لجان الدفعات

PHYSICAL PHARMACY

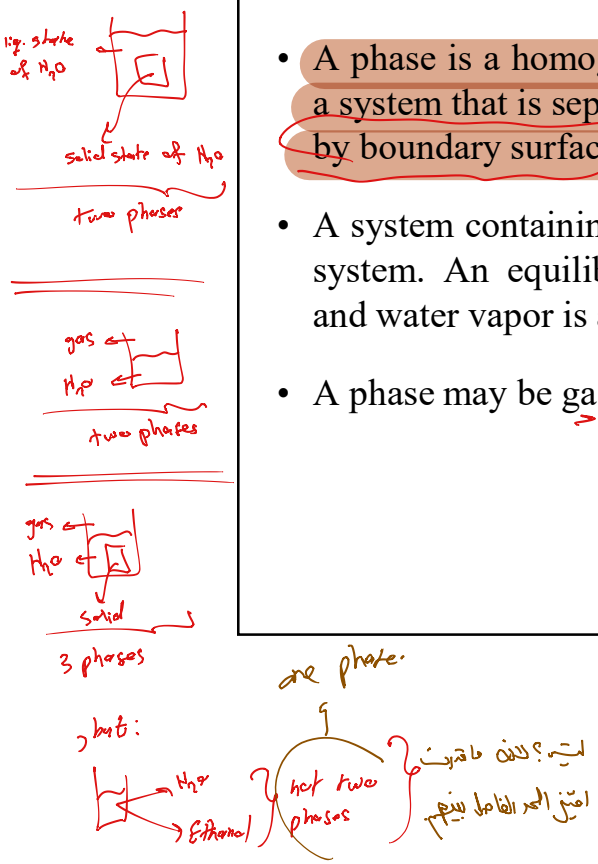
MORPHINE ACADEMY

MORPHINE ACADEMY

Phase equilibria and the phase rule

The Phase

- A phase is a homogenous physically-distinct portion of a system that is separated from other parts of the system by boundary surfaces.
- A system containing water and its vapor is a two-phase system. An equilibrium mixture of ice, liquid water, and water vapor is a three phase system.
- A phase may be gas, liquid or solid.



The Phase

- A gas or a gaseous mixture is a single phase.
- Completely miscible liquids constitute a single phase.
- In an immiscible liquid system, each layer is counted as a separate phase.
- Every solid constitutes a single phase except when a solid solution is formed.
- A solid solution is considered as a single phase.
- Each polymorphic form constitutes a separate phase.

The Phase diagram

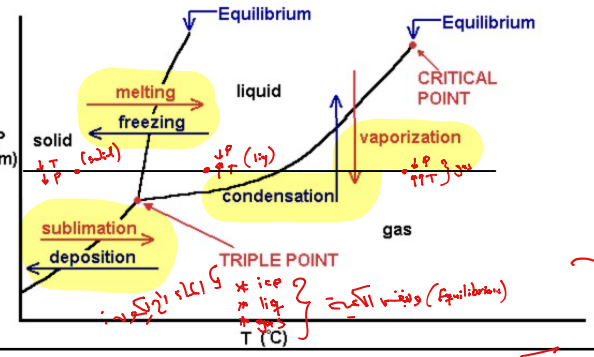
- Phase diagram shows the multisystem state changes with the temperature, pressure, composition and other intensive properties.

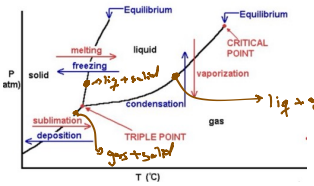
Intensive properties are properties that do not depend on size; e.g. pressure and temperature.

The Phase diagram: One component system

- The simplest phase diagrams are pressure-temperature diagrams of a single simple substance.
- The axes correspond to the pressure and temperature.
- The lines in the phase diagram represent two phase systems, while the spaces between the lines represent one phase systems.

➢The triple point represents the temperature and pressure where all three physical states are in equilibrium (for water 0.01 °C and 0.00603659 atm).

