8. Vapor-liquid equilibrium

In the previous chapters, we have studied ways to compute either the density of a gas, or of a liquid at reservoir conditions. Knowing this density, we can compute the volume at reservoir conditions and are therefore able to compute formation volume factors of gas or oil.

But these methods cannot be used if in the reservoir we have liquid as well as gas, in other words, if we are in the two-phase region between the bubble point curve and the dew-point curve. Then we must first find out what compositions the liquid and the gas have. Once that is known, we can compute the appropriate densities and other interesting values such as the formation volume factor. We will see that analysis involves solving so-called equilibrium equations. In the computations we assume that the total mole fractions of the components (in liquid + gas) are known, as well as the temperature and pressure in the reservoir (or separator if we are interested in the composition there).

8.1 Formulating the equilibrium equations

The situation that we investigate in this chapter is as illustrated in figure 8-1:

Figure 8-1a:	At reservoir conditions, both liquid and gas co-exist.
Figure 8-1b:	In the separator, gas evolves from the liquid. Large volumes of gas are formed at separator conditions (density of gas quite low in general). The liquid volume shrinks because of decreased temperature and also because a portion of the fluid escapes into the gas phase.
Figure 8-1c:	The liquid and gas phases formed in the separator are withdrawn separately (which explains the name "separator"). The liquid enters the stock tank where further gas may evolve from it as additional temperature and pressure drops may occur.

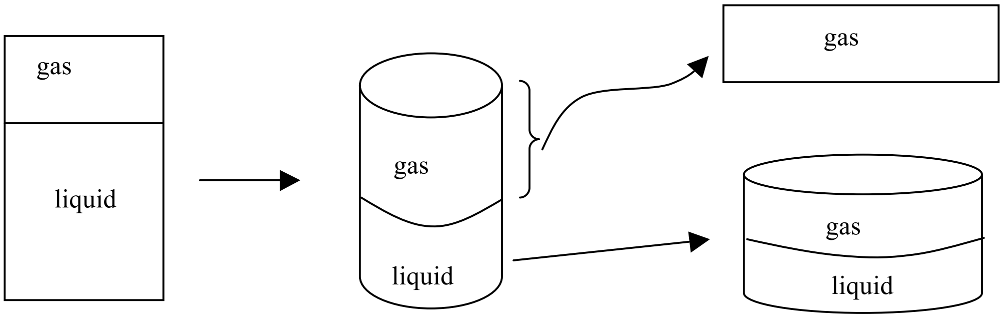


Fig 8-1 a: reservoir conditions; b: separator; c: stock tank

To find the equations that govern this problem we make use of two laws:

1. Dalton's law, which we have seen before.
2. Raoult's law.

Dalton's Law tells us that the partial pressure exerted by component j in a gas mixture is equal to the gas mole fraction y_j of the component times the total pressure. In other words,

$$p_j = y_j p.$$

Raoult's law states that for an ideal liquid solution, the partial pressure exerted in gas phase by a component is equal to the vapor pressure of that component times its mole fraction x_j in the liquid. This gives

$$p_j = x_j p_{vj},$$

where p_{vj} is the vapor pressure of component j.

When a gas and a liquid are in equilibrium, these partial pressures must be the same. In other words

$$y_j p = x_j p_{vj}, \quad \text{or}$$

$$\frac{y_j}{x_j} = \frac{p_{vj}}{p}.$$

This result is used to define the so-called equilibrium ratio K_j of the j-th component, as

$$K_j \equiv \frac{y_j}{x_j} = \frac{p_{vj}}{p}.$$

The K-values are determined experimentally as we will discuss in section 8.4. If we know the K-values of a mixture, then we can compute the composition of the gas and liquid in the two-phase region. K-values are very important in petroleum engineering, and will be revisited and discussed in great detail in the PE251 and PE255 courses.

What do you think K-values depend upon?

Please note that

- Dalton's law only holds for ideal gases. For practical purposes, the ideal-gas assumption limits the use the equations to pressures of about 100 psia and moderate temperatures.
- Raoult's law assumes that the liquid is an ideal liquid solution. This assumption can only be made if the components are similar.
- A pure component has a vapor pressure only up to its critical temperature.

This means that we have to be a little careful in our use of the above equations. We will discuss the consequences of these limitations in later sections.

