CH2351 Chemical Engineering Thermodynamics II

Unit – I, II

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Excess Gibbs Free Energy

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Activity Coefficient

$$\gamma_i = \exp\left(\frac{\bar{G_i}^{\mathrm{E}}}{RT}\right)$$

$$\ln\gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{T,P,n_j}$$

Models for Activity Coefficient

Porter equation

$$\frac{G^E}{RT} = Ax_1x_2 \longrightarrow \boxed{\begin{aligned} \ln\gamma_1 &= Ax_2^2 \\ \ln\gamma_2 &= Ax_1^2 \end{aligned}}$$

Margules one parameter equations

Models for Activity Coefficient

Redlich-Kister Expansion form

$$\frac{G^E}{RT} = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots\right]$$

$$\frac{G^E}{RT} = x_1 x_2 \left[A + B(x_1 - x_2)\right]$$

$$\frac{G^E}{RT} = x_1 x_2 \left[A(x_1 + x_2) + B(x_1 - x_2)\right]$$

$$\frac{G^E}{x_1 x_2 RT} = (A + B)x_1 + (A - B)x_2 \longrightarrow$$

$$= A_1 x_1 + A_2 x_2$$

$$\boxed{\begin{aligned} \ln \gamma_1 &= x_2^2 \left[A_2 + 2x_1(A_1 - A_2)\right] \\ \ln \gamma_2 &= x_1^2 \left[A_1 + 2x_2(A_2 - A_1)\right] \end{aligned}}$$

Margules two parameter equations

$$\frac{x_1 x_2}{G^E/RT} = A' + B'(x_1 - x_2) = A' + B'(2x_1 - 1)$$

The above equation may also be written as

$$\frac{x_1 x_2}{G^E/RT} = A'(x_1 + x_2) + B'(x_1 - x_2) = (A' + B')x_1 + (A' - B')x_2$$

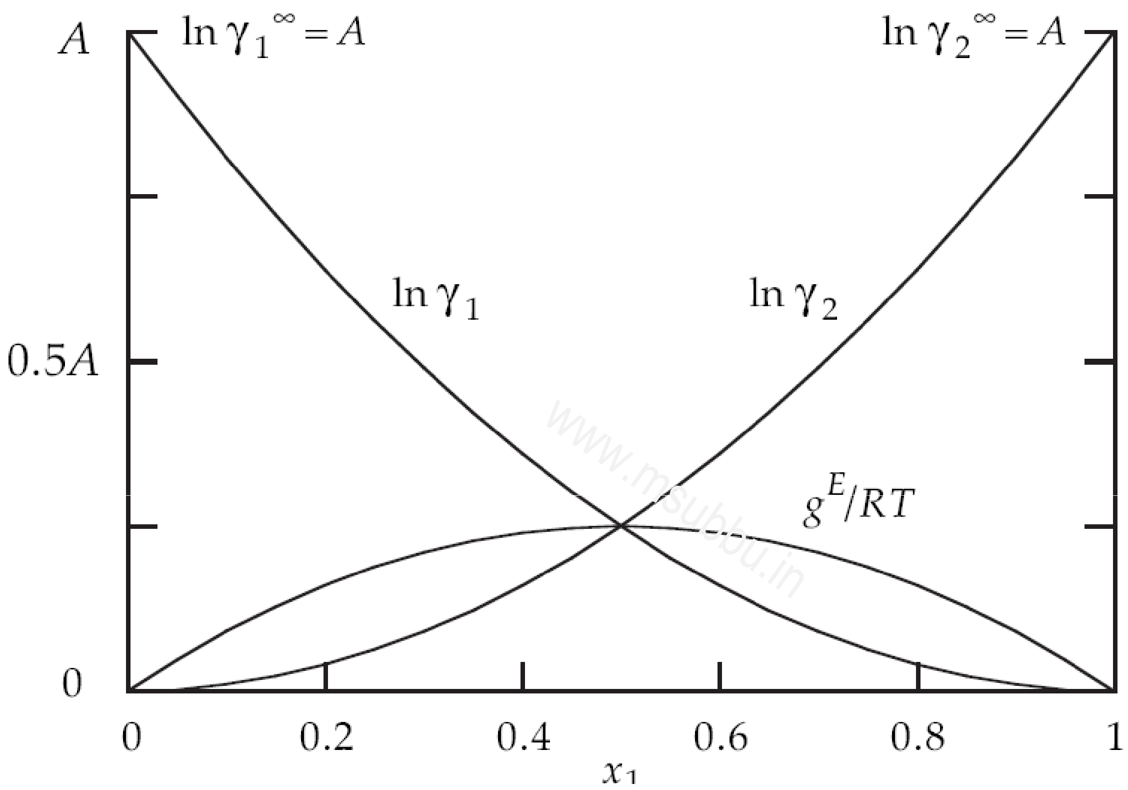
By using $A' + B' = 1/A'_1$ and $A' - B' = 1/A'_2$, we get

$$\frac{x_1 x_2}{G^E/RT} = \frac{x_1}{A'_1} + \frac{x_2}{A'_2} = \frac{A'_2 x_1 + A'_1 x_2}{A'_2 A'_1}$$

$$\frac{G^E}{x_1 x_2 RT} = \frac{A'_2 A'_1}{A'_2 x_1 + A'_1 x_2} \longrightarrow \boxed{\begin{aligned} \ln \gamma_1 &= A'_2 \left(1 + \frac{A'_2 x_1}{A'_1 x_2}\right)^{-2} \\ \ln \gamma_2 &= A'_1 \left(1 + \frac{A'_1 x_2}{A'_2 x_1}\right)^{-2} \end{aligned}}$$

van Laar equations

Two-suffix Margules Equation or Porter Equation



$$\ln\gamma_1 = Ax_2^2$$

$$\ln\gamma_2 = Ax_1^2$$

Figure 5.8 Substantial symmetry exists in the composition dependence of the excess Gibbs energy and activity coefficients for binary mixtures that obey the Porter equation (5.6.1).

This model provide a good representation for many simple mixtures. Typically, this require that the molecules are of similar size, shape, and chemical nature

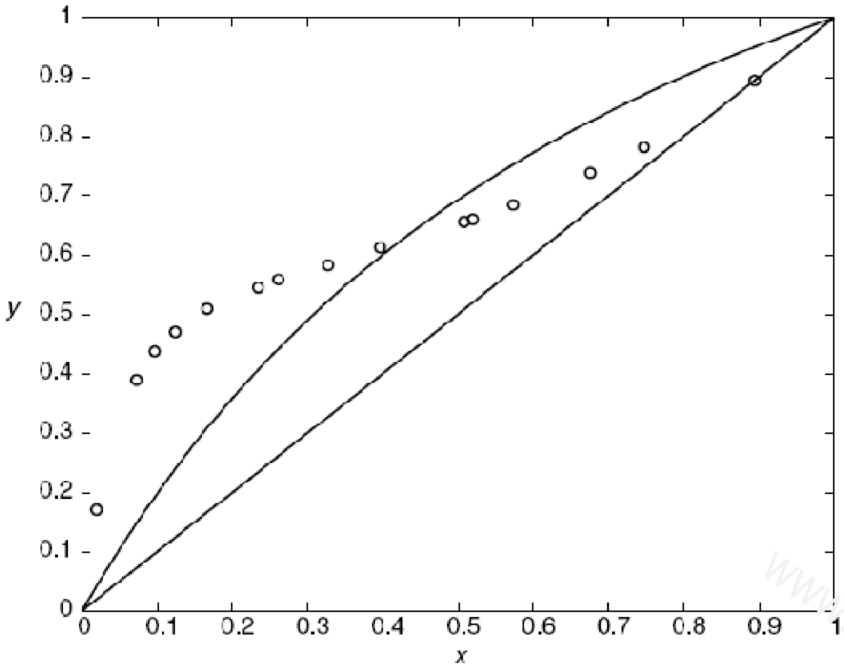


Figure 3.6. Ethanol–water vapor–liquid diagram for ideal thermodynamics

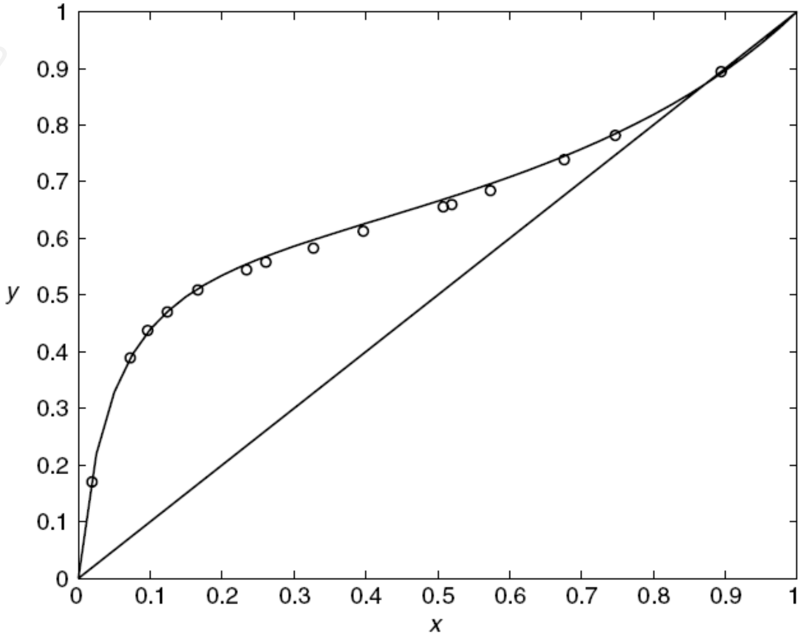


Figure 3.7. Ethanol–water vapor–liquid diagram with Wilson binary interaction parameters.