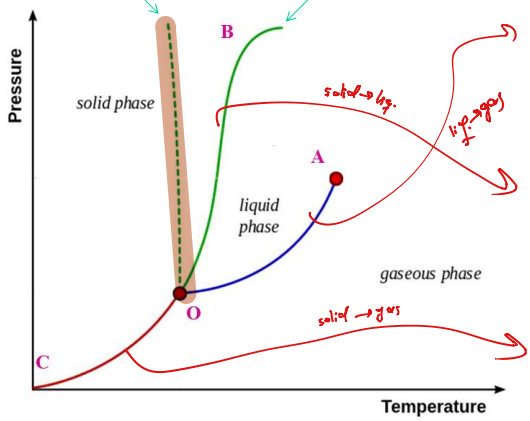




The Phase diagram: One component system

The frozen state of water (ice) is actually less dense than the liquid state. Therefore; increasing pressure (which favors compactness of the molecules) will favor the liquid state.

For most substances the solid is denser than the liquid. Therefore; an increase in pressure usually favors the more dense solid phase.



Curve OA: vapor pressure curve

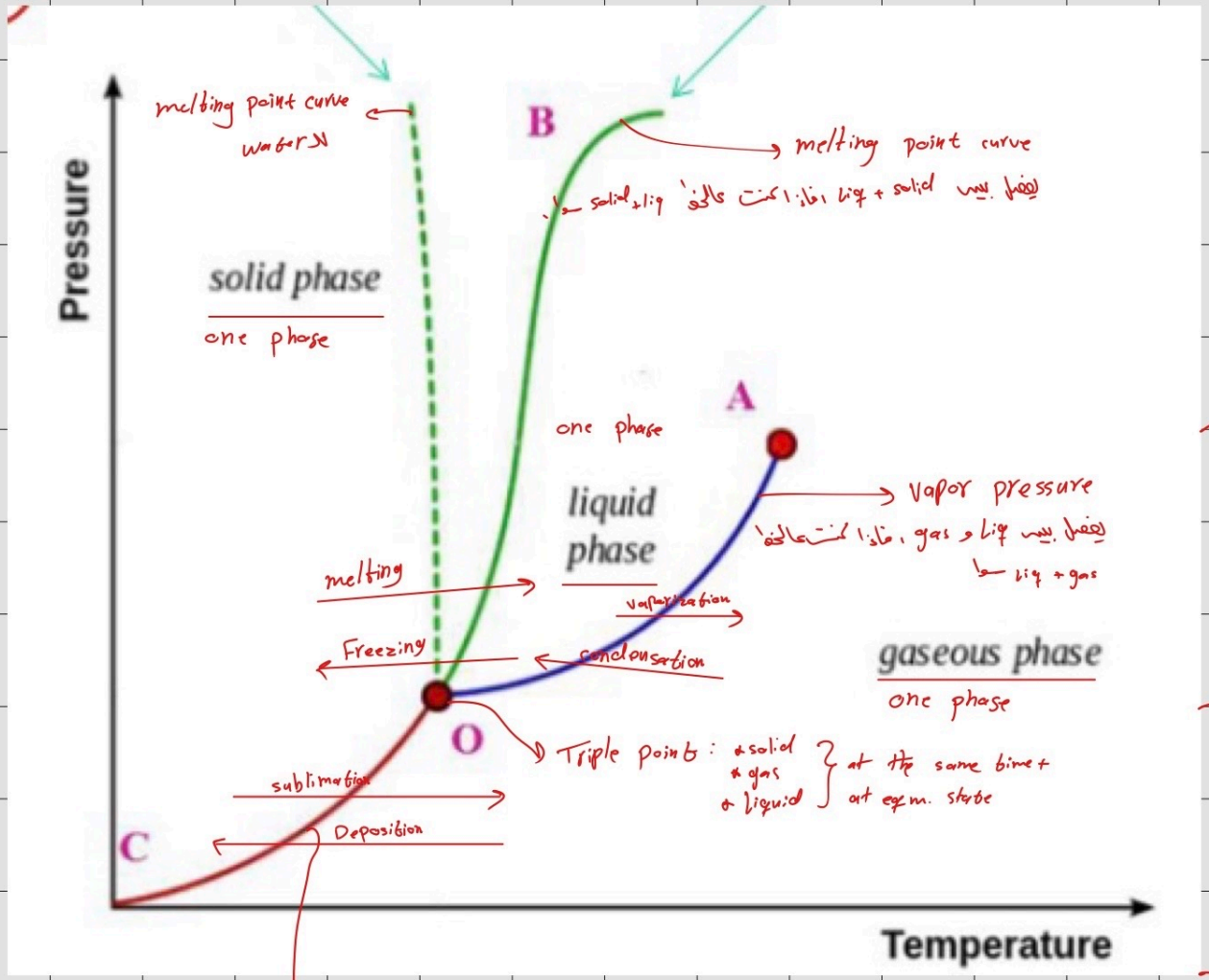
Curve OB: Melting point curve

Curve OC: Sublimation curve

إذا كان عندك ثلج عند صفر سيليسيوس،وزدنا الضغط بس (بدون تغيير درجة الحرارة) شو بصير؟
بتحول إلى ماء سائل،ليش ؟لانه درجة الحرارة ثابتة واللي تغير هو بس الضغط،وبما انه الماء السائل اكثف من الثلج،فالضغط بفضل الحالة اللي حجمها أصغر واللي هي الماء

الضغط بفضل الاشي اللي كثافته اعلى (يعني حجمه اصغر) ليش؟ لانه بقرب الجزيئات من بعض ،يعني لو كان سائل وزدت الضغط عليه بصير صلب،ولو كان غاز وضغطته بزيادة بصير سائل
هاد بالوضع الطبيعي
بس بحالة المي،كلما زدت الضغط عليه بميل انه يضل سائل،لانه الحالة السائلة للماء اكثف من حالة الثلج،لانه الثلج حجمه اكبر من حجم الماء،فكلما زاد الحجم قلت الكثافة،فكثافة الماء السائل اعلى من كثافة الثلج

