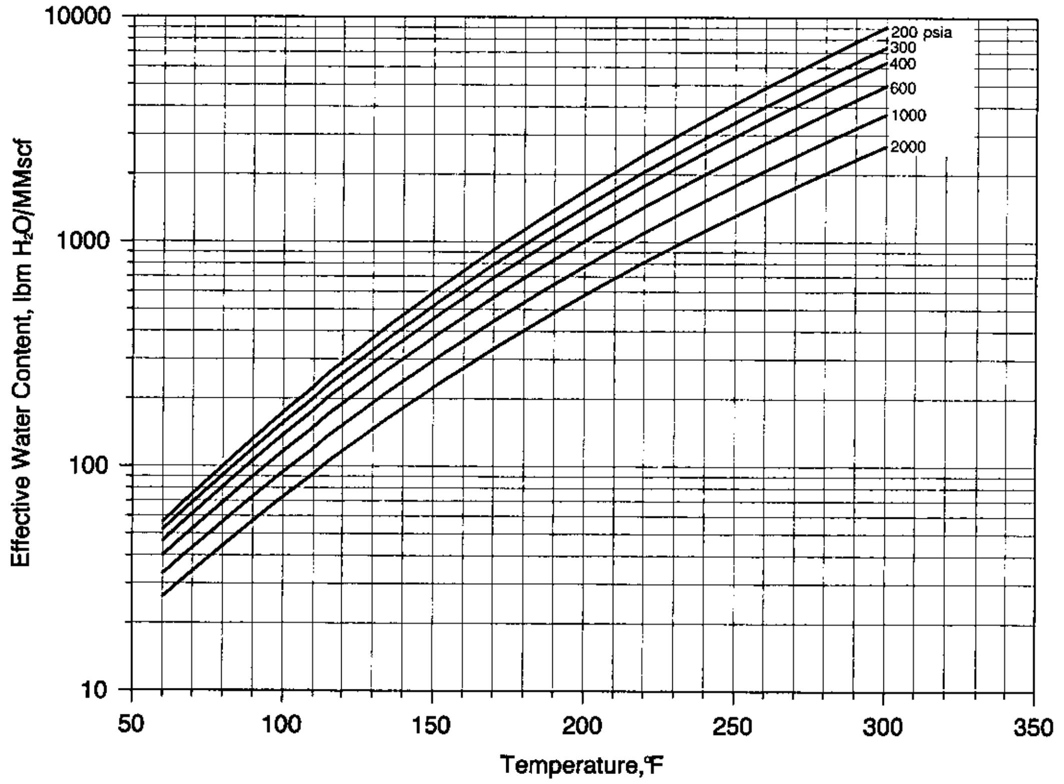


Figure 6.5(a) Water Content Contribution of H_2S

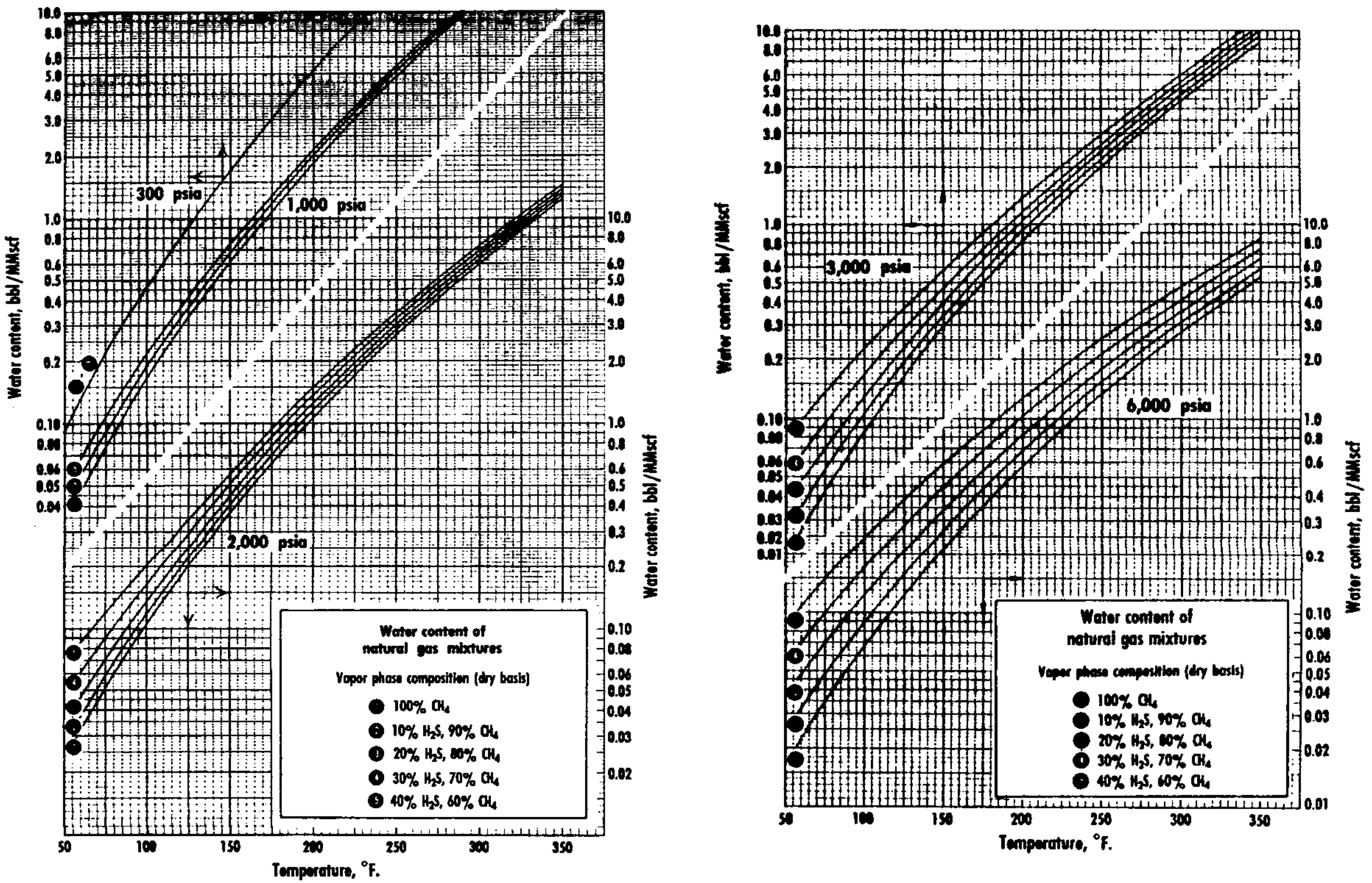


Figure 6.6 Another Correlation for Sour Natural Gases

Another Equation of State Approach

Suresh Sharma and the author have combined the Eykman Molecular Refraction concepts with standard physical chemistry equations to provide a basic correlation for sour gases. It too is empirical. It is more tedious manually than the others but represents a reliable alternative approach in the suite of methods presented. All of the figures shown herein are of course unnecessary when using the computer program for this method.

The first workable method for predicting water content was based on the concepts of EMR shown in Chapter 3 and standard physical chemistry principles.(6.7, 6.8) The method has been designed as a computer solution but can be performed manually using Figures 6.7-6.9

