

Very often the ideal gas physical state is used, even though it is not always physically stable, since it is convenient for thermodynamic calculations.

As an example, a “standard state” for the vapour phase may be used. However, there is no common agreement as to its exact definition as it can be appreciated in table 2.1. The table also shows the standard volume for each of these standards, using the ideal gas law.

Table 2.1 Principal definitions of the standard state for the vapour properties

Temperature (K)	Pressure (kPa)	Used by	Known as	$v(T, P)$ ($\text{m}^3 \text{ kmol}^{-1}$)
273.15 (0 °C)	101.325 (1 atm)	IUPAC (before 1982), NIST	Standard conditions, Normal cubic meter, DIN 1343	22.414
273.15 (0 °C)	100	IUPAC (since 1982)	Standard temperature and pressure (STP), Standard conditions, ISO 13443	22.711
288.15 (15 °C)	101.325 (1 atm)	European gas companies	International standard atmosphere (ISA), Normal cubic meter, ISO 2533	23.645
293.15 (20 °C)	101.325 (1 atm)	NIST [10]	Ambient, Room	24.055
298.056 (60 °F)	101.325 (14.696 psi)	American gas companies, SPE	Standard cubic feet	24.458
298.056 (60 °F)	101.5598 (14.73 psi)	American gas companies, OPEC	Standard cubic feet	24.401
298.15 (25 °C)	101.325 (1 atm)		Ambient, Room	24.465
298.15 (25 °C)	100	NBS [11]		24.790

2.1.3 Gibbs phase rule, or how to read a phase diagram

The Gibbs phase rule is of great help when drawing phase diagrams. In this case, no feed composition is required. It states that:

The number of intensive properties that must be fixed for a system to be entirely determined is given by:

$$\mathfrak{S} = \mathcal{N} - \phi + 2 - \mathcal{R} \quad (2.7)$$

Where \mathcal{N} is the number of components in the system, ϕ is the number of phases and \mathcal{R} are the number of additional relationships (constraints) as for example known chemical reactions, azeotropy, critical points or fixed compositions. Note that the “intensive

properties” according to this definition are mole fractions within the phases along with temperature and pressure. This phase rule does not consider the relative amount of each phase and as a result it does not consider the so-called extensive properties which are proportional to the amount of substance. Examples below will illustrate the use of this rule.

2.1.3.1 Pure component application

For a pure component without additional relationships equation (2.7) reduces to:

$$\mathfrak{F} = 3 - \phi \quad (2.8)$$

This is why on a pure component phase diagram, where pressure is shown as a function of temperature, the single phase ($\phi = 1$) region is a two-dimensional region, the two-phase ($\phi = 2$) regions are lines (vapour-liquid or **vapour pressure** line associated to evaporation/condensation; vapour-solid or **sublimation/deposition** line and liquid-solid or **melting or fusion/crystallisation** line), and the three-phase “region” ($\phi = 3$) is a point. Figure 2.1 is an example of a pure component phase diagram.

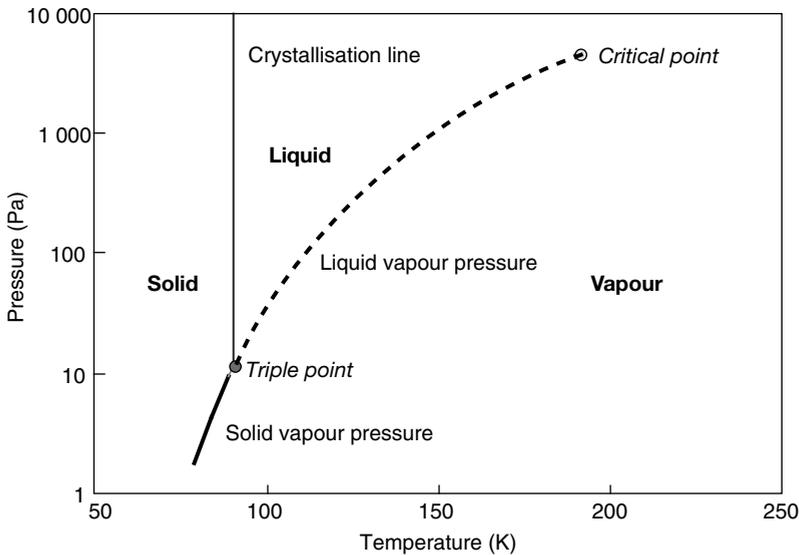


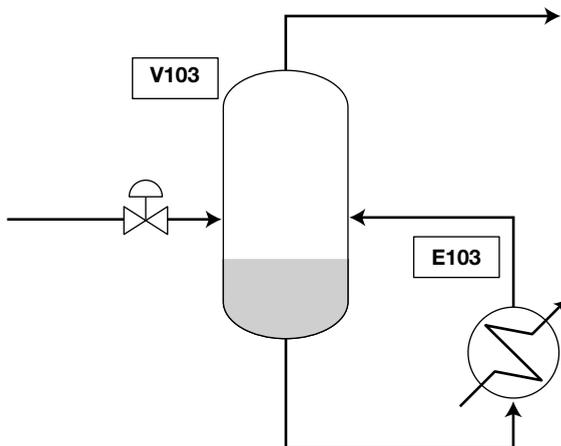
Figure 2.1

Behaviour of methane as a pure component (from DIPPR [12]).