the simplest phase diagram: pressure - temperature diagram ⇒ single phase.



ارجعولهم بس تخلصوا إنتبه

$F = 1 - 3 + 2 = 0$ ← 3 phases (gas, liq, solid) ← triple point عند

$F = 1 - 2 + 2 = 1$ ← two phases ← على أي خط منحنى

$F = C - P + 2$

$F = 1 - 1 + 2 = 2$ ← one phase ← داخل أي منطقة سواء solid / liquid / gas

Deposition ⇐ من الغاز للصلب ، sublimation ⇐ من الصلب للغاز

solid تجيب بالة ⇐ Gas ، solid بيصير ⇐ إذا كنت على الخط فأنت

The Phase diagram: One component system

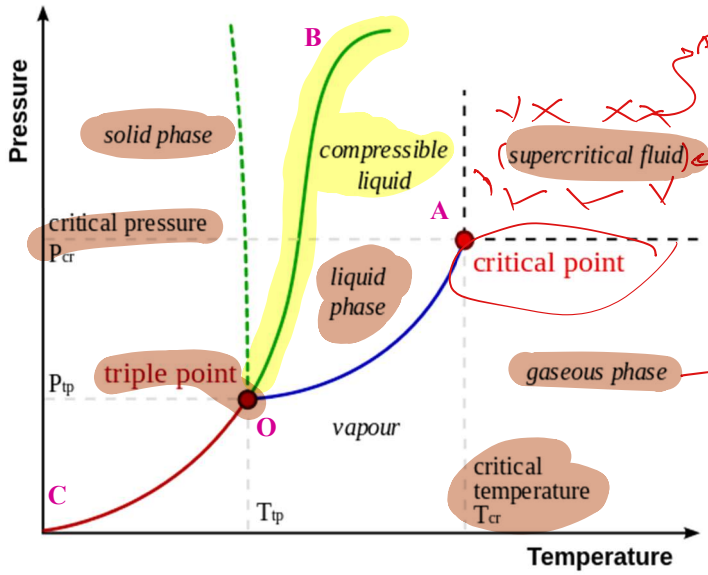
- The critical point is the point on a phase diagram that indicates the critical temperature and pressure.
- The critical temperature of a substance is the temperature above which that substance can no longer exist as a liquid, no matter how much the pressure is increased.
- In the same way, the critical pressure is the pressure above which the substance can no longer exist as a gas, no matter how high the temperature is.
- Supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