- The options for the activity coefficient of the gaseous phase are: ideal gas, Redlich–Kwong or Redlich–Kwong–Soave, Peng–Robinson, plus a few specialized ones (i.e., HF hexamerization and Hayden–O’Connell).

- In the liquid phase, the simplest option is an ideal liquid, with an activity coefficient equal to 1.0. That choice leads to Raoult’s law, which may suffice for similar chemicals. Other models include regular solution theory using solubility parameters (although not in Aspen Plus), NRTL, Electrolyte NRTL, UNIFAC, UNIQUAC, Van Laar, and Wilson.

Characteristics of the models

- The Electrolyte NRTL is especially suited for acid gas adsorption, which includes the removal of carbon dioxide and hydrogen sulfide from a gas stream. Refineries routinely use this process when making hydrogen. This is also one way of capturing carbon dioxide from a power plant to capture and sequester it.
- The UNIFAC model is a group contribution method that allows the model parameters to be estimated using the molecular structure of each chemical. When experimental data is not available, this is the only method that can be used.
- The UNIQUAC model uses binary parameters, which must be determined from experimental data. Once found, however, the same parameters can be used in multicomponentmixtures of three or more chemicals.
- Both UNIFAC and UNIQUAC can be used when two liquid phases or azeotropes are present.
- The Van Laar options are less recommended in Aspen Plus; they are simpler to use than the others, but less successful in general. In Aspen Plus the ease of use is immaterial since someone else has created the program.
- The Wilson equation is an option if there is only one liquid phase, and it does handle azeotropes.

Example 9-40. ***VLE of Non-ideal Solution***

Given in what follows are values of infinite dilution activity coefficients and pure-species vapor pressures for binary systems at specified temperatures. Determine the Margules parameters, and then apply the Margules equation to a sufficient number of x_1 and construct Pxy diagram.

(a) *For chloroform(1) / diethyl ether(2) at 30°C,*

$$\gamma_1^\infty = 0.57; \gamma_2^\infty = 0.71; P_1^{sat} = 86.59\ kPa; P_2^{sat} = 33.73\ kPa$$

(b) *For acetone(1) / benzene(2) at 45°C,*

$$\gamma_1^\infty = 1.60; \gamma_2^\infty = 1.47; P_1^{sat} = 68.36\ kPa; P_2^{sat} = 29.82\ kPa$$

$$\ln\gamma_1 = x_2^2\left[A_2 + 2x_1(A_1 - A_2)\right]$$
$$\ln\gamma_2 = x_1^2\left[A_1 + 2x_2(A_2 - A_1)\right]$$

Model the following vapor–liquid equilbria data of ethyl acetate and water at 760 mmHg using the WilsonRK model in Aspen Plus (Ellis and Garbett, 1960):

x_1	y_1	T (°C)
0.0006	0.0405	98.85
0.0011	0.1256	96.20
0.0049	0.5910	86.50
0.0086	0.6680	76.20
0.0459	0.7140	70.55
0.1440	0.7025	70.55
0.2690	0.7060	70.50
0.3540	0.7090	70.45
0.4080	0.7090	70.55
0.5140	0.7100	70.50
0.6080	0.7025	70.50
0.6900	0.7070	70.45
0.7750	0.6990	70.50
0.8737	0.7650	71.45
0.9444	0.8650	73.35

Azeotrope Composition

Determination of γ_1 and γ_2 at a single known composition permits evaluation of these constants and complete γ curves. Measurements of a single set of equilibrium liquid and vapor compositions, together with a knowledge of the vapor pressures of pure components, suffice for calculations of γ_1 and γ_2.

From the γ values ideality of solutions can be found, and prediction of azeotropic compositions is possible.

Gibbs-Duhem Equation - Applications

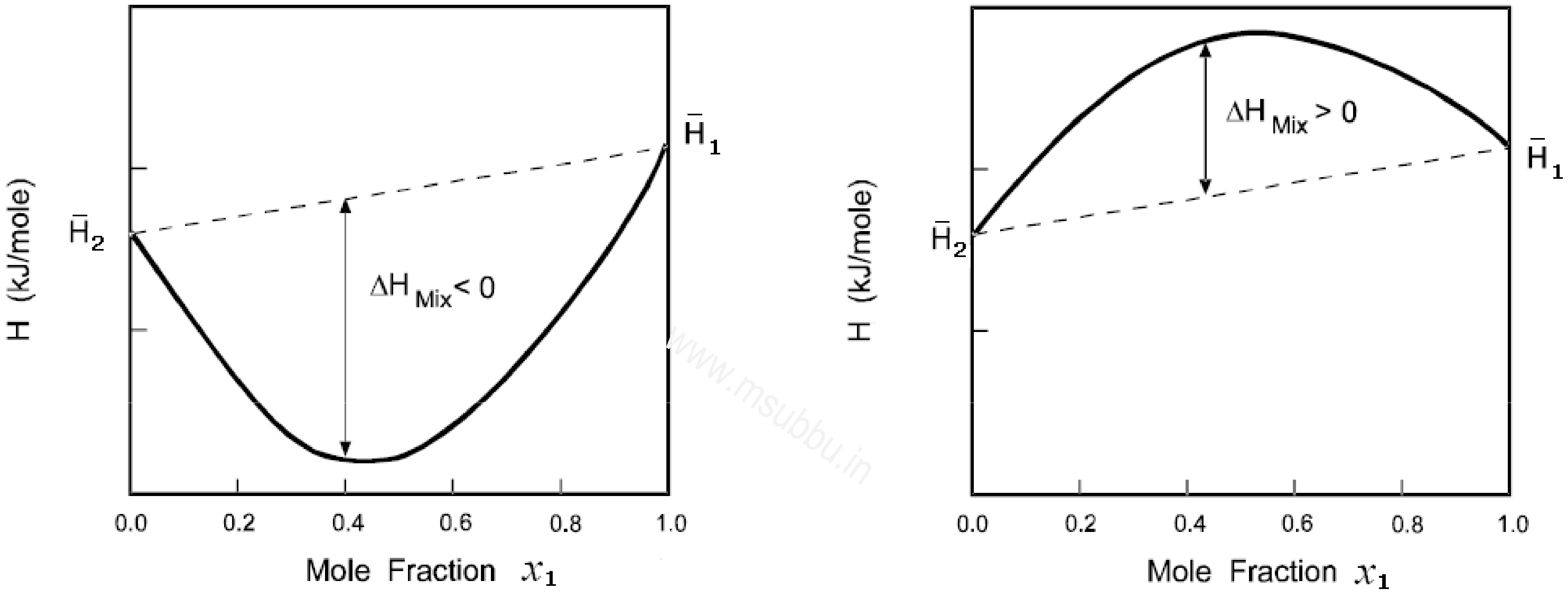
$$x_1 \left(\frac{\partial \ln \gamma_i}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P}$$

1. If we have experimental data for γ_1 as a function of x_1, we can integrate the above equation and calculate γ_2 as a function of x_2. That is, in a binary mixture, activity coefficient data for one component can be used to predict the activity coefficient of the other component.

2. If we have extensive experimental data for *both* γ_1 and γ_2 as a function of composition, we can test the data for thermodynamic consistency by determining whether or not the data obey the above equation. If the data show serious inconsistencies with the above equation, we may conclude that they are unreliable.

3. If we have limited data for γ_1 and γ_2, we can use an integral form of the Gibbs-Duhem equation; the integrated form provides us with thermodynamically consistent equations that relate γ_1 and γ_2 to x. These equations contain a few adjustable parameters that can be determined from the limited data.

