Contents

Chapter 1

Equilibrium and Stability in Single Component Systems

1.1 Equilibrium Criteria

1.1.1 *Closed System at Constant U and V*

Imagine that we have a closed system with a mass m subjected to a disturbance. We need to know the evolution of this system with time from the old state to its final equilibrium state. Naturally, since this system is closed to mass, its material balance will end up in the simple form:

$$\frac{dm}{dt} = 0 \rightarrow m_{\text{Initial}} = m_{\text{Final}} \tag{1.1}$$

The energy and entropy balances for such a closed system can be given in differential form as

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} \tag{1.2}$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \tag{1.3}$$

Furthermore, assume that the system is subject to the following constraints

- Constant volume.
- No heat exchanged between the system and its surroundings i.e., adiabatic system.

The energy and entropy balances reduces to

$$\frac{dU}{dt} = 0 \rightarrow U_{\text{Initial}} = U_{\text{Final}} \tag{1.4}$$

$$\frac{dS}{dt} = \dot{S}_{\text{gen}} \geq 0 \tag{1.5}$$

The entropy generation term is well known to be greater than or equal to zero being zero for a reversible process. Therefore, what equation 1.5 tells us is that the entropy function is monotonically increasing during the approach to equilibrium.

Hence, entropy is usually called the arrow of time since it increases with time. At equilibrium in a closed system at constant U and V entropy must be a maximum.

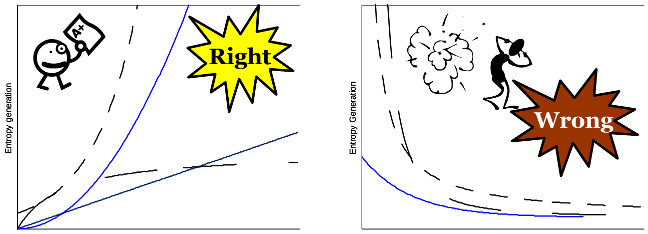


Fig. 1.1 Illustration of the entropy maximum principle.

1.1.2 *Closed System at Constant T and V*

Suppose that we have a constant volume system, and there is heat exchange between the system and its surroundings to keep the system isothermal. Similar treatment to the isolated system case. We need to know the evolution of this system with time from the old state to its final equilibrium state. Naturally, since this system is closed to mass, its material balance will end up in the simple form:

$$\frac{dm}{dt} = 0 \rightarrow m_{\text{Initial}} = m_{\text{Final}}$$

The energy and entropy balances for such a closed system can be given in differential form as

$$\frac{dU}{dt} = \dot{Q}$$
$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \rightarrow \dot{Q} = T\frac{dS}{dt} - T\dot{S}_{\text{gen}}$$

Substitute the rate of heat transfer obtained from the entropy balance in the energy balance to obtain

$$\frac{dU}{dt} = T\frac{dS}{dt} - T\dot{S}_{\text{gen}}$$
$$\frac{d(U - TS)}{dt} = \frac{dA}{dt} = -T\dot{S}_{\text{gen}} \leq 0.$$

The entropy generation term is well known to be greater than or equal to zero being zero for a reversible process. Furthermore, the absolute temperature is always positive. Therefore, the product $T\dot{S}_{\text{gen}}$ is positive. Consequently, Helmholtz free energy must be a minimum at equilibrium.

1.1.3 *Closed System at Constant T and P*

Suppose that we have a system maintained at a constant pressure, and there is heat exchange between the system and its surroundings to keep the system isothermal. Similar treatment to the isolated system case. We need to know the evolution of this system with time from the old state to its final equilibrium state. Naturally, since this system is closed to mass, its material balance will end up in the simple form:

$$\frac{dm}{dt} = 0 \rightarrow m_{\text{Initial}} = m_{\text{Final}}$$

The energy and entropy balances for such a closed system can be given in differential form as

$$\begin{aligned}\frac{dU}{dt} &= \dot{Q} - P\frac{dV}{dt}\\ \frac{dS}{dt} &= \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \rightarrow \dot{Q} = T\frac{dS}{dt} - T\dot{S}_{\text{gen}}\end{aligned}$$

Substitute the rate of heat transfer obtained from the entropy balance in the energy balance to obtain

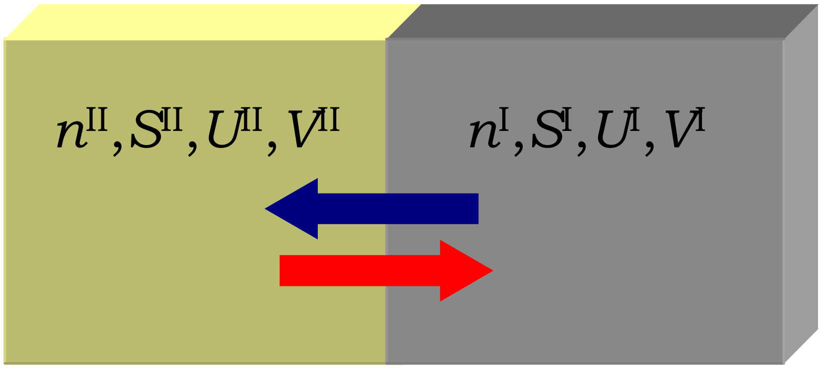
$$\begin{aligned}\frac{dU}{dt} &= T\frac{dS}{dt} - T\dot{S}_{\text{gen}}\\ \frac{d(U - TS + PV)}{dt} &= \frac{d(H - TS)}{dt} = \frac{dG}{dt} = -T\dot{S}_{\text{gen}} \leq 0.\end{aligned}$$

