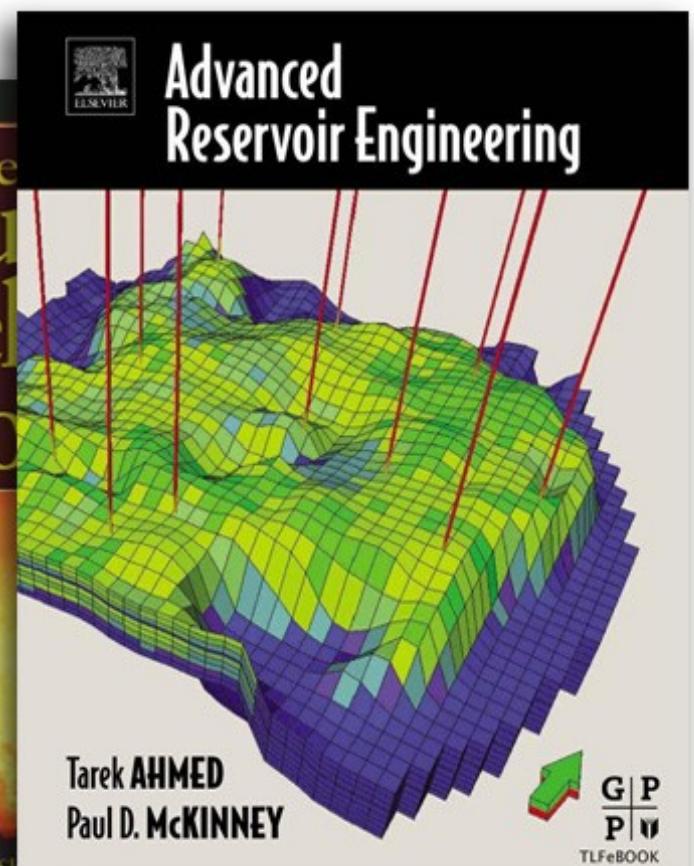
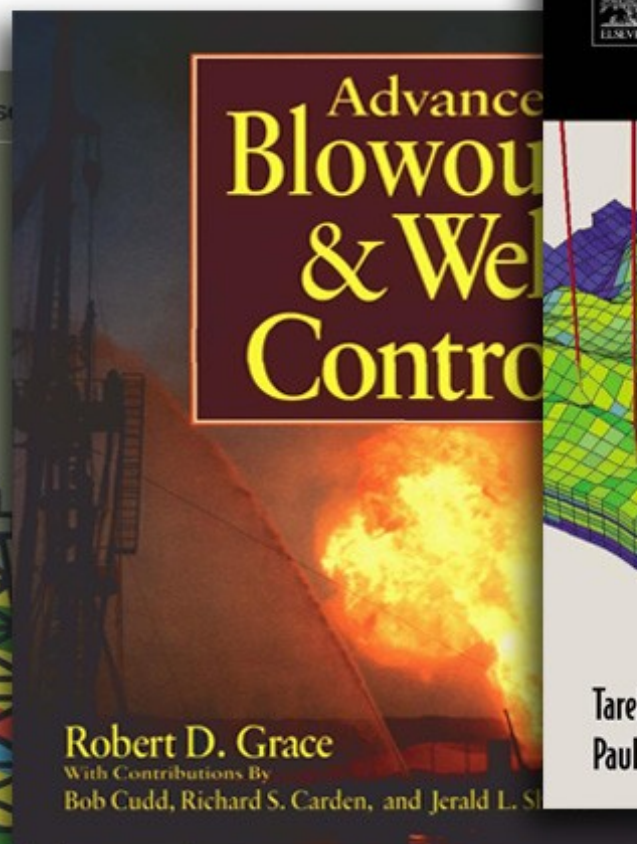
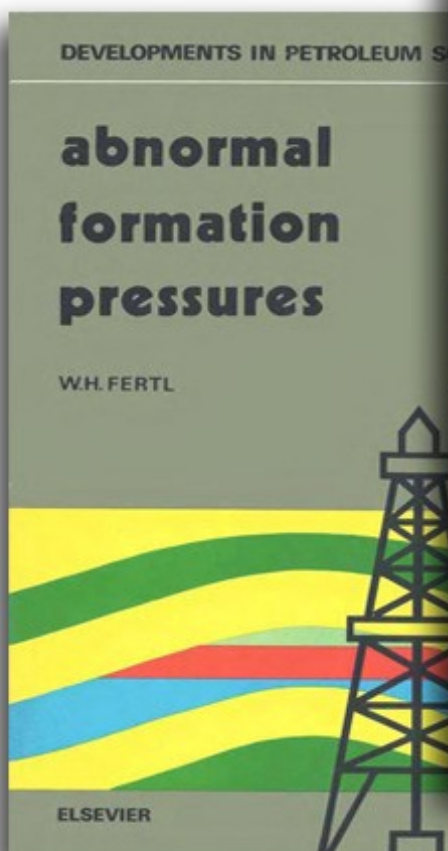


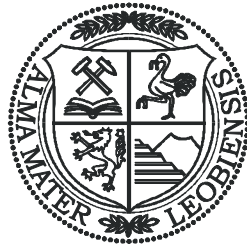


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# **TEXTBOOK SERIES**

VOLUME 2

# **RESERVOIR FLUIDS**

by

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Leoben, October 2004



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# Chapter 1

## Review of Thermodynamic Terminology

When considering hydrocarbon reservoirs, terms such as “oil reservoirs” and “gas reservoirs” are used both in colloquial speech and technical literature. However, these terms are insufficient. Changes in the state of aggregation during production should always be taken into account, in consequence of changes of the reservoir pressure and changes of pressure and temperature in the production system (tubing, pipe lines, separator, tank).

Thermodynamics has evolved to a science of studying changes in the state of a system with changing conditions, i.e. temperature, pressure, composition. Therefore, it may be helpful to refurbish the thermodynamic terminology at the beginning, as far as it is indispensable to the understanding of these tools.

Thermodynamic studies are generally focused on arbitrarily chosen systems while the rest of the universe is assumed as “surroundings”. The surface of the system - real or imaginary - is called a “boundary”. A system is called a “closed system” if it does not exchange matter with the surroundings, in opposite to an “open system” which exchanges matter with the surroundings. Both systems may exchange energy with the surroundings.

The concept of a closed system is of major interest in applied hydrocarbon thermodynamics. It is called a “homogeneous” closed system if it only contains a single phase, e.g. natural gas phase or oil. A “heterogeneous” closed system contains more than one phase.

A “phase” is defined as a physically homogeneous portion of matter. The phases of a heterogeneous system are separated by interfaces and are optically distinguishable. It is not obligatory that a phase is chemically homogeneous. It may consist of several compounds, e.g. of a large number of various hydrocarbons.

The properties of a system are classified into “intensive” and “extensive” properties. Intensive properties such as temperature and pressure are independent of the size of the system, i.e. of the amount of the substance in the system. Extensive properties depend on the amount of the substances, such as volume, enthalpy, entropy etc. However, extensive properties per unit of mass or mole are intensive properties, e.g. the mole volume.

“State functions” or “state variables” are those properties for which the change in state only depends on the initial and final state of the system. It is this path-independent characteristic of the state functions that makes it possible to quantify any change of a system.

“Equilibrium” has been defined as a “state of rest”. In an equilibrium state, no further change or - more precisely - no net-flux will take place unless one or more properties of the system are altered. On the other side, a system changes until it reaches its equilibrium state.. Any change of a system is called a “thermodynamic interest” in the thermodynamic study of the system:

- adiabatic (no heat added to or removed from the system),
- isothermal (constant temperature),
- isobaric (constant pressure),
- isochoric (constant volume).

A process is called “reversible” if it proceeds through a series of equilibrium states in such a way that the work done by forward change along the path is identical to the work attained from the backward change along the same path. However, all real processes are “irreversible” with varying degrees of departure from a reversible one.

## Chapter 2

# Phase Behavior

Hydrocarbon reservoirs consist of rock and fluids. Water in brine form and a gaseous and/or liquid hydrocarbon phase are regarded as reservoir fluids. The phase behavior of the actual hydrocarbon mixture in the reservoir can be described as a function of the state of the system.

A system in thermodynamic equilibrium possesses an accurately defined relationship between the state variables. These are united in the so-called “equation of state”:

$$F(p, V, T) = 0. \quad (2.1)$$

By specification of two variables, the third one will be stipulated.

## 2.1 GIBBS' Phase Rule

When referring to the number of phases coexisting in the thermodynamical equilibrium, the phase rule introduced by GIBBS (1928) is applied.

$$F = C - P + 2 \quad (2.2)$$

where

- **P**: number of phases,
- **C**: number of components,
- **F**: number of degrees of freedom.

**C** is defined as the smallest number of constituents by which the coexisting phases can be completely described. **F** is defined as the number of quantities - such as pressure, temperature, concentrations - which can be varied within finite boundaries without changing the number of phases in the system.

Eq. 2.2 describes the system in a qualitative and very general manner. However, no reference to the state variables ( $p$ ,  $T$ ), to the composition of the particular phases or to the proportions of the phases are given.

To gain a full understanding, it is best to discuss the phase behavior of pure substances (single-component systems) first. The circumstances in case of binary or even multi-component systems are much more complicated.

## 2.2 Single-Component System

### 2.2.1 Water

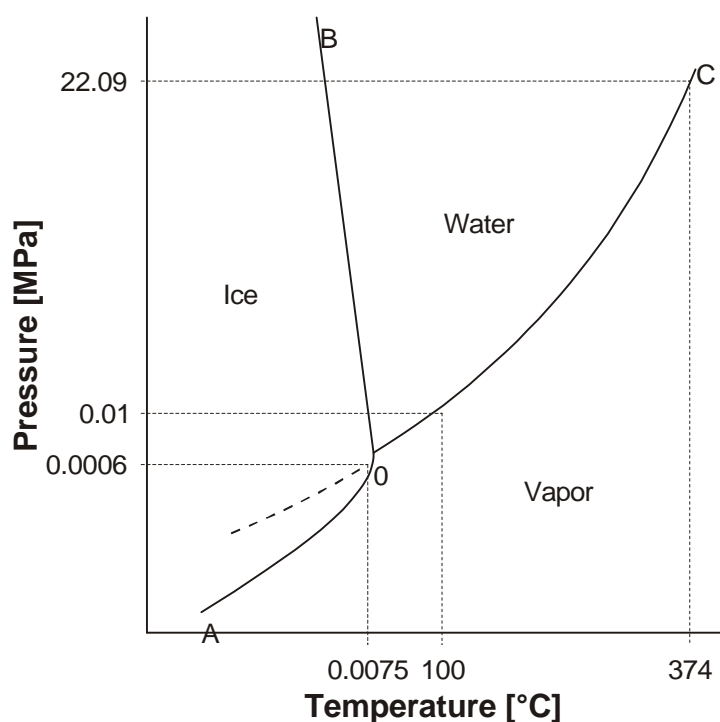


Figure 2.1: Water system - schematic (not drawn to scale)

Water is one of the most thoroughly studied chemical compounds. Therefore, it is discussed as a single-component system in this context. The possible phases are ice (solid state), water (liquid state) and vapor (gaseous state). The phase diagram in Figure 2.1 illustrates at which state of the system - characterized by  $p$  and  $T$  - two or all three phases are in equilibrium:

- The **sublimation curve OA** signifies the equilibrium between the solid and vapor.
- The **melting point curve OB** combines the states of equilibrium between the solid

and liquid state.

- The **vapor pressure curve OC** specifies the states of the system at which the liquid and vapor coexist. On this curve, the "wet" vapor is in equilibrium with the "saturated" liquid.
- At the **triple point O**, all three phases are in equilibrium. In case of water, the thermodynamical data at this point are  $p = 610.6 \text{ Pa}$  and  $T = 273.16 \text{ K}$ .
- The end point **C** of the vapor pressure curve is the **critical point** and signifies the highest temperature and pressure at which the liquid and vapor coexist ( $p_c(\text{H}_2\text{O}) = 22.09 \text{ MPa}$ ,  $T_c(\text{H}_2\text{O}) = 647.15 \text{ K}$ ).

### Example 2.1

The degree(s) of freedom in different states of a single-component system. by use of Eq. 2.2 (GIBBS' phase rule) and Figure 2.1:

- $F = 0$  at the tripel point ( $P = 3$ ).
- $F = 1$  on the curves describing the 2-phase ( $P = 2$ ) equilibria. Either the temperature or the pressure is freely eligible without counteracting any given phase equilibrium.
- $F = 2$  in any area of single phase state ( $P = 1$ ). Both pressure and temperature (naturally inside finite boundaries) are freely eligible without transforming the system into a multi-phase system.

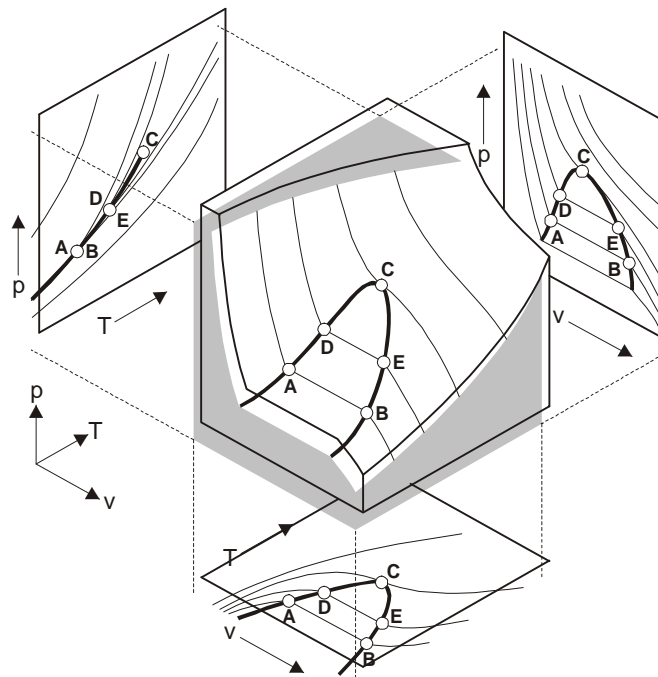


Figure 2.2: Phase equilibrium surface of a pure substance (from GYULAY, 1967)

The state variables,  $p$ ,  $T$ ,  $V$  can only assume positive values. Thus, the graphical illustration of the state of any system is only located in the positive section of the  $(p, V, T)$  coordinate system. An example for an equilibrium surface is given in Figure 2.2. The shape of such an equilibrium surface is substance specific.

Assuming that the partial derivatives are steady, it is possible to draw only one single tangential plane at an optional point of the surface. However, a plane is defined by two vectors which infers that the differential quotients

$$\left(\frac{\partial p}{\partial T}\right)_V, \left(\frac{\partial V}{\partial T}\right)_p, \left(\frac{\partial V}{\partial p}\right)_T$$

are not independent of one another. It is proven that

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \quad (2.3)$$

The three differential quotients describe three fundamental properties of the system: (i) the isothermal compressibility  $\kappa$ , (ii) the cubic expansion coefficient  $\alpha$ , and (iii) the pressure coefficient  $\beta$ :

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \quad (2.4)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad (2.5)$$

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \quad (2.6)$$

Then, according to Eq. 2.3, the following is valid:

$$\alpha = p\kappa\beta \quad (2.7)$$

Since the specific volume - in contrast to Figure 2.1 - appears now as a state variable, the 2-phase state (e.g. water in equilibrium with vapor) is characterized by any area surrounded by two curves which converge at the critical point:

- On the **bubble point curve**, an infinitesimal small amount of vapor is in equilibrium with the “saturated” liquid.
- The **dew point curve** characterizes states in which a negligible small amount of liquid is in equilibrium with “wet” vapor.

It is common to simplify the complex spatial illustration of the equilibrium surface by

applying normal projections. Figure 2.2 displays that

- the projection into the  $(p, V)$  plane results in **isotherms** ( $T = \text{const}$ ),
- the projection into the  $(V, T)$  plane results in **isobares** ( $p = \text{const}$ ),
- the projection into the  $(p, T)$  plane results in **isochores** ( $V = \text{const}$ ).

Considering the projection which represents the 2-phase area (liquid-vapor) in the  $(p, T)$  plane, the bubble point curve and dew point curve coincide. The resulting single curve is called **vapor pressure curve**.

Of course, the vapor pressure curve is not isochoric. However, it is possible to draw isochores: One upwards into the liquid phase and one downwards into the gas phase. This aspect will be described in detail by discussing the phase behavior of the simple hydrocarbon n-butane.

## 2.2.2 n-Butane

Projections of the equilibrium surface into two planes of the positive section of the  $(p, V, T)$  coordinate system are shown in Figure 2.3 and Figure 2.4.

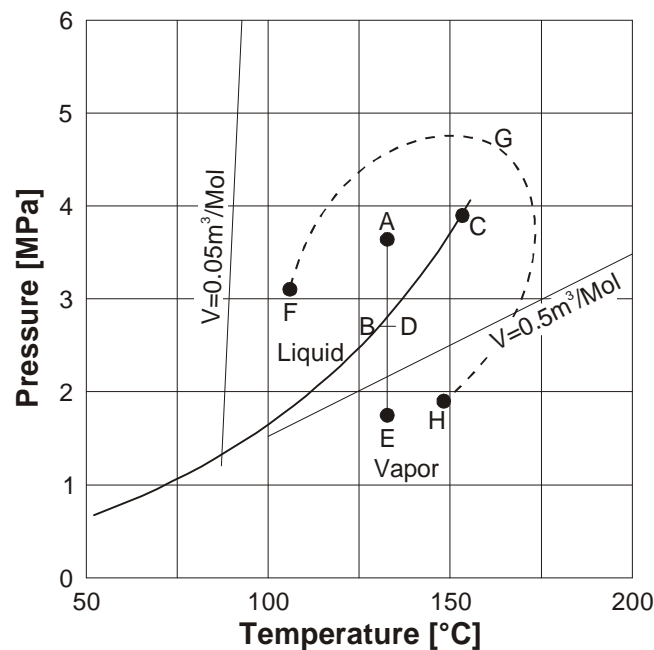


Figure 2.3: Vapor pressure diagram of n-butane (from GYULAY, 1967)

Figure 2.3 illustrates the vapor pressure curve of n-butane, including the critical point  $C$ . In addition, the isochores  $V = 0.05 \text{ m}^3/\text{kmole}$  inside the liquid phase region and  $V = 0.5 \text{ m}^3/\text{kmole}$  inside the vapor region are shown. In case of the state  $A$ , butane is an

undersaturated liquid. When moving to the bubble point **B** by isothermal expansion, vaporization commences. Then the continuation of this isothermal expansion includes no further pressure drop in the system until the last molecule has passed over to the gas phase. From this moment, further expansion will result in further pressure decrease. At the point **E**, *n*-butane is in the state of a “dry” vapor. An isochoric change of state must be analogously discussed.

By applying the projection of the equilibrium surface into the ( $p$ ,  $V$ ) plane (see Figure 2.4), it is possible to comprise the whole 2-phase region. In this region, the isothermal vaporization or condensation takes place as an isobaric process.

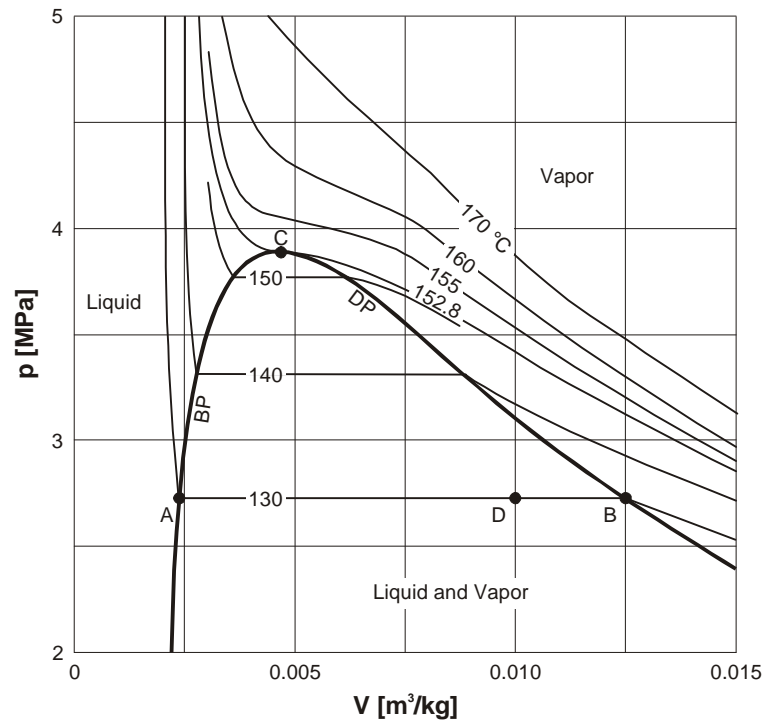


Figure 2.4: Pressure - volume phase diagram of *n*-butane (from GYULAY, 1967)

Isotherms, which do not intersect the 2-phase region, describe those states of the system without any phase transformation by changing the pressure. The intersection point of all other isotherms with the bubble point curve (e.g. **A**) marks the specific volume of the saturated liquid which is in phase equilibrium with the specific volume of the wet vapor (e.g. marked by point **B**). Considering point **D** within the 2-phase region of the system (specific volume of the system in total), the mass ratio of the liquid and vapor phase being in equilibrium with one another can be calculated by the principle of the lever:

$$m_L/m_v = \overline{DB}/\overline{AD} \quad (2.8)$$

**Example 2.2**

100 kg n-butane are filled up in a sealed 10 m<sup>3</sup> container. The volume of the vapor phase at T = 130°C and p = 2.7 MPa can be evaluated from Figure 2.4 using Eq. 2.8

From Figure 2.4:

$$m_L/m_v = \overline{DB}/\overline{AD} = 0.3333,$$

$$m_L + m_v = 100 = 0.3333 m_v + m_v$$

$$m_v = 75 \text{ kg.}$$

The specific volume of the vapor phase is marked by point B in Figure 2.4:

$$V = 0.0125 \text{ m}^3/\text{kg}.$$

The vapor volume of the system, V<sub>v</sub>, can be now calculated by multiplying V with m<sub>v</sub>:

$$V_v = 0.9375 \text{ m}^3.$$

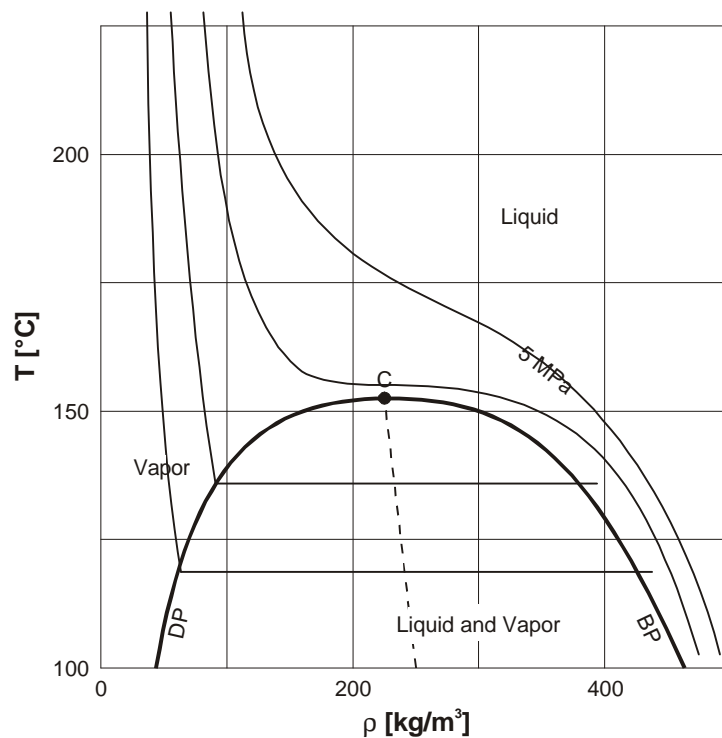


Figure 2.5: Temperature - density phase diagram of n-butane (from GYULAY, 1967)

Figure 2.5 demonstrates the (T, ρ) diagram of n-butane. The isobare touching the critical point has an inflection point just as the critical isotherm in Figure 2.4. Inside the 2-phase region, average values of fluid and vapor density are located on a straight line. With the help of this rule (CAILLETET-MATHIAS rule (1886)), the critical density can be calculated

by extrapolation.

### Example 2.3

Use the CAILLETET-MATHIAS rule to evaluate the critical density of methane. The densities of the liquid and the vapor phase being in equilibrium have been measured at different temperatures (see table below). The values of averaged densities have already been calculated.

Temperature T °C	Liquid Density $\rho_{liq,eq}$ kg/m <sup>3</sup>	Vapor Density $\rho_{v,eq}$ kg/m <sup>3</sup>	Averaged Density $\overline{\rho_{eq}}$ kg/m <sup>3</sup>
- 158.3	4.192 E + 2	2.311 E + 0	2.1076 E + 02
- 148.3	4.045 E + 2	2.798 E + 0	2.0365 E + 02
- 138.3	3.889 E + 2	7.624 E + 0	1.9825 E + 02
- 128.3	3.713 E + 2	1.240 E + 1	1.9185 E + 02
- 118.3	3.506 E + 2	1.925 E + 1	1.8493 E + 02
- 108.3	3.281 E + 2	2.899 E + 1	1.7855 E + 02

It is known as the CAILLETET-MATHIAS rule that the averaged densities are situated on a straight line. The slope of a straight line can be evaluated by regression analysis. On the basis of the averaged densities given above:

$$tg \alpha = -0,654 kg/m^3.$$

To evaluate the critical density,  $\rho_c$ , the line must be extrapolated to the critical temperature of methane,  $T_c = -82,3^\circ C$ :

$$\rho_c = 178.55 - 26 \times 0.654 \text{ kg/m}^3,$$

$$\rho_c = 161.546 \text{ kg/m}^3.$$

## 2.3 Critical State and Quantities of Corresponding States

Figure 2.4 illustrates the inflection point of the critical isotherm at the critical point. At the point of the inflection, both the first and the second partial derivatives of  $p = p(V)$  equal zero that

$$\left(\frac{\partial p}{\partial V}\right) = 0 = \left(\frac{\partial^2 p}{\partial V^2}\right). \quad (2.9)$$

The state of the system at this point is characterized by the critical specific volume  $V_c$ , the critical pressure  $p_c$ , and the critical temperature  $T_c$ .

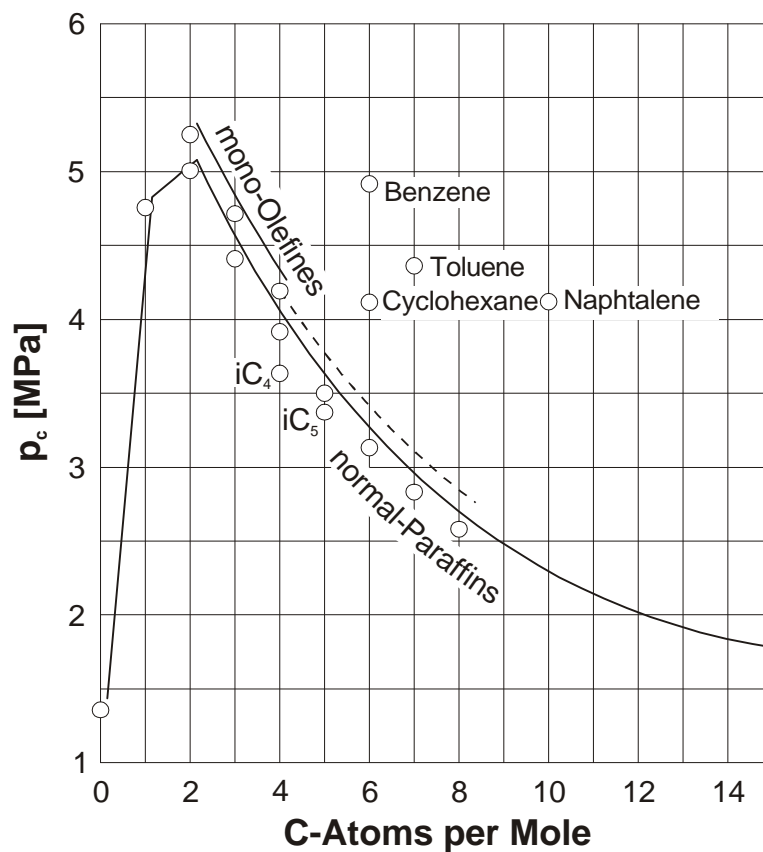


Figure 2.6: Critical pressure as a function of number of C-atoms in homologous series (after GYULAY, 1967)

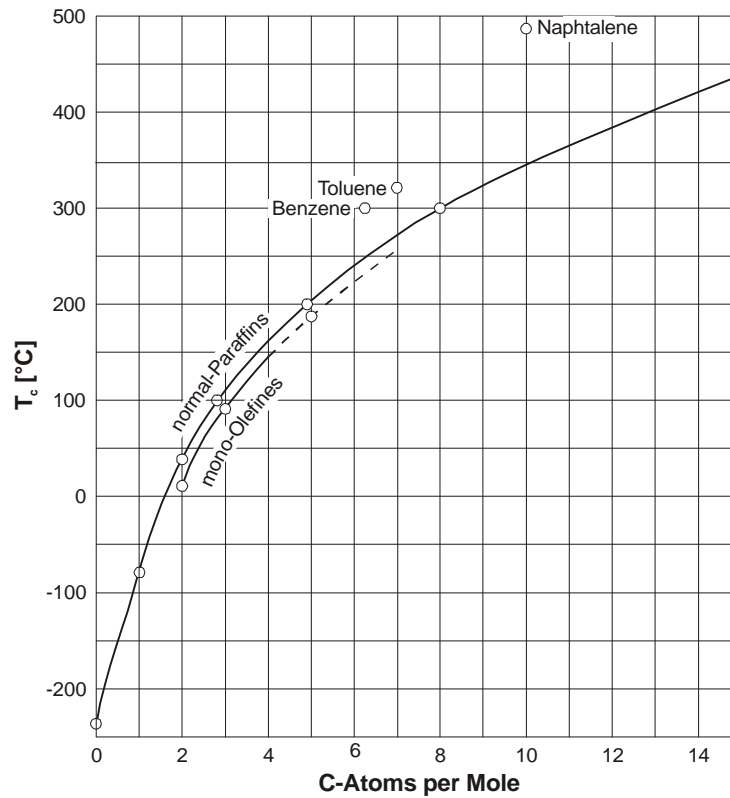


Figure 2.7: Critical temperature as a function of numbers of C-atoms in homologous series (after GYULAY, 1967)

Considering the critical data  $p_c$  and  $T_c$ , the homologous series of hydrocarbons show regularities which can be used for extrapolation. The experimental data in Figure 2.6 and Figure 2.7 refer to the homologous series of paraffins,  $C_nH_{2n+2}$ , and olefins,  $C_nH_{2n}$  ( $n = 1, 2, \dots, k$ ), with a margin of error 1 to 2 %. Because of thermal decomposition in case of high molecular weight, it is not possible to obtain experimentally information about the critical data. However, the critical data of homologous compounds with longer carbon chains can be extrapolated though an increasing error has to be taken into consideration.

The “*principle of corresponding states*” for chemically similar substances - e.g. for homologous series - results in a close relation between the  $(p, V, T)$  properties of pure hydrocarbons if the state variables are substituted by the so called “reduced quantities” which are

$$p_r = \frac{p}{p_c}; \quad V_r = \frac{V}{V_c}; \quad T_r = \frac{T}{T_c} \quad (2.10)$$

Figure 2.8 shows a  $(p_r, V_r)$  phase diagram which is valid for paraffins from methane ( $CH_4$ ) to hexane ( $C_6H_{14}$ ).

## 2.4 Binary Systems

If a system consists of more than one component, its state is also a function of composition. In general, the composition is defined by “*mole fractions*”.

The mole fraction is defined as the ratio between the number of moles of a certain component and the sum of moles of all components. A system being composed of  $k$  components is defined by the specification of  $(k - 1)$  mole fractions because the sum of the mole fractions always equal  $1$ . Considering a 2-component system, every change in state is described by the equation of state  $F(p, V, T, z) = 0$ .  $z$  may be the mole fraction of one (lighter) component.

The phase behavior of the ethane/n-heptane system is graphically illustrated by the  $(p, T, z)$  coordinate system in Figure 2.9. The volume is equivalent to the mole volume.

In the plane  $z = 1$ , the vapor pressure curve of ethane appears, whereas in the plane  $z = 0$  the one of n-heptane appears. Covering all other  $z$  planes, an envelope surface encloses the 2-phase state. This is demonstrated by the example of three additional  $z$  planes.

The upper broken line marks the critical points of all compositions which are possible. This curve divides the envelope surface into two parts: the **bubble point surface** and the **dew point surface**. The region of an undersaturated liquid state is positioned outside the bubble point surface (low temperature). Outside of the dew point surface (high temperature), the state of a dry gas is given.

Analogous to the pure substance, the critical state of binary systems is defined as the state at which the intensive properties of the phases are no more distinguishable. Just as in case of single-component systems, the critical isotherms have an inflection point according to Eq. 2.9.

Figure 2.10 shows the projection of Figure 2.9 into the  $(p, T)$  plane. At a given pressure, the bubble point temperature of the mixture is always higher than that of the pure lighter component. Physically, it can be explained by the fact that the thermal motion of the lighter molecules is obstructed by the heavier ones which exhibit more inertia.

On the other side, the dew point temperature of the mixture at a given pressure is always lower than that of the pure heavier component. This is due to the fact that lighter molecules partially transfer their higher kinetic energy to the heavier ones by collision. Consequently, the system maintains the state of a gas phase.

Figure 2.10 also shows that  $T_c$  of a mixture lies between the critical temperatures of the pure substances. In contrast to this,  $p_c$  of the mixture may be obviously higher than the one of the pure substances.

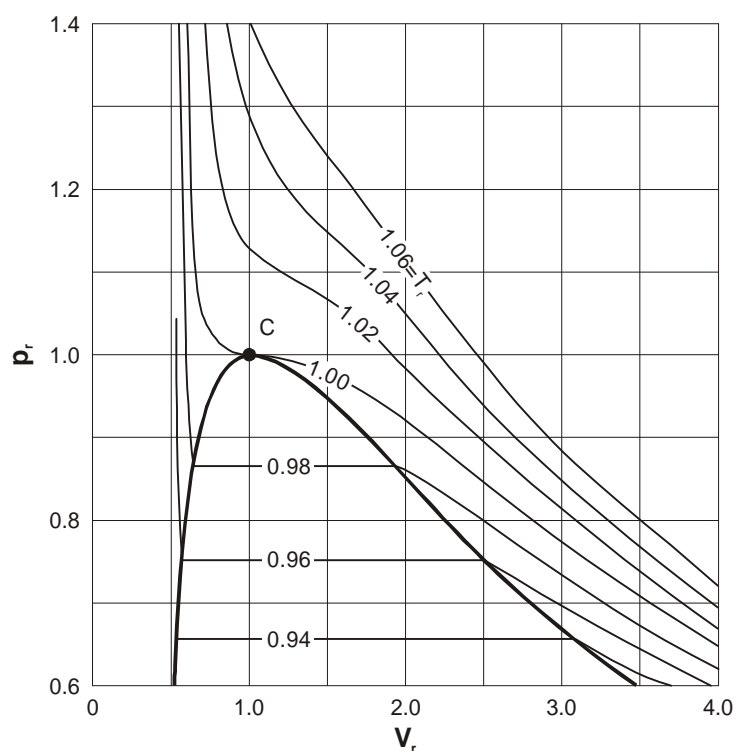


Figure 2.8: Combined reduced pressure - reduced volume phase diagram of paraffins with low molecular weight (after GYULAY, 1967)

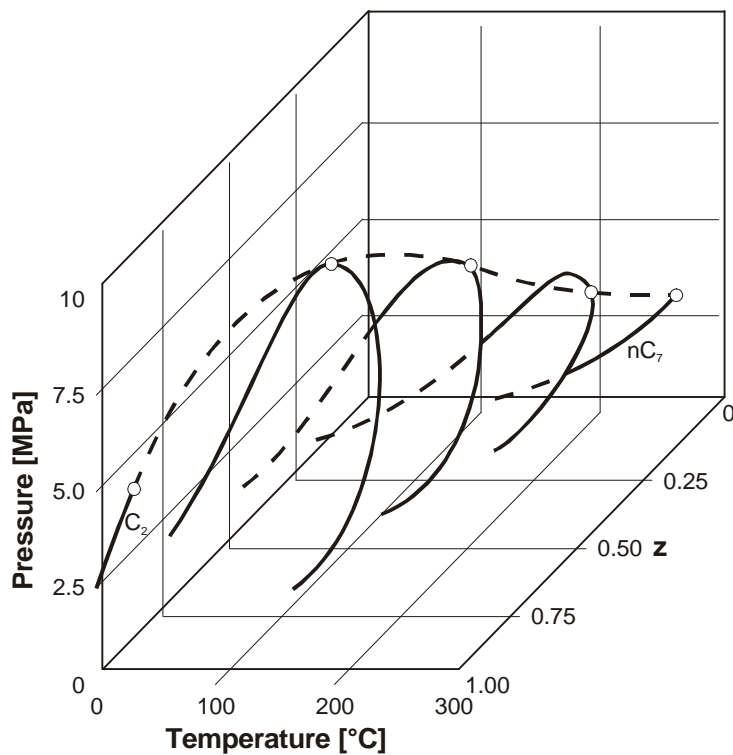


Figure 2.9: Phase equilibrium surface of the binary system ethane/n-heptane (from GYULAY, 1967)

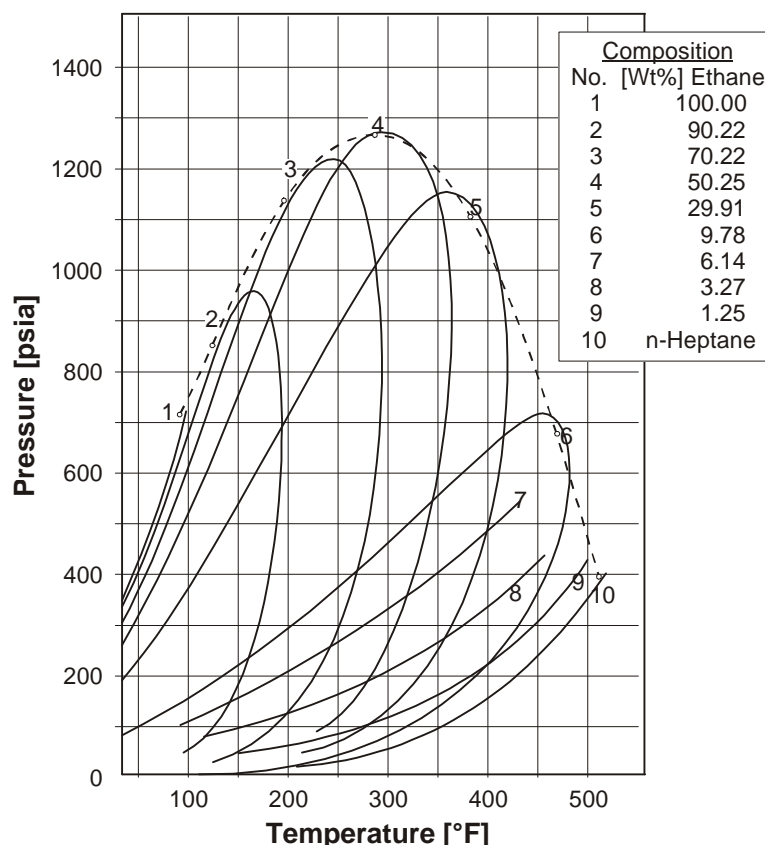


Figure 2.10: Pressure - temperature phase diagram of the binary system ethane/n-heptane (from KAY, 1938)

If the mixture consists of two homologous compounds with quite different volatility (in consequence of quite different molecular weights), the critical data curve envelopes a very extensive temperature and pressure region. For example, the maximum of the critical pressure of a methane/n-decane system equals 37 MPa. The smaller the difference between the molecular weights and thus between the volatility, the more flat the envelope curve will be.

Figure 2.11 illustrates the phase behavior of a certain ethane/n-heptane system. Besides the critical point, the curve enveloping the 2-phase region possesses two additional characteristic points:

- $C'$ : the point of highest pressure on the curve that is called **cricondenbare**.
- $C''$ : the point of highest temperature on the curve that is called **cricondentherm**.

As on Figure 2.11, so called "**quality lines**" are shown on  $(p, T)$  diagrams. A quality line represents a certain mole percentage being liquid or vapor in the state of phase equilibrium. In Figure 2.11, the quality line "20 %" represents the states in which 20 % of the system account for the liquid phase. The bubble point curve and the dew point curve represent 100 % and 0 % liquid, respectively. All the quality lines (isochores) converge at the critical point.