The Phase diagram: One component system

Curve OA: vapor pressure curve

Curve OB: Melting point curve

Curve OC: Sublimation curve



The supercritical fluids

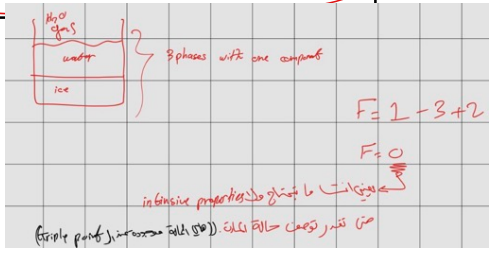
- In general terms, supercritical fluids have properties between those of a gas and a liquid.
- Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes.
- Supercritical fluids have the viscosity of a gas, but the densities and solvent power of a liquid, making SC fluids ideal for extraction.

The Gibbs phase rule

- To understand and define the state of a phase, knowledge of several independent variables is required.
- Independent variables (also called intensive variables) are the variables that do not depend on the volume or size of the phase, e.g. temperature, pressure, density, boiling point and concentration.
- The Gibbs phase rule is expressed as follows:

$$F = C - P + 2$$

- **F**: is the number of degrees of freedom of the system which is the least number of intensive variables required to define the system completely (vary independently).
- **C**: number of components, **P**: number of phases present



Application of phase rule to one component system

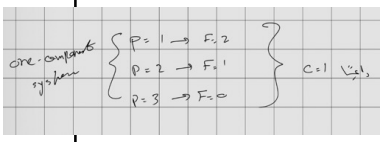
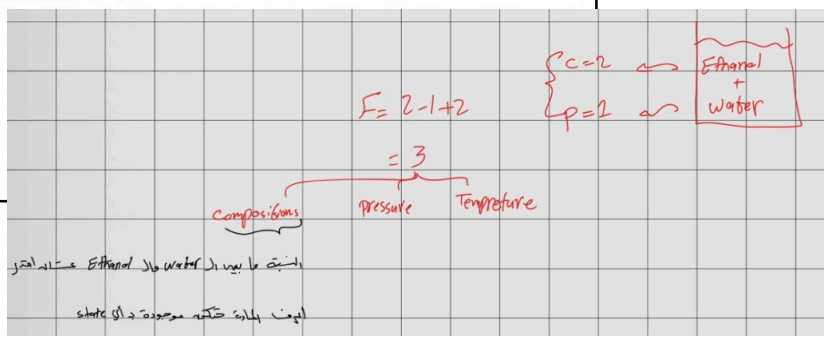


TABLE 2–7
APPLICATION OF THE PHASE RULE TO SINGLE-COMPONENT SYSTEMS*

System	Number of Phases	Degrees of Freedom	Comments
Gas, liquid, or solid	1	$F = C - P + 2$ $= 1 - 1 + 2 = 2$	System is *bivariant* ($F = 2$) and lies anywhere within the area marked vapor, liquid, or solid in Figure 2–22. We must fix two variables, e.g., P_2 and t_2, to define system D.
Gas–liquid, liquid–solid, or gas–solid	2	$F = C - P + 2$ $= 1 - 2 + 2 = 1$	System is *univariant* ($F = 1$) and lies anywhere along a *line* between two-phase regions, i.e., AO, BO, or CO in Figure 2–22. We must fix one variable, e.g., either P_1 or t_2, to define system E.
Gas–liquid–solid	3	$F = C - P + 2$ $= 1 - 3 + 2 = 0$	System is *invariant* ($F = 0$) and can lie only at the *point* of intersection of the lines bounding the three-phase regions, i.e., point O in Figure 2–22.

*Key: C = number of components; P = number of phases.



Two component system containing liquid phases

- Systems in which the vapor phase is ignored and only solid and liquid phases are considered are termed condensed systems.