Enthalpy Change of Mixing

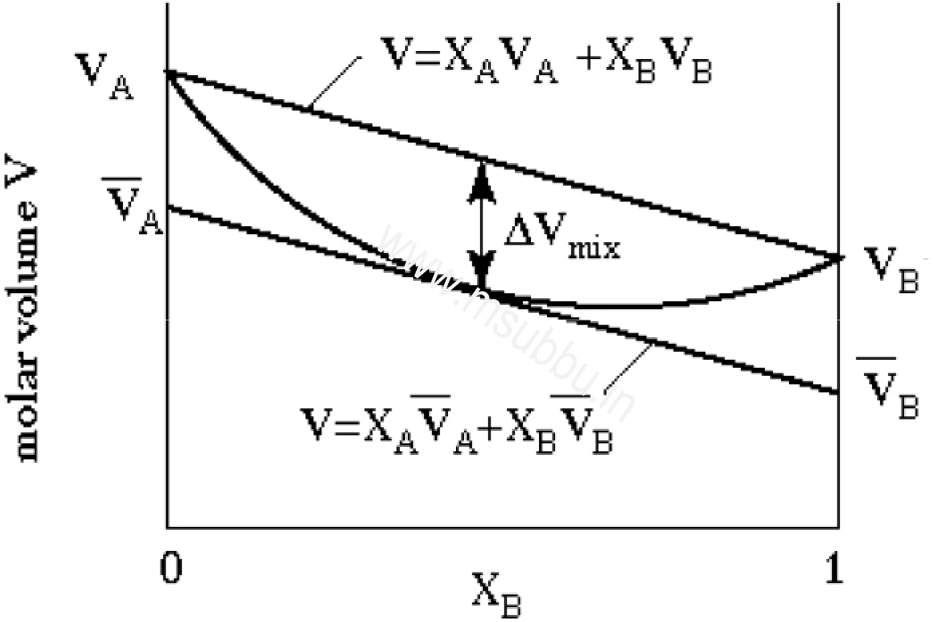


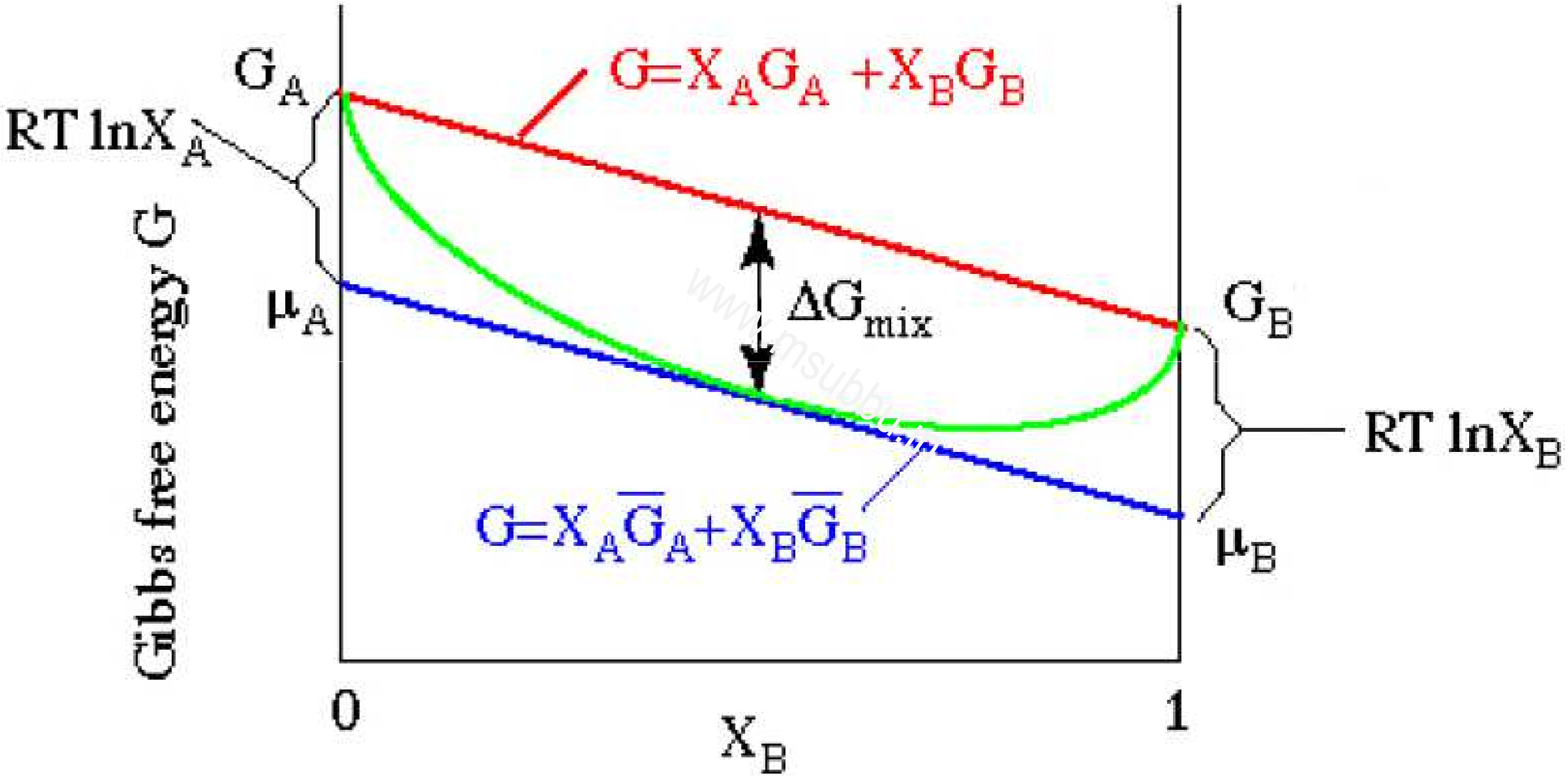
(a)

(b)

Enthalpies of mixing (at constant T and P) for a hypothetical binary solution. A negative enthalpy of mixing (a) means that heat is released upon mixing (exothermic) while a positive enthalpy of mixing (b) means that heat is absorbed upon mixing (endothermic).

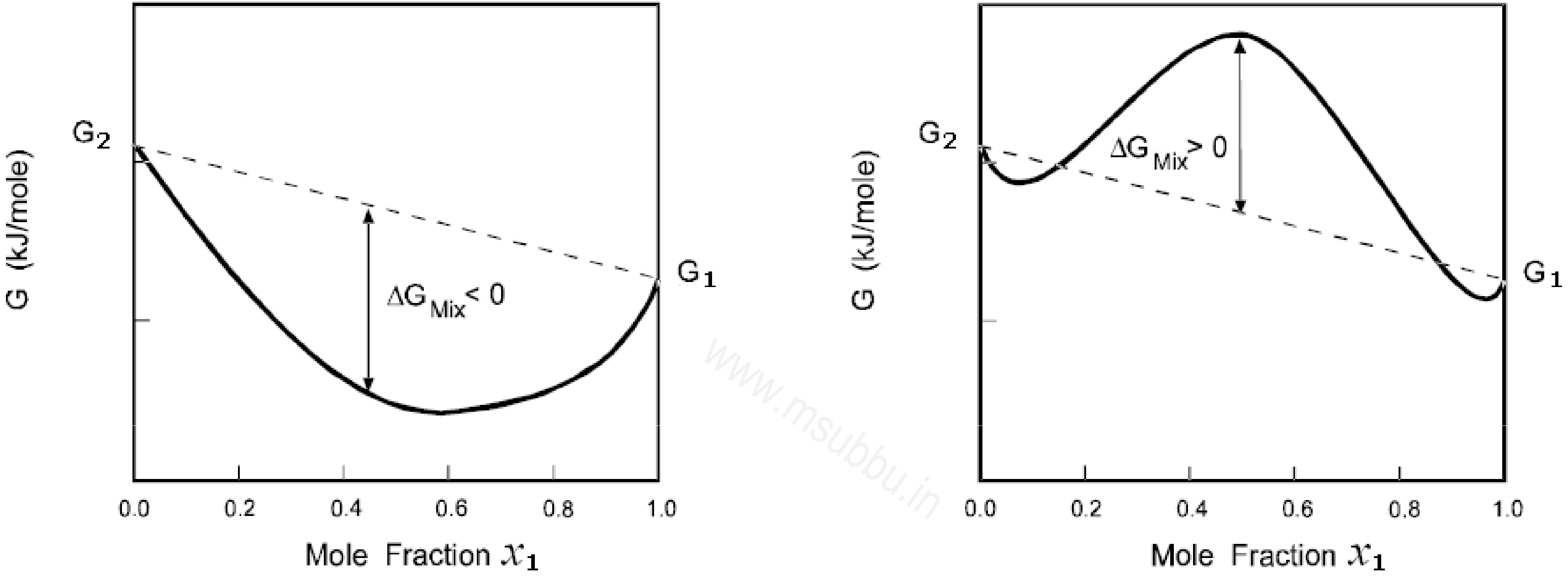
- ΔH_{mix} is negative for mixing of sulfuric acid with water


$V=X_AV_A+X_BV_B$
V_A
$\overline{V}_A$
ΔV_{mix}
V_B
$\overline{V}_B$
$V=X_A\overline{V}_A+X_B\overline{V}_B$
molar volume V
0
1
X_B



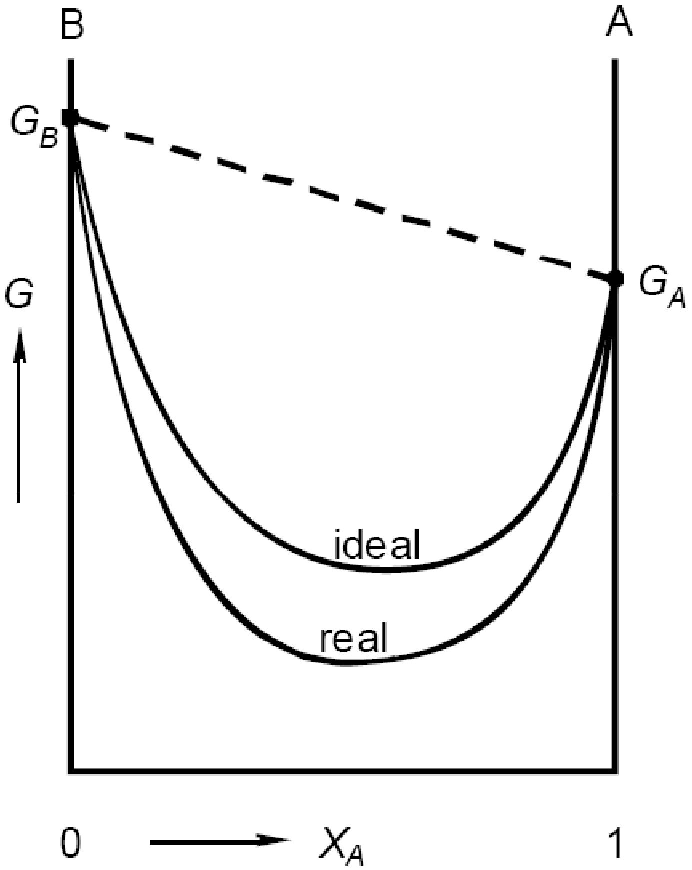
G_A
$RT \ln X_A$
$G = X_A G_A + X_B G_B$
μ_A
ΔG_{mix}
G_B
$RT \ln X_B$
$G = X_A \overline{G}_A + X_B \overline{G}_B$
μ_B
Gibbs free energy G
0
1
X_B