The entropy generation term is well known to be greater than or equal to zero being zero for a reversible process. Furthermore, the absolute temperature is always positive. Therefore, the product $T\dot{S}_{\text{gen}}$ is positive. Consequently, Gibbs free energy must be a minimum at equilibrium. The same result can be obtained for a system open to mass. Consequently, *Gibbs free energy must be a minimum for true equilibrium to be established.*

1.2 Equilibrium Conditions for a Closed System at Constant *U* and *V*

Consider a single component, single phase closed adiabatic system with constant volume. Divide into two nonuniform subsystems by an imaginary boundary. Nonuniform may include different T and/or P initially. These two subsystems are open to flow of heat and mass across the internal boundary.

Carry out overall material and energy balances, noting that the total volume is



the sum of the two subsystems' volumes

$$n = n^I + n^{II} = \text{constant} \rightarrow dn^I = -dn^{II} \tag{1.6}$$

$$U = U^I + U^{II} = \text{constant} \rightarrow dU^I = -dU^{II} \tag{1.7}$$

$$V = V^I + V^{II} = \text{constant} \rightarrow dV^I = -dV^{II} \tag{1.8}$$

This is natural since the system is isolated from the surroundings. The loss in one subsystem must appear in the other as gain. Consider the entropy to be a function of (U, V, N). From the definition of partial and total derivatives we have

$$dS^I = \left(\frac{\partial S^I}{\partial U^I}\right)_{n^I,V^I} dU^I + \left(\frac{\partial S^I}{\partial V^I}\right)_{n^I,U^I} dV^I + \left(\frac{\partial S^I}{\partial n^I}\right)_{U^I,V^I} dn^I \tag{1.9}$$

$$dS^{II} = \left(\frac{\partial S^{II}}{\partial U^{II}}\right)_{n^{II},V^{II}} dU^{II} + \left(\frac{\partial S^{II}}{\partial V^{II}}\right)_{n^{II},U^{II}} dV^{II} + \left(\frac{\partial S^{II}}{\partial n^{II}}\right)_{U^{II},V^{II}} dn^{II} \tag{1.10}$$

The first law of thermodynamics states that

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{g}{T}dn \tag{1.11}$$

From the equality of the thermodynamic function and the energy balance for each subsystem we can write the following equivalents of the partial derivatives

$$dS^I = \frac{1}{T^I}dU^I + \frac{P^I}{T^I}dV^I - \frac{g^I}{T^I}dn^I \tag{1.12}$$

$$dS^{II} = \frac{1}{T^{II}}dU^{II} + \frac{P^{II}}{T^{II}}dV^{II} - \frac{g^{II}}{T^{II}}dn^{II} \tag{1.13}$$

The total entropy change is given by

$$\begin{aligned} dS &= dS^I + dS^{II} \\ &= \left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) dU^I + \left(\frac{P^I}{T^I} - \frac{P^{II}}{T^{II}}\right) dV^I - \left(\frac{g^I}{T^I} - \frac{g^{II}}{T^{II}}\right) dn^I \end{aligned} \tag{1.14}$$

We know that for such a system at constant (U, V, N), the entropy (S) is a maximum or the differential of entropy must be equal to zero $(dS = 0)$. Consequently, the individual terms are zeros implying that the equilibrium conditions are

$$\begin{aligned}
\left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) &= 0 \rightarrow T^I = T^{II} \\
\left(\frac{P^I}{T^I} - \frac{P^{II}}{T^{II}}\right) &= 0 \rightarrow P^I = P^{II} \\
\left(\frac{g^I}{T^I} - \frac{g^{II}}{T^{II}}\right) &= 0 \rightarrow g^I = g^{II}.
\end{aligned}$$

Consequently, three types of equilibria must be satisfied to have equilibrium established under all constraints for various phases coexisting at equilibrium

(1) Thermal equilibrium

$$T^I = T^{II} = \cdots = T^N \tag{1.15}$$

(2) Mechanical equilibrium

$$P^I = P^{II} = \cdots = P^N \tag{1.16}$$

(3) Chemical equilibrium

$$g^I = g^{II} = \cdots = g^N \tag{1.17}$$

$$\mu^I = \mu^{II} = \cdots = \mu^N \tag{1.18}$$

where μ is called the chemical potential.

1.3 Stability Analysis

A stable equilibrium state will be established when S is a maximum or the first derivative is equal to zero. To check for maximum conditions, we have three possible values of the second derivative

(1) $d^2S < 0$ provides a maximum value of S or a true equilibrium state,
(2) $d^2S = 0$ is an inflection point of S or a metastable equilibrium state,
(3) $d^2S > 0$ provides a minimum value of S or an unstable equilibrium state.