Figure 2.11 also shows an isothermal decrease along the path  $EF$  where  $E$  defines the system to be a dry gas. If the constant temperature is higher than  $T_c$  but lower than the cricondentherm - like in case of the path  $EF$  -, the path surpasses the dew point line twice. Consequently, a condensate drops out at the dew point  $D'$ . At some point between  $D'$  and  $D''$ , the volume of condensate (liquid) will be at its maximum. This maximum is given by the intersection point of the path  $EF$  with the dotted line connecting the critical point  $C$  and  $C'$ . If the decrease in pressure will be continued, the condensate will be vaporized again. As soon as the dew point  $D''$  has been reached, the condensed phase has been vaporized in total. This process is called a “*retrograde condensation*”.

Similar phenomena occur when the temperature is changed by an isobaric process where the constant pressure is higher than  $p_c$  but lower than the cricondenbar of the system.

In Figure 2.11, the dotted line connecting point  $C$  with point  $C'$  marks the states of the system which exhibit the highest volume percentage of condensate dropout.

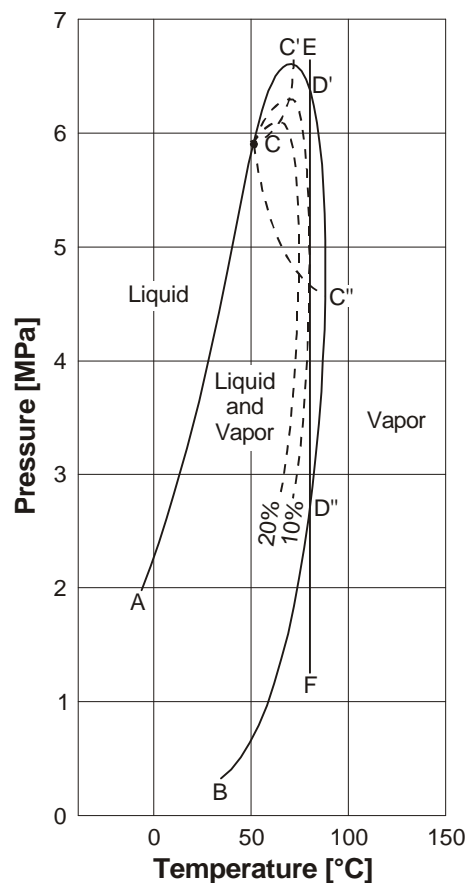


Figure 2.11: Pressure - temperature phase diagram of the binary system ethane ( $z = 0.9683$ )/n-heptane

It depends on the composition of the system if the cricondenbar is located on the dew point curve or on the bubble point curve. As far as the system ethane/n-heptane is concerned, Figure 2.10 elucidates that the cricondenbar is located on the bubble point curve at low mole fractions of ethane.

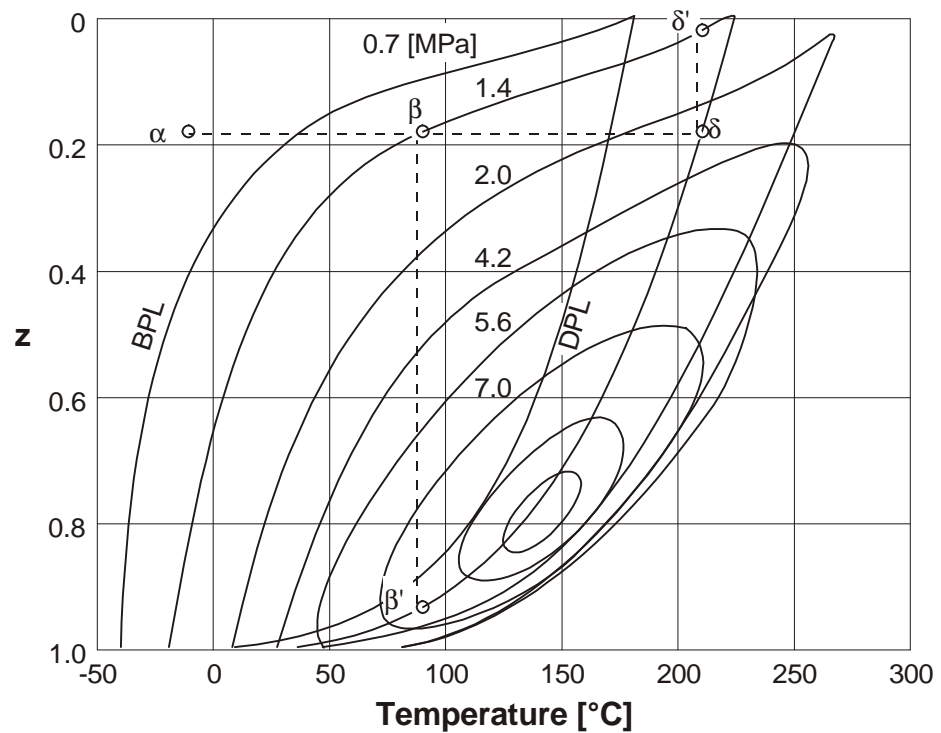


Figure 2.12: Mole fraction(ethane) - temperature diagram of the binary system ethane/n-heptane (from GYULAY, 1967)

In Figure 2.12, the phase behavior of ethane/n-heptane systems is graphically illustrated in the  $(z, T)$  plane corresponding to another possible projection of the surface in Figure 2.9. The mixture  $\alpha$  achieves bubble point  $\beta$  due to an isobaric (1.4 MPa) heat supply. Point  $\beta$  symbolizes the composition of the liquid phase which is in equilibrium with an infinitesimal small vapor phase whose composition is symbolized by the point  $\beta'$ . During further increase of temperature, dew point state is reached at point  $\delta$ . The composition of the infinitesimal small liquid phase in equilibrium with the vapor phase corresponds with point  $\delta'$ .

The design of the corresponding  $(p, z)$  diagram is also possible (see Figure 2.13). An example may be the composition at the point **A** ( $T = 150$  °C). The composition of the liquid phase is given by point  $A'$ , the one of the vapor phase by point  $A''$ . Again the relative masses of both phases can be determined by applying the principle of the lever (see Example 2.4).

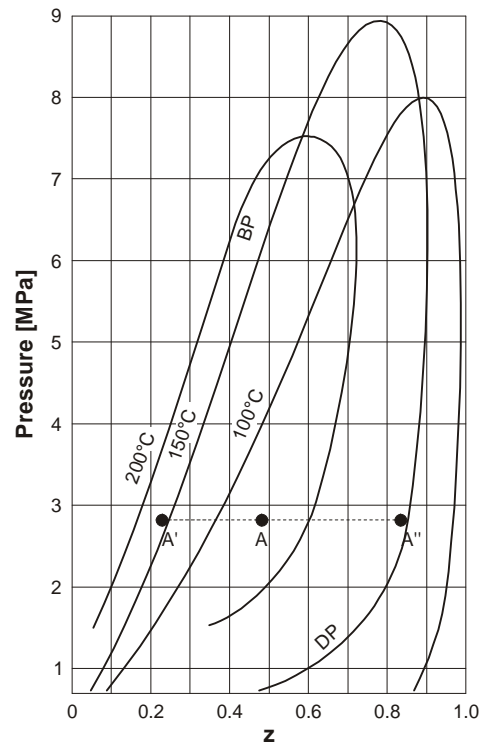


Figure 2.13: Mole fraction (ethane) - Pressure diagram of the binary system ethane/n-heptane (from GYULAY, 1967)

**Example 2.4.**

Determination of the phase composition and distribution of the components.

A sealed container ( $p = 2.86 \text{ MPa}$ ),  $T = 150^\circ\text{C}$ ) is filled up with 100 kg of a ethane( $z = 0.47$ )/n-heptane mixture. The mole number of ethane in the liquid phase and in the vapor phase, respectively, can be evaluated from Figure 2.13 by using the principle of lever.

At first, the mole weights ( $M_{C2} = 30 \text{ kg/mole}$ ,  $M_{C7} = 100 \text{ kg/mole}$ ) are inserted into

$$z = \frac{\left(\frac{m_{C2}}{30}\right)}{\left(\frac{m_{C2}}{30}\right) + \left(\frac{m_{C7}}{100}\right)}$$

to evaluate the weight of n-heptane in the system,  $m_{C7}$ . The weight of ethane,  $m_{C2}$ , is given by  $m_{C2} = 100 - m_{C7}$ .

$$z = 0.47 = \frac{\left(\frac{100 - m_{C7}}{30}\right)}{\left(\frac{100 - m_{C7}}{30}\right) + \left(\frac{m_{C7}}{100}\right)}$$

$$m_{C7} = 78.95 \text{ kg}$$

$$m_{C2} = 100 - 78.95 = 21.05 \text{ kg}$$

Now the total mole number of the system,  $n = n_{C2} + n_{C7}$ , can be calculated:

$$n_{C2} = \frac{m_{C2}}{M_{C2}} = \frac{21.05}{30} = 0.702 \text{ kmole} ,$$

$$n_{C7} = \frac{m_{C7}}{M_{C7}} = \frac{78.95}{100} = 0.790 \text{ kmole} ,$$

$$n = 0.702 + 0.790 = 1.492 \text{ kmole} .$$

From Figure 2.12

$$\frac{n_{liq}}{n_{vap}} = \frac{\overline{A A''}}{\overline{A A'}} = 1.346$$

where

$n_{liq}$ : total mole number in the liquid phase

$n_{vap}$ : total mole number in the vapor phase

Thus the total mole number in the vapor phase results in

$$n_{vap} = 0.636 \text{ kmole}$$

The composition of the vapor phase is given by point  $A''$  in Figure 2.12:

$$z = 0.82$$

The mole number of ethane in the vapor phase can now be calculated by

$$n_{C2, vap} = z \times n_{vap} = 0.82 \times 0.636 = 0.521 \text{ kmole} .$$

The composition of the liquid phase is given by point  $A'$  in Figure 2.12:

$$z = 0.23 .$$

The total mole number in the liquid phase results in

$$n_{liq} = n - n_{vap} = 1.432 - 0.636 = 0.856 \text{ kmole} .$$

The mole number of ethane in the liquid phase can now be calculated by

$$n_{C2, liq} = 0.23 \times 0.856 = 0.188 \text{ kmole} .$$

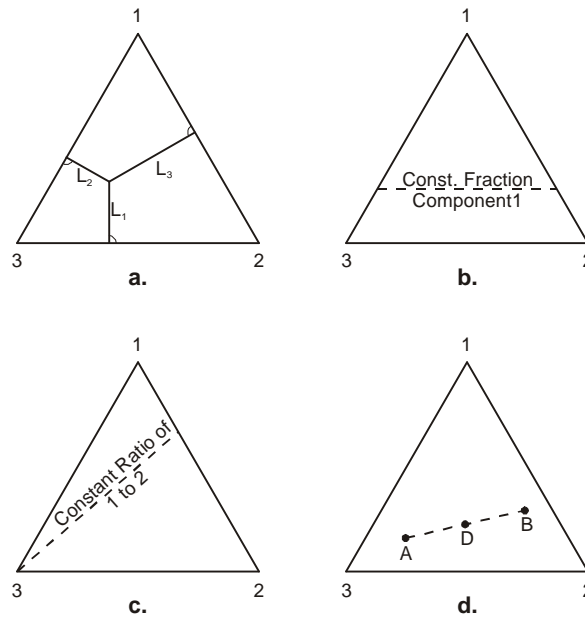


Figure 2.14: Properties of ternary diagrams

## 2.5 Multi-Component Systems

### 2.5.1 Ternary Phase Diagrams

It is common to illustrate the phase behavior of 3-component systems at constant pressure and temperature in so called triangular diagrams. Each corner of the triangle represents one pure component. On the basis of the equilaterality of the triangle, the sum of the perpendicular distances from any point to each side of the diagram is a constant equal to length of any of the sides. Thus, the composition - expressed in mole fractions - of a point in the interior of the triangle is given by

$$z_1 = \frac{L_1}{L_T}, \quad z_2 = \frac{L_2}{L_T}, \quad z_3 = \frac{L_3}{L_T}, \quad (2.11)$$

where

$$L_T = L_1 + L_2 + L_3. \quad (2.12)$$

Several other useful properties of the triangular diagrams are also illustrated by Figure 2.14:

- For mixtures along any line parallel to a side of the diagram, the fraction of the component of the corner opposite to that side is constant.
- Mixtures lying on any line connecting a corner with the opposite side contain a constant ratio of the component at the ends of the side.
- Mixtures of any two compositions lie on a straight line connecting the two initial points on the ternary diagram. The principle of the lever finds application again and

$$\frac{n_A}{n_B} = \frac{\overline{DB}}{\overline{DA}} \quad (2.13)$$

gives the mixing ratio leading to mixture **D**.

Figure 2.15 shows the 2-phase region for chosen **p** and **T**. Any mixture with an overall composition lying inside the binodal curve will split into a liquid and a vapor phase. The “**tie lines**” connect compositions of liquid and vapor phases in equilibrium. Any overall composition on a certain tie line gives the same liquid and vapor composition being in equilibrium. Only the amounts of the phases change as the overall composition changes.

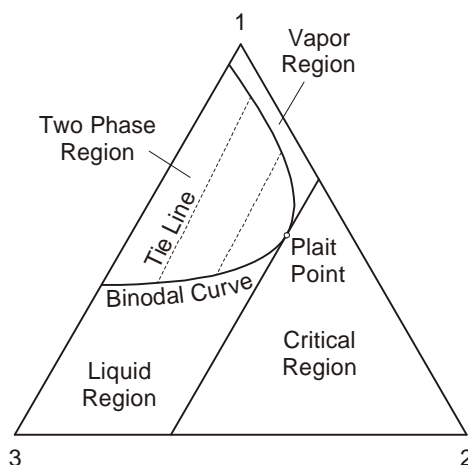


Figure 2.15: Typical features of a ternary phase diagram

The liquid and vapor portion of the binodal curve meet at the “**plait point**” which represents the critical composition. By drawing the tangent in the plait point on the binodal curve, the single-phase region is splitted into three sections. Mixtures of a composition being located in the critical region with another one being located in the liquid or vapor region will, in any case, also result in a single-phase system if the straight

line connecting the two initial compositions does not intersect the 2-phase region.

Figure 2.16 illustrates the influence of pressure on the phase behavior of a certain ternary system at constant temperature. As pressure increases, the 2-phase region shrinks.

It is useful to comprise the two heavier components of a ternary system and to reduce this system to a fictitious binary system, on the basis of a hypothetical component. Figure 2.17 illustrates a corresponding application by the respective  $(p, T)$  diagram of the methane/propane/n-pentane system. The mole-% of methane are specified along the outermost envelope curve. All envelope curves are characterized by the portion of propane in the hypothetical component (propane/n-pentane) which is given by

$$C = \frac{z_3}{z_3 + z_5} \quad (2.14)$$

In accordance to this aspect, the critical state properties,  $p_c$  and  $T_c$ , can be determined for any mixture of the three components (see Example 2.5).

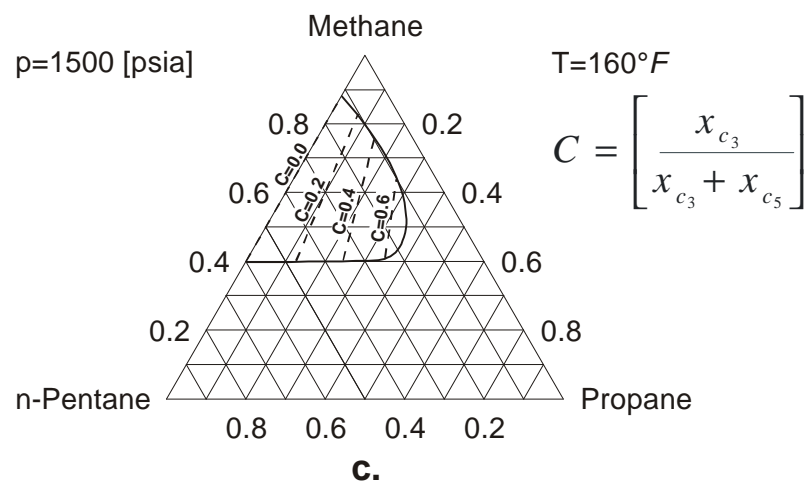
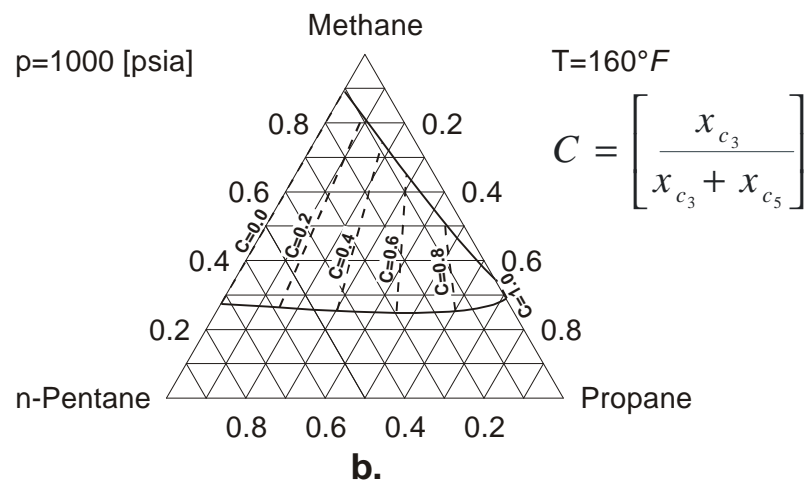
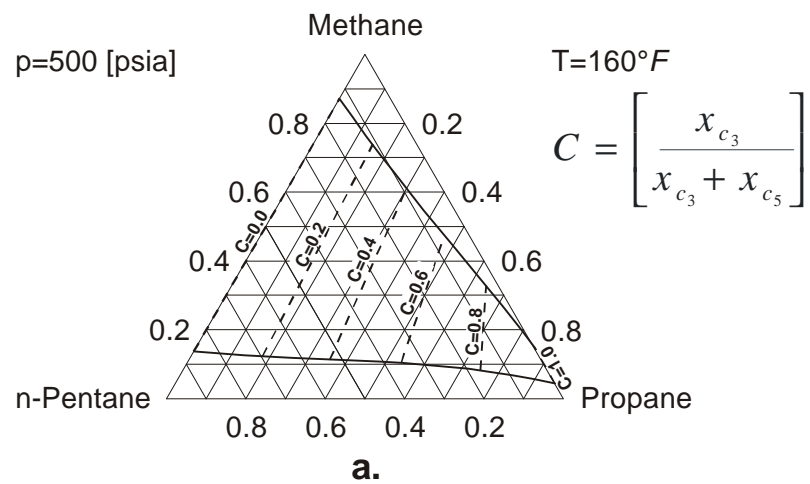


Figure 2.16: Triangular diagrams for the methane/propane/n-pentane system at 160 °F (71 °C) (after DOURSON et al., 1943)

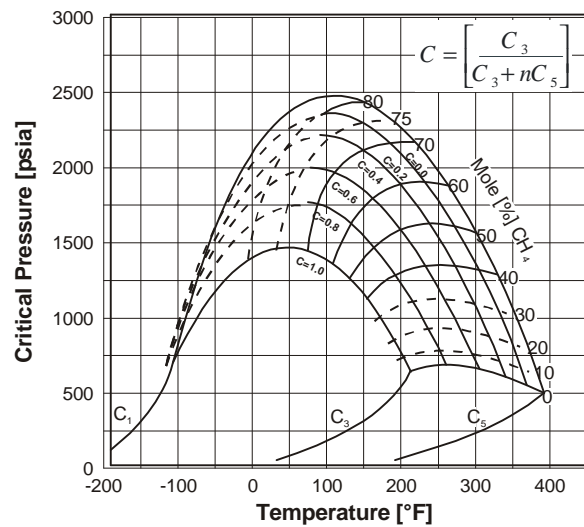


Figure 2.17: Critical loci of methane/propane/n-pentane systems  
(from KATZ et al., 1959)

### Example 2.5

The hydrocarbon mixture is composed of 8 kg methane ( $M = 16$  kg/kmole), 13.2 kg propane ( $M = 44.1$  kg/kmole) and 32.5 kg n-pentane ( $M = 72.2$  kg/kmole). The critical data of this mixture can be evaluated by use of Figure 2.17.

At first, the mole numbers and the respective mole fractions must be calculated.

$$n_1 = \frac{8}{16} = 0.5 \text{ kmole},$$

$$n_3 = \frac{13.2}{44.1} = 0.3 \text{ kmole},$$

$$n_5 = \frac{32.5}{72.2} = 0.45 \text{ kmole},$$

$$z_1 = \frac{0.5}{0.5 + 0.3 + 0.45} = 0.4,$$

$$z_3 = \frac{0.3}{0.5 + 0.3 + 0.45} = 0.24,$$

$$z_5 = \frac{0.45}{0.5 + 0.3 + 0.45} = 0.36.$$

The portion of propane in the hypothetical component propane/n-pentane is given by

$$C = \frac{z_3}{z_3 + z_5} = \frac{0.24}{0.24 + 0.36} = 0.4.$$

From Figure 2.17 at  $C = 0.4$  and 40 mole percent methane:

$$T_c = 262.5^\circ F = 128^\circ C$$

and

$$p_c = 1344 \text{ psia} = 9.26 \text{ MPa}.$$

The application of the triangular diagram is not solely confined to ternary systems. For example it is possible to partition the paraffinic hydrocarbons into three pseudo-components which are

- methane ( $C_1$ ) as the light component,
- the lighter pseudo-component including ethane to hexane ( $C_2-C_6$ ),
- the heavier pseudo-component including heptane and higher hydrocarbons ( $C_{7+}$ ).

Anyway, only poor information of complex natural hydrocarbon systems has been reported until now. Nevertheless, some generalization makes a description of these complex systems possible - according to known data. The phase behavior of several complex and natural hydrocarbon systems are demonstrated in Figure 2.18 to Figure 2.22 by  $(p,T)$  phase diagrams. For the classification of natural hydrocarbon systems, it is essential to know

- if the critical temperature is lower or higher than the reservoir temperature,
- which state will be achieved at surface conditions (separator).

Not considered in this classification are changes in composition during production.

Figure 2.18 represents a hydrocarbon system whose critical temperature is significantly lower than the reservoir temperature. In case of an isothermal pressure decrease (full line from point **1** to **2**), which occurs in the reservoir adjacent to the production well the the course of production, the system remains in the single-phase (gaseous) state. Even in case of both pressure and temperature decrease (dotted line), no liquid phase will drop out. Consequently, the considered hydrocarbon mixture is called a “**dry gas**”. Dry gases contain mainly methane, small amounts of ethane, possibly propane and some hydrocarbons of higher molecular weights.

A so called “**wet gas**” (see Figure 2.19) remains in a single-phase (gaseous) state in the reservoir during production (line **1-2**). Anyway, condensate will drop out under separator conditions.

In case of the system shown in Figure 2.20, the reservoir temperature is higher than the critical one but lower than the cricondentherm. The initial conditions given by Point **1** specifies the hydrocarbon mixture as a dry gas. If the pressure will decrease adjacent to the production well during production, the dew point of the system is reached at point **2**. Consequently, condensate drops out inside the reservoir. The pressure at point **3** corresponds to the state in which the condensed liquid phase reaches the maximum (in mole%). In the separator, the amount of condensate is larger than in case of wet gases. Systems as shown in Figure 2.20 are called “**gas condensates**”.

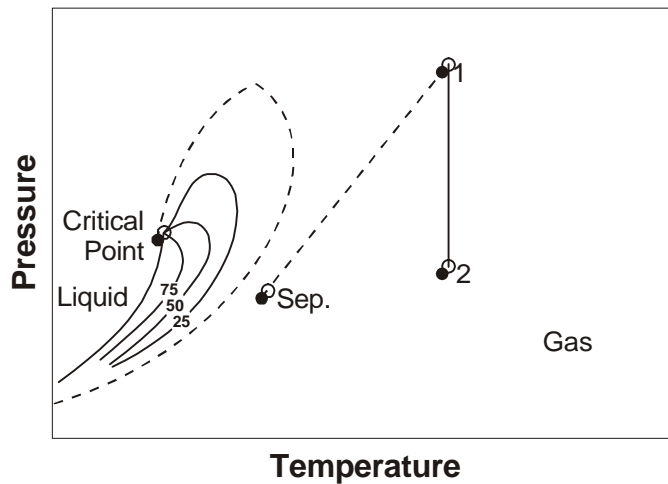


Figure 2.18: Phase diagram of a dry gas (from MCCAIN, 1973)

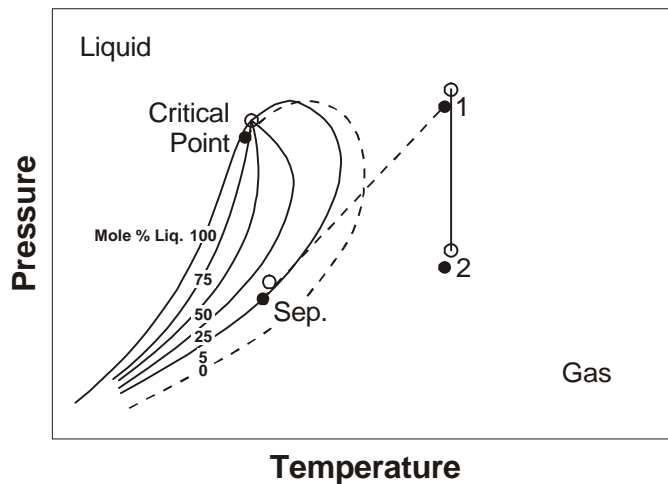


Figure 2.19: Phase diagram of a wet gas (from MCCAIN, 1973)

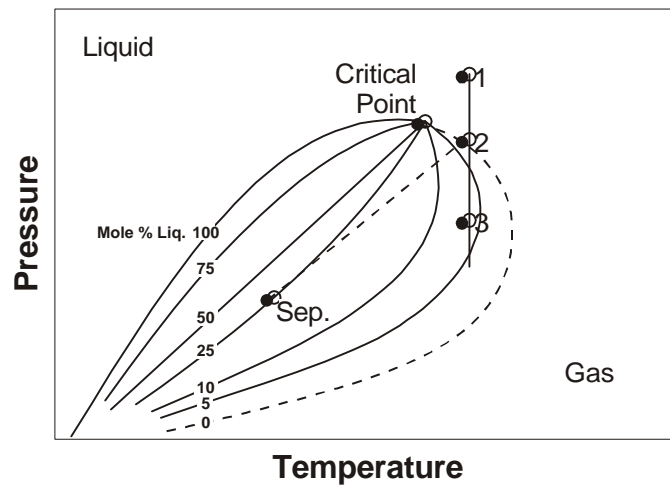


Figure 2.20: Phase diagram of a retrograde gas condensate (from MCCAIN, 1973)

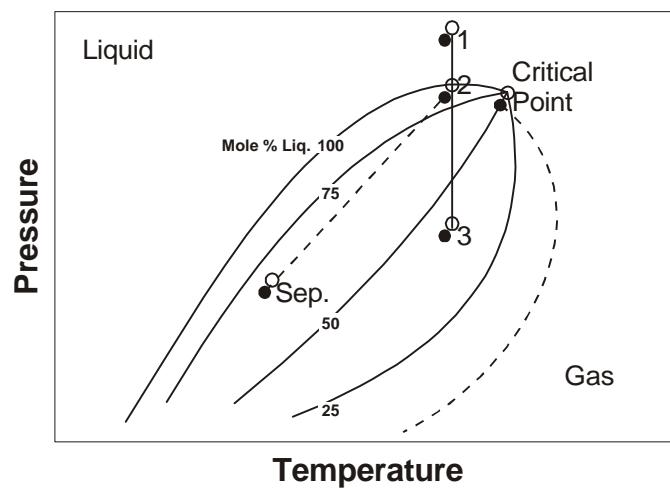


Figure 2.21: Phase diagram of a high-shrinkage crude oil (from MCCAIN, 1973)

The so called “*white oils*” - as characterized in Figure 2.21 - are referred to as “*high shrinkage oils*”. The reservoir temperature is below the critical temperature. Since the bubble point curve will be reached by the decrease in pressure due to production, from the initial pressure (point *1*) to the pressure *2*, a further pressure drop in the reservoir will lead to point *3* and thus to an increased development of the vapor phase. At separator conditions, about 65% of the produced hydrocarbon mixture will exist as liquid phase if the reservoir is produced at bubble point conditions.

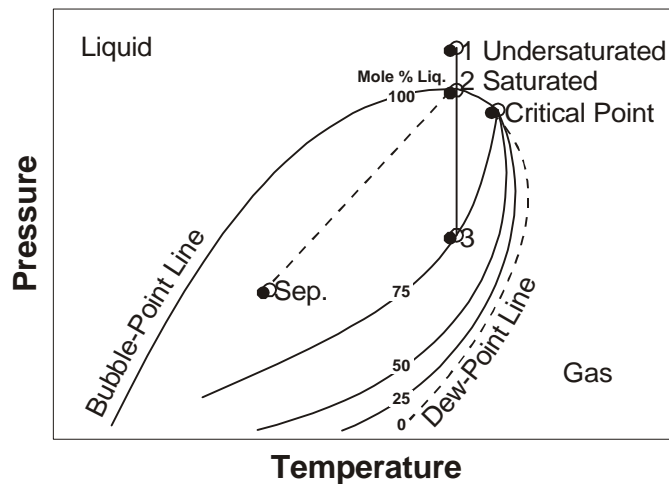


Figure 2.22: Phase diagram of a low shrinkage crude oil (from MCCAIN, 1973)

Figure 2.22 shows a “black oil” or “*low shrinkage oil*”. The initial state is characterized by point **1** at which the state of the system can be regarded as “undersaturated” liquid. If the pressure in the neighbourhood of the production well will decrease during production to point **2**, the bubble point curve is reached and the state of the system is now considered “saturated”. The separator conditions are near the bubble point curve. Consequently, about 85 mole% of the produced hydrocarbon mixture is in the liquid phase at separator conditions. In accordance to this fact, the shrinkage of the oil due to gas liberation is less pronounced than in case “white oils” (see Figure 2.21).

If the hydrocarbon mixture in the reservoir is a 2-phase state under initial reservoir conditions, oil and gas phase can be considered apart from one another (see Figure 2.23). The equilibrium conditions at the initial state of the system are given by the intersection point of the dew point curve of the gas cap and the bubble point curve of the oil zone. The gas cap shows a “retrograde” behavior, if the intersection point is located on the dew point curve of the gas cap between the critical point and the cricondentherm.

Just as in case of binary systems (see Figure 2.9), the phase behavior of natural hydrocarbon mixtures can also be illustrated in  $(p, T, z)$  diagrams.

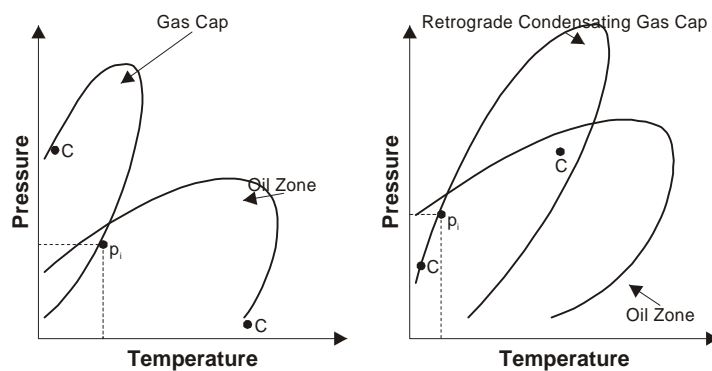


Figure 2.23: Phase diagram pairs of gas cap and oil zone

In Figure 2.24, composition **I** represents the separator gas while composition **IV** represents the corresponding separator oil of the well stream. Furthermore, the phase behavior of two representative mixtures of **I** and **IV** are given by the compositions **II** and **III**. The system of composition **II** corresponds to a gas-condensate system, the one of composition **III** to a white oil. Inside the 2-phase region of system **II** and **III**, isochores of the liquid phase and - as dotted lines - the locations of maximum retrograde condensation are drawn. Again an envelope surface comprises the 2-phase region in dependence on the composition. The spatial curve, which connects the critical points, splits the surface into two parts which are the dew point surface and the bubble point surface. Outside the envelope surface, the system is in a single-phase state.

By projecting the phase surface into the  $(p, z)$  plane, information about the composition of the system will be obtained. If the state of the system is represented by point **1**, the equilibrium composition of the liquid ( $x_1$ ), and the one of the vapor phase, ( $y_1$ ), is given by point **4** in the  $(p, z)$  plane.

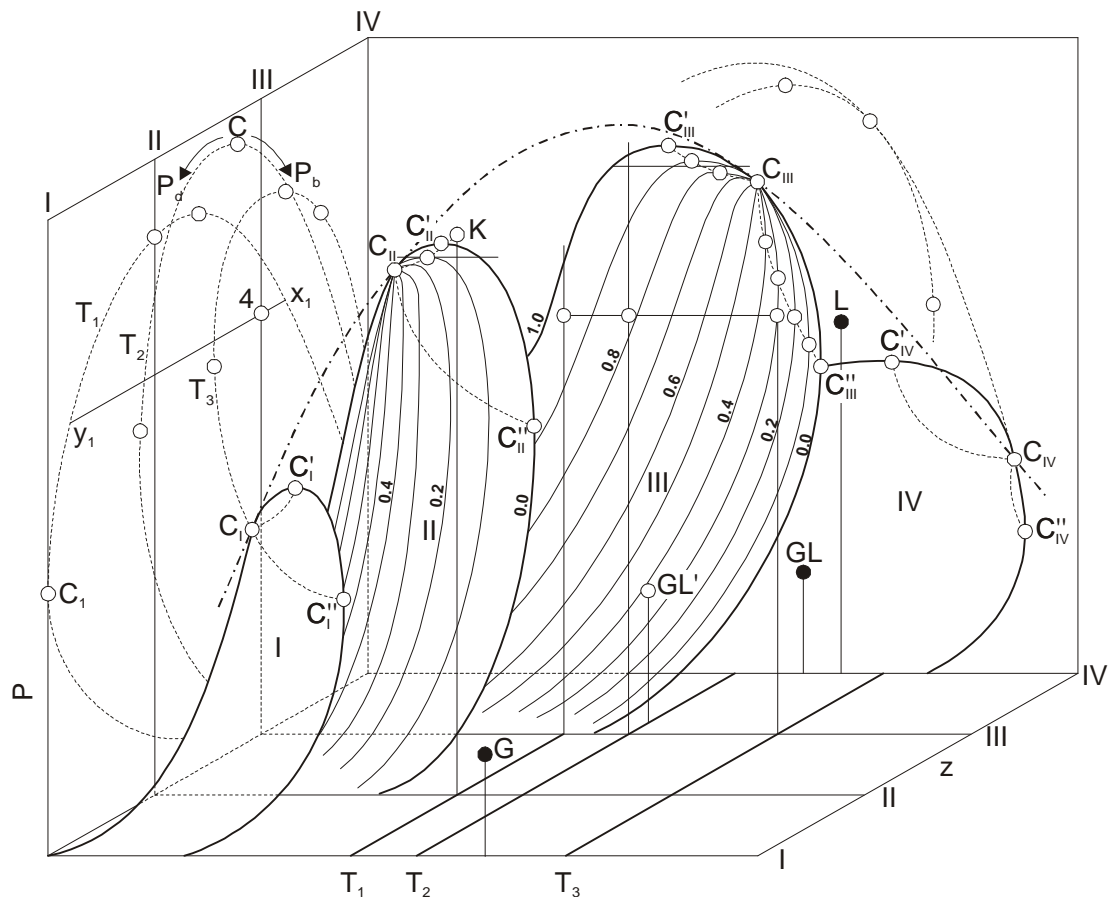


Figure 2.24: Phase equilibrium surface of oil/natural gas systems (from GYULAY, 1967)



## Chapter 3

### Equations of State

The preliminary chapter included graphical illustrations of equilibrium surfaces and their normal projections into the  $(p, T)$ ,  $(p, V)$ ,  $(p, z)$  etc. planes. The application of such diagrams enable the determination of the respective volume for certain states defined by the corresponding pressure  $p$  and temperature  $T$ . However, a pure graphical application of the state functions is not very practical and - on top of that - impossible for multi-component systems. This aspect obviously makes a mathematical consideration of these problems necessary.

On the basis of Eq. 2.1, the following relation regarding the  $(p, V, T)$  data is valid in case of any chemically homogeneous phase:

$$V = V(p, T) \quad (3.1)$$

In this context,  $V$  must be defined as the volume of one mole (intensive property). In case of a 2-phase system:

$$n = n_{liq} + n_{vap} \quad (3.2)$$

and therefore

$$nV_t = n_{liq}V_{liq} + n_{vap}V_{vap} \quad (3.3)$$

where

- $V_t$ : mole volume of the system
- $V_{liq}$ : mole volume of the liquid phase
- $V_{vap}$ : mole volume of the vapor phase
- $n$ : number of moles in the system
- $n_{liq}$ : number of moles in the liquid phase
- $n_{vap}$ : number of moles in the vapor phase.

If phase equilibrium is given, the phases can be regarded as separate thermodynamic systems. If a phase - may be the liquid - consists of  $k$  components, the corresponding equation of state may be written as follows:

$$F(p, V, T, x_1 x_2, \dots x_p) = 0 \quad (3.4)$$

or

$$V = V(p, T, x_1 x_2, \dots x_k) \quad (3.5)$$

where  $x_i$  is defined as the mole fraction of the component  $i$  in the (liquid) phase. Considering the mole fractions, the so called “constraint equation” is valid:

$$\sum_{i=1}^k x_i = 1. \quad (3.6)$$

In various cases of even practical interests, a multi-component phase behaves as an ideal mixture and the volumes are strictly additive. If  $V_i$  is defined as the mole volume of component  $i$  in the phase, the mole volume of the phase will result in

$$V = \sum_{i=1}^k x_i V_i \quad (3.7)$$

If Eq. 3.7 is valid, the enthalpy of the system must be generally considered additive. This means that the enthalpy of the system is equal to the sum of the enthalpies of the single components. In this case, no thermal effect will take place during the mixing procedure. Put into other words: The mixing energy will be zero.

Regarding Eq. 3.6 in discussing Eq. 3.5, it is obvious that  $V$  is a function of  $2 + (k - 1) = k + 1$  variables. It is impossible to approximate the equilibrium surface for the entire  $(p, V, T, x_k)$  space by one single equation of state. Therefore some procedure bit by bit is necessary.

### 3.1 Change of State at Low Compressibility

The expansion of Eq. 3.1 - or just the same of Eq. 3.5 at constant composition - into a TAYLOR-Series leads to

$$\begin{aligned} V(p, T) = V(p_o, T_o) + \left(\frac{\partial V}{\partial p}\right)_T (p - p_o) + \frac{1}{2} \left(\frac{\partial^2 V}{\partial p^2}\right)_T (p - p_o)^2 + \\ + \left(\frac{\partial V}{\partial T}\right)_p (T - T_o) + \frac{1}{2} \left(\frac{\partial^2 V}{\partial T^2}\right)_p (T - T_o)^2 + \dots \end{aligned} \quad (3.8)$$

By assuming that the higher derivations are neglectable, Eq. 3.8 may be truncated to

$$V(p,T) = V_o \left[ 1 + \frac{1}{V_o} \left( \frac{\partial V}{\partial p} \right)_T (p - p_o) + \frac{1}{V_o} \left( \frac{\partial V}{\partial T} \right)_p (T - T_o) \right] \quad (3.9)$$

where

$$V_o = V(p_o, T_o).$$

Considering the Eq. 2.4 and Eq. 2.5, Eq. 3.9 may be transformed to

$$V(p, T) = V_o [1 - \kappa(p - p_o) + \alpha(T - T_o)] \quad (3.10)$$

where

$\kappa$ : isothermal compressibility

$\alpha$ : cubic expansion coefficient

Eq. 3.10 can at best be applied for fluids in a 1-phase state. Experience and practice have shown that the cubic equations of state are most sufficient and beneficial for calculating the state of gases and of 2-phase systems. Of course, there may exist equations which approximate the measured values more accurately. Anyway, the constants included in these equations are not always given. Therefore, only the cubic equations of state, particularly the PENG-ROBINSON equation, will be discussed in this textbook. In doing so, the proceedings of generalization in derivating this equation of state will be elucidated.

## 3.2 Equation of State of Perfect and Real Gases

A gas is defined as perfect, if the intermolecular (VAN DER WAALS) forces are neglectable. Then for a molar system:

$$pV = RT \quad (3.11)$$

where  $R$  is the universal gas constant ( $R = 8.31434 \text{ J/mole K}$ ).

The compressibility factor  $Z$  is defined as

$$Z = \frac{pV}{RT} \quad (3.12)$$

or

$$Z = \frac{V_{actual}}{V_{ideal}}, \quad (3.13)$$

respectively.

For ideal gases, the factor  $Z$  equals 1. For real gases,  $Z$  is a state variable and depends on the pressure, the temperature and the composition. The critical point is defined by the pressure  $p_c$ , temperature  $T_c$ , and specific volume  $V_c$  and may be determined experimentally for 1-component systems.