- Systems containing liquids might be:

1. Completely immiscible (such as mercury and water)
2. Completely miscible in all proportions (e.g.ethanol and water)
3. Partially miscible (e.g. phenol and water)

Two component system containing liquid phases

For two component systems:

$C=2 \quad F = C - P + 2 \implies F = 4 - P$

$P \geq 1 \implies F \leq 3$

Three variables are required: temperature, pressure, and composition.

If the pressure is fixed, only temperature and composition are required.

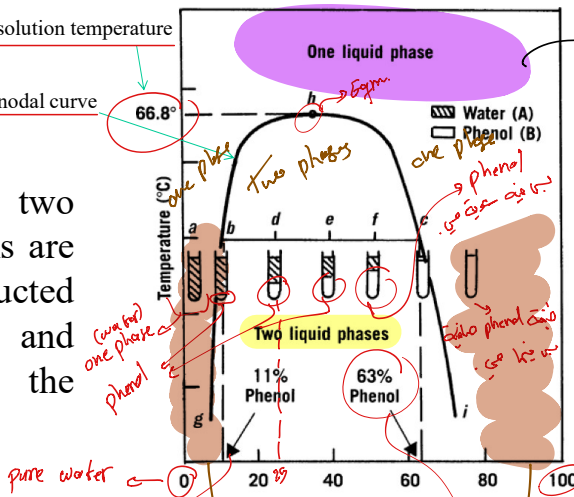
$F = C - P + 1$

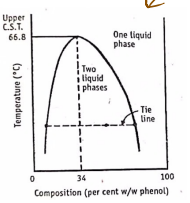
Two component system containing liquid phases

Upper consolute temperature = critical solution temperature

Binodal curve

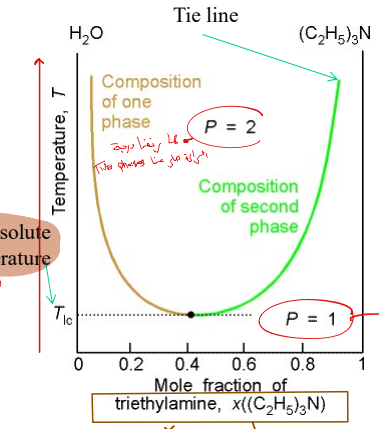
Phase diagrams for two component systems are commonly constructed with temperature and composition as the coordinates.





Two component system containing liquid phases

Other liquid mixtures show no upper consolute temperature but lower consolute temperature.



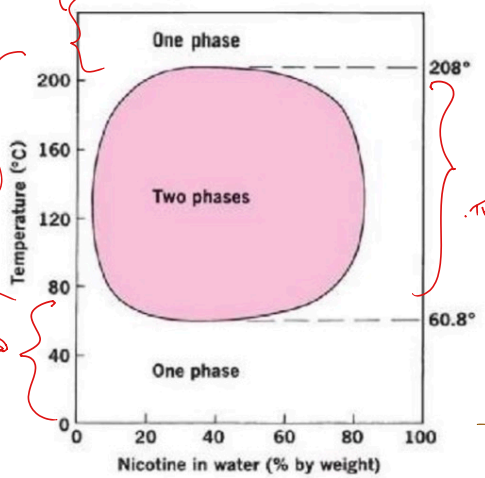
[في نظام Lower CST]

رفع الحرارة ⟵ تقل الذائبية ⟵ يتسع المنحنى ⟵ يميل إلى (Two Phases)

تقليل الحرارة ⟵ تزيد الذائبية ⟵ يضيق المنحنى ⟵ يميل إلى (One Phase)

Two component system containing liquid phases

Other liquid mixtures show both upper and lower consolute temperatures.



التسخين في الحرارات المنخفضة: يقلل الذائبية ⟵ يوصلنا لـ Two phases.