We mentioned that if we know the K-values for some pressure and temperature we can find the composition of the gas and the liquid in that point in the two-phase region. We'll now set up the equations that tell us how this is done.

We define

n	total moles of both gas and liquid present at any p and T
n_L	total moles of material in the liquid phase
n_V	(in McCain this is n_g) total moles of material in the vapor phase
z_j	mole fraction of component j in the total mixture
x_j	mole fraction of component j in the liquid phase
y_j	mole fraction of component j in the vapor phase
K_j	ratio of y_j over x_j

We can now write down the following five equations:

(8.1) $$n = n_L + n_V,$$

(8.2) $$K_j = \frac{y_j}{x_j}.$$

Also,

(8.3) $$z_j n = x_j n_L + y_j n_V,$$

and

(8.4) $$\sum_j x_j = \sum_j y_j = \sum_j z_j = 1.$$

Convince yourself that all these equations are valid.

Substitution of equation (8.2) in (8.3) gives, after some reworking,

(8.5) $$x_j = \frac{nz_j}{n_L + K_j n_V}.$$

Similarly, we get

(8.6) $$y_j = \frac{nz_j K_j}{n_L + K_j n_V}.$$

Substitution of these expressions in equation (8.4) gives

(8.7) $$\sum_j \frac{nz_j}{n_L + n_V K_j} = 1, \quad \text{or}$$

(8.8) $$\sum_j \frac{nz_j K_j}{n_L + K_j n_V} = 1.$$

Equations (8.7) and (8.8) are two equations in the two unknown n_L and n_V, and can therefore be used to solve for these values. When we know these, we can find x_j and y_j (assuming of course that we know the total mole fractions z_j).

Alternatively, these equations can be subtracted from each other. This gives

(8.9) $$\sum_j \frac{(K_j - 1) nz_j}{(K_j - 1) n_V + n} = f(n_V, K_j, z_j) = 0.$$

This is one equation in one unknown. It can be used to solve for n_V, which in turn leads to n_L and so to x_j and y_j.

8.2 Solving the equilibrium equations

We can solve for the equilibrium values using either equation (8.9), or equations (8.7) and (8.8). If we use (8.9) the problem boils down to finding the zero of the function f. This can be done using standard software packages (or you can write your own method using, for example, the regula falsi method).

Solving equations (8.7) and (8.8) can be done in an iterative fashion. A possible procedure is:

1. Find K_j for the given p, T and composition
2. Guess n_L if you think that liquid is the major mole fraction, otherwise guess n_V
3. Evaluate the left hand side of equation (8.7), so compute the x_j's and sum the values. If you are working with n_V, use equation (8.8).
4. If this sum is not equal to 1, repeat steps 2-4 with a different guess for n_L

A separator is at 35 psia and 40 °F. The following total mole fractions are found in the separator (the K-values at 35 psia and 40 °F are given also):

Component	***total mole fraction***	***K-values at***
C1	*0.3396*	*61.0*
C2	*0.0646*	*9.00*
C3	*0.0987*	*2.20*
C4	*0.0434*	*0.610*
C5	*0.0320*	*0.157*
C6	*0.0300*	*0.0350*
C7+	*0.3917*	*0.0032*

(Note, here the C4 and C5 values are averages of iso- and n-. The C7+ is treated as octane).

Compute the liquid and gas mole fractions.

A spreadsheet that could be used in this iterative process is shown in figure 8-2 and is available on the Q-drive as well.

	A	B	C	D	E	F
1				n_L=	n_V=	
2				**0.521**	**0.479**	
3						
4		z_j	K_j	$x_j=z_j/(n_L+K_jn_V)$	$y_j=z_jK_j/(n_L+K_jn_V)$	$y_j=K_jx_j$
5	**C1**	3.396E-01	6.100E+01	1.142E-02	6.966E-01	6.966E-01
6	**C2**	6.460E-02	9.000E+00	1.337E-02	1.203E-01	1.203E-01
7	**C3**	9.870E-02	2.200E+00	6.267E-02	1.379E-01	1.379E-01
8	**C4**	4.340E-02	6.100E-01	5.337E-02	3.256E-02	3.256E-02
9	**C5**	3.200E-02	1.570E-01	5.367E-02	8.427E-03	8.427E-03
10	**C6**	3.000E-02	3.500E-02	5.579E-02	1.953E-03	1.953E-03
11	**C7+**	3.917E-01	3.200E-03	7.496E-01	2.399E-03	2.399E-03
12						
13	**Total**	1.000E+00		9.999E-01	1.000E+00	1.000E+00

The user inputs the guess for n_L in cell D2. Column D computes x_j. The guess shown gives a very good agreement (sum of x_j's sum to 1).