The critical compressibility factor,  $Z_c$ , can be evaluated by substituting the critical data  $p_c$ ,  $T_c$  and  $V_c$  into Eq. 3.12:

$$Z_c = \frac{p_c V_c}{RT_c}. \quad (3.14)$$

### Example 3.1

Evaluation of a Z-factor from laboratory data. A cylinder with volume of 0.075 m<sup>3</sup> has been filled with a gas under atmospheric pressure and at a temperature of 90.5°C. Then the volume of the cylinder has been isothermally reduced to 0.00035 m<sup>3</sup> (volume reduction in consequence of mercury insertion). After the volume reduction, the pressure has been recorded as 13.79 MPa.

If the gas would show an ideal behavior at 90°C and 13.79 MPa, the specific volume could be calculated by

$$P_1 V_1 = P_2 V_2$$

and so

$$V_2 = V_1 \frac{P_1}{P_2},$$

$$V_2 = 75 \times 10^{-3} \frac{0.101}{13.79} = 55 \times 10^{-5} \text{ m}^3.$$

By use of Eq. 3.13 and considering the measured volume amounting to 0.00035 m<sup>3</sup>:

$$Z = \frac{35 \times 10^{-5}}{55 \times 10^{-5}} = 0.64$$

### 3.3 Cubic Equations of State

If the pressure of any gaseous system is low, the ideal gas equation remains sufficient to describe the volumetric behavior. In the year 1873, VAN DER WAALS deduced the first equation of state which is able - up to a certain degree - to describe the continuity from gaseous to the liquid state:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (3.15)$$

$a$  and  $b$  are substance specific constants.  $b$  can be interpreted as the inherent volume of the molecules which is not available for the thermal motion of the molecules. The term  $a/V^2$  regards the pressure reduction in consequence of intermolecular attraction.

Eq. 3.15 may also be written in the following form:

$$p = \frac{RT}{(V - b)} - \frac{a}{V^2}. \quad (3.16)$$

Figure 3.1 illustrates the VAN DER WAALS isotherms in the vicinity of the critical point. The dotted section of the isotherms represents the data which are predicted by using the VAN DER WAALS equation. Obviously, Eq. 3.16 cannot predict the real behavior of the system during the vaporization, respectively condensation. The real behavior is shown by the straight full line **BD** inside the 2-phase region.

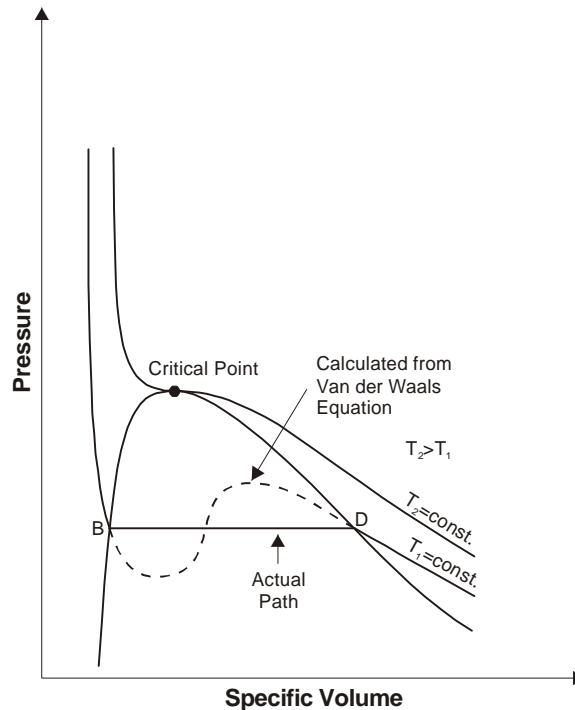


Figure 3.1: The VAN DER WAALS isotherms near the critical point

The cubic equations of state, which have been formulated by REDLICH and KWONG (1949), SOAVE (1972), and PENG and ROBINSON (1976), have achieved much better results.

The REDLICH-KWONG equation is given as

$$p = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} \quad (3.17)$$

where  $b$  again is a substance specific constant. Anyway,  $a$  is now a function of the temperature. It is useful to write the parameter  $a$  as follows:

$$a = a'f(T) \quad (3.18)$$

where  $a'$  is constant. The original REDLICH-KWONG equation included

$$f(T) = T^{-0.5}.$$

By multiplication of Eq. 3.17 with

$$V(V+b)(V-b)/p$$

and after arrangement of  $V$  corresponding to its order of power:

$$V^3 - \frac{RT}{p}V^2 + \left(\frac{a}{p} - \frac{bRT}{p} - b^2\right)V - \frac{ab}{p} = 0. \quad (3.19)$$

At the critical point ( $V = V_c$ ):

$$(V - V_c)^3 = V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \quad (3.20)$$

The comparison of Eq. 3.19 and Eq. 3.20 leads to

$$3V_c = \frac{RT_c}{p_c}, \quad (3.21)$$

$$3V_c^2 = \frac{a_c}{p_c} - \frac{bRT_c}{p_c} - b^2, \quad (3.22)$$

$$V_c^3 = \frac{a_c b}{p_c} \quad (3.23)$$

where

$$a_c = a'f(T_c). \quad (3.24)$$

Substitution of Eq. 3.21 and Eq. 3.23 into Eq. 3.22 results in

$$3V_c^2 = \frac{V_c^3}{b} - 3bV_c - b^2 \quad (3.25)$$

or after rearrangement, in

$$b^3 + 3b^2V_c + 3bV_c^2 + V_c^3 = 2V_c^3, \quad (3.26)$$

$$(b + V_c)^3 = 2V_c^3, \quad (3.27)$$

$$b = (2^{1/3} - 1)V_c. \quad (3.28)$$

Furthermore, Eq. 3.28 and Eq. 3.21 can be combined to

$$b = \frac{2^{1/3} - 1 RT_c}{3p_c} = \Omega_b \frac{RT_c}{p_c}. \quad (3.29)$$

Inserting Eq. 3.21 and Eq. 3.23 into Eq. 3.29:

$$a_c = \frac{(RT_c)^2}{9(2^{1/3} - 1)p_c} = \Omega_b \frac{(RT_c)^2}{p_c} \quad (3.30)$$

The constants  $\Omega_b$  and  $\Omega_a$  have the following numerical values:

$$\Omega_b = 0.08664,$$

$$\Omega_a = 0.42748.$$

From Eq. 3.18 and Eq. 3.24:

$$a = a_c \frac{f(T)}{f(T_c)} = a_c \alpha. \quad (3.31)$$

It is obvious that  $\alpha = 1$ , if  $T = T_c$ .

The substitution of  $V = ZRT/p$  into the Eq. 3.19 and the arrangement of  $Z$  corresponding to its order of power results in

$$\left(\frac{ZRT}{p}\right)^3 - \frac{RT}{p} \left(\frac{ZRT}{p}\right)^2 + \left(\frac{a}{p} - \frac{bRT}{p} - b^2\right) \frac{ZRT}{p} - \frac{ab}{b} = 0. \quad (3.32)$$

Therefore:

$$Z^3 - Z^2 + \left[ \frac{ap}{(RT)^2} - \frac{bp}{RT} - \frac{b^2 p^2}{(RT)^2} \right] Z - \frac{ap}{(RT)^2} \frac{bp}{RT} = 0 \quad (3.33)$$

or

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (3.34)$$

where

$$A = \frac{ap}{(RT)^2} \quad (3.35)$$

and

$$B = \frac{bp}{RT}. \quad (3.36)$$

The substitution of Eq. 3.29 and Eq. 3.30 into Eq. 3.35 and Eq. 3.36 leads to

$$A = 4.2748 \left( \frac{p_r}{T_r^2} \right) \alpha \quad (3.37)$$

and

$$B = 0.8664 \frac{p_r}{T_r}. \quad (3.38)$$

In the original REDLICH-KWONG equation:

$$f(T) = T^{-0.5} \quad (3.39)$$

and so

$$\alpha = T_r^{-0.5}. \quad (3.40)$$

Eq. 3.29 - 3.31 only include two parameters which are  $p_c$  and  $T_c$ . Please note that the ideal gas equation contains no substance-specific parameters. Since the Redlich-Kwong cubic equations of state consider these two substance-specific parameters, it has improved the calculation of  $(PVT)$  properties in a fundamental way. Anyway, the increasing yield of experimental data has more and more indicated that the behavior of many liquids with a

non-spherical molecule structure deviates greatly from the predicted one. This made the introduction of a third factor necessary.

Beginning with the year 1951 (MEISSNER and SEFERIAN), several proposals for a third parameter have been made. The so called “*acentric factor*”,  $\omega$ , has become the one with greatest acknowledgement:

$$\omega = -\left(\lg p_r^s + 1\right) \text{ at } T_r = 0.7 \quad (3.41)$$

where  $p_r^s = p^s/p_c$  is the reduced boiling point pressure.

The equation of state from SOAVE (1972) only differs from the REDLICH-KWONG equation with respect to the definition of the factor  $\alpha$

$$\alpha^{0.5} = 1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5}). \quad (3.42)$$

The weakness of all these equations ranging from the original REDLICH-KWONG equation to all its modifications (including the SOAVE equation) is the fact of an universal unrealistic value  $Z_c = 1/3$ . Moreover, the prediction of liquid density is combined with large errors.

Improved approximation has been achieved with the PENG-ROBINSON equation:

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (3.43)$$

where  $a$  is given by Eq. 3.18 and  $b$  is further a substance specific constant.

Just as in case of the REDLICH-KWONG equation, the following terms and equations can be obtained:

$$V^3 - \left(\frac{RT}{p} - b\right)V^2 + \left(\frac{a}{b} - \frac{2bRT}{p} - 3b^2\right)V - \left(b\frac{a}{p} - \frac{RT}{p}b - b^2\right) = 0, \quad (3.44)$$

$$V_c = 0.307 \frac{RT_c}{p_c}, \quad (3.45)$$

$$b = 0.077796 \frac{RT_c}{p_c}, \quad (3.46)$$

$$a = a_c \alpha, \quad (3.47)$$

$$a_c = 0.457236 \frac{(RT_c)^2}{p_c}, \quad (3.48)$$

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - AB - B^2 - B^3 = 0, \quad (3.49)$$

$$A = 0.457325 \cdot \left( \frac{p_r}{T_r^2} \right) \alpha, \quad (3.50)$$

$$B = 0.07796 \frac{p_r}{T_r}, \quad (3.51)$$

$$\alpha^{0.5} = 1 + (0.3676 + 1.54226\omega - 0.26992\omega^4)(1 - T_r^{1/2}). \quad (3.52)$$

Analogies between Eq. 3.44 to Eq. 3.52 on the one side and Eq. 3.19, Eq. 3.29 to Eq. 3.31, Eq. 3.34 to Eq. 3.38, and Eq. 3.42 on the other side are obvious. The universal critical Z-factor of the PENG-ROBINSON equation results in 0.307 which is much better than 1/3 but still far away from reality. Anyway, the calculated fluid densities are much more accurate than the ones calculated by the equations of state previously discussed.

Eq. 3.16, Eq. 3.17, and Eq. 3.43 have been established for pure substances. The extension for multi-component systems requires the calculation of the respective data of the pure components and mixing rules in order to get the parameters of the mixture.

The mixing rule for the parameter  $b$ , which is included in the equations of REDLICH-KWONG, SOAVE and PENG-ROBINSON, is universally defined as an arithmetic average by using

$$b = \sum_{i=1}^k x_i b_i. \quad (3.53)$$

For the temperature-dependent coefficient  $a$ , different mixing rules exist and are presented below.

REDLICH-KWONG:

$$a = \left[ \sum_{i=1}^k x_i a_i^{0.5} \right]^2. \quad (3.54)$$

where  $a_i$  can be calculated on the basis of the critical data of each component by using Eq. 3.30 and Eq. 3.40 into Eq. 3.31.

SOAVE:

$$a = \sum_{i=1}^k \sum_{j=1}^k x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (3.55)$$

where  $a_i$  and  $a_j$ , respectively, can be evaluated by Eq. 3.30 and Eq. 3.42.

PENG-ROBINSON:

$$a = \sum_{i=1}^k \sum_{j=1}^k x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (3.56)$$

where  $a_i$  is defined by Eq. 3.48 and Eq. 3.52.

The mixing rules used by SOAVE and PENG-ROBINSON consider the binary interaction between the molecules of the components  $i$  and  $j$ . In Eq. 3.55 and Eq. 3.56, the terms  $k_{ij}$  are **binary interaction coefficients** which are assumed to be independent of pressure and temperature.

Values of the binary interaction coefficients must be obtained by fitting the equation of state to gas-liquid equilibria data for each binary mixture. They have different values for each binary pair and also take on different values for each equation of state.

Obviously, Eq. 3.55 and Eq. 3.56 reduce to the form of Eq. 3.54 if all binary interaction coefficients are zero.

Another possibility of obtaining this coefficient - if no data are available - is by mean of matching the phase behavior of multi-component systems.

### Example 3.2

Calculation of the pressure by use of the PENG-ROBINSON equation of state. A laboratory cell at temperature of 100 °C with volume of 0.00025 m<sup>3</sup> contains 0.25 mole of gas. The composition of the system, the critical data and the acentric factors of the components are tabled below.

Component	Composition $y_i$	Critical Data		Acentric Factor $\omega_i$
		$T_{c,i}$ K	$P_{c,i}$ MPa	
C <sub>1</sub>	0.75	190.6	4.60	0.0115
C <sub>2</sub>	0.20	305.4	4.88	0.0908
n - C <sub>4</sub>	0.05	425.2	3.80	0.1928

First, the parameters  $b$  and  $a$  must be calculated for each component.

For methane from Eq. 3.46:

$$b_{C1} = 0.077796 \frac{8.31434 \times 190.6}{4.6 \times 10^6} = 2.6801 \times 10^{-5} ,$$

from Eq. 3.48:

$$a_{c,C1} = 0.457236 \frac{(8.31434 \times 190.6)^2}{4.6 \times 10^6} = 0.2494 ,$$

from Eq. 3.52 by inserting the acentric factor for methane

$$\omega_{C1} = 0.0115$$

and the reduced temperature of methane

$$T_{r,1} = \frac{373.15}{190.6} = 1.958 :$$

$$\alpha_{C1}^{0.5} = 0.8426$$

and thus

$$\alpha_{C1} = 0.7100 ,$$

and from Eq. 3.47:

$$\alpha_{C1} = 0.2494 \times 0.71 = 0.1771 .$$

Correspondingly to the calculations for methane, the parameters of ethane and n-butane were evaluated. They are tabled below.

Component	$b_i$	$a_{c,i}$	$a_i$	$a_i$
C <sub>1</sub>	2.680 E-5	0.2496	0.7100	0.1770
C <sub>2</sub>	4.048 E-5	0.6041	0.8945	0.5404
n - C <sub>4</sub>	7.238 E-5	1.5038	1.1691	1.7581

The parameter  $b$  can be calculated by use of Eq. 3.53:

$$b = 0.75 \times 2.68E - 5 + 0.20 \times 4.048E - 5 + 0.05 \times 7.238E - 5$$

$$b = 3.182 E - 5 .$$

To calculate the coefficient  $a$  by use of Eq. 3.56, the interactive coefficients,  $K_{ij}$ , must be known. They are given below:

	$C_1$	$C_2$	$n - C_4$
$C_1$	0.0000 E+0	0.2648 E-2	0.1464 E-1
$C_2$	0.2648 E-2	0.0000 E+0	0.4904 E-2
$n - C_4$	0.1464 E-1	0.4904 E-2	0.0000 E+0

$$\begin{aligned}
 a = & 0.75 \times 0.75 (0.1770 \times 0.1770)^{0.5} (1 - 0.000000) + \\
 & + 0.75 \times 0.20 (0.1770 \times 0.5404)^{0.5} (1 - 0.002648) + \\
 & + 0.75 \times 0.05 (0.1770 \times 1.7581)^{0.5} (1 - 0.014640) + \\
 & + 0.20 \times 0.75 (0.5404 \times 0.1770)^{0.5} (1 - 0.002648) + \\
 & + 0.20 \times 0.20 (0.5404 \times 0.5404)^{0.5} (1 - 0.000000) + \\
 & + 0.20 \times 0.05 (0.5404 \times 1.7581)^{0.5} (1 - 0.004904) + \\
 & + 0.05 \times 0.75 (1.7581 \times 0.1770)^{0.5} (1 - 0.014640) + \\
 & + 0.05 \times 0.20 (1.7581 \times 0.5404)^{0.5} (1 - 0.004904) + \\
 & + 0.05 \times 0.05 (1.7581 \times 1.7581)^{0.5} (1 - 0.000000) = 0.2787
 \end{aligned}$$

Now the pressure can be calculated through Eq. 3.43 and by inserting

$$V = \frac{0.00025}{0.25} = 0.001 \text{ m}^3/\text{mole} ,$$

$$T = 373.15 \text{ K} ,$$

$$R = 8.31434 \text{ J/K} \times \text{mole}$$

$$b = 3.182 \times 10^{-5}$$

and

$$a = 0.2787 .$$

The calculation procedure results in  $p = 2.939 \text{ MPa}$ .

**Example 3.3**

Calculation of the density of methane by use of the PENG-ROBINSON equation of state. 2.0 kg methane ( $M_I = 16 \text{ kg k/mole}$ ) is hold at temperature of 305.12 K and at pressure of 9.26 MPa. The critical data and the acentric factor of methane are known as

$$T_c = 190.6 \text{ K} ,$$

$$p_c = 4.6 \text{ MPa} ,$$

$$\omega = 0.0115 .$$

First, the parameters  $a$  and  $b$  have to be calculated.

From Eq. 3.46:

$$b = 0.077796 \frac{8.31434 \times 190.6}{4.6 \times 10^6} = 2.6801 \times 10^{-5} .$$

From Eq. 3.48:

$$a_c = 0.457236 \frac{(8.31434 \times 190.6)^2}{4.6 \times 10^6} = 0.2496 .$$

From Eq. 3.52 by inserting the acentric factor and the reduced temperature of the system

$$T_{r,1} = \frac{305.12}{190.6} = 1.601 ,$$

$$\alpha^{0.5} = 0.8954$$

and thus

$$\alpha = 0.8017 ,$$

and from Eq. 3.47:

$$a = 0.2496 \times 0.8017 = 0.2001 .$$

Now the mole volume of methane at the given state variables has to be evaluated through Eq. 3.44. To solve this cubic equation of state, the CARDAN equation is applied for

$$x^3 + rx^2 + sx + t = 0$$

where

$$r = -\left(\frac{RT}{p} - b\right) ,$$

$$s = \left( \frac{a}{p} - \frac{2bRT}{p} - 3b^2 \right)$$

and

$$t = -b \left( \frac{a}{p} - \frac{RT}{p} b - b^2 \right).$$

The calculation of  $r$ ,  $s$  and  $t$  result in

$$r = -0.2472 \times 10^{-3},$$

$$s = 0.476 \times 10^{-8},$$

and

$$t = -0.3736 \times 10^{-12}.$$

By substitution of

$$x = y - \frac{r}{3},$$

the formula

$$x^3 + rx^2 + sx + t = 0$$

is reduced to

$$y^3 + py + q = 0$$

where

$$p = \frac{3s - r^2}{3}$$

and

$$q = \frac{2r^3}{27} - \frac{rs}{3} + t.$$

The calculation of  $p$  and  $q$  result in

$$p = -1.561 \times 10^{-8}$$

and

$$q = -1.014 \times 10^{-12}.$$

The discriminant  $D$  is defined as

$$D = \left( \frac{p}{3} \right)^3 + \left( \frac{q}{2} \right)^2$$

and thus

$$D = 1.161 \times 10^{-25}$$

Based on the relationships

$$u = \sqrt[3]{-\frac{q}{2} + \sqrt{D}} ,$$

$$v = \sqrt[3]{-\frac{q}{2} - \sqrt{D}}$$

and

$$y = u + v ,$$

the mole volume can be calculated through

$$x = y - \frac{r}{3} :$$

$$u = 9.33 \times 10^{-5} ,$$

$$v = 5.87 \times 10^{-5} ,$$

$$y = 1.52 \times 10^{-4}$$

and thus

$$V = 2.344 \times 10^{-4} \text{ m}^3/\text{mole} ,$$

and

$$\rho = \frac{m}{nV} = \frac{M}{V} = 68.522 \text{ kg/m}^3 .$$

### 3.4 Virial Equation of State

All cubic equations of state mentioned above are more or less empirical or at best semi-theoretical. Anyway, they are obviously qualified for practical application.

In contrast, the virial equation of state has some theoretical background in statistical mechanics. However, the form of an infinite series concerning the volume is not very appropriate for practical application.

The pressure is expressed as

$$p = RT \left( \frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3} \dots \right). \quad (3.57)$$

The virial coefficients **B**, **C** etc. are solely a function of temperature. Sometimes Eq. 3.57 is applied for the calculation of gaseous states (e.g. natural gas) by considering only the first two or three terms (depending on the availability of the virial coefficients).

If **V** is substituted into Eq. 3.57 according to the gas law by  $Z RT/p$ , then:

$$Z = 1 + \frac{Bp}{ZRT} + \frac{Cp^2}{(ZRT)^2} + \dots \quad (3.58)$$

The second virial coefficient **B** can be shown to be the slope of isotherms on a plot of  $Z = Z(p)$  at  $p = 0$ . When **p** approaches zero, the third term in Eq. 3.58 may be neglected so that

$$B = ZRT \lim_{p \rightarrow 0} \left( \frac{Z-1}{p} \right). \quad (3.59)$$

Since also **Z** becomes *zero* as **p** goes to zero, de l'Hospital's rule can be applied resulting at constant temperature in

$$B = RT \lim_{p \rightarrow 0} \left( \frac{\partial Z}{\partial p} \right)_T. \quad (3.60)$$

Eq. 3.60 implies that the second virial coefficient vanishes at the BOYLE-temperature. The BOYLE temperature is defined as the temperature above which **Z**-values become greater than 1 for all pressures.



## Chapter 4

# Calculation of Phase Equilibria

## 4.1 Mixtures

### 4.1.1 Definitions

In case of thermodynamical phase equilibrium of a multi-component system, all phases are - in physical terms - homogeneous mixtures. Vaporized compounds are always mixable in all relations, independent of their chemical characteristics. Therefore, only one vapor phase exists.

Compounds existing in a liquid phase are only mixable in all relations if they are chemically similar. Since hydrocarbons - especially those which belong to the same homologous series - exhibit such chemical conformity, their mixtures will be physically homogeneous, independent of the composition of the mixture.

The composition of the system and its phases are specified by mole fractions. The mole fraction of the component  $i$  is given by the ratio between its mole number,  $n_i$ , and the total mole number in the system (in the respective phase),  $n$ . The sum of all mole fractions equals 1. In the following, the different mole fractions are marked by

$z_i$ : mole fraction of the component  $i$  in the total system

$x_i$ : mole fraction of the component  $i$  in the liquid phase

$y_i$ : mole fraction of the component  $i$  in the vapor phase,

so that in the system in total

$$z_i = \frac{n_i}{\sum_{i=1}^k n_i}, \quad (4.1)$$

$$x_i = \left( \frac{n_i}{\sum_{i=1}^k n_i} \right)_{liq}, \quad (4.2)$$

$$y_i = \left( \frac{n_i}{\sum_{i=1}^k n_i} \right)_{vap}. \quad (4.3)$$

If a multi-component system is in the state of thermodynamic phase equilibrium, the distribution of the component  $i$  among the vapor and the liquid phase is characterized by its distribution coefficient, the so called “**K-factor**”:

$$K_i = \frac{y_i}{x_i}. \quad (4.4)$$

The numerical value of  $K_i$  depends on the state of the system. Accordingly, the composition of the phases will change at any variation in state.

### 4.1.2 K-factors

Ideal liquid mixtures have the property of being met by RAOULT’s law so that

$$x_i = \frac{p_i}{p_i^o} \quad (4.5)$$

where

$p_i$ : partial pressure of the component  $i$

$p_i^o$ : tension of component  $i$  as a single-component system

$x_i$ : mole fraction of component  $i$  in the liquid phase.

The total pressure of the system adds up to

$$p = \sum_{i=1}^k p_i = \sum_{i=1}^k x_i p_i^o \quad (4.6)$$

If a vapor phase exhibits perfect behavior, DALTON’s law can be applied and

$$y_i = \frac{p_i}{p} \quad (4.7)$$

The combination of Eq. 4.5 and Eq. 4.7 results in

$$K_{i(id)} = \frac{y_i}{x_i} = \frac{p_i^o}{p} \quad (4.8)$$

Anyway, certain limitations are placed on the definition of the  $K$ -factor given above. It is evident that any pure component has a vapor pressure only up to its critical temperature. In practice, the extrapolation of the vapor pressure curves to higher temperatures than  $T_c$  does not yield satisfactory results in most cases. Since  $T_c = 190.6 \text{ K}$  for methane, it becomes evident that some other means must be obtained for the determination of  $K$ -factors if they are to be used for hydrocarbon mixtures.

On the basis of the thermodynamic concept of fugacity, the vapor pressures in Eq. 4.8 can be corrected and extrapolated to cover a wider range of conditions. A first approach originated from DODGE and NEWTON (1937) who have shown that at any given  $p$  and  $T$

$$f_{i(liq)} = x_i f_{i(liq)}^o \quad (4.9)$$

and

$$f_{i(vap)} = y_i f_{i(vap)}^o \quad (4.10)$$

respectively, where

$f_{i(liq)}$  : fugacity of component  $i$  in a liquid mixture

$f_{i(vap)}$  : fugacity of component  $i$  in a vapor mixture

$f_{i(liq)}^o$  : fugacity of pure component  $i$  as liquid

$f_{i(vap)}^o$  : fugacity of pure component  $i$  as vapor.

If the phases are in equilibrium at given conditions and thus

$$f_{i(vap)} = f_{i(liq)}, \quad (4.11)$$

the definition of the  $K$ -factor is given by

$$K'_{i(id)} = \frac{y_i}{x_i} = \frac{f_{i(liq)}^o}{f_{i(vap)}^o}. \quad (4.12)$$

A generalized fugacity chart for natural gases based on reduced temperatures and pressures is given in Figure 4.1 in terms of  $f/p$ , the so called “**activity coefficient**”. The fugacities serve to provide ideal equilibrium constants as defined by Eq. 4.12.

Figure 4.2 shows that the  $K'_{i(id)}$ -values are not sufficiently accurate to describe phase equilibria at high pressures. Anyway, the extrapolation of the fugacities on the basis of Eq. 4.10 - though also limited by the critical state conditions - covers a wider range of state conditions than the vapor pressure relations.

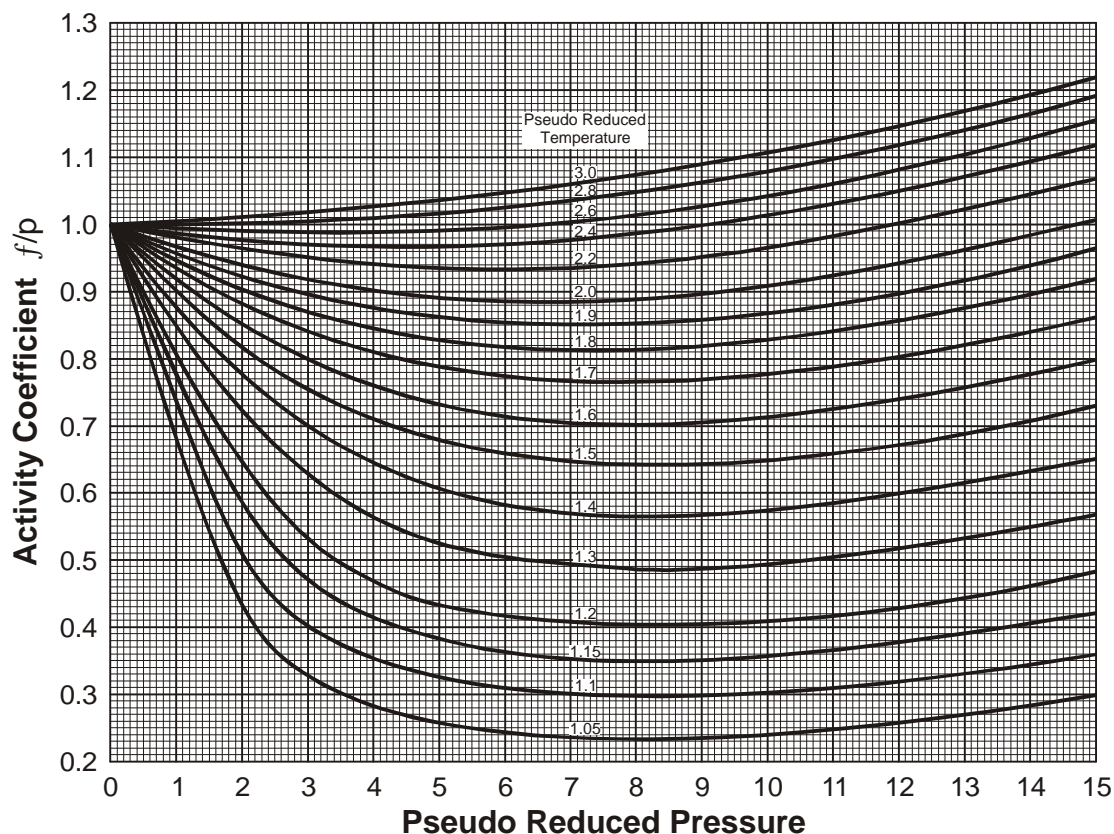
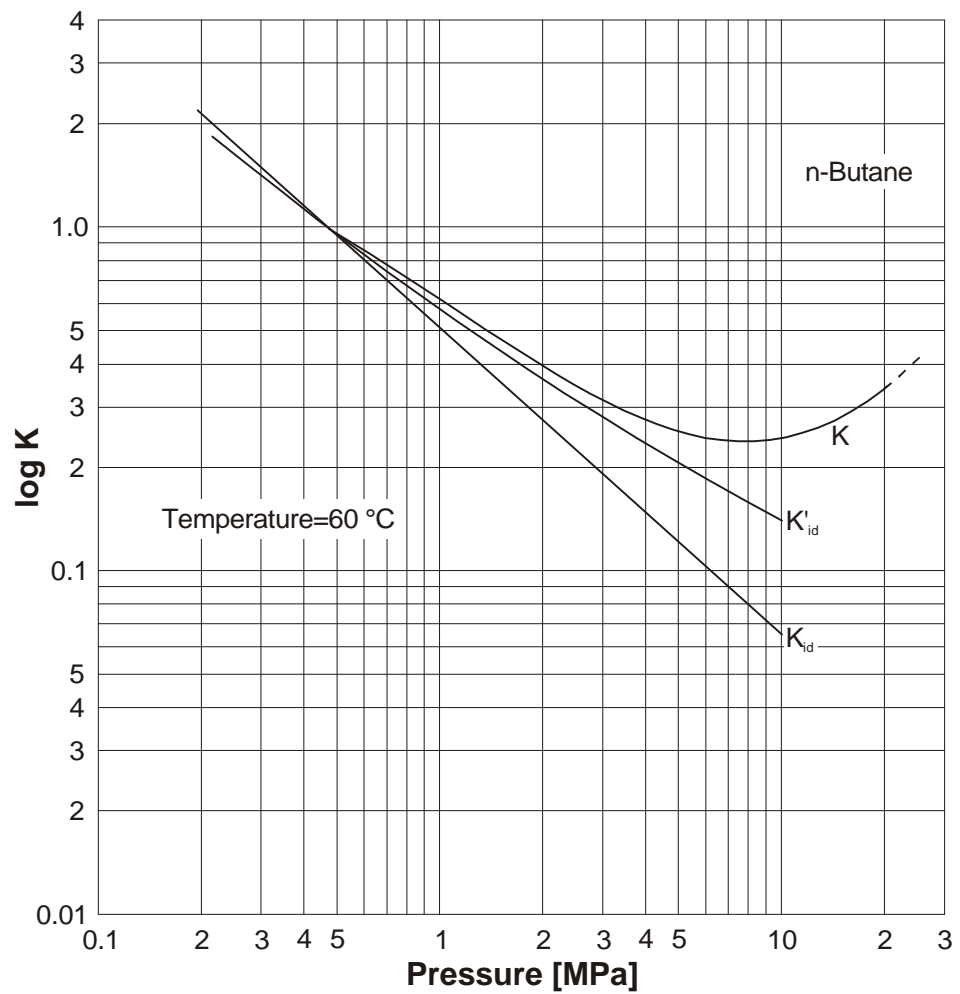


Figure 4.1: Fugacity of natural gases (from BROWN, 1945)

In case of multi-component hydrocarbon systems, attraction forces between the molecules affect the vapor-liquid equilibria at higher  $p$  and  $T$ . Since both RAOULT's and DALTON's laws and the fugacity relations given above (see Eq. 4.9 and Eq. 4.10) result in the calculation of K-factors without considering the composition, it is necessary to find another solution for the determination of the K-factors.

Figure 4.2: Ideal and real K-factors of *n*-butane at 60[°C]

K-factors can be evaluated in satisfactory accordance with the measured data by the application of the “successive solution method”. This method - it will be discussed through Example 5.5 - consists in an iterative process. It is based on the definition of the “*fugacity coefficient*” of the component *i* ( $i = 1, 2, \dots, k$ ) in a multi-component phase *P* - in analogy of the “activity coefficient”  $f/p$  - as

$$\phi_{i,P} = \frac{f_{i,P}}{x_{i,P} p} \quad (4.13)$$

where *p* is used for the total pressure of the system.

After introducing not only the PENG-ROBINSON equation of state

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)}$$

in

$$\ln \frac{f}{p} = Z - 1 - \ln Z + \frac{1}{RT} \int_{\infty}^V \left( \frac{RT}{V} - p \right) dV$$

but also other terms which have been defined by PENG-ROBINSON (see Chap. 3), NGHIEM, AZIZ and LI (1983) have calculated fugacity coefficients by use of

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left[ \frac{2 \sum_{j=1}^k x_j a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left( \frac{Z + 2.414 B}{Z - 0.414 B} \right) \quad (4.14)$$

where  $a_{ij}$  is defined by

$$a_{ij} = (1 - K_{ij}) (a_i^{0.5} a_j^{0.5}). \quad (4.15)$$

If the phases are in equilibrium at given conditions and thus

$$\frac{f_{i(vap)}}{f_{i(liq)}} = 1$$

(see Eq. 4.11), the definition of the  $K$ -factor is given by

$$K_i = \frac{\phi_{i(liq)}}{\phi_{i(vap)}} \quad (4.16)$$

(see Eq. 4.13),

where

$\phi_{i(liq)}$ : fugacity coefficient of component  $i$  in the liquid phase

$\phi_{i(vap)}$ : fugacity coefficient of component  $i$  in the vapor phase.

## 4.2 Composition of Phases in Equilibrium

### 4.2.1 Definitions

If the system at a given pressure, temperature and composition is in a liquid-vapor phase equilibrium, the following must be valid (on the basis of an overall and particular material balance, respectively):

$$n = n_{liq} + n_{vap} \quad (4.17)$$

$$z_i n = x_i n_{liq} + y_i n_{vap}; \quad (i = 1, \dots, k) \quad (4.18)$$

where

$n$ : total mole number of the system

$n_{liq}$ : mole number of the liquid phase

$n_{vap}$ : mole number of the vapor phase

$x_i$ : mole fraction of component  $i$  in the liquid phase

$y_i$ : mole fraction of component  $i$  in the vapor phase

$z_i$ : mole fraction of component  $i$  in the system

After substitution of Eq. 4.4 into Eq. 4.18 and after rearrangement, the following is valid:

$$x_i = \frac{z_i n}{n_{liq} + n_{vap} K_i}, \quad (4.19)$$

$$y_i = \frac{z_i n}{n_{liq}/K_i + n_{vap}} \quad (4.20)$$

If the numerical values for  $n_{liq}$  and  $n_{vap}$  have been chosen correctly, the calculations of  $x_i$  and  $y_i$  ( $i = 1, \dots, k$ ) (Eq. 4.19 and Eq. 4.20) result in

$$\sum_{i=1}^k x_i = \sum_{i=1}^k \frac{z_i n}{n_{liq} + n_{vap} K_i} = 1 \quad (4.21)$$

and

$$\sum_{i=1}^k y_i = \sum_{i=1}^k \frac{z_i n}{n_{liq}/K_i + n_{vap}} = 1. \quad (4.22)$$

Example 5.1 will demonstrate that it is possible to use the Eq. 4.21 and Eq. 4.22 for iterative calculation purposes which result in the evaluation of the phase compositions at given pressure, temperature and system composition.

If  $n = 1$ , Eq. 4.17 gives

$$n_{vap} = 1 - n_{liq}$$

and Eq. 4.21 becomes

$$\sum_{i=1}^k x_i = \sum_{i=1}^k \frac{z_i}{n_{liq} + K_i(1 - n_{liq})} = 1. \quad (4.23)$$

Eq. 4.23 elucidates that

$n_{liq}$  must be chosen larger in the following iteration if  $\sum x_i > 1$ ,

$n_{liq}$  must be chosen smaller in the reverse case of  $\sum x_i < 1$ .

#### Example 4.1

Determination of the gas and liquid phase compositions at  $p = 14$  MPa and  $T = 92$  °C through an iterative calculation procedure on the basis of the constraint of Eq. 4.23. The actual composition of the hydrocarbon system is tabled below. Assumption:  $K_{C7+} = 0.15 K_{C7}$ .

**FIRST ITERATION:**  $n_{liq} = 0.790$ ,  $n_{vap} = 0.210$

Component	Composition $z_i$	K-Factor $K_i$	Iteration I $x_i = \frac{z_i}{n_{liq} + n_{vap}K_i}$
C <sub>1</sub>	0.4404	2.85	0.3173
C <sub>2</sub>	0.0432	1.17	0.0417
C <sub>3</sub>	0.0405	0.68	0.0434
C <sub>4</sub>	0.0284	0.41	0.0324
C <sub>5</sub>	0.0174	0.24	0.0207
C <sub>6</sub>	0.0290	0.15	0.0353
C <sub>7+</sub>	0.4011	0.01	0.5055
<b>S</b>	<b>1.0000</b>		<b>0.9963</b>

SECOND ITERATION:  $n_{liq} = 0.776, n_{vap} = 0.224$

THIRD ITERATION:  $n_{liq} = 0.778, n_{vap} = 0.222$

Component	Iteration II $x_i = \frac{z_i}{n_{liq} + n_{vap} K_i}$	Iteration III $x_i = \frac{z_i}{n_{liq} + n_{vap} K_i}$	Iteration III $y_i = \frac{z_i}{n_{liq}/K_i + n_{vap}}$
C <sub>1</sub>	0.3114	0.3123	0.8896
C <sub>2</sub>	0.0416	0.0416	0.0487
C <sub>3</sub>	0.0436	0.0436	0.0296
C <sub>4</sub>	0.0327	0.0327	0.0134
C <sub>5</sub>	0.0210	0.0209	0.0051
C <sub>6</sub>	0.0358	0.0357	0.0054
C <sub>7+</sub>	0.5145	0.5132	0.0082
S	<b>1.0006</b>	<b>0.9999</b>	<b>1.0000</b>

At the bubble point of the system, the amount of vapor is infinitesimal small and thus

$$n_{vap} = 0, n_{liq} = n \text{ and } x_i = z_i.$$

Eq. 4.22 then becomes

$$\sum_{i=1}^k \frac{z_i n}{n_{liq}/K_i + n_{vap}} = \sum_{i=1}^k K_i z_i = \sum_{i=1}^k K_i x_i = 1. \quad (4.24)$$

Example 4.2 illustrates the iterative process of calculating the bubble point pressure,  $p_b$ , for a given hydrocarbon composition and for a fixed temperature. Naturally,  $K_i = K_{i(p)}$  must be known.

In the vicinity of the bubble point,  $K_i x_i$  are in a linear relation to pressure. Therefore, linear interpolation can be applied for acceleration purposes.

**Example 4.2**

Determination of the bubble point pressure of a crude oil. The composition of the system is given in Example 4.1.