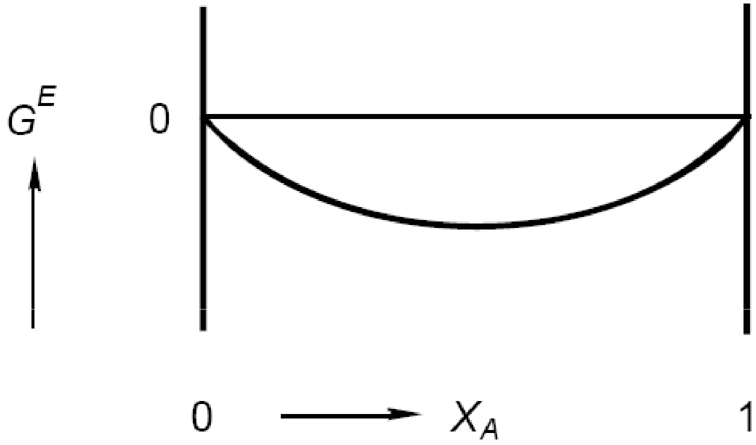
Gibbs Free Energy Change of Mixing



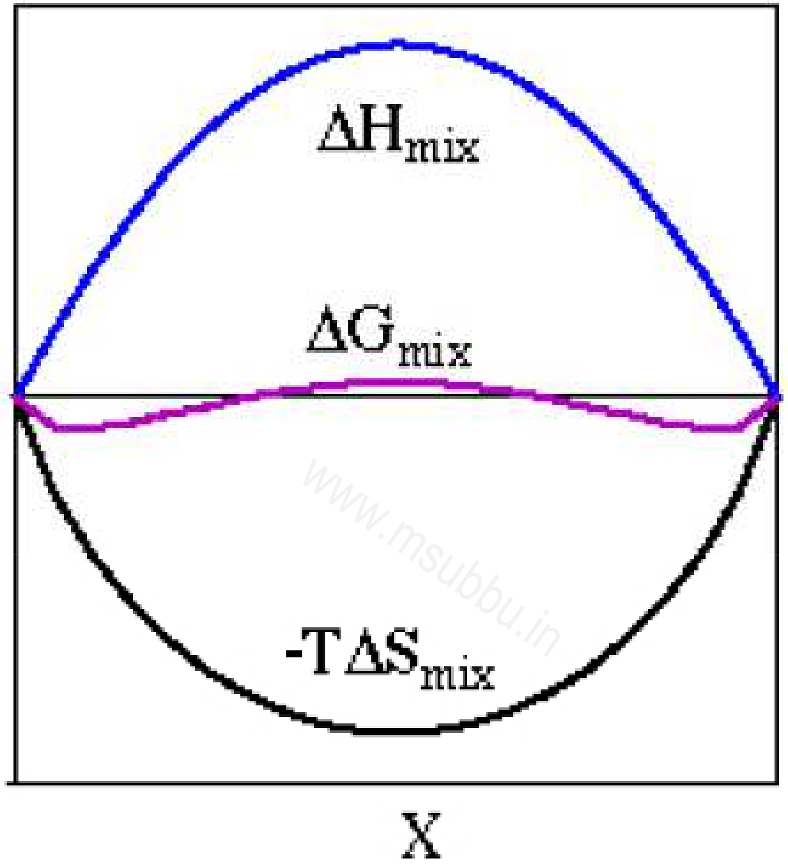
(a) (b)

Gibbs free energies of mixing for a hypothetical binary solution. A negative free energy of mixing (a) means that there is a thermodynamic driving force for mixing to occur (i.e. it will occur spontaneously), while a positive free energy of mixing (b) means that the pure components will not mix.





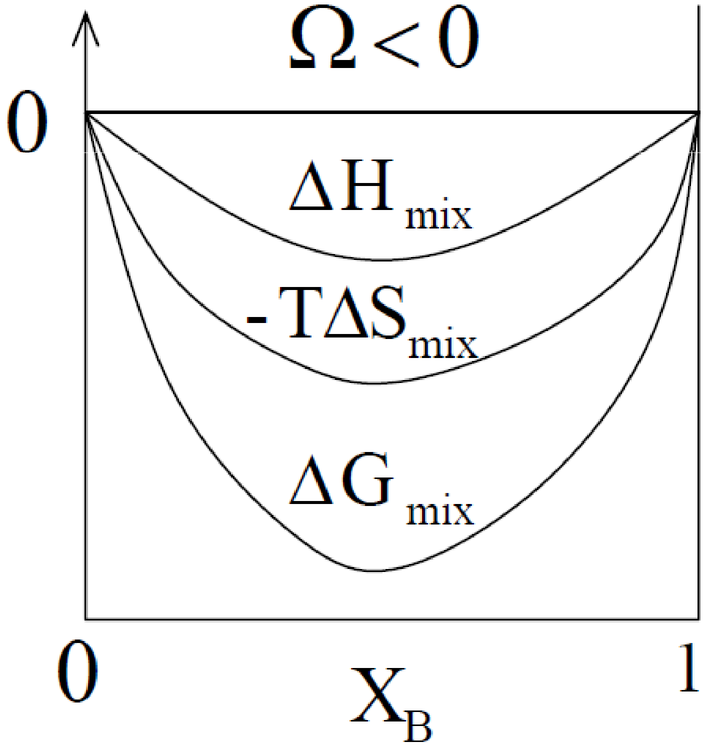
For given temperature and pressure, the Gibbs energy of a real mixture differs from the Gibbs energy of the hypothetical ideal mixture of the same components. The difference between the two is the excess Gibbs energy



Depending on the relative values of ΔH_{mix} and $-T\Delta S_{mix}$, the free energy of mixing may be negative throughout the whole composition range if the entropic energy contribution outweighs the enthalpy increase; this is more likely at higher temperature.

ΔG_{mix} for Exothermic Systems

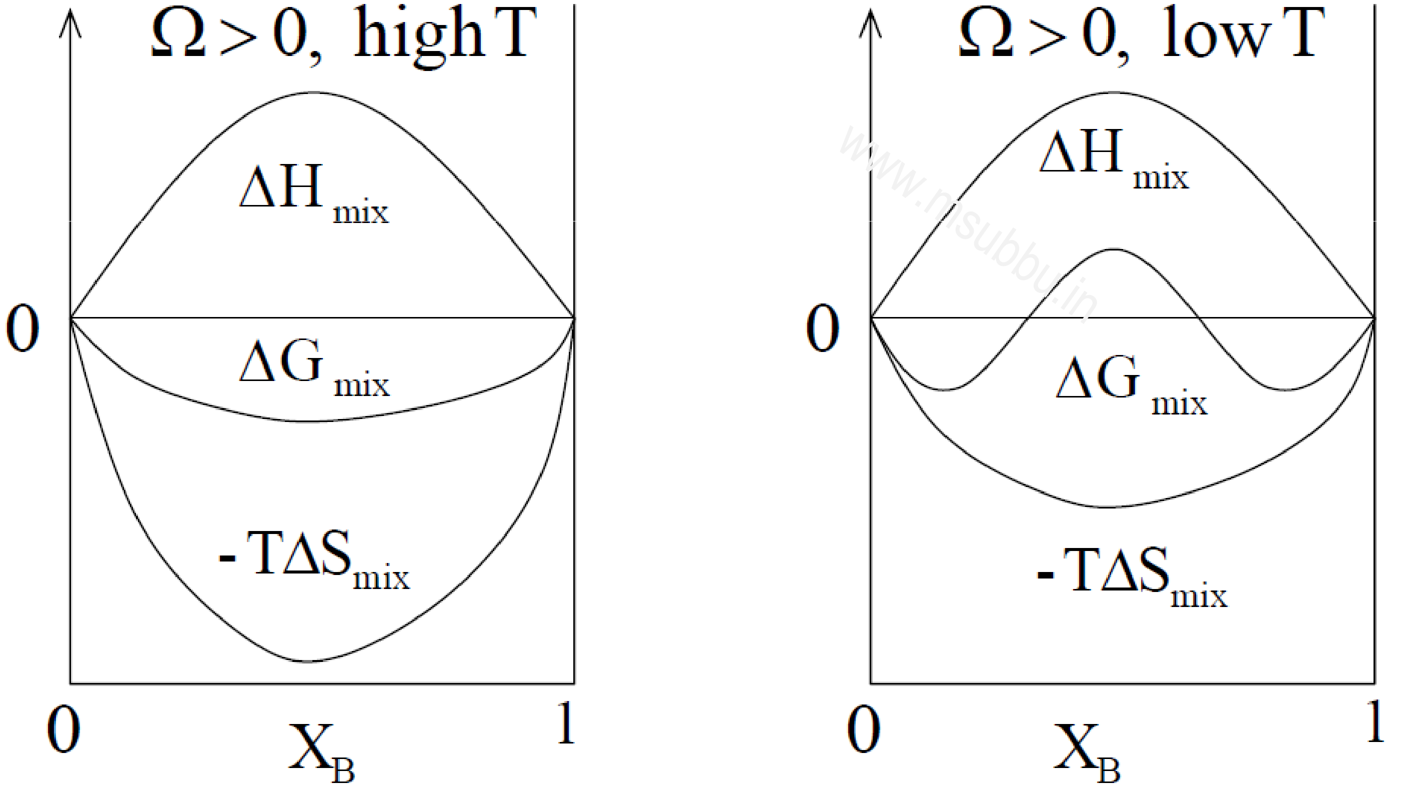
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