In this example, we used n_L and computed the xj values. The y_j values can be computed using $y_j=x_jK_j$. This is done in column F. In column E we compute y_j using equation (8.2). Both columns add up to 1. This shows that there is also excellent agreement for the y_j's. This may not always be the case. If the K-values are not accurate (they are determined experimentally so may suffer from measurement errors) we may find that the sum of the y-values does not exactly add up to 1.

If there is no convergence of the method, it may be that either the K-values are very inaccurate, or that we are not actually in the two-phase region. There is a simple test to find out if we are, which we will discuss below. First, let's see what happens if we are at the boundary of the two-phase region.

8.3 The two-phase region and its boundaries

The two-phase region is bounded by the dew-point curve and the bubble-point curve. What happens at these boundaries? Suppose that the liquid is at bubble point, can we determine the composition of the first vapor to form? Suppose that the vapor is at its dew point, can we determine the composition of the first liquid drops to form?
To answer these questions let's find out what happens to the equations (8.1) through (8.5) at these points.

Bubble-point

At the bubble point, the total number of moles in the vapor phase is zero, so

$$n_V = 0.$$

This gives immediately in equation (8.3) that

$$z_j = x_j.$$

In turn that leads to

$$y_j = K_j z_j,$$

where y_j gives the composition of the first vapor to form. Also, from (8.4), we see that

$$\sum_j z_j K_j = 1. \tag{8.10}$$

Dew-point

At the dew point, the total number of moles in the liquid phase is zero, so

$$n_L = 0.$$

Equation (8.3) now gives that

$$y_j = z_j.$$

Therefore

$$x_j = z_j/K_j,$$

where x_j gives the composition of the first drops to form. From equation (8.4) we see that

$$\sum_j \frac{z_j}{K_j} = 1. \qquad (8.11)$$

Finding the bubble point and dew point

The equations that we just found are unique for the bubble point pressure and the dew point pressure. We can therefore use them to find the bubble point or dew point pressure of a substance. This is quite a cute application of the equations. Let's see how it works. We know that at the bubble point pressure, $\sum_j z_j K_j = 1$. So if for a set of K values this equation holds we know that the pressure for which we have these K-values is the bubble point pressure. Of course the K values can only be found if we know the pressure, so it seems that we are in a catch-22 again. But, we can step out of this using an iteration:

Step 1. Guess a bubble point pressure p_b.

Step 2. Determine K_j.

Step 3. Evaluate $\sum_j z_j K_j$. If this sum is not equal to 1, repeat steps 1-3 with a new intelligent guess.

In a similar fashion, the dew point pressure can be found.

Are we inside the two-phase region?

The procedure outlined to find the equilibrium compositions in the two-phase region will of course only converge if the mixture is indeed in the two-phase region at the given pressure and temperature. Can we check this beforehand?

We know that at the bubble-point $\sum_j K_j z_j = 1$. The mixture will be all liquid if the selected temperature is less than the bubble-point temperature, or if the selected pressure is greater than the bubble-point pressure. It can be shown that this will be the case if $\sum_j K_j z_j < 1$.

Similarly, we know that at the dew-point $\sum_j z_j / K_j = 1$. The mixture will be all gas if the selected temperature is greater than the dew-point temperature or the selected pressure is less than the dew-point pressure. It can be shown that this situation occurs for $\sum_j z_j / K_j < 1$.

So, to ensure that the z- and K-values we have indeed correspond to condition in the two-phase region we should check that $\sum_j K_j z_j > 1$, and $\sum_j z_j / K_j > 1$. Check this before you perform any equilibrium calculations.