Component	Compos. $z_i$	1. Assumption $p_b = 21 \text{ MPa}$		2. Assumption $p_b = 22.5 \text{ MPa}$		3. Assumption $p_b = 23.2 \text{ MPa}$	
		$K_i$	$y_i = K_i z_i$	$K_i$	$y_i = K_i z_i$	$K_i$	$y_i = K_i z_i$
C <sub>1</sub>	0.4404	2.1500	0.9469	2.060	0.9072	2.020	0.8896
C <sub>2</sub>	0.0432	1.0300	0.0445	1.025	0.0443	1.020	0.0441
C <sub>3</sub>	0.0405	0.6720	0.0272	0.678	0.0274	0.680	0.0275
C <sub>4</sub>	0.0284	0.4400	0.0125	0.448	0.0127	0.450	0.0128
C <sub>5</sub>	0.0174	0.3000	0.0052	0.316	0.0055	0.323	0.0056
C <sub>6</sub>	0.0290	0.2150	0.0062	0.230	0.0067	0.239	0.0069
C <sub>7+</sub>	0.4701	0.0235	0.0094	0.250	0.0100	0.026	0.0104
S	1.0000		1.0519		1.0138		0.9969

By interpolation:  $p_b = 23 \text{ MPa}$

At the dew point of the system, the amount of liquid phase is infinitesimal small and thus

$$n_{liq} = 0, n_{vap} = n \text{ and } y_i = z_i.$$

From Eq. 4.21:

$$\sum_{i=1}^k \frac{z_i n}{n_{liq} + n_{vap} K_i} = \sum_{i=1}^k \frac{z_i}{K_i} = \sum_{i=1}^k \frac{y_i}{K_i} = 1. \quad (4.25)$$

In analogy of the iterative process demonstrated by Example 4.2 (evaluation of  $p_b$ ), it is theoretically possible to evaluate the dew point pressure by use of Eq. 4.25 by summing up the  $y_i/K_i$  values and by varying the pressure as long as  $\sum y_i/K_i = 1$ .

However, the evaluation of the  $K$ -factor for heavier components is crucial. Therefore, the calculation of the dew point pressure of hydrocarbon systems by using Eq. 4.25 may be too inaccurate. This notion is mostly used to check the  $K$ -factors which have been evaluated for certain state conditions.

In evaluating hydrocarbon systems, two characteristic processes are of importance. These are illustrated schematically in Figure 4.3.

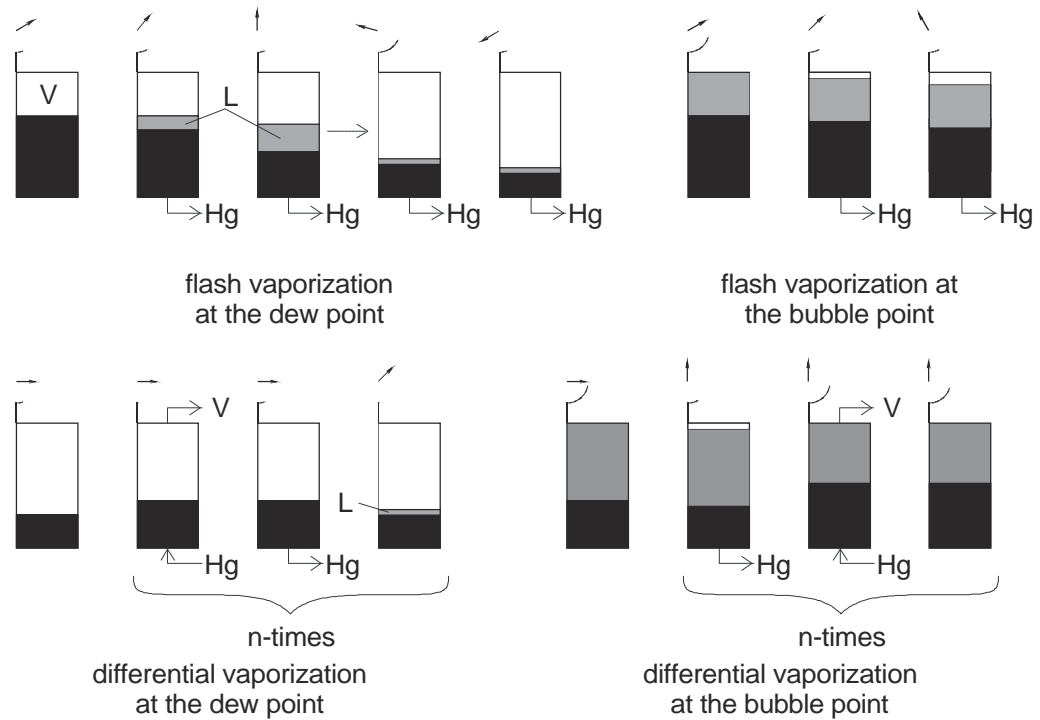


Figure 4.3: Flash and differential vaporization

- “**Flash vaporization (condensation)**”: Mass and composition of the system remain constant (closed system) while  $p$  and  $V$  are changed isothermally.  $V$  increases with decreasing pressure. The portions of the phases and their compositions (variables) are evaluated for any state of thermodynamic equilibrium.
- “**Differential vaporization (condensation)**”: Preceding every further change of state, mass and composition of the system are changed in removing one phase - generally the vapor phase - partly or completely as soon as the previous phase equilibrium has been achieved (open system).

In case of a flash vaporization, the phase compositions in any state of equilibrium can be calculated by Eq. 4.19 to Eq. 4.21. However, the  $K$ -factors must always correspond to the given pressure and temperature.

In case of a differential vaporization (open system), some material balance has to be applied. Assumption: The volume remains constant meanwhile any change in state is connected with a change of the mole number in the system and the composition of the system. This would correspond to the following reflections: In case of a saturated liquid, the amount of component  $i$  will decrease by  $y_i dn_v$ , resulting from the liberation and production of an infinitesimal small amount of gas  $dn_v$ , and

$$y_i dn_{vap} = n_{liq} x_i - (n_{liq} - dn_{vap})(x_i - dx_i). \quad (4.26)$$

Since  $y_i = K_i x_i$  and  $dn_{vap} = dn_{liq}$ , the following is obtained after neglect of the term  $dn_{vap} dx_i$ :

$$K_i x_i dn_{liq} = x_i dn_{liq} + n_{liq} dx_i \quad (4.27)$$

Eq. 4.27 cannot be integrated, because  $K_i$  is a function of pressure. Therefore, the method of finite differences is often applied. The integral is then substituted by summation formulae. Results have been often proved to correspond accurately with the experimental data (see Example 4.3).

### Example 4.3

Determination of tank oil composition after 3-stage separation using the procedure of Example 5.1 and known  $K_i$  values.

**FIRST SEPARATOR:**  $p = 3.33 \text{ MPa}$ ,  $T = 48.7 \text{ }^\circ\text{C}$ ,  $n_{liq} = 0.582$ ,  $n_{vap} = 0.418$

Component	Well Stream Composition $z_i$	K-Factor $K_i$	Fluids	
			Liquid	Vapor
			$x_i$	$y_i$
$C_1$	0.4404	8.100	0.1110	0.8991
$C_2$	0.0432	1.650	0.0339	0.0560
$C_3$	0.0405	0.590	0.0489	0.0288
$C_4$	0.0284	0.230	0.0419	0.0096
$C_5$	0.0174	0.088	0.0281	0.0025
$C_6$	0.0290	0.039	0.0485	0.0019
$C_{7+}$	0.4011	0.003	0.6877	0.0021
$\Sigma =$	1.0000		1.0000	1.0000

**SECOND SEPERATOR:**  $p = 0.44 \text{ MPa}$ ,  $T = 48.7 \text{ }^\circ\text{C}$ ,  $n_{liq} = 0.844$ ,  $n_{lvap} = 0.156$

Component	Feed Composition $z_i$	K-Factor $K_i$	Fluids	
			Liquid	Vapor
			$x_i$	$y_i$
$C_1$	0.1110	60.000	0.0109	0.6530
$C_2$	0.0339	10.600	0.0135	0.1430
$C_3$	0.0489	3.400	0.0355	0.1207
$C_4$	0.0419	1.250	0.0403	0.0504
$C_5$	0.0281	0.415	0.0309	0.0128
$C_6$	0.0485	0.170	0.0557	0.0095
$C_{7+}$	0.6877	0.013	0.8132	0.0106
$S =$	1.0000		10000	10000

**Tank:**  $p = 0.01 \text{ MPa}$ ,  $T = 48.7^\circ\text{C}$ ,  $n_{\text{liq}} = 0.9486$ ,  $n_{\text{vap}} = 0.0514$

Component	Feed Composition $z_i$	K-Factor $K_i$	Fluids Liquid Vapor $x_i$ $y_i$	
$C_1$	0.1090	265.000	0.0007	0.1965
$C_2$	0.0135	46.600	0.0038	0.1885
$C_3$	0.0355	14.300	0.0210	0.3022
$C_4$	0.0403	5.350	0.0330	0.1775
$C_5$	0.0309	1.720	0.0299	0.0513
$C_6$	0.0557	0.700	0.0566	0.0396
$C_{7+}$	0.8132	0.052	0.8550	0.0444
<b>S =</b>	<b>1.0000</b>		<b>10000</b>	<b>10000</b>

One mole reservoir crude oil produced amounts to

$$n_{\text{liq}1} \times n_{\text{liq}2} \times n_{\text{liq}3} = 0.582 \times 0.844 \times 0.9486 = \mathbf{0.466 \text{ mol tank oil}}$$

## 4.2.2 Evaluation of K-Factors Using Convergence Pressures

As already mentioned, the  $K_i$ -factors in real systems not only depend on temperature and pressure, but also on composition. KATZ and HACKMUTH have been the first to provide for appropriate data of gas-oil systems. Since then the collection of data has been continuously enlarged.

The most simple relations exist in any 2-component system. Figure 4.4 is a plot of the K-factors for the methane-propane system at the critical temperature of the mixture ( $T_c = 100^\circ\text{F}$ ).  $K > 1$  for the highly volatile component methane at any pressure at which the vapor and the liquid phase are in equilibrium. If the pressure increases, its K-factor will decrease.

On the other side  $K < 1$  for the less volatile component propane since its concentration in the vapor phase is less than in the liquid. At any isothermal change in state,  $K$  for the less volatile component propane will equal 1 at two different pressures. One corresponds - just as in case of the highly volatile component - with the critical pressure of the mixture and the other one with the vapor pressure of the pure substance. Above the critical pressure of the system, K-factors have no longer any physical meaning.

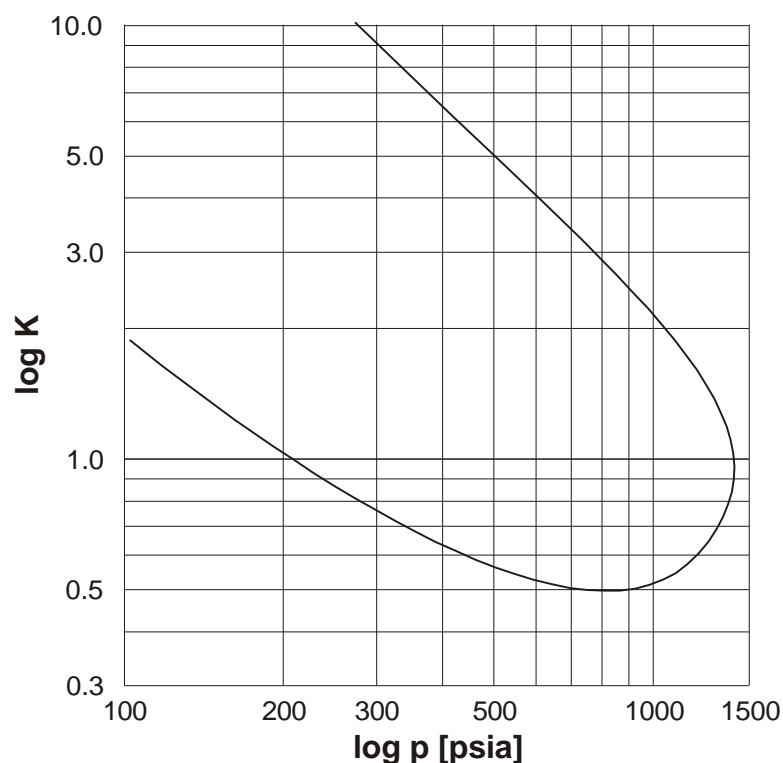


Figure 4.4:  $K$ -factors for methane-propane at  $T_c = 100\text{ }^{\circ}\text{F}$   
(from SAGE, LACEY and SCHAAFSMA) (1934)

Generally, the  $K$ -factors increase with increasing temperature at constant pressure. However, methane shows some irregular behavior. Its  $K$ -factor increases with temperature up to a certain limit and decreases beyond that.

According to observations, the two  $K$ -isotherms of a binary system will also converge at other temperatures than  $T_c$ . This point is also characterized by  $K = 1$  ( $y = x$ ). However, this convergence is only an “apparent” convergence. In contrast to the critical isotherms, the  $K$ -values have no physical meaning up to the point of apparent convergence because of the existence of only one phase beyond the critical pressure. Anyway, the isotherms may be extrapolated to  $K = 1$  defining the pressure at this point as the “**convergence pressure**”  $p_k$  of the system at the actual temperature.

It has been proved that multi-component systems have properties very similar to those of the binary systems with respect to the convergence of all  $K$ -isotherms. Figure 4.5 emphasizes the dependence of the  $K$ -factors on the (apparent) convergence pressure  $p_k$  which is a function of the system composition. The differences in  $K$ -values for the two convergence pressures at pressures below 0.7 MPa (100 psia) are not significant for the lighter hydrocarbons ethane through pentane. It becomes apparent that at low pressures and temperatures, the  $K$ -factors are nearly independent of composition.

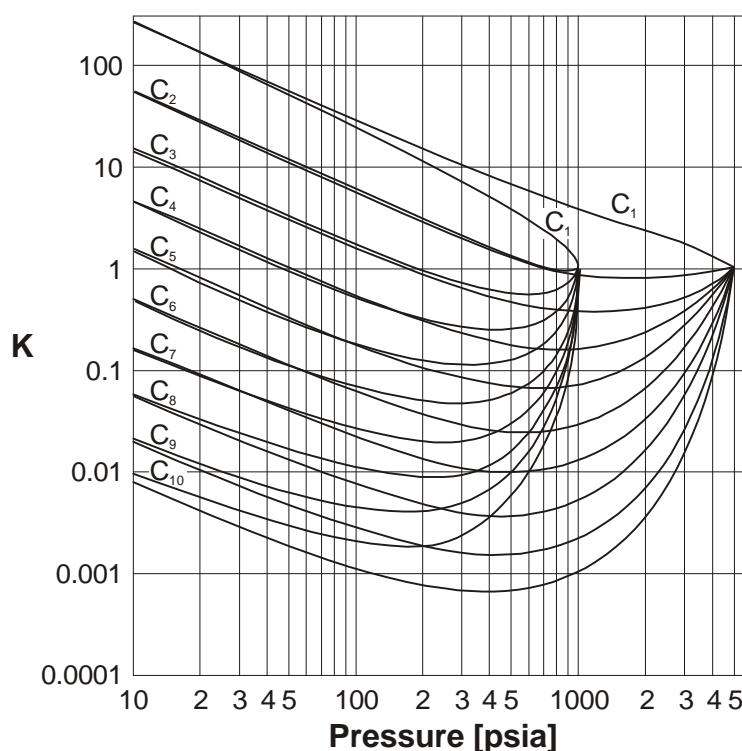


Figure 4.5: Comparison of  $K$ -factors at  $100^{\circ}\text{F}$  for 1,000 and 5,000- $\text{psia}$  convergence pressure (from NGAA, 1957)

Note:

- If the evaluation of the  $K$ -factors is based on the convergence pressure of the mixture, the  $K$ -factors depend only on  $p$  and  $T$  and are independent of composition.
- At a given temperature, the convergence pressure of a mixture coincides with the critical pressure of another mixing ratio of its components.

In 1957, the NGAA (**Natural Gasoline Association of America**) published a diagram series  $\lg K = f(\lg p)_T$  in its “Equilibrium Ratio Data Book”. The diagrams are based on average values of already available data from various gas condensates and gas/crude oil-systems. This series includes the paraffinic homologous compounds - methane through decane - just as ethylene, propylene, nitrogen, carbon dioxide and hydrogen sulfide within the pressure range from 0.07 to 140 MPa and for temperatures ranging from - 148 to +260 °C.

Figure 4.6 and Figure 4.7 present the respective charts for methane and hexane, respectively ( $p_k = 34.5 \text{ MPa}$  (5000  $\text{psia}$ )). The values for this convergence pressure can be used for a large number of hydrocarbon systems. Today, these data are already available for electronic data-processing.

If  $p_k$  is known, it is possible to choose from the measured series those  $K$ -factors which are best suited to describe the phase equilibrium vapor-liquid of the given system.

The second parameter, which has to be evaluated to proceed with the prediction of the phase and volumetric behavior of complex hydrocarbon systems, is the  $K$ -factor of the heaviest component. In conventional analyses of hydrocarbon fluids, the components heavier than hexane are grouped together and reported as the pseudo-component " $C_{7+}$ ". This fraction is a mixture of materials of varying volatility. Anyway, the vapor pressure curves and the critical properties of the hydrocarbons heavier than hexane are fairly close together. Thus, it is possible to characterize the mixture " $C_{7+}$ " by an average set of  $K$ -values.

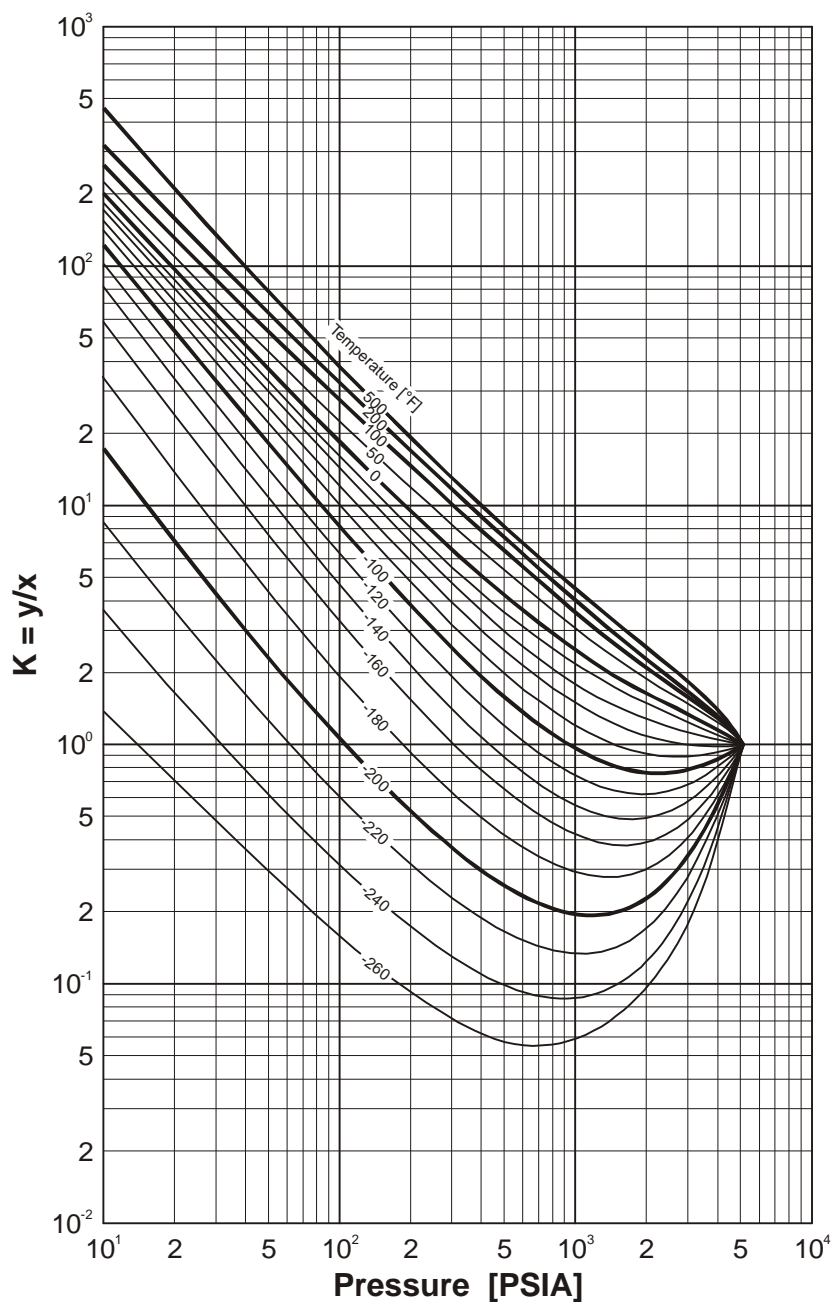


Figure 4.6:  $K$ -factors for methane, 5,000 psia convergence pressure (from NGAA, 1957)

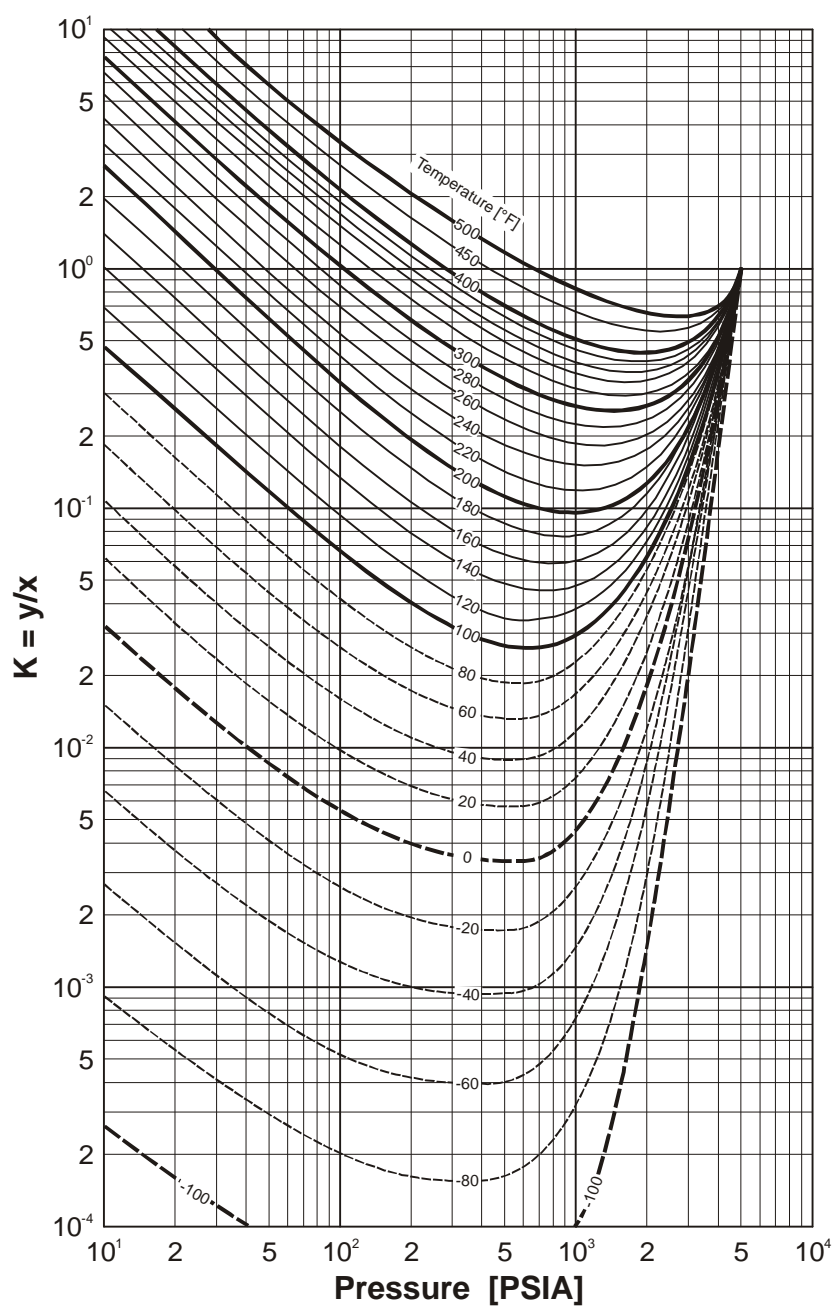


Figure 4.7: K-factors for hexane, 5,000 psia convergence pressure (from NGAA, 1957)

### 4.2.3 Evaluation of Convergence Pressure

Several iterative methods have been proposed in order to estimate  $p_k$ . One of the most convenient methods is based on the assumption of a pseudo-binary system and consists of the following steps:

- A certain convergence pressure is assumed, Then the  $K$ -factors of the components are evaluated from the NGAA-diagrams (examples are given through Figure 4.6 and Figure 4.7).
- The respective composition of the liquid phase being in equilibrium is evaluated by the iterative process shown in Example 4.1.
- Excluding the lightest component methane, all the other components are summarized as a pseudo-component  $C_{2+}$ . The pseudo-critical temperature of  $C_{2+}$  in the liquid phase is evaluated in calculating its mole weight in the liquid phase,  $W_i$ , through
- $W_i = x_i M_i$  ( $i = 2, 3, 4, \dots, k$ ) and the pseudo-critical temperature of  $C_{2+}$  through

$$T_{pc} = \frac{\sum_{i=2}^k W_i T_{ci}}{\sum_{i=2}^k W_i} \quad (4.28)$$

- The critical point of the pseudo-component  $C_{2+}$  is plotted on Figure 4.8 which shows the vapor pressure curves of homologous hydrocarbons.
- The “binary” critical envelope curve between the critical point of methane and the one of the pseudo-component  $C_{2+}$  is drawn.
- In entering Figure 4.8 at the temperature of the system, the convergence pressure can be read off from the critical envelope curve methane- $C_{2+}$  because  $p_k$  coincides with the critical pressure of one of the possible mixing ratios in the “binary” system.
- If this numerical value of the convergence pressure does not coincide with the  $p_k$ -value initially assumed, the whole procedure has to be repeated, starting with the assumption of another convergence pressure. The iterative process must go on until correspondence of the assumed convergence pressure and the evaluated one have been achieved.

This iterative method will be demonstrated by Example 4.4.

The  $K$ -factors obtained through this method exhibit only satisfactory results if the operating pressure is considerably lower than  $p_k$ . If the operating pressure approaches  $p_k$ , the  $K$ -factors become very sensitive to the convergence pressure used and care must be taken in the selection of the correct value of  $p_k$ . However, charts exist only for some distinct convergence pressures (800, 1000, 1500, 2000, 3000, 5000 and 10,000 psia). Thus

the interpolation - inevitable for estimating the  $K$ -values - may lead to great errors.

#### 4.2.4 $p_K$ Evaluation Using PENG-ROBINSON Equation of state

With help of the “*successive solution method*”, the  $K$ -factors of the components of the system can be evaluated by an iterative process like the one presented in Example 4.5:

- The composition of the system, the pressure and temperature as well as the critical data of the components, their acentric factors and the interactive coefficients must be known.
- On the basis of assumed  $K$ -factors, the phase compositions are calculated through an iterative calculation procedure (see Example 4.1).
- On the basis of the calculated phase compositions, the PENG-ROBINSON EOS-parameters  $a$ ,  $b$ ,  $A$ , and  $B$  are calculated.
- The  $Z$ -factors both for the liquid and the vapor phase are evaluated by solving the equation of state (Eq. 3.49) through the use of the method of CARDAN (see Example 3.3).
- The fugacity coefficients for both phases are evaluated by using Eq. 4.14 and Eq. 4.15:

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left[ \frac{2 \sum_{j=1}^k x_j a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left( \frac{Z+2 \cdot 414B}{Z-0.414B} \right)$$

and

$$a_{ij} = (1 - K_{ij})(a_i^{0.5} a_j^{0.5}).$$

- New  $K$ -values can be evaluated by inserting these values in Eq. 4.16:

$$K_i = \frac{\phi_{i, liq}}{\phi_{i, vap}}$$

- On the basis of the evaluated  $K$ -values, the calculation procedure is repeated. The steps described above will be repeated until the  $K$ -factors converge within a certain limit.
- The last flash iteration results in the evaluation of the mole number in the liquid phase,  $n_{liq}$ , the mole number in the vapor phase  $n_{vap}$  and in the evaluation of the composition of the phases.

- Using  $Z_{liq}$  and  $Z_{vap}$ , the volume and the density of the two phases can be calculated, too.

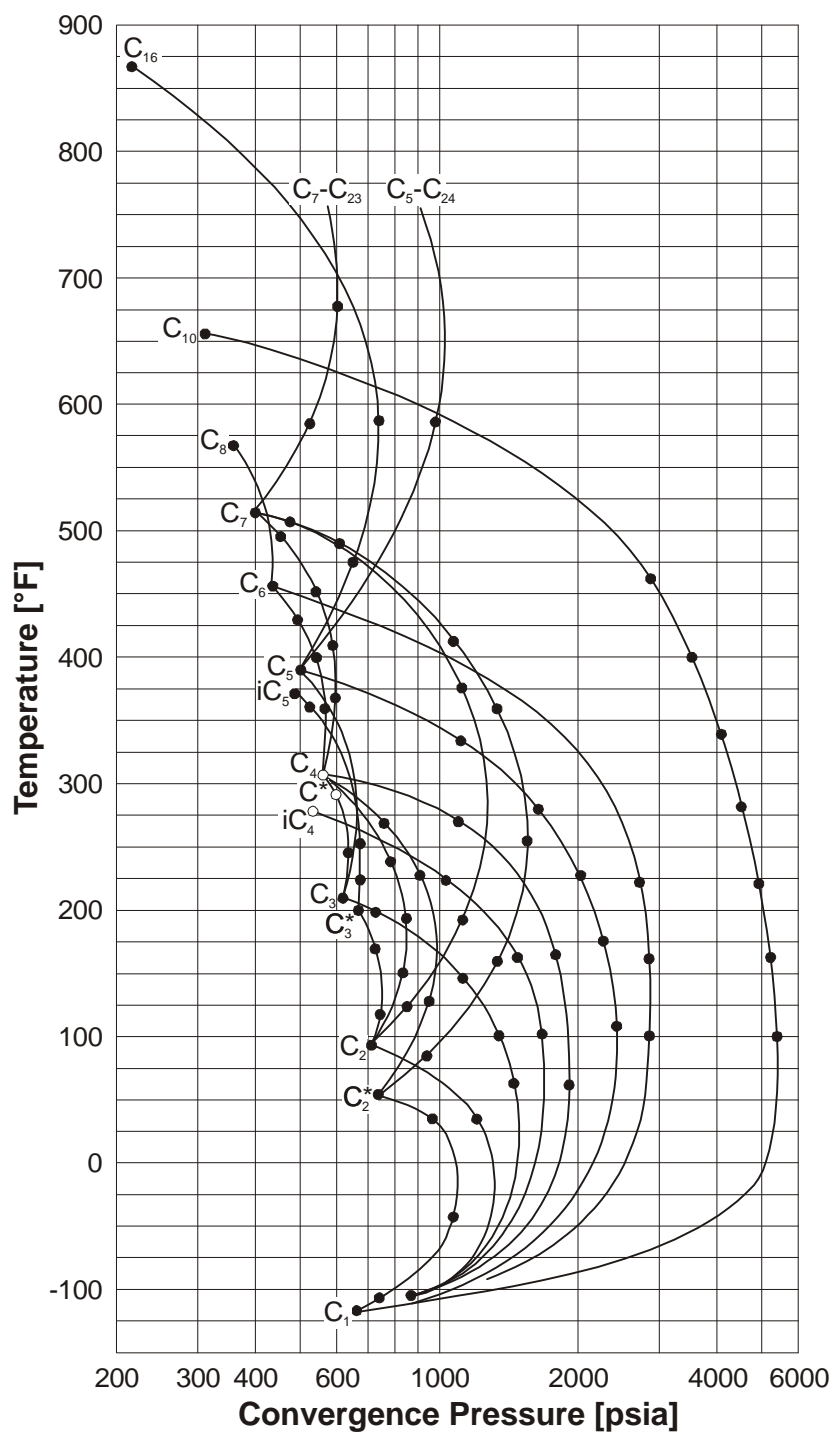


Figure 4.8: Convergence pressure data - methane for binary hydrocarbon mixtures (from WINN, 1952)

**Example 4.4**

Evaluation of the convergence pressure by the iterative NGAA process described above. The composition of the system and the liquid phase is tabled below,  $T = 49^\circ\text{C}$  and  $p = 15.5\text{ MPa}$ , assumption:  $C_{7+} \approx nC_8$

**FIRST ITERATION:  $p_k = 26.7\text{ MPa}$  (4000 psia),  $n_{\text{liq}} = 0.5876$ ,  $n_{\text{vap}} = 0.4124$**

Component	$z_i$	$M_i$ kg/kmole	$T_{c,i}$ K	$K_i$	$x_i$	$W_i = x_i M_i$	$W_i T_{c,i}$
$C_1$	0.6973	—	—	1.6500	0.5499	—	—
$C_2$	0.0318	30.07	305.4	0.9000	0.0332	0.998	304.79
$C_3$	0.0194	44.09	369.8	0.6300	0.0229	1.010	373.50
$nC_4$	0.0223	58.12	425.2	0.4300	0.0292	1.697	721.56
$nC_5$	0.0221	72.15	469.7	0.2250	0.0325	2.345	1101.45
$nC_{6*}$	0.0309	86.17	507.4	0.1700	0.0470	4.050	2054.97
$C_{7*}$	0.1762	114.22	568.8	0.0720	0.2854	32.598	18541.74
<b>S</b>	<b>1.0000</b>				<b>1.0000</b>	<b>42.698</b>	<b>23098.01</b>

$$T_{pc} = \frac{\sum_{i=2}^k W_i T_{c,i}}{\sum_{i=2}^k W_i} = \frac{23098.01}{42.698} = 540.96\text{ K} = 514.06^\circ\text{F}$$

On Figure 4.8,  $T_{pc} = 514.06^\circ\text{F}$  is close to  $T_c$  of pure n-heptane. Considering the operating temperature ( $T = 120^\circ\text{F}$ ), the convergence pressure  $p_k$  can be read off on the envelope curve between methane and n-heptane at

**$p_k = 3150\text{ psia} = 21.72\text{ MPa}$ .**

This value does not coincide with the initially assumed value. Thus a second iteration must be done.

SECOND ITERATION:  $p_k = 20.4 \text{ MPa} (3000 \text{ psia})$ ,  $n_{\text{liq}} = 0.5604$ ,  $n_{\text{vap}} = 0.4496$

Component	$K_i$	$x_i$	$W_i = x_i M_i$	$W_i T_{C_i}$
$C_1$	1.700	0.5332	—	—
$C_2$	0.8800	0.0336	1.010	308.45
$C_3$	0.6200	0.0233	1.027	379.78
$nC_4$	0.4200	0.0299	1.738	739.00
$nC_5$	0.2200	0.0336	2.424	1138.55
$nC_6^*$	0.1800	0.0483	4.162	2111.80
$C_7^*$	0.0700	0.2980	34.038	19360.81
S		1.0000	44.399	24038.39

$$\frac{\sum_{i=2}^k W_i T_{C_i}}{\sum_{i=2}^k W_i} = \frac{24038.39}{44.399} = 541.42 K = 514.9 ^\circ F$$

From Figure 4.8:  $p_k = 3150 \text{ psia}$ , and thus

$$p_k = 21.72 \text{ MPa}.$$

The agreement with the assumption is now satisfactory. Further refinement is impossible ( $K$ -values only evaluated for 1000  $\text{psia}$  steps in  $p_k$ ).

### Example 4.5

Evaluation of the  $K$ -factors of the three components of a system at  $p = 1.38 \text{ MPa}$  and  $T = 338.7 \text{ K}$ . The successive solution method is used on the basis of the composition of the system, the critical and reduced data, the acentric factors and the interaction coefficients  $K_{ij}$  are given in Table I and Table II.

TABLE I: Data of the System

Component	Composition	Critical Data		Reduced Data		Acentric Factor
	$z_i$	$T_c \text{ K}$	$p_c \text{ MPa}$	$T_r$	$p_r$	$W_i$
$C_3$	0.61	369.8	4.245	0.916	0.325	0.152
$n - C_4$	0.28	425.2	3.800	0.797	0.363	0.193
$n - C_5$	0.11	469.6	3.374	0.721	0.409	0.251

**TABLE II: Interaction Coefficients of the Components**

	$C_3$	$n - C_4$	$n - C_5$
$C_3$	0.000	0.001	0.003
$n - C_4$	0.001	0.000	0.001
$n - C_5$	0.003	0.001	0.000

For the first iteration of the flash process,  $K$ -factors as well as the mole numbers in the phases,  $n_{liq}$  and  $n_{vap}$ , are assumed. The gas and the liquid phase compositions are calculated through an iterative calculation procedure (see Example 4.1). The assumed  $K$ -factors as well as the evaluated phase compositions are given in Table III.

**TABLE III: First Iteration ( $n_{liq} = 0.52$ ,  $n_{vap} = 0.48$ , Phase Composition Evaluation)**

Component	K-Factor	$x_i = \frac{z_i}{n_v K_i + n_L}$	$y_i = \frac{z_i}{n_L / K_i + n_v}$
$C_3$	1.745	0.440	0.767
$n - C_4$	0.537	0.369	0.198
$n - C_5$	0.182	0.191	0.035
S		<b>1.000</b>	<b>1.000</b>

Then the flash iteration starts with the evaluation of  $a$  and  $b$ . At first the parameters  $b$  and  $a$  for each component have to be evaluated through

$$b_i = 0.0778 \frac{RT_c}{p_c},$$

(see Eq. 3.46),

$$a_{c,i} = 0.45724 \frac{R^2 T^2}{p_c},$$

(see Eq. 3.48),

$$\alpha_i^{0.5} = 1 + (0.37646 + 1.54226\omega - 1.54226\omega^2)(1 - T_r^{0.5}),$$

(see Eq. 3.52) and through

$$a_i = (a_c \alpha)_i.$$

(see Eq. 3.47).

The results of these calculations are shown in Table IV.

**TABLE IV: First Iteration, Evaluation of  $b_i$  and  $a_i$**

Component	$b_i$	$a_i$
C <sub>3</sub>	5.635 E-5	1.072
n - C <sub>4</sub>	7.247 E-5	1.729
n - C <sub>5</sub>	9.003 E-5	2.557

By use of Eq. 3.53

$$b = \sum_{i=1}^k x_i b_i$$

and Eq. 3.56

$$a = \sum_{i=1}^k \sum_{j=1}^k x_i x_j (a_i a_j)^{0.5} (1 - K_{ij}),$$

$a$  and  $b$  for the liquid phase as well as for the vapor phase are calculated on the basis of phase compositions evaluated through the first evaluation (see Table III). The calculation procedure is presented through Example 3.2.

Then the parameters  $A$  and  $B$  are calculated after PENG-ROBINSON using Eq. 3.35

$$A = \frac{ap}{R^2 T^2}$$

and Eq. 3.36

$$B = \frac{b p}{R T}.$$

The evaluated numerical values of the parameters  $a$ ,  $b$ ,  $A$  and  $B$  for both phases are summarized in Table V.

**TABLE V: First Iteration, Evaluation of  $a$ ,  $b$ ,  $A$  and  $B$**

	$a$	$b$	$A$	$B$
Liquid Phase	1.551	6.873 E-5	0.2699	3.368 E-2
Vapor Phase	1.232	6.072 E-5	0.2144	2.975 E-2

Now the  $Z$ -factors both for the liquid and the vapor phase can be evaluated solving the equation of state given by Eq. 3.49:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0.$$

To solve this cubic equation of state, the CARDAN equation is applied for

$$x^3 + rx^2 + sx + t = 0$$

where

$$r = -(1 - B),$$

$$s = (A - 2B - 3B^2)$$

and

$$t = -(AB - B^2 - B^3).$$

The factors  $r$ ,  $s$  and  $t$  have to be evaluated both for the liquid and the vapor phase.

By substitution of

$$x = y - \frac{r}{3},$$

the formula

$$x^3 + rx^2 + sx + t = 0$$

is reduced to

$$y^3 + py + q = 0$$

where

$$p = \frac{3s - r^2}{3}$$

and

$$q = \frac{2r^3}{27} - \frac{rs}{3} + t.$$

The discriminant  $D$  is defined as

$$D = \left(\frac{p}{3}\right)^3 + \left(\frac{q}{2}\right)^2$$

Contrary to Example 3.3,  $D < 0$  both in case of the liquid phase and in case of the vapor phase. Thus the cubic equation of state has three real solutions, respectively. In defining

$$\varsigma = 2\sqrt[3]{-\frac{p}{27}}$$

and

$$\cos \varphi = -\frac{q}{2\zeta},$$

the three solutions for the reduced form

$$y^3 + py + q = 0$$

are given by

$$y_1 = 2\sqrt[3]{\zeta} \cos(\varphi/3)$$

$$y_2 = 2\sqrt[3]{\zeta} \cos(\varphi/3 + 2\pi/3)$$

and

$$y_3 = 2\sqrt[3]{\zeta} \cos(\varphi/3 + 4\pi/3).$$

Introducing  $y_1$ ,  $y_2$ , and  $y_3$  into

$$x = y - \frac{r}{3},$$

the Z-factors(=x) of the phases can be evaluated. The solutions are summarized in Table VI.