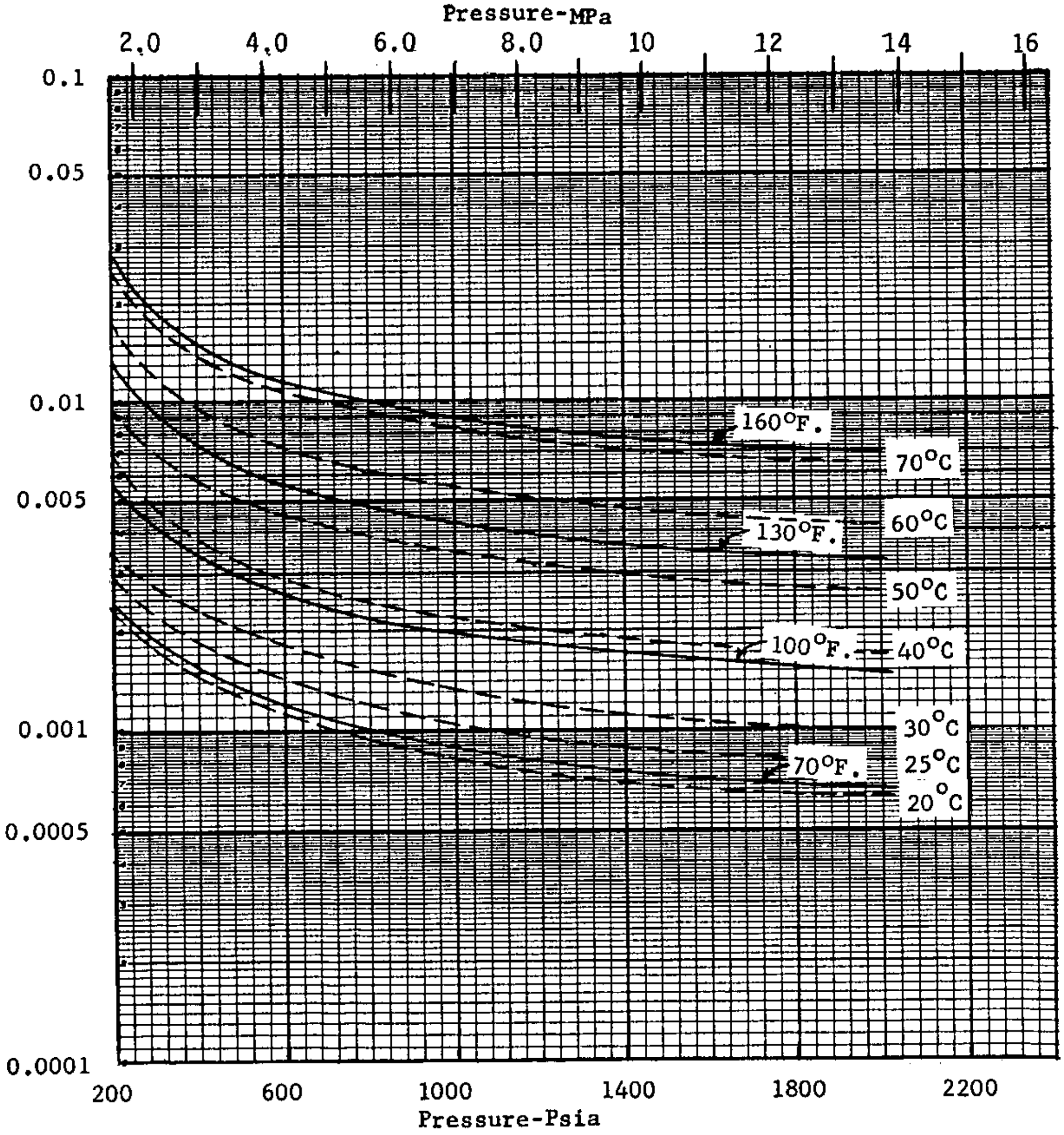


Figure 6.7 **Constant ’k" as a Function of Pressure and Temperature**

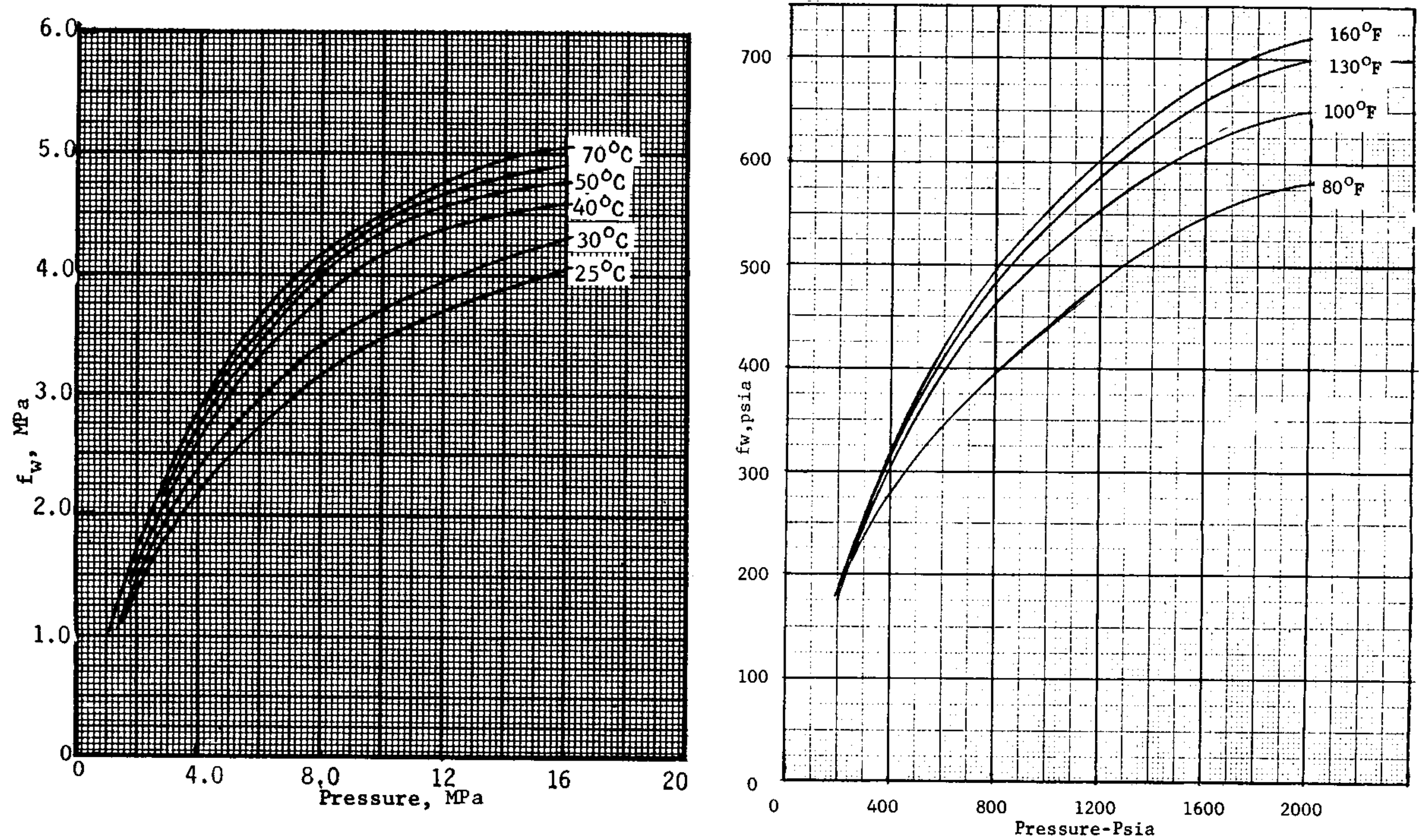
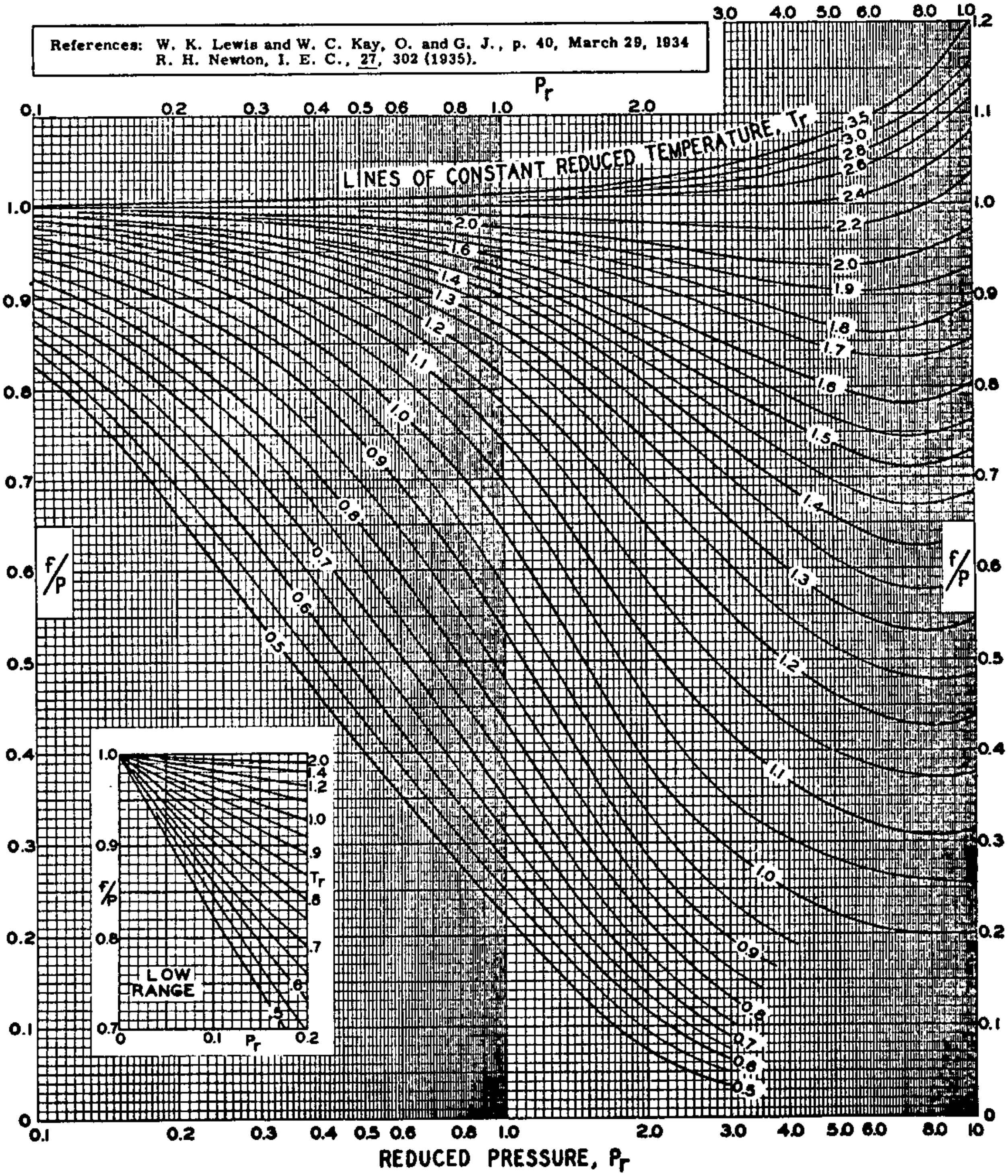


Figure 6.8 Water Fugacity as a Function of Pressure and Temperature



References: W. K. Lewis and W. C. Kay, O. and G. J., p. 40, March 29, 1934
R. H. Newton, I. E. C., 27, 302 (1935).

Figure 6.9 General Fugacity Coefficient Chart

The procedure is as follows.

1. Calculate the critical pressure and temperature of the mixture, using the technique of McLeod and Campbell summarized in Chapter 3, which utilizes molecular refraction as a third parameter.
2. Calculate reduced pressure and temperature for the gas system. Determine "Z" from EMR approach.
3. Find the value for constant "k" from Figure 6.7, or calculate by the equation.

$$k = \left(\frac{P_w^o}{P}\right)\left(\frac{f_w^o/P_w^o}{f_w/P}\right)\left(\frac{P}{P_w^o}\right)^{0.0049} \tag{6.3}$$

Where: P_w^o = vapor pressure of water at system temperature (T)
P = system pressure
f_w^o = fugacity of water at P_w^o and T
f_w = fugacity of water at P and T
0.0049 = semi-empirical constant

4. Determine the fugacity of water (f_w) from Figure 6.8, or calculate from Figure 6.9, using P_c and T_c for water.
5. Determine value of (f/P), the fugacity coefficient from Figure 6.9, using the reduced parameters from Step 2. Calculate "f."
6. Determine the water content by the equation

$$y = k\,(f_w/f)^Z \tag{6.4}$$

Where: y = mol fraction of water in vapor

In solving Equation 6.4 note that the Z must be from the EMR combination rule and no other source.

I use all of the above methods when calculating a sour gas water content. The reason – the random behavior of such systems. The repeatability of data is very poor, even in the laboratory. One should recognize this in applying such information.

You likely will get four different answers with the four correlations above. If dehydrator design or operation is involved, I suggest you use the highest of the results to be on the safe side.

Effect of Nitrogen and Heavy Ends

Nitrogen will hold less water than methane. At pressures to about 7.0 MPa [1000 psia] the water content of nitrogen is about 6-9% less than for methane. This deviation increases with pressure. Thus, including nitrogen as a hydrocarbon is practical and offers a small safety factor.

The presence of heavy ends tends to increase the water capacity of the gas. Once again the deviation is relatively small at normal system pressures. The nitrogen and heavy end effects tend to cancel out each other in many production systems.

Example 6.1: Calculate the saturated water content of a gas with the analysis shown below at 1100 psia and 120°F. EMR $Z = 0.79$, $P_c = 867$ psia, $T_c = 436$°R.

Comp.	y_i
N_2	0.0046
CO_2	0.0030
H_2S	0.1438
C_1	0.8414
C_2	0.0059
C_3	0.0008
iC_4	0.0003
nC_4	0.0002
	1.0000

1. From Figure 6.1(a), $W = 97$ lbm/MMscf
2. $y_1 = 0.0030$, $y_2 = 0.1438$
   From Figure 6.1(a), $W_{hc} = 97$ lbm/MMscf
   From Figure 6.2, $W_1 = 130$
   From Figure 6.3, $W_2 = 230$
   $W = (0.8532)(97) + (0.003)(130) + (0.1438)(230) = 116$ lbm/MMscf
3. From Figure 6.4(a), $W_1 = 120$
   From Figure 6.5(a), $W_2 = 150$
   $W = (0.8532)(97) + (0.003)(120) + (0.1438)(150) = 105$ lbm/MMscf
4. Effective % $H_2S = (0.3)(0.75) + (14.38) = 14.6\%$
   From Figure 6.6, $W = (350)(0.31) = 109$ lbm/MMscf
5. From Figure 6.7, $k = 0.0031$
   From Figure 6.8, $f_w = 555$
   $P_r' = 1100/867 = 1.27$, $T_r' = 580/436 = 1.33$
   $f/P = 0.85$, $f = (0.85)(1100) = 935$
   $y = (0.0031)(555/935)^{0.79} = 0.00205$
   $W = (0.00205)(47\,448) = 97.3$ lbm/MMscf

In Example 6.1 the water content from Equation 6.2 is greater than from Figure 6.1. This is expected for the sour gas in question. From my experience, a value as high as 116 is not likely but it does happen. The value of 97 represents a practical minimum.

Using probability principles, the numbers would be regarded as a distribution. The mode is the most likely value but any value within the range shown has some probability of occurring. This fact must be accepted in making any decision resulting from this calculation. Merely averaging the numbers or arbitrarily picking one as "sacred" is not consistent with the true facts of the matter.

One can estimate the water content, or relative saturation of the gas entering a dehydrator, from the water content correlations.

Example 6.2: Water is separated in an inlet scrubber to a compressor plant at 7.0 MPa and 35°C. The gas is then compressed and aftercooled to 14.0 MPa and 50°C before entering a dehydrator. Is the gas saturated?

From Figure 6.1, water content at 7.0 MPa and 35°C = 810 kg/10^6 std m^3

From Figure 6.1, water content at 14.0 MPa and 50°C = 1050 kg/10^6 std m^3

The gas is capable of holding 1050 kg but has only 810 kg. Therefore, it is not saturated. There is less than the maximum amount of water to be removed. Also, there is less driving force available to aid water removal. One must consider both factors.

In other cases the maximum water capacity of the gas downstream may be less than that upstream. In this case water must condense in the section involved. The water content correlation may be used to estimate the amount of liquid water present.

If no separation occurs between the wellhead and the dehydration plant, it is reasonable to assume that the gas was saturated at the formation pressure and temperature.

Saturated Water Content in Equilibrium with Hydrates

Figure 6.1 is based on the assumption that the condensed water phase is a liquid. However, at temperatures below the hydrate temperature of the gas, the "condensed" phase will be a solid (hydrate). The water content of a gas in equilibrium with a hydrate will be lower than equilibrium with a metastable liquid.

Hydrate formation is a time dependent process. The rate at which hydrate crystals form depends upon several factors including gas composition, presence of crystal nucleation sites in the liquid phase, degree of agitation, etc. During this transient "hydrate formation period" the liquid water present is termed "metastable liquid." Metastable water is liquid water which, at equilibrium, will exist as a hydrate.

References 6.9-6.11 present experimental data showing equilibrium water contents of gases above hydrates. Data from Reference 6.10 is presented in Figure 6.10. For comparative purposes, the "metastable" water content of a sweet gas from Figure 6.1 is also shown. The water content of gases in the hydrate region is a strong function of composition. Figure 6.10 should not be extrapolated to other compositions.

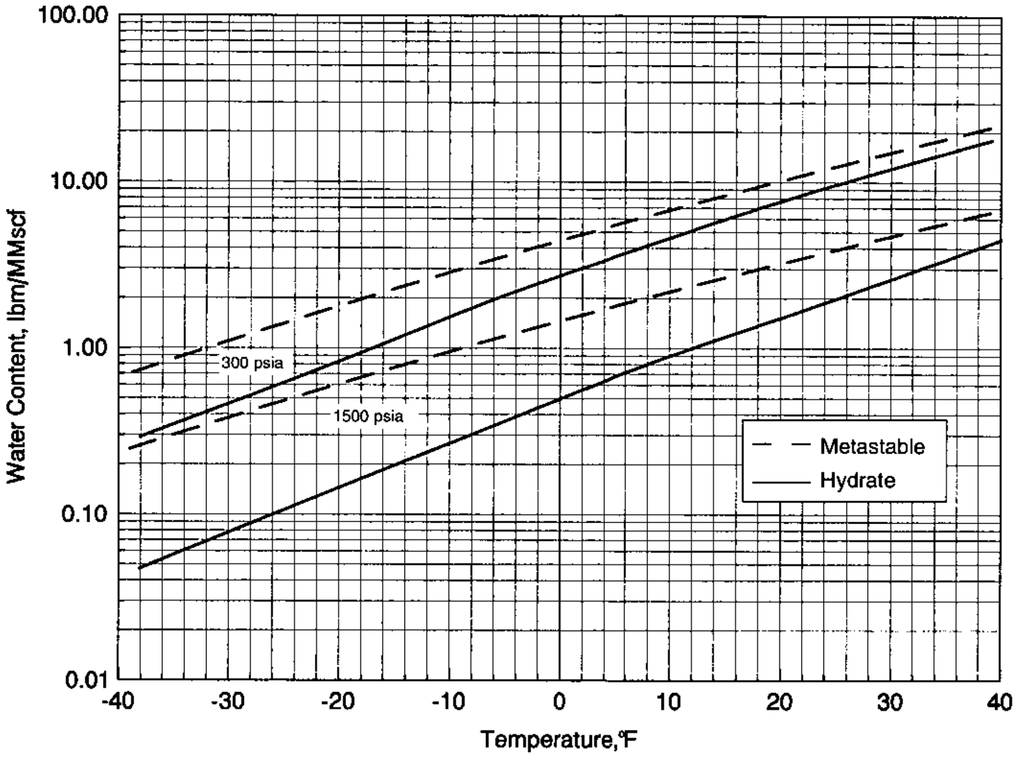


Figure 6.10 Water Content of 5.31% C_3 - 94.69% C_1 Gas in Equilibrium with Hydrate

When designing dehydration systems, particularly TEG systems to meet extremely low water dewpoint specifications, it is necessary to determine the water content of the gas in equilibrium with a hydrate using a correlation like that presented in Figure 6.10. If a metastable correlation is used, one will overestimate the saturated water content of the gas at the dewpoint specification. This, in turn, may result in a dehydration design which is unable to meet the required water removal. Where experimental data is unavailable, utilization of a sound thermodynamic-based correlation can provide an estimate of water content in equilibrium with hydrates.

WATER MONITORS

Measurement of the water content of gas is a normal part of the gas conditioning process. There are many instruments on the market for this purpose, in a wide price range. The choice is not routine. Some are difficult, or certainly inconvenient, to calibrate. Some will not stand hard physical treatment. Others are not suitable for hazardous atmospheres.

The grandfather of this family of instruments is what is often called the Bureau of Mines Dewpoint Tester. It consists of a polished mirror that can be cooled at a steady rate. When the first drops of liquid "dew" appear visually on this mirror the technician records the temperature and pressure. It is simple and rugged. But, it depends on the visual judgment of the technician. Different people get different results.

One problem is the fact that hydrocarbons often condense at a higher temperature than water and flood the mirror. That little opaque spot may be hard to detect. One solution for this is to place an activated carbon chamber in the test line ahead of the tester. Carbon has little affinity for water. Once it has been saturated the gas leaving will be representative of the gas being tested. At best though this type of tester is not a completely satisfactory instrument when used as a guide in custody transfer operations.

There is also a visual type based on expanding gas across a valve to produce a fog. One finds the vanishing point of the fog to determine the dewpoint. It is a low pressure instrument requiring gas expansion.

A more sophisticated form of the mirror concept uses a gold plated mirror bonded to a copper thermocouple holder. As this assembly is cooled an optical sensing bridge detects the change in light level that occurs when dew forms on the mirror.