Without further derivation, the following two criteria must be satisfied to have a stable phase:

(1) Heat capacity at a constant volume must be positive (Thermal stability criteria)

$$c_V > 0 \tag{1.19}$$

(2) Isothermal compressibility must be positive (Mechanical stability criteria)

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T > 0 \rightarrow \left(\frac{\partial P}{\partial v}\right)_T < 0. \tag{1.20}$$

The derived stability and equilibrium are valid for multicomponent and multiphase equilibria. Similar analysis for various systems leads to the table below

		Criterion	
System	**Constraint**	**Equilibrium**	**Stability**
Isolated, adiabatic, fixed boundary	Constant (U, V)	$S = \text{Max}, dS = 0$	$d^2S < 0$
Isothermal, closed, fixed boundary	Constant (T, V)	$A = \text{Min}, dA = 0$	$d^2A > 0$
Isothermal, isobaric, closed	Constant (T, P)	$G = \text{Min}, dG = 0$	$d^2G > 0$
Isothermal, isobaric, open	Constant (T, P, m)	$G = \text{Min}, dG = 0$	$d^2G > 0$

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Chapter 2

Raoult's Law and Its Related Calculations

Many calculations are related to the use of the Raoult's law for vapor-liquid equilibria (VLE) including condensation and boiling. A similar derivation leads to the same form of equation for the solid-vapor equilibria (SVE) case such as sublimation and deposition. Typical calculations involving Raoult's law are

- Bubble P: determine total pressure , P, given the composition in the liquid phase, $\mathbf{x}$, and temperature , T.
- Bubble T: determine the temperature , T, given the composition in the liquid phase, $\mathbf{x}$, and total pressure , P.
- Dew P: determine total pressure , P, given the composition in the vapor phase, $\mathbf{y}$, and temperature , T.
- Dew T: determine the temperature , T, given the composition in the vapor phase, $\mathbf{y}$, and total pressure , P.
- Generation of Pxy phase diagram.
- Generation of Txy phase diagram.
- Flash calculations.

In the next sections, many of these calculations will be illustrated using the ternary system benzene (1) - toluene (2) - m-xylene (3). This system is expected to behave close to ideality i.e., follow Raoult's law due to the minor differences in the shape and size of the molecules as well as interactions.

2.1 Derivation of Raoult's Law

The derivation of Raoult's law is a straightforward application of the equilibrium criteria (isofugacity) subject to the following constraints:

(1) The vapor phase is an ideal gas mixture (IGM),

$$f_i^v = y_i P \tag{2.1}$$

(2) The liquid phase is an ideal mixture (IM),

$$f_i^l = x_i P_i^{\text{vap}} \tag{2.2}$$

(3) The pressure is low enough such that the fugacity of the gas goes to the total pressure and that of the liquid to the vapor pressure of the pure species. Also, the Poynting factor is reduced to unity.

The equilibrium criteria requires that

$$\begin{aligned} f_i^v &= f_i^l \\ y_i \phi_i^v P &= x_i \phi_i^{\text{vap}} P_i^{\text{vap}} \exp\left[\frac{v_i^l (P - P_i^{\text{vap}})}{RT}\right] \end{aligned} \tag{2.3}$$

Simplify using the assumptions aforementioned to reduce equation 2.3 to the well known Roault's law

$$y_i P = x_i P_i^{\text{vap}}. \tag{2.4}$$

Derivation for solid-vapor or solid-supercritical phase equilibria subject to the same simplifying assumptions leads to similar expressions as that of equation 2.4.

2.2 Vapor Pressure is King

In the application of Raoult's law and its related calculations remember the golden rule: vapor Pressure is king! You need accurate values of the vapor pressure of all components in your system. In process simulators; EOS are used to estimate the vapor pressure. Alternatively, one can estimate the vapor pressure using equations such as Antoine and Wagner equations. Obtain the vapor pressure for the components of interest from any reference you deem useful. I am using the properties package coming with Sandler's book and the species databank with the Thermosolver package coming with Kortesky. The data are given as coefficients in the Antoine vapor pressure equation

$$\ln P^{\text{vap}} = A - \frac{B}{T + C}, \tag{2.5}$$

The Antoine equation constants for benzene, toluene, and m-xylene are given below with P^{vap} given in bar when T is given in K.

	A	B	C
Benzene	9.2806	2788.51	−52.36
Toluene	9.3935	3096.52	−53.67
m-Xylene	9.5188	3366.99	−58.04

.

2.3 Bubble P Calculation

The bubble P type calculation assumes knowledge of composition in the liquid phase and the temperature. Subsequently, it evaluates the pressure and composition in the vapor phase. This type of calculation is one of the easiest due to the wise choice of temperature and liquid composition. At a given temperature, the vapor pressure for both components is calculated using the vapor pressure model equation e.g., equation 2.5. The pressure is given by summing up all the partial pressures to obtain,

$$P = \sum x_i P_i^{\text{vap}}, \tag{2.6}$$

Example 2.1 Determine the bubble pressure for a mixture of benzene, toluene and m-xylene with a composition given by the vector $\mathbf{x} = \{0.4, 0.3, 0.3\}$ at 300 K.

It is usually easiest to solve such type of problems using tables instead of sequential calculations. Each component is assigned a number in sequence that is benzene is component 1, toluene is 2 and m-xylene is component 3.