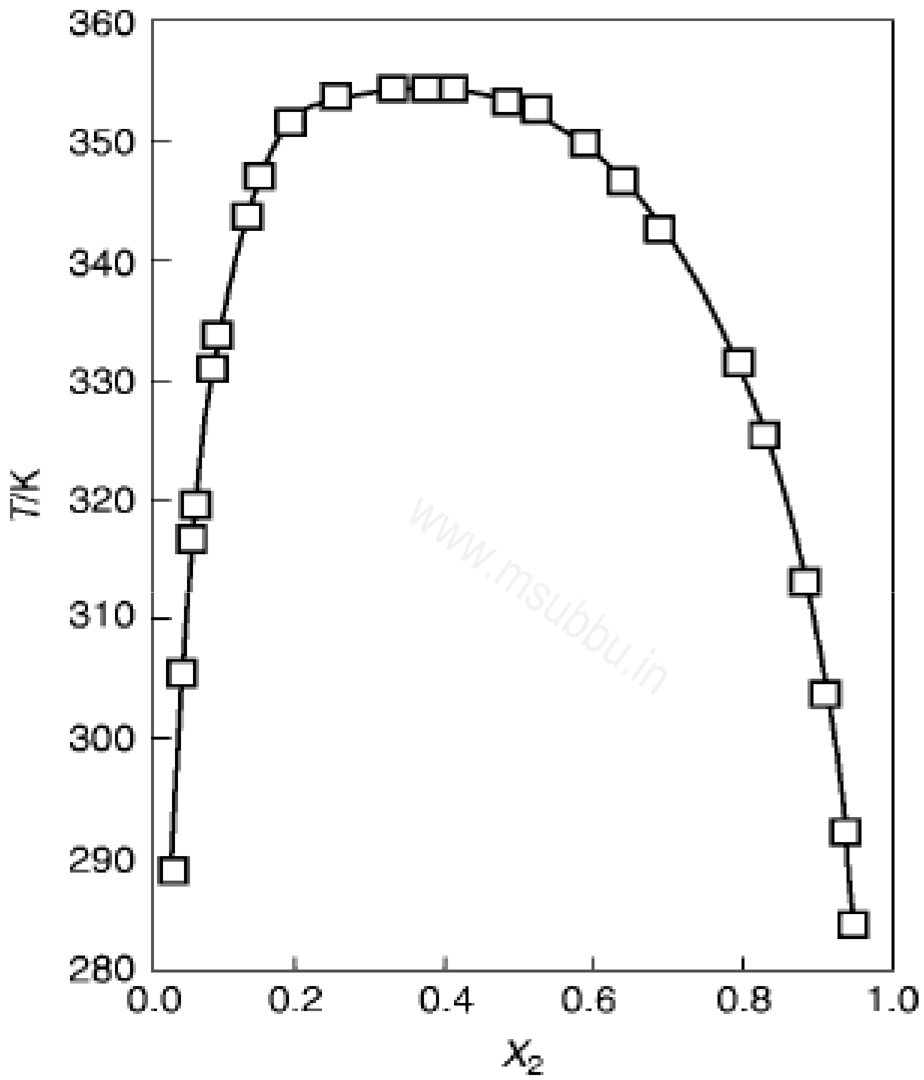


For $\Omega < 0$, $\Delta H_{mix} < 0$ – exothermic solution – mixing is favorable at all T

ΔG_{mix} for Endothermic Systems

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$





Liquid–liquid equilibrium curve for ethanenitrile (1) and 2,2,4-trimethylpentane (2), with a critical upper solution temperature of 354.55 K

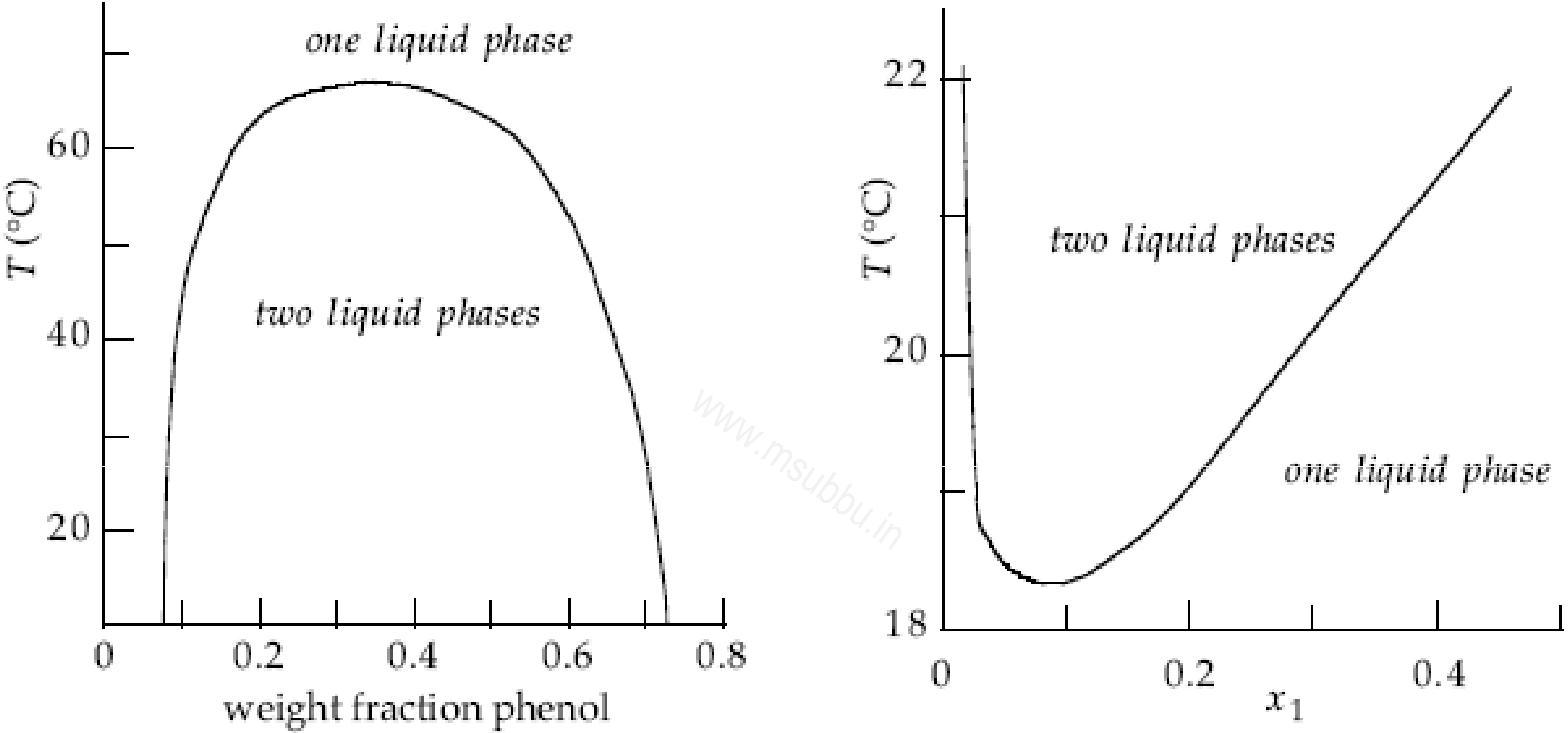


Figure 9.13 *Left*: Mixtures of phenol (C_6H_6O) and water have a UCST near 67°C and 0.35 weight fraction phenol [8–11]. *Right*: Mixtures of triethylamine(1) ($C_6H_{15}N$) and water(2) have an LCST near 18.3°C and $x_1 \approx 0.095$ [12].