One of the better (and more expensive) instruments uses two hygroscopically coated quartz crystal oscillators which vibrate at nine million cycles per second. Water vapor is alternately adsorbed and desorbed on each crystal. The mass change involved is reflected by changes in frequency, which are compared electronically. Each crystal is exposed alternately to the moist sample gas for 30 seconds while the other is exposed to a dry reference gas.

Still another instrument uses an anodized aluminum strip providing an aluminum oxide layer on which a thin layer of gold has been deposited. Two conductors are used. When water adsorbs on the oxide surface it changes the dielectric properties. The impedance is measured and converted to water content in equilibrium with the sensor.

There are many variations of the electrolytic moisture analyzer available. The exact system varies with the manufacturer. One type consists of a glass tube with two platinum wires wound in a double helix on the inside surface. The space on this surface, between the wires, is coated with phosphorous pentoxide (P_2O_5). When moisture wets the P_2O_5 an electrolysis current is produced as a potential is applied to the wires. The magnitude of this current is used to measure water content.

Another instrument measures water content by measurement of the heat energy exchanged when gas is adsorbed or desorbed on the surface of a solid adsorbent. The sample is split into two streams, one of which is thoroughly dried.

One also can measure water content in a chromatograph. In one method the gas is passed through calcium carbide. The water reacts producing equivalent amounts of acetylene which can be measured in the chromatograph. Another chromatographic method measures the water content using two identical columns coated with glycerol.

Many of the instruments described briefly above may be satisfactory in a given case. None are perfect. Some require calibration which at best is a nuisance. If you have sour gases the choice becomes very limited and none may be truly satisfactory. The electrolytic cells are particularly susceptible to poisoning.

WATER CONTENT APPLICATIONS

Water content correlations are used primarily for dehydration calculations and to determine how much water (if any) will condense from the gas. The latter involves considerations of disposal, corrosion/erosion and hydrate inhibition.

The amount of condensed water is relative small. The real danger is underestimating the quantity. Be sure that your estimates are on the "safe" side of the possible range of values. The additional capital expenditure normally will be trivial. There is a tendency to predict flowing temperatures lower than they turn out to be. Notice in Figure 6.1 that the water content is a log scale. A change in temperature of only 10% in the ambient range causes about a 33% increase in water content. A common cause of poor dehydrator performance is underprediction of the water loading.

References 6.1-6.12 all address water content correlations; 6.12 is an excellent review of water content correlations.

GAS HYDRATES

Gas hydrates are a form of clathrate first discovered by Davy in 1810. Villard in 1888 presented performance data on hydrocarbon hydrates. Thus, the scientific study of these physical compounds has been very extensive.

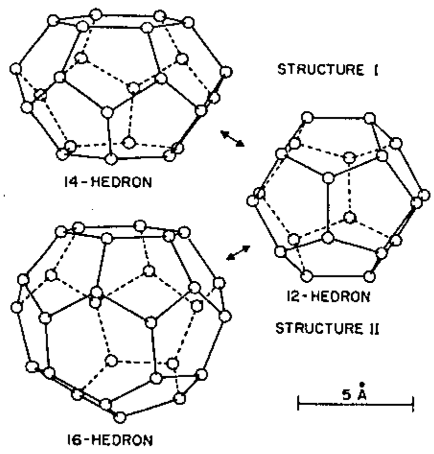


Figure 6.11 Schematic of Natural Gas Hydrate Lattice

A clathrate is any compound wherein guest molecules are entrapped in a cage structure composed of host molecules. With the natural gas hydrate the lattice is formed by water molecules as shown in Figure 6.11. The circles represent water molecules and the lines hydrogen bonds. Contained within each lattice is a series of cavities or cages that must be occupied by enough guest molecules to stabilize this lattice crystal.

X-ray diffraction analysis shows the gas hydrate crystal structure to be a derivative of the pentagonal dodecahedron, a twelve sided structure whose faces have five edges. Since the bonding angle is 108° and that of ice is 109.5°, the structure was long thought to be the probable basic hydrate building structure; yet, no orderly packing arrangement can be made with the regular pentagonal dodecahedron. Claussen proposed two separate crystal lattices of modified dodecahedron configurations designated as Structures I and II.

The basic lattice of Structure I has a cell constant of 12 A° and contains forty-six water molecules arranged to form eight voids, two of which are pentagonal dodecahedra. The remaining six voids are somewhat larger cavities having fourteen faces. Designated as tetrakaidecahedron, each large void has twelve pentagonal faces and two hexagonal faces. Molecules of methane are able to enter either size void, while a larger hydrocarbon such as ethane can be entrapped only in the larger voids. During formation it is also possible that some cavities are left unoccupied due to the lattice forming and closing when no hydrocarbon molecule is properly oriented. Other hydrocarbon molecules such as propane and larger are not entrapped in this structure due to their unfavorable size.

A second crystal form, Structure II, designated as a pentagonal dodecahedral-diamond lattice, is formed in the presence of hydrocarbons larger than ethane. For this structure, a unit cell having 136 water molecules and a cell constant of 17 A° is present. There are sixteen small pentagonal dodecahedral voids and eight larger voids. The large voids, termed hexakaidecahedron, have four hexagonal and twelve pentagonal faces. Entrapment of propane, n-butane, and isobutane occurs in these structures as well as possible entrapment of ethane and methane. It can be surmised that the absence of propane and heavier molecules would cause only Type I hydrates to be formed, while the presence of both ethane and propane would result in both. This is possible since the availability of excess water and hydrocarbons during hydrate formation may be limited.

It is apparent from the above that molecular size is an important factor. A second important factor is gas solubility. Solubility primarily affects the rate of clathration since it governs the statistical probability that a given molecule will be present when the lattice is closing. Hence, the greater the solubility of a given component, the faster a hydrate will form.

It is believed that the guest molecule dictates which type of structure will be formed, and its solubility governs the rate of formation. Size also affects the formation rate. This may be seen from the hydrate behavior of methane, hydrogen sulfide, and propane. At a given temperature the pure methane hydrate requires a higher pressure to form than the propane hydrate, although its solubility in water is considerably greater than that of propane. It is much easier for a small molecule to avoid entrapment as the cage is closing than a larger one. There are more methane molecules present, but their more active, random movement, and smaller size make clathration more difficult. The similarly sized hydrogen sulfide molecule is far more soluble than methane, forms in the same structure, and requires about one-twentieth the time to hydrate.

The actual imprisonment conditions are considered satisfied when the gas molecule is properly oriented within the water structure such that the aggregation of water and gas molecules have best utilized the available space. This corresponds to the state of lowest potential energy for the aggregation such that attractive, repulsive, rotational, and bonding forces are as much in equilibrium as possible. Once formed, the hydrogen bonded structure will not be broken until these forces become so unbalanced that the strength of the hydrogen bond is exceeded and fracturing occurs.

The guest molecules provide stability to the lattice structure in the same manner that liquid in the pores of a subsurface sand prevents subsidence. Not all cages must be full. Therefore, there is no specific formula for hydrates.

The following is representative of typical hydrate crystals formed by a given component.(6.13)

$$CH_4\ 5.9\ H_2O\ ,\quad C_2H_6\ 8.2\ H_2O\ ,\quad H_2S\ 6.1\ H_2O\ ,\quad CO_2\ 6.0\ H_2O$$

$$N_2\ 6.0\ H_2O\ ,\quad C_3H_8\ 17.0\ H_2O\ ,\quad i\text{-}C_4H_{10}\ 17.0\ H_2O$$

Normal butane can form a hydrate but it is very unstable. All paraffin hydrocarbons larger than the butanes are nonhydrate formers.

A natural gas mixture forms hydrates more readily than any pure component. It is necessary to have all three sizes of cages relatively full in order to stabilize the lattice. The cell constant quoted above is the length of one side of a cube which would fit into the cavities. So a mixture of molecular sizes is conducive to hydrate formation.

The individual hydrate crystals form in the liquid water phase. Only in the liquid phase does one have the necessary concentration and energy level to allow hydrogen atom bonding. These crystals are very small. But, they can grow by sharing the faces composed of 5- and 6-membered water molecules. It is only when this growth continues to form a plug are hydrates a known problem.

HYDRATE EQUILIBRIUM

Figure 6.12$^{(6.14)}$ shows the hydrate forming characteristics of common natural gas components. The lines shown are the hydrate forming conditions. Below and to the right of the line no hydrates can form. At some temperature the hydrate forming line becomes vertical. This happens at the point where the hydrate forming curve intersects the vapor pressure curve of that component.

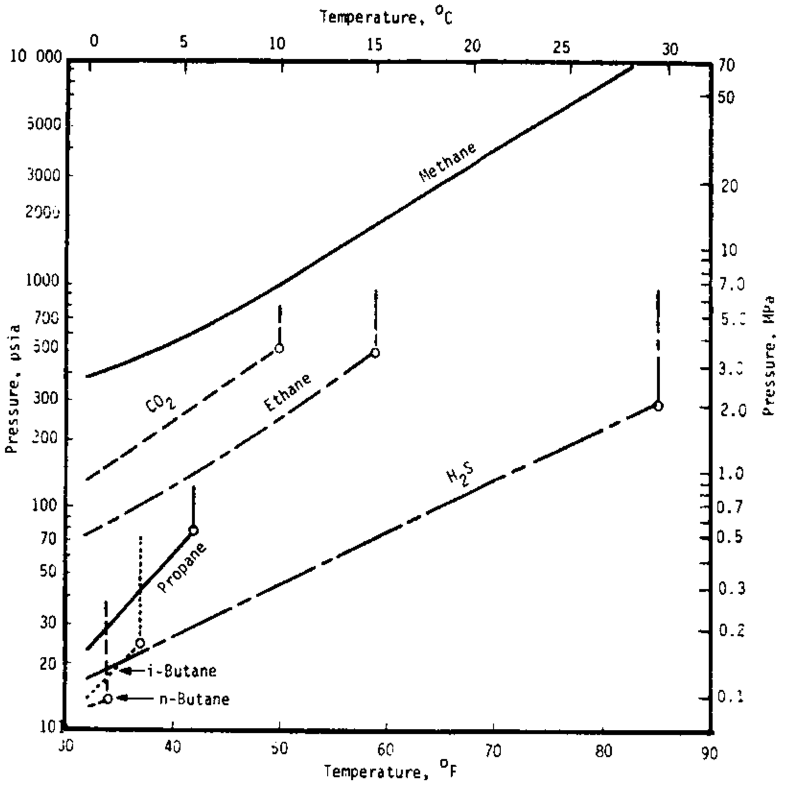
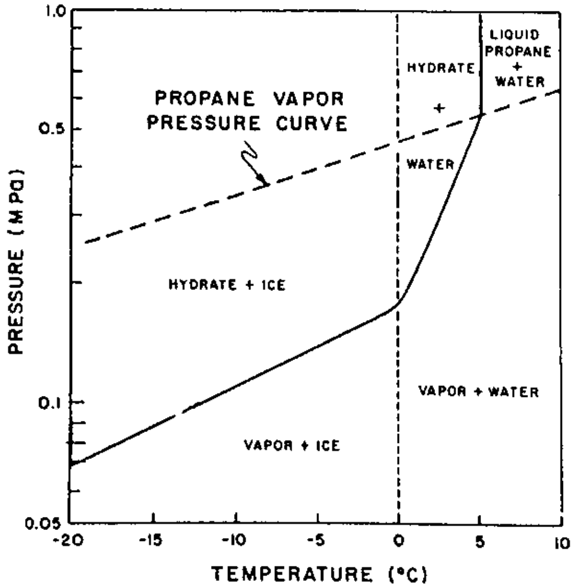


Figure 6.12 Hydrate Forming Conditions for Natural Gas Components



The figure at left illustrates the general behavior for propane.

Below 0°C [32°F] both ice and hydrate are present above the curve; only vapor and ice are below. Above the freezing point, hydrate is the only solid phase to the left of the hydrate forming curve. At the intersection of the vapor pressure and hydrate curves the latter becomes essentially vertical. This intersection establishes the *maximum hydrate forming temperature* for pure components.

The same general behavior occurs for a gas mixture, as shown in Figure 6.13. Line FEGC is the dewpoint line for the mixture. The slope of the hydrate curve (FGH) becomes increasingly vertical along the quadruple line (FG). The slope of the quadruple line is dependent upon the amount of hydrocarbon liquid in the system. Increasing amounts of liquid steepen

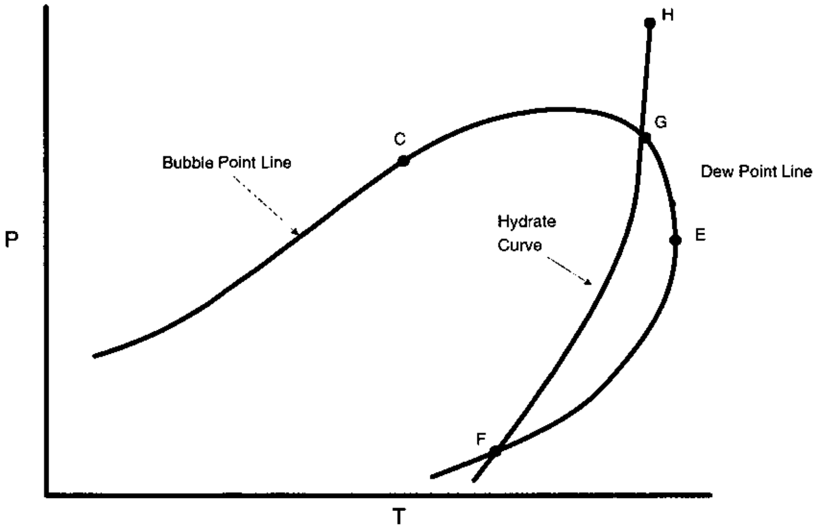


Figure 6.13 General Hydrate Formation Characteristics of a Gas Mixture

the slope. If the quadruple line intersects the phase envelope to the left of the critical point (bubble point line) the hydrate curve will be essentially vertical in the single phase region.

The general procedure for hydrate prediction involves two basic steps.

1. Use a suitable correlation to establish the position of the dewpoint line FEGC.
2. Use a suitable correlation to find hydrate line FGH.

The first step was covered in Chapter 5. The correlations which follow may be used for Step 2.

HYDRATE PREDICTION CORRELATIONS

All basic hydrate prediction correlations are for a system containing only gas and water in a static test cell that was rocked only to provide good equilibrium. In most cases the data shown are the hydrate melting conditions, a more reproducible data point than the formation point, and more reliable for calculation use.

Early correlations showed hydrate forming curves as a function of gas relative density. Although they are simple to use and may happen to apply for a lean gas, they are not recommended for engineering calculations.