Determine the vapor pressure at the given temperature from Antoine's equation

$$\begin{aligned}
P_1^{\text{vap}} &= \exp\left(9.2806 - \frac{2788.51}{300 - 52.36}\right) = 0.138105 \text{ bar} \\
P_2^{\text{vap}} &= \exp\left(9.3935 - \frac{3096.52}{300 - 53.67}\right) = \ 0.041706 \text{ bar} \\
P_3^{\text{vap}} &= \exp\left(9.5188 - \frac{3366.99}{300 - 58.04}\right) = \ 0.012318 \text{ bar}
\end{aligned}$$

Determine the total pressure at the given temperature as below

	No.	x_i	P_i^{vap}(bar)	$x_i P_i^{\text{vap}}$(bar)	$y_i = x_i P_i^{\text{vap}}/P$
Benzene	1	0.4	0.138105	0.055242	0.773166
Toluene	2	0.3	0.041706	0.012512	0.175113
m-Xylene	3	0.3	0.012318	0.003695	0.051721
			$P = \sum x_i P_i^{\text{vap}}$	0.071449	1

.

Thus, the bubble pressure for this mixture at 300 K is 0.071449 bar. The composition in the vapor phase at equilibrium with the liquid, then, is

$$y_i = \frac{x_i P_i^{\text{vap}}}{\sum x_i P_i^{\text{vap}}} = \frac{x_i P_i^{\text{vap}}}{P} \tag{2.7}$$

$$y_1 = \frac{x_1 P_1^{\text{vap}}}{P} = \frac{(0.4)(0.138105)}{0.071449} = 0.773166$$

You can always check your answer to see if the sum of the mole fractions in the vapor phase adds up to unity

$$\sum y_i = 0.773166 + 0.175113 + 0.051721 = 1.00.$$

2.4 Dew P Calculation

The dew P type calculation assumes knowledge of composition in the vapor phase and the temperature. Subsequently, it evaluates the pressure and composition in the liquid phase. This type of calculation is one of the easiest due to the wise choice of temperature and vapor composition. At a given temperature, the vapor pressure for both components is calculated using the vapor pressure model equation e.g., equation 2.5. The pressure is given by summing up with respect to the liquid phase mole fraction,

$$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}, \tag{2.8}$$

Example 2.2 Determine the dew pressure for a mixture of benzene, toluene and m-xylene with a composition given by the vector $\mathbf{y} = \{0.4, 0.3, 0.3\}$ at 300 K.

Determine the vapor pressure for each component at the given temperature. Subsequently, determine the total pressure at the given temperature as below

	No.	y_i	P_i^{vap}(bar)	y_i/P_i^{vap}(bar)	$x_i = \frac{y_i P}{P_i^{\text{vap}}}$
Benzene	1	0.4	0.138105	2.896337	0.084089
Toluene	2	0.3	0.041706	7.193255	0.20884
m-Xylene	3	0.3	0.012318	24.35432	0.707072
			$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$	0.029033	1

.

Thus, the dew pressure for this mixture at the specified composition is 0.029033 bars and the composition in the vapor phase, then, is

$$x_i = \frac{y_i \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}}{P_i^{\text{vap}}} = \frac{y_i P}{P_i^{\text{vap}}} \tag{2.9}$$

$$x_1 = \frac{y_1 P}{P_1^{\text{vap}}} = \frac{(0.4)(0.029033)}{0.138105} = 0.084089$$

You can always check your answer to see if the sum of the mole fractions in the liquid phase adds up to unity

$$\sum x_i = 0.084089 + 0.20884 + 0.707072 = 1.00.$$

2.5 Bubble T

The total pressure of the system and the compositions in the liquid phase are known. The composition in the vapor phase and bubble point temperature are to be determined. The bubble T is harder than the bubble P and dew P calculations. This is due to the nonlinear dependence of vapor pressure on temperature. The calculations require trial and error solution. Two approaches can be used to solve such kind of problems:

(1) Solution using the root of a single nonlinear equation

$$0 = P - \sum x_i P_i^{\text{vap}} \tag{2.10}$$

(2) Solution using an optimization technique

$$\text{Minimize } \left(P - \sum x_i P_i^{\text{vap}}\right)^2 \tag{2.11}$$

The following procedure is suitable to solve without particular use of any numerical technique. The first step is to try and find an initial guess for the bubble temperature. The idea is rather simple: the bubble temperature should be within the boiling temperatures, at the given pressure, for the least and most volatile components. Assuming that the bubble temperature is linearly proportional to composition, one can find a reasonable initial guess for the bubble temperature.

Example 2.3 Determine the bubble temperature for a mixture of benzene, toluene and m-xylene with a composition given by the vector $\mathbf{x} = \{0.4, 0.3, 0.3\}$ at a total pressure of 0.071449 bar.