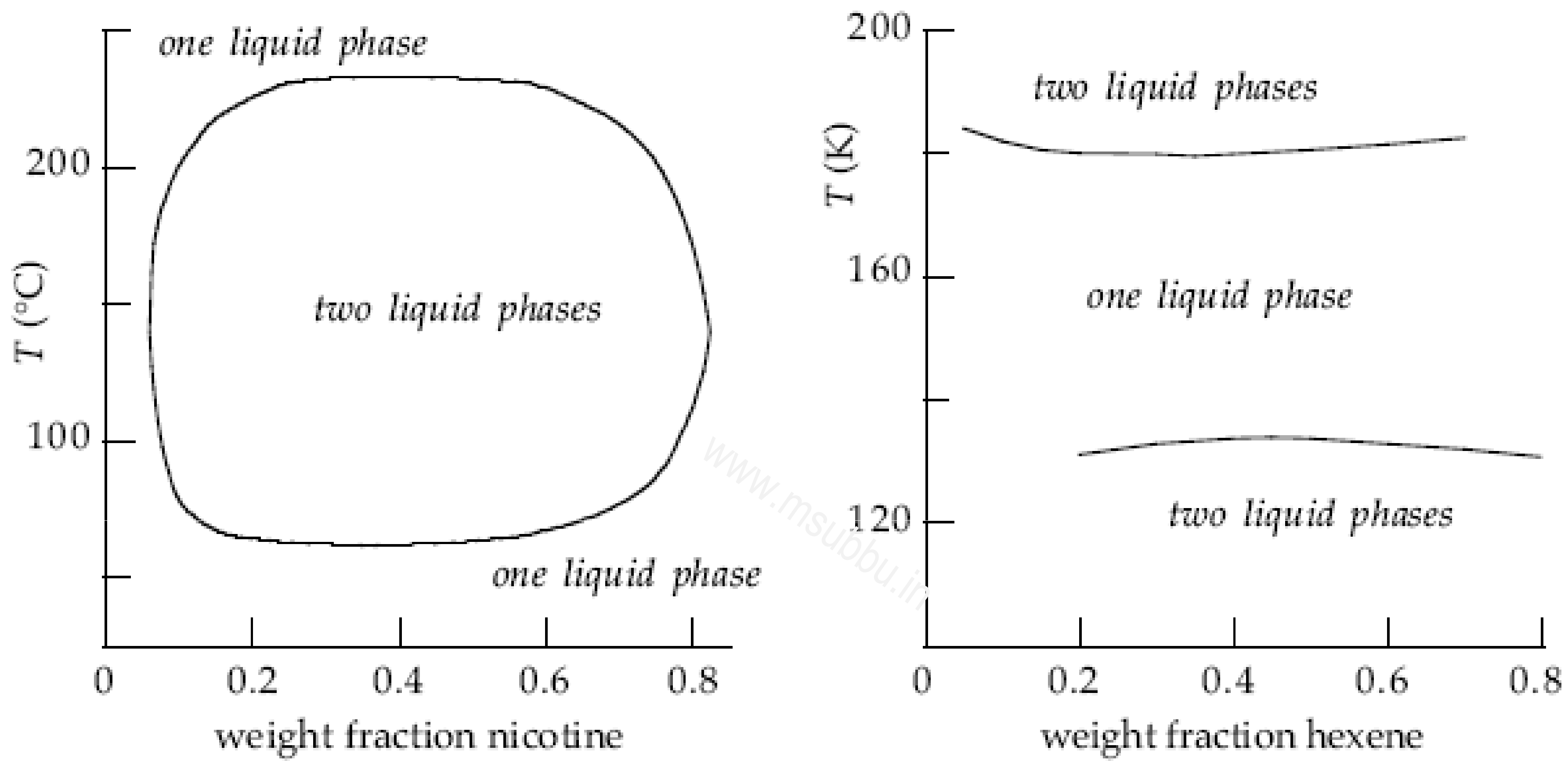
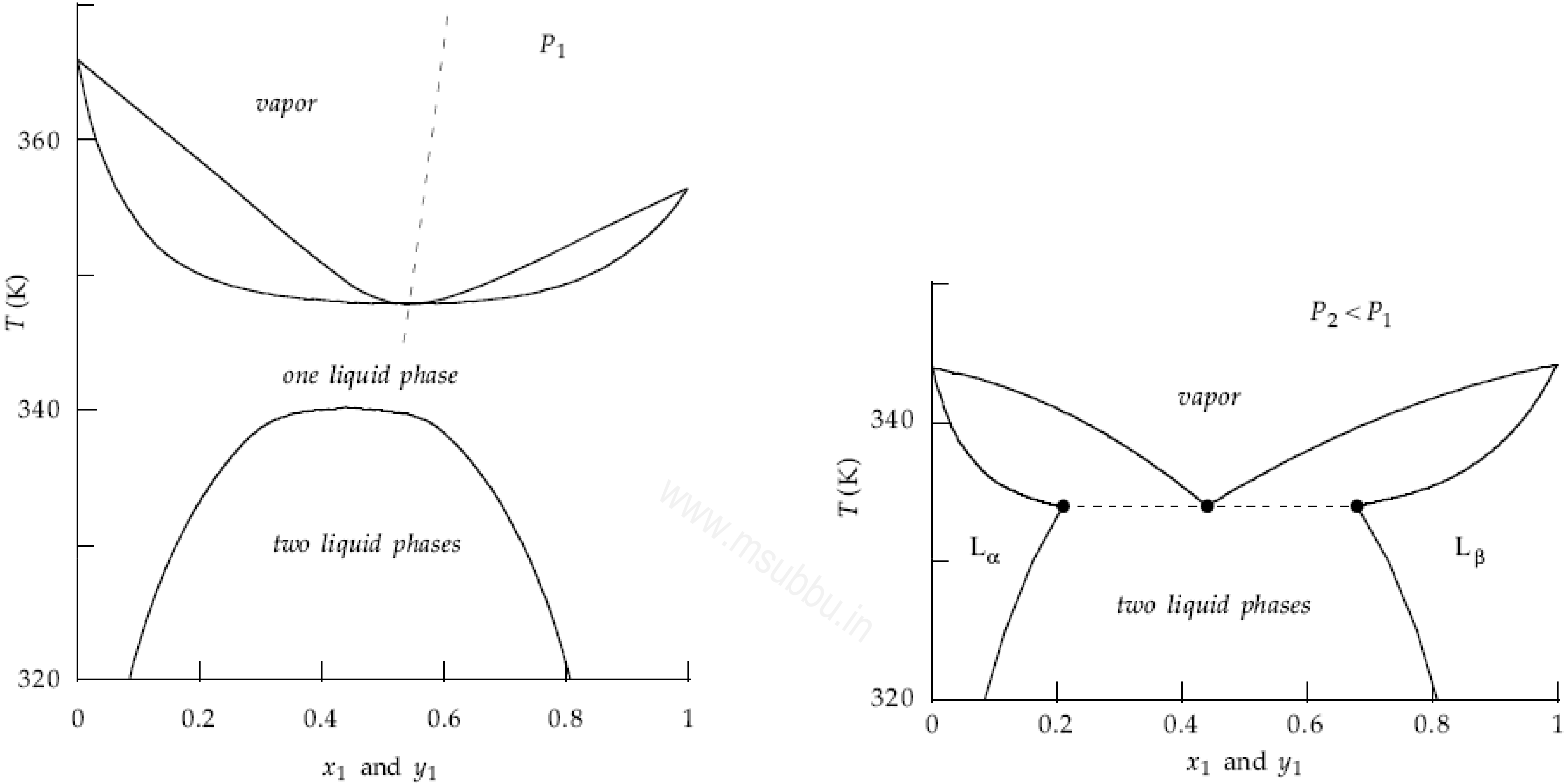
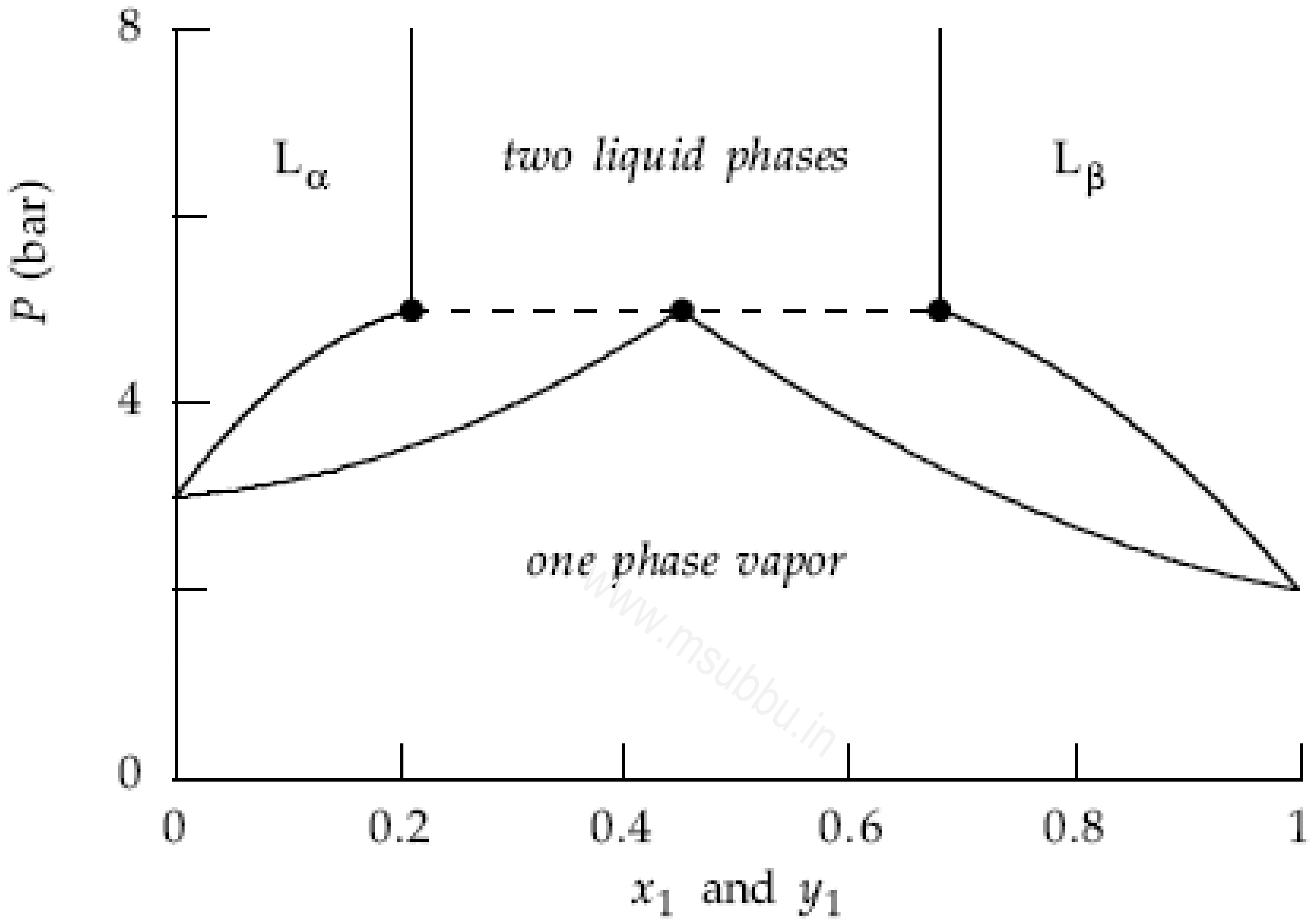


Figure 9.14 Examples of binary mixtures that have both a UCST and an LCST. *Left*: Mixtures of nicotine ($C_{10}H_{14}N_2$) and water have a closed solubility loop, with UCST = 233°C and LCST = 61.5°C [13]. *Right*: Mixtures of 1-hexene (C_6H_{12}) and methane have a miscibility gap, with UCST = 133.8 K and LCST = 179.6 K [14]. Pure hexene solidifies at 133.3 K, so the UCST occurs just above the melting curve of the mixtures.