Vapor-Solid Equilibrium Constants

Katz and his co-workers developed a set of $K_{v\text{-}s}$ values for hydrate prediction.(6.15-6.18) Figures 6.14- - 6.18 are the $K_{v\text{-}s}$ charts for use of this method as redrafted by the GPSA and modified for use herein. Figure 6.17 replaces the figure in the original work.(6.19)

In spite of some theoretical flaws in the method it has proven very reliable up to about 7 MPa [1000 psia]. Some of the curves do not exceed this pressure. With others the accuracy begins to decrease as the values converge to $K_{v\text{-}s} = 1.0$.

In the original work it was assumed that nitrogen was a nonhydrate former and that n-butane had the same $K_{v\text{-}s}$ value as ethane. Later work has shown these to be technically incorrect. A $K_{v\text{-}s}$ curve is now provided for n-butane, however, as a practical matter using $K_{v\text{-}s}$ = infinity for nitrogen gives very satisfactory results.

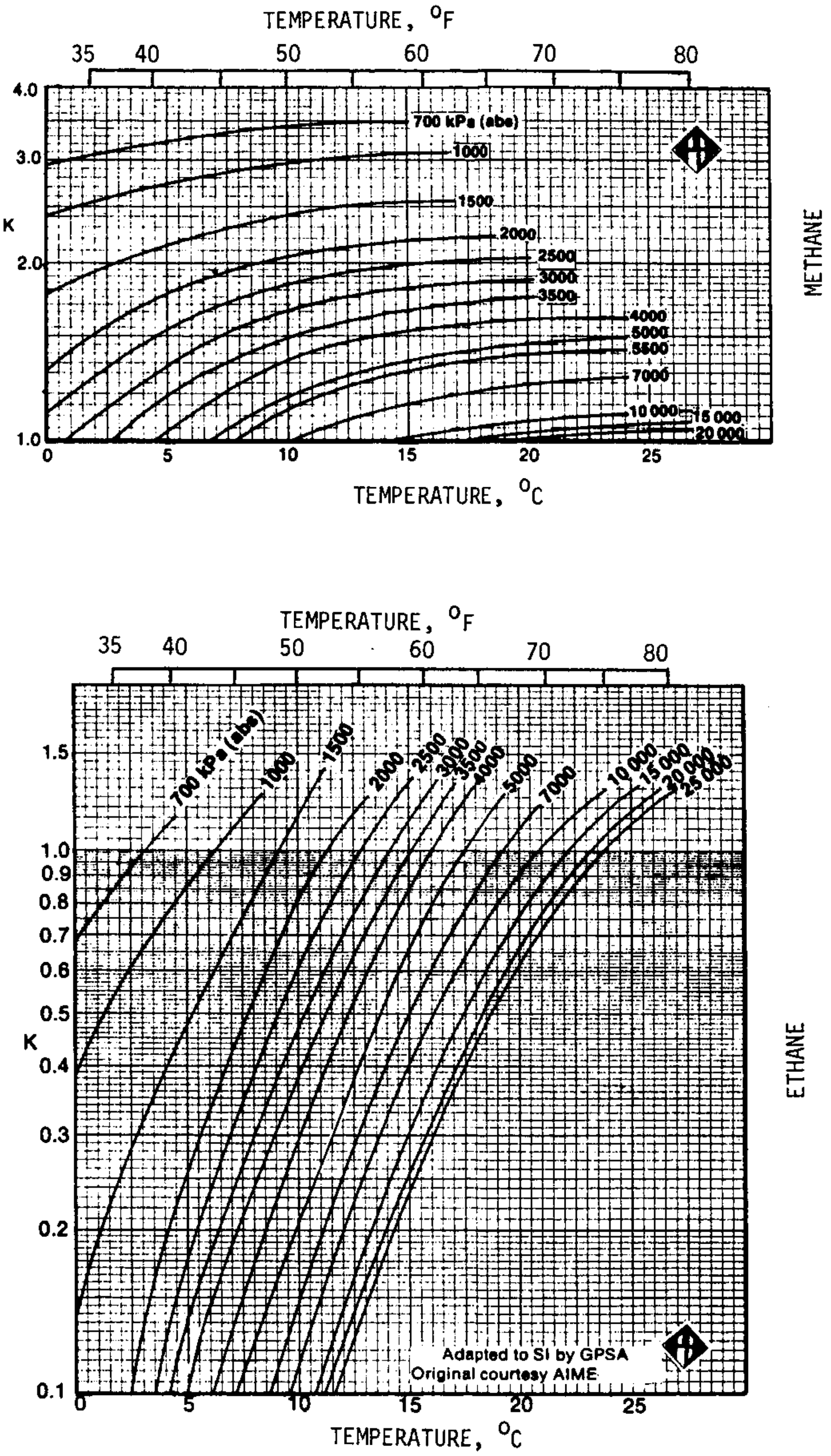
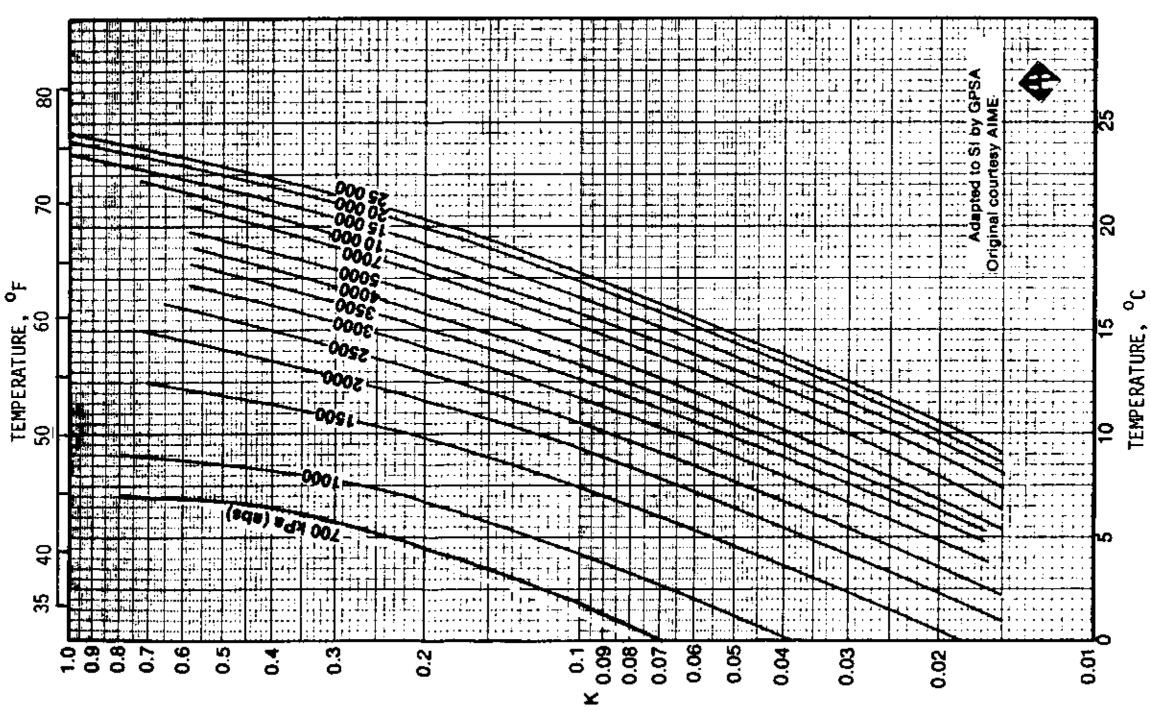
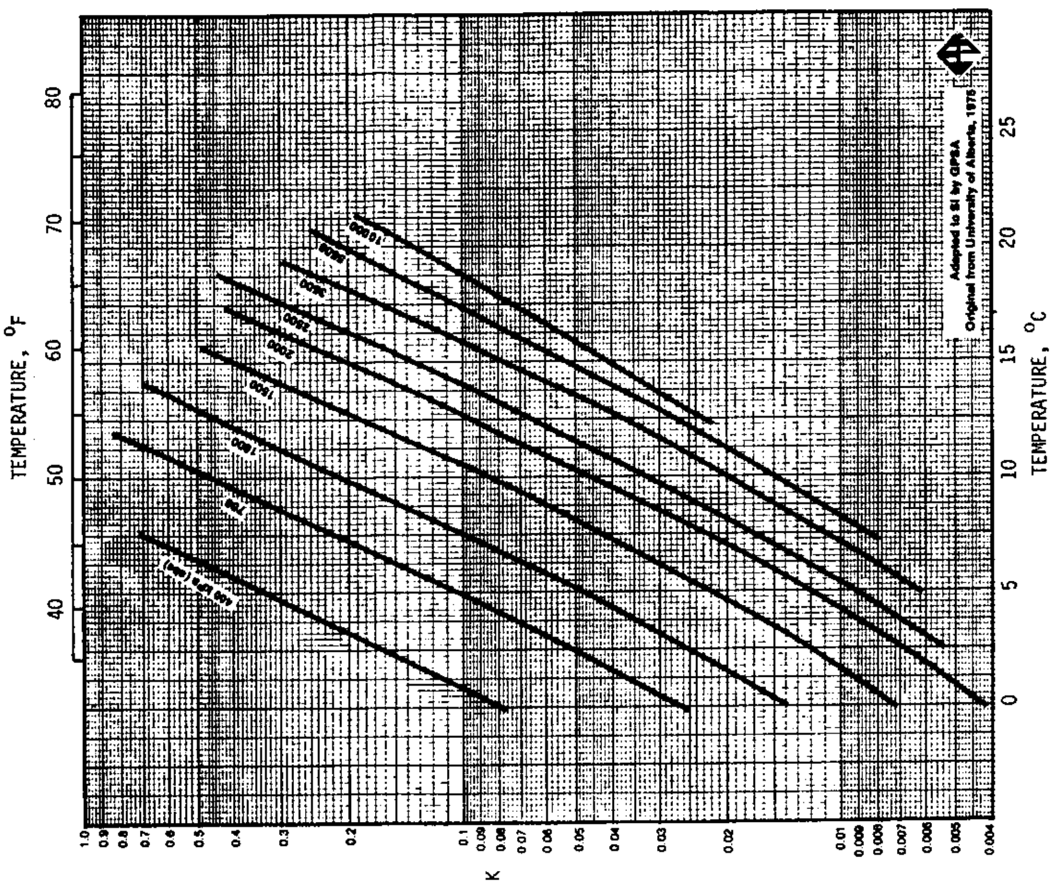


Figure 6.14 **Vapor-Solid K Values for Methane and Ethane**



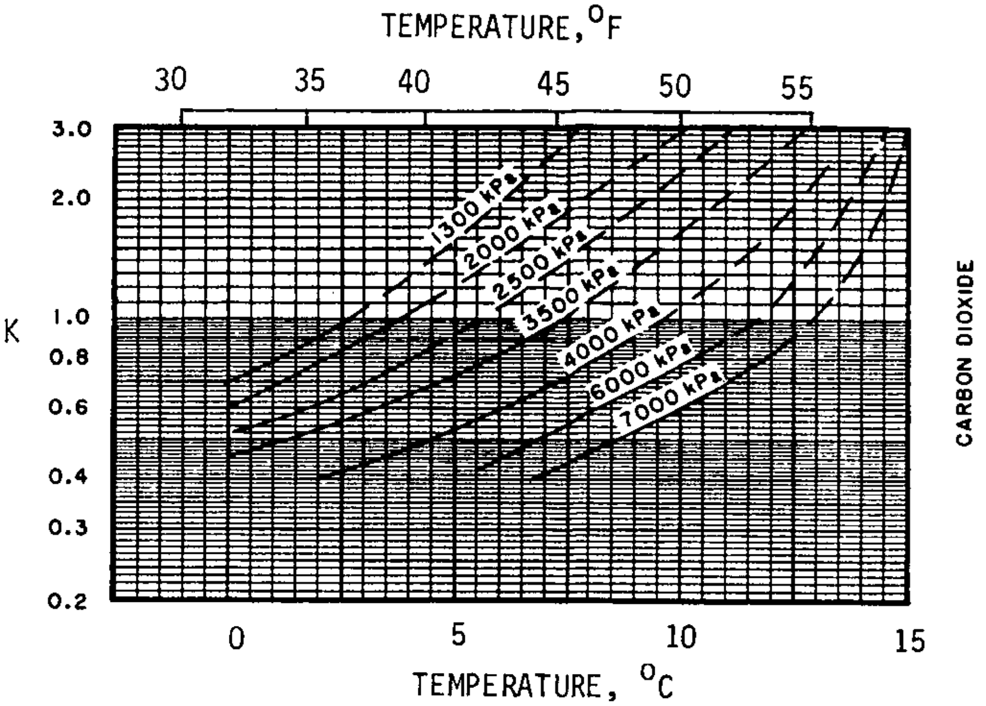
Adapted to SI by GPSA
Original courtesy AIME

