10. VAPOR-LIQUID EQUILIBRIUM

It will be recalled from the phase behavior discussions presented previously that an area bounded by the bubble point and dew point curves on the pressure-temperature diagram of a multicomponent system defines the conditions for vapor and liquid to exist in equilibrium. At different points within the limits of the phase boundary, the quantity and composition of both phases vary. The purpose of this chapter is to present methods of calculating the quantity and composition of equilibrium vapor and liquid existing at a specified temperature and pressure. These methods have wide applicability to calculations of reservoir fluid behavior and to calculations concerned with processing reservoir fluids at the surface for their natural gas and heavier oil components.

The distribution of a component of a system between vapor and liquid is expressed by the equilibrium constant, K. The equilibrium constant is defined as the ratio of the mole fraction of the component in the vapor phase, y, to the mole fraction of the component in the liquid phase, x, mathematically, then

$$K = \frac{y}{x} \tag{10.1}$$

where

K = equilibrium constant of a component
y = mole fraction of a component on the vapor phase
x = mole fraction of a component in the liquid phase

The equilibrium constants of the various components of petroleum are functions of pressure, temperature, and the over-all composition of the system. At low pressure the effect of the system composition is small; but above 1000 psia the over-all composition of the system considerably affects the equilibrium constant. The word "constant" is a misnomer, but is used widely in the petroleum industry. Muskat [1] has proposed the term "equilibrium ratio" to indicate that the ratio is not solely a function of pressure and temperature. Although his term is more meaningful than "equilibrium constant," the old term will be used here.

Equilibrium constants can be evaluated by three methods :

(1) From Raoult's and Dalton's laws.

(2) From data on vapor and liquid fugacities of pure compounds.

(3) Direct analysis of the vapor and liquid in equilibrium at any specified pressure and temperature.

After the three methods of evaluating equilibrium constants are discussed in detail, several methods of using them will be explained.

10.1 Raoult's and Dalton's Laws

For ideal solutions at equilibrium, Raoult's law and Dalton's law may be combined to calculate concentration of each component in the vapor and liquid phases.

Raoult's law (liquids) states that the partial pressure of a component is equal to the mole fraction of the component in the liquid phase times the vapor pressure of the pure component.

$$P_i = x_i \cdot P_{v_i} \tag{10.2}$$

Dalton's law states that the partial pressure of a component in a vapor is equal to the total pressure exerted by the vapor times the mole fraction of the component in the vapor.

$$P_i = y_i \cdot P \tag{10.3}$$

where

P_i = partial pressure of component i in the vapor phase
x_i = mole fraction of component i in the liquid phase
P_{v_i} = vapor pressure of the pure component at the temperature of the system
y_i = mole fraction of component i in the vapor phase
P = total pressure of the system

Combining the equations of Raoult's and Dalton's gives:

$$x_i \cdot P_{v_i} = y_i \cdot P \tag{10.4}$$

which can be arranged to give:

$$\frac{P_{v_i}}{P} = \frac{y}{x} = K \tag{10.5}$$

K is the equilibrium constant at the particular temperature and total pressure.

Two factors that restrict the use of equilibrium constants calculated by Raoult's and Dalton's laws are immediately apparent.

(1) A pure compound cannot have a vapor pressure at temperatures above its critical temperature. Thus, Raoult's law is limited to temperatures less than the critical temperature of all compounds in the system. This means, for example, that an equilibrium constant for methane cannot be evaluated by Raoult's law at temperatures above — 116°F.

(2) Dalton's partial pressure law assumes that each component in the vapor behaves as an ideal gas. In practice, the ideal gas assumption places an upper limit of pressure of 50 to 100 psia.

Equilibrium constants calculated from Eq. (10.5) take the form of straight lines of unit slope on log K vs. log P coordinates, and have values of unity at the pressure corresponding to the vapor pressure of the component at the temperature under consideration. For example, the vapor pressure of propane at 120°F is 240 psia, so that the equilibrium constant for propane at 120°F takes the form shown in Fig. 10.1. Constants calculated from Raoult's Jaw are no longer important because ideal equilibrium constants and empirical constants far more accurately describe multicomponent system behavior.

10.2 Ideal Equilibrium Constants

A better approximation of actual equilibrium constants is obtained by defining the constants in terms of the fugacities of the compounds. [2,3] The fugacity may be looked upon as a vapor pressure modified to represent, correctly the escaping tendency of the molecules from one phase into the other.[4]

By using fugacities to define equilibrium constants, the departure of the vapor from ideal gas behavior and the effect of the total system pressure on the vapor pressure of the components are taken into account.

In an ideal solution the fugacity of any compound in the system is equal to fugacity of the compound in the pure state times its mole fraction. Thus, if $\left(f_i^L\right)_{mix}$ and $\left(f_i^G\right)_{mix}$ are the fugacities of a compound in the liquid and vapor phases, and $\left(f_i^L\right)_{pure}$, and $\left(f_i^G\right)_{pure}$ are fugacities in the pure states,

$$\left(f_i^G\right)_{mix} = y_i \cdot \left(f_i^G\right)_{pure} \tag{10.6}$$

and :

$$\left(f_i^L\right)_{mix} = x_i \cdot \left(f_i^L\right)_{pure} \tag{10.7}$$

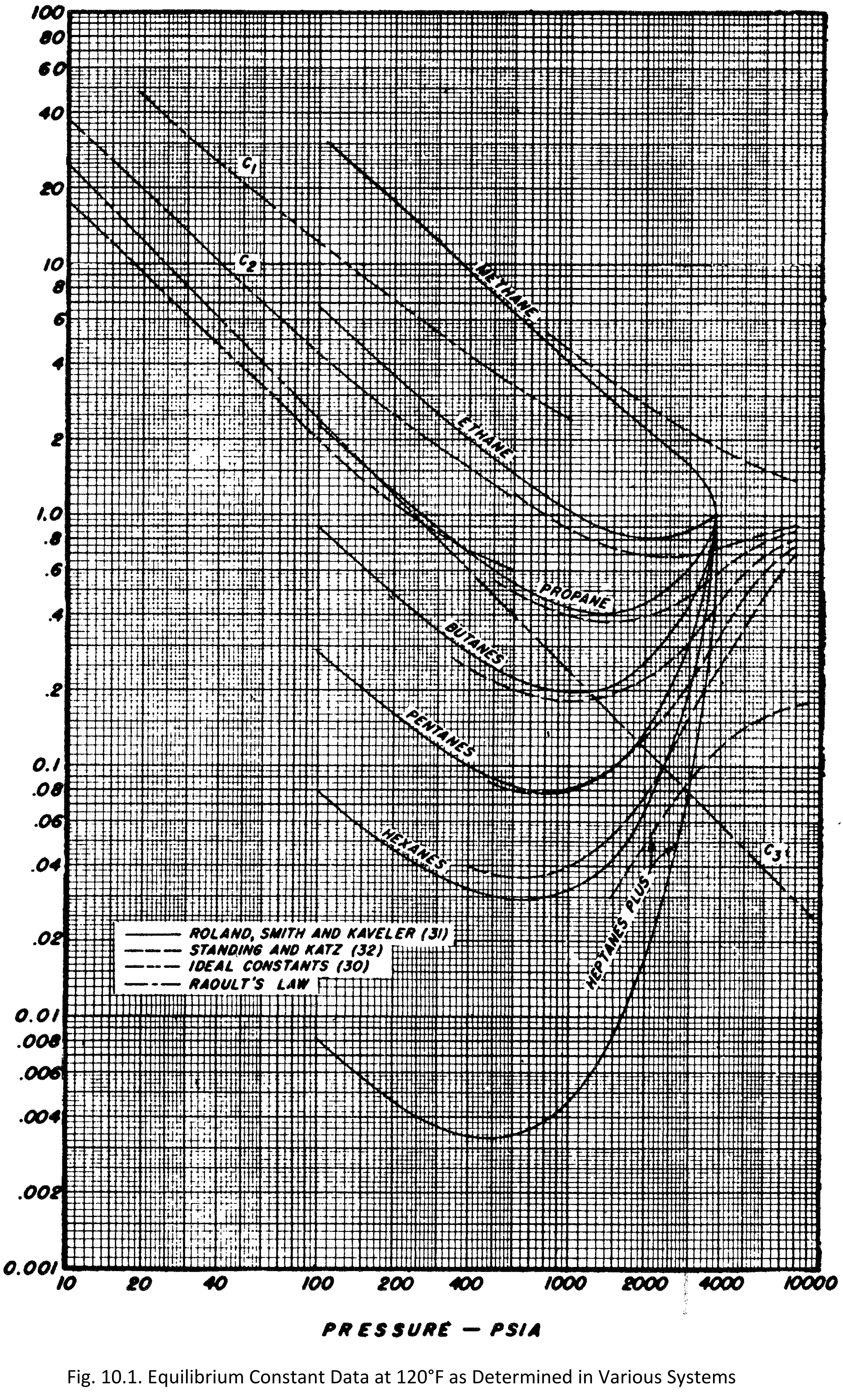


Fig. 10.1. Equilibrium Constant Data at 120°F as Determined in Various Systems

At equilibrium conditions the fugacities of the compound are equal in the liquid and vapor phase:

$$\begin{gathered}\left(f_i^G\right)_{mix} = \left(f_i^L\right)_{mix} \\ y_i \cdot \left(f_i^G\right)_{pure} = x_i \cdot \left(f_i^L\right)_{pure}\end{gathered} \tag{10.8}$$

and :

$$\frac{y_i}{x_i} = \frac{\left(f_i^L\right)_{pure}}{\left(f_i^G\right)_{pure}} = K \tag{10.9}$$

Ideal constants are limited by one important fact. At a given temperature a compound can exist only as a single phase at any pressure other than the vapor pressure, so that the fugacity of either the vapor or liquid (depending upon whether the pressure is greater or less than the vapor pressure of the compound) must be obtained by extrapolation of the fugacity-pressure relation. As the extrapolation is somewhat arbitrary, the farther the pressure is from the vapor pressure, the more uncertain the equilibrium constant becomes. Usually the ideal equilibrium constants are considered undependable at pressures more than twice the vapor pressure of the compound. For this reason, they have limited usefulness for calculations dealing with petroleums reservoir conditions.