Note that the vapour pressure line ends with a *critical point*. This point is defined as the conditions where the properties of the two phases merge, so that these phases become indistinguishable (same density, energy, etc.). This is a particularity of the fluid phases. When equation (2.7) is used, the critical point is considered as an additional constraint $\mathcal{R} = 1$ on top of the two-phase line, which explains why it is presented as a point (zero dimension).

Example 2.1 Refrigeration system

Propane is used to cool a process, as shown in the diagram of figure 2.2. The fluid that must be cooled in exchanger E103 should have an outlet temperature of $-30\text{ }^{\circ}\text{C}$. At the inlet of the exchanger, propane is a bubbling liquid while it is a saturated vapour at the outlet. What pressure will the exchanger work at?

**Figure 2.2**

Sketch of the heat exchanger in a propane cooling example.

Analysis:

Only propane appears in the process. It is a well-known light hydrocarbon.

Propane will evaporate to cool the process. It is a vapour-liquid equilibrium of a pure component.

Only temperature is given. Saturation pressure (vapour pressure) must be calculated.

Model requirement:

A vapour pressure curve is enough to solve the question asked. As long as the temperature remains within the limits provided by the database, the Antoine [13] equation is sufficient (see chapter 3):

$$\ln\left(\frac{P^\sigma(T)}{P_c}\right) = A + \frac{B}{(T/T_c) + C}$$

For propane, the parameter values are given in table 2.2:

Table 2.2 Constants for Example 2.1

Parameter	T_c (K)	P_c (MPa)	A	B	C
Value	369.82	4.24	5.75442079	-5.48259492	-0.04723775

Solution:

The refrigeration system uses the heat of vapourisation of propane to cool the process fluid. The propane, a pure component ($\mathcal{N} = 1$), is at vapour-liquid equilibrium, *i.e.* a two-phase equilibrium ($\phi = 2$). The Gibbs phase rule (2.7) indicates that $\mathfrak{S} = 1$. If temperature is set to $-30\text{ }^\circ\text{C}$ (to ensure a reasonable driving force for heat exchange), then pressure is automatically fixed to the vapour pressure.

We therefore find, at $-30\text{ }^\circ\text{C}$, a pressure of 5.6 bar. With this information, the thermodynamic state is defined, indicating that temperature was a sufficient piece of information.

This example is discussed on the website:

<http://books.ifpenergiesnouvelles.fr/ebooks/thermodynamics>

The behaviour of the properties as a function of pressure and temperature in the single phase region is further discussed in the first section of chapter 4.

2.1.3.2 Binary systems

For a binary system, the single phase region of the phase diagram, according to equation (2.7), is a three-dimensional volume. It can be presented in a pressure-temperature-composition diagram as shown in figure 2.3 (top). In order to keep these figures readable, the solid regions are not represented (see for example [14]). The two-phase regions are two-dimensional surfaces on this plot, and the three-phase regions (not shown on the figure) are lines.

Due to the difficulty of reading this type of diagram, cuts or projections of isolines on one plane are preferred (figure 2.3, bottom). It is important to understand their meaning correctly.

A. Two phase temperature-composition or pressure-composition phase diagrams

When the phase diagram is cut at a given pressure (isobar), a temperature-composition, or Txy diagram appears (an example is shown in figure 2.4). Similarly, if figure 2.3 is cut at a given temperature (isotherm), a pressure-composition or Pxy plot is found, as shown in figure 2.5.

Two saturation lines are shown on both of these diagrams: they show the compositions of the phases at equilibrium (bubble and dew curves). They merge at the end of the diagram, for pure components (vapour pressure or boiling temperature are the same). For systems whose composition, pressure and temperature values are represented by a point located between the two lines, two phases (liquid and vapour) coexist.

A single liquid phase appears at higher pressures (for isothermal plots) or at lower temperatures (for isobaric plots). The bubble curve marks the boundary between the liquid phase and the two-phase region. It describes the **saturated liquid** composition. **Any liquid that coexists with a vapour phase is at its bubble point.**

A single phase vapour is observed at lower pressure (for isothermal plots), or higher temperatures (for isobaric plots). The dew curve is at the limit between the vapour region and the two-phase region. This curve describes the **saturated vapour** composition. **Any vapour that coexists with a liquid is at its dew point.**