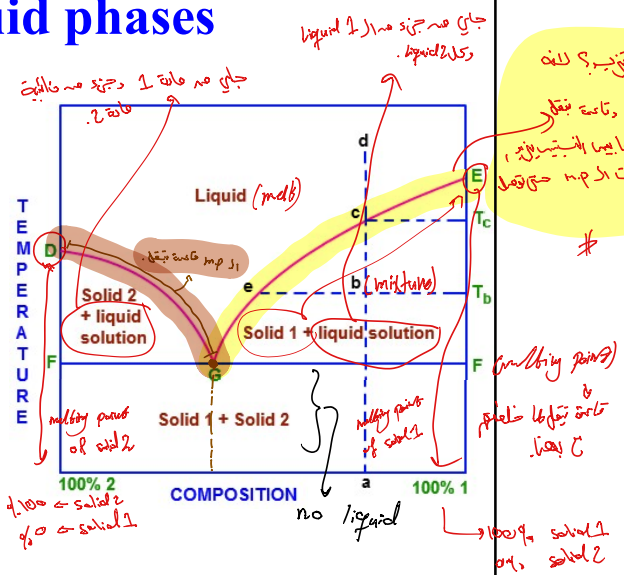
التسخين العالي جداً (فوق 208) يرفع الذائبية ⟵ يرجعنا لـ One phase.

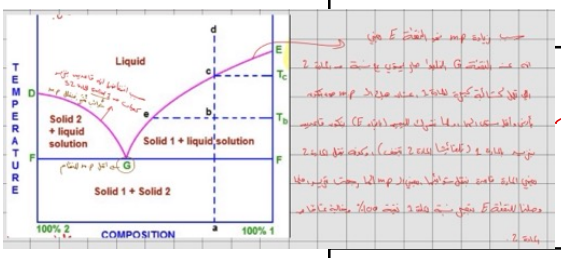
Two component system containing solid and liquid phases

The points of **D** and **E** represent the melting points of **solids 2 and 1**.

Two component system consisting of two solids (**2 and 1**) when heated to a temperature above the melting points of both (**point d**), a one-phase system will form consisting of a liquid solution of **2 and 1**.

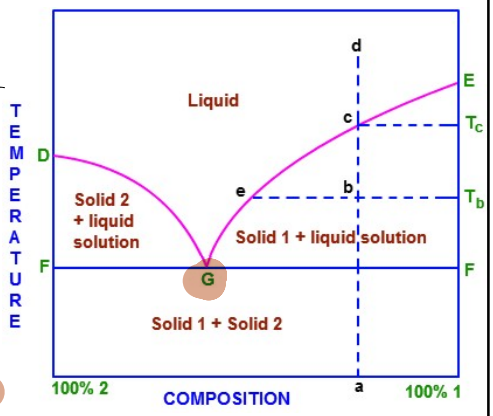
When the temperature fall to point c, pure solid 1 will form dispersed in a liquid solution of 1 and 2.





Two component system containing solid and liquid phases

- At point **G** solid **1**, solid **2** and solution phase are in mutual equilibrium (exist together).
- The solid phase at this point is a finely divided two-phase dispersion of crystalline 1 and 2 called a eutectic, and G is the eutectic point. Eutectic melts at a lower temperature than either of its pure components.



Phase equilibria in three-component systems

For three component systems:

$C = 3 \quad F = C - P + 2 \Rightarrow F = 5 - P$

$P \geq 1 \Rightarrow F \leq 4$

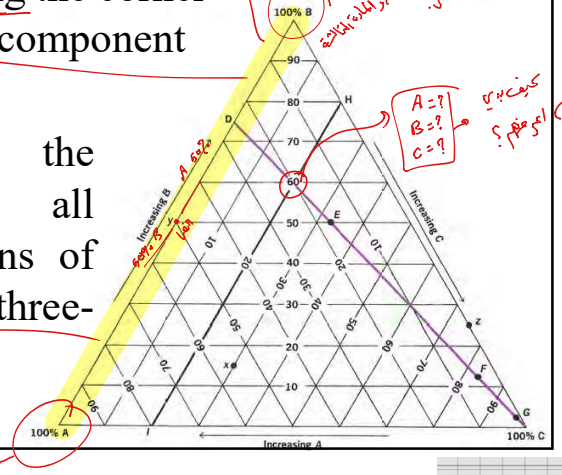
Four variables are required: temperature, pressure, and two compositions.