**TABLE VI: First Iteration, Solution for the Z-Factors after CARDAN**

	$Z_1$	$Z_2$	$Z_3$
Liquid Phase	0.0523	0.2172	0.6968
Vapor Phase	0.0526	0.1325	0.7852

Obviously, the actual Z-factor of the liquid phase must be identical with the smaller one of the three solutions for the liquid phase, meanwhile the actual Z-factor for the vapor phase is equal to the greatest one of the three solutions for the vapor phase. Thus the first iteration results in

$$\mathbf{Z_{liq} = 0.0523}$$

and

$$\mathbf{Z_{vap} = 0.7852}$$

The Z-factors are introduced into Eq. 4.14 to evaluate the fugacity coefficients  $\phi_3$  (of propane),  $\phi_4$  (of n-butane) and  $\phi_5$  (of n-pentane) both for the liquid and the vapor phase. The results of this calculation procedure are summarized in Table VII.

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left[ \frac{\sum_{i=1}^k x_i a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left( \frac{Z + 2 \cdot 414B}{Z - 0.414B} \right)$$

**TABLE VII: First Iteration: Fugacity Coefficients**

	$f_3$	$f_4$	$f_5$
Liquid Phase	1.2580	0.4707	0.1831
Vapor Phase	0.8473	0.7519	0.6672

As a result of the first iteration flash, K-factors are evaluated through Eq. 4.16

$$K_i = \frac{\phi_{i,liq}}{\phi_{i,vap}}$$

and summarized in Table VIII.

**TABLE VIII: First Iteration, K-Factors**

Components	K-Factor
C <sub>3</sub>	1.4847
n - C <sub>4</sub>	0.6260
n - C <sub>5</sub>	0.2744

These K-factors are the basis of the second iteration which starts again with the iterative calculation procedure presented through Example 4.1., in using the data given in Table I and Table IV. The results are shown in Table IX. The numerical values of the parameters  $a$ ,  $b$ ,  $A$  and  $B$  for both phases are evaluated again and summarized in Table X.

Now the Z-factors both for the liquid and the vapor phase can be evaluated solving the equation of state given by Eq. 3.49

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0$$

through the CARDAN equation. The solutions are summarized in Table XI.

**TABLE IX: Second Iteration ( $n_{\text{liq}} = 0.556, n_{\text{vap}} = 0.444$ ), Phase Composition Evaluation)**

Component	K-Factor	$x_i = \frac{z_i}{n_v K_i + n_L}$	$y_i = \frac{z_i}{n_L / K_i + n_v}$
C <sub>3</sub>	1.4847	0.5020	0.7453
n - C <sub>4</sub>	0.6260	0.3358	0.2102
n - C <sub>5</sub>	0.2742	0.1623	0.0445
S		<b>1.0001</b>	<b>1.0000</b>

**Table X: Second Iteration, Evaluation of a, b, A and B**

	a	b	A	B
Liquid Phase	1.490	6.725 E-5	0.2592	3.296 E-2
Vapor Phase	1.249	6.116 E-5	0.2173	2.997 E-2

**TABLE XI: Second Iteration, Solution for the Z-Factors after CARDAN**

	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>
Liquid Phase	0.0521	0.1988	0.7161
Vapor Phase	0.0525	0.1364	0.7812

Once more again, the actual Z-factor of the liquid phase must be identical with the smallest one of the three solutions for the liquid phase, and the actual Z-factor for the vapor phase is equal to the greatest one of the three solutions for the vapor phase. Thus the second iteration results in

$$Z_{\text{liq}} = 0.0521$$

and

$$Z_{\text{vap}} = 0.7812$$

The Z-factors are introduced into Eq. 4.14

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left[ \frac{\sum_{i=1}^k x_i a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left( \frac{Z + 2 \cdot 414B}{Z - 0.414B} \right)$$

to evaluate the fugacity coefficients. The results of this calculation procedure are summarized in Table XII.

**TABLE XII: Second Iteration, Fugacity Coefficients**

	$f_3$	$f_4$	$f_5$
Liquid Phase	1.2520	0.4717	0.1846
Vapor Phase	0.8477	0.7511	0.6655

The K-factors are evaluated through Eq. 4.16

$$K_i = \frac{\phi_{i,liq}}{\phi_{i,vap}}$$

and given in Table XIII.

**TABLE XIII: Second Iteration, K-Factors**

Components	K-Factor
C <sub>3</sub>	1.4769
n - C <sub>4</sub>	0.6280
n - C <sub>5</sub>	0.2773

The K-factors from the two flash iterations exhibit satisfactory convergence. On the basis of the K-factors given in Table XIII, a final iterative calculation procedure analogous to Example 4.1 results in the mole numbers and in the composition of the phases (see Table XIV).

**Table XIV: Final Results**

$$n_{liq} = 0.562$$

$$n_{vap} = 0.438$$

Component	K-Factor	$x_i = \frac{z_i}{n_v K_i + n_L}$	$y_i = \frac{z_i}{n_L / K_i + n_v}$
C <sub>3</sub>	1.4769	0.5046	0.7452
n - C <sub>4</sub>	0.6280	0.3345	0.2101
n - C <sub>5</sub>	0.2773	0.1609	0.0446
S		1.0000	0.9999



# Chapter 5

## Phase Properties

### 5.1 Natural Gases

#### 5.1.1 Volume

As previously discussed in Chap. 3, the state of ideal gases is defined by the following equation of state:

$$pV = nRT \quad (5.1)$$

where **R** is the universal gas constant and *n* is the number of moles. The value **R** depends on the system of units. In the **SI** system:

$$R = 8.31432 \text{ J / K mole.}$$

In case of ideal gases, no intermolecular forces are acting. At any isothermal change of state, the decrease in volume is directly proportional to the increase in pressure. It has been observed that in many cases - e.g. in case of natural gases - the volume becomes less than half if the pressure is doubled. This behavior of a gas is called a real one.

Below the BOYLE temperature, the real gases are more compressible than an ideal one, because of intermolecular forces of attraction and repulsion. If the pressure is low (the forces of attraction can be neglected because of the great distance of molecules) or in case of high temperatures (dominance of the kinetic energy of the molecules), real gases behave similarly to perfect gases.

In case of real gases, the change in state can be well described by the equations of state which are also presented in Chap. 3 (VAN DER WAALS, REDLICH-KWONG, PENG-ROBINSON). In petroleum industry, the basic relation of Eq. 3.12

$$pV = ZnRT$$

is generally used because of its easy applicability.

The Z-factor is the so called “*deviation factor*” or “*compressibility factor*”. It is defined as the ratio of the volume of a real gas to the volume of a perfect one at identical temperature and pressure.

By introducing

$$n = \frac{m}{\bar{M}}$$

where  $m$  is the mass of the system and  $\bar{M}$  the averaged molecular weight of the components.

Eq. 3.12 can be transformed into

$$pV = \frac{mZRT}{\bar{M}}. \quad (5.2)$$

If  $m$  is defined as the unit of mass of 1 g, the reciprocal of the specific volume  $V$  is the density and so

$$\rho_g = \frac{1}{V} = \frac{p\bar{M}}{ZRT}. \quad (5.3)$$

The atmospheric density of the gas is often related to the atmospheric density of air at standard temperature. In doing so, the “*specific gravity*” of the gas  $\gamma_g$  is defined by

$$\gamma_g = \frac{\rho_g^0}{\rho_{g,a}^0} = \frac{\bar{M}_g}{\bar{M}_a} = \frac{\bar{M}_g}{28.97} \quad (5.4)$$

where the subscript “ $a$ ” indicates the values for air and the superscript “ $o$ ” those at standard conditions (atmospheric pressure).

If Eq. 5.4 is combined with Eq. 5.2, the gas density results in

$$\rho_g = \frac{1}{V} = \frac{M_a}{R} \gamma_g \frac{p}{ZT} = 0.003473 \gamma_g \frac{p}{ZT} \quad (5.5)$$

As expected, the Z-factor not only depends on pressure and temperature but also on the molecular weight. Z-factors of different gases, which can be determined experimentally, vary considerably. Figure 5.1 shows the Z-factor of methane, ethane and propane as a function of the pressure.

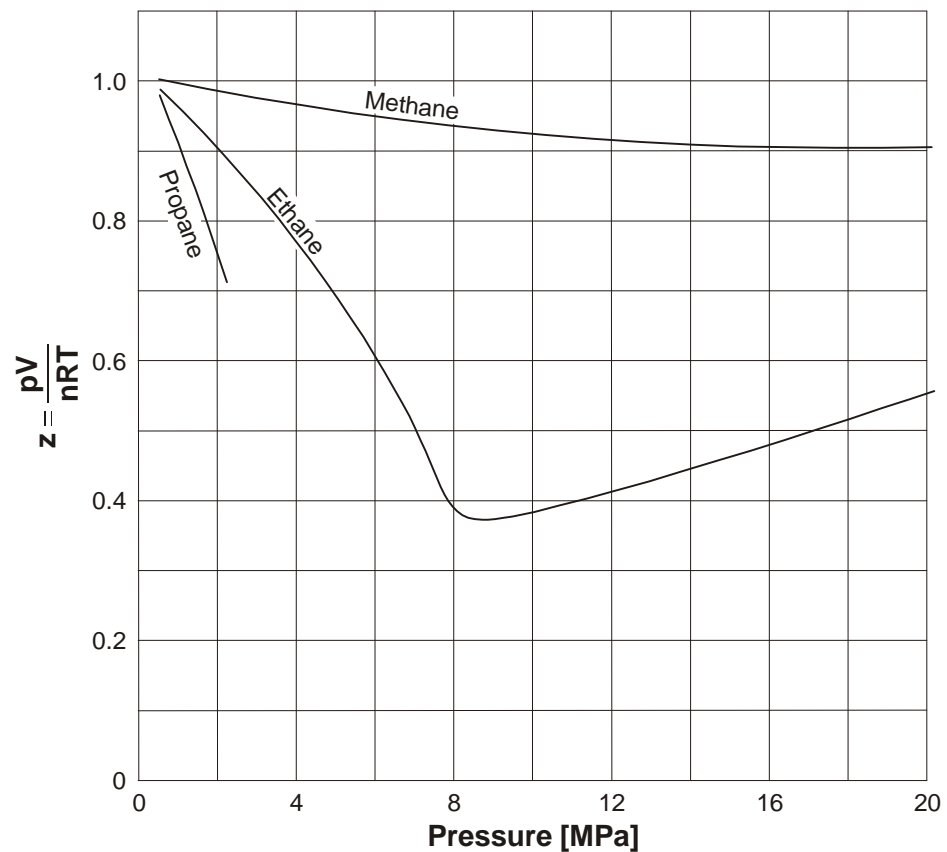


Figure 5.1: Z-factor of methane, ethane and propane versus pressure at  $T = 140^{\circ}F$  (from STANDING, 1977)

### 5.1.2 Formation Volume Factor

In petroleum industry, the term “formation volume factor” is widely used. It expresses the volume taken at  $p$  and  $T$  by the volume at standard state conditions, ( $p^{\circ}$  and  $V^{\circ}$ ).

The formation volume factor for gases,  $B_g$ , is defined by

$$B_g = B_g(p, T) = \frac{V}{V^{\circ}} \quad (5.6)$$

where the standard conditions  $p^{\circ}$  and  $T^{\circ}$  are generally defined in

Europe:  $p^{\circ}$ : 1.00 bar

$T^{\circ}$ : 273.15 K

and

USA:  $p^{\circ}$ : 14.7 psia (1.01325 bar)

$T^{\circ}$ : 60.0 °F (15 °C).

In case of one mole and standard conditions, Eq. 5.1 results in

$$p^{\circ} V^{\circ} = Z^{\circ} R T^{\circ} \quad (5.7)$$

If Eq. 5.1 and Eq. 5.7 are substituted in Eq. 5.6, then:

$$B_g(p, T) = \frac{Z T}{p} C \quad (5.8)$$

where

$$C = \frac{p^{\circ}}{Z^{\circ} T^{\circ}}.$$

### 5.1.3 Compressibility

On the basis of the gas law, the isothermal gas compressibility results in

$$c_g = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{B_g} \left( \frac{\partial B_g}{\partial p} \right)_T = \frac{1}{p} - \frac{1}{Z} \left( \frac{\partial Z}{\partial p} \right). \quad (5.9)$$

For ideal gases:  $Z = 1$ , i.e.  $\frac{\partial Z}{\partial p} = 0$ .

Therefore, the gas compressibility is only a function of pressure and is inversely proportional to the pressure.

### 5.1.4 Correlation of Z-Factor on the Basis of Reduced State Variables

In general, the components of natural gases are homologous paraffins with similar molecular structures. Therefore, the theorem of corresponding states can be applied. Figure 5.2 shows the excellent correspondence of the Z-factors of methane, propane and pentane as a function of reduced pressure for a series of reduced temperatures.

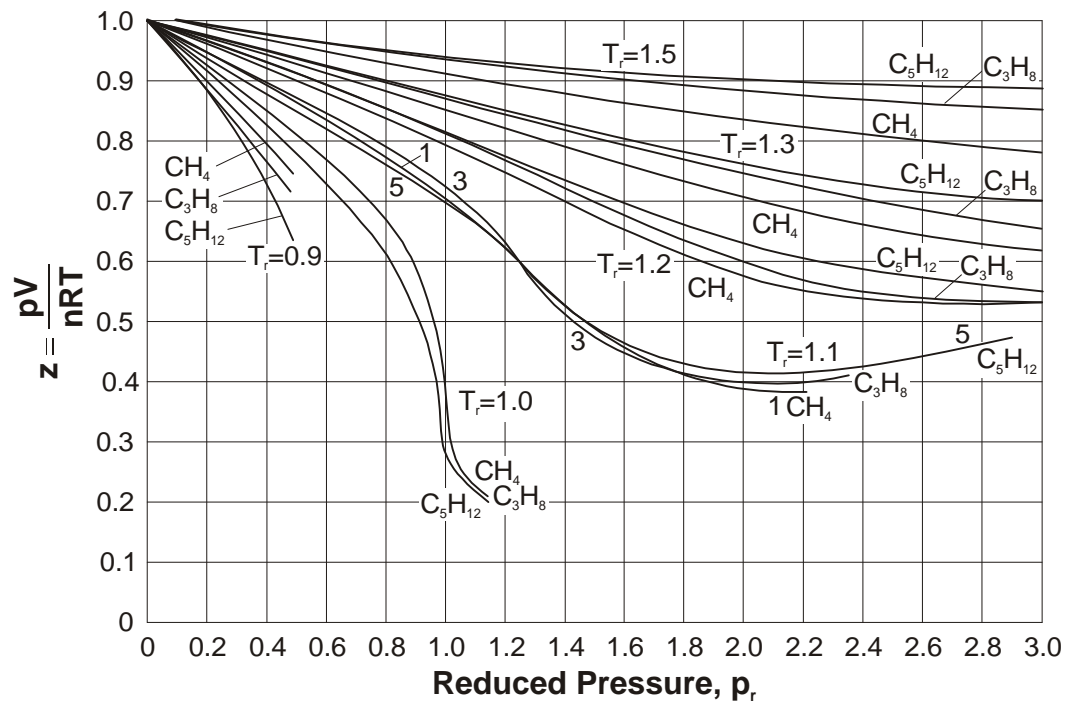


Figure 5.2: Z-factor as a function of reduced pressure for a series of reduced temperatures (from SAGE and LACEY, 1949)

The theorem of corresponding states can also be applied to gas mixtures through the evaluation of “*pseudo-critical*” data,  $T_{pc}$  and  $p_{pc}$ , which are given by

$$T_{pc} = \sum_{i=1}^k y_i T_{c,i} \quad (5.10)$$

and

$$p_{pc} = \sum_{i=1}^k y_i p_{c,i} \quad (5.11)$$

where

$p_{c,i}$ : critical pressure of component  $i$

$T_{c,i}$ : critical temperature of component  $i$

$y_i$ : mole fraction of component  $i$  in the gas phase.

Then the “pseudo-reduced” data,  $T_{pr}$  and  $p_{pr}$ , can be evaluated:

$$T_{pr} = \frac{T}{T_{pc}}, \quad (5.12)$$

$$p_{pr} = \frac{p}{p_{pc}} \quad (5.13)$$

where

$T$ : operating temperature

$p$ : operating pressure

Note that both  $T$  and  $T_{pc}$  in Eq. 5.12 must be absolute temperatures, either given in  $K$  (Kelvin, SI unit) or in  $R$  (Rankin, Field Unit).

The definition of corresponding states on the basis of the pseudo-reduced data results in a generalized plot of  $Z$ -factors for natural gases (see Figure 5.3). This plot can be used to evaluate the  $Z$ -factor of a natural gas on the basis of its composition and the critical data of the components (see Example 5.1).

Several natural gases contain a considerable amount of heavy components which will be combined - depending on the feasibility of chemical analysis - to the pseudo-components  $C_{7+}$  or  $C_{9+}$ . The compositions of these mixtures cannot exactly be defined. In the laboratory practice, the  $C_{7+}$  fraction is obtained as a liquid residue from a fractional distillation and two properties - averaged molecular weight and specific gravity - are determined. These properties have been correlated with the pseudo-critical data of this fraction (see Figure 5.4). On the basis of these correlations, the engineer is able to calculate pseudo-reduced properties of natural gases for which conventional analyses are available.

In many cases, the data of fractional distillation are not available. Anyway, several diagrams have been published which correlate the pseudo-critical state variables with the gas gravity. By means of these diagrams, the  $Z$ -factor can be determined even if the gas composition is not known. These diagrams are only valid for a given quality or only for one area, formation, reservoir, basin, etc. The respective diagram for Oklahoma City gases is given in Figure 5.5 (see also Example 5.2.)

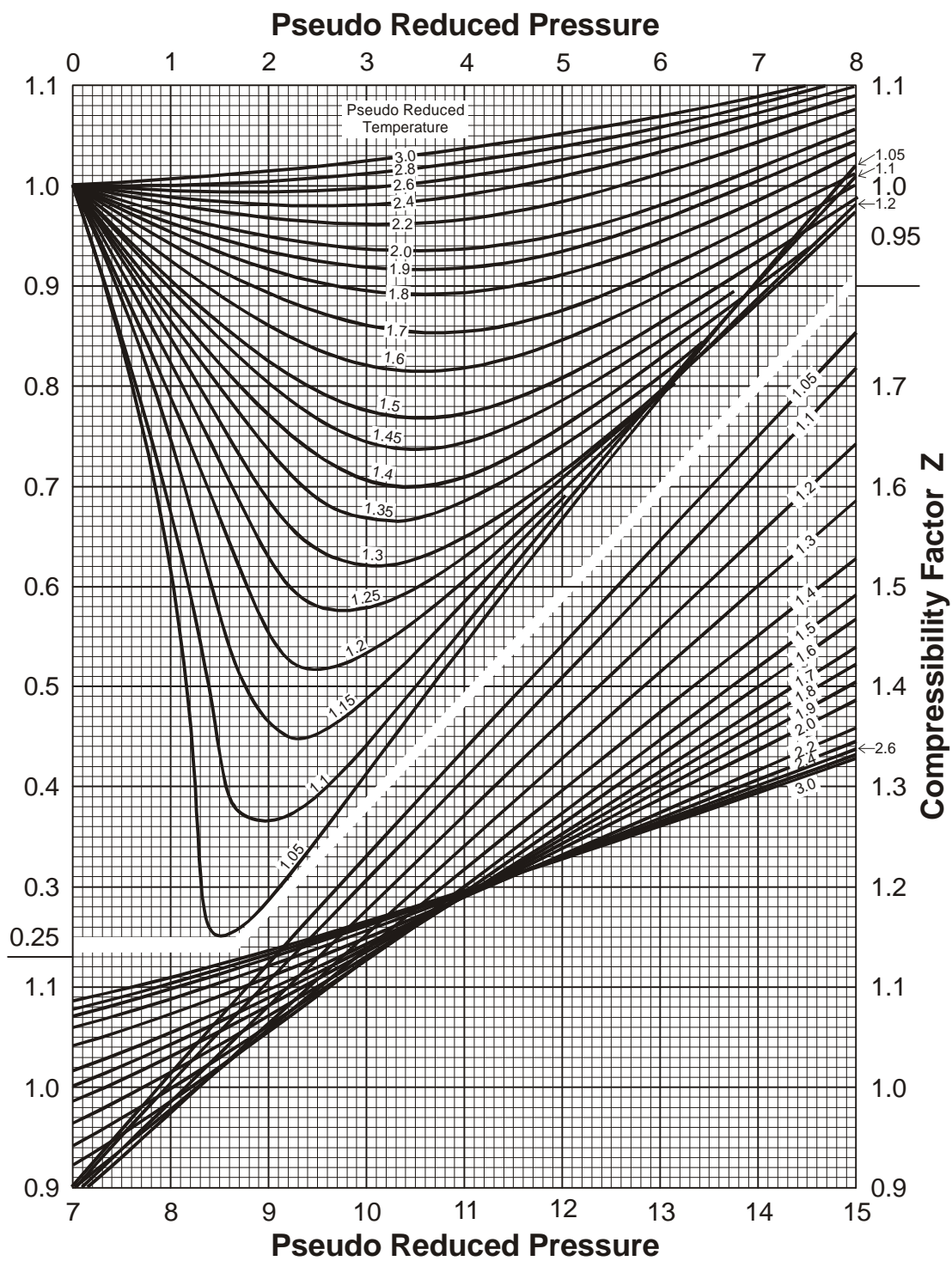


Figure 5.3:  $Z$ -factor for natural gases (from BROWN et al., 1948)

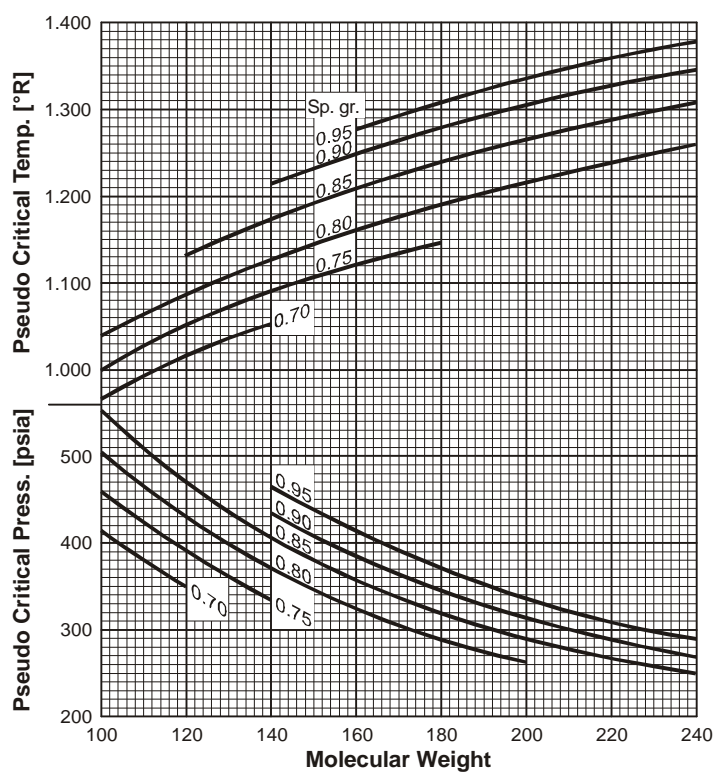


Figure 5.4: Pseudo-critical temperatures and pressures for heptanes and heavier  
(from MATTHEWS et al, 1942)

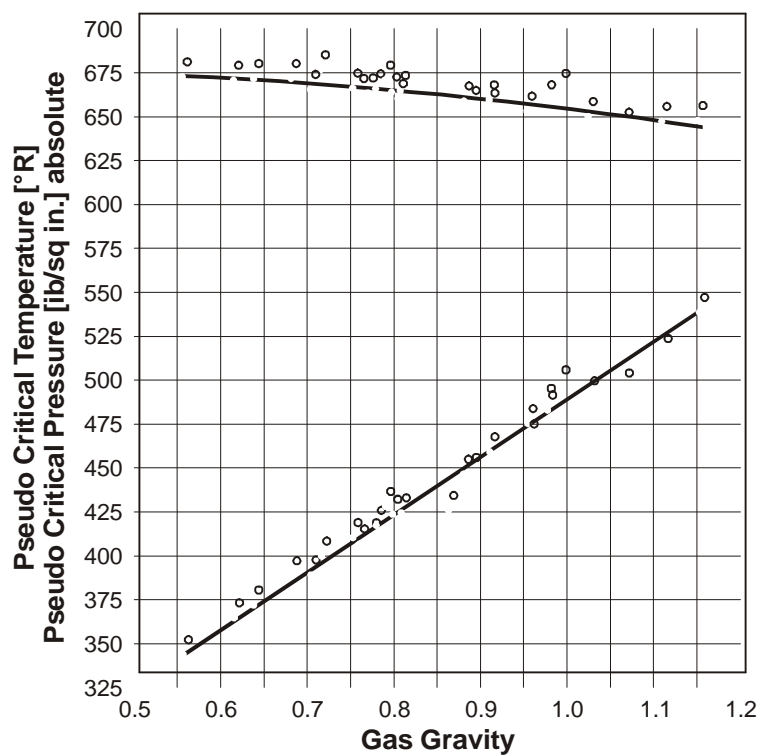


Figure 5.5: Pseudo-critical properties of Oklahoma City Gases  
(from MATTHEWS et al., 1942)

**Example 5.1**

Evaluation of the density of a natural gas at  $T = 105\text{ }^{\circ}\text{C}$  and at  $p = 22.55\text{ MPa}$ . The  $Z$ -factor is determined by using Figure 5.12 The table below summarizes the composition of the gas, the critical data as well as the calculated reduced data of the components.

Assumption:  $C_{7+} \approx C_8$

Component	Mi kg/kmole	y <sub>i</sub>	y <sub>i</sub> Mi kg/kmole	T <sub>c,i</sub> K	y <sub>i</sub> x T <sub>c,i</sub> K	p <sub>ci</sub> MPa	y <sub>i</sub> x p <sub>ci</sub> MPa
C <sub>1</sub>	16.0	0.9443	15.109	190.6	179.98	4.60	4.344
C <sub>2</sub>	30.1	0.0158	0.476	305.4	4.83	4.88	0.077
C <sub>3</sub>	44.1	0.0132	0.582	369.8	4.88	4.25	0.056
iC <sub>4</sub>	58.1	0.0051	0.296	408.1	2.08	3.65	0.019
nC <sub>4</sub>	58.1	0.0053	0.308	425.2	2.25	3.79	0.020
iC <sub>5</sub>	72.2	0.0023	0.166	461.4	1.06	3.38	0.008
nC <sub>5</sub>	72.2	0.0021	0.152	469.7	0.99	3.37	0.007
C <sub>6</sub>	86.2	0.0033	0.284	507.4	1.67	3.01	0.010
c <sub>7+</sub> <sup>*</sup>	114.23	0.0086	0.982	568.8	4.89	2.48	0.021
<b>S</b>		<b>1.000</b>	<b>18.355</b>		<b>202.63</b>		<b>4.562</b>

$$T_{pr} = \frac{T}{T_{pc}} = \frac{105 + 273.15}{202.63} = 1.87$$

$$p_{pr} = \frac{p}{p_{pc}} = \left( \frac{22.5}{4.562} = 4.93 \right)$$

From Figure 5.12

$$Z = 0.925$$

which is introduced in

$$\rho_g = \frac{p \sum_{i=1}^k y_i M_i}{ZRT}$$

where

$$R = 8.31432 \text{ J/ K mole.}$$

$$\rho_g = \frac{22.5 \text{ E} + 5 \times 18.355 \text{ E} - 3}{0.925 \times 8.31432 \times 378.15} = 142.32 \text{ kg/m}^3$$

**Example 5.2**

Evaluation of the density and the formation volume factor of an Oklahoma City Gas of the specific gravity  $\gamma_g = 0.7018$  at  $T = 90.5^\circ\text{C}(655\text{ R})$  and  $p = 12.5\text{ MPa}(1813\text{ psia})$ .

From Figure 5.12:

$$T_{pc} = 390\text{R}$$

and

$$p_{pc} = 670\text{psia}.$$

Calculation of the pseudo-reduced data:

$$T_{pr} = \frac{T}{T_{pc}} = \frac{655}{390} = 1.68$$

and

$$p_{pr} = \frac{p}{p_{pc}} = \frac{1813}{670} = 2.71.$$

From Figure 5.3:

$$Z = 0.86$$

The gas density can be calculated by using Eq. 5.5:

$$\rho_g = \frac{M_a}{R} \gamma_g \frac{p}{ZT},$$

$$M_a = 28.97 \text{ E-3 kg/mole},$$

and

$$R = 8.31432 \text{ J/K mole},$$

$$\rho_g = \frac{0.02897 \times 0.7018 \times 125 \text{ E} + 5}{8.31432 \times 0.86 \times 363.65} = 97.774 \text{ kg/m}^3$$

The formation volume factor can be evaluated through Eq. 5.8

$$B_g(p,T) = \frac{ZT}{p} C$$

where

$$C = \frac{p^o}{Z^o T^o}.$$

Assuming that the gas is a perfect one at European standard conditions ( $p^o = 1$  bar,  $T^o = 273.15$  K), then  $Z^o = 1$  and the gas formation volume factor results in

$$B_g = \frac{0.86 \times (90.5 + 273.15)}{12.5} \frac{0.1}{273.15},$$

$$B_g = 0.00916.$$

### 5.1.5 Water Content

The conventional gas analysis does not indicate any water content. However, the natural gas in a reservoir is in thermodynamic equilibrium with the interstitial water. Therefore, the gas must be assumed to be saturated with water vapor whose mole fraction,  $y_w$ , can be calculated by the DALTON law:

$$y_w = \frac{p_w}{p} \quad (5.14)$$

where

$p_w$ : vapor pressure of water at operating temperature

$p$ : operating pressure of the system.

It could be deduced from numerous measurements that the water vapor content of the natural gas can be well correlated with pressure and temperature while the influence of the gas composition has been found to be insignificant (see Figure 5.6 a Example 5.3).

Natural gas and liquid water will combine to form solids resembling wet snow at temperatures somewhat above the crystallization temperature of pure water. These solids are called “**gas hydrates**”. Because these solids can form at temperatures and pressures normally encountered in natural-gas pipelines, this phenomenon is of particular interest to the petroleum industry since it may cause severe plugging problems. The conditions for the gas hydrate formation will be summarized later on.

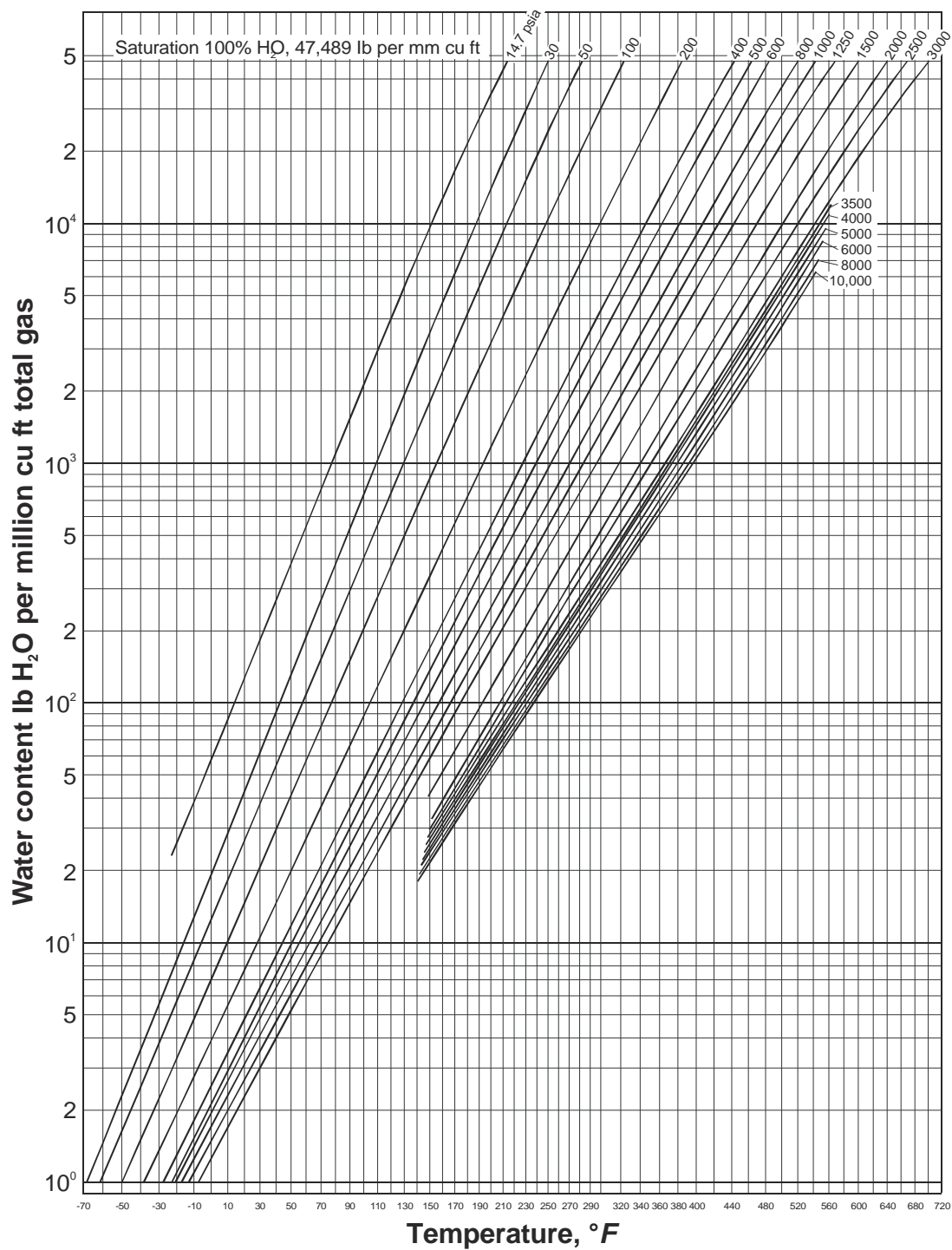


Figure 5.6: Water content of natural gas in equilibrium with liquid water  
(from KATZ et al., 1959)

**Example 5.3**

The evaluation of the water content of a natural gas as a function of operating pressure and temperature. This can be done by correlation through Figure 5.12.

**FIRST STATE:**  $p = 13.8 \text{ MPa (2000 psia)}$

$$T = 93.3 \text{ }^{\circ}\text{C (200 }^{\circ}\text{F)}$$

The water content at this state is evaluated through Figure 5.12 as

$$3.8 \text{ E-4 lb/cu ft} = 6.1 \text{ E-3 kg/m}^3$$

**SECOND STATE:**  $p = 3.45 \text{ MPa (500 psia)}$

$$T = 60 \text{ }^{\circ}\text{C (140 }^{\circ}\text{F)}$$

The water content at this state was evaluated through Figure 5.12 as

$$3.25 \text{ E-4 lb/cu ft} = 5.2 \text{ E-3 kg/m}^3$$

**THIRD STATE:**  $p = 2.8 \text{ MPa (400 psia)}$

$$T = 60 \text{ }^{\circ}\text{C (140 }^{\circ}\text{F)}$$

The water content at this state was evaluated through Figure 5.12 as

$$3.8 \text{ E-4 lb/cu ft} = 6.1 \text{ E-3 kg/m}^3$$

## 5.1.6 Viscosity

Like all intensive physical properties, the viscosity of a natural gas is completely described by

$$\mu = F(p, T, y_1, y_2, y_3, \dots, y_{k-1}) \quad (5.15)$$

In case of an oil phase:

$$\mu = F(p, T, x_1, x_2, x_3, \dots, x_{k-1}) \quad (5.16)$$

Eq. 5.15 and Eq. 5.16 simply state that the viscosity is a function of pressure, temperature and composition. LOHRENZ et.al. (1964) presented respective calculations which are useful for

- determining viscosities of reservoir fluids in compositional material balance computations, and
- predicting the decrease in viscosity which occurs when gases dissolve in reservoir oils.

The correlations presented below may be seen as modifications of Eq. 5.15. The assumptions are practical because the composition is frequently not known. Anyway, the assumptions are sufficiently valid so that these correlations are frequently used for reservoir engineering computations.

The gas viscosity  $\mu_g$  increases with the temperature. Figure 5.7 shows the dependence of the viscosity of pure gases on the temperature at atmospheric pressure ( $0.1 \text{ MPa}$  and  $14.7 \text{ psi}$ , respectively).

Figure 5.8 presents the viscosity of natural gases at atmospheric pressure as a function of the averaged molecular weight. This diagram elucidates that the viscosity decreases along with increasing molecular weight. It also contains correction functions for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{S}$ .

The theorem of corresponding states has been proved to be valid once more again. The viscosity at any state of the gaseous system can be predicted through the reduced viscosity which is defined by

$$\mu_{g,r}(p_{pr}, T_{pr}) = \frac{\mu_g(p, T)}{\mu_{g,1}(p = 1, T)} \quad (5.17)$$

The procedure to evaluate  $m$  at a certain pressure and temperature is the following (see Example 5.4):

- From Figure 5.8, the atmospheric viscosity  $m_{g,1}$  has to be evaluated for the given gravity (or averaged molecular weight) of the gas and the operating temperature.
- According to Figure 5.4 or Figure 5.5, the pseudo-critical pressure,  $p_{pc}$ , and the pseudo-critical temperature,  $T_{pc}$ , are determined.
- After the calculation of the pseudo-reduced state quantities  $p_{pr}$  and  $T_{pr}$ , the reduced viscosity  $m_{g,r}$  which is given by the ratio between the actual viscosity and the one at atmospheric pressure, is evaluated by using Figure 5.9.
- The actual gas viscosity can be calculated through Eq. 5.17 where

$$\mu_g = \mu_{g,r} \mu_{g,1}$$

The gas viscosity determined through this method deviates from laboratory measurements by 3% at the maximum. This is a satisfactory solution for practical purposes.

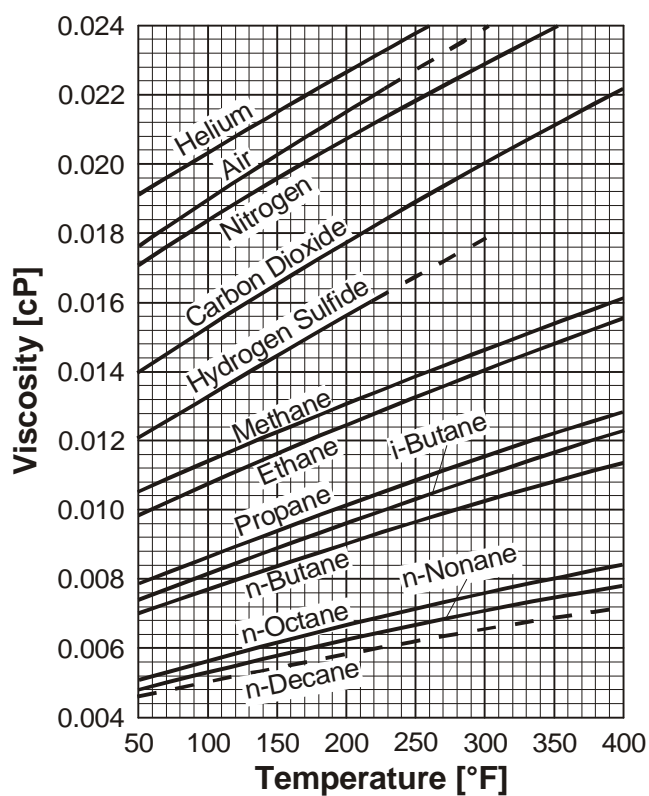


Figure 5.7: Viscosity of paraffin hydrocarbon gases natural gases at atmospheric pressure (from CARR et al., 1954)

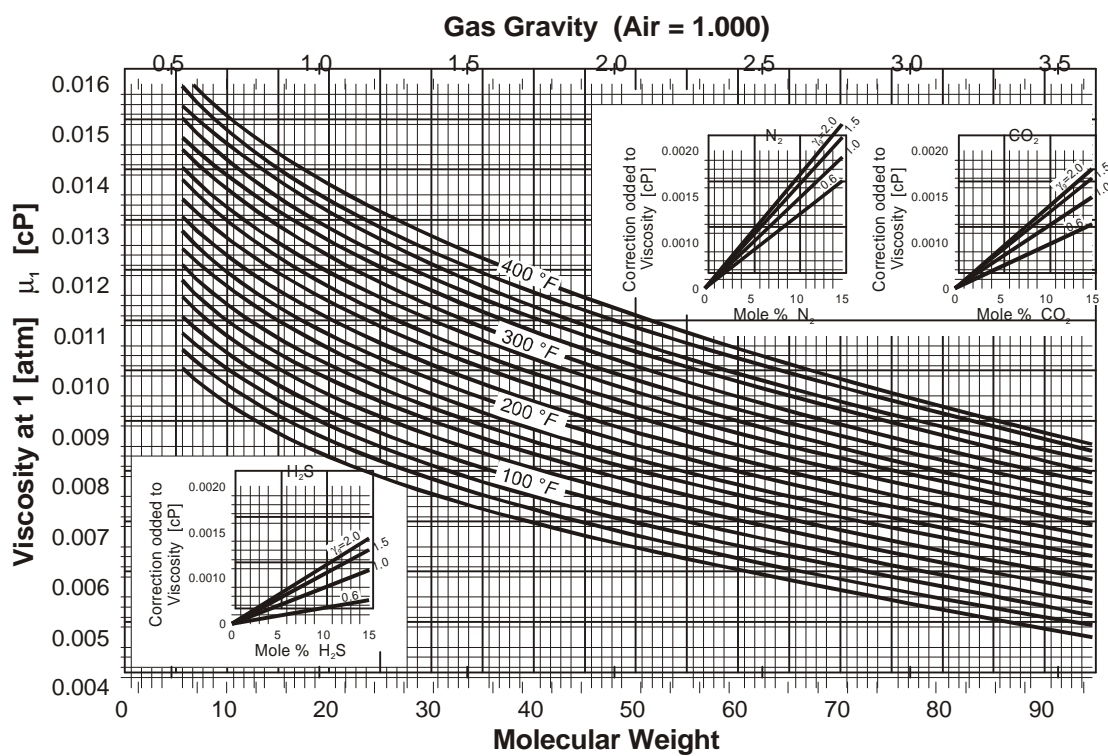


Figure 5.8: Viscosity of natural gases at atmospheric pressure (from CARR et al, 1954)

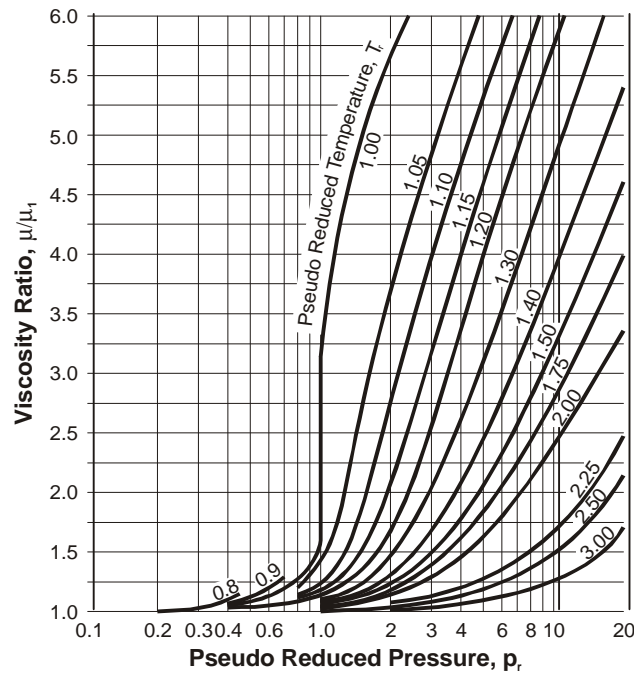


Figure 5.9: Correlation of viscosity ratio with pseudo-reduced pressure and temperature (from CARR et al., 1954)

#### Example 5.4

Determination of the viscosity of an Oklahoma City gas of  $\gamma_g = 0.7018$  at  $T = 90.5^\circ\text{C}$  ( $194.9^\circ\text{F}$ ,  $654.7\text{ R}$ ) and  $p = 12.5\text{ MPa}$  ( $1800\text{ psia}$ ).