8.4 A closer look at the K-values

Combining Dalton's law and Raoult's law we can write

$$(8.12) \qquad K_j = \frac{p_{vj}}{p},$$

for ideal solutions. This equation would tell us that the K-values only depend on pressure and temperature (because the vapor pressure is solely a function of temperature). In reality the mixture will not be ideal. Therefore K-values will also depend on the types of molecules present and their quantities in the gas and liquid. But for low pressures and temperatures equation (8.12) can be used to estimate the K-values. In McCain examples 12-1 and 12-4, a comparison is made between computations using (8.12) to find the K-values, and computations with more accurate, experimentally determined, K-values. A difference of 10 percent in the computation of n_L was found. This is quite substantial.

What does a typical curve for K-values as function of pressure look like? Below is an example for various hydrocarbons at three different temperatures. The experimental data are shown as dots. Experimentally determined K-values normally are plotted against pressure on a log-log scale as is done here.

The shapes of the K-value curves in figure 8-2 are typical of most multicomponent mixtures. At low pressures, the slope of each curve is approximately –1.

Check that this is the slope predicted by equation (8.12).

At higher pressure the non-ideal behaviour is seen. The curves tend to converge toward a K-value near 1.0. If the mixture is at its critical temperature, the curves will converge to exactly 1.0.

Why a value of 1.0?

The value of pressure for which the K-factors appear to converge to unity is known as the *convergence pressure.* For the critical temperature, this convergence pressure is in fact the critical pressure. At any temperature other than the critical temperature, the K-value curves actually do not extent past the bubble-point or dew-point pressure of the mixture. The curves can be extrapolated however to determine the point of apparent convergence.

The convergence pressure is not equal to the critical pressure of the mixture, but it does characterize the properties of the mixture and is therefore very useful to estimate. More about this in section 8.5.

We note that instead of equation (8.12) the K-values can also be computed from the fugacity f_j of a component. The fugacity is a thermodynamic quantity that defines the change in free energy, or chemical potential, that is required to pass from one state to another state. K_j can be defined as

$$(8.13) \qquad K_j = \frac{f_{Lj}}{f_{Vj}}.$$

The fugacity definition of K_j can be extrapolated higher above the pure substance critical point than can the vapor pressure definition. This will be discussed in detail in PE251.

On the side: Free energy, or Gibbs free energy, is the amount of energy that is available in a system to do work. The free energy per mole is also referred to as the chemical potential. A chemical potential can also be seen as a measure of the escaping tendency of a component in a solution.

8.5 Determining the convergence pressure

We start by emphasizing again that, at any temperature other than the critical temperature, the K-value curves do not actually extend past the two-phase region enclosed by the bubble point and dew point pressures of the mixture. The parts of the curves outside the two-phase region are simply obtained by extrapolation.

At the high pressure end, the extrapolated curves seem to meet in one point which is called the *point of apparent convergence*. The pressure in this point is called the *convergence pressure*, or the *apparent convergence pressure*, and is denoted by p_k. The K-values in the points of apparent convergence are 1.0 (as is the case at the critical point).

The convergence pressure determined by extrapolation is not always very accurate. If the operating pressure is close to the possible convergence pressure, it is important to get a more accurate value of the convergence pressure, so that a more accurate K-value curve can be found. Here, we discuss a possible approach. If the operating pressure is much less than the convergence pressure is likely to be, then an accurate estimate of the convergence pressure is not at all necessary.

The convergence pressure of the hydrocarbon mixtures found in oil fields generally depends on temperature and the liquid phase composition. So again we are in a catch 22 situation: to determine the convergence pressure we must know the liquid phase composition, but to determine the liquid phase composition we must solve the equilibrium equations which require the K-values which require the location of the convergence pressure. Again, a trial and error approach can be used to solve this problem:

Step 1. Get a first rough estimate for the convergence pressure. This first guess may be obtained using the formula

$$p_k = 60M_{C7+} - 4200,$$

where M_{C7+} is the molecular weight of heptane+.

Step 2 Solve the equilibrium equations.

Step 3. Split the mixture into C1 and C2+. Compute the weight averaged critical pressure and temperature of the C2+ mixture (note: these are NOT the pseudo critical values. Pseudo critical values were mole averaged, not weight averaged).

Step 4. Go to figure 8-3. This figure gives the critical loci of convergence pressures for binary mixtures. Find the point in this graph corresponding to the weight averaged critical pressure and temperature computed in step 3.