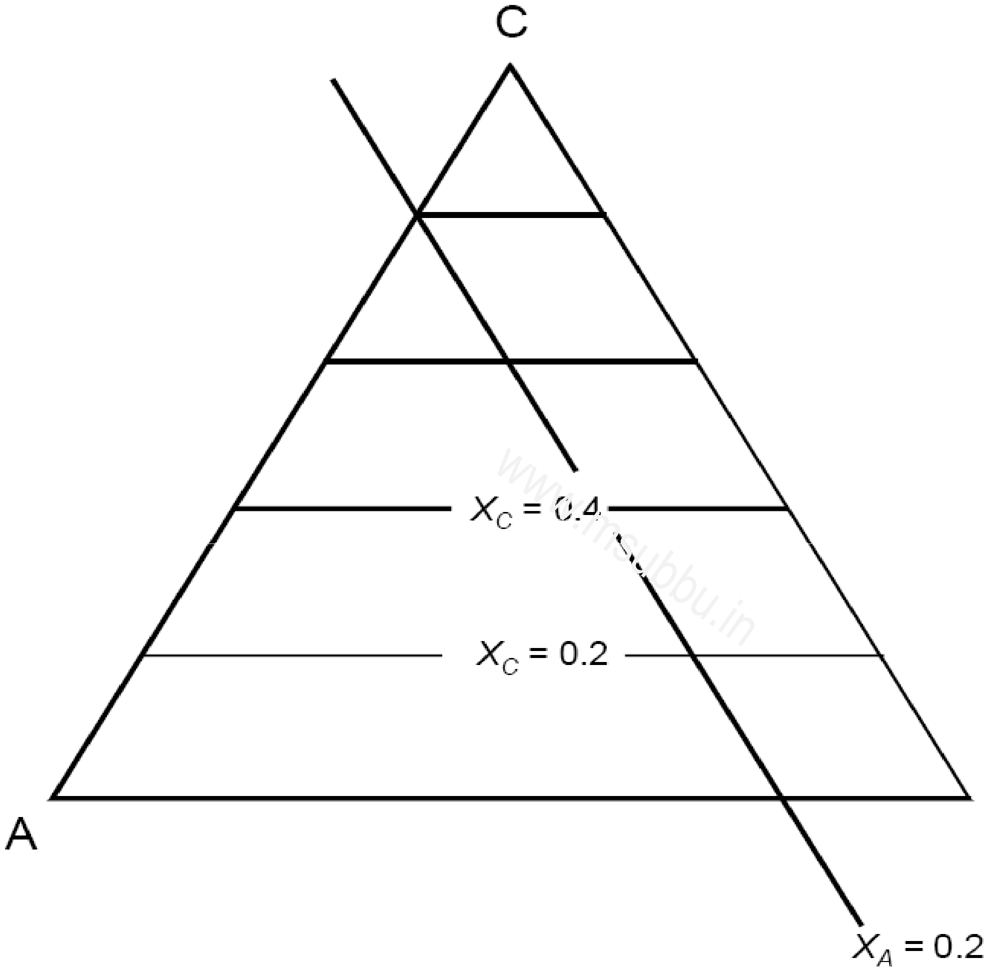


Effect of pressure on *Txy diagram for a binary mixture that exhibits vapor-liquidliquid* equilibrium via a heterogeneous azeotrope. At high pressures (*left) the VLE and LLE* regions are separated by a one-phase liquid region, and no VLLE occurs. Broken line at top is locus of homogeneous azeotropes. But at low pressures (*right) the VLE and LLE regions intersect* along an isotherm (broken horizontal line) at which the three phases coexist. Filled circles give compositions of the three phases in equilibrium; center circle gives composition of the vapor. Note that the change in pressure has little effect on the LLE envelope.

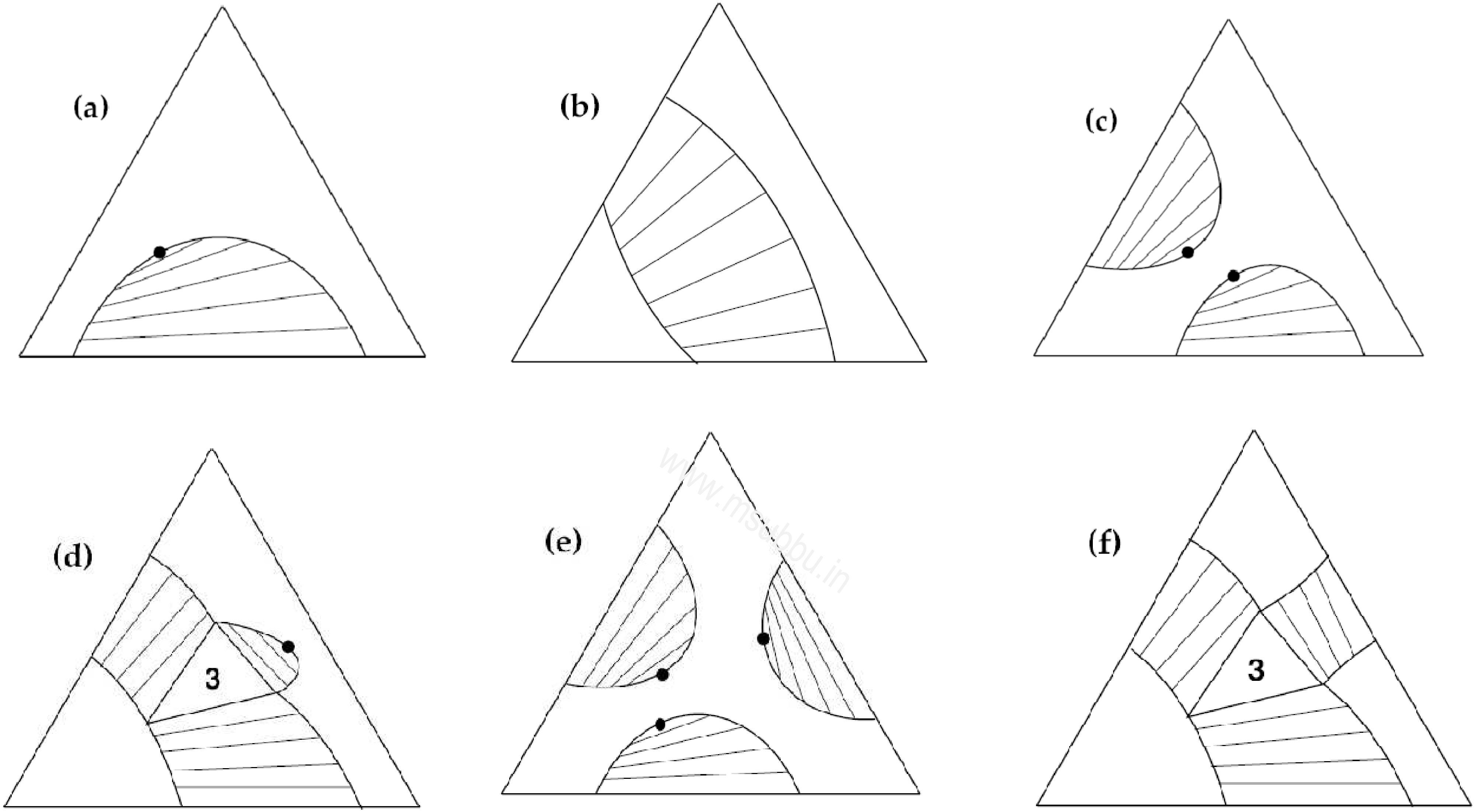


Schematic isothermal *Pxy diagram for the binary shown in previous slide. Broken horizontal* line is the three-phase tie line for VLLE (heterogeneous azeotrope). At this temperature, LLE occurs at high pressures and VLE occurs at low pressures.