From Figure 5.12, the viscosity at atmospheric pressure and operating temperature can be read off as

$$\mu_{g,1} = 0.0122\text{cP}.$$

Then the pseudo-critical data of the system are evaluated from Figure 5.12 where

$$p_{pc} = 670\text{ psia}$$

and

$$T_{pc} = 385^\circ\text{R}.$$

The calculation of the pseudo-reduced data of the system result in

$$p_{pr} = \frac{p}{p_{pc}} = \frac{1800}{670} = 2.69$$

and

$$\frac{T}{T_{pc}} = \frac{654.6}{385} = 1.70.$$

The ratio between the actual gas viscosity,  $\mu_g$ , and its viscosity at atmospheric pressure,  $\mu_{g,1}$ , can now be read off from Figure 5.9:

$$\mu_{g,r} = 1.35$$

so that

$$\mu_g = \mu_{g,r} \times \mu_{g,1} = 1.35 \times 0.0122 = 0.0165 \text{ cP}$$

and

$$\mu_g = 0.0165 \text{ mPa s},$$

respectively.

## 5.2 Hydrocarbon Liquids

### 5.2.1 Volume

For practical purposes, it is sufficient to consider hydrocarbon liquids as ideal mixtures whose volumes can be calculated by adding up the volumes of the components.

The interesting properties (density, viscosity, etc.), which depend on the oil composition, can easily be determined at the standard conditions (atmospheric pressure and  $T = 60^\circ F$  ( $15^\circ C$ )).

However, a crude oil does not remain in the single-phase state at standard conditions since light components are liberated at atmospheric pressure and surface temperature. This inconvenience can be handled by attributing “apparent liquid densities” or “apparent specific liquid volumes” at standard conditions to the dissolved and easily volatilized components. Then the respective “pseudo-liquid” data of any hydrocarbon liquid at standard conditions may be evaluated from the real one at standard conditions and from the apparent data of the liberated light components.

STANDING and KATZ (1942) examined the properties of many crude oils. They established that the apparent densities of the two light components methane and ethane depend on the density of the system (see Figure 5.10). Based on these data and assuming that propane and heavier components follow the rule of additive volumes, they developed a method for computing the apparent liquid density of hydrocarbon mixtures. This calculation procedure is presented through Example 5.5. It is based on Figure 5.11 which presents the correlation of the density of a system containing methane and ethane with the density of

the propanes-plus fraction, the weight -% ethane in the ethanes-plus material and the weight-% methane in the entire system. Finally, the evaluated pseudo-liquid density of the system containing methane and ethane has to be corrected with regard to the operating temperature and pressure. Figure 5.12 and Figure 5.13 serve this purpose.

The correlation method after STANDING and KATZ is satisfactory for stock-tank liquids which have low concentrations of methane and ethane.

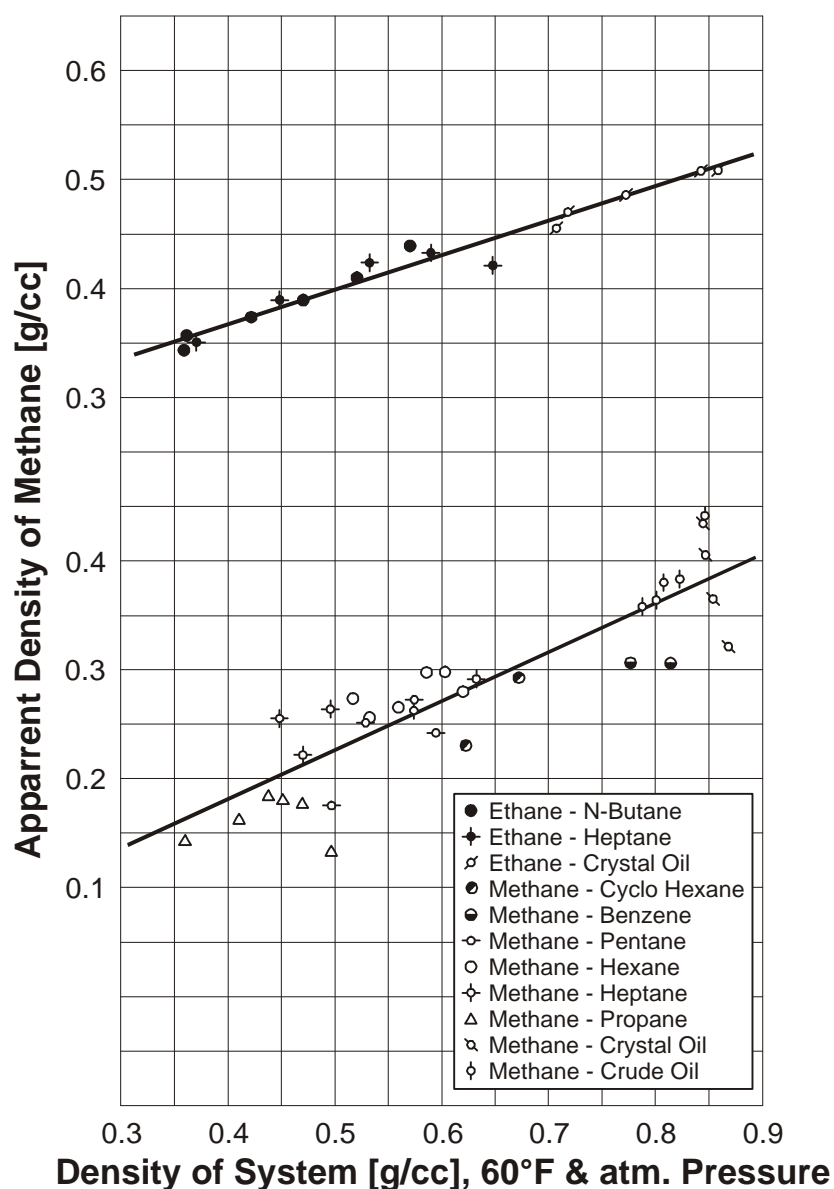


Figure 5.10: Variation of apparent density of methane and ethane with density of the system (from STANDING and KATZ, 1942)

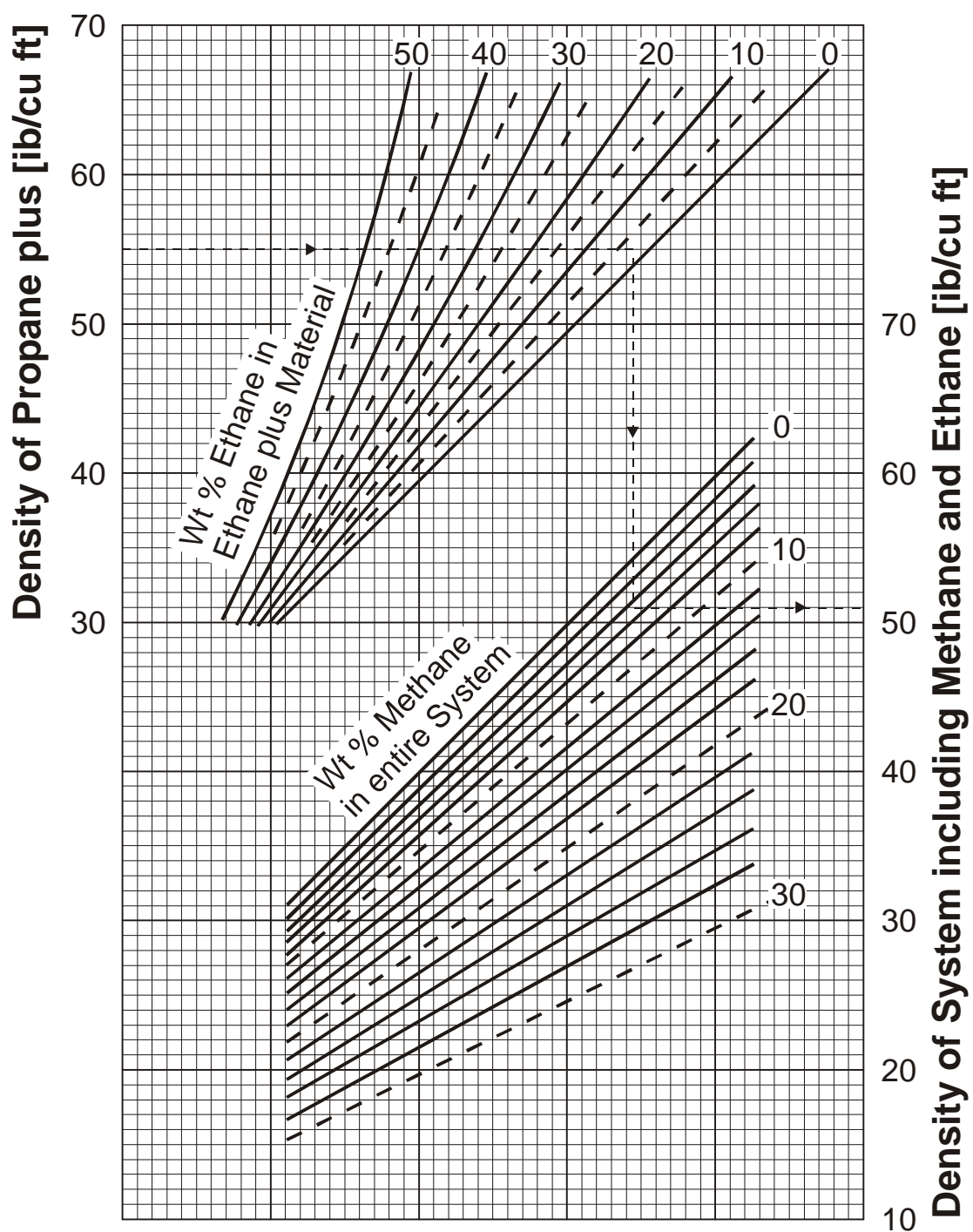


Figure 5.11: Pseudo-liquid density of systems containing methane and ethane (from STANDING, 1952)

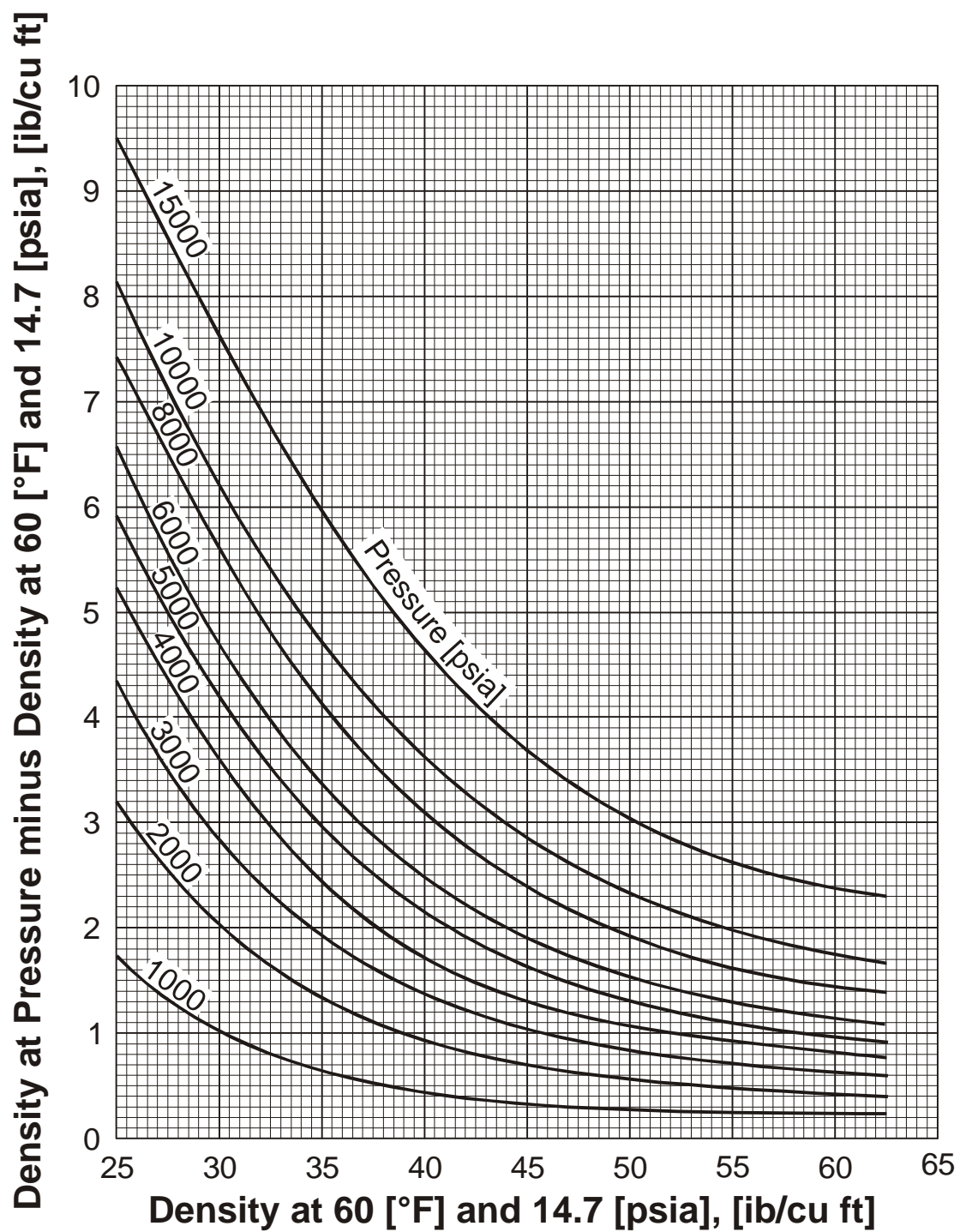


Figure 5.12: Density correction for compressibility of liquids (from STANDING, 1952)

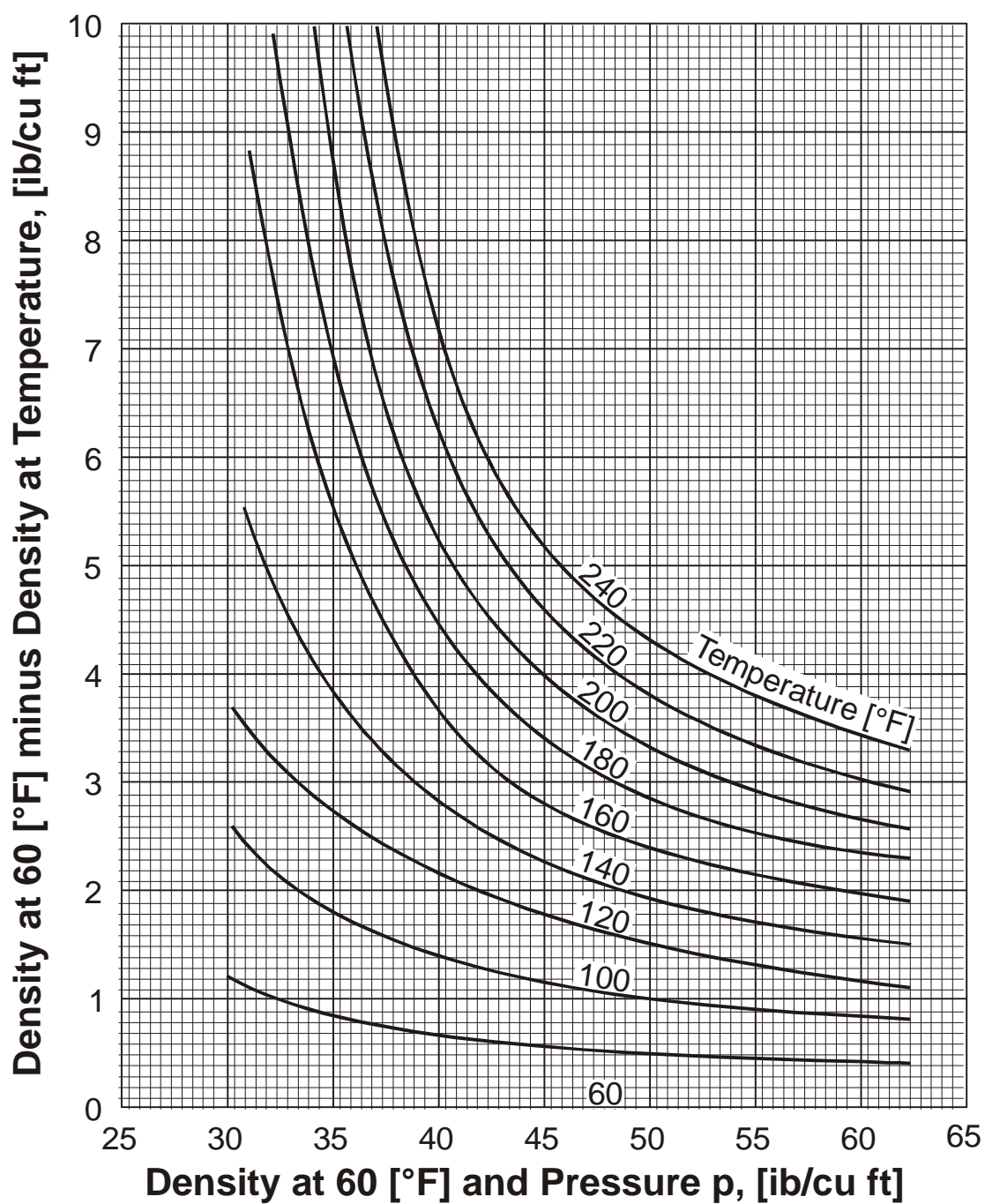


Figure 5.13: Density correction for thermal expansion of liquids  
(from STANDING, 1952)

**Example 5.5**

Determination of the density of an oil at bubble point conditions by using the STANDING-KATZ correlations. The bubble point is defined by

$$p_{o,b} = 3300 \text{ psia} (22.55 \text{ MPa})$$

and

$$T_{o,b} = 220^\circ \text{F} (105^\circ \text{C}).$$

The composition of the entire system is tabled below.

Composition	Mole Fraction $z_i = x_i$	Mole Weight $M_i$ kg/kmole	$z_i M_i$	Density $\rho_i$ kg/m <sup>3</sup>	Volume $V_i^*$ m <sup>3</sup>
C <sub>1</sub>	0.4404	16.0	7.046		
C <sub>2</sub>	0.0432	30.1	1.300		
C <sub>3</sub>	0.0405	44.1	1.786	507.5	0.0035
C <sub>4</sub>	0.0284	58.1	1.650	575.0	0.0029
C <sub>5</sub>	0.0174	72.2	1.256	626.0	0.0020
C <sub>6</sub>	0.0290	86.2	2.500	662.5	0.0038
C <sub>7+</sub>	0.4001	287.0	114.829	907.0	0.1271
<b>S</b>	<b>1.0000</b>		<b>130.367</b>		<b>0.1393</b>

\*) at standard conditions: 0.1 MPa, 15°C

Calculation of the density of the propane-plus fraction:

$$\frac{\sum_{i=3}^k z_i M_i}{\sum_{i=3}^k V_i} = \frac{122.021}{0.1393} = 876 \text{ kg/m}^3 = 54.69 \text{ lb/cuft.}$$

Calculation of the weight-% ethane in the ethane-plus material:

$$\frac{z_2 M_2}{\sum_{i=2}^k z_i M_i} \times 100 = \frac{1.300}{123.321} \times 100 = 1.05 \text{ \%}.$$

Calculation of the weight-% methane in the entire system:

$$\frac{z_1 M_1}{\sum_{i=1}^k z_i M_i} \times 100 = \frac{7.046}{130.367} \times 100 = 5.4 \text{ \%}.$$

From Figure 5.11, the **pseudo-liquid density** of the hydrocarbon mixture at standard conditions is read off as **51.5 lb/cu ft.**

From Figure 5.12, the **pressure correction** for  $p_{ob}$  (3300 psia) is read off as **0.9 lb/cu ft.**

Consequently, the **liquid density at 3300 psia and 60°F** is found to be **51.5 + 0.9 = 52.4 lb/cu ft.**

Then the **temperature correction** for 220° F is read off from Figure 6.13 as **3.7 lb/cu ft.** Consequently, the **oil density at 3300 psia and 220 °F** (bubble point conditions) is found to be

$$\rho_{o,b} = 52.4 - 3.7 = 48.7 \text{ lb/cu ft}$$

and

$$\rho_{o,b} = 780.1 \text{ kg/m}^3,$$

respectively.

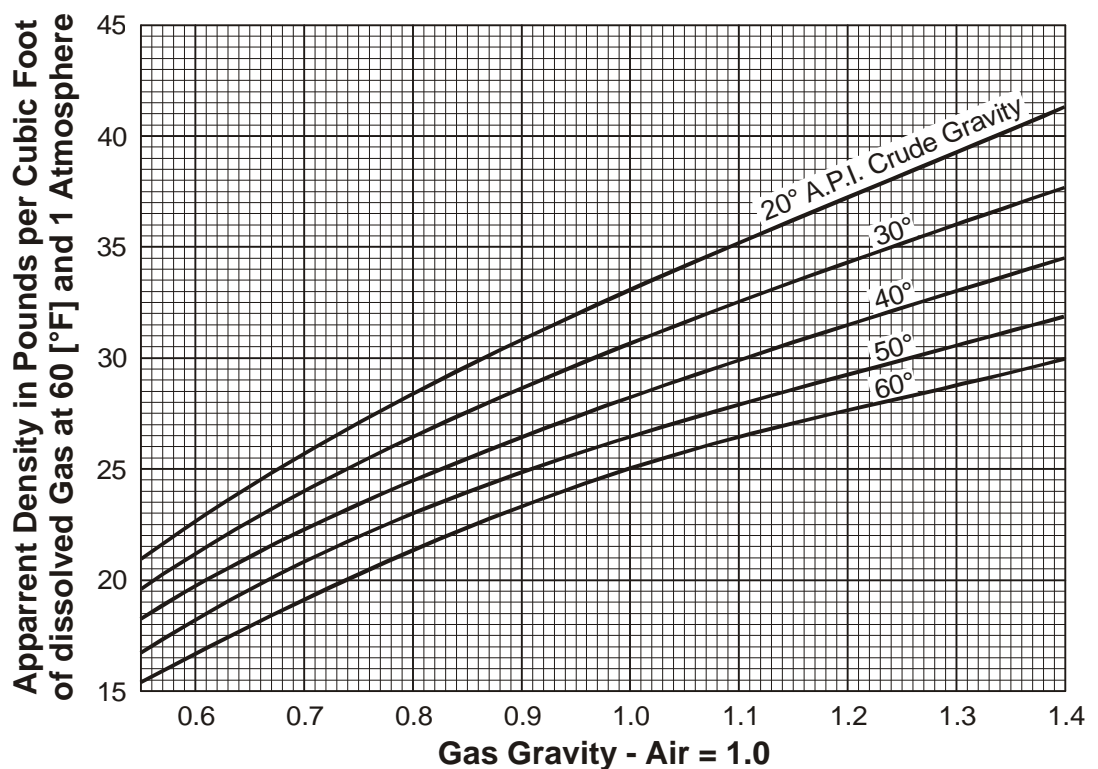


Figure 5.14: Apparent liquid density of natural gases in various API gravity oils (from KATZ, 1952)

Natural gases (dissolved gas) predominantly consist of methane. Therefore, KATZ (1942) has applied the method of the apparent liquid volume also to crude oil - natural gas systems. The easily volatilized component is marked by its gravity,  $\gamma_g$ , and the scarcely volatilized fraction is the tank oil with the density  $\rho_o$  and its gravity  $\gamma_o$  (in °API) at standard conditions. The apparent liquid density of the respective natural gas can be determined according to Figure 5.14.

The amount of the dissolved gas is always indicated as the volume of gas at standard conditions which has been liberated from one unit of volume tank oil, either as *normal*  $m^3/m^3$  or *scu ft/STB* (*stock tank barrel*). This ratio of volumes is designated as  $R_s$  (solution ratio). In terms of the production, the ratio is also often designated as **GOR** (producing gas - oil ratio).

In other words:  $R_s$  expresses how much gas (*cubic meter or cubic feet*) will be dissolved in one cubic meter or barrel oil (volume at standard conditions) at the operating conditions. Therefore,  $R_s$  depends on pressure and temperature, but also on the oil quality.

## 5.2.2 Formation Volume Factor

The oil volume inside the tank (surface conditions) differs from the volume of the oil leaving the reservoir. This change in volume has three main sources:

- The most important factor is the gas liberation below bubble point pressure  $p_{ob}$ .
- The difference between the reservoir pressure and atmospheric pressure causes slight expansion of the remaining oil phase.
- The increase in volume because of expansion is more or less compensated by the shrinkage of the oil resulting from the transfer from reservoir to surface temperature.

The formation volume factor of the oil phase, which must be taken into account, is defined as

$$B_o = \frac{\text{oil volume and volume of dissolved gas at reservoir conditions}}{\text{oil volume at standard conditions}}$$

Consequently,  $B_o$  can be defined as the volume of one cubic meter tank oil (oil at standard conditions) at any operating pressure and temperature.

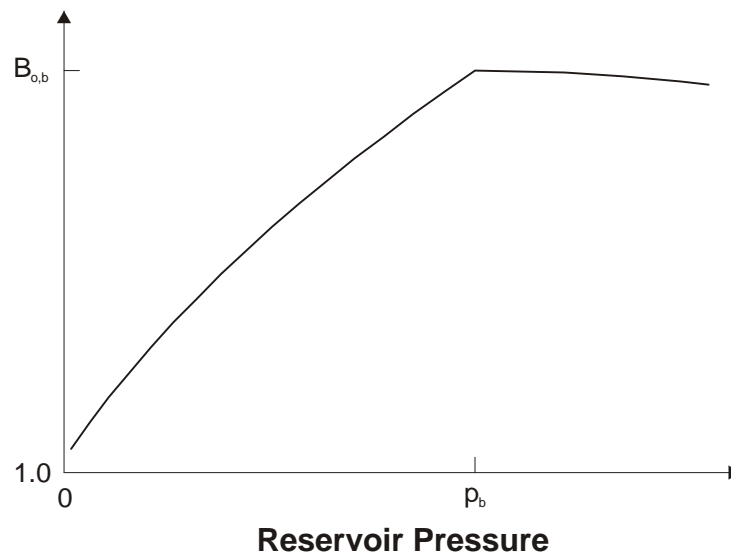


Figure 5.15: Typical graph of formation-volume factor of oil against pressure

Figure 5.15 illustrates typical characteristics the relationship between  $B_o$  and  $p$ . As long as the pressure does not fall below the bubble point pressure  $p_{ob}$  during a pressure decrease from initial reservoir conditions, the change in  $B_o$  will be ruled by the expansion of the oil. As soon as the reservoir pressure falls below  $p_{ob}$ , gas will be liberated. This gas liberation results in a shrinkage of the oil volume. Thus,  $B_o$  decreases at decreasing pressure as soon as  $p_{ob}$  has been crossed.

The reciprocal value of  $B_o$  is called “*shrinkage factor*”. By multiplying the tank oil volume with the actual  $B_o$ , the volume of the oil inside the reservoir is obtained. On the other side, the multiplication of the shrinkage factor with the volume inside the reservoir will result in the stock oil volume.

On the basis of many investigations, STANDING (1947) amplified the correlation to permit the calculation of bubble point pressure and formation volume factors at bubble point conditions. The respective STANDING charts are appended at the end of this textbook:

- Working with Chart 1, it is possible to take the solution ratio in total, gas gravity, tank oil gravity and reservoir temperature to determine the pressure at which the given amount of gas would be in solution. This pressure is the bubble point pressure of the respective hydrocarbon system,  $p_{ob}$ .
- Charts 2 permits the evaluation of  $B_o$  at bubble point conditions if  $GOR$  represents the solution ratio in total.
- The total formation volume factor,  $B_t$ , can be estimated by use of Chart 3.  $B_t$  is defined by

$$B_t = B_o + (R_{si} - R_s)B_g \quad (5.18)$$

where

$B_o$ : volume factor of the actual oil phase

$B_g$ : volume factor of the actual gas phase

$R_{s,i}$ : solution ratio at initial conditions (solution ratio in total)

$R_s$ : solution ratio at operating conditions.

$B_o$  can be evaluated

- by use of the KATZ correlation (see Figure 5.14) and the STANDING diagrams (see Figure 5.12 and Figure 5.13)
- or by use of the Charts from STANDING (see appendix).

In most cases, these empirical correlations (see Example 5.6) yield values which are comparable within 3 or 4 % to measured laboratory data.

#### Example 5.6

Evaluation of  $B_o$  at bubble point conditions. The operating data are tabled below in SI-units and Field-units. The calculation is based on one cubic meter tank oil.

$$p_{o,b} = 3300 \text{ psia} (22.55 \text{ MPa})$$

$$T_{o,b} = 220^\circ \text{F} (105^\circ \text{C})$$

	GOR $nm^3/m^3]$	GOR $cu \text{ ft}/bbl$	$\gamma_g$	$\rho_o$ $kg/m^3$	$\gamma_o$ $^\circ \text{API}$
Separator 1	74	415.5	0.640		
Separator 2	16	89.8	0.897		
Tank	4	22.5	1.540	876.2	30
<b>S</b>	<b>94</b>	<b>527.8</b>			

In summing up the producing gas/oil ratios GOR, the initial solution ratio  $R_{si}$  results in

$$R_{s,i} = 94 \text{ nm}^3/\text{m}^3$$

and

$$R_{s,i} = 527.8 \text{ cuft/bbl}$$

respectively.

The computation of the average specific gas gravity results in

$$\gamma_g = \frac{(74 \times 0.64) + (16 \times 0.897) + (4 \times 1.54)}{74 + 16 + 4} = \frac{67.9}{94} = 0.722.$$

Now the amount of gas can be calculated through

$$m_g = R_{si} \rho_a \gamma_g$$

where  $\rho_a$  is the air density.

$$m_g = 94 \times 1.225 \times 0.722 = 83.1 \text{ kg}$$

Because the specific gravities are given as

$$\gamma_g = 0.722$$

and

$$\gamma_o = 30^\circ \text{ API},$$

the apparent liquid density of the gas can be evaluated through Figure 5.14 as

$$\rho_{g,a} = 24.3 \text{ lb/cu ft}$$

and

$$\rho_{g,a} = 389.2 \text{ kg/m}^3,$$

respectively.

Now the apparent liquid volume of the liberated gas at standard conditions ( $T = 15^\circ \text{C}$  and atmospheric pressure) can be calculated through

$$V_{g,app} = \frac{m_g}{\rho_{g,a}}$$

and so

$$V_{g, app} = \frac{83.1}{389.2} = 0.214 \text{ m}^3 .$$

In summarizing 1 m<sup>3</sup> tank oil and 0.214 m<sup>3</sup> apparent liquid volume of the liberated gas, as well as 876.2 kg tank oil and 83.1kg liberated gas, the pseudo-liquid density of the given hydrocarbon system at standard conditions results in

$$\rho_{o, app} = \frac{876.2 + 83.1}{1000 + 0.214} = 790.2 \text{ kg/m}^3$$

and so

$$\rho_{o, app} = 49.3 \text{ lb/cu ft} .$$

From Figure 5.12, the pressure correction of this density for  $p = 3300$  psia results in

$$\rho_o = 49.3 + 0.9 = 50.2 \text{ lb/cu ft} .$$

From Figure 5.13, the final temperature correction for  $T = 220$  °F results in

$$\rho_o = 50.2 - 3.8 = 46.4 \text{ lb/cu ft}$$

or, in SI-units, respectively, in

$$\rho_o = 743.7 \text{ kg/m}^3 .$$

On the basis of the calculated oil density under the conditions of the reservoir, the volume of one cubic meter oil under reservoir conditions results in

$$V_{ob} = \frac{959.3}{743.7} = 1.29 \text{ m}^3$$

and so

$$B_{ob} = 1.29 .$$

In other words: 1.29 m<sup>3</sup> saturated reservoir liquid under reservoir conditions shrinks to 1 m<sup>3</sup> tank oil. The shrinkage results in

$$\frac{1.29 - 1.000}{1.29} \times 100 = 22.48 \%$$

### 5.2.3 Compressibility of Undersaturated Liquids

An undersaturated oil is a compressed liquid in the pressure range above the bubble point pressure  $p_b$ . Its isothermal compressibility is to be calculated in the same way as for the gases (see Eq. 5.9) so that

$$c_o = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{1}{B_o} \left( \frac{\partial B_o}{\partial p} \right)_T \quad (5.19)$$

and after integration

$$B_o = B_{ob} e^{-c_o(p-p_b)} \quad (5.20)$$

Because

$$\rho_o = \frac{C}{B_o}$$

where  $C$  is a constant, the density of an undersaturated oil phase can be calculated through

$$\rho_o = \rho_{ob} e^{c_o(p-p_b)} \quad (5.21)$$

In general, the bubble point pressure,  $p_b$ , is chosen as reference. Eq. 5.20 and Eq. 5.21 will develop in a Taylor series. Because  $c_o$  is very small, the terms of higher order can be disregarded so that

$$B_o \sim B_{ob} [1 - c_o(p - p_b)] \quad (5.22)$$

and

$$\rho_o = \rho_{o,b} [1 + c_o(p - p_b)] \quad (5.23)$$

Similar formulae are also valid for water.

The compressibility of undersaturated liquids is constant within wide pressure intervals. Therefore, it can be calculated between any two states of the system,  $(V_1, p_1)$  and  $(V_2, p_2)$  by

$$c_o = -\frac{V_1 - V_2}{\bar{V}(p_1 - p_2)} \quad (5.24)$$

where  $\bar{V}$  is averaged volume between  $p_1$  and  $p_2$ .

TRUBE (1957) has reported a method of calculating the compressibility of undersaturated liquids. This method is based on the determination of the pseudo-critical data of the system and on the evaluation of the pseudo-reduced compressibility of the undersaturated liquid,  $c_r$  as a function the pseudo-reduced pressure,  $p_{pr}$ , and pseudo-reduced temperature,  $T_{pr}$  (see Figure 5.16). Then the oil compressibility can be calculated through

$$c_o = c_r / p_{pc} \quad (5.25)$$

If the composition of the undersaturated system is not known, the pseudo-reduced pressure and temperature can be approximately evaluated through Figure 5.17 on the basis of

- the calculation of the pseudo-liquid density of the hydrocarbon mixture at standard conditions (see procedure of Example 5.6),
- the pressure correction of this pseudo-liquid density from Figure 5.12,
- relation of the evaluated oil density to the density of water at standard temperature,  $\rho_w = 1000 \text{ kg/m}^3$ .

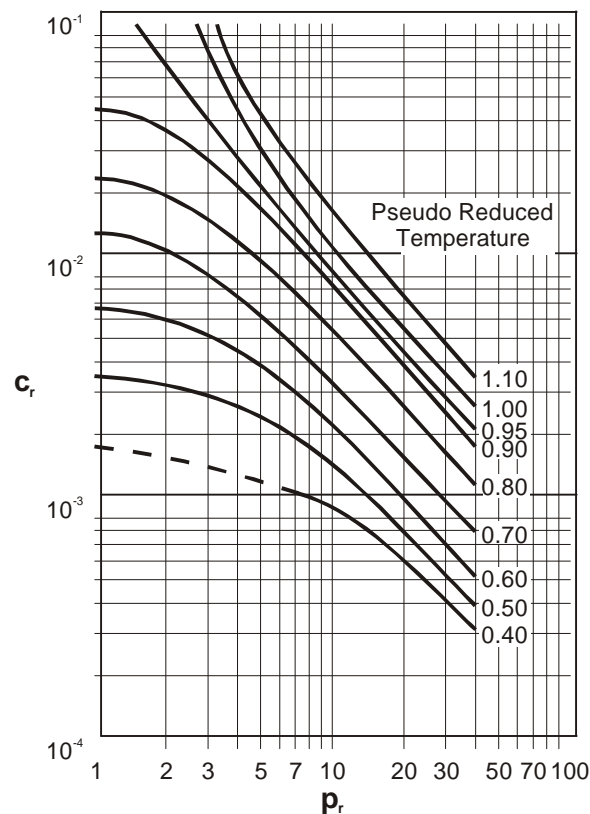


Figure 5.16: Pseudo-reduced compressibility for undersaturated reservoir fluids (from TRUBE, 1957)

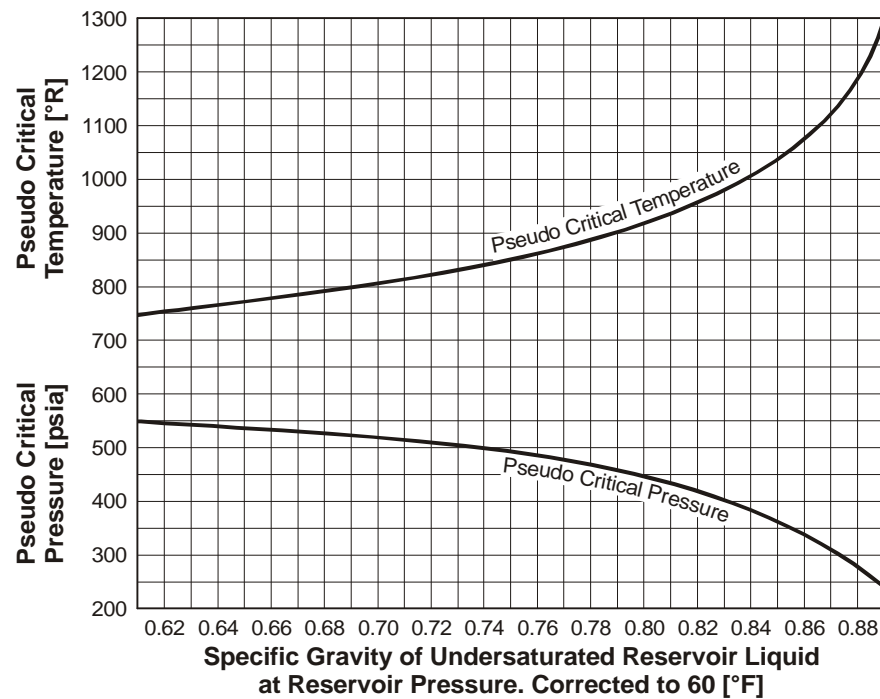


Figure 5.17: Pseudo-critical conditions of undersaturated reservoir liquids  
(from TRUBE, 1957)

#### Example 5.7

Evaluation of  $B_{oi}$  for an undersaturated oil at reservoir temperature  $T = 105^\circ\text{C}$  and under the initial pressure  $p_i = 25\text{ MPa}$  through the reduced compressibility from TRUBE. The composition of the system, the pseudo-critical data and  $p_b$  are given in Example 5.5.  $B_{ob}$  has been calculated through Example 5.6.