10.3 Empirical Equilibrium Constants

The third method of evaluating equilibrium constants is to determine experimentally the equilibrium compositions of vapor and liquid phases at various temperatures and pressures. The equilibrium constant of each component can then be valuated by calculating the ratio of the mole fractions in the vapor and liquid phases.

When done correctly, this procedure results in a set of equilibrium constants representing a specific system. Fig.10.1 shows two sets of such constants at 120°F. The data of Roland, Smith, and Kaveler [5] were determined for a Gulf Coast condensate system containing roughly 70 mole% of methane and 21 % of hexanes plus material.

The system studied by Standing and Katz [6] also was a condensate system. It contained about 83 mole % of methane and 6 mole % of hexanes plus. The constants of both systems are in good agreement at 1000 psia and, on the basis of other data, are expected to continue in agreement at lower pressures. However, the wide differences in the constants of the two systems at pressures approaching 3000 psia reflect the effect of system composition. Unfortunately, too few systems have been studied to define the manner in which the composition influences the values of the constants.

The shape of the log K - log P curves shown in Fig.10.1 is characteristic of all multicomponent system curves. At low pressures the slope of the curves is near minus one. As pressure increases, all the equilibrium constants decrease and, with the exception of methane, all pass through a minimum value. The constants tend to converge to unity at some high pressure.

The apparent convergence of the equilibrium constants to unity at some pressure is often misinterpreted to mean that the system is near its critical state. Unless the temperature at which the constants are determined is the critical temperature of the system, it is impossible for the equilibrium constants actually to converge, because it is only at the critical pressure and temperature of the system that the phase compositions are the same. At any temperature other than the critical temperature, the equilibrium constants become meaningless after the bubble point or dew point pressure of the system is reached. Nevertheless, isothermal log X – log P curves are often extrapolated to pressure regions wherein two phases cannot possibly exist. Quite often the curves have an appearance of converging. Therefore, in order to forestall confusion between actual behavior of systems at their critical state and their behavior postulated from extrapolated equilibrium constant data, it should be recognized that in the great majority of instances equilibrium constants converge to an "apparent convergence pressure, " and that this pressure actually may be quite different from the critical pressure of the system.

The equilibrium constants of the plus fraction often behave in a manner different from the other components of a system. This is because the plus fraction in itself is a mixture of compounds, and both its vapor and liquid phase composition can vary with pressure.

In Fig. 10.2 are plotted the specific gravities and molecular weights of the heptanes plus fraction [6] whose equilibrium constants are shown in Fig. 10.1.

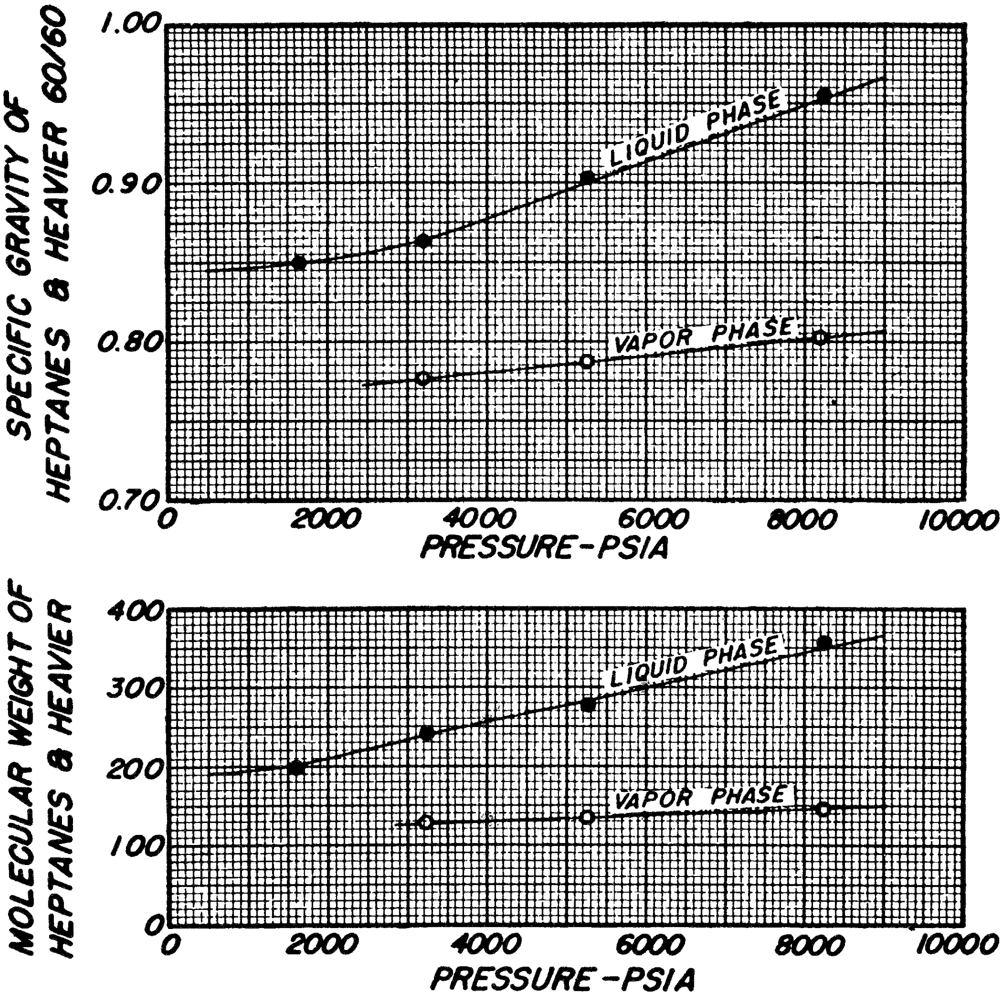


Fig. 10.2. Effect of Pressure on Specific Gravity and Molecular Weight of Heptanes and Heavier [6] (After Standing and Katz, Trans. AIME, 1944)

At 4000 psia, for example, the equilibrium was between 130 molecular weight material in the vapor phase and 255 molecular material in the liquid phase. Increasing the pressure to 6000 psia caused the lighter portions of the liquid heptanes plus material to transfer to the vapor, raising the molecular weight of the vapor heptanes plus from 130 to 138. In so doing, the heptanes plus remaining in the liquid phase increased from 255 to 300. Therefore it is apparent that at, 6000 psia the heptanes plus equilibrium constant is for a material completely different from the material in equilibrium at 4000 psia. As a result, the log K-log P curve of the heptanes plus fraction has a shape different from that of the pure compounds in the system.

At present there are too few data with which to study the pressure behavior of the plus fraction. The explanation offered above is logical and, on the basis of the explanation, it is expected that the effect would be more noticeable when approaching dew point conditions than when near bubble points.

10.4. Construction of Log K-Log P Curves

At pressures less than 1000 psia, the influence of system composition on the equilibrium constant values usually is small. Calculations concerned with dissolved gas systems normally are made by using equilibrium constants determined by Katz and Hachmuth" for mixtures of natural gas and crude oil from the Oklahoma City field. The equilibrium constant data of Roland, Smith, and Kaveler [5] are used for condensate system calculations. Often these data are used also for dissolved gas and condensate system calculations at pressures above 1000 psia.

Above 3000 psia, the data of Katz and Hachmuth [7]and of Roland, Smith, and Kaveler [5]become less useful because of the apparent convergence of the constants near 4000 psia. It therefore becomes necessary to employ several empirical factors, in addition to pressure and temperature, to evaluate the constants in and above this pressure region.

Gilliland and Scheeline [8] and Brown and White [9] have shown how the apparent convergence pressure and the general shape of the log K – log P isotherms can be used to estimate equilibrium constants when experimental data are lacking. Referring to the general-shape curves shown in Fig. 10.3, it can be seen that the components of a system can be divided into two groups.

(1).The first group, referred to as more volatile components, contains those components whose equilibrium constants are never less than unity.

(2) The equilibrium constants of the less volatile components comprising the second group have minimum values, as well as two values of unity, one at the apparent convergence pressure and the other at the vapour pressure of the component. Thus, in the example shown in Fig. 10.3, the equilibrium constant of butane has a minimum value of 0.32 at about 1500 psia and unity values at 4000 psia and 180 psia.

Brown and White [9] found that by using the ratio of the apparent convergence pressure to the vapor pressure as one correlating factor, a correlation could be obtained with the ratio of the pressure for minimum K to the apparent convergence pressure. In other words, the ratio of distance C, Fig. 10.3, to distance A can be used to obtain an estimate of the ratio of the distance B to distance C. Referring to the correlation of these factors shown in Fig. 10.4, the value of the ordinate of the example cited above is 4000/180 = 22.2. From the correlation, the ratio of the minimum K pressure to the apparent convergence pressure is found to be 0.28. Therefore the pressure at which the minimum butane K occurs is 4000 · 0.28 = 1120 psia.

The ratio of the apparent convergence pressure to the vapor pressure of a component also has been correlated to give values of the minimum constant. Referring to Fig. 10.5, the minimum value of the butane constant in the example is 0.37. The equilibrium constants of other less volatile components can be obtained in like manner by using the apparent convergence pressure of the system and the vapor pressures of the component (from Handbooks).

The equilibrium constants of the more volatile components cannot be correlated by the methods outlined above. Sage, Hicks, and Lacey [10] have presented methane equilibrium constants as a function of the average molecular weight of the less volatile components in the system. Their correlations can be used at pressures below 1500 psi to define the general course of the methane curve. At pressures approaching the apparent convergence pressure, it usually is necessary to sketch in the curve.