If the temperature and pressure are both fixed then, only two compositions are required

- Because we are dealing with a three-component system, it is more convenient to use triangular coordinate graphs

Rules relating to triangular diagram

- Each of the three corners represent 100% by weight of one component.
- The three lines joining the corner points represent two component mixture.
- The area within the triangle represent all possible combinations of A, B , and C to give three-component system



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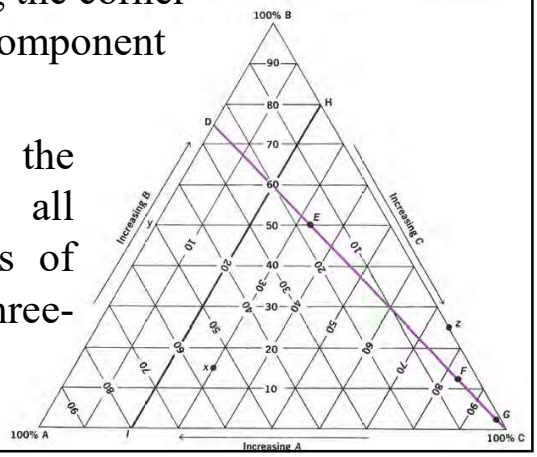


Ternary systems with one pair of partially miscible liquids

- E.g. Water, benzene and ethanol mixture
- Water and benzene are partially miscible
- Ethanol is miscible with both water and benzene

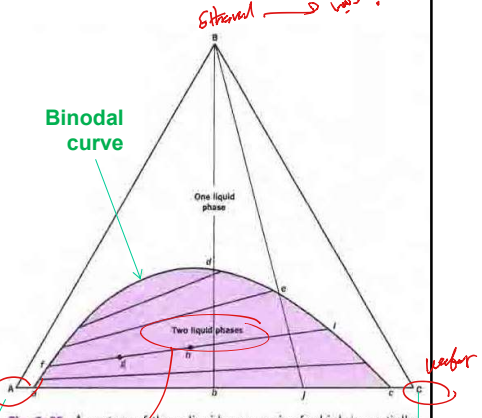
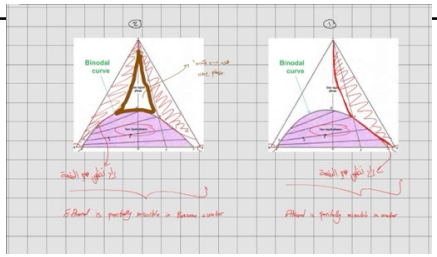


Fig. 2–28. A system of three liquids, one pair of which is partially miscible.

Partially miscible liquids



Ternary systems with one pair of partially miscible liquids

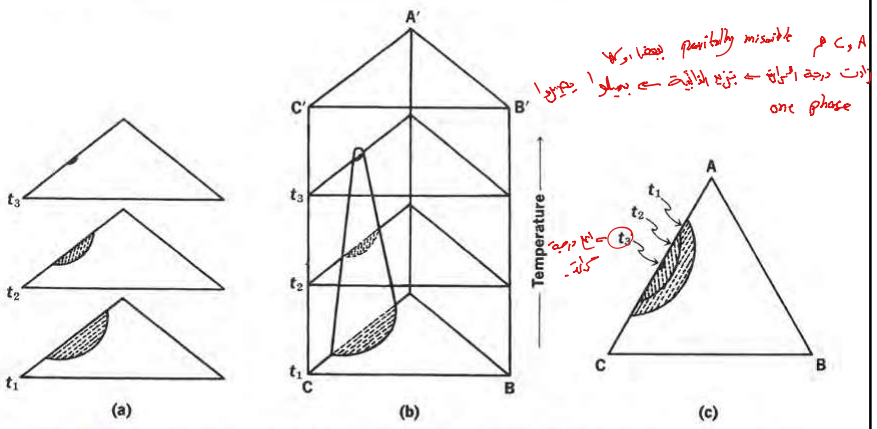


Fig. 2–29. Alterations of the binodal curves with changes in temperature. (*a*) Curves on the triangular diagrams at temperatures t_1, t_2, and t_3. (*b*) The three-dimensional arrangement of the diagrams in the order of increasing temperature. (*c*) The view one would obtain by looking down from the top of (*b*).