Figure 6.15 Vapor-Solid K Values for Propane



Adapted to SI by GPSA
Original from University of Alberta, 1978

Figure 6.16 Vapor-Solid K Values for iso-Butane



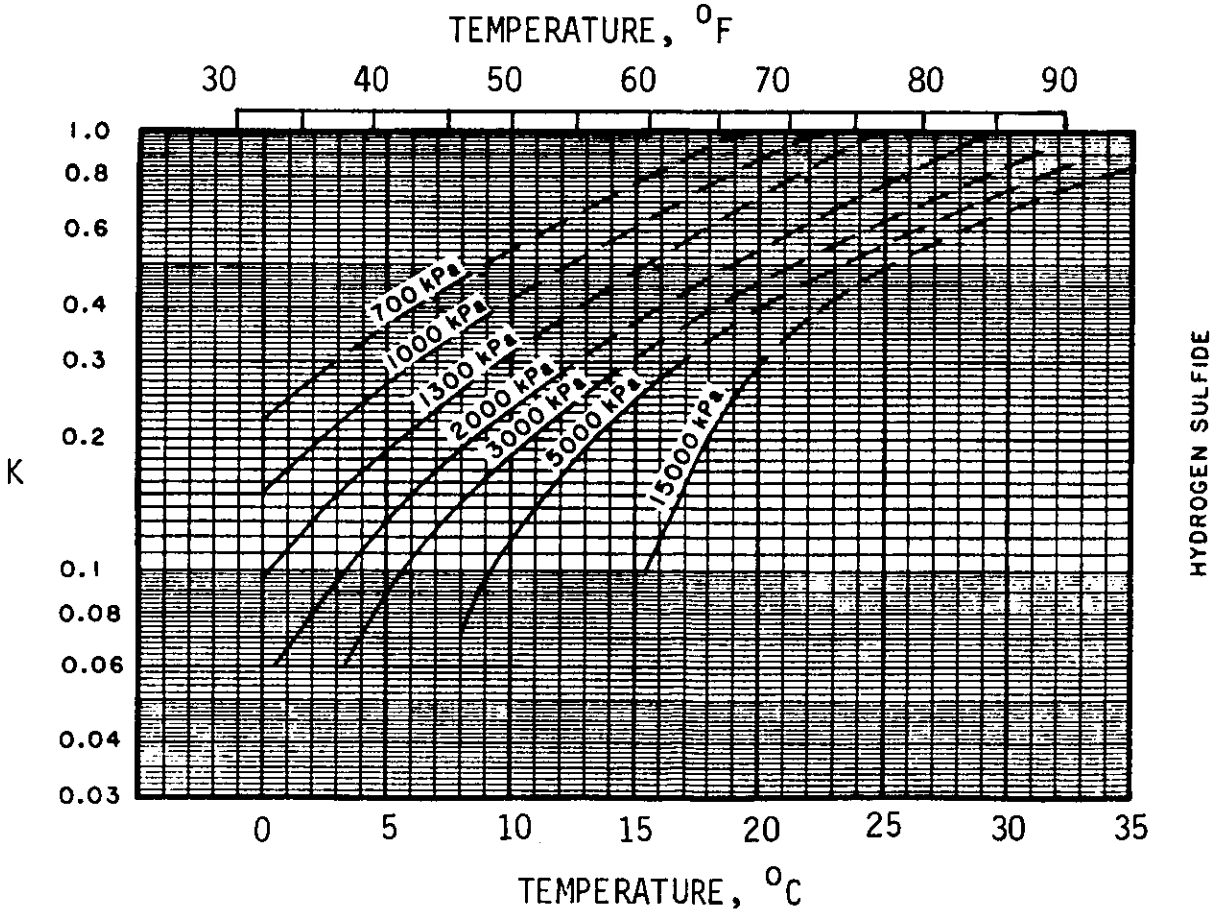


Figure 6.17 Vapor-Solid K Values for CO_2 and H_2S

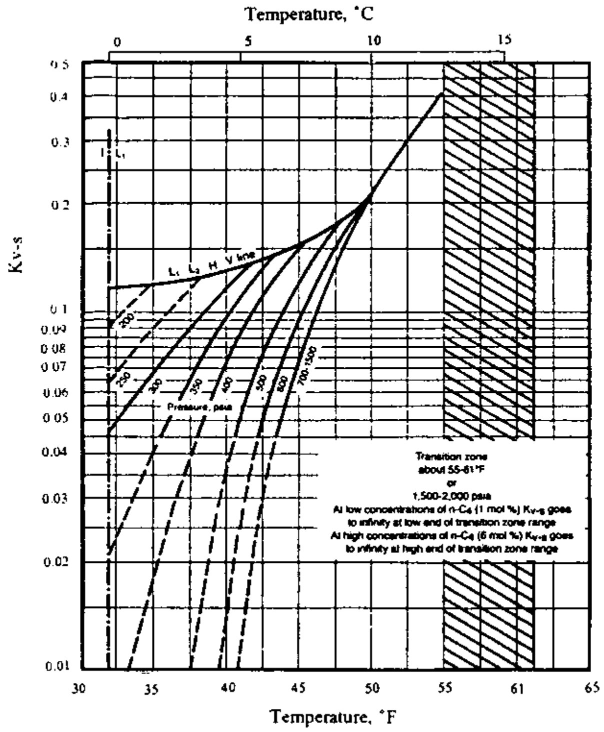


Figure 6.18 Vapor-Solid Equilibrium Constants for n-Butane

A dewpoint type calculation is made using the $K_{v\text{-}s}$ values shown. The term "y_i" is the mol fraction of each component in the gas. $K_{v\text{-}s}$ equals infinity for all nonhydrate formers present.

$$\sum(y_i/K_{v-s}) = 1.0 \tag{6.5}$$

Example 6.3: Find the hydrate formation temperature of the gas below at 2.0 MPa [290 psia].

Kc,12
method

Component	y_i	At 10°C [50°F]	
		$K_{v\text{-}s}$	$y_i/K_{v\text{-}s}$
Nitrogen	0.094	Inf	0.0
Methane	0.784	2.04	0.384
Ethane	0.060	0.82	0.073
Propane	0.036	0.113	0.319
Iso-Butane	0.005	0.047	0.106
n-Butane	0.019	0.21	0.090
CO_2	0.002	2.9	0.001
	1.000		0.974

One can assume a new temperature and repeat the calculation. In Example 6.3 the result will be a hydrate formation temperature of about 9.5°C [49°F].

The preceding approach may also be applied using a different set of $K_{v\text{-}s}$ values. Sloan *et al.*$^{(6.20)}$ present $K_{v\text{-}s}$ values which are dependent upon composition and type of hydrate structure (I or II).

Trekell-Campbell Method

The Katz method possesses pressure limitations and fails to address the hydrate depression effects of molecules too large to fit into the cavities. Too many of these in one location makes it difficult for a stable lattice to form around them.

The molecules larger than methane increase the ease of stable hydrate formation. This method(6.21) uses methane as the reference condition. The additive effect of other molecules is then plotted in Figures 6.19-6.21 for a pressure range 6.9-41.4 MPa [1000-6000 psia]. Each figure is for a specific pressure and the corresponding methane hydrate forming temperature. The abscissa shows the displacement of this methane hydrate forming temperature for the percentage of each component shown on the ordinate.

Notice in Figure 6.19 that n-butane has a slightly positive effect on hydrate formation. In Figures 6.20 and 6.21 the temperature displacement is negative (n-butane becomes a nonhydrate former). This change probably is due to distortion of the lattice with pressure which does not allow even the largest cavities to hold a molecule as large as n-butane.

Figure 6.22 is the negative correction (depression) for nonhydrate formers (pentanes plus). The key parameter is

$$\frac{y_{C_5+}}{1 - y_{C_1} - y_{C_5+}}(100)$$

or the ratio of the mol fraction of pentanes plus to the sum of the mol fractions ethane, propane and butanes. Increasing this ratio is unfavorable to hydrate formation; there are too many large molecules present.

The following general procedure is recommended for this method:

1. Calculate the hydrocarbon dewpoint curve to locate line FEGC in Figure 6.13.
2. Using the 6.9 MPa prediction chart, determine the hydrate formation temperature by algebraically summing temperature displacements. Use the dry gas analysis for the ordinate values and sum the ΔT values found on the abscissa to the temperature for methane hydrate given on the figure. Correct this temperature for the effect of pentanes and heavier if present.
3. Repeat the previous step at 13.8 MPa and correct for pentanes and heavier.
4. Calculate the hydrate temperature at each remaining pressure for which there is a graph until the hydrocarbon dewpoint pressure is reached.
5. Plot the calculated temperatures and fit the best curve through the points.

The procedure shows that pentane and heavier have a calculable effect on hydrate point, and the "K" value is not infinity.

Limited data show that H_2S and CO_2 elevate the hydrate point less in natural gases containing reasonable amounts of ethanes through propanes than would be expected from their binary data with methane. In fact, the correction for CO_2 is negligible for most gases tested. In the final analysis, one does not need an exact hydrate forming prediction. A narrow range of 1-2°C is suitable for design and operation.

I do not recommend that you extrapolate the curves in Figure 6.19-6.22. At some composition the lines approach the vertical (infinite slope) and any increase in concentration produces no further temperature deflection. But, one also must remember that the correlation is empirical and that any extrapolation tends to increase the risk.