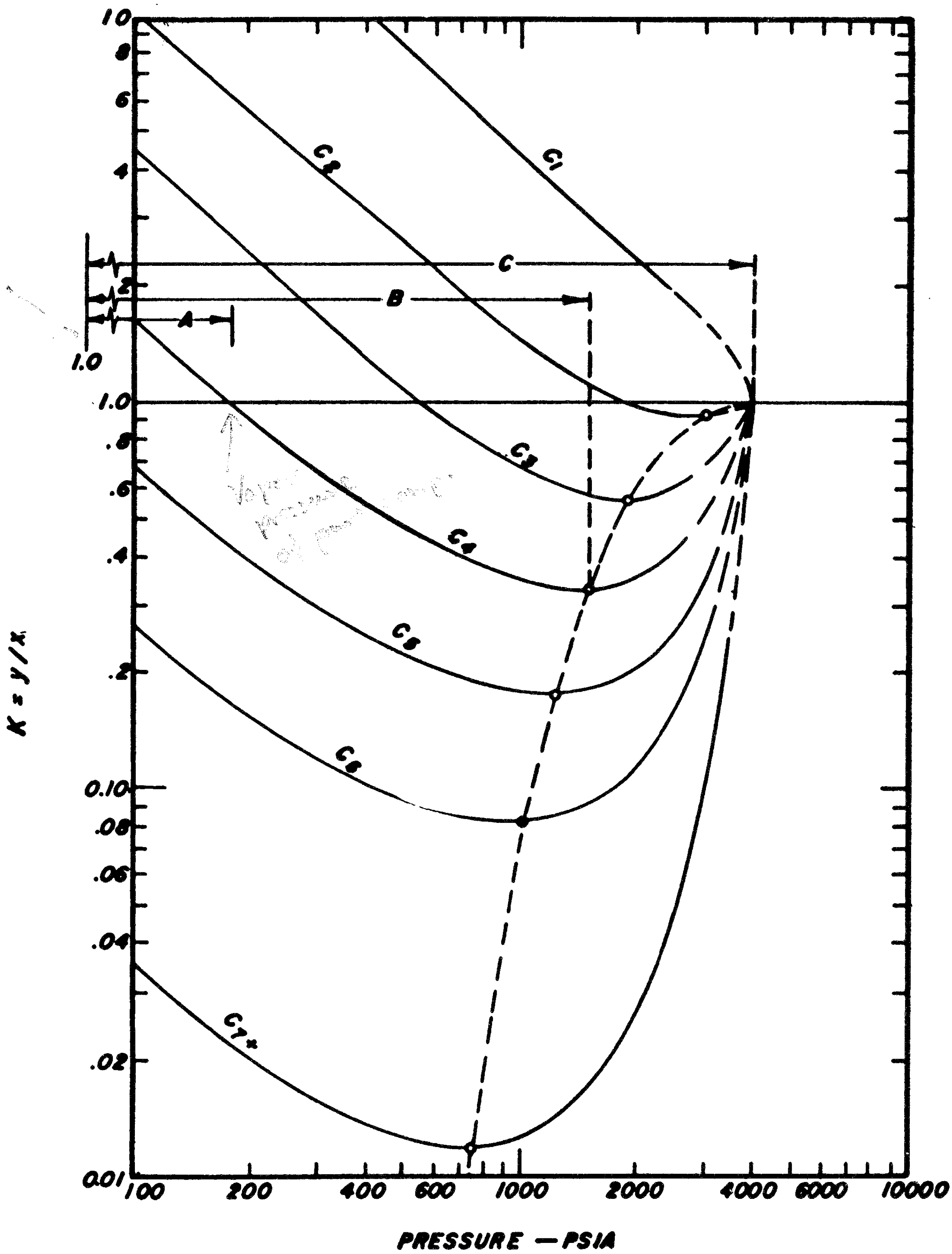


Fig. 10.3. Sketch illustrating Method of Constructing Equilibrium Constant-Pressure Isotherms.

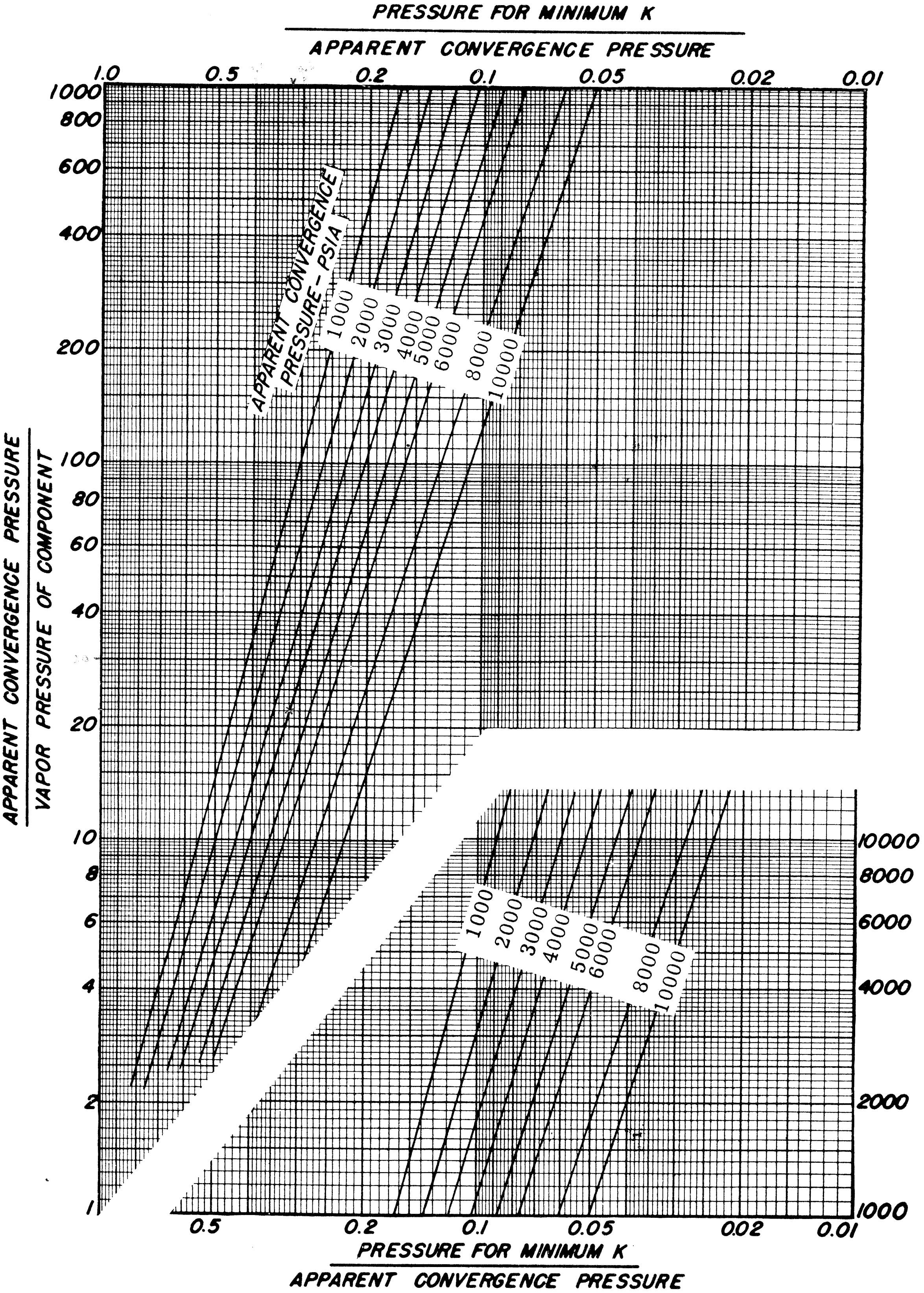


Fig.10.4. Correlation of the Pressure at Which the Minimum Equilibrium Constant Occurs with the Ratio of Apparent Convergence Pressure to the Vapor Pressure of the Component

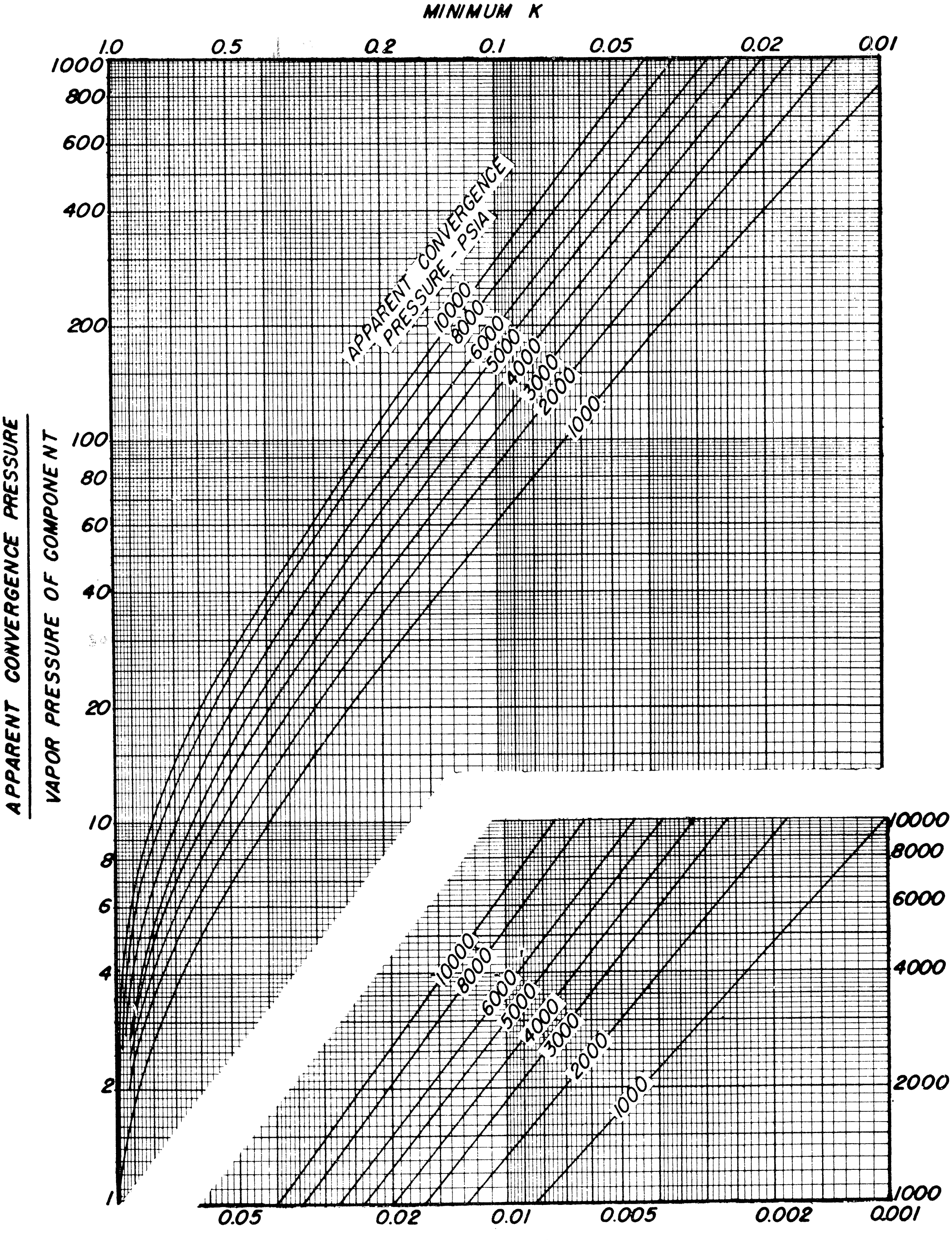


Fig. 10.5. Correlation of Minimum Equilibrium Constant with the Ratio of Apparent Convergence Pressure to the Vapor Pressure of the Component