The solution assumes using the Antoine equation for vapor pressure which can be inverted to give temperature as a function of vapor pressure

$$T_i = \frac{B_i}{A_i - \ln P_i^{\text{vap}}} - C_i$$

At the given total pressure, the boiling temperature for each compound is given as:

$$T_1 = \frac{B_1}{A_1 - \ln P_1^{\text{vap}}} - C_1 = \frac{2788.51}{9.2806 - \ln 0.071449} + 52.36 = 286.31 \text{ K}.$$
$$T_2 = \frac{B_2}{A_2 - \ln P_2^{\text{vap}}} - C_2 = \frac{3096.52}{9.3935 - \ln 0.071449} + 53.67 = 311.02 \text{ K}.$$
$$T_3 = \frac{B_3}{A_3 - \ln P_3^{\text{vap}}} - C_3 = \frac{3366.99}{9.5188 - \ln 0.071449} + 58.04 = 334.99 \text{ K}.$$

Find an initial guess for the bubble temperature using linear weighted average of the pure components' boiling temperatures

$$T^{(0)} = \sum x_i T_i = (0.4)(286.31) + (0.3)(311.02) + (0.3)(334.99) = 308.33 \text{ K}.$$

The solution now is straightforward as a Bubble P calculation with the initial guess of bubble temperature

	No.	x_i	P_i^{vap}(bar)	$x_i P_i^{\text{vap}}$(bar)	$y_i = x_i P_i^{\text{vap}}/P$
Benzene	1	0.4	0.19919	0.07968	$\frac{(0.4)(0.19919)}{0.071449} = 1.11514$
Toluene	2	0.3	0.0629	0.01887	$\frac{(0.3)(0.0629)}{0.071449} = 0.26412$
m-Xylene	3	0.3	0.01957	0.00587	$\frac{(0.3)(0.01957)}{0.071449} = 0.08217$
			$P = \sum x_i P_i^{\text{vap}} =$	0.10442	$\sum y_i = 1.46143$

.

The total pressure is higher than the system pressure indicating that the guessed bubble temperature is too high and needs to be reduced! Scaling using the obtained sum of mole fractions will do the job for us. Benzene is picked as a key component to do the scaling of vapor pressure which will scale the temperature accordingly. Thus providing a new refined estimate of the bubble temperature

$$P_1^{\text{vap}\prime} = P_1^{\text{vap}} / \sum y_i = \frac{0.19919}{1.46143} = 0.1363 \text{ bar}$$

$$T^{(1)} = \frac{2788.51}{9.2806 - \ln 0.1363} + 52.36 = 299.\,71 \text{ K.}$$

Again, use the new estimate to carry out the bubble pressure for the mixture

	No.	x_i	P_i^{vap}(bar)	$x_i P_i^{\text{vap}}$(bar)	$y_i = x_i P_i^{\text{vap}}/P$
Benzene	1	0.4	0.1363	0.05452	$\frac{(0.4)(0.1363)}{0.071449} = 0.76305$
Toluene	2	0.3	0.04109	0.01233	$\frac{(0.3)(0.04109)}{0.071449} = 0.17254$
m-Xylene	3	0.3	0.01211	0.00363	$\frac{(0.3)(0.01211)}{0.071449} = 0.05087$
			$P = \sum x_i P_i^{\text{vap}} =$	0.07048	$\sum y_i = 0.98646$

.

This iteration improved the summation of mole fractions as well as the calculated pressure is close to the system pressure. One can keep on calculating in this manner until a certain convergence tolerance is achieved.

$$P_1^{\text{vap}\prime} = P_1^{\text{vap}} / \sum y_i = \frac{0.1363}{0.98646} = 0.138\,17 \text{ bar}$$

$$T^{(2)} = \frac{2788.51}{9.2806 - \ln 0.13817} + 52.36 = 300.01 \text{ K.}$$

	No.	x_i	P_i^{vap}(bar)	$x_i P_i^{\text{vap}}$(bar)	$y_i = x_i P_i^{\text{vap}}/P$
Benzene	1	0.4	0.13817	0.05527	$\frac{(0.4)(0.136817)}{0.071449} = 0.77352$
Toluene	2	0.3	0.04173	0.01252	$\frac{(0.3)(0.04173)}{0.071449} = 0.1752$
m-Xylene	3	0.3	0.01233	0.0037	$\frac{(0.3)(0.01233)}{0.071449} = 0.05175$
			$P = \sum x_i P_i^{\text{vap}} =$	0.07148	$\sum y_i = 1.00048$

.

The assumed temperature essentially yielded the same system pressure and the sum of mole fractions is unity. Therefore, the bubble point temperature is 300.01 K.

2.6 Dew *T*

The total pressure of the system and the compositions in the vapor phase are known. The composition in the liquid phase and dew point temperature are to be determined. The dew T is harder than the bubble P and dew P calculations. This is due to the nonlinear dependence of vapor pressure on temperature. The calculations require trial and error solution. Two approaches can be used to solve such kind of problems:

(1) Solution using the root of a single nonlinear equation

$$0 = P - \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}} \tag{2.12}$$

(2) Solution using an optimization technique

$$\text{Minimize } \left(P - \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}} \right)^2 \tag{2.13}$$

The following procedure is suitable to solve without particular use of any numerical technique. The first step is to try and find an initial guess for the dew temperature similar to that of bubble T calculations.

Example 2.4 Determine the dew temperature for a mixture of benzene, toluene and m-xylene with a composition given by the vector $\mathbf{y} = \{0.4, 0.3, 0.3\}$ at a total pressure of 0.029033 bar.