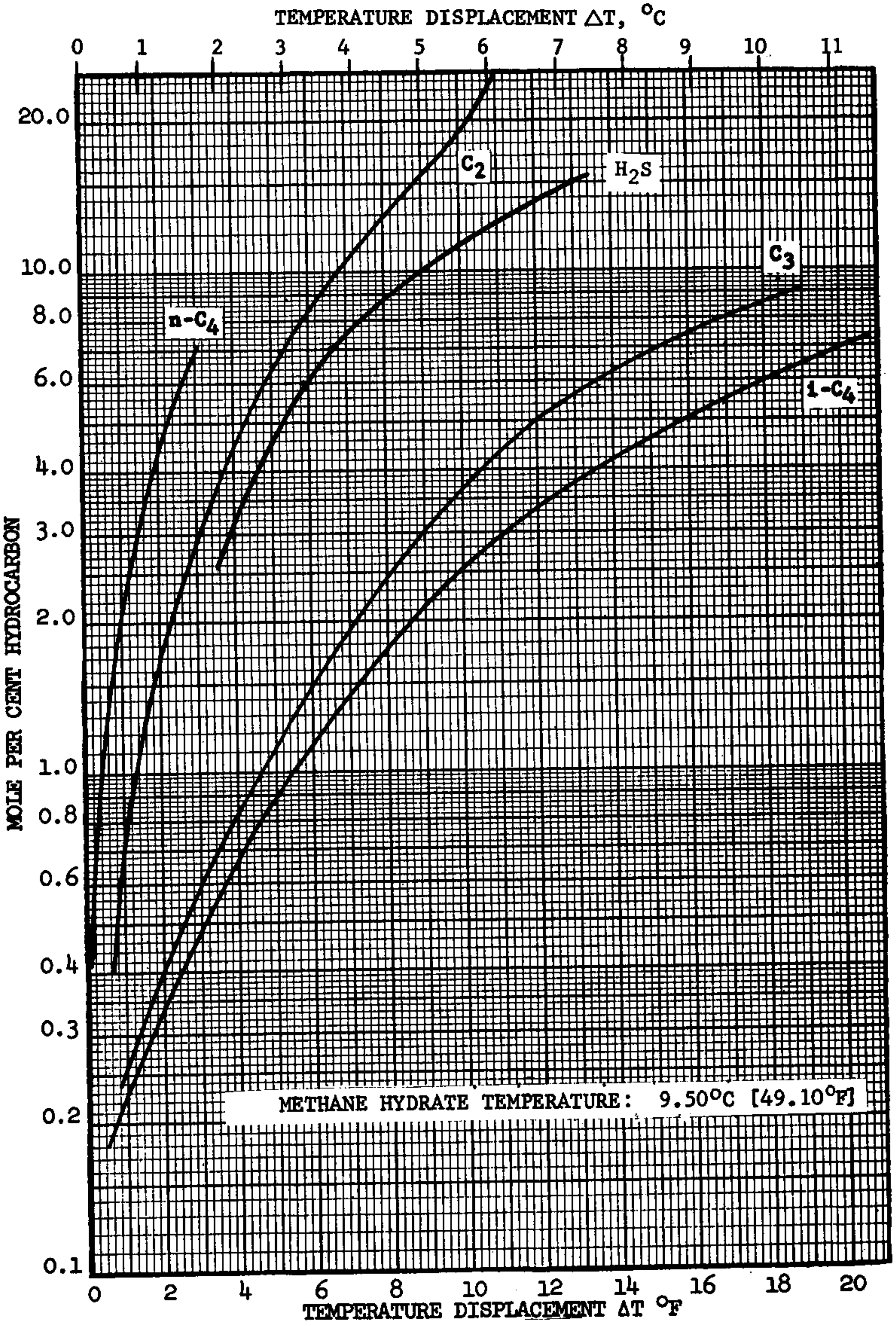


Figure 6.19 Hydrate Prediction Correlations at 6.9 MPa

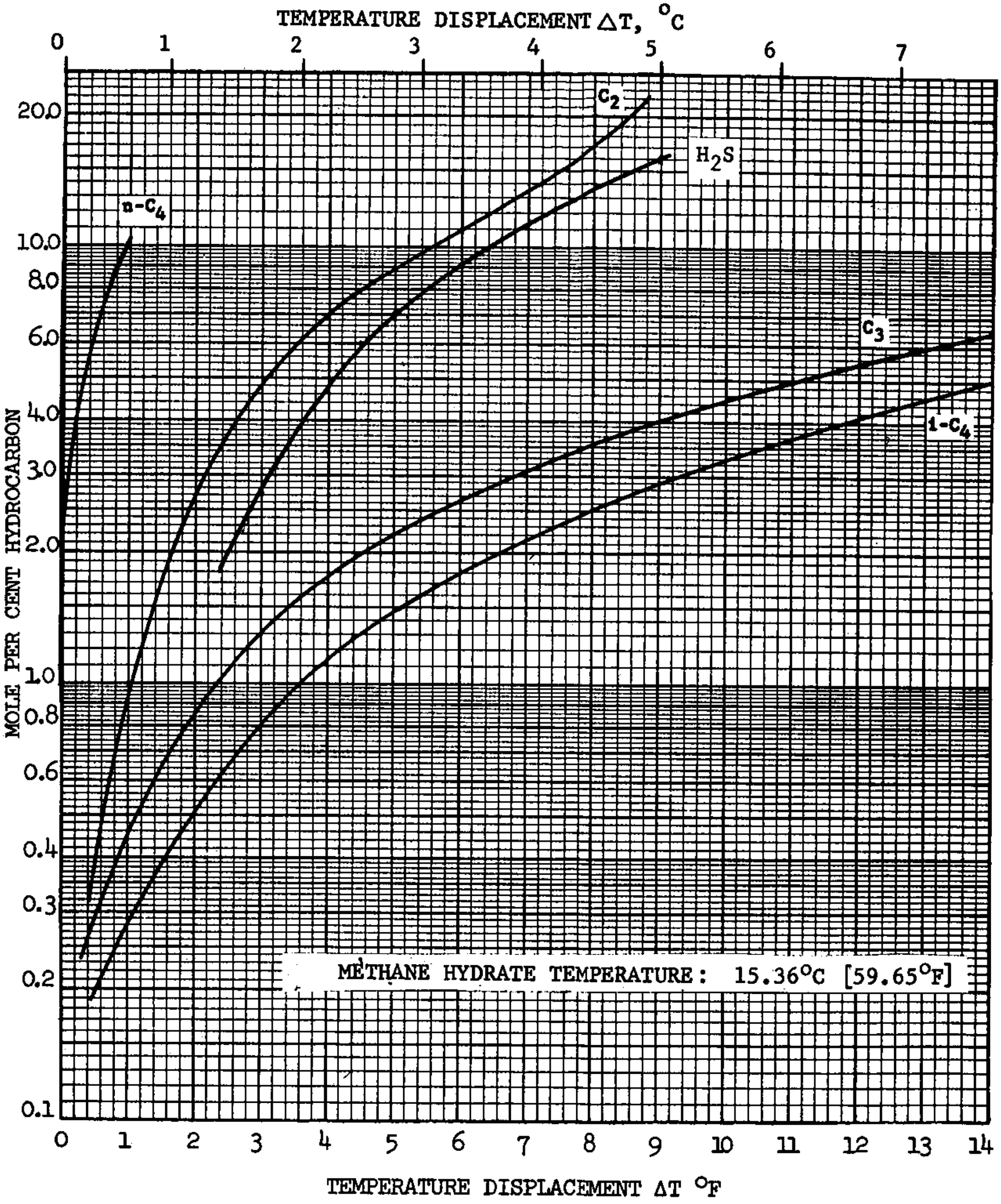


Figure 6.19(a) Hydrate Prediction Correlations at 13.8 MPa

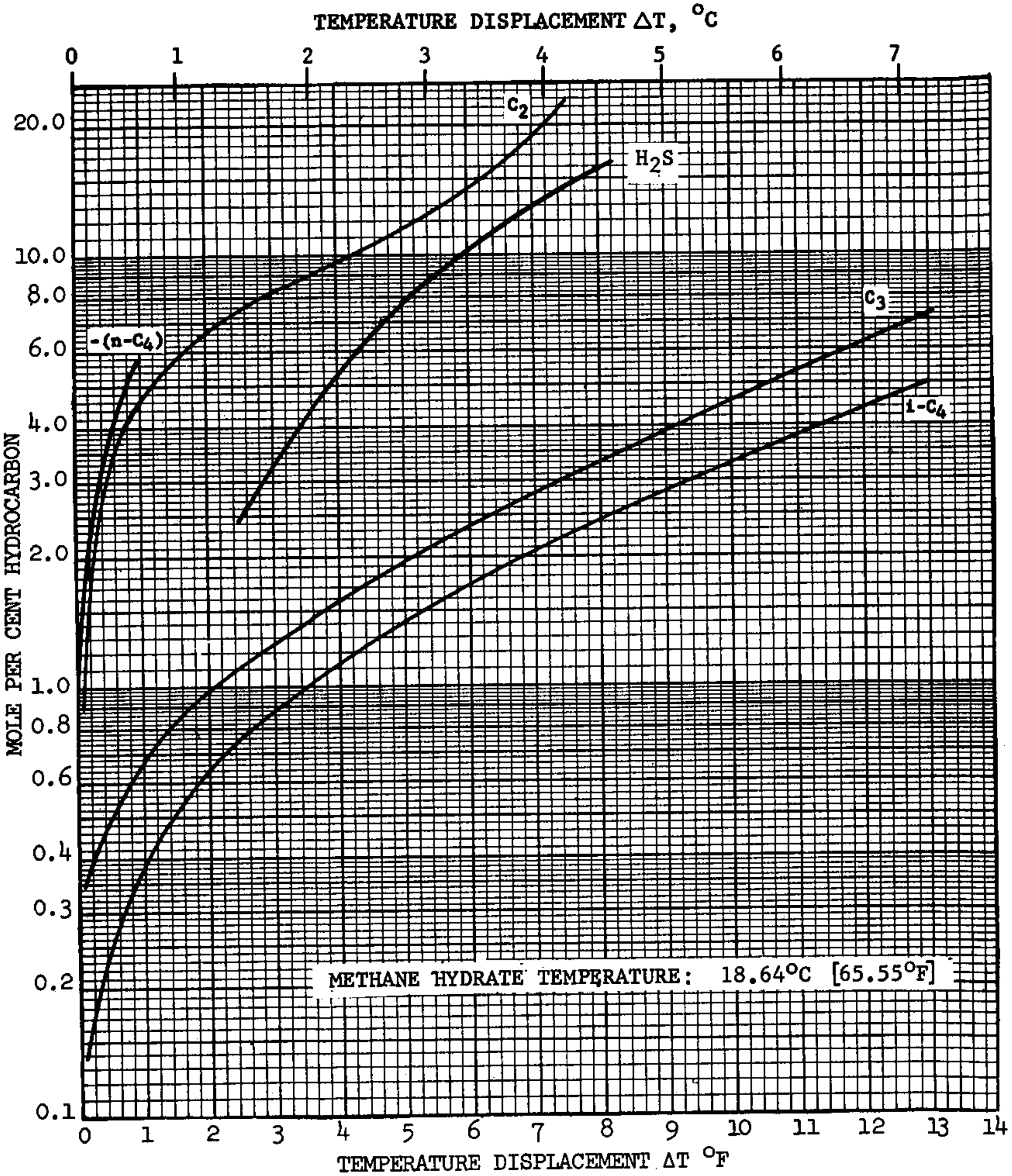


Figure 6.20 Hydrate Prediction Correlations at 20.7 MPa

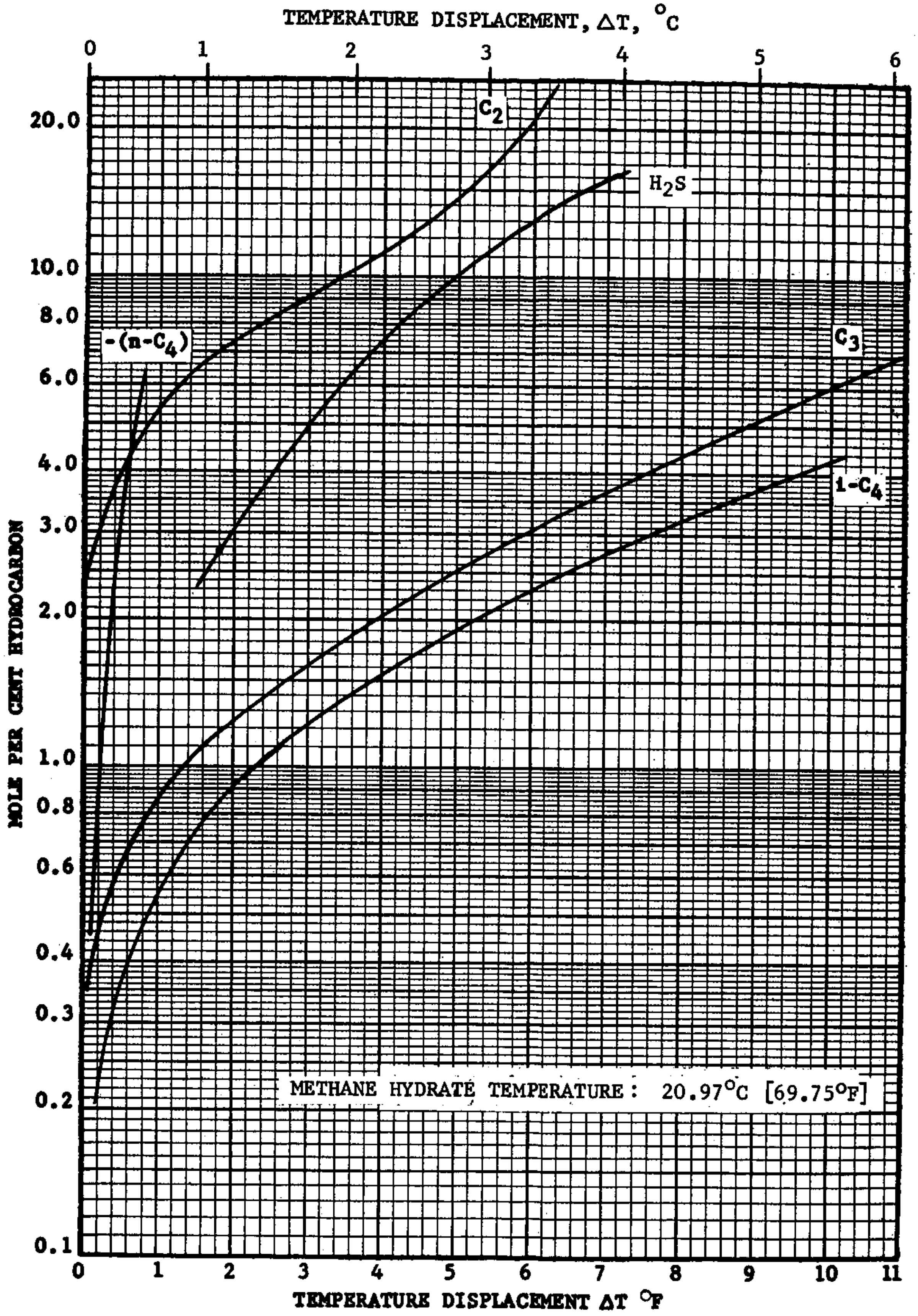


Figure 6.20(a) Hydrate Prediction Correlations at 27.6 MPa

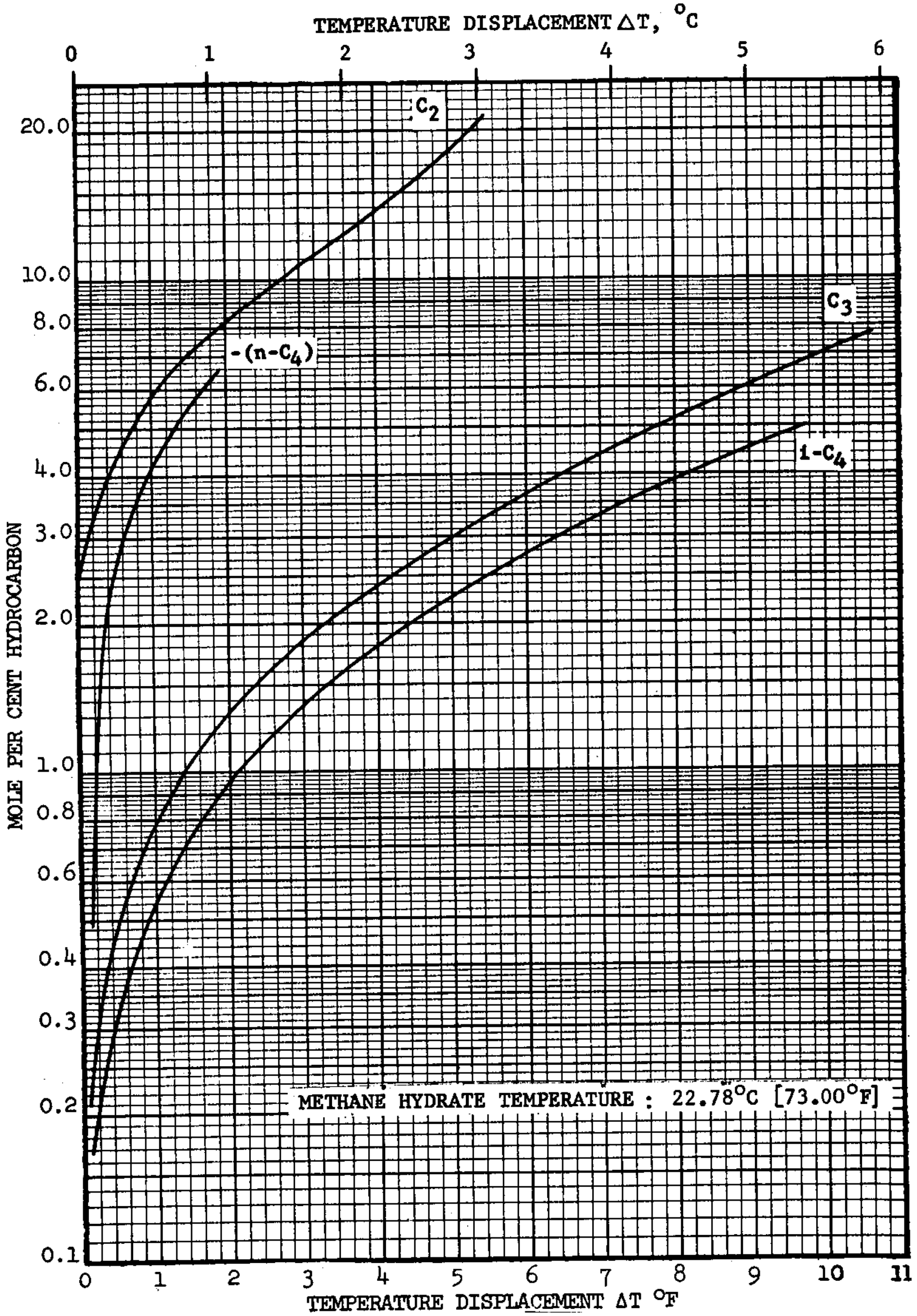


Figure 6.21 Hydrate Prediction Correlations at 34.5 MPa

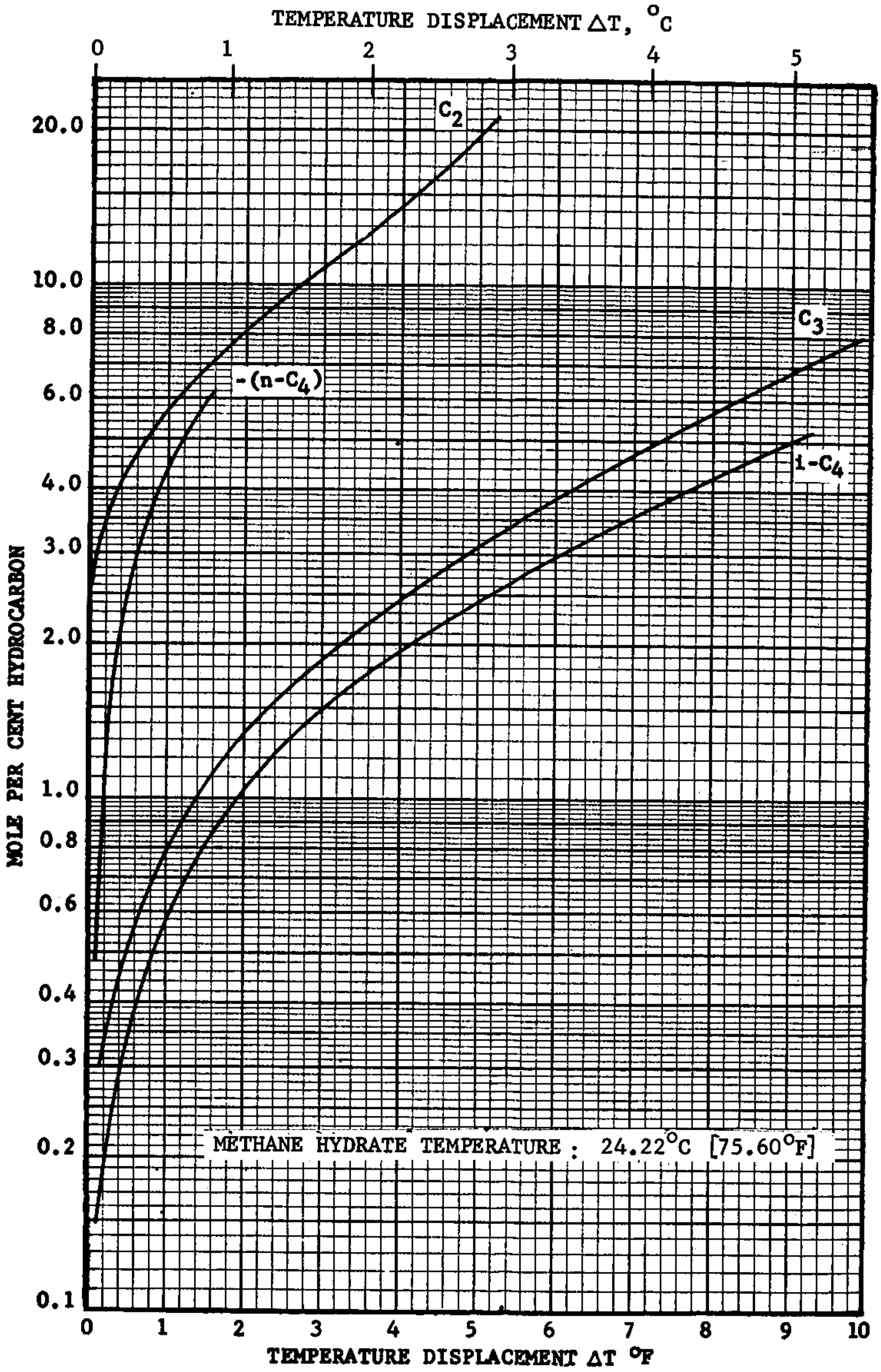
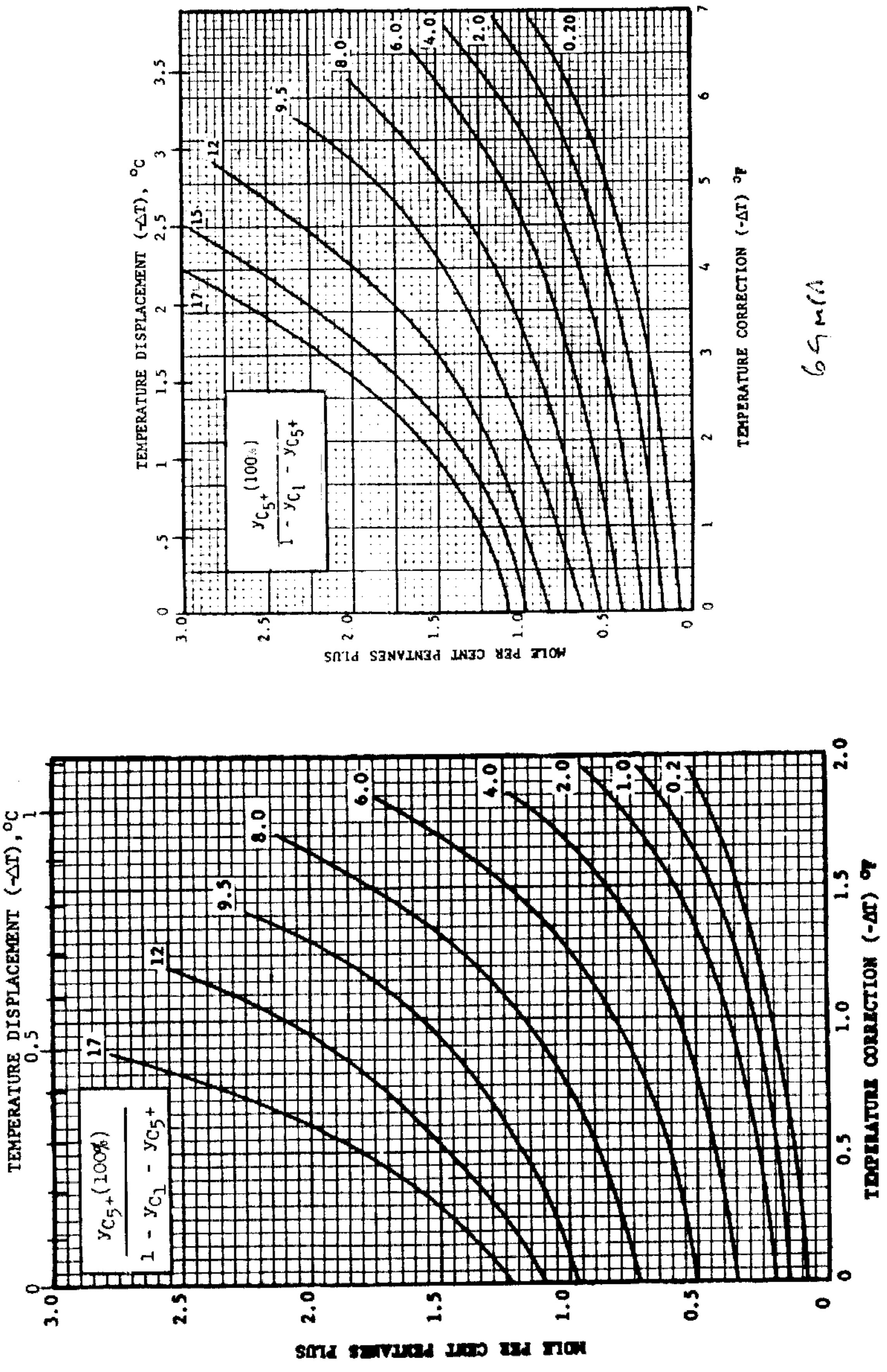


Figure 6.21(a) Hydrate Prediction Correlations at 41.4 MPa



6.9 MPA

13.8 - 41.4 MPA

Figure 6.22 Hydrate Prediction Correlations for Non-Hydrate Formers

McLeod-Campbell Method

This work(6.22) is for use with high pressure gases above about 35-40 MPa [5000-6000 psia].(6.21) Early work indicated erroneously that gas hydrate forming curves approach the pure methane curve at these high pressures. This work proves that said curves are parallel to the methane curve and have essentially the same slope for all gas mixtures.

A specific correlation was prepared from 41.4-69 MPa [6000-10 000 psia] using a modified Clapeyron equation to describe the energy of phase transformation. Using available data this was reduced to the simple equation

$$T = A\,(C')^{0.5} \qquad (6.6)$$

Where:			Metric	English
	T	= hydrate forming temperature	K	°R
	A	= correlation factor	2.16	3.89
	C'	= component factors from the following table		

Pressure		C Values				
MPa	psia	C_1	C_2	C_3	iC_4	nC_4
41.4	6000	18 933	20 806	28 382	30 696	17 340
48.3	7000	19 096	20 848	28 709	30 913	17 358
55.2	8000	19 246	20 932	28 764	39 935	17 491
62.1	9000	19 367	21 094	29 182	31 109	17 868
69.0	10 000	19 489	21 105	29 200	30 935	17 868

In using Equation 6.6 one expresses the gas composition in terms only of the relative quantity of methane through n-butane. All heavier molecules are ignored. Multiply this pseudo mol fraction by each component's "C" value from the table to find a composite value for substitution into Equation 6.6.

Example 6.5: Calculate the hydrate forming temperature of a gas at 41.4 MPa [6000 psia] with the pseudo analyses shown.

Component	Mol Fr.	C	C′
C_1	0.906	18 933	17 153
C_2	0.066	20 806	1373
C_3	0.018	28 382	511
iC_4	0.005	30 696	153
nC_4	0.005	17 340	87
Total	1.000		19 277

From Eqn. 6.6, $T = (2.16)(19\,277)^{0.5} = 300\text{ K} = 27°\text{C}$ $\qquad T = (3.89)(19\,277)^{0.5} = 540°\text{R} = 80°\text{F}$

Reference 6.23 presents hydrate data for a lean natural gas at pressures to 100MPa [14 500 psia].

Equation of State Calculations

A series of computer solutions have been developed for prediction of hydrate forming conditions.(6.1, 6.24-28) These, unlike the calculations discussed previously are based on equations of state. In general, they are as good as, and maybe better than, the methods discussed above. The models presented here provide a good basis for developing more sophisticated calculations.

APPLICATION OF HYDRATE CALCULATIONS

Remember that hydrates can form only when the gas is saturated with water. This assumption is implicit in any hydrate correlation.

In addition, when using the correlations presented in this text it is assumed that no liquid hydrocarbon or ice is present in the system. (Small amounts of liquid hydrocarbon have little effect on the hydrate temperature.)

Hydrates are a problem only if they are allowed to agglomerate to a degree where they restrict or stop flow. Turbulent flow with liquids present, coupled with sound mechanical design, will reduce the observed hydrate point below that calculated. One should expect all of the above calculation methods to predict hydrate formation temperatures within 1-2 °C of the test value, within the range of their application. In past tests the Trekell-Campbell approach tends to give high values.

One of the best reasons for effective dehydration is to prevent hydrates by eliminating liquid water. Piping, design and valve selection likewise can lower the effective hydrate point. In a multi-phase pipeline the liquid can literally keep the hydrates from attaching themselves and growing. The same is true of well-bore flow. Hydrates may be a problem only when flow stops.

Because of factors like these, hydrate calculations yield somewhat theoretical numbers for planning purposes. If these are used as a proper guideline and the system is designed properly, hydrates should not present a problem.

If you have an unusual gas, outside the normal composition, I recommend laboratory determination of hydrating conditions.

HYDRATE INHIBITION

The positive manner to prevent hydrates (and corrosion) is to keep the lines and equipment "dry" of liquid water. There are occasions (rightly or wrongly) when the decision is made to operate a line containing liquid water. If this decision is made, and minimum line temperature is below the hydrate point, inhibition of this water is necessary.