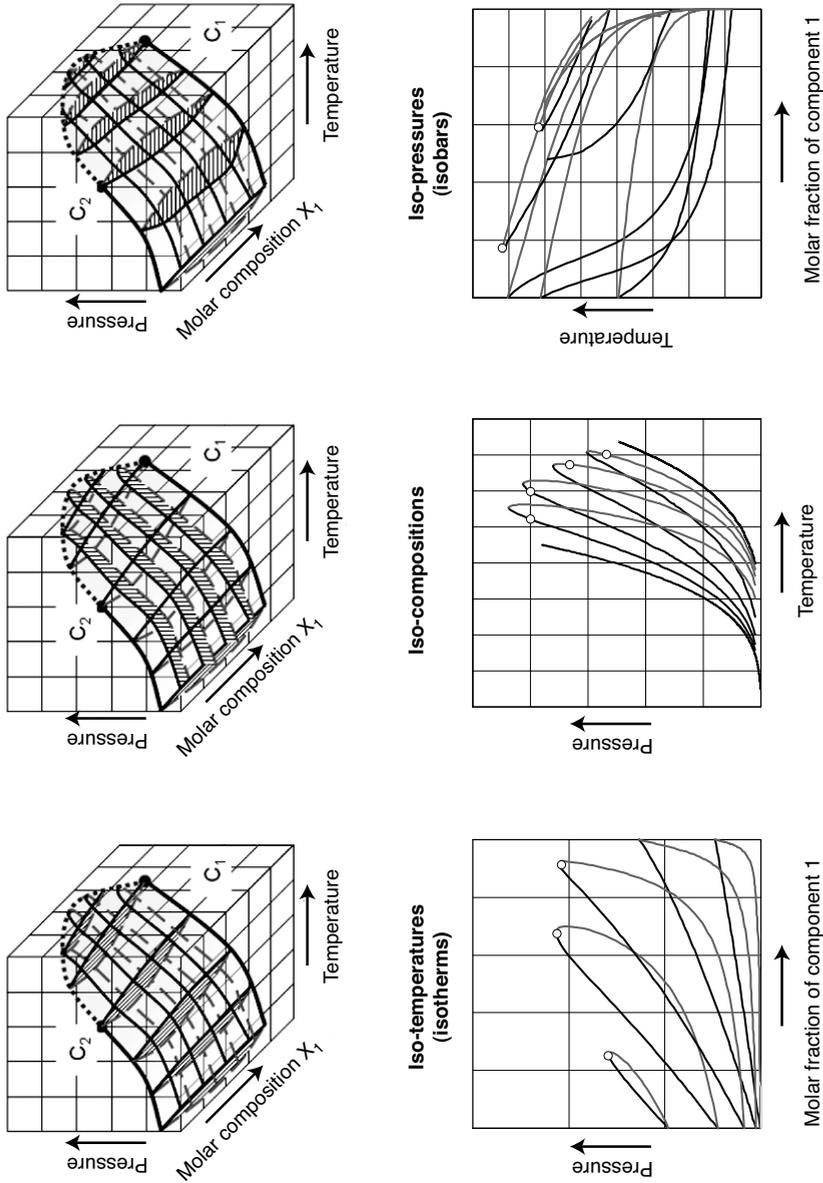


Figure 2.3

Three dimensional phase diagrams of a binary mixture and three types of cuts.

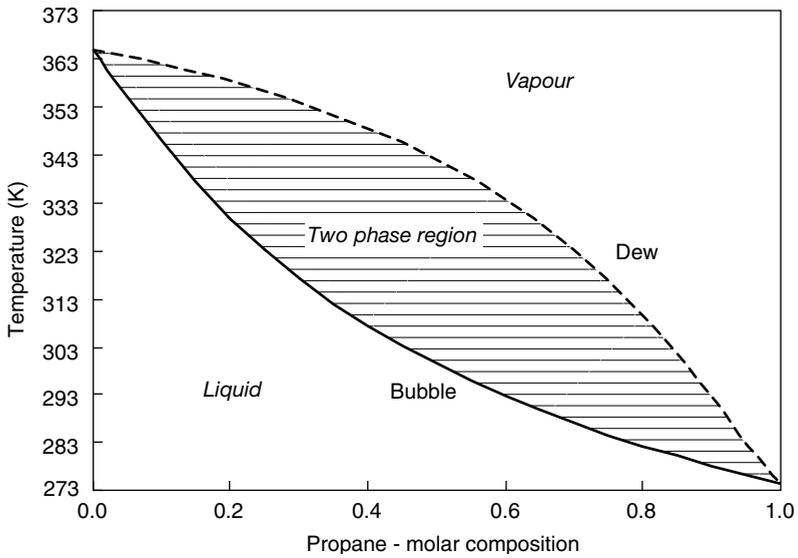


Figure 2.4

Example of a T_{xy} vapour-liquid phase diagram (model of propane + n -pentane mixture at 0.5 MPa).

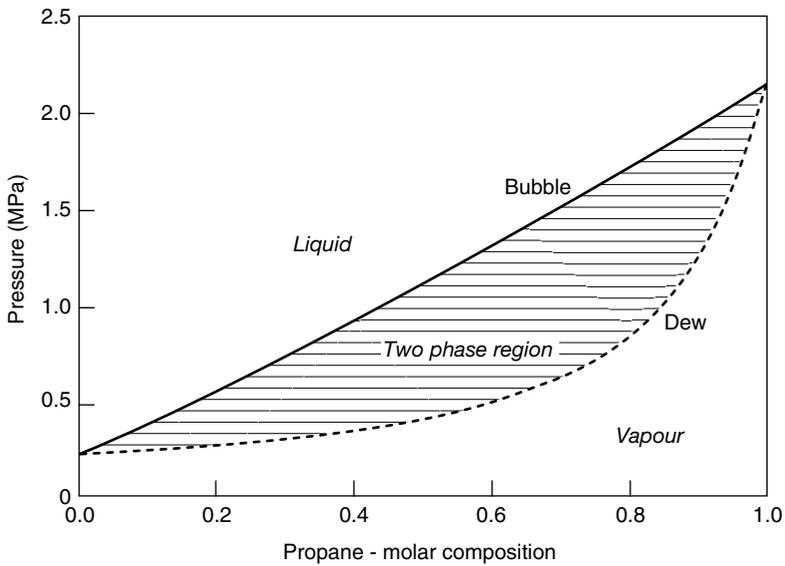


Figure 2.5

Example of a P_{xy} phase diagram (case of a nearly ideal mixture of propane + n -pentane at 333.15 K).

B. Pressure-temperature phase diagrams

Projections or cuts (iso-composition) are also provided on the PT plane. An example of such a projection is shown in figure 2.6. The vapour pressure curves of the pure components can be identified. These curves end with their critical point. The PT projection also shows a line that links these two points. It connects the critical points of all intermediate compositions and is called the **critical point locus**.

For intermediate compositions (e.g. 80% ethane), a number of PT cuts are shown in figure 2.6. The two-phase region in this representation has become a surface, rather than a line as it was for a pure component. Application of the Gibbs phase rule (2.7), with $\mathcal{N} = 2$ and $\phi = 2$ ($\mathcal{R} = 0$) indicates that it is not sufficient to know that two phases coexist to have a single relationship between pressure and temperature. Yet, this two-phase region (or envelope) is limited by two distinct curves. One (the bubble curve, on the upper left) is the line where the liquid feed starts forming a first bubble of vapour, while the dew curve (on the lower right) is the line where a first drop of liquid condenses from the vapour feed. Both curves join at the critical point of the mixture (open circle). Points on the critical locus have an additional constraint (criticality: $\mathcal{R} = 1$), which explains why the critical locus is a line on this plot.

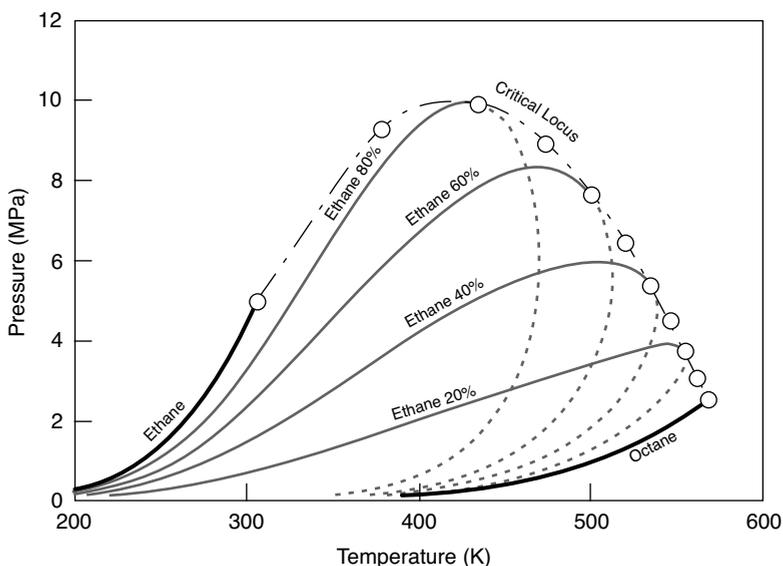


Figure 2.6

PT projection of the phase diagram of the ethane + octane binary mixture.

Bold lines are pure component vapour pressures; full lines are bubble points, dotted lines are dew points. The open circles represent the mixtures critical points and the dash-dot line the critical locus.

Example 2.2 VLE observation

A binary mixture of propane and *n*-pentane is available at 0.5 MPa. Using the information on figure 2.4, indicate the temperature range where vapour-liquid equilibrium can be observed.

If a system containing 40% (molar) propane is known to be at vapour-liquid equilibrium at 333.15 K, which is the proportion of each component in each phase? Can this reading be made on figure 2.5?

Analysis:

The properties to deal with are pressure, temperature and composition.

The mixture is a binary system with two light hydrocarbons.

Vapour and liquid are present together at equilibrium conditions.

Solution:

The Gibbs phase rule indicates that the degree of freedom of the system is $\mathfrak{S} = 4 - \phi$. If two phases are present, two intensive properties are necessary to specify the phase conditions. In a Txy diagram, pressure is fixed. Hence, a single additional property is required, which can be either temperature, liquid composition or vapour composition.

The corresponding extreme temperatures at 0.5 MPa are the boiling points of propane (275.15 K on the right of the figure) and of *n*-butane (367.15 K on the opposite side).

At 333.15 K, two phases can be observed with a liquid composition of propane of 0.18 and a vapour composition of 0.62. If composition of the overall mixture is less or greater than these two specified limits, only one phase will be observed. Any mixture with an overall composition included in this range will split into two phases. For example, the 40% mole propane mixture will lead to the following material balance:

$$F = L + V$$

$$Fz_1^F = Lx_1^L + Vy_1^V$$

Defining the vapour fraction as $\theta = V/F$ yields:

$$\theta = \frac{z_1^F - x_1^L}{y_1^V - x_1^L} = \frac{0.4 - 0.18}{0.62 - 0.18} = 0.5$$

This equation is known graphically as the **lever rule**.

When reading on the Pxy diagram, the compositions obtained are exactly the same.

This example is discussed on the website:

<http://books.ifpennergiesnouvelles.fr/ebooks/thermodynamics>

2.1.3.3 Three phases Txy or Pxy diagrams

When three phases are at equilibrium in a binary mixture, the Gibbs phase rule indicates that a single degree of freedom remains. When represented on a Txy or Pxy diagram, this means that either pressure or temperature is fixed and hence that no degree of freedom remains.

Figure 2.7 shows an example of three-phase equilibrium. It is represented by a straight, horizontal line to describe the three-phase conditions: temperature, as well as the composition of the three phases are fixed. On the left of the horizontal line, composition of the heavy liquid phase (aqueous) is found (liquid 1 on the figure with 0.035 isobutanol mole fraction). On the opposite side the composition of the light liquid phase (organic) is shown as liquid 2 (0.4 isobutanol mole fraction). The third point in the middle of the line indicates the composition of the vapour (0.34 isobutanol mole fraction) in equilibrium with the two liquids. At this temperature (362.65 K or 89.5 °C), cooling a system that contains a vapour will result in condensation of the vapour and formation of two liquids, while the temperature remains constant, as with a pure component.

In between the two almost vertical lines and below the rigorously horizontal three-phase line, two liquids coexist. Outside this zone, at temperatures below the three-phase temperature (89.5 °C) only liquid 1 or liquid 2 can be found. At the top of the diagram, there are two different vapour-liquid equilibrium zones. On the left, the dew line starts from the normal boiling point of water and ends at the vapour composition on the three-phase line. On the right side, the dew line starts from the normal boiling point of isobutanol and reaches the same point. Bubble lines join the normal boiling points to the liquid compositions on the three-phase line. A horizontal line at the three-phase temperature separates the two-phase regions from the single-phase regions. The region below this line is divided into two single-phase regions (Liquid 1 and Liquid 2) and one two-phase region (Liquid 1 + Liquid 2). The region above this line is divided into two two-phase regions (Vapour + Liquid 1 and Vapour + Liquid 2) and one single-phase region (Vapour).

This type of diagram, where the vapour composition on the three phase line lies between the two liquid compositions is called a *heteroazeotrope*. However, other types of three-phase diagrams may exist, as will be illustrated in chapter 4 of this book.

In all cases for binary systems, the three phase conditions are represented by a straight horizontal line.

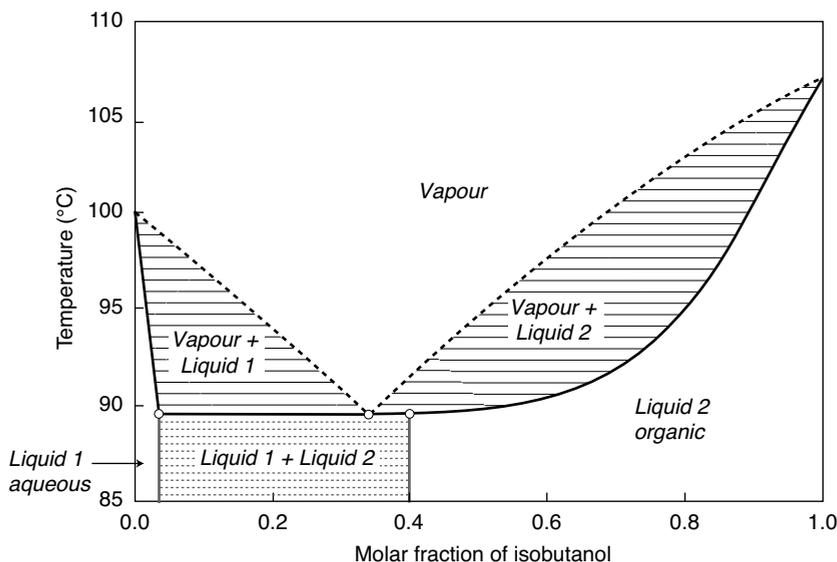


Figure 2.7

Atmospheric vapour-liquid-liquid diagram of the water-isobutanol system.

2.1.3.4 Ternary mixtures

The study of ternary mixtures is of great interest for a number of process applications, as it helps us understand the role of solvents or co-solvents. The Gibbs phase rule indicates that there are 3 degrees of freedom for a two-phase equilibrium (vapour-liquid or liquid-liquid). The two-phase zone can therefore be represented by a volume and the single phase zone by a four-dimensional hyper-volume. Very often, triangular cuts at fixed pressure and temperature are used (see, for example, figures 2.8, 2.9 and 2.10).

A. Vapour-liquid equilibrium

For ternary mixtures, if either pressure or temperature is fixed, a three-dimensional diagram is found again. This technique can be used to visualise the aspect of two-phase vapour-liquid equilibrium. A triangle is used as a basis to describe the composition of each component

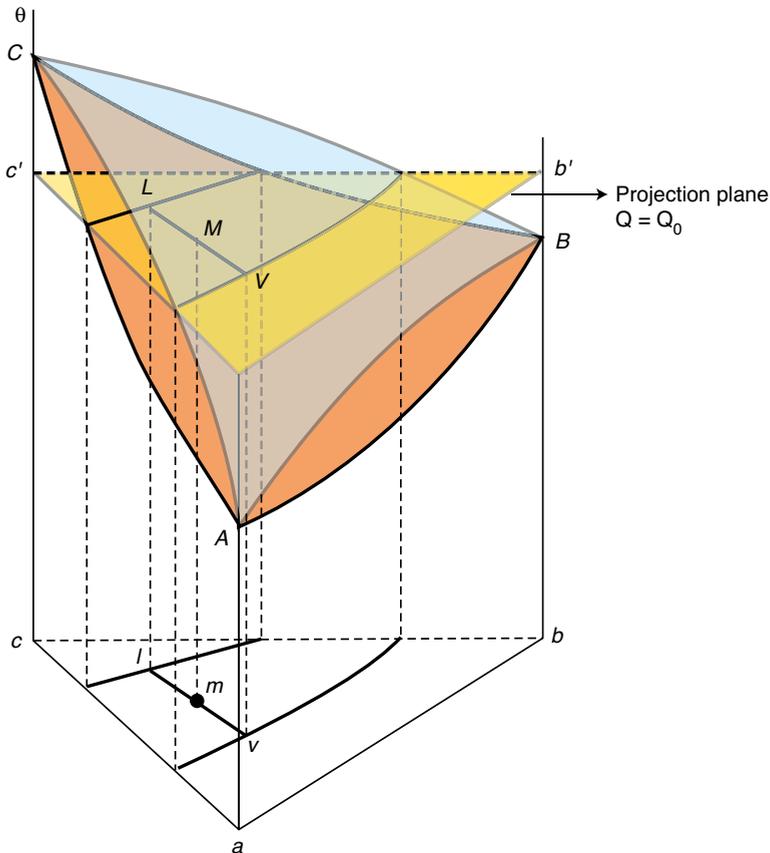


Figure 2.8

Isobaric vapour-liquid equilibrium representation for a ternary mixture.

(note that the sum of the heights is constant in a triangle, which is why it is used to describe composition). On this diagram bubble and dew locus are surfaces. In the constant pressure diagram as shown in figure 2.8, the vapour lies on top, at high temperature, above the dew surface. The liquid zone is found below the bubble surface.

B. Liquid-liquid equilibrium

Ternary mixtures of partially miscible products are commonly used in industry to purify one of the products by extraction. Pressure and temperature are usually constant in such processes and the Gibbs phase rule shows that the two remaining degrees of freedom can describe the system. Two molar fractions are sufficient to describe a single-phase system. If two phases are present, the phase compositions are located on the saturation lines, and only one molar fraction is necessary. Triangular phase diagrams are used, as in figure 2.9. The two-phase zones are bordered by *saturation lines* (similar to bubble and dew lines except that, since both describe a liquid phase, this terminology can no longer be used), and hatched by the *tie-lines*, that are straight lines connecting the compositions of the two liquids in equilibrium with each other. Often, a *plait point* or *critical point* can be seen, at the limit where the two liquid phases become identical (the tie-line is reduced to a point).

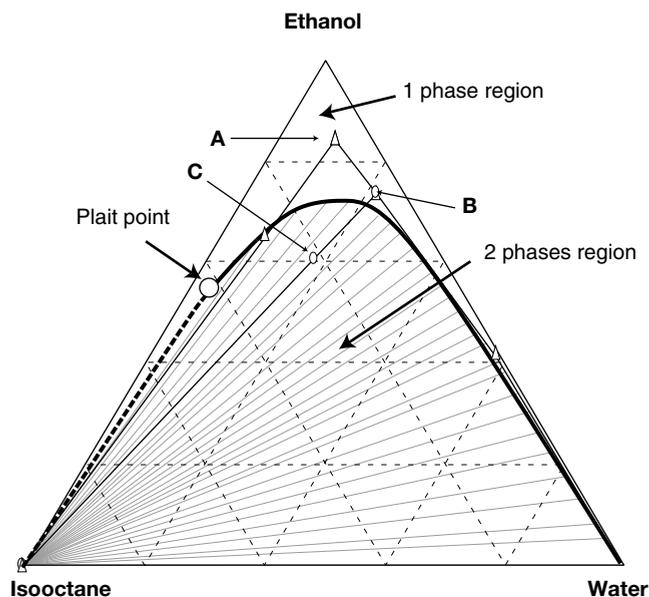


Figure 2.9

Liquid-liquid equilibrium for the ternary mixture of isooctane + ethanol + water at 298.15 K and 101.32 kPa (kind I). The A, B, C labels refer to example 2.3.

Different kinds of phase diagram can be encountered (figure 2.10). Kind I corresponds to two partially miscible components and one fully miscible with both others, as in figure 2.9. In kind II, two components are fully miscible and both are partially miscible with the third. Kind III implies that no two components are fully miscible: in this case, a three-phase equilibrium can be encountered. Note that three phase equilibrium in a ternary mixture, at fixed pressure and temperature, leaves no degrees of freedom. Hence, the compositions of the three phases are fixed. They are represented by the summits of the internal triangle.

It is quite common to observe that the size of the two-phase zone decreases with a temperature increase. This effect is represented in figure 2.10 for the different types of diagrams. Diagrams of type II may have one or two two-phase zones. For type III, the three different zones that may exist at lower temperature may merge, yielding a single three-phase zone.

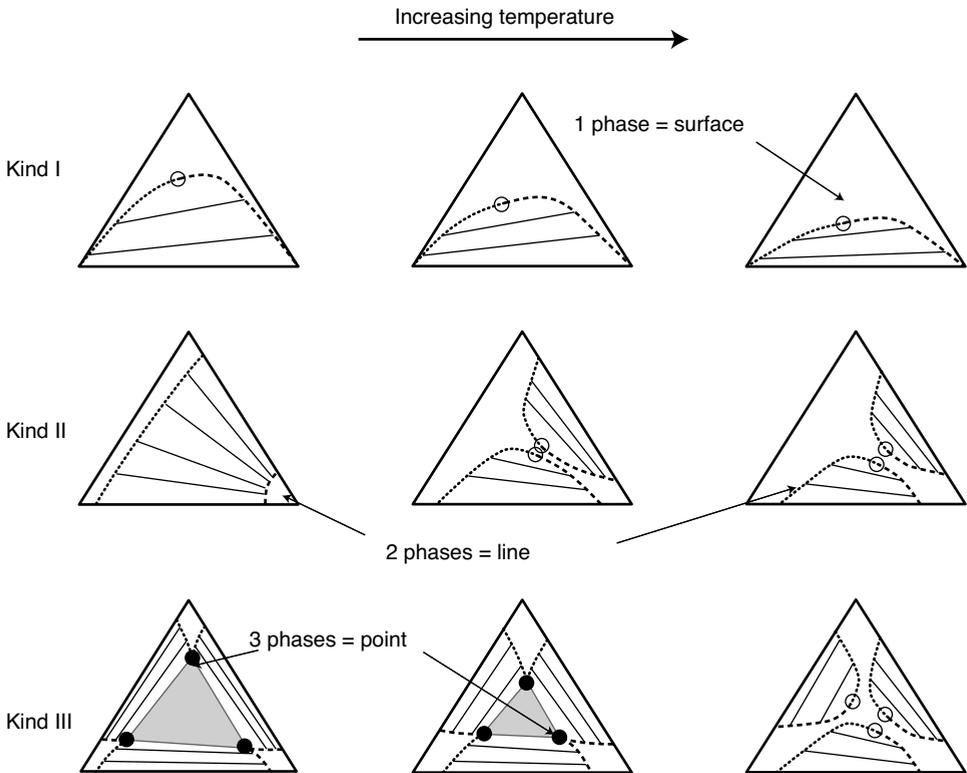


Figure 2.10

Different kinds of liquid-liquid equilibrium for a ternary mixture.

Example 2.3 Flexfuel model

E85 gasoline may be represented in a simplified way using a mixture of isooctane for the hydrocarbon (15% volume) and ethanol (85% volume). For the sake of the example we consider that the alcohol used for the mixing has been obtained by simple distillation: its composition in ethanol is very close to the binary azeotrope between water and ethanol. A 0.965 volume fraction composition will be used. The mixture is made at 298.15 K (25 °C) and the molar volumes are available at this temperature for each component.

Locate this E85 gasoline on figure 2.9.

In a distillery region, a driver adds 5 litres of a 70% volume alcohol to the 25 litres of E85 in the car fuel tank. What happens?

To repair the “mistake”, the driver decides to fill up the tank with only gasoline (isooctane) since the flex motor is designed to work with any of these fuels. Suppose he fills the contaminated tank with 20 litres of isooctane. What happens? Is the phenomenon due to the “mistake”? Some data related to the components are given in table 2.3:

Table 2.3 Constants for example 2.3

Component	Molar mass (kg kmol ⁻¹)	Molar density (mol L ⁻¹) at 298.15 K
Isooctane	114.2	6.0205
Ethanol	46.1	17.04
Water	18.0	55.384

Analysis:

Pressure and temperature are near ambient. Only compositions and phase behaviour are of interest.

Components are hydrocarbon, alcohol and water. Water is known not to mix with hydrocarbons. Ethanol is a solvent for both other fluids. A two-phase liquid-liquid zone will be observed. The diagram is kind I.

Solution:

First of all, equilibrium data are given in molar composition and gasoline measurements are made on a volume basis. Conversion must be carried out using molar volume.

Location of the point describing the E85 is known exactly (table 2.4). It is made from 15% isooctane and 85% of the ethanol-water mixture. If the “Ethanol” mixture contains 0.965 of pure ethanol then the net ethanol volume fraction will be 0.82025. With a total volume of 25 L, the molar fractions are calculated in table 2.4.

Table 2.4 Original E85 gas for example 2.3

Component	<i>x</i> (vol/vol)	Vol (L)	Amount (mol)	<i>x</i> (mol/mol)
Isooctane	0.1500	3.75	22.58	0.0546
Ethanol	0.82025	20.51	349.42	0.8457
Water	0.02975	0.74	41.19	0.0997
Total		25.00	413.19	

With 0.8457 of ethanol in the mixture, the E85 is very near the top of the triangle (point A on figure 2.9). Water composition is almost on the 10% isoline. This point belongs to the single-phase zone, so the fuel mix is OK.

5 litres of raw alcohol from a retort is now added to the fuel. The same table starting with a volume composition of {0,0.7,0.3} is created. The mixture is obtained adding the moles of each component, resulting in the composition given in table 2.5:

Table 2.5 First mixture of gas for example 2.3

Component	Vol (L)	x (vol/vol)	Amount (mol)	x (mol/mol)
Isooctane	3.75	0.1250	22.58	0.0406
Ethanol	24.01	0.8002	409.07	0.7359
Water	2.24	0.0748	124.27	0.2235
Total	30.00		555.91	

The resulting point is slightly below the former (point B on figure 2.9). On the 323.15 K diagram, the point is still in the one-phase area, but on the 298.15 K diagram the point is located very near the two-phase limit. If the temperature drops a few degrees, the liquid will split into two phases. It can be considered a dangerous mistake.

Will adding 20 litres of pure isooctane correct this mistake? Another balance of the same kind is made to obtain the composition shown in table 2.6:

Table 2.6 Second mixture of gas for example 2.3

Component	Vol (L)	x (vol/vol)	Amount (mol)	x (mol/mol)
Isooctane	23.75	0.4750	142.99	0.2114
Ethanol	24.01	0.4801	409.06	0.6049
Water	2.25	0.0449	124.27	0.1837
Total	50.00		676.32	

Now the mixture contains close to 60% ethanol and a similar amount of water and isooctane (point C on figure 2.9). This point is located in the two-phase zones indicating a separation into two layers: at the bottom, the aqueous phase (with 66% ethanol and 20% water at 323.15 K) and an organic phase with very little ethanol and essentially isooctane on top. The cause is the excessive presence of water. Industrial E85 is made of very pure (99.8% volume) ethanol. Water is removed using a special dehydration column or molecular sieves. Check the result in this case.

This example is discussed on the website:

<http://books.ifpenergiesnouvelles.fr/ebooks/thermodynamics>

2.1.3.5 Multicomponent systems

Equation (2.7) is valid for any number of components. It is clear, however, that a multidimensional plot is almost impossible to use. However, the PT type diagram discussed in the previous section remains identical: whatever the number of components, the bubble curve and the dew curve keep their significance and the mixture critical point is located at the point where both curves merge.

Note however that if a three-phase region exists, it is located by a PT curve if the mixture is binary (the projection of the three-phase line seen in figure 2.7). When more components are present in the mixture, the three-phase region becomes a surface in the same way as the two-phase regions.

Whatever the number of components, equation (2.7) indicates that if the mixture composition is known, the number of supplementary constraints is equal to $\mathcal{R} = \mathcal{N} - 1$, and the number of remaining degrees of freedom is

$$\mathfrak{S} = (\mathcal{N} - \phi + 2) - (\mathcal{N} - 1) = 3 - \phi \quad (2.9)$$

Then, in a two-phase system for example, if the pressure is given, the temperature is fixed as well as the phase compositions (bubble or dew lines). This case is also discussed below and will be called a $T\theta$ or $P\theta$ calculation.

2.1.4 Duhem phase rule (theorem)

In process simulation calculations, the feed composition is generally provided, yet it is not known how many phases may be present. In this case Duhem's phase rule states that:

If the amount of substance of all components in the feed is given, any combination of two state properties are sufficient to fully define the system.

As a result, a system may be defined according the classification provided in table 2.7. It will be seen later that in the case of phase equilibrium calculations, they will be called "Flash types".

The abbreviations used in table 2.7 will be kept throughout this book in order to simplify the notations.

Table 2.7 Most frequently encountered combinations of data types given

Flash type	Meaning	Example applications
PT	Pressure and temperature given	Basic case Used in all calculations
$T\theta$ or $P\theta$	Temperature or pressure and vapour fraction given	Bubble point Dew point Partially vapourised flash
TV	Temperature and volume given	Closed vessel at known temperature
PH	Pressure and enthalpy given	Adiabatic distillation columns Adiabatic expansions
PS	Pressure and entropy given	Ideal adiabatic compressors Pumps Turbines