Ternary systems with two or three pairs of partially miscible liquids

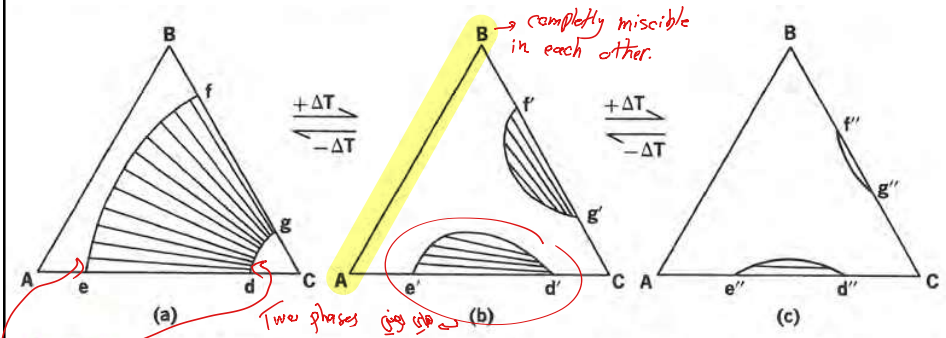


Fig. 2–30. Effect of temperature changes on the binodal curves representing a system of two pairs of partially miscible liquids.

Ternary systems with two or three pairs of partially miscible liquids

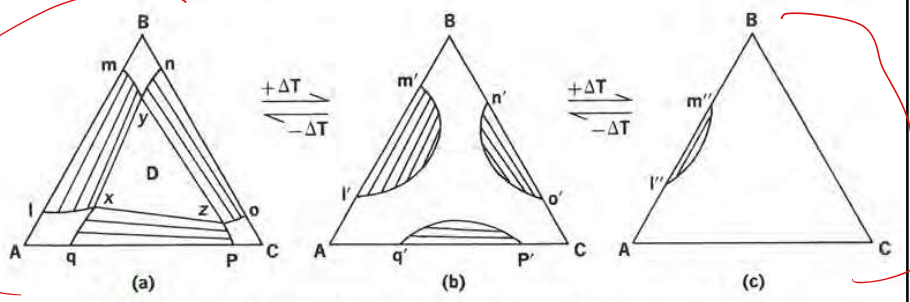


Fig. 2–31. Temperature effects on a system of three pairs of partially miscible liquids.

وجه المقارنة	One-Component System (نظام المكون الواحد)	Two-Component System (نظام المكونَين)	Three-Component System (نظام المكونات الثلاثة)
أمثلة شهيرة	الماء (H_2O)	Phenol + Water، Menthol + Camphor	Water + Benzene + Ethanol
قانون الأطوار ($F = C - P + 2$)	$F = 1 - P + 2 = \mathbf{3} -$	$F = 2 - P + 2 = \mathbf{4} -$ (أو $F = 3 - P$ عند تثبيت الضغط)	$F = 3 - P + 2 = \mathbf{5} -$ (أو $F = 4 - P$ عند تثبيت T, P)
أقصى درجات حرية (F_{max})	$\mathbf{F = 2}$ (T, P حرارة وضغط)	$\mathbf{F = 3}$ (T, P وتركيز مادة واحدة)	$\mathbf{F = 4}$ (T, P وتركيز مادتين)
شكل الرسم البياني	رسم ثنائي الأبعاد عادي (محور T ضد محور P)	رسم ثنائي الأبعاد (محور T ضد التركيز $Composition$ عند ضغط ثابت	مثلث متساوي الأضلاع (Triangular Graph) عند ثبات T, P
النقاط/المناطق المميزة	• Triple Point: تعايش 3 أطوار ($F = 0$) • Critical Point: بعد الحرارة والضغط الحرجين	• Eutectic Point: أقل درجة انصهار لخليط صلب • Upper/Lower Consolute Temp: للامتزاج الجزئي	• Binodal Curve (القبة): تفصل بين طور سائل واحد وطورين • Tie-lines: لربط التراكيز الممتزجة
تأثير تغيير الحرارة	يغير حالة المادة من صلب إلى سائل إلى غاز	يغير الامتزاجية أو حالة الانصهار للخليط	كلما زادت الحرارة: تزداد الذائبية وتتقلص قبة الـ $Two - phase$