Many materials may be added to water to depress both hydrate and freezing temperatures. For many practical reasons an alcohol or one of the glycols is injected as an inhibitor, usually methanol, diethylene glycol (DEG) or ethylene glycol (EG). All may be recovered and recirculated, but the economics of methanol recovery may not be favorable in many cases.

Methanol may be used effectively at any temperature. I do not recommend DEG generally below about –10°C because of its viscosity and the difficulty of separation if oil is present. Above –10°C it might be preferred because there is less vaporization loss.

The total injection rate is that needed to provide the necessary inhibitor concentration in the liquid water plus that inhibitor which enters the vapor phase. Any inhibitor in the vapor phase has little effect on hydrate formation conditions.

Equation 6.7(6.29) has been found reliable for prediction of the necessary inhibitor concentration in the water phase to lower the hydrate point a given amount.

$$X = \frac{(d)(M)}{K_i + (d)(M)}(100) \tag{6.7}$$

Where:		Metric	English
	d = °C depression of hydrate point	°C	°F
	X = weight percent inhibitor in the liquid water phase	–	–
	M = mol wt of inhibitor	–	–
	K_i = constant	1297	2335

Equation 6.7 is a simplification of the actual thermodynamic relationship between hydrate depression (d) and inhibitor concentration (X). However, when using the constants shown above, Equation 6.7 does an excellent job of matching laboratory equilibrium data for hydrate suppression with methanol solutions up to about 25 wt% and ethylene glycol to about 50-60 wt%.

Correlating Equation 6.7 with data collected on actual flowing systems is more difficult. On some glycol injection tests the back calculated values for K_i were nearly twice the numbers quoted above.

In truth, no one number applies to all systems, because it is affected by system dynamics, configuration, location and method of injection, etc. Most experienced operators will adjust the injection rate by trial-and-error following initial start-up. This is one of many process calculations that provides little more than a "safe" or "ballpark" estimate to guide operations.

Correlations other than Equation 6.7 have been proposed. For methanol concentrations up to about 50 wt% the following equation(6.30) may be more accurate.

$$d = A \ln (1 - x_m) \tag{6.8}$$

Where:		Metric	English
	d = °C depression of hydrate point	°C	°F
	x_m = mol fraction of methanol in the liquid water phase	–	–
	A = constant	–72	–129.6

Note that the inhibitor concentration in Equation 6.8 is expressed as a mol fraction rather than a weight percent.

Maddox, *et al.*(6.31) has also proposed a correlation to estimate hydrate depression versus inhibitor concentration. Based on the limited amount of empirical data available, it appears to be more reliable at high inhibitor concentrations (> 50 wt%).

The quantity "d" is found by first predicting the hydrate forming temperature at the maximum pressure in the line segment being protected. The minimum flowing temperature is then estimated. The quantity "d" is the difference between these two numbers. In the absence of a more definitive number, 4°C may be used as a reasonable minimum flowing temperature for buried lines and lines at the bottom of a body of water over 30-40 meters deep.

Total inhibitor injection rate to satisfy the inhibitor concentration needed is found from the equation

$$m_I = m_W\left(\frac{X_R}{X_L - X_R}\right) \tag{6.9}$$

Where:		Metric	English
m_I =	mass of inhibitor solution	kg	lbm
m_W =	mass of liquid water	kg	lbm
X_R =	rich inhibitor concentration	wt %	
X_L =	lean inhibitor concentration	wt %	

The lean inhibitor concentration, X_L, is almost always 100% for methanol and typically varies from 60-80% for glycols. The rich inhibitor concentration, X_R, is determined from Equation 6.7 for field and pipeline inhibition. For inhibition in gas processing plants, the ability to adequately mix the inhibitor and gas in the piping or exchanger is the primary concern. In these cases, the rich inhibitor concentration is set based on two criteria: 1) hydrate depression and 2) mixing. The mixing requirement usually dominates and often results in a specified dilution (X_L to X_R) of 5% or less. The concentrations of both the lean and rich glycol are kept in the non-freezing region (see Figure 6.24).

The following factors are useful for the above calculation.

	MeOH	EG	DEG
Molecular Weight	32	62	106
Density: g/cm^3	0.80	1.11	1.12
kg/m^3	800	1110	1120
lb/ft^3	49.7	69.4	69.6

The injection rate will be in m^3 or liters per unit time in metric units. If water content of gas is found in m^3/10^6 std m^3, this can be converted to liters by remembering that

$$1\ \text{m}^3 = 1000\ \text{liters}\quad,\quad \text{g/cm}^3 = \text{kg/L}$$

One converts the mass rate of inhibitor injection from Equation 6.9 into volumetric rate using an appropriate conversion factor.