At the given total pressure, the boiling temperature for each compound is given as:

$$T_1 = \frac{B_1}{A_1 - \ln P_1^{\text{vap}}} - C_1 = \frac{2788.51}{9.2806 - \ln 0.029033} + 52.36 = 269.87 \text{ K}.$$
$$T_2 = \frac{B_2}{A_2 - \ln P_2^{\text{vap}}} - C_2 = \frac{3096.52}{9.3935 - \ln 0.029033} + 53.67 = 293.1 \text{ K}.$$
$$T_3 = \frac{B_3}{A_3 - \ln P_3^{\text{vap}}} - C_3 = \frac{3366.99}{9.5188 - \ln 0.029033} + 58.04 = 315.89 \text{ K}.$$

Find an initial guess for the dew temperature using linear weighted average of the pure components' boiling temperatures

$$T^{(0)} = \sum y_i T_i = (0.4)(269.87) + (0.3)(293.1) + (0.3)(315.89) = 290.65 \text{ K}.$$

The solution now is straightforward as a dew P calculation with the initial guess of dew temperature

	No.	y_i	P_i^{vap}(bar)	y_i/P_i^{vap}(bar)	$x_i = \frac{y_i P}{P_i^{\text{vap}}}$
Benzene	1	0.4	0.088763	4.506384	$\frac{(0.4)(0.029033)}{0.088763} = 0.130833$
Toluene	2	0.3	0.025392	11.81486	$\frac{(0.3)(0.029033)}{0.025392} = 0.343017$
m-Xylene	3	0.3	0.007039	42.62029	$\frac{(0.3)(0.029033)}{0.007039} = 1.237382$
			$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$	0.016966	$\sum x_i = 1.711232$

.

Clearly, the calculated dew pressure is less than the given pressure and the sum of mole fractions is larger than one. This is indicative of the guessed temperature being low and needs to be increased. Scaling with a key component is used again to scale the vapor pressure and the temperature subsequently. Notice, however, that this time we multiply the vapor pressure by the sum of mole fractions instead of dividing

$$P_1^{\text{vap}\prime} = P_1^{\text{vap}} \sum x_i = 0.088763(1.711232) = 0.151\,89 \text{ bar}$$
$$T^{(1)} = \frac{2788.51}{9.2806 - \ln 0.151\,89} + 52.36 = 302.\,11 \text{ K}.$$

	No.	y_i	P_i^{vap}(bar)	y_i/P_i^{vap}(bar)	$x_i = \frac{y_i P}{P_i^{\text{vap}}}$
Benzene	1	0.4	0.151894	2.633415	$\frac{(0.4)(0.029033)}{0.151894} = 0.076455$
Toluene	2	0.3	0.046406	6.464622	$\frac{(0.3)(0.029033)}{0.046406} = 0.187685$
m-Xylene	3	0.3	0.013893	21.59295	$\frac{(0.3)(0.029033)}{0.013893} = 0.626902$
			$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$	0.032583	$\sum x_i = 0.891043$

.

Still, the sum of mole fractions is not as close to unity as desired, more iterations are required.

$$P_1^{\text{vap}\prime} = P_1^{\text{vap}} \sum x_i = 0.151894(0.891043) = 0.135\,34 \text{ bar}$$
$$T^{(2)} = \frac{2788.51}{9.2806 - \ln 0.135\,34} + 52.36 = 299.\,56 \text{ K}.$$

	No.	y_i	P_i^{vap}(bar)	y_i/P_i^{vap}(bar)	$x_i = \frac{y_i P}{P_i^{\text{vap}}}$
Benzene	1	0.4	0.135344	2.955431	$\frac{(0.4)(0.029033)}{0.135344}$ =0.085804
Toluene	2	0.3	0.040771	7.358174	$\frac{(0.3)(0.029033)}{0.040771}$ =0.213628
m-Xylene	3	0.3	0.012007	24.98451	$\frac{(0.3)(0.029033)}{0.012007}$ =0.725368
			$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$	0.02833	$\sum x_i$ =1.0248

.

Still, the sum of mole fractions is not as close to unity as desired, more iterations are required.

$$P_1^{\text{vap}\prime} = P_1^{\text{vap}} \sum x_i = 0.135344(1.0248) = 0.138\,7 \text{ bar}$$

$$T^{(3)} = \frac{2788.51}{9.2806 - \ln 0.138\,7} + 52.36 = 300.\,09 \text{ K.}$$

: :

	No.	y_i	P_i^{vap}(bar)	y_i/P_i^{vap}(bar)	$x_i = \frac{y_i P}{P_i^{\text{vap}}}$
Benzene	1	0.4	0.138701	2.88391	$\frac{(0.4)(0.029033)}{0.138701}$ = 0.083728
Toluene	2	0.3	0.041907	7.158626	$\frac{(0.3)(0.029033)}{0.041907}$ = 0.207834
m-Xylene	3	0.3	0.012385	24.22222	$\frac{(0.3)(0.029033)}{0.012385}$ = 0.703237
			$P = \frac{1}{\sum \frac{y_i}{P_i^{\text{vap}}}}$	0.029185	$\sum x_i$ = 0.994799

.

After these iterations, the pressure is close enough to the system pressure and the sum of mole fractions is approximately unity. Consequently, the dew temperature for this mixture is 300.09 K.

2.7 Flash Calculations

The

2.8 Phase Diagram Generation

Generate the phase diagram for a binary mixture using the assumptions inherent in Raoult's law.