- Evaluation of the specific gravity of the undersaturated oil at  $60^\circ\text{F}$ :
  - From Example 5.6:  $\rho_{o, app} = 49.3\text{ lb/cu ft}$
  - pressure correction of  $\rho_{o, app}$  for  $p = 25\text{ MPa}$  (3626 psia) by using Fig.5.12:

$$\rho_o = 49.3 + 0.98 = 50.28\text{ lb/cu ft } (805.41\text{ kg/m}^3).$$

- Specific gravity of the undersaturated oil:

$$\gamma_o = \frac{\rho_o}{\rho_{water}} = \frac{805.41}{1000} = 0.805$$

- Evaluation of the pseudo-critical data on the basis of Fig. 5.17 and  $\gamma_o = 0.805$  and the pseudo-reduced data ( $T = 105^\circ\text{C}$  ( $680.7^\circ\text{R}$ );  $p = 25\text{ MPa}$  (3626 psia)).

$$T_{pr} = \frac{680.7}{925} = 0.74$$

$$p_{pr} = \frac{3626}{440} = 8.24$$

From Fig. 5.16, the reduced compressibility can be read off as  $c_r = 0.004$

$$c_o = \frac{c_r}{p_{pc}} = \frac{0.004}{3.0337} = 0.00132 \text{ MPa}^{-1}$$

- Considering  $B_{o,b} = 1.29$  (see Example 5.6) and Eq. 5.23:

$$B_{oi} = 1.29[1 + 0.00132(25 - 22.5)] = 1.286$$

## 5.2.4 Viscosity

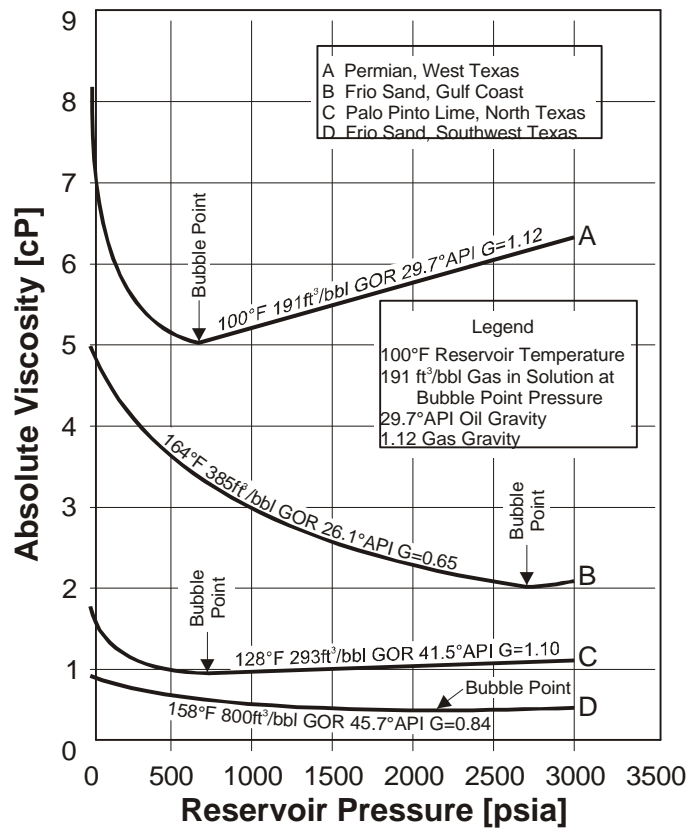


Figure 5.18: Viscosity of subsurface samples of crude oil (from HOCOTT and BUCKLEY, 1941, after BEAL, 1946)

In general, the viscosity of liquids decreases with increasing temperature and increases with increasing pressure. HOCOTT and BUCKLEY (1941) presented measurements of the viscosity of crude oils containing dissolved gases. Figure 5.18 demonstrates that the viscosity decreases with increasing pressure up to the bubble point because of the increasing fraction of light components. The dependence on pressure is more significant

for high viscous oils than for low viscous ones. Anyway, above the bubble point pressure, the viscosity increases with increasing pressure.

The viscosity of the crude oil can be determined with sufficient accuracy. The data basis has to include the viscosity of the tank oil  $\mu_1$ , the reservoir temperature, the initial solution ratio  $R_{si}$  and the undersaturated pressure in the reservoir,  $\Delta p = p_i - p_b$ . Example 5.8 elucidates the respective correlation procedure.

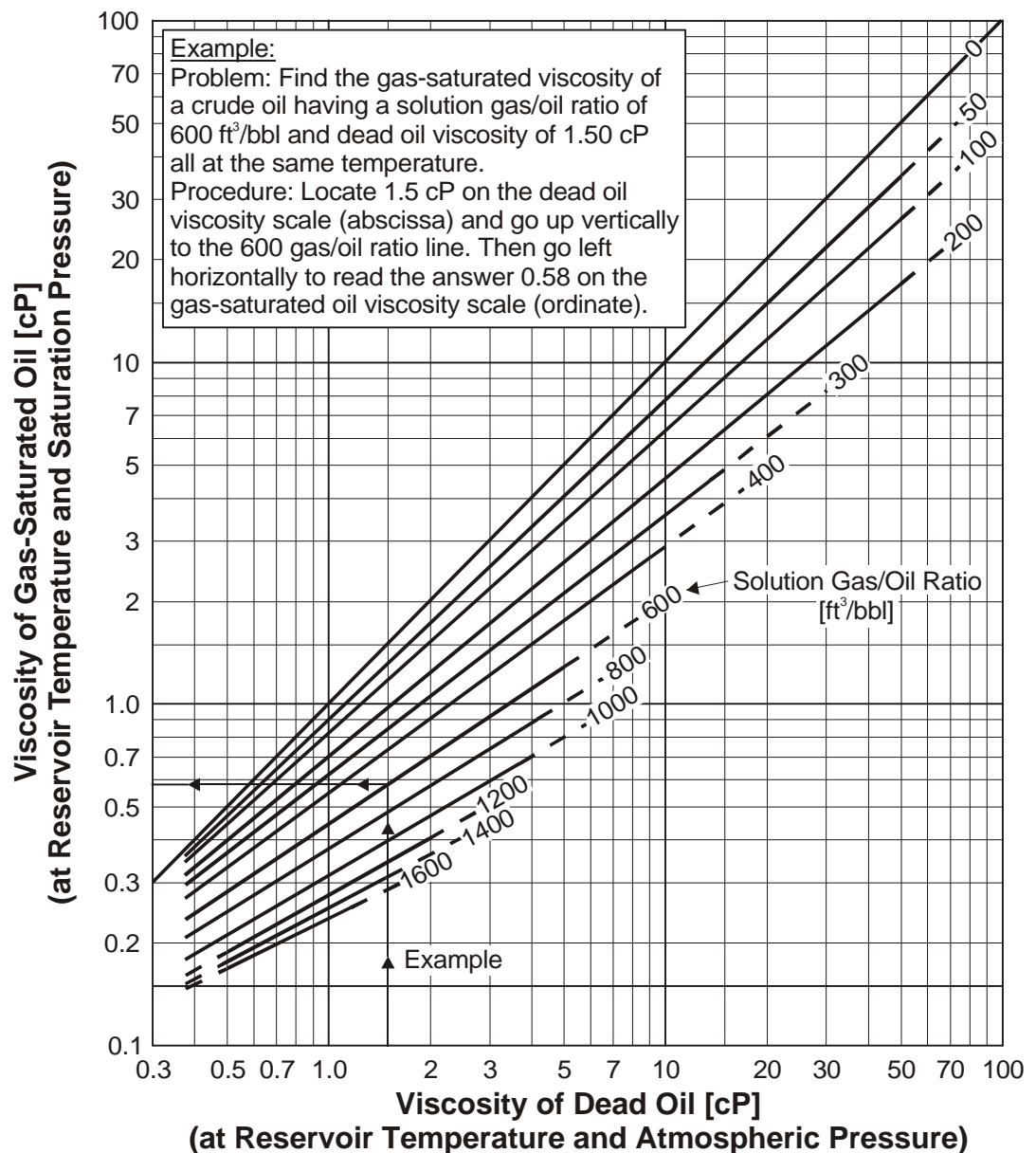


Figure 5.19: Viscosity of gas-saturated reservoir crude oils at reservoir conditions (from CHEW and CONNALLY, 1959)

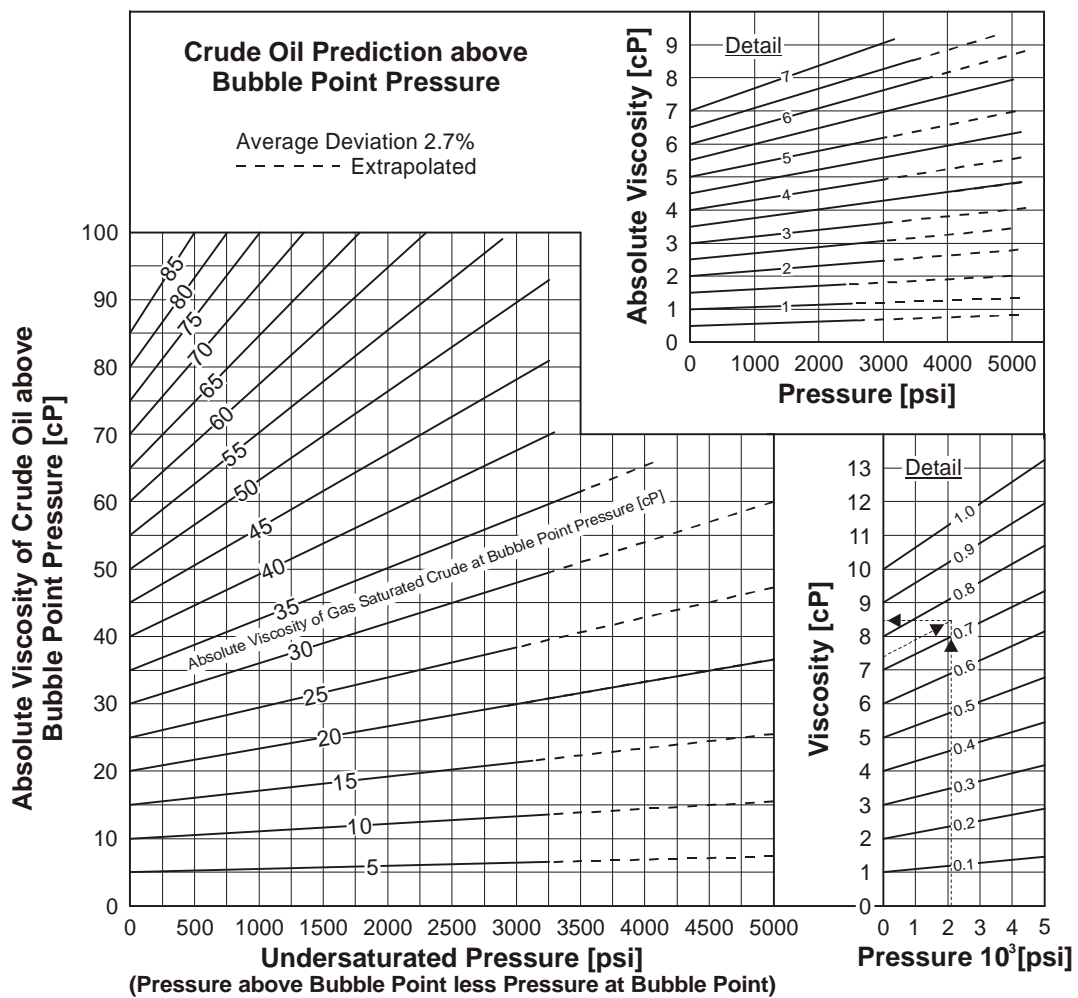


Figure 5.20: Prediction of crude oil viscosity above bubble point pressure (from BEAL, 1946)

### Example 5.8

Evaluation of the oil viscosity at reservoir conditions. The following production data are known:

		SI-Units	Field Units
Reservoir Temperature	T	105 °C	220 °F
Bubble Point Pressure	pb	22.55 MPa	3300 psia
Reservoir Pressure	p	25.00 MPa	3600 psia
Initial Solution Ratio	Rsi	94 nm <sup>3</sup> /m <sup>3</sup>	527.8 cu ft/bbl
Standard Oil Viscosity	$\mu_1$	0.9 mPas	0.9 cP

From Figure 5.19, the oil viscosity at bubble point conditions can

be read off as

$$\mu_{ob} = 0.45 \text{ cP}$$

From Figure 5.20, the viscosity of the undersaturated crude oil at  $p = 3300 \text{ psia}$  can be evaluated:

at bubble point conditions can

$$\mu_{oi} = 0.48 \text{ mPas}$$

or

$$\mu_{oi} = 0.48 \text{ cP}$$

## 5.3 Brines

It has been recognized relatively late that water is - without any exception - one of the reservoir fluids. GARRISON (1935) and SCHILTHUIS (1938) have been the first who presented detailed information on the distribution of oil and water in porous rock and on the origin and occurrence of “*connate water*” (formation water, capillary water, interstitial water). Furthermore, they established a relationship between the water saturation and the rock permeability.

Nowadays, knowledge of the chemical and physiochemical data of the respective reservoir water is of great importance for the petroleum engineer. Water analyses

- give valuable information about the area of prospecting,
- help to answer questions about the origin of the produced water,
- make sure that injected water is chemically compatible with the reservoir water or with added water (plugging by precipitations must be avoided),
- are indispensable for feasibility studies in case of chemical EOR processes.

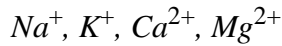
Last but not least, data such as density, compressibility, formation volume factor and viscosity are required for calculating the displacement process and for establishing a material balance.

Additionally, this section presents an unusual phenomenon, the so-called “*gas hydrate formation*”, by which water and natural gas form a solid phase at temperatures above the freezing point of water.

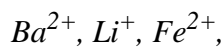
### 5.3.1 Composition of Brines

Reservoir water always contains dissolved inorganic salts, above all sodium chloride, *NaCl*. Therefore, these waters are sometimes called “brines” although they are not comparable with sea water because of differences in both the total salt concentration and the content of distinct ions.

A reservoir brine usually contain the cations

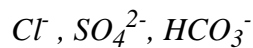


and, in certain cases,

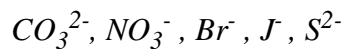


and sometimes  $Sn^{2+}$ .

The anions, which generally are present in reservoir brines, are



and, in some cases, also



The elements are present in reservoir water within the following concentration ranges:

<i>Na, Cl</i>	<i>in%</i>
<i>Ca, SO<sub>4</sub></i>	<i>in% or ppm</i>
<i>K, Sr</i>	<i>in 100 ppm</i>
<i>Al, B, Ba, Fe, Li</i>	<i>in 1 - 100 ppm</i>
<i>Cr, Cu, Mn, Ni, Sn, Ti, Zr</i>	<i>in ppb (in most cases)</i>
<i>Be, Co, Ga, Ge, Pb, V, W, Zn</i>	<i>in ppb (in some cases)</i>

where

<b>% :</b>	g substance per 100 g brine
<b>ppm:</b>	mg substance per 1 kg brine
<b>ppb:</b>	mg substance per 10 <sup>3</sup> kg brine

Usually micro-organisms of different species are also present in oil field brines. The origin of these organisms is not yet totally clear. They contribute to corrosion in the bore hole and to permeability reduction during water flooding.

There is a wide variability of concentrations and chemical characteristics resulting from many factors. Such factors may be

- the non-marine origin of a few sediments,
- dilution with ground water,
- enrichment because of vaporization by migrating gas,
- adsorption and cation exchange with clay minerals,
- dissolution of mineral salts in the migrating formation water,
- the chemical reaction with components of adjacent sediments.

Therefore, it is important that water from a certain horizon is characteristically distinct from all the other brines, even those from the immediate neighbourhood. Thus, water analyses are mainly used for identifying the produced water with regard to the geological formation it originates from. In doing so, a simple and easily readable representation of the great data set from a water sample is desired. The graphical method proposed by STIFF (1951) may be the simplest graphical method, has maximum utility and, hence, is the most popular.

This graphical method is shown in Figure 5.21. Horizontal lines extend right and left from a centrally located vertical line. The positive ions are plotted on the left of the vertical line, while the anions are plotted on the right. Characteristic positions are designated for the ions which are most frequently found in reservoir brines.

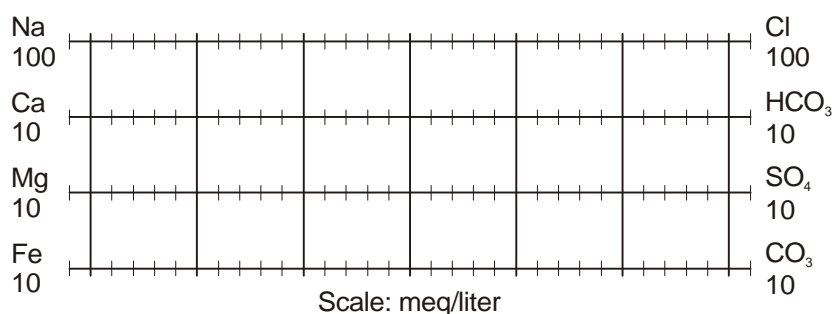


Figure 5.21: Essential feature of the water pattern analysis system (from STIFF, 1951)

The analysis data for all ions in question are indicated in *ppm* (milligram per liter). To make these values comparable with each other, the contents have to be converted to **meq** (milliequivalents) by dividing the respective value with the milliequivalent weight (ionic weight in mg per valence). If there is a difference between  $\Sigma$  meq of the positive and  $\Sigma$  meq of the negative ions, the difference is presented as sodium.

Although various scales can be employed, most reservoir waters may be plotted with sodium and chloride on a scale of *100 meq* and a scale of *10 meq* for the others. When the data of the water analysis are plotted on the graph and the adjacent points are connected

by straight lines, a closed “pattern” is formed as a “fingerprint” of the respective brine.

One of many practical applications in correlating producing formations is illustrated by Figure 5.22. The characteristic pattern of the formations is evident.

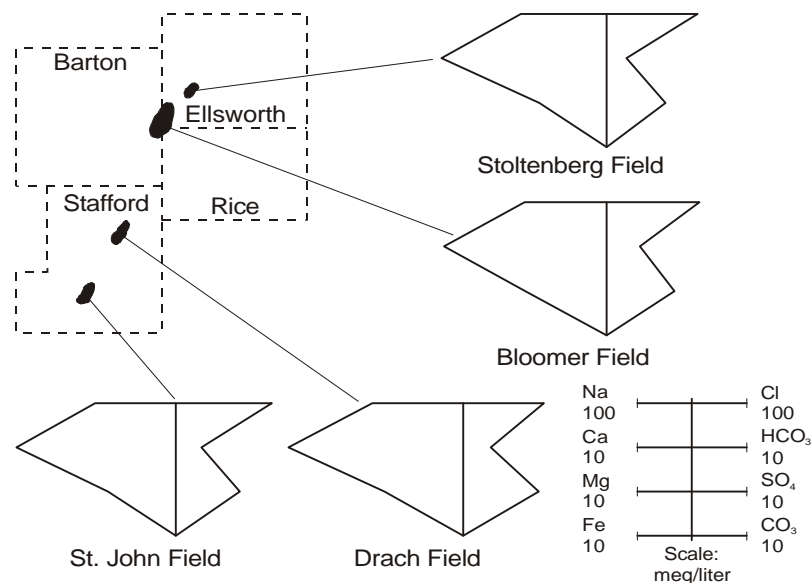


Figure 5.22: Course of Arbuckle formation through Kansas shown by water patterns (from STIFF, 1951)

### 5.3.2 Formation Volume Factor

The definition of the formation volume factor of water  $B_w$  corresponds to the definition of  $B_o$ . Similarly to the hydrocarbon liquids, the change in volume may have three reasons:

- liberation of dissolved gas due to pressure decrease,
- expansion of the brine because of pressure decrease,
- contraction of the brine due to temperature reduction.

In contrast to the solubility of natural gases in oil, their solubility in water is low (see Figure 5.23a). Additionally, the solubility decrease with increasing salinity of the brine (see Figure 5.23b). Consequently, the contribution of the gas liberation to  $B_w$  is low.

Since the expansion due to the decrease in pressure and the contraction because of temperature decrease are also insignificant,  $B_w$  is always numerically small, rarely above 1.06.

Figure 5.24 shows a typical relationship between  $B_w$  and  $p$ . In the present case, the initial

reservoir pressure is higher than the bubble point pressure. If the reservoir pressure is reduced from initial pressure to the bubble point pressure,  $B_w$  increases because of the water expansion. A further pressure reduction leads to gas liberation. This loss of liquid volume only balances partly the continuing expansion so that  $B_w$  further increases with further pressure drop. Along with the reduction of the pressure to atmospheric pressure,  $B_w$  will reach its maximum value. The difference between this value and 1.0 represents the thermal contraction resulting from the cooling of the brine from the reservoir temperature to the standard temperature of 15 °C. However,  $B_w$  will be smaller than 1.0, if the increase in volume by dissolved gas is too small to compensate the volume reduction resulting from high pressure.

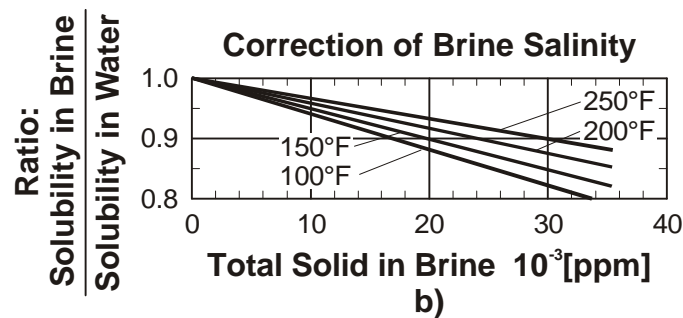
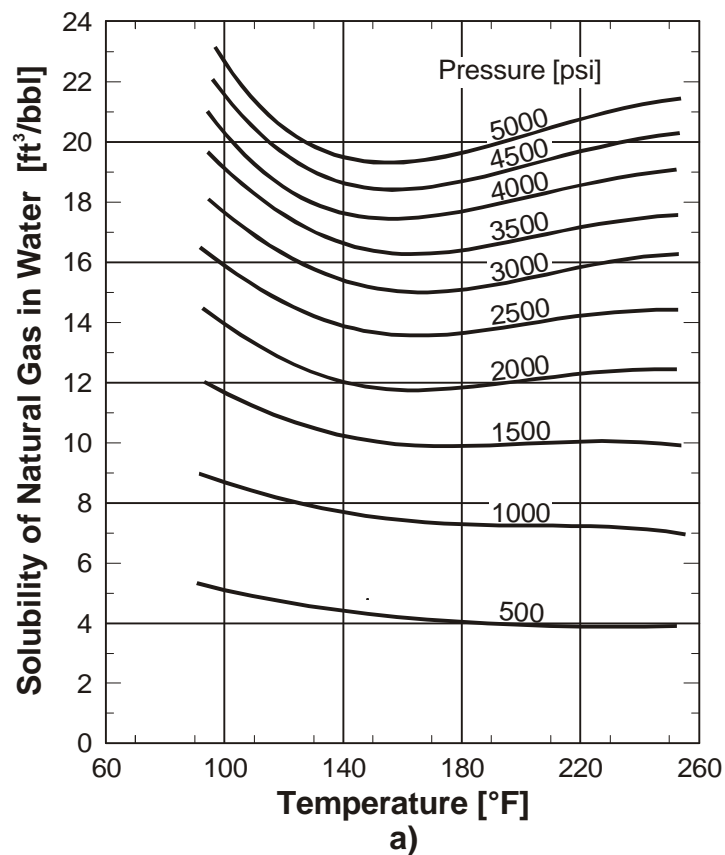


Figure 5.23: Solubility of natural gas in water (from DODSON and STANDING, 1944)

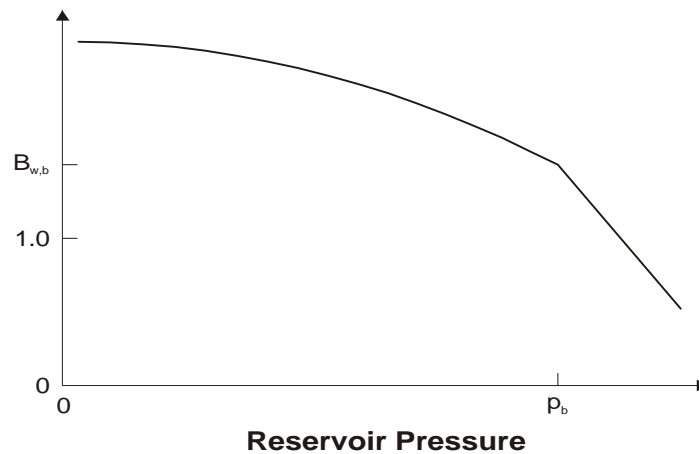


Figure 5.24: Typical graph of formation volume factor of water against pressure

The assumption is customary that the bubble point pressure of a gas-saturated brine is equal to the bubble point pressure of the crude oil inside the corresponding reservoir.

Figure 5.25 presents data of  $B_w$  for pure water saturated with natural gas (solid lines). Naturally, gas saturated pure water has a higher volume factor than pure water at a given pressure and temperature (dashed lines).  $B_w$  for a reservoir water can be computed with aid of Figure 5.25 and Figure 5.23 as follows:

- The volume factors for pure water and pure water saturated with natural gas are read from Figure 5.25 for the given reservoir data.
- The gas solution ratio,  $R_{sw}$ , for pure water is read from Figure 5.23a. and corrected for salinity using Figure 5.23b.
- Assuming the effect of gas solubility on  $B_w$  to be linear, the volume factor is computed by interpolation.

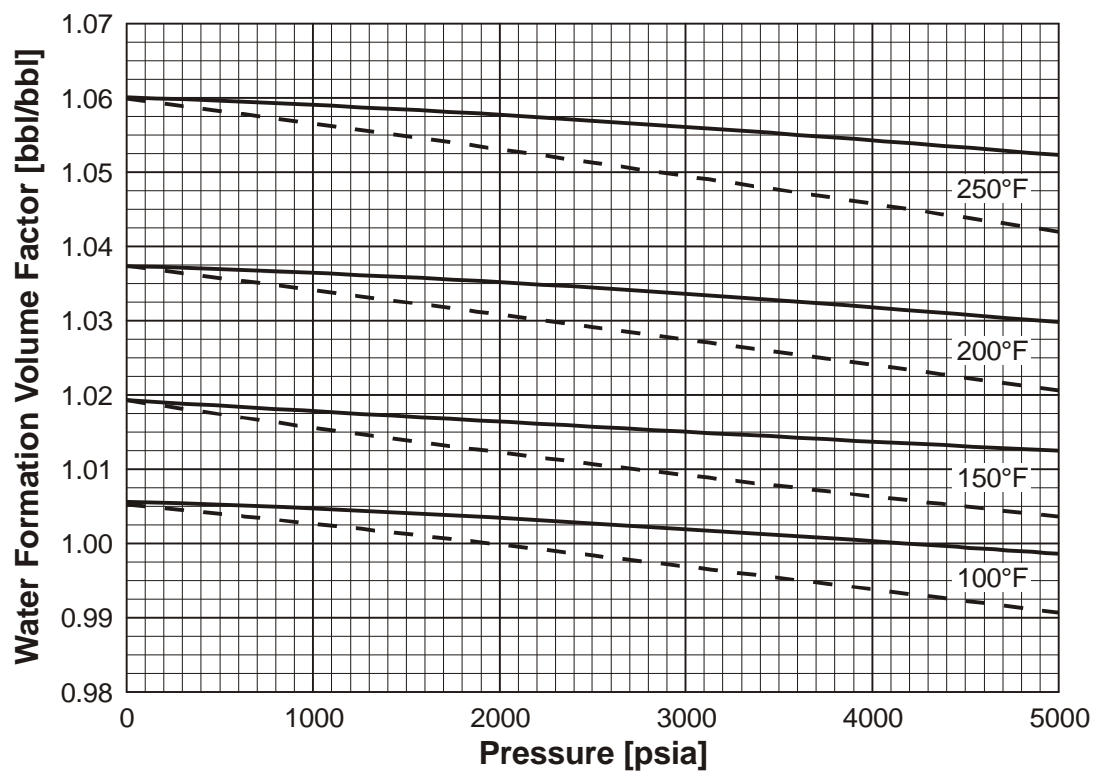


Figure 5.25:  $B_w$  for pure water (dashed lines) and pure water saturated with natural gas (solid lines) as a function of pressure and temperature (from DODSON and STANDING, 1944)

#### Example 5.9

Formation volume factor of reservoir water. The reservoir conditions as well as the salinity of the brine are given below both in SI- and Field units.

		SI Units	Field Units
Reservoir Temperature	T	93.3 °C	200 °F
Reservoir Pressure	p	20.56 MPa	3000 psia
Salinity		30,000 ppm	30,000 ppm

The evaluation of  $B_w$  for pure water from Figure 5.25 results in

$$B_w = 1.0275$$

$B_w$  for pure water saturated with natural brine can be read off from Figure 5.25 as

$$B_w = 1.034.$$

The gas solution ratio in pure water from Figure 5.23a results in

$$R_{sw} = 15.3 \text{ cu ft/bbl}$$

After correction of the gas solubility by using Figure 5.23b,  $R_{sw}$  results in

$$R_{sw} = 15.3 \times 0.88 = 13.46 \text{ cu ft/bbl}$$

Then the formation volume factor of the reservoir water results in

$$B_w = 1.0275 + (1.034 - 1.0275) \frac{13.46}{15.3} = 1.033.$$



Figure 5.26: Density of brine as a function of total dissolved solids  
(from MCCAIN, 1973)

In Figure 5.26, the density of reservoir water at standard conditions is plotted as a function of the total salt concentration. By dividing the respective density with  $B_w$ , the corresponding density under reservoir conditions can be received.

From Figure 5.27a, the coefficient of the isothermal water compressibility,  $c_w$ , can be evaluated without considering the gas in solution. At a given pressure and temperature, gas in solution causes an increase  $c_w$  (see Figure 5.27b).

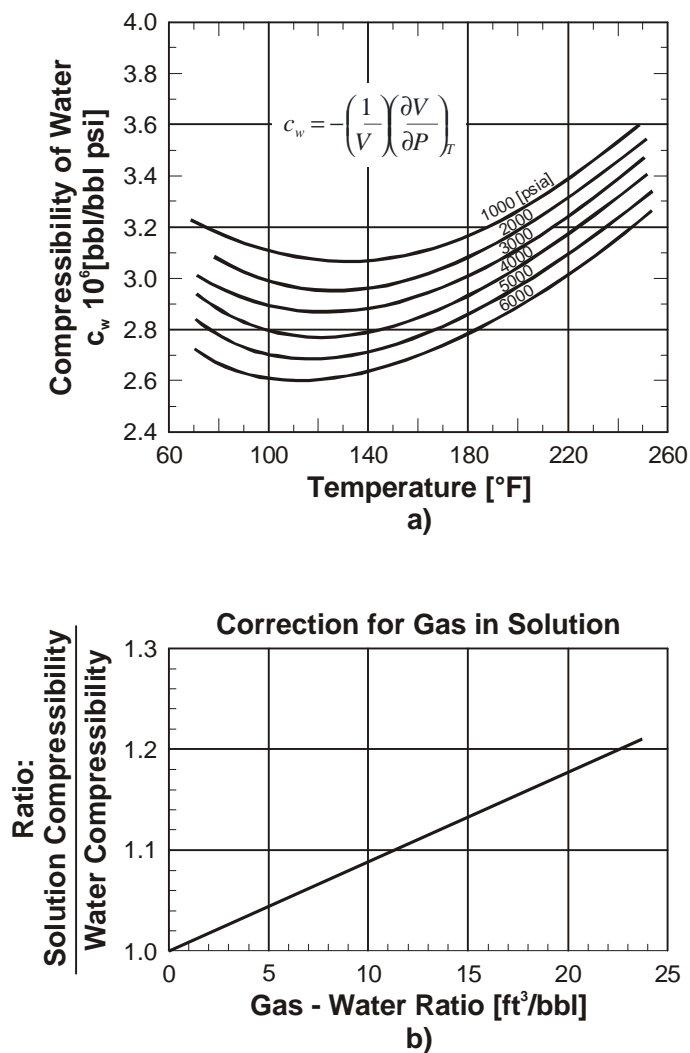


Figure 5.27: The isothermal coefficient of compressibility of pure water, including effects of gas in solution (from DODSON and STANDING, 1944)

#### Example 5.10

Evaluation of the compressibility of reservoir water at the reservoir data of Example 5.9.

From Figure 5.12a at 3000 psia and  $200^{\circ}\text{F}$ ,  $c_w$  can be read off as

$$c_w = 3.1 \text{ E} - 6 \text{ psi}^{-1}.$$

From Figure 5.23a, the gas solubility in pure water results in 15.3 cu ft/bbl.

Correction of gas solubility from Figure 5.12b:

$$R_w = 15.3 \times 0.88 = 13.46 \text{ cu ft/bbl}.$$

After evaluating the effect of the dissolved gas from Figure 5.23b, the compressibility of the reservoir brine results in

$$c_w = 1.12 \times 3.1 \text{ E} - 6 = 3.47 \text{ E} - 6 \text{ psi}^{-1},$$

or

$$c_w = 5.03 \text{ E} - 10 \text{ Pa}^{-1},$$

respectively.

### 5.3.3 Viscosity

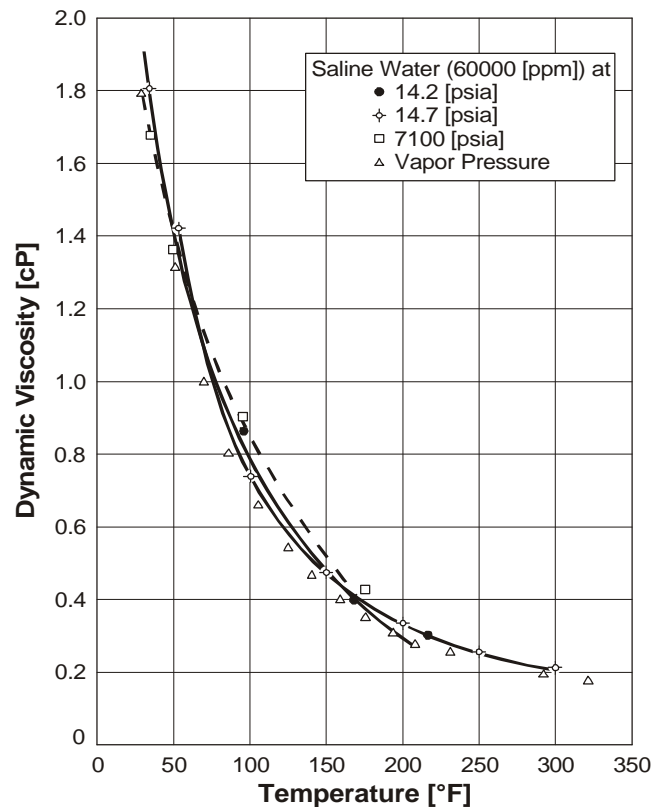


Figure 5.28: The viscosity of water at oil field temperature and pressure (from VAN WINGEN, 1950)

Regarding the viscosity of oil field brines, only few data are available. Figure 5.28 shows the water viscosity as a function of the temperature. The viscosity should rise with pressure and increase significantly with increasing salt concentration. These dependencies can be observed in Figure 5.28. It is recommended to use this graph for estimating the viscosity of reservoir waters without considering both the pressure and the salinity of the brine.

Low molecular paraffins are dissolved in water under reservoir conditions. This fact should furthermore lead to a considerable reduction of the brine viscosity. Unfortunately, no corresponding data have been published until now.

### 5.3.4 Natural Gas Hydrates

Natural gas and liquid water can form solid material which remind of wet snow. This process takes place at temperatures slightly higher than the freezing point of pure water. These solid substances are called “*gas hydrates*”.

The phenomenon is of special interest for petroleum industry. For example, the pressure decreases in the production line, such as across a choke or in a separator. This can cause a reduction in the temperature of the gas (adiabatic process) and, therefore, the condensation of water from the gas. The conditions necessary for hydrate formation could be established.

Gas hydrates behave rather like dissolutions of gases in ice than like chemical compounds. The lattice of the hydrate crystal is mainly formed by water molecules while the hydrocarbon molecules occupy vacancies within the lattice. Therefore, the hydrate formation is rather of physical than of chemical nature. The water lattice seems to be similar to ice, because the formation enthalpy is comparable.

Although gas hydrates can be compared rather to solid solutions than to chemical compounds, a certain number of water molecules is associated to each gas molecule. This may be caused by the crystal structure. The ratio of hydrocarbon to water depends mainly on the size of gas molecules.

The presence of liquid water is the most important prerequisite for hydrate formation. However, even if liquid water is present, a meta-stable equilibrium between water and hydrocarbon gas may occur (under conditions at which generally hydrate formation takes place). Seed crystals can immediately induce the hydrate formation.

Figure 5.29 shows a part of the phase diagram of a mixture of water and a light hydrocarbon. The point  $Q_2$  is a “quadruple point” at which four phases are in equilibrium. The quadruple point  $Q_1$  is at approximately  $0^\circ\text{C}$  (ice, gas hydrate, water and natural gas are in equilibrium). The connection  $Q_1 - Q_2$  represents the equilibrium natural gas-water-hydrate. This line is of special interest.

Figure 5.30 presents the hydrate formation conditions for natural gases of different gravities. The curves can be used to estimate the conditions of hydrate formation. Anyway, the results should be applied with caution because of the large discrepancies of the few published experimental data and the correlation present, especially in case of high gas gravity and temperature.

Additionally, it has to be taken into account that electrolytes present in the water will lead

to decreasing temperatures at which hydrate formation will occur. Thus, water-soluble substances are often added to the system to inhibit or suppress the hydrate formation. The effect of the concentration of various inhibitors on the hydrate-formation temperatures of a natural gas is plotted in Figure 5.31.

Hydrate portion of the phase diagram for a typical mixture of water and a light hydrocarbon (from MCCAIN, 1973)

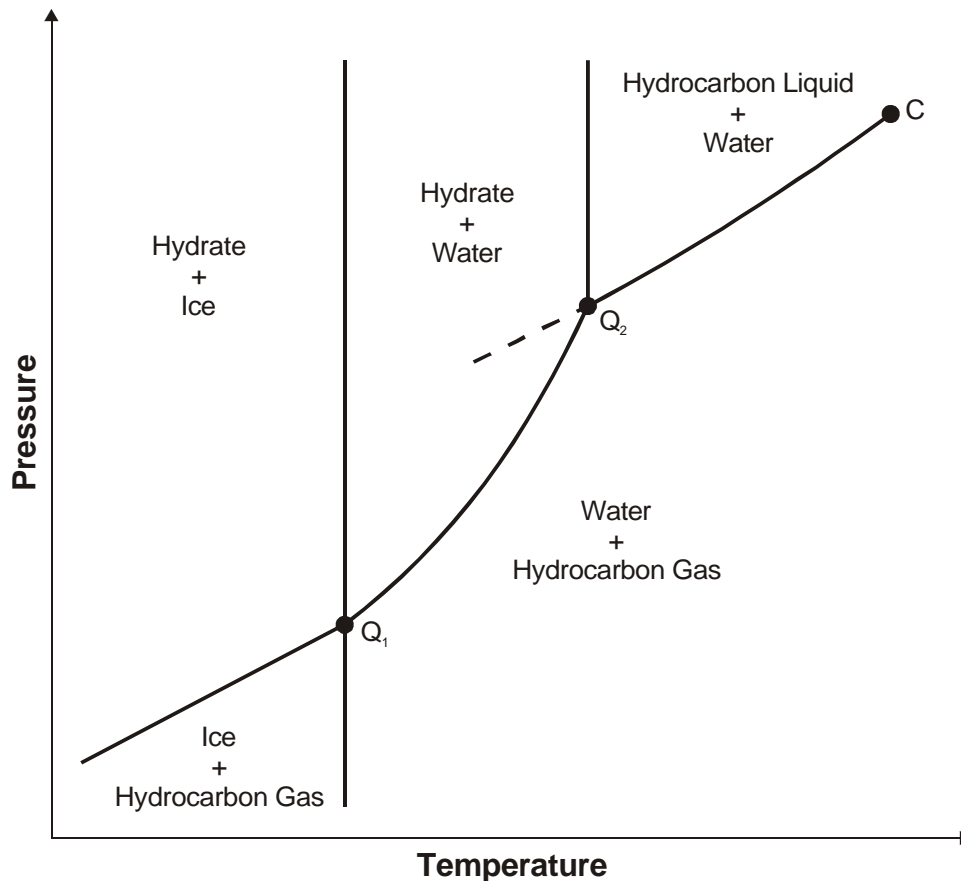


Figure 5.29: Hydrate portion of the phase diagram for a typical mixture of water and a light hydrocarbon (from MCCAIN, 1973)

Temperature calculations have been carried out for typical natural gases, and the results have been combined with the hydrate formation conditions given in Figure 5.30. This has been done to evaluate diagrams by which the maximum adiabatic pressure reduction without gas hydrate formation can be estimated. One of these diagrams is given by Figure 5.32.