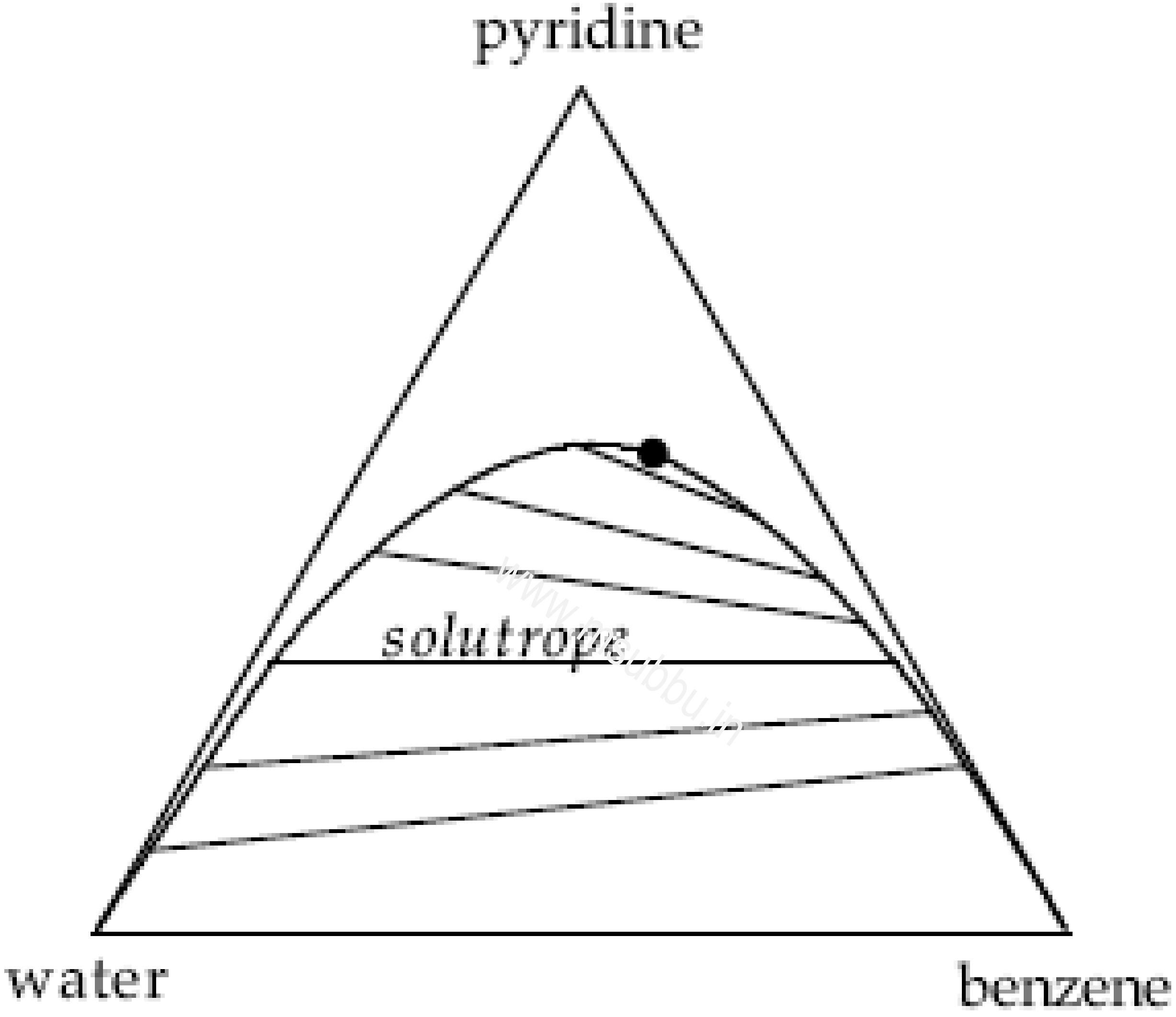
Ternary Liquid Equilibrium



The component of common composition is the one represented by the vertex that lies opposite the tie line.



Six common types of isothermal-isobaric triangular diagrams for ternary mixtures that exhibit liquid-liquid equilibria. Filled circles locate consolute points. Numeral 3 inside a triangle identifies three-phase LLLE; the compositions of the three phases are given by the vertices of the triangles. These six diagrams are arranged by the number of two-phase regions: (a) and (b) each have one, (c) has two, and (d)-(f) each have three.

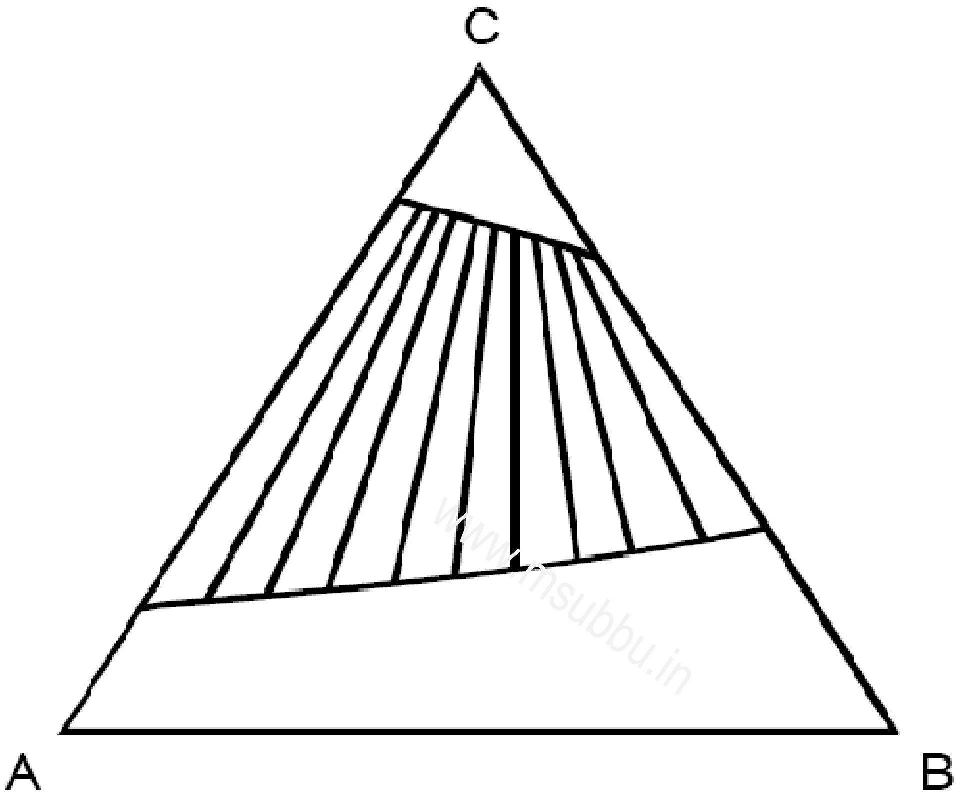


Formation of a solutrope in mixtures of water, benzene (C_6H_6), and pyridine (C_5H_5N). Filled circle marks consolute point

Solutropes

- Invariance in composition that occurs when a line on a triangular diagram lies parallel to an edge of the triangle. This invariance takes on special significance when the parallel line is a tie line across a two phase region. When this occurs, the two phases in LLE have the same composition in one component, and the mixture is called a solutrope.

- Their practical significance arises from their ability to inhibit separations by liquid extraction, because transfers of components between phases are often hindered when a mole fraction becomes the same in both phases. Such inhibitions may be compounded if the densities of the phases also become equal, as they may near solutropes. Since liquid extractions exploit density differences, no separation occurs in an extraction process when the densities of the two phases become equal, even if their compositions differ.



The system methylcyclohexane (A) + n-hexane (B) + methanol (C) at 1 atm, 30 °C. Phase diagram showing the boundaries of the region of demixing and *tie lines* connecting the positions of the two coexisting liquid phases (Schuberth 1986)

Effect of Temperature on TLE

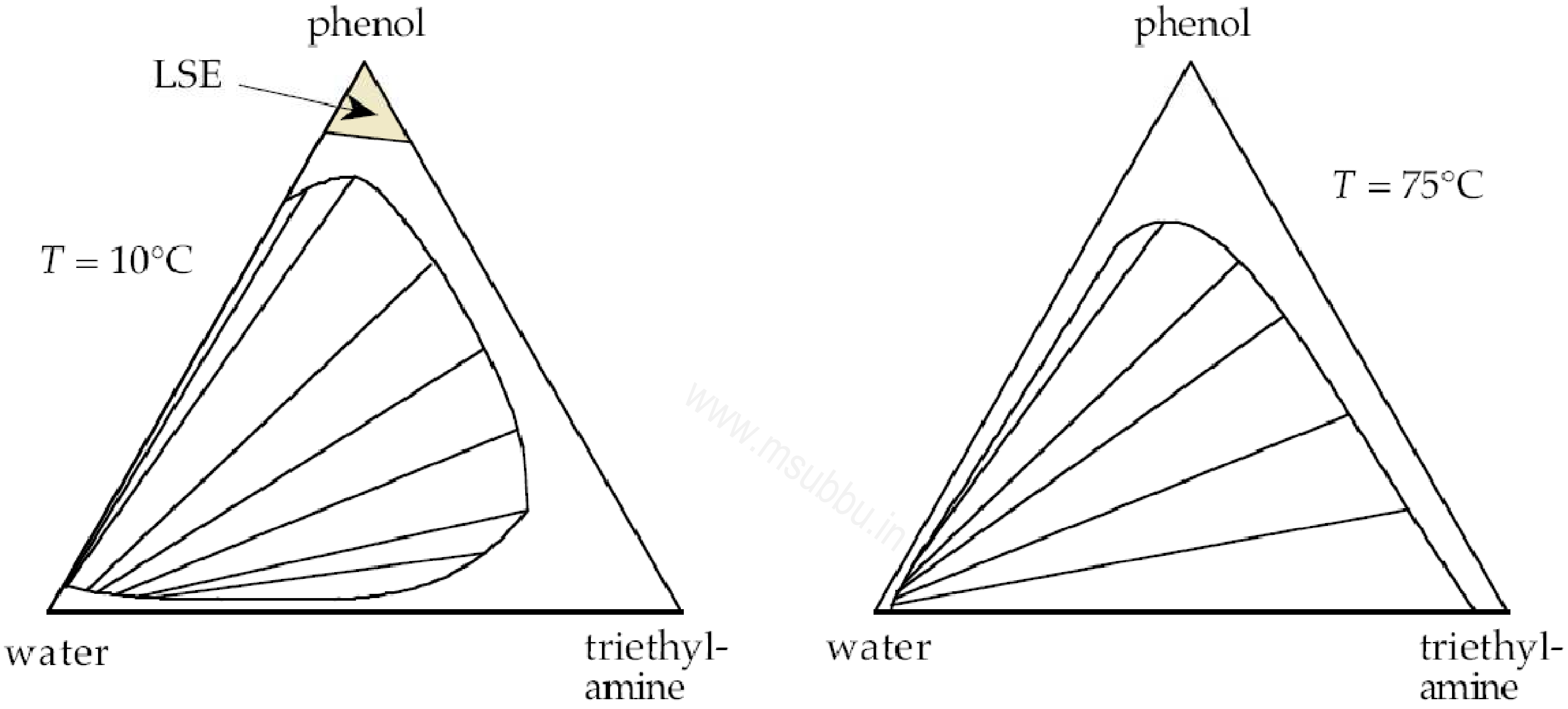


Figure 9.27 Effect of temperature on LLE in mixtures of phenol, water, and triethylamine. At 10°C a consolute point occurs in mixtures lean in phenol, while at 75°C a consolute point occurs in mixtures lean in triethylamine. At 10°C pure phenol solidifies. Compositions plotted here as weight fractions. Adapted from Walas [5].

Gamma-Gamma Method Applied to LLE Calculations

$$x_i^{\alpha}\gamma_i^{\alpha}(T,\{x^{\alpha}\}) = x_i^{\beta}\gamma_i^{\beta}(T,\{x^{\beta}\})$$

- The gamma-gamma method is commonly applied to low-pressure, liquid-liquid equilibrium calculations