



The Hashemite University
Faculty of Pharmaceutical Science

Physical Pharmacy I

Phase equilibria and the phase rule

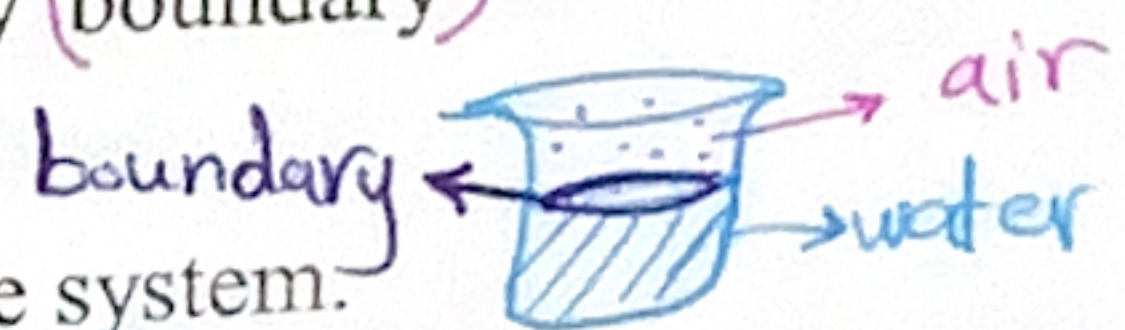
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The Phase

- 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.
(3 phases) لوضيعة ice
- A phase may be gas, liquid or (solid).
(most condensed)



Ice



Water



Water vapor

The Phase

gases they mix easily
& Spontaneously
(1 Phase) ←

$CO_2, O_2, NO_2, \dots$
(atmospheric air) مثال

A gas or a gaseous mixture is a single phase.

Completely (miscible liquids) constitute a single phase.

Suspension/emulsion

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.

(Solid) ← فواليا هو
liquid من