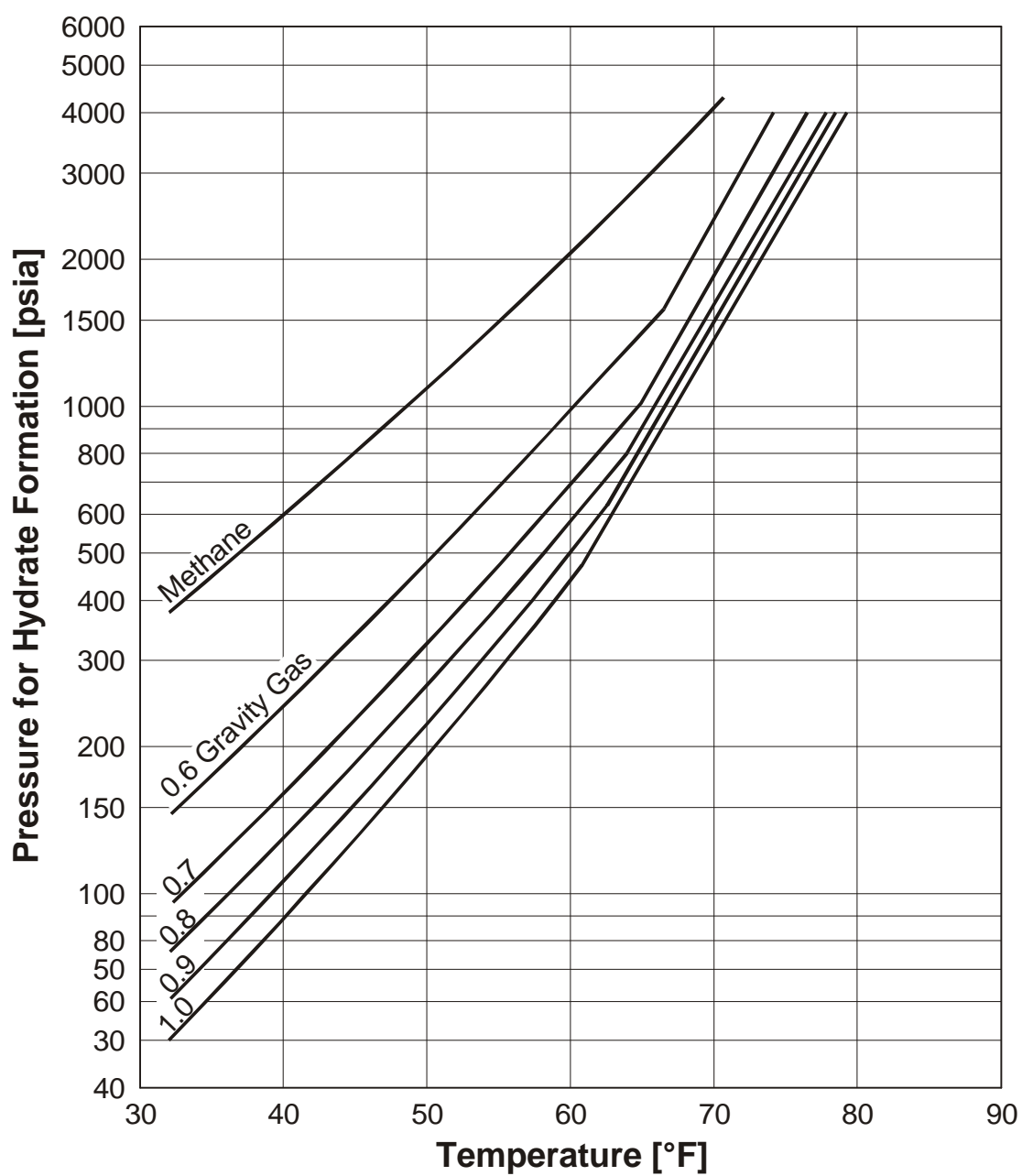


Figure 5.30: Pressure-temperature curves for predicting hydrate formation  
(from KATZ, 1945)

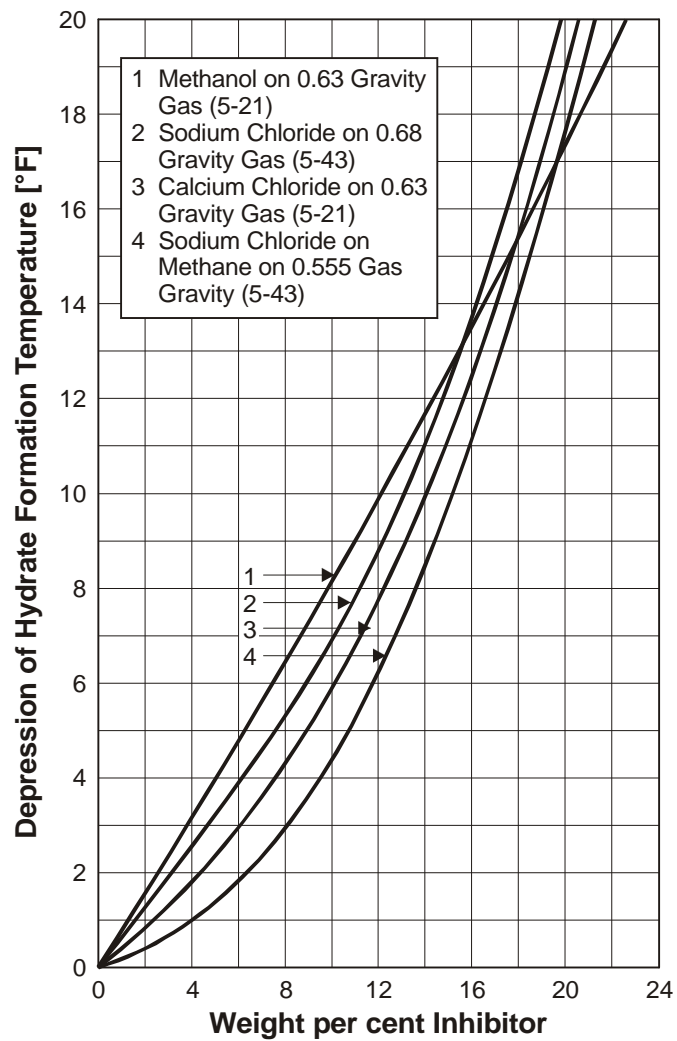


Figure 5.31: Depression of hydrate formation temperature by inhibitors (from KATZ et al., 1959)

#### Example 5.11

Evaluation of the maximum of adiabatic expansion of a natural gas without any danger of hydrate formation.

Problem: Up to which pressure can this gas be expanded

		SI-Units	Field-Units
Gas Gravity	$\gamma_g$	0.80	0.80
Initial Pressure	$p_i$	20.68 MPa	3000 psia
Initial Temperature	$T_i$	71°C	160 °F

adiabatically without hydrate formation and what will the temperature be?

Solution steps:

- The ordinate of Figure 5.32 was entered at  $p_i = 3000$  psia.
- It follows a horizontal movement to the 160 °F isotherm.
- The next step consists of the vertical movement to the abscissa. 800 psia is the lowest final pressure which will preclude hydrate formation.

The intersection of the 800 psia line with the dashed line results in 65 °F (18.3 °C) after expansion to 800 psia (5.52 MPa).

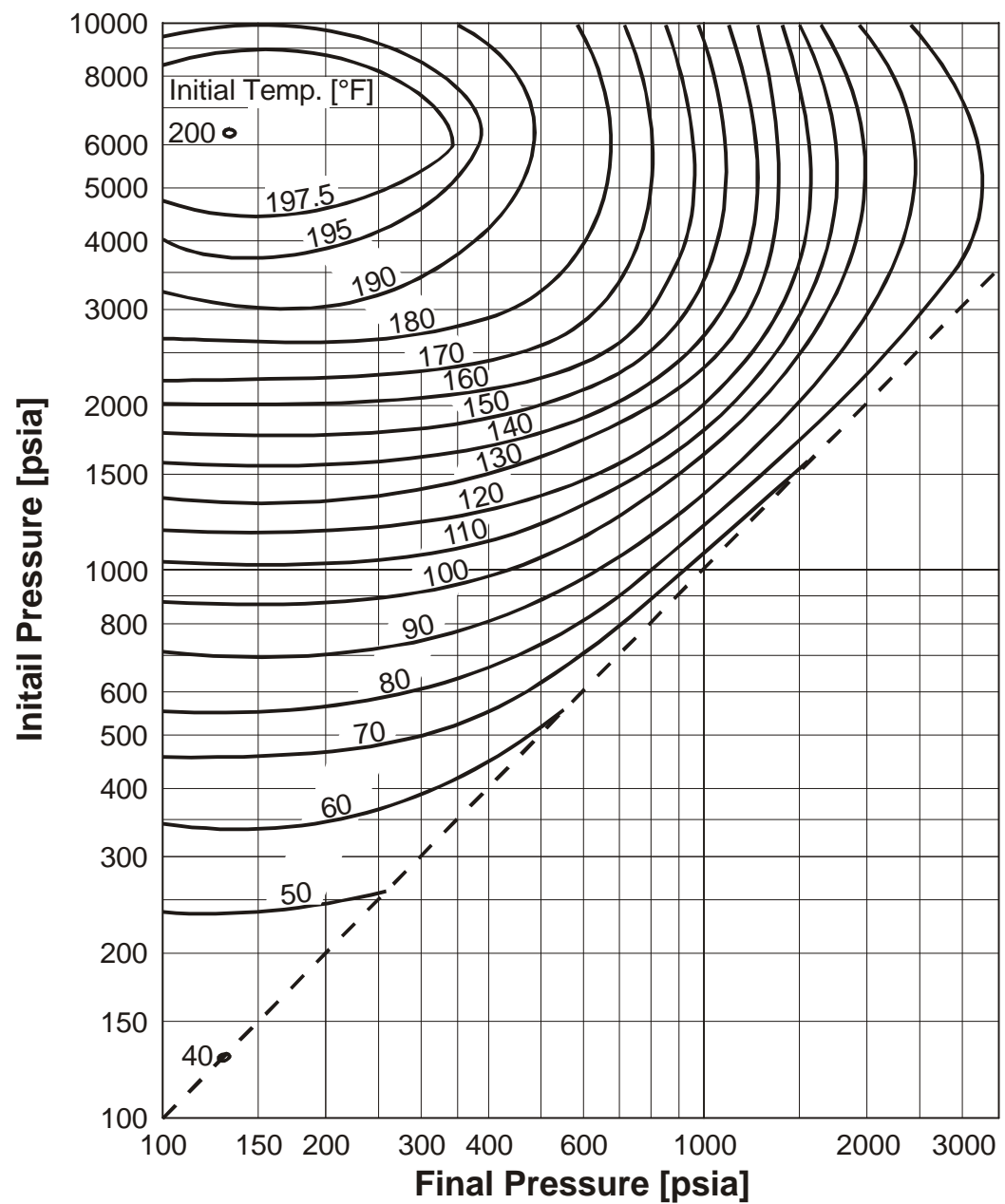


Figure 5.32: Permissible expansion of 0.8 gravity gas without hydrate formation (from KATZ, 1945).



## Chapter 6

# pVT-Measurements

Accurate crude oil data are necessary to control the production of a hydrocarbon reservoir efficiently. They are of importance for further calculations of the processes which take place inside a reservoir.

## 6.1 Sampling

### 6.1.1 Objectives

The objectives of sampling are to receive samples from a suitable place in the production wells or surface facilities. The samples should represent the system in the reservoir under its initial conditions. Only then, the determination of its type, volumetric and phase behavior, and its composition is assured to supply data for

- geological and reservoir engineering evaluation and forecasting,
- laboratory studies concerning enhanced oil recovery (**EOR**) methods modifying  $pVT$  properties (and the viscosity) of the system.

### 6.1.2 General Criteria

Based on the general remarks about the types and behavior of hydrocarbon systems, conclusions can be drawn about general sampling criteria. It is obvious that - except in case of dry and wet gases - characteristic samples can be received only in the early life of the reservoir. Therefore, it can be generally stated that the best time of sampling is at the beginning of production.

Table 6.1: Types of natural gas and oil

Type	Density of the produced liquid [ $\text{kg}/\text{m}^3$ ]	Gas/liquid ratio [ $\text{m}^3/\text{m}^3$ ]
Dry gas	-	
Wet gas	$\leq 740$	11000 - 20000
Gas/condensate system	740 - 780	1000 - 13000
High shrinkage oils	780 - 800	200 - 1500
Low shrinkage oils	$\geq 800$	$\leq 200$

To meet all requirements, the careful selection of wells for sampling is very important. Representative samples cannot be received from wells which are perforated at the water/oil or gas/oil contact and are producing water and/or non-equilibrium gas. The wells should be allocated at characteristic sections of the reservoir. Number of samples will depend on the dip of the structure as well as on the pay thickness. To determine the fluid properties along with the depth of the pay zone (where monophasic system exists), a minimum of one sample per 30 m can be recommended.

There are restrictions which must always be considered:

- Considering the gravitational effect, it is clear that the sampling in closed wells could easily lead to misleading data.
- No characteristic fluid can be received within the flowing wells, where a multiphase system exists or is developing.
- Reliable sampling conditions in the flowing wells and at the wellhead only exist, if the total composition of the system entering the well and leaving it at the wellhead remains constant.

Favorable conditions at steady state flow are indicated by stabilization of the pressure and temperature at the wellhead and in the separator. Moreover, the production gas/liquid ratio, *GOR*, should remain constant during a long period of time.

### 6.1.3 Sampling Methods

There are three methods of sampling. Samples can be taken from the flowing wells (**subsurface sampling**) or from the equilibrium phases of the separators (**separator samples**). The third possibility is to get representative samples from the wellhead

(**wellhead sampling**). In every case, steady state conditions must be maintained. The method used depends on the type of system to be sampled.

There are certain approximations for selecting sampling methods which consider some of the properties of the produced fluids. Values summarized in Table 6.1 represent average characteristics which can be used as some rule of thumb. It is clear, however, that the behavior of any system also depends on reservoir conditions which are missing on the tabulated data. Therefore, preliminary screening must be used cautiously.

On the basis of the general remarks on the phase behavior of different systems in their initial state and on the changes in their behavior in the depression zone and in the wells, the following guidelines can be applied in screening sampling methods.

Sampling of equilibrium phases from separators can be used for all systems, but steady state conditions must exist. Note, that no separator sampling is needed for dry gases and for saturated and undersaturated oils, if no free water enters the production well and if there is a considerable length along which a 1-phase oil.

For sampling, only those separators can be used whose construction ensures highly efficient separation of the entering phases. In a wide region of flow rates, no liquid droplets should depart the system with the gas.

Separators must contain pressure gauges and thermometers as well as devices for the accurate measurement of the gas volumes (liberated and/or delivered), liquid hydrocarbons, and of water. Each phase can be sampled through sampling valves built in the separator at that part where pure gas, oil, and water exist.

To determine the phase boundary during the time of sampling, separators often contain high pressure windows for visual control. When highly paraffinic systems are produced exhibiting a cloud point in the vicinity of the separator temperature, separators should be heated. The continuous monitoring of the concentration of some key components in the gas phase is recommended. This procedure should be considered to control the development and maintenance of steady-state flow.

Samples of the equilibrium phases should be taken using specially designed bottles with valves at their extreme ends. These bottles are in vertical position during sampling. The upper valve is connected with the sampling valve of the separator by a flexible tubing which is resistant to pressure and corrosion by phases sampled.

Sometimes, the bottles and the connecting tube are filled up with an indifferent liquid (mercury or water from the separator or from other sources) to maintain pressure and to exclude air. It is then displaced by the sampled phase (gas or liquid). Whenever the temperature in the separator is lower than the ambient temperature, the use of mercury (or brine) is recommended in sampling the liquid phase. In doing so, about 90% of mercury (or brine) has to be displaced by the separator liquid. After closing the valves into the container and in the separator and after dismantling the container, additional 10% of mercury (or brine) should be removed by opening the lower valve. The created gas cap will prevent uncontrollable pressure increase during shipping. The valves in the container

must be protected by steel caps during shipping. Data for identification must be delivered with the sample.

### **Bottom hole sampling**

Bottom hole sampling can be used when only the phase to be sampled is present at the perforated zone. If water is also produced with the hydrocarbons but remains at the bottom under steady-state conditions, samples can be taken above the water level. However, the flow of a 1-phase hydrocarbon fluid must be assured. The method can be controlled by sampling at different depths and by analyzing the water content of samples. No sampling within the wells is needed for dry gases or - in general - for systems which exist in a 1-phase state up to the wellhead.

Bottom hole samplers are specially designed devices containing one valve or two valves at their extreme ends. They are run into the well through a sealed tube mounted to the christmas tree by a mechanically driven cable. After reaching the desired depth (usually with open valves to allow the flushing of the sampler by the flowing fluids), the valves are closed. The valves are operated mechanically or electrically from the surface or within the sampler at the predetermined depth or time.

At the surface, the sample should immediately be transferred to containers through a flexible steel tube which - together with the shipping bottle - is filled up with an inert liquid (e.g. mercury). The sample is displaced by injection of the inert liquid into the sampler using a volumetric pump or - in a simple manner - by gravitational effects. The protection of the samples in the shipping bottles and their correct marking for identification are important as it has already been mentioned.

### **Sampling at the wellhead**

Sampling at the wellhead is a suitable process in case of the production of dry gas or undersaturated oil at wellhead conditions.

The container is connected with a valve at the wellhead and flushed with the fluid produced. The previous remarks referring to the protection and identification of the shipping bottles are also valid for wellhead samples.

## **6.1.4 Special Problems**

Sometimes problems arise from low permeability oil reservoirs (wells being produced with high depression). As a result, the ratio of the phases entering the wells does not characterize the initially-in-place fluids (bubble point oil system), especially if water is also present. In this case, it is only possible to take samples from the equilibrium phases of the separator and to recombine them under separator conditions corresponding to their volume ratio. Afterwards, pressure and temperature are increased up to the reservoir conditions.

If the liquid is in equilibrium with other phase(s), the basic concept of this method is that the composition of the oil phase is not influenced by the contacted volume of the other phase(s) being in equilibrium with the oil. However, no processes in the reservoir-well system should take place which may result in a difference between the overall composition of the reservoir fluid and the produced fluid.

A similar approach can also be used for gas-condensate systems.

Whenever water production cannot be avoided and the volume of the produced water is high, dissolved gases may be liberated from the water having a composition which could largely differ from that of the equilibrium hydrocarbon system. In this case, a similar procedure as above should be used to restore the composition of the hydrocarbon phase.

However, the samples must be preserved in their original state. As for liquids, it is important

- to prevent any loss - especially considering the lighter fractions -,
- to avoid the contact with air because oxidation processes could drastically modify the composition of hydrocarbon liquids, primarily those of oils.

Specially designed sampling is needed to determine the microbiological contamination of the produced fluid(s). This procedure is often necessary in case of reservoirs containing only water from which water will be produced for industrial or public supply. Sterile samplers and shipping bottles but also anaerobic conditions (in the course of sample transfer) must be guaranteed.

## 6.2 Experimental Determination of the Volumetric and Phase Behavior

To determine the volumetric and phase behavior of naturally occurring systems under reservoir/well/surface conditions, equipments and methods have been developed for the petroleum industry. A general scheme of the set of equipments used for *PVT* studies shown in Figure 6.1.

## 6.2.1 Equipment

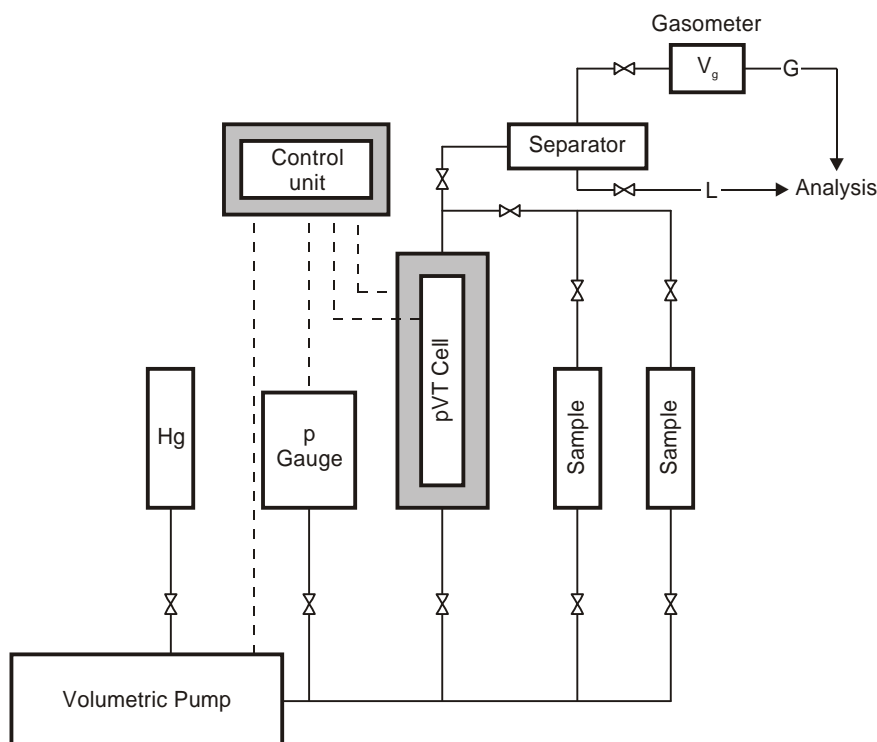


Figure 6.1: Scheme of *PVT* equipments

Samples to be studied are transferred to the **pVT cell**. Some known volume of an inert liquid is injected into the sampling bottle(s), while the same liquid is withdrawn from the cell initially filled with it.

The selection criteria for the inert liquid are:

- It must exhibit low volatility under (i) ambient conditions and also (ii) under temperatures and pressures which represent the working conditions.
- It should not react with the fluids contacted.
- Its physical and chemical properties must be well known.

Although mercury is widely used, sometimes low melting point alloys are used. No restriction is needed, however, if the liquid transported by the volumetric pump(s) is separated from the samples. In this case, the samples will be transferred and measured by a piston built into the containers and the **pVT** cell.

Double-acting or two single-acting volumetric pump(s) are needed for this process. Sometimes only one pump may be used for this purpose, if the inert liquid leaves the cell through a suitable operated valve at the bottom of the cell. This valve controls the rate and volume of the out-flowing inert liquid.

The sample being transferred into the cell must be in a 1-phase state. Therefore, liberated gas or condensate in the shipping bottle has to be dissolved or evaporated in advance. Referring to separator samples, the proportions of gas and liquid to be injected into the *PVT* cell must be equal to those measured into the field separator at the time of sampling.

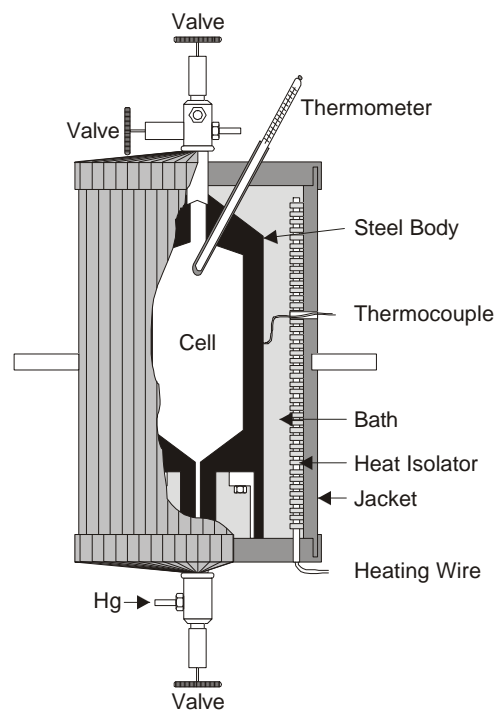
### 6.2.2 PVT-Cells

Evaluation of the *pVT* behavior is carried out on the system transferred into the *PVT* cell. The cell has to be a heat- and pressure-resistant vessel which is equipped with valves made of non-corrosive materials. The cell is mounted into a thermostatic bath which ensures from detrimental temperature inconstancy in the cell. The electrically heated (or cooled) medium circulating around the cell could be air or liquid. To obtain the desired rapid establishment of the equilibrium conditions at any given pressure and/or temperature, the cell is agitated or stirred inside.

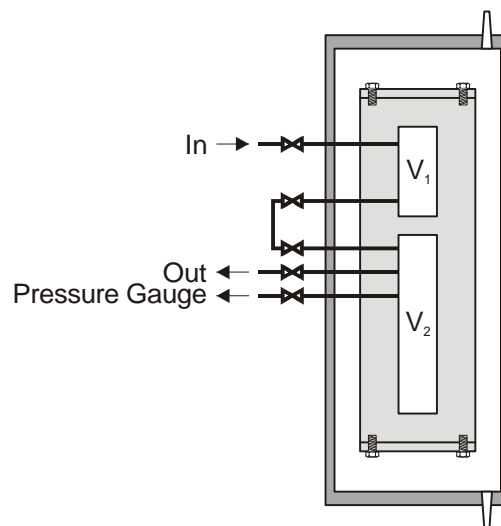
However, the accuracy of measurements depends on the resolution of the measuring instruments. Nevertheless, the relative error can be decreased by a reasonable increase of the sample volume studied. Therefore, “micro *PVT* cells” are not used in practice. Moreover, considering the change in volume of the system within the pressure range applied in the *PVT* studies, larger cell volumes are used to study (i) gases, (ii) gas-condensate systems, (iii) critical oils, and (iv) water. On the other hand, relatively smaller ones are used to investigate characteristic oil systems.

Although many different *PVT* cells are specified, two basic types can be distinguished:

- **blind *PVT* cells** (without any possibility of visual observation of the system to be measured),
- **windowed *PVT* cells**, where the volumetric and phase behavior can directly be observed through one or more pressure- and temperature- resistant windows built into the cell body. The inside of the cell is lighted from outside by transmitted or reflected (from the inner wall of the cell) light.

Figure 6.2: Blind *PVT* cell

Blind *PVT* cells are usually used to study systems in which no phase transition takes place or phase transition can easily be determined using the isothermal  $p - V$  relationship (dry gases, oil systems, water). A characteristic blind cell is shown in Figure 6.2. Its volume is about  $0.001[m^3]$  which is large enough to be used for gas and oil studies as well.

Figure 6.3: *PVT* cell (after BURNETT)

A special *PVT* cell for gases was developed by BURNETT (see Figure 6.3). It contains two or more chambers with different volumes which are separated by valves. The chamber possessing the smaller volume contains the gas under given pressure. By opening

successively the valves of the evacuate other chambers with known volume, the change in pressure can be measured. No volumetric pumps are needed in this case.

### Windowed $PVT$ cells

Windowed  $PVT$  cells are usually used to evaluate systems where the knowledge of the volumes of coexisting phases is necessary (e.g. wet gases under well or separator conditions, gas condensate systems). It is also required whenever phase transition cannot exactly be determined by isothermal ( $pV$ ) relationships (volatile oils or partially miscible liquid-liquid systems with or without free gas phase).

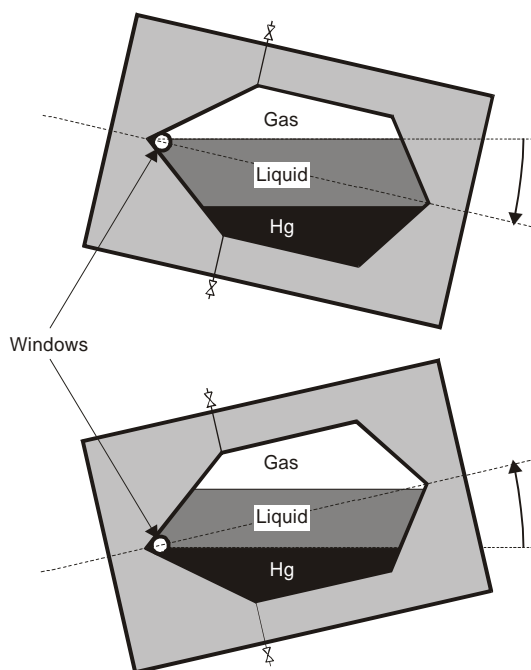


Figure 6.4:  $PVT$  cell (after DEAN-POETTMAN)

A typical one-windowed cell is shown in Figure 6.4. The volumes of the liquid phase can be determined by the angle of rotating the cell until liquid phases appear in the window.

A  $PVT$  cell with variable volume is presented in Figure 6.5. The condensed phase can be moved to the window by simultaneous lifting (or sinking) the two built-in plungers. The volume corresponding to that motion can be read on the calibrated stem of the plungers.

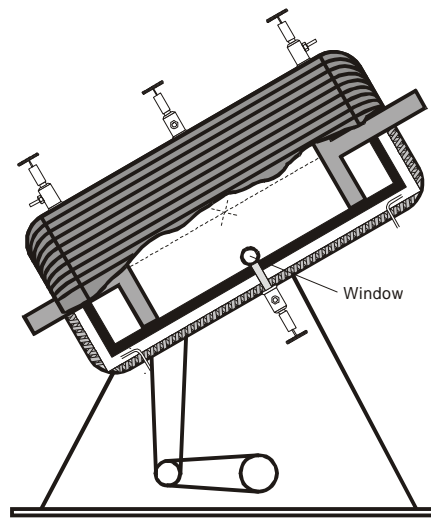


Figure 6.5: Variable volume cell (after VELOKIVSKIY et al.)

As far as SLOAN's windowed cell (see Figure 6.6) is concerned, there are three sections. In the upper part, a plunger is moved by the fluid injected or withdrawn by a volumetric pump. In the lower part, the condensed liquid is collected and can be lifted up to the windows which are built into the middle part. This can be done by injecting inert fluid. Meanwhile, pressure can be kept at the desired constant value by the simultaneous lifting of the plunger.

Another type contains one capillary glass tube within the cell through which the inner volume can be lighted and observed using an optical system. It serves also for the measurement of the volume of phases. The scheme of this cell is shown in Figure 6.7. Three windows are built into the body of the most generally used cell as shown in Figure 6.8.

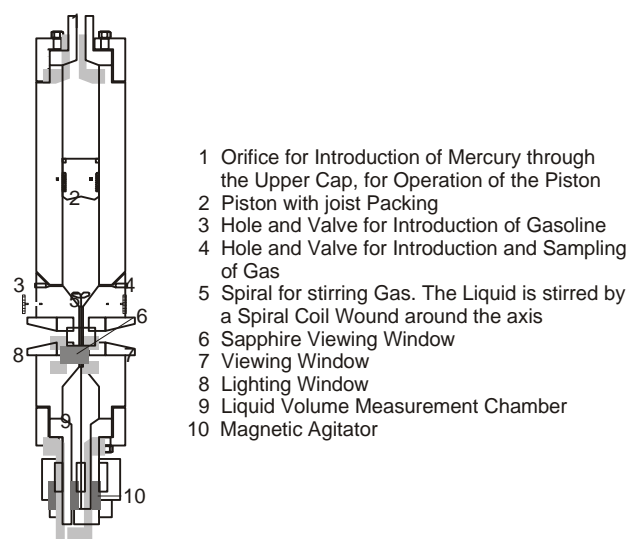


Figure 6.6: PVT cell (after SLOAN)

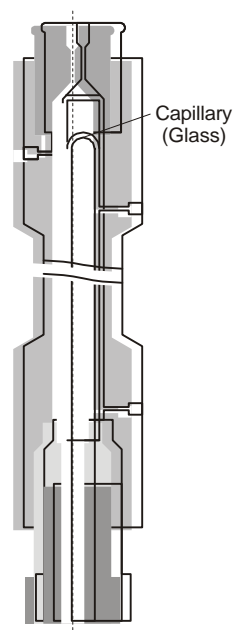


Figure 6.7: *PVT* cell (after WELLS-ROOF)

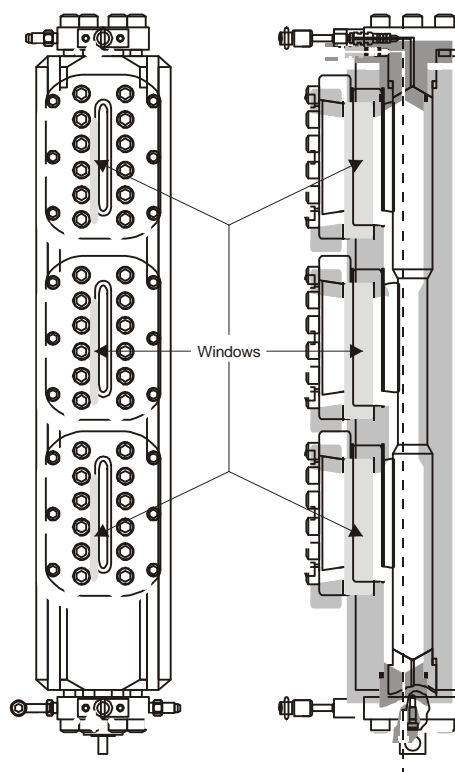


Figure 6.8: RUSKA cell

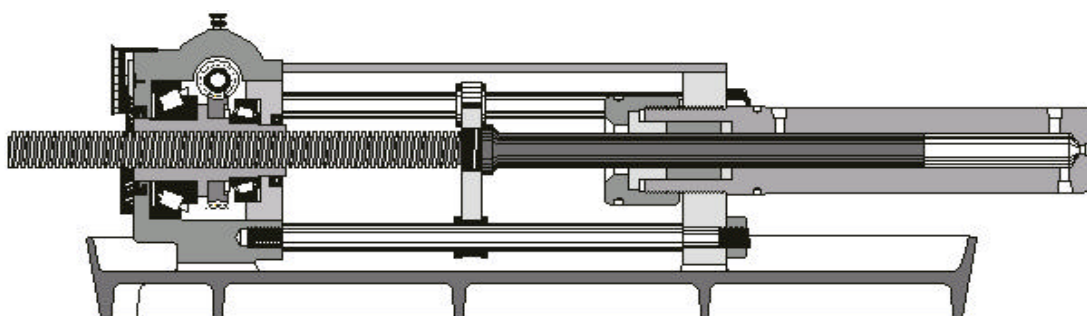


Figure 6.9: RUSKA volumetric mercury pump

### 6.2.3 Volumetric Pumps

Volumetric pumps - the so called **positive displacement pumps** - are used to measure the volume of the inert liquid injected to and withdrawn from the cell respectively. The pressure can be increased or decreased. The transported volume is proportional to the change in volume of the system studied.

In the generally used types, the inert liquid is displaced by a plunger from a pressure resistant and thermostatically controlled cylinder. The movement of the connecting screw-spindle can be read on a calibrated rod and on a dial to increase the accuracy.

In practice, hand- and mechanically operated pumps are used, the latter sometimes with variable speed. A special type of volumetric pumps is the **double-acting** one: Two plungers are working simultaneously, but in opposite directions.

A scheme of a hand-operated volumetric pump is shown in Figure 6.9. Its general construction does not differ from the pump which is mechanically driven.

### 6.2.4 Auxiliary Equipment

The *PVT* cell, the volumetric pump(s), and other parts of the *PVT* system are interconnected by pressure-resistant stainless steel tubes. In order to separate single parts of the equipment, valves are mounted in the network of tubes.

Pressure in the system is measured by gauges containing BOURDON-tubes. However, also dead weight gauges can be used for this purpose and for the calibration of the BOURDON-tube-gauges as well. There are also gauges in which an electric signal is proportional to the pressure measured. These gauges are also built into the tube network. They are filled with the inert liquid used in the volumetric pumps.

In order to store the inert liquid (mercury), a container is used which is also interconnected

through valves with the different parts of the *PVT* system.

The temperature of the volumetric pump(s), in the *PVT* cells, and in the thermostat around the cell is usually measured by thermocouples (may be controlled by thermometers). Whenever pressure, temperature, and the volume in the pumps are measured electrically, the process can be automated and computerized.

If the gas phase liberated in the *PVT* cell will be displaced, its volume must be measured. For this purpose gasometers are used. However, gas could condense under ambient conditions or at pre-selected pressures. Therefore, a laboratory separator must be inserted between the *PVT* cell and the gasometer.

## 6.3 Methods

Basically, there are three methods generally used in *PVT* studies. They are distinguishable by considering the change and the direction of change in the composition of the system.

### 6.3.1 Flash Process

In the course of flash processes, pressure is gradually increased or decreased at constant temperature under equilibrium conditions. At each pressure step, the volumes of the system and that of the existing phases are measured and the development of phases is observed. Measurements are usually repeated at other temperatures, too, covering some range between reservoir and surface temperatures (in the separator or in the stock tanks).

Measurements start at or above the reservoir pressure. The lowest pressure applied is determined by the system studied. For systems in which no phase transition takes place, the lowest pressure selected could be the atmospheric one. In this case the flash process simulates the whole course of production.

Whenever phase transition occurs, measurements should be carried out in a pressure region which correctly characterizes the phase transition and the 2-phase (or multiphase) behavior of the system. In this case the flash process - carried out at reservoir temperature - simulates the behavior of the system far inside the reservoir where its composition is not influenced by the production. A scheme of the flash process has been presented in Figure 4.3.

### 6.3.2 Differential Process

The differential process describes the change in the volumetric and phase behavior of the system at reservoir temperature and under equilibrium conditions, where any decrease in the reservoir pressure results from the stepwise production of one of the equilibrium phases (usually liberated or free gas).

In contrast to the flash process during which the composition is maintained and the volume is varied, the differential process is carried out at constant volume and by variation of the system composition.

In the course of the differential study - also explained in Figure 4.3 -, the volumes of the system and those of the existing phases are measured. The development or disappearance of phases is observed. To follow the change in composition of the system and to characterize the displaced phase (gas), the composition of the latter is also determined. By use of a laboratory separator in which pressure and temperature correspond to those during the field separation process, further information on the volume (and composition) of phases separated can be given.

The differential process is repeatedly carried out, usually down to the lowest possible reservoir (separator) pressure. As a result of the gradually changing composition, the values of characteristic parameters will differ from those determined by the flash process, except the starting point representing the intact system under initial reservoir conditions.

### 6.3.3 Reverse Differential Process

The reverse differential process is used to study the effect of any gas injection process on the volumetric and phase behavior of systems. This can be done under initial conditions (gas cycling) or by starting from a given depleted state (gas injection with pressure increase). Both are constant volume processes. In the course of gas injection (using a pre-selected gas), the phase volumes are measured and phase transition(s) are observed at reservoir temperature. There are two subgroups of the reverse differential process.

If the effect of **pressure maintenance by gas injection** is being studied after each step of the differential measurement,  $p$  is re-established by injecting a measured volume of the pre-selected gas. This method is used, when

- in the initial state of a gas condensate system, the liquid phase exists beyond the restriction of retrograde condensation,
- partial or total evaporation of the immobile liquid condensate is needed.

In depleted (gas condensate or oil) reservoirs, the effect of **increasing the pressure by pre-selected gas** can also be studied. In the course of a stepwise process, an isothermal pressure increase is realized under constant volume conditions. The highest pressure to be

reached corresponds to the fracturing pressure of the formation, or - if this information is not available - it is about 10% higher than the initial reservoir pressure. If some 1-phase system develops below this pressure, it is obviously no need to continue the process in a higher pressure region. The effect of gas injection is often the combination of the methods discussed above.

# SI Metric Conversion Factors

°API		141.5/(131.5+°API)	E+03	=	kg/m <sup>3</sup>
bar	x	1.0	E-01	=	MPa
bbl	x	1.589 873	E-01	=	m <sup>3</sup>
cal	x	4.1896	E+00	=	J
cp	x	1.0	E-03	=	Pas
cu ft	x	2.831 685	E-02	=	m <sup>3</sup>
°F		(°F-32)/1.8	E+00	=	°C
g/cm <sup>3</sup>	x	1.0	E+3	=	kg/m <sup>3</sup>
lb/cu ft	x	1.601846	E+01	=	kg/m <sup>3</sup>
psi	x	6.894 757	E-03	=	MPa
psia	x	6.894 757	E-03	=	MPa
°R		(°R/1.8)-273.15	E+00	=	°C