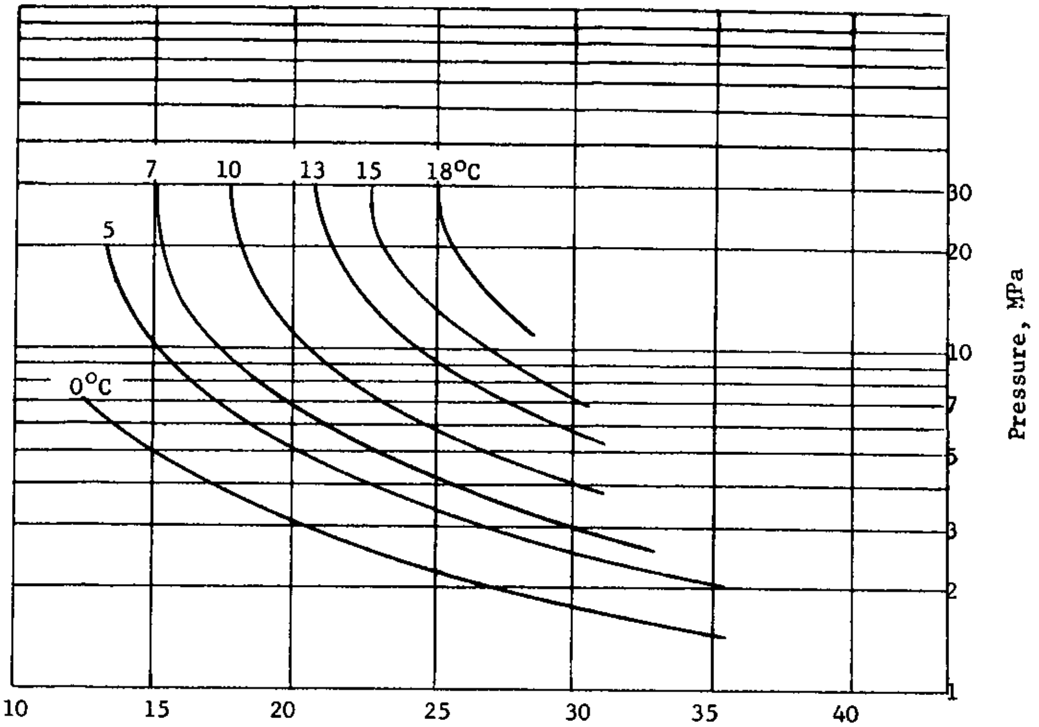
Inhibitor Losses to the Hydrocarbon Phase

Inhibitor may be lost due to its solubility in the hydrocarbon liquid and vapor phases. For glycol systems these losses are small. The following provides useful guidelines.

	Losses	
Vapor	3.5 L/10^6 std m^3	0.23 lbm/MMscf
Liquid	nil	nil

Methanol losses are more significant, particularly vapor phase losses.

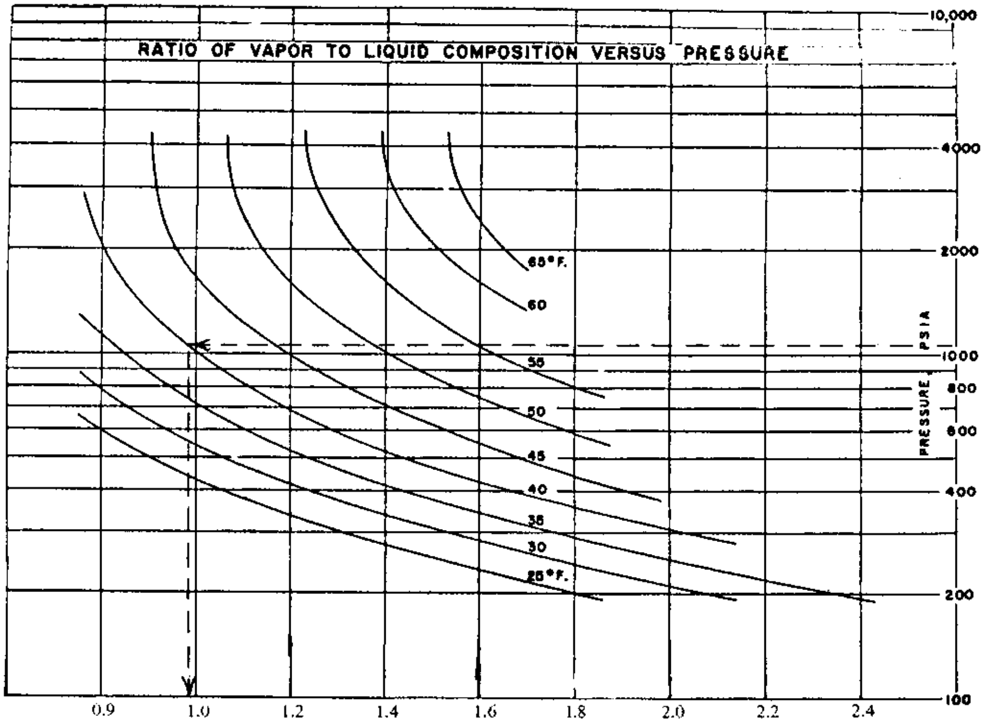
Figure 6.23 provides reliable estimates of vaporization loss for pressures less than about 6900 kPa [1000 psia] and water phase methanol concentrations less than about 40 wt%. Enter the ordinate at the minimum pressure of the line segment. Proceed horizontally to the minimum temperature. From this point read vertically to the abscissa, loss per unit volume of gas flowing divided by X, the weight percent methanol in the liquid phase. Knowing X from Equation 6.7 you can solve for methanol vaporization loss per unit volume of gas flowing.



kg MeOH per 10^6 normal m^3 (100 kPa & 0°C)

[illegible] Wt % MeOH in Water Phase

Note: multiply value from chart by 0.95 to convert to std m^3 (100 kPa and 15°C)



lbs MeOH per Million ft^3 Gas (14.7 psia, 60°F)

wt % MeOH in Water Phase

Figure 6.23 Vapor-Liquid Equilibrium of Methanol over Water

At pressures greater than about 6900 kPa [1000 psia] vapor losses may be several times higher than those indicated in Figure 6.23, particularly at high methanol concentrations.*(6.33)*

Methanol solubility in the hydrocarbon liquid phase is low, however, in systems containing substantial amounts of hydrocarbon liquid the total liquid phase losses can be significant. At typical pipeline inhibition conditions, a solubility of about 0.4 kg/m^3 [0.15 lbm/Bbl] is generally adequate for planning purposes.*(6.23)* This assumes a paraffinic hydrocarbon liquid. Methanol solubility in aromatic hydrocarbons can be 4-5 times higher than this!

Calculation Summary

The inhibition calculation procedure may be summarized as follows:

1. Determine the hydrate formation temperature of the gas.
2. Establish the lowest temperature expected in the system.
3. Compute the amount of liquid water present at the temperature in Step 2, using the water dewpoint at that temperature and a suitable water content correlation.
4. Use Equation 6.7 to solve for "X." In the equation "d" is the temperature in Step 1 minus that in Step 2. Calculate the weight of inhibitor from Equation 6.9, using X from Equation 6.7. (Note, if Equation 6.8 is used to calculate x_m, it must be converted to a weight percent, X, before being used in Equation 6.9.)

   The volume rate of injection of solution will be the weight of inhibitor per unit time divided by its density, after correcting for concentration.
5. If methanol is used, one must correct for that amount lost to the hydrocarbon vapor and liquid phases. Figure 6.23 is used for this purpose. Enter the righthand ordinate at the pressure at which the temperature in Step (2) occurs. Read horizontally to the lowest temperature and then vertically to the abscissa. The denominator of the abscissa value is the value of "X" previously determined from Equation 6.7 (step 4). Liquid losses may be estimated using a solubility of 0.2 mol %.
6. Total injection rate equals that found from Step 5 plus that from Step 4. This is the rate of inhibitor solution.

Exampble 6.6: 3.5 x 10^6 std m^3/d [124 MMscf] of natural gas leaves an offshore platform at 40°C and 8000 kPa. The hydrate temperature of the gas is 17°C [63°F]. The gas arrives onshore at 5°C and 6500 kPa. Associated condensate production is 60 m^3/10^6 std m^3 [10.7 Bbl/MMscf]. Calculate the amount of methanol and 80 wt% EG inhibitor required to prevent hydrate formation in the pipeline.

Methanol:

Step 1 – Hydrate temperature = 17°C

Step 2 – Lowest temperature in system = 5°C
"d" = 17 – 5 = 12°C

Step 3 – Water content @ 40°C and 8000 kPa = 1000 kg/10^6 std m^3

Water content out at 5°C and 6500 kPa = 160 kg/10^6 std m^3

$$\text{Water condensed} = \left(\frac{3.5 \times 10^6 \text{ std m}^3}{\text{d}}\right)\left(1000 - 160 \frac{\text{kg}}{10^6 \text{ std m}^3}\right)$$

$$= 2940 \text{ kg H}_2\text{O/d}$$

Exampble 6.6 (Cont'd.):

Step 4 – Calculate inhibitor concentration from Equation 6.7

$$X = \frac{(12)(32)(100)}{1297 + (12)(32)} = 22.8 \text{ wt\%}$$

Calculate mass of inhibitor required in water phase from Equation 6.9

$$m_I = \frac{(2940)(22.8)}{(100 - 22.8)} = 868 \text{ kg/d}$$

Step 5 – Calculate losses to the hydrocarbon phases

Vapor – from Figure 6.23 at 4°C and 6500 kPa

$$\text{Losses} \approx 15.7 \frac{\text{kg}/10^6 \text{ std m}^3}{\text{wt\% MeOH}}$$

$$\text{Vapor Losses} = \left(15.7 \frac{\text{kg}/10^6 \text{ std m}^3}{\text{wt\% MeOH}}\right)\left(\frac{3.5 \times 10^6 \text{ std m}^3}{\text{d}}\right)(\text{ 22.8 wt\% MeOH })$$

$$= 1253 \text{ kg/d}$$

Liquid - use 0.4 kg MeOH/m^3 condensate

$$\text{Liquid Losses} = \left(0.4 \frac{\text{kg MeOH}}{\text{m}^3 \text{ condensate}}\right)\left(\frac{60 \text{ m}^3 \text{ condensate}}{10^6 \text{ std m}^3}\right)\left(\frac{3.5 \times 10^6 \text{ std m}^3}{\text{d}}\right)$$

$$= 84 \text{ kg/d}$$

$$\text{Total Injection Rate} = 868 + 1253 + 84$$

$$= 2205 \text{ kg/d} = 0.11 \text{ m}^3\text{/h}$$

For 80% EG solution – calculate X from Equation 6.7

$$X = \frac{(12)(62)(100)}{1297 + (12)(62)} = 36.5\%$$

Calculate mass of inhibitor required in the water from Equation 6.9

$$m_I = \frac{(2940)(36.5)}{80 - 36.5} = 2467 \text{ kg/d} = 0.095 \text{ m}^3\text{/h}$$

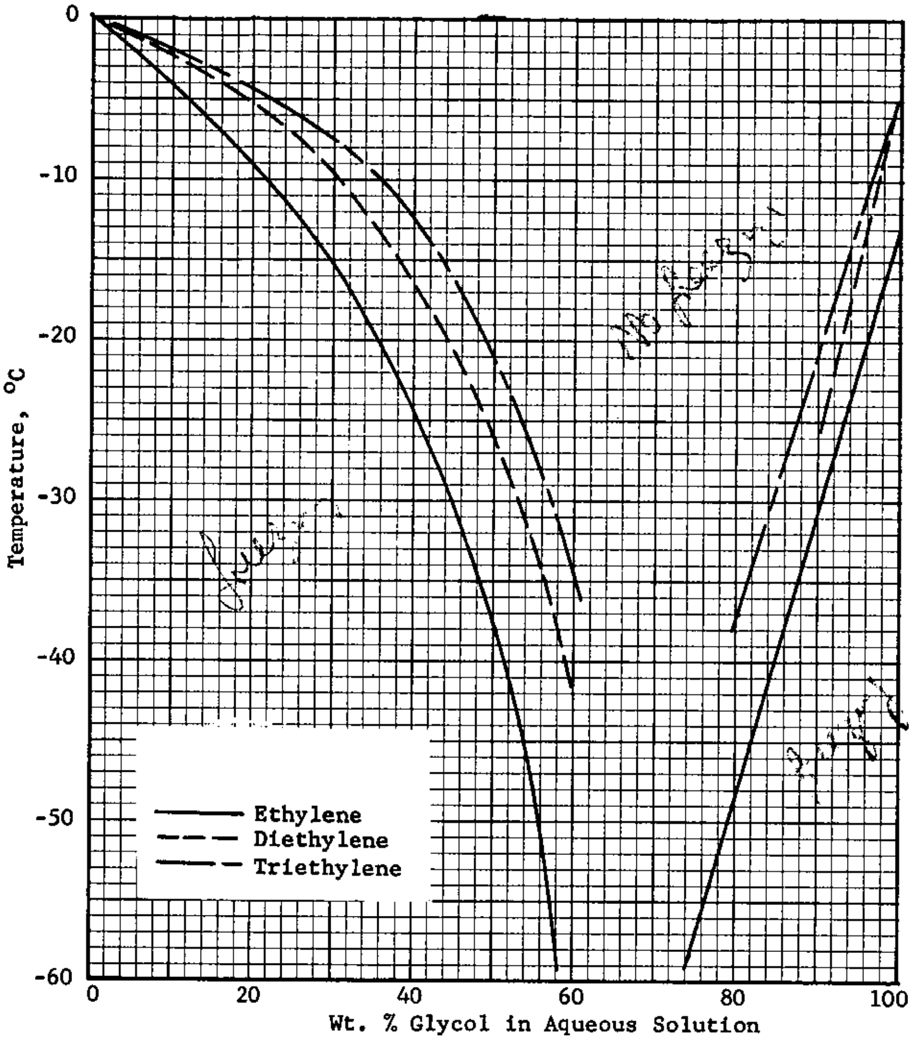
Crystallization (Freezing) of Glycols

Glycols do not freeze solid but form a "mushy" solution that nevertheless does not flow very well. The concentration must be such that this is avoided.

Figure 6.24 shows the "freezing point" for the three most common glycols. The curves go through a minimum. At a given temperature the concentration should be kept between the lines. A value of about 60 wt % glycol is safe at any likely temperature.

If the minimum system temperature is below –10°C [14°F], the injection rate must satisfy both Figure 6.24 and Equations 6.7 and 6.9. Typically the lean glycol solution injected will contain 15-25 wt % water. Thus, the total mount of water to be protected is that in the system plus that injected with the glycol. Equation 6.9 accounts for this water.

With EG and DEG the reboiler should not be operated above 150-160°C [300-320°F] to minimize thermal decomposition.



Benzene
Toluene

MeOH
can also
[illegible]
aromatics
to liquid.

Figure 6.24 Freezing Points of Glycol-Water Solutions

Glycol Losses

The major loss of glycol does not occur from vaporization. It is from losses in the regeneration system, spillage, salt contamination and losses in the separation of oil from the glycol water phase.

Regeneration losses should be small in a well designed unit unless salt contamination tends to plug the still column. Salt is a problem in its own right for the water is distilled off and leaves the salt behind. Salt can be removed from glycol only by vacuum distillation reclaiming.

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