Step 5. Trace the closest locus to the point (or interpolate between the closest curves) and find the pressure on this locus corresponding to the temperature of the mixture. Take this pressure as the new convergence pressure. If this convergence pressure is very different than the first guess, repeat steps 1-5 with a new guess.

Example: The compositions of a gas and liquid mixture at a pressure of 1300 psia and a temperature of 160 F are calculated with an estimate of the convergence pressure of 5000 psia. The values obtained are listed below. Was this a good first estimate?

Component	***xj***	***yj***
C1	*0.2752*	*0.8705*
C2	*0.0730*	*0.0806*
C3	*0.0390*	*0.0217*
i-C4	*0.0151*	*0.0052*
n-C4	*0.0442*	*0.0122*
i-C5	*0.0178*	*0.0029*
n-C5	*0.0247*	*0.0033*
C6	*0.0259*	*0.0018*
C7+	*0.4851*	*0.0018*

Properties of C7+:

Specific gravity	*0.8600*
Molecular weight	*225 lb/lb mole*

So here, steps 1 and 2 in the above procedure are already performed. Next, we split the mixture in C1 and C2+ and we determine the weight averaged critical pressure and temperature of the C2+ mixture. So first, we find the composition weight fraction of the components in the C2+ mixture given by

$$w_j = \frac{x_j M_j}{\sum_{j=2} x_j M_j}.$$

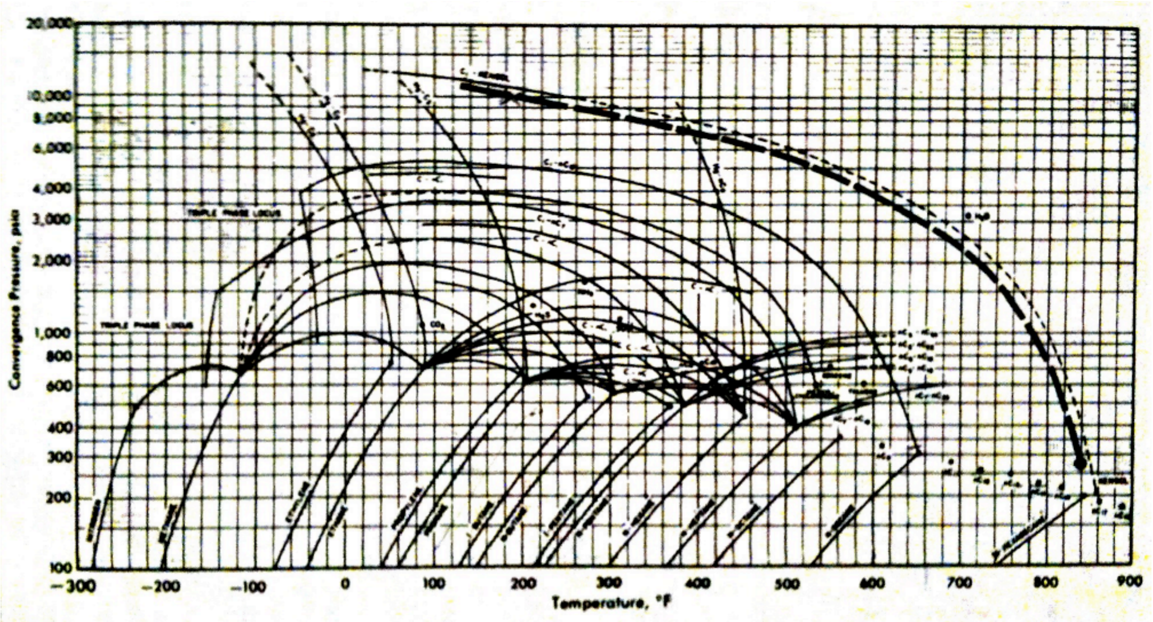
Then we compute the weight averaged critical temperature and pressure of the C2+ mixture using

$$\text{wt avg } T_c = \sum_{j=2} w_j T_{cj}, \quad \text{wt avg } p_c = \sum_{j=2} w_j p_{cj}.$$

If we do this for the given C2+ mixture, we obtain a weight averaged critical temperature of 1297 °R and a weight averaged critical pressure of 274 psia.