One major difficulty hinders the use of the correlations presented in Fig. 10.4 and Fig. 10.5 to determine K's for systems occurring in petroleum reservoirs. At the present time the apparent convergence pressure of a system cannot be evaluated from the composition of the system. Consequently, while Fig. 10.4 and Fig. 10.5 will assist one to draw log K – log P isotherms, there is no direct way of knowing whether valid curves have been constructed for the particular system being studied. If PVT data are available from which to predict bubble point or dew point pressures, the selection of an apparent convergence pressure is simplified because the apparent convergence pressure must be higher than a bubble point or dew point pressure. The question then is: When the composition of a system is known, what is the procedure for determining constants for use at high pressures? The following proposed method leans heavily on the construction of curves "by eye." The absence of other published methods or correlations almost forces the use of this or some comparable method.

(1) Katz and Hackmuth's constants are accepted for use with dissolved gas systems. Roland, Smith, and Kaveler's constants are applied to condensate systems. When PVT data are available to define the bubble point or dew point pressure of the system, the constants are modified so that the calculated bubble point (or dew point) pressure is in agreement with the experimentally determined bubble point pressure. The modifications involves the following steps:

  (a) The published data at the desired temperature are plotted on log K – log P coordinates. The bubble point pressure is then calculated, using the unmodified data. This procedure establishes a set of constants that will give a calculated bubble point, although the calculated bubble point pressure and the experimental bubble point pressure may not agree. By using the unmodified data, the experimentally determined relationship of the constants to each other is maintained.

  (b) The set of K's that satisfactorily calculate a bubble point condition are then plotted at the experimentally determined bubble point pressure. Curves are sketched in through these values to give an approximate apparent convergence pressure.

  (c) The locations of the minimum K values are determined by use of Fig. 10.4 and Fig. 10.5, the estimated apparent convergence pressure, and vapor pressure values of the individual components.

  (d) Smooth curves are drawn that connect the apparent convergence pressure, the bubble point pressure, the minimum K values, and the vapor-pressure points. In the low pressure region the curves are given slopes of 45 degrees.

  (e) If the curves do not look right, the apparent convergence is changed slightly and another set of curves is constructed. This is continued until a set is obtained that has the appearance of those illus trated in Fig. 10.3.

  (f) The methane equilibrium constant curve is constructed parallel to the unmodified curve at pressures below 1000 psia. The curve is brought into the apparent convergence pressure, maintaining the form illustrated in Fig. 10.3.

(2) When PVT data are not available to give the bubble point pressure, apparent convergence pressures are assumed roughly as follows:

Molecule weight M of C7+ fraction	Apparent Convergence Pressure (psia)
120	3000
170	6000
220	9000

Admittedly, the above method has many faults. However, in the region of pressures wherein the system composition influences the equilibrium constants, it is better to use such a method of taking into account the system composition than to neglect the effect completely.

10.5. Equilibrium constants in Vapor-Liquid Equilibrium calculations

The use of equilibrium constants makes possible the calculation of bubble point pressures, dew point pressures, and the proportions of vapor and liquid in equilibrium at pressures and temperatures where two phases can exist. The mathematical equations used in making these calculations are derived in the following section.

10.5.1 Flash Vaporization of a System.

In all calculations it is assumed that the system is in thermodynamic equilibrium at the given temperature and pressure. The equations used for the calculation of the relative proportions of vapor and liquid are obtained from a material balance, as follows:

If we let

F = total moles in the system
V = total moles of gas at equilibrium
L = total moles of liquid at equilibrium
x = mole fraction of any component in the liquid
y = mole fraction of any component in the gas
n = mole fraction of any component in the system
$K = \frac{y}{x}$ = - equilibrium constant for any component

A material balance of the system gives:

$$F = L + V \tag{10.10}$$

A material balance of any component, k, gives :

$$n_k F = x_k \cdot L + y_k \cdot V \tag{10.11}$$

Substituting $x_k \cdot K_k$ for y_k in Eq. (10.11) and solving forx_k gives the mole fraction of the component k in the liquid phase:

$$x_k = \frac{F \cdot n_k}{L + V \cdot K_k} \tag{10.12}$$

At equilibrium, the mole fractions of the components in both phases must sum to unity, or:

$$\sum_{k=1}^{k=j} x_k = 1 \tag{10.13}$$

$$\sum_{k=1}^{k=j} y_k = 1 \tag{10.14}$$

Applying the requirements of Eq. (10.13) to Eq. (10.12),

$$\sum_{k=1}^{k=j} x_k = \sum_{k=1}^{k=j} \frac{F \cdot n_k}{L + V \cdot K_k} = 1 \tag{10.15}$$

A similar equation can be obtained by solving for the composition of the vapor phase. The equation is

$$\sum_{k=1}^{k=j} y_k = \sum_{k=1}^{k=j} \frac{Fn_k}{\frac{L}{K_k}+V} = 1 \tag{10.16}$$

Eq. (10.15) and Eq. (10.16) must be solved by trial and error methods. The calculations are simplified by letting F equal 1, in which case the sum of L and V must equal 1. The procedure is to assume a value of L or V and calculate values of $\frac{n_k}{L+V\cdot K_k}$. By plotting the summation of $\frac{n_k}{L+V\cdot K_k}$ against the assumed L or V and using the resulting curve to guide the next assumption, a satisfactory solution can be obtained, usually by the third trial. This procedure is illustrated in Example 10.1 by the calculation of the quantities and composition of vapor and liquid in equilibrium at 2000 psia and 218°F. [11]

Example 10.1.

Calculation of Equilibrium Quantities of Gas and Liquid Pressure = 2000 psia, Temperature = 218°F.

1	2	3	4	5	6	7
Comp.	Mole frac. n	K 2000 psia and 218°F	Assume L=0.790 V=0.210			Vapor comp. $y = K \cdot x$
			$V \cdot K$	$L + V \cdot K$	$\frac{n}{L + V \cdot K}$	
C1	0.4404	2.85	0.598	1.388	0.3173	
C2	0.0432	1.17	0.246	1.036	0.0413	
C3	0.0405	0.680	0.143	0.933	0.0434	
C4	0.0284	0.410	0.0860	0.876	0.0324	
C5	0.0174	0.244	0.0512	0.8412	0.0207	
C6	0.0290	0.150	0.0315	0.8215	0.0353	
C7+	0.4011	0.0160	0.00336	0.7934	0.5055	
	1.0000				0.9959	
			Assume L=0.776 V=0.2240			
C1			0.638	1.414	0.3114	
C2			0.262	1.038	0.0416	
C3			0.153	0.929	0.0436	
C4			0.0918	0.8678	0.0327	
C5			0.0546	0.8306	0.0210	
C6			0.0336	0.8096	0.0358	
C7+			0.00359	0.7796	0.5145	
					1.006	
			Assume L=0.778 V=0.222			
C1			0.632	1.410	0.3123	0.8901
C2			0.260	1.038	0.0416	0.0487
C3			0.151	0.929	0.0436	0.0296
C4			0.0910	0.869	0.0327	0.0134
C5			0.0542	0.8322	0.0209	0.0051
C6			0.0333	0.8118	0.0357	0.0054
C7+			0.00355	0.7815	0.5132	0.0082
					1.0000	1.0000

The calculations outlined in Example 10.2 and summarized in Fig. 10.6 illustrate a typical problem concerned with the separation of gas and liquid by surface traps. In Table 12 each stage separation involves the application of Equation (28) to the material entering that stage. From .experience it has been found easiest to treat each stage separately on the basis of one mole input to that stage. The actual quantities of vapor and liquid are calculated later from the results of the individual computations.

Example 10.2.

Example of Trap Separation of a Well Effluent

Primary Trap, 500 PSIA, 120°F

1	2	3	4	5
Comp	Well effluent n	K 500 psia and 120°F	Assume L=0.582 V=0.418	
			$\frac{n}{L+VK}$	$y = Kx$
C1	0.4404	8.1	0.1110	0.8991
C2	0.0432	1.65	0.0339	0.0560
C3	0.0405	0.59	0.0489	0.0288
C4	0.0284	0.23	0.0419	0.0096
C5	0.0174	0.088	0.0281	0.0025
C6	0.0290	0.039	0.0485	0.0019
C7+	0.4011	0.0030*	0.6877	0.0021
	1.0000		1.0000	1.0000

Secondary Trap, 65 PSIA, 120°F

1	2	3	4	5
Comp	Primary Trap Liquid n	K 65 psia and 120°F	Assume L = 0.844 V=0.156	
			$\frac{n}{L+VK}$	$y = Kx$
C1	0.1110	60.0	0.0109	0.6530
C2	0.0339	10.6	0.0135	0.1430
C3	0.0489	3.4	0.0355	0.1207
C4	0.0419	1.25	0.0403	0.0504
C5	0.0281	0.415	0.0309	0.0128
C6	0.0485	0.170	0.0557	0.0095
C7+	0.6877	0.013*	0.8132	0.0106
	1.0000		1.0000	1.0000

Moles secondary trap liquid per mole well effluent = 0.582 . 0.844 = 0.491

Moles secondary trap gas per mole well effluent = 0.582 . 0.156 = 0.091

*Equilibrium constant of C7+ assumed to be 0.15 times that of C7.[7]

Tank, 14.7 PSIA, 120°F

1	2	3	4	5
Comp	Secondary Trap Liquid n	K 14.7 psia and 120°F	Assume L = 0.844 V=0.156	
			$\frac{n}{L+VK}$	$y = Kx$
C1	0.0109	265	0.0007	0.1965
C2	0.0135	46.5	0.0038	0.1885
C3	0.0355	14.3	0.0210	0.3022
C4	0.0403	5.35	0.0330	0.1775
C5	0.0309	1.72	0.0299	0.0513
C6	0.0557	0.70	0.0566	0.0396
C7+	0.8132	0.052*	0.8550	0.0444
	1.0000		1.0000	1.0000

Moles tank oil per mole well effluent = 0.491 . 0.949 = 0.466

Moles tank vapors per mole well effluent = 0.491 . 0.051=0.025

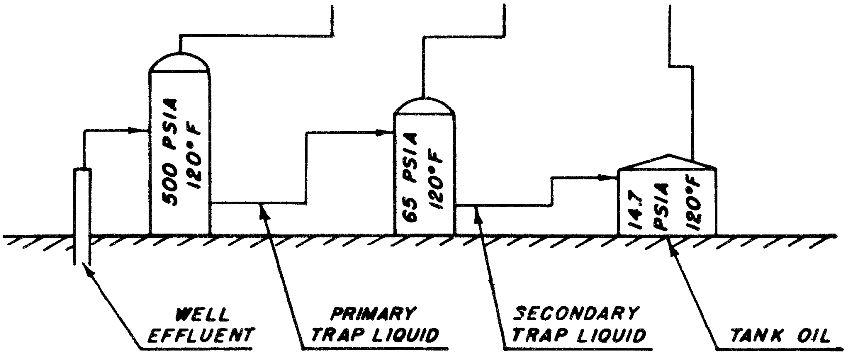
1	2	3	4
Comp	Tank Oil n	Lb mole /Gal 14.7 psia and 120°F	Gal/mole Tank Oil
C1	0.0007	0.129	-
C2	0.0038	0.104	0.04
C3	0.0210	0.0958	0.22
C4	0.0330	0.0821	0.40
C5	0.0299	0.0724	0.41
C6	0.0566	0.0641	0.88
C7+	0.8550	0.0263	32.53
	1.0000		34.48

$$\frac{bbl\ STO}{lb\ mole\ Well\ effluent} = \frac{0.466 \cdot 34.48}{42} = 0.383$$

Molecular Weight C7+= 287

Specific Gravity C7+ = 0.9071

	PRIMARY TRAP GAS	SECONDARY TRAP GAS	TANK VAPORS
METHANE	0.8991	0.6530	0.1965
ETHANE	0.0560	0.1430	0.1885
PROPANE	0.0288	0.1207	0.3022
BUTANES	0.0096	0.0504	0.1775
PENTANES	0.0025	0.0128	0.0513
HEXANES	0.0019	0.0095	0.0396
HEPTANES PLUS	0.0021	0.0106	0.0444
	1.0000	1.0000	1.0000
POUND MOLE.	0.418	0.091	0.025
GAS-OIL RATIO-CFB*	414	90	25
GAS GRAVITY-AIR=1	0.640	0.897	1.54



	WELL EFFLUENT	PRIMARY TRAP LIQUID	SECONDARY TRAP LIQUID	TANK OIL
METHANE	0.4404	0.1110	0.0109	0.0007
ETHANE	0.0432	0.0339	0.0135	0.0038
PROPANE	0.0405	0.0489	0.0355	0.0210
BUTANES	0.0284	0.0419	0.0403	0.0330
PENTANES	0.0174	0.0281	0.0309	0.0299
HEXANES	0.0290	0.0485	0.0557	0.0566
HEPTANES(+)	0.4011	0.6877	0.8132	0.8550
	1.0000	1.0000	1.0000	1.0000
POUND MOLE.	1.000	0.582	0.491	0.466 ≅ 0.383 BBL

TANK OIL GRAVITY = 27.4°API

*GAS-OIL RATIO = CU FT PER BBL TANK OIL

Fig. 10.6. Stage Separation of Well Production

10.5.2 Bubble Point Pressure of a System.

The bubble point of a system has been defined as the state at which an infinitesimal quantity of gas is in equilibrium with a large quantity of fluid. This definition leads to an equation for calculating the bubble point pressure of a system. Starting with Eq. (10.16), it can be seen that as the vapor quantity becomes infinitesimal.

$$V \to 0\,, \qquad L \to F\,, so\ that$$

$$\sum_{k=1}^{k=j} y_k = \lim_{V\to 0} \sum_{k=1}^{k=j} \frac{Fn_k}{\frac{L}{K_k} + V} = \sum_{k=1}^{k=j} K_k n_k = 1 \qquad (10.17)$$

Thus, to calculate the bubble point pressure of a system, it is necessary to determine by trial and error methods the pressure at which the summation of the products of the mole fractions of the entire system times the equilibrium constants is equal to unity. An example calculation illustrating this procedure is shown in Example 10.3. The composition of the bubble point vapor is given by the values of $K_k n_k$ in column 4.

Example 10.3.

Calculation of the Bubble Point Pressure of a Well Effluent at 218°F

1	2	3	4
Comp.	Well effluent mole frac. n	Assume pressure P = 3000 psia	
		Eq.Const K	Kn
C1	0.4404	2.15	0.9469
C2	0.0432	1.03	0.0445
C3	0.0405	0.672	0.0272
C4	0.0284	0.440	0.0125
C5	0.0174	0.300	0.0052
C6	0.0290	0.215	0.0062
C7+	0.4011	0.0235	0.0094
			1.0519

1	2	3	4
Comp.	Well effluent mole frac. n	Assume pressure P = 3200 psia	
		Eq.Const K	Kn
C1	0.4404	2.06	0.9072
C2	0.0432	1.025	0.0443
C3	0.0405	0.678	0.0274
C4	0.0284	0.448	0.0127
C5	0.0174	0.316	0.0055
C6	0.0290	0.230	0.0067
C7+	0.4011	0.0250	0.0100
			1.0138

1	2	3	4
Comp.	Well effluent mole frac. n	Assume pressure P = 3300 psia	
		Eq.Const K	Kn
C1	0.4404	2.02	0.8896
C2	0.0432	1.02	0.0441
C3	0.0405	0.680	0.0275
C4	0.0284	0.450	0.0128
C5	0.0174	0.323	0.0056
C6	0.0290	0.239	0.0069
C7+	0.4011	0.0260	0.0104
			1.0138

By interpolation, bubble point pressure P_b = 3280 PSIA.

10.5.3 Dew Point Pressure of a System.

The equation for the dew point condition can be developed from Eq. (10.15). Because the liquid phase is infinitesimal at the dew point state.

$$\sum_{k=1}^{k=j} x_k = \lim_{V \to 0} \sum_{k=1}^{k=j} \frac{F n_k}{L + V K_k} = \sum_{k=1}^{k=j} \frac{n_k}{K_k} = 1 \qquad (10.18)$$

The evaluation of the dew point pressure requires a trial and error solution in the same manner as the bubble point pressure. The values of $\frac{n_k}{K_k}$ give the composition of the dew point liquid.

10.5.4 Accuracy of Vapor-Liquid Calculations with equilibrium constants

The accuracy of calculated vapor and liquid quantities, using equilibrium constants and the over-all system composition, is dependent on the composition of the system, the relative proportions of vapor and liquid in equilibrium, and errors in the individual equilibrium constants. Because of the several variables, it is impossible to make a general statement regarding accuracy, but examples of several individual cases will illustrate a method of evaluating the effects of the variables.

The calculations in Example 10.4 show the effect that an error in any one equilibrium constant can have on the quantity of liquid phase computed by use of Eq. (10.15).

Example 10.4.

Errors in Equilibrium Constants on the Calculated Quantity of Liquid Phase in a Dissolved Gas System

1	2	3	4	5	6	7	8	9	10	11
Comp	Mole frac. n	K at 2000 psia and 218®F	Assume L = 0.770 V=0.230							Error in K %
			VK	$L+VK$	Liq. comp x	Adj.Liq. comp x′	$L+VK'$	VK'	K'	
C1	0.4404	2.850	0.6555	1.4255	0.3089	0.3064	1.4373	0.6673	2.901	+1.8
C2	0.0432	1.170	0.2691	1.0391	0.0416	0.0391	1.1048	0.3348	1.456	+24.4
C3	0.0405	0.680	0.1564	0.9264	0.0437	0.0412	0.9830	0.2130	0.926	+36.2
C4	0.0284	0.410	0.0943	0.8643	0.0328	0.0303	0.9372	0.1672	0.727	+77.3
C5	0.0174	0.244	0.0561	0.8261	0.0211	0.0186	0.9355	0.1655	0.720	+195.1
C6	0.0290	0.150	0.0345	0.8045	0.0360	0.0355	0.8656	0.0956	0.416	+177.3
C7+	0.4011	0.016	0.0037	0.7737	0.5184	0.5159	0.7775	0.0075	0.033	+106.2
	1.0000				1.0025					

NOTE: Correct liquid quantity is 0.778 mole fraction

The dissolved gas system having the composition shown in column 2 has been shown in Example 10.1 to form 0.778 mole fraction liquid and 0.222 mole fraction vapor at 2000 psia and 218°F. The equilibrium constants used to calculate these quantities are shown in column 3. Columns 4, 5, and 6 pertain to an erroneous calculation that assumes 0.770 mole fraction of the system is liquid. The fact that the summation of the mole fraction of the components in the liquid phase does not equal unity proves that L = 0.770 is an incorrect assumption. The adjusted mole fractions, x′, shown in column 7, are the values to which each component would have to be changed in order that L = 0.770 be judged a correct value. For example, if the mole fraction of methane in the liquid phase were 0.3064, rather than 0.3089, the summation of the mole fraction in the liquid phase would have been unity, and L = 0.770 would have been a valid assumption. Likewise, the conditions;

$$\sum_{k=1}^{k=j} x_k = 1$$

would be satisfied if the ethane liquid fraction were 0.0025 unit lower. Columns 8 and 9 present the calculation of $L + VK'$ and K', resulting from values of x' shown in column 7. The equilibrium constant, K' in column 10 is the value which, used with the correct constants of the other components, would cause a calculated liquid quantity of 0.770 mole fraction, rather than the correct value of 0.778 mole fraction. Thus, for the particular system at 2000 psia and 218°F, a +1.8 % error in the methane constant would cause a —1.0 % error in the calculated liquid quantity. To cause the same —1.0 % error in the calculated liquid requires that the pentane equilibrium constant be in error by +195.1 %.

Results of calculations similar to those presented in Example 10.4 are shown in Fig. 10.7, Fig. 10.8, and Fig. 10.9. The curves of Fig. 10.9 are of interest because they show that calculations near the dew point pressure of a condensate system can be influenced greatly by both the methane and heptanes plus equilibrium constant. For the particular conditions under study in Fig. 10.9, an error of —2.5% in the value of the methane equilibrium constant results in an error of +40% in the quantity of calculated liquid. An error of +8% in the same constant results in the calculation of a dew point state, rather than the correct 0.051 mole fraction liquid content. Errors in the heptanes plus constant, while not as drastic in their effect on calculated liquid volumes as errors in the methane constant, also cause large errors in the calculated phase quantities.

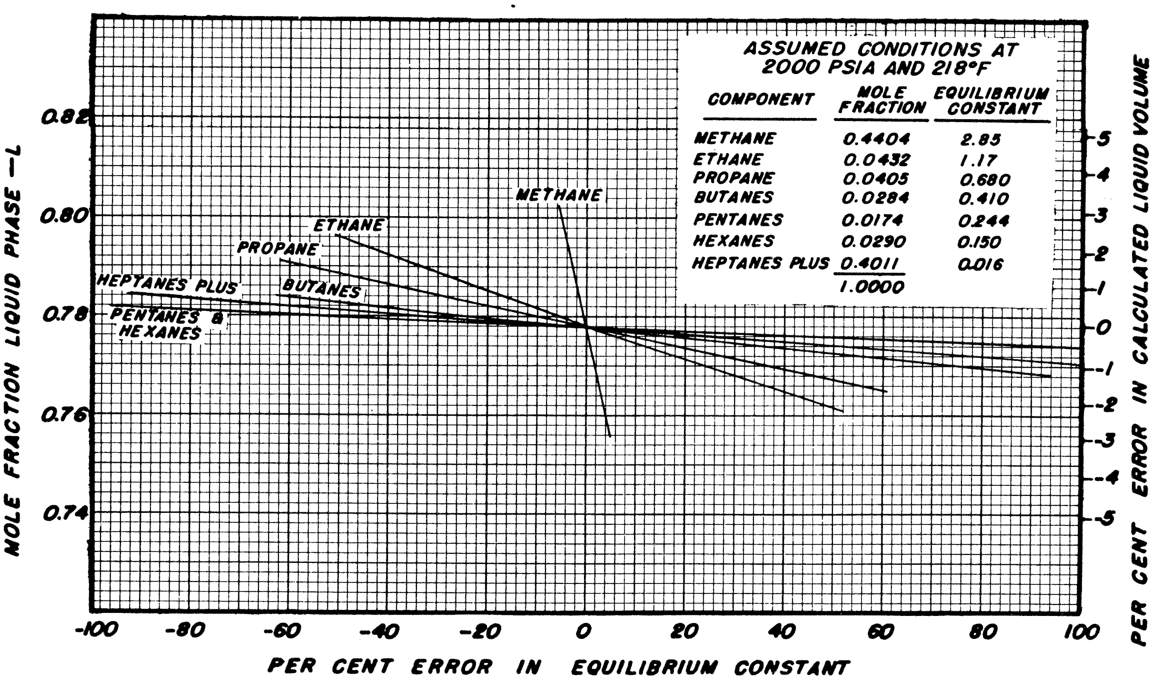
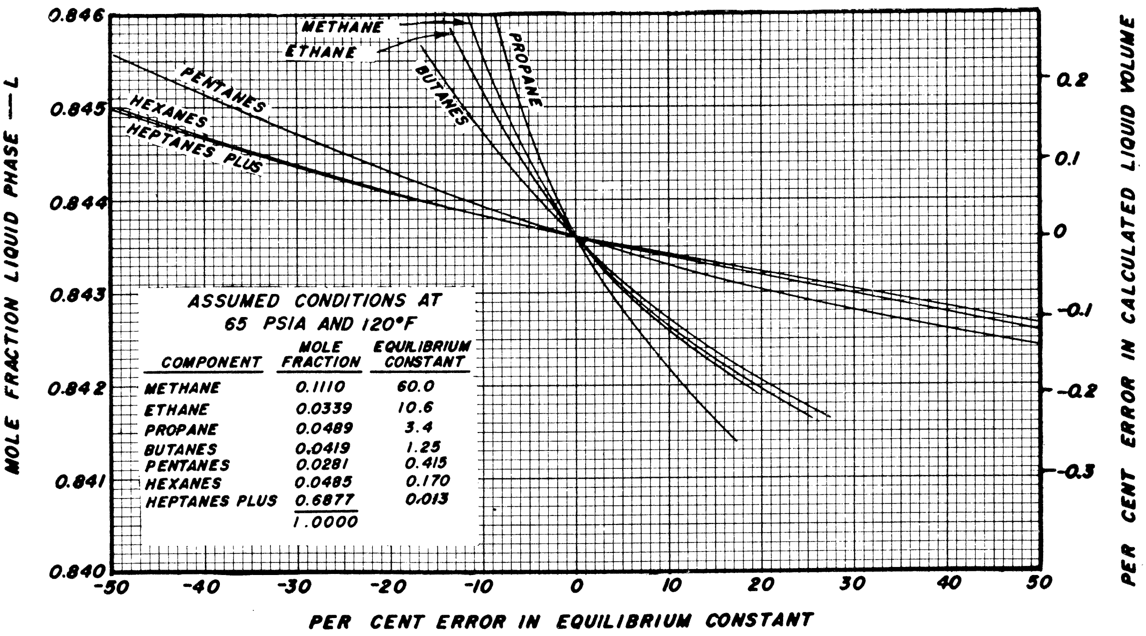


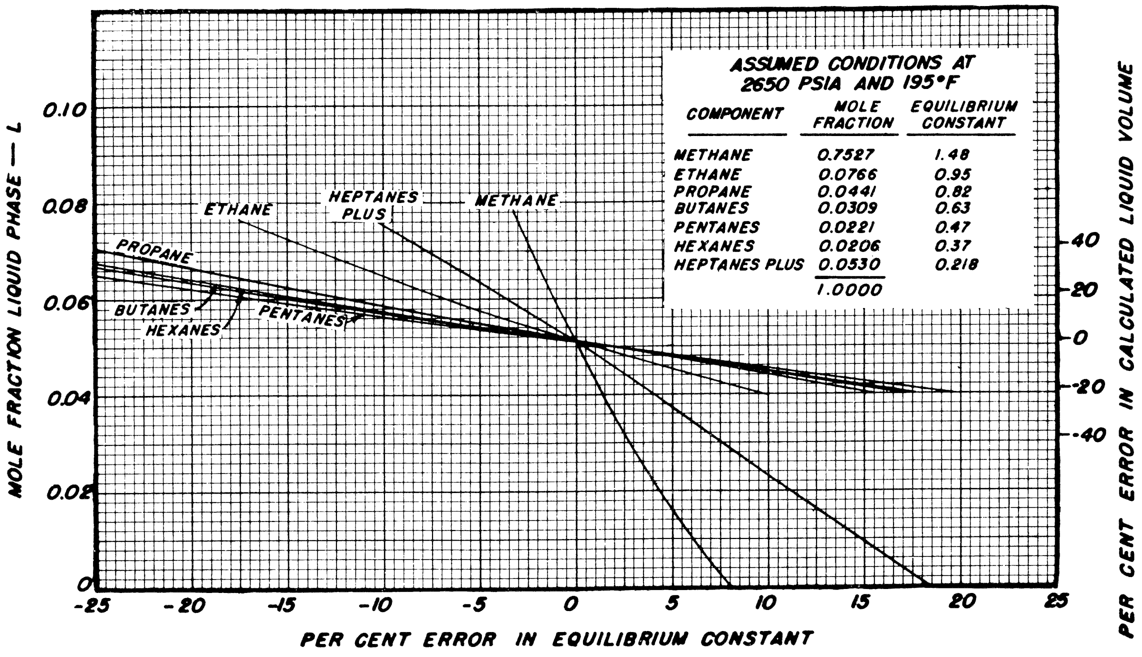
Fig. 10.7. Effect of Errors in Equilibrium Constants on the Calculated Quantity of Liquid Phase in a Dissolved Gas System



ASSUMED CONDITIONS AT 65 PSIA AND 120°F

COMPONENT	MOLE FRACTION	EQUILIBRIUM CONSTANT
METHANE	0.1110	60.0
ETHANE	0.0339	10.6
PROPANE	0.0489	3.4
BUTANES	0.0419	1.25
PENTANES	0.0281	0.415
HEXANES	0.0485	0.170
HEPTANES PLUS	0.6877	0.013
	1.0000	

Fig. 10.8. Effect of Errors in Equilibrium Constants on the Calculated Quantity of Liquid Phase in a Dissolved Gas System



ASSUMED CONDITIONS AT 2650 PSIA AND 195°F

COMPONENT	MOLE FRACTION	EQUILIBRIUM CONSTANT
METHANE	0.7527	1.48
ETHANE	0.0766	0.95
PROPANE	0.0441	0.82
BUTANES	0.0309	0.63
PENTANES	0.0221	0.47
HEXANES	0.0206	0.37
HEPTANES PLUS	0.0530	0.218
	1.0000	

Fig. 10.9. Effect of Errors in Equilibrium Constants on the Calculated Quantity of Liquid Phase in a Gas-Condensate System

10.6 Summary of Principal Points

The equilibrium constants, K, used in calculating the relative proportions and compositions of vapor and liquid in equilibrium are functions of pressure, temperature, and over-all composition of the system. As yet, too few systems have been investigated to determine the manner in which the system composition influences the equilibrium constants.

At pressures less than 1000 psia, the constants determined by Katz and Hachmuth are best for calculating the behavior of dissolved gas systems. Above 1000 psia, they may require some adjusting in order to be consistent with experimentally determined phase behavior.

Condensate systems are best handled by use of Roland, Smith, and Kaveler's constants. Major revisions of the constants may be required to give correct phase behavior in the high pressure region.

The fact that log K – log P isotherms appear to converge to unity should not be interpreted as meaning that the system is at its critical state. Equilibrium constants can converge only at the critical temperature of the system; at all other temperatures the convergence is an "apparent convergence."

Calculations of bubble point pressures and the relative phase volume near bubble point conditions are most sensitive to inaccuracies of the methane equilibrium constant. Calculations at or near dew point conditions are sensitive to inaccuracies of both methane and heptanes plus constants.

10.7 Equilibrium Calculations

Equilibriums between gas and Liquid are formed in the Reservoirs, through the process system in Separators, and at Standard conditions (SC). Calcuations of Vapor-Liquid (V/L) equilibriums are based on determining equilibrium constants (K_i) and partitioning constants of the individual compounds in the 2 phases.

Suppose that the system is in the two-phase region at given T and P. The calculations are based on 1 mole initial fluid.

The following equation are valid:

$$L + V = 1 \tag{10.19}$$

where

L: mole fraction of liquid
V: mole fraction of gas

and the total fluid composition could then be expresses by:

$$z_i = x_i L + y_i V \tag{10.20}$$

where

z_i: mole fraction of comp. i in the total fluid
x_i: mole fraction of comp. i in the liquid
y_i: mole fraction of comp. i in the gas

The equilibrium constant (K_i) could be expressed by

$$K_i = \frac{y_i}{x_i} \tag{10.21}$$

K_i: equilibrium constant of compounent i at given T and P

$$\sum x_i = \sum y_i = \sum z_i = 1 \tag{10.22}$$

10.7.1 Flash calculations

Suppose that the system is in the 2 phase region ant P and T as descrived in Fig. 10.10:

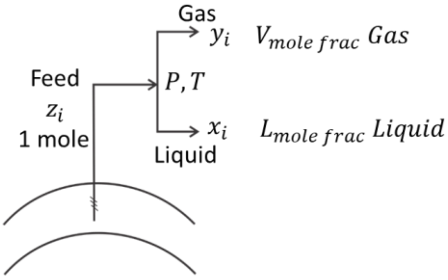


Fig. 10.10 Schematic figure describing a flash of reservoir fluid into a 2-phase region at P and T with gas and liquid.

Combining Eq. 10.20, Eq. 10.21, and Eq.10.22, gives:

$$\sum x_i = \sum \frac{z_i}{(L + K_i V)} = 1 \tag{10.23}$$

$$\sum y_i = \sum \frac{z_i}{\left(\frac{L}{K_i} + V\right)} = 1 \tag{10.24}$$

Eq. (10.23) and Eq. (10.24) are called “Flash Equations”, and they are not independent. One of the equations is solved by iteration, supposing values of L and V so that $L + V = 1$, until convergence is obtained. Each term in the flash equation is then similar to the composition of component i in the actual phase.

The iteration can be done by using the Newton-Ralphson method.

10.7.2 Calculation of bubble point, P_b

Bubble point (Pb) calculations could be performed by the use of Flash equations. Flash Eq. 10.24 could be used to describe the composition in the first bubble of gas that is formed when the pressure is reduced and bubble point is reached, Fig. 10.11.

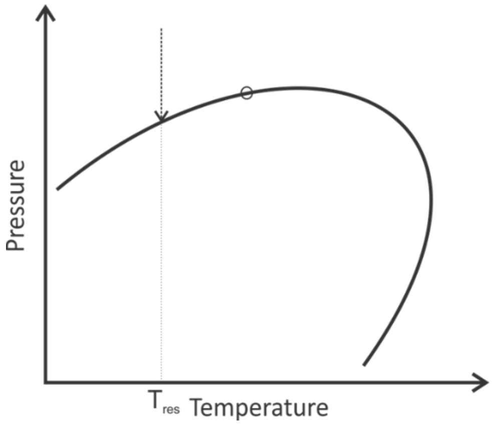


Fig. 10.11 Bubble point (P_b) deterimation at constant temperature (T_{res}). P_b reached when the first droplet of gas is formed.

$$\sum y_i = \sum \frac{z_i}{\left(\frac{L}{K_i} + V\right)} = 1$$

At the bubble point; $L = 1, V = 0$, and $x_i = z_i$ which gives :

$$\sum y_i = \sum z_i K_i = 1 \tag{10.25}$$

P$_b$ is determined by determine K$_i$ values at different supposed values of P$_b$ until convergence is obtained. As a rule of thumb:

if $\sum z_i K_i > 1 \Rightarrow two - phase\ region$

if $\sum z_i K_i < 1 \Rightarrow liquid\ phase$

10.7.3 Calculation of dew point, P$_d$:

Similary, dew point calculation could be performed using Flash calculations. Flash Eq. 10.23 could be used to describe the composition in the first droplet of liquid that is formed when the pressure is reduced and the dew point pressure is obtained, Fig.10.12.

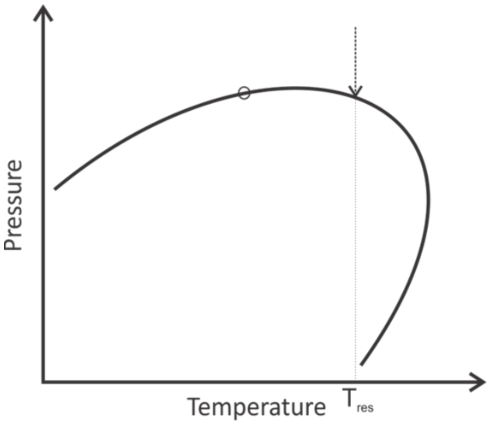


Fig. 10.12 Dew point (P$_d$) deterimation at constant temperature (T$_{res}$).
P$_d$ reached when the first droplet of liquid is formed.

$$\sum x_i = \sum \frac{z_i}{(L + K_i V)} = 1$$

At dew point: $L \approx 0,\ V \approx 1$, and $y_i = z_i$. Then Flash Eq.10.23 could be expressed as :

$$\sum x_i = \sum \frac{z_i}{K_i} = 1 \tag{10.26}$$

P$_d$ is determined by determining K_i values at different supposed values of P$_d$ until converge is obtained. As a rule of Thumb:as a rule of thumb:

if $\sum \frac{z_i}{K_i} > 1 \Rightarrow two - phase\ region$

if $\sum \frac{z_i}{K_i} < 1 \Rightarrow gas\ phase$

10.7.4 Separator Calculations

The equilibrium calculations are also used in separator calculations with a separator system consisting of k separators, as seen in Fig. 10.13.

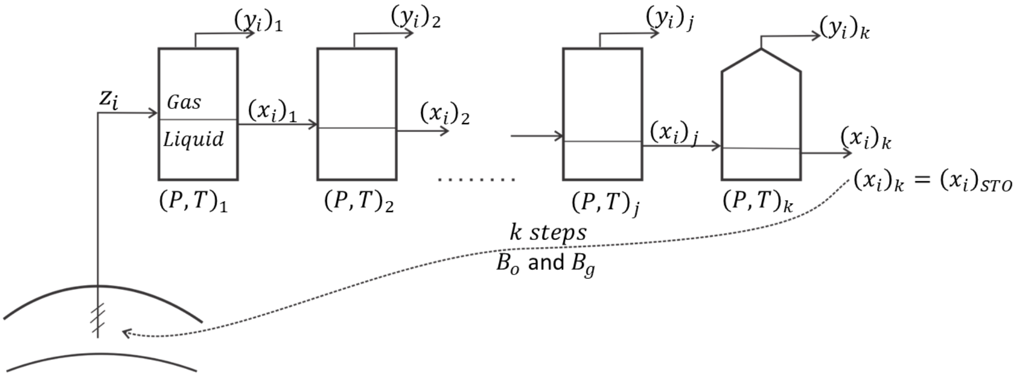
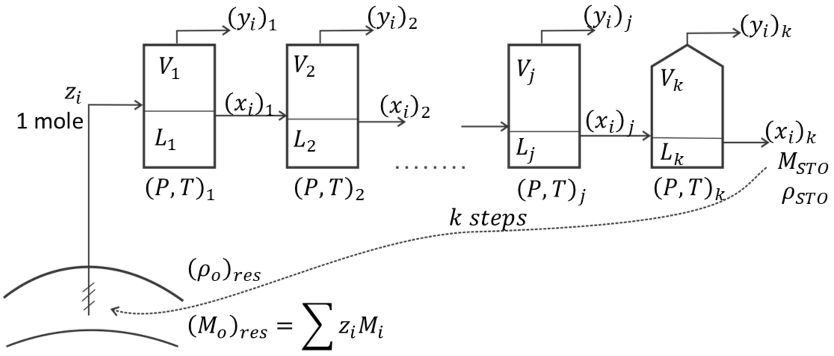


Fig. 10.13 Separator system with k separators

Based upon the compositional analysis of the reservoir fluid (z_i), the composition of gas and liquid from each of the separators at given values of T and P are calculated using the Flash Equations. Based on 1 mole reservoir fluid, calculation of the mole fractions of gas (V_j) and liquid (L_j) for each of the separators are performed using the flash equations. Notice that the feed for next separator is the composition of the liquid phase (x_i) in the former separator, Fig 10.14.



Fif. 10.14 Mole fraction of Gas (V_i) and Liquid (L_i) at each separator pressure stage.

The following equations are then valid for the liquid phase:

$$\begin{aligned}(n_o)_1 &= 1 \cdot L_1 \\ (n_o)_2 &= L_2 \cdot (n_o)_1 = L_1 \cdot L_2 \\ (n_o)_3 &= L_3 \cdot (n_o)_2 = L_1 \cdot L_2 \cdot L_3\end{aligned} \tag{10.27}$$

where :

$(n_o)_j$: mole fluid to separator j (j = 1, 2,....k)

L_j: mole fraction of liquid in separator j

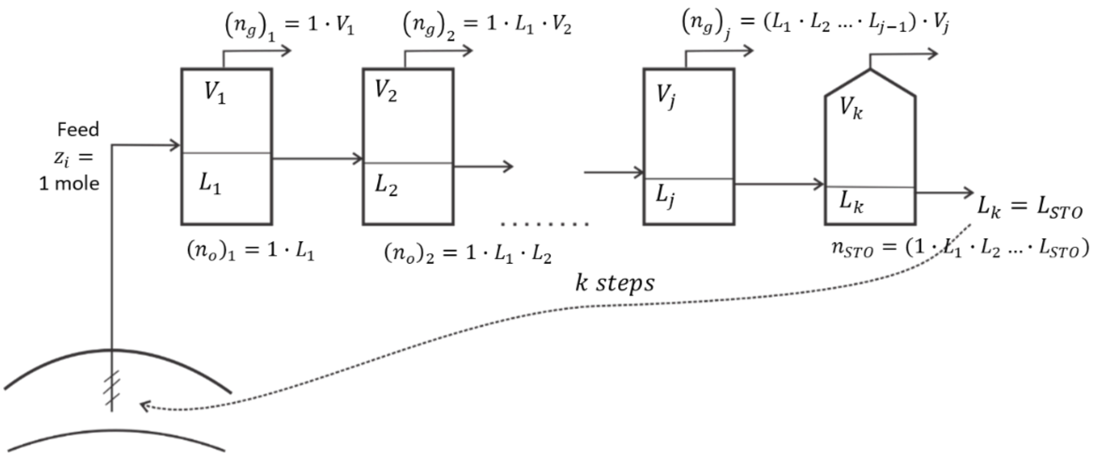


Fig. 10.15 Molar distribution of Gas and liquid in the separator system with k stages

The mole fraction of STO (n_{STO}) :

$$n_{STO} = (n_o)_k = L_1 \cdot L_2 \cdot L_3 \cdot \cdots\cdots \cdot L_k = \prod_{j=1}^{k} L_j \tag{10.28}$$

The total mole fraction of gas from the separators $\left((n_g)_{SC}\right)$ could be expressed by the equation:

$$(n_g)_{SC} = 1 - n_{STO} = 1 - \prod_{j=1}^{k} L_j \tag{10.29}$$

where the gas at each separator could be expressed by the following equations:

$$\begin{aligned}
(n_g)_1 &= 1 \cdot V_1 \\
(n_g)_2 &= L_1 \cdot V_2 = V_2 \cdot (n_o)_1 \\
(n_g)_3 &= L_1 \cdot L_2 \cdot V_3 = V_3 \cdot (n_o)_2 \\
(n_g)_j &= (L_1 \cdot L_2 \ldots \cdot V_{j-1}) \cdot V_j = V_j \cdot (n_o)_{j-1}
\end{aligned} \tag{10.30}$$

where:

V_j: mole fraction vapor in separator *j*

10.7.5 Calculation of GOR

Thus, based on 1 mole reservoir fluid it is easy to calculate $(V_g)_{SC}$, V_{STO}, total gas oil ratio, GOR, B_o. The total gas production, $(V_g)_{SC}$, culd be expresses by:

$$(V_g)_{SC} = (n_g)_{SC} \cdot V_m = \left(1 - \prod_{j=1}^{k} L_j\right) \cdot V_m \tag{10.31}$$

The STO production, V_{STO}, is equal to:

$$V_{STO} = \frac{m_{STO}}{\rho_{STO}} = \frac{n_{STO} \cdot M_{STO}}{\rho_{STO}} \tag{10.32}$$

and the total GOR could then be expressed by:

$$(GOR)_{tot} = \frac{(V_g)_{SC}}{V_{STO}} = \frac{(n_g)_{SC} \cdot V_m}{\frac{n_{STO} \cdot M_{STO}}{\rho_{STO}}} \tag{10.33}$$

The GOR at each separator stage j could could then be derrived from the equation:

$$(GOR)_j = \frac{(V_g)_j}{V_{STO}} = \frac{(n_g)_j \cdot V_m}{\frac{n_{STO} \cdot M_{STO}}{\rho_{STO}}} \tag{10.34}$$

This could be further derived by:

$$(GOR)_j = \frac{(L_1 \cdot L_2 \ldots \cdot L_{j-1}) \cdot V_j \cdot V_m}{\frac{(L_1 \cdot L_2 \ldots \cdot L_{j-1})(L_j \cdot L_{j+1} \ldots \cdot L_{STO}) \cdot M_{STO}}{\rho_{STO}}} = \frac{V_j \cdot V_m}{\frac{(L_j \cdot L_{j+1} \ldots \cdot L_{STO}) \cdot M_{STO}}{\rho_{STO}}} \tag{10.35}$$

Optimizing separator pressures during the process design is important for reduceing the GOR both at the individual separator stages, $(GOR)_j$, and the total GOR, $(GOR)_{tot}$ for the system.

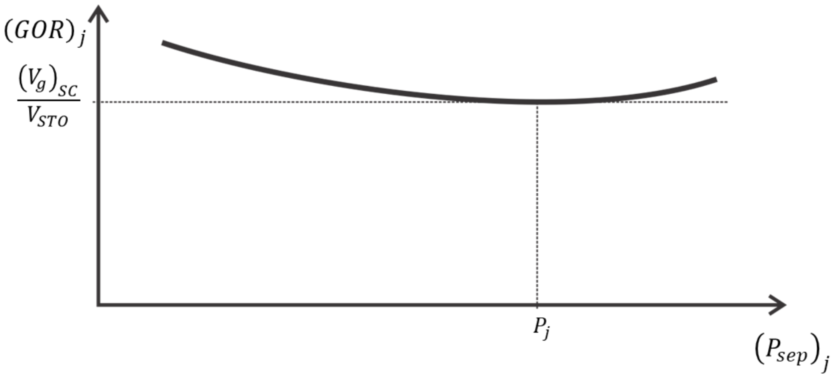


Fig. 10.16 Optimising separator pressures for lowest GOR

The separator temperatures are mainly controlled by the sorroundings.

10.7.5 Formation volume factors B_o and B_g from separator data

The data obtained during separator calculations could also be used to calculate the reservoir formation volume factors B_o and B_g.

The mole fraction of Gas (n_g) and STO (n_{STO}) at SC after separators are visualized in Fig. 10.17.

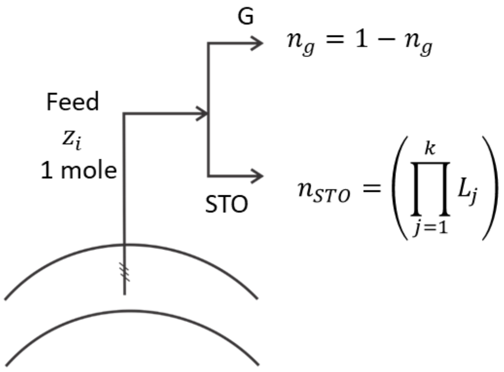


Fig. 10.17 Mole fraction of Gas (n_g) and STO (n_{STO}) at SC for after separators

The production of 1 mole reservoir fluid from an undersaturated oil reservoir would give a B_o factor:

$$B_o = \frac{(V_o)_{res}}{V_{STO}} = \frac{\frac{(m_o)_{res}}{(\rho_o)_{res}}}{\frac{n_{STO} \cdot M_{STO}}{\rho_{STO}}} = \frac{\frac{(n_o)_{res} \cdot (M_o)_{res}}{(\rho_o)_{res}}}{\left(\prod_{j=1}^{k} L_j\right) \frac{M_{STO}}{\rho_{STO}}} \tag{10.36}$$

where

$(M_o)_{res} = \sum z_i \cdot M_i$:

$(n_o)_{res}$ = mole res.fluid = 1

$(\rho_o)_{res}$: density of reservoir oil

M_{STO}: molecular weight of STO

ρ_{STO}: density of STO

$n_{STO} = \prod_{j=1}^{k} L_j$: mole fraction of STO

The B_o factor is larger than 1,and up to 2.5 for undersaturated Oil Reservoirs.

For wet gas rerservoirs or undersaturated gas condensate, theB_o could be expressed by:

$$B_o = \frac{(V_o)_{res}}{V_{STO}} = \frac{\frac{ZRT_{res}}{P_{res}}}{\frac{n_{STO} \cdot M_{STO}}{\rho_{STO}}} = \frac{Z \cdot R \cdot T_{res} \cdot \rho_{STO}}{P_{res} \cdot n_{STO} \cdot M_{STO}} \tag{10.37}$$

Where:

M_{STO}: molecular weight of STO

ρ_{STO}: density of STO

Z: compressibility factor of gas at T_{res} and P_{res}.

T_{res}: reservoir temperature (absolute)

P_{res}: reservoir pressure.

$n_{STO} = \prod_{j=1}^{k} L_j$: mole fraction of STO

The gas formation volume factor, B_g, will then be:

$$B_g = \frac{(V_g)_{res}}{(V_g)_{SC}} = \frac{\frac{Z \cdot n \cdot R \cdot T_{res}}{P_{res}}}{n_g \cdot V_m} = \frac{\frac{Z \cdot n \cdot R \cdot T_{res}}{P_{res}}}{(1 - n_{STO}) \cdot V_m} \tag{10.38}$$

where:

n_g: molefraction of gas

V_m: molar volume of gas at SC (379.51 SCF/lbmole or 23.6447 Sm^3/kgmole)

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