The easiest way to generate phase diagrams using Raoult's law is to specify the temperature and liquid phase composition. Remember that the phase rule requires specification of two intensive variables for a two phase-two component system. Specification of temperature eliminates solving for the nonlinearly dependent vapor pressure. Therefore, specifying temperature and liquid composition results in production of Pxy diagram. Alternatively, one may specify total pressure and liquid, or vapor phase, composition. This specification results in generation of Txy diagram. Generation of xy diagrams is projecting the results of either the Txy or Pxy diagrams on the xy plane.

2.8.1 *Generation of Pxy Diagrams*

The equilibrium temperature (T) and liquid phase composition (x_1) are specified in this case. Therefore, we are carrying out bubble P type calculation many times. Varying the composition in the liquid phase, arbitrarily, between the pure component limits will yield the required Pxy table (refer to 2.2 for example). This table, in turn, can be used to plot the required diagram. 2.1 is a Pxy diagram for n-hexane (1)– n-heptane (2) at 300 K. The xy diagram can be generated from the information contained in the Pxy diagram. 2.2 illustrates a xy diagram for n-hexane (1)–n-heptane (2) at 300 K.

P (bar)	0.0666	0.0817	0.0968	0.112	0.127	0.142	0.158	0.173	0.188	0.203	0.218
x	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.00
y	0.000	0.267	0.450	0.584	0.686	0.766	0.831	0.884	0.929	0.967	1.00

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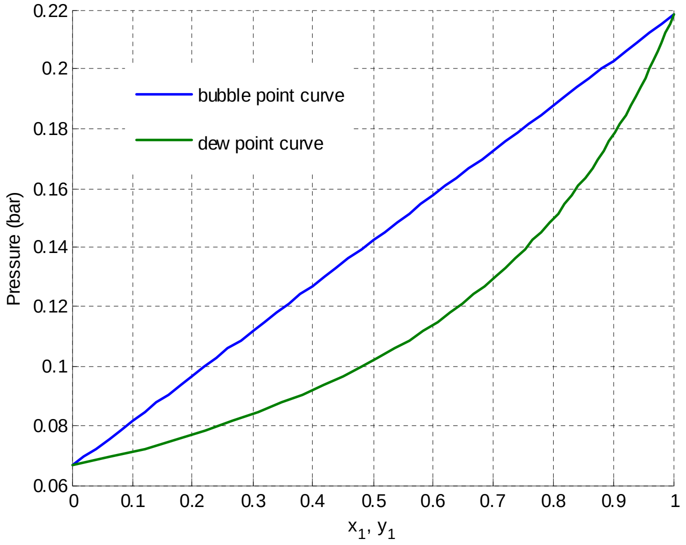

Fig. 2.1 Pxy phase diagram for n-hexane – n-heptane binary system at T = 300 K assuming Raoult's law applies.

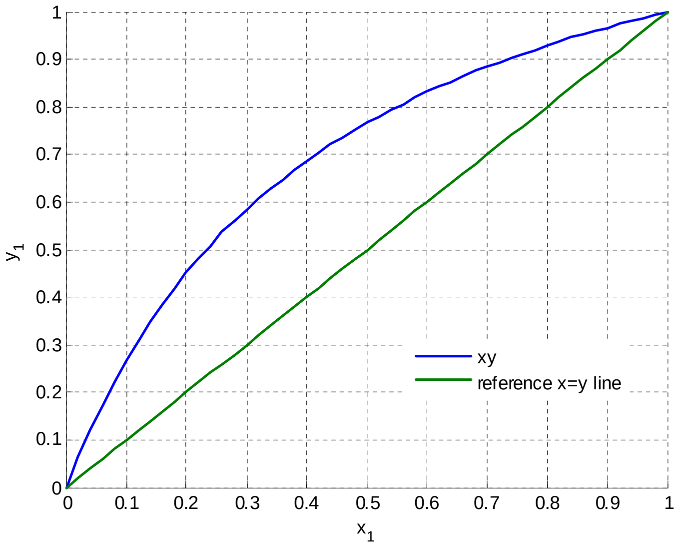

Fig. 2.2 xy phase diagram for n-hexane – n-heptane binary system at $T = 300$ K assuming Raoult's law applies.

2.8.2 *Generation of Txy diagrams*

The generation of

Chapter 3

Modified Raoult's Law

Many calculations are related to the use of the modified Raoult's law for vapor-liquid equilibria (VLE) including condensation and boiling. The same type of calculations for Raoult's law can be used with the modified Raoult's law given that the activity coefficients are known. There is a hierarchy of the calculations in this case different that of the Raoult's law. The calculations are ranked as below:

1. Bubble point pressure is the easiest since the liquid composition is specified and the activity coefficients are known. Also temperature is known which makes the vapor pressures readily available. Trial and error solution is not required for this case
2. Bubble point temperature is second in calculation difficulty. Liquid composition is specified while temperature is to be determined. This requires trial and error solution for the temperature.
3. Dew point pressure is a little bit harder since liquid phase composition is not known while temperature is specified. This necessitates trial and error solution for the liquid phase composition.
4. Dew point temperature is the hardest among these calculations since both temperature and liquid phase compositions are not known. This requires trial and error on both the temperature and liquid phase composition.