We plot this point in figure 8-3. The point is very close to the C1-kensol locus. We trace back a curve very close to this locus from our point back to a temperature of 160 °F and find that the convergence pressure is close to 10,000 psia for this mixture. So, the first guess of 5000 psia was not too great! In this case though the operating pressure is considerably less than the convergence pressure so we do not expect the new convergence pressure to have that much influence on the solution of the equilibrium equations.

We note that black oils usually have convergence pressures of about 10,000 psia, volatile oils about 7000 psia and retrograde gases about 5000 psia.



8.6 Reservoir Fluid Studies

From McCain Chapter 10.
What is the best way to produce petroleum? What pressure and temperature should a separator be at to get most out of the reservoir fluid? Should there be more than one separator? In order to answer these questions and at the same time obtain a good idea of the composition of the reservoir fluid, several laboratory tests are performed on reservoir fluid. We briefly discuss flash vaporization, differential vaporization and separator tests. An example of a typical black oil reservoir fluid study is handed out separately (table 10-1 in McCain). Included is a table with the nomenclature used in the report. To find out more about separation tests read chapter 13 in McCain (not examinable, just for interest).

Flash vaporization

Equilibrium equation calculations are often called flash vaporization calculations, or simply flash calculations. Flash vaporization is performed in a laboratory to help determine the composition of the petroleum during production. In flash vaporization, the reservoir fluid is placed in a cell. The pressure in the cell is adjusted to a value equal to or greater than the initial reservoir pressure. Temperature is set at the reservoir temperature. Now, the pressure is reduced by increasing the volume in increments. The cell is agitated regularly to ensure that the contents are at equilibrium. No gas or liquid is removed from the cell during this process. The temperature is kept constant. At each step, pressure and total volume of the liquid and gas are measured and plotted against each other. This will give an isotherm in the PV diagram for the petroleum.

How can the bubble point pressure be determined from this graph?

Results for the black oil example study are given on page 4 of the extra handout.

Differential vaporization

In differential vaporization, again the reservoir fluid is placed in a cell. The pressure is brought to bubble point pressure and the temperature is set at reservoir temperature. Again, the pressure is reduced by increasing the cell volume and the cell is agitated to ensure equilibrium between the liquid and the vapor.

But in contrast to flash vaporization, the gas is now expelled from the cell whilst keeping the pressure in the cell constant (which requires a reduction in volume). The gas is collected and its quantity and specific gravity are measured. The volume of the remaining liquid is measured also. The process is repeated in small steps until atmospheric pressure is reached. Then the temperature is reduced to standard temperature and the volume of remaining liquid is measured. Results for the study are shown on page 5 of the extra handout. Here, the relative oil volume B_{oD} is equal to the volume of the cell liquid divided by the volume of the residual oil (the volume of the remaining liquid at the end of the differential vaporization process). The R_{sDb} values are the computed by dividing the total volume of removed gas during the entire process by the volume of residual oil (so it measures the amount of gas in solution at the bubble point in standard cubic feet of gas removed per barrel of residual oil). R_{sD} measures the gas remaining in the solution at any lower pressure than bubble point.

Separator tests

In separators tests, a sample of reservoir fluid is places in a laboratory cell and brought to reservoir temperature and bubble-point pressure. Then the liquid is expelled from the cell through two stages (usually) of separation: stage 1 in the separator and stage 2 in the stock tank. Pressure in the cell is held constant at bubble point pressure by reducing the volume as the fluid is expelled. A series of separator conditions is usually tested. In the example study results are shown for 4 different separator conditions (page 7 of the extra handout). Here, the situation modeled is a primary separator operating at 50, 100, 200 or 300 psig. The stock tank is separating at 0 psig (1 atmosphere). What is interesting here is that the formation volume factors shown are clearly dependent on the separator conditions (although not by that much). It is therefore important to determine the optimum separator conditions for each reservoir.
Note on page 7, B_{oSb} is the formation volume factor of oil measured as the volume of liquid expelled from the cell divided by the volume of liquid arriving in the stock tank. The solution gas-oil ratio R_{sSb} is calculated as the volume of separator gas + stock tank gas divided by the volume of liquid in the stock tank.

In the field, more than two stages of separation may be used. They are operated in series at successively lower pressures to obtain the maximum amount of liquid.