In the next sections, many of these calculations will be illustrated using the binary system toluene (1) - n-butanol (2).

3.1 Derivation of Modified Raoult's Law

The derivation of modified Raoult's law is a straightforward application of the equilibrium criteria (isofugacity) subject to the following constraints:

(1) The vapor phase is an ideal gas mixture (IGM),

$$f_i^v = y_i \phi_i^v P \tag{3.1}$$

for an IGM this fugacity is reduced to

$$f_i^v = y_i P$$

(2) The liquid phase is a nonideal mixture described by any g^{ex} model i.e. the nonideality is described by activity coefficients,

$$f_i^l = x_i \gamma_i P_i^{\mathrm{vap}} \exp\left[\frac{v_i^l (P - P_i^{\mathrm{vap}})}{RT}\right] \tag{3.2}$$

(3) The pressure is low enough such that the fugacity of the gas goes to the total pressure and that of the liquid to the vapor pressure of the pure species. Also, the Poynting factor is reduced to unity.

The equilibrium criteria requires that the fugacities are equal between the two phase. Simplify using the assumptions aforementioned to reduce equation 2.3 to the modified Roault's law

$$y_i P = x_i \gamma_i P_i^{\mathrm{vap}}. \tag{3.3}$$

3.2 Bubble P Calculation

Example 3.1 It is desired to find the bubble point pressure of a mixture of 0.3 mole fraction toluene (1) and 0.7 mole fraction 1-butanol (2) at 108.255°C. The vapor pressures are given by:

$$\log P_1^{\mathrm{vap}} = 6.95508 - \frac{1345.087}{219.516 + T}$$
$$\log P_i^{\mathrm{vap}} = 8.19659 - \frac{1781.719}{217.675 + T}$$

where P_i^{vap} is in mm Hg and T is in °C. The activity coefficient γ_i is given by the van Laar equation for a binary system as

$$\log \gamma_1 = \frac{A x_2^2}{\left(\frac{A}{B} x_1 + x_2\right)^2}$$
$$\log \gamma_2 = \frac{B x_1^2}{\left(x_1 + \frac{B}{A} x_2\right)^2}$$

the constants in the van Laar equation are given as $A = 0.38969$ and $B = 0.55954$.

It is usually easiest to solve such type of problems using tables instead of sequential calculations. Determine the vapor pressure at the given temperature from Antoine's equation

$$P_1^{\mathrm{vap}} = 10^{\left[6.95508 - \frac{1345.087}{219.516 + 108.255}\right]} = 710.133 \text{ mmHg}$$
$$P_2^{\mathrm{vap}} = 10^{\left[8.19659 - \frac{1781.719}{217.675 + 108.255}\right]} = 537.057 \text{ mmHg}.$$

Calculate the activity coefficients from the van Laar equation as

$$\gamma_1 = 10^{\left[\frac{0.38969(0.7)^2}{\left(\frac{0.38969}{0.55954}(0.3)+0.7\right)^2}\right]} = 1.70266$$
$$\gamma_2 = 10^{\left[\frac{0.55954(0.3)^2}{\left(0.3+\frac{0.55954}{0.38969}(0.7)\right)^2}\right]} = 1.07045.$$

Determine the total pressure at the given temperature as below

	No.	x_i	P_i^{vap}(mmHg)	γ_i	$x_i\gamma_iP_i^{\text{vap}}$(mmHg)	y_i
Toluene	1	0.3	710.133	1.70266	362.734	0.47406
n-Butanol	2	0.7	537.057	1.07045	402.424	0.52594
				$P = \sum x_i\gamma_iP_i^{\text{vap}}$	765.158	1

Thus, the bubble pressure for this mixture at 108.255°C is 765.158 mmHg. The composition in the vapor phase at equilibrium with the liquid, then, is

$$y_i = \frac{x_i\gamma_iP_i^{\text{vap}}}{\sum x_i\gamma_iP_i^{\text{vap}}} = \frac{x_i\gamma_iP_i^{\text{vap}}}{P} \tag{3.4}$$
$$y_1 = \frac{x_1\gamma_1P_1^{\text{vap}}}{P} = \frac{(0.3)(1.70266)(710.133)}{765.158} = 0.47406.$$

You can always check your answer to see if the sum of the mole fractions in the vapor phase adds up to unity.

3.3 Bubble T Calculation

Example 3.2 It is desired to find the bubble point temperature of a mixture of 0.3 mole fraction toluene (1) and 0.7 mole fraction 1-butanol (2) at 765.158 mmHg. The vapor pressures are given by:

$$\log P_1^{\text{vap}} = 6.95508 - \frac{1345.087}{219.516+T}$$
$$\log P_i^{\text{vap}} = 8.19659 - \frac{1781.719}{217.675+T}$$

where P_i^{vap} is in mm Hg and T is in °C. The activity coefficient γ_i is given by the van Laar equation for a binary system as

$$\log\gamma_1 = \frac{Ax_2^2}{\left(\frac{A}{B}x_1+x_2\right)^2}$$
$$\log\gamma_2 = \frac{Bx_1^2}{\left(x_1+\frac{B}{A}x_2\right)^2}$$

the constants in the van Laar equation are given as $A = 0.38969$ and $B = 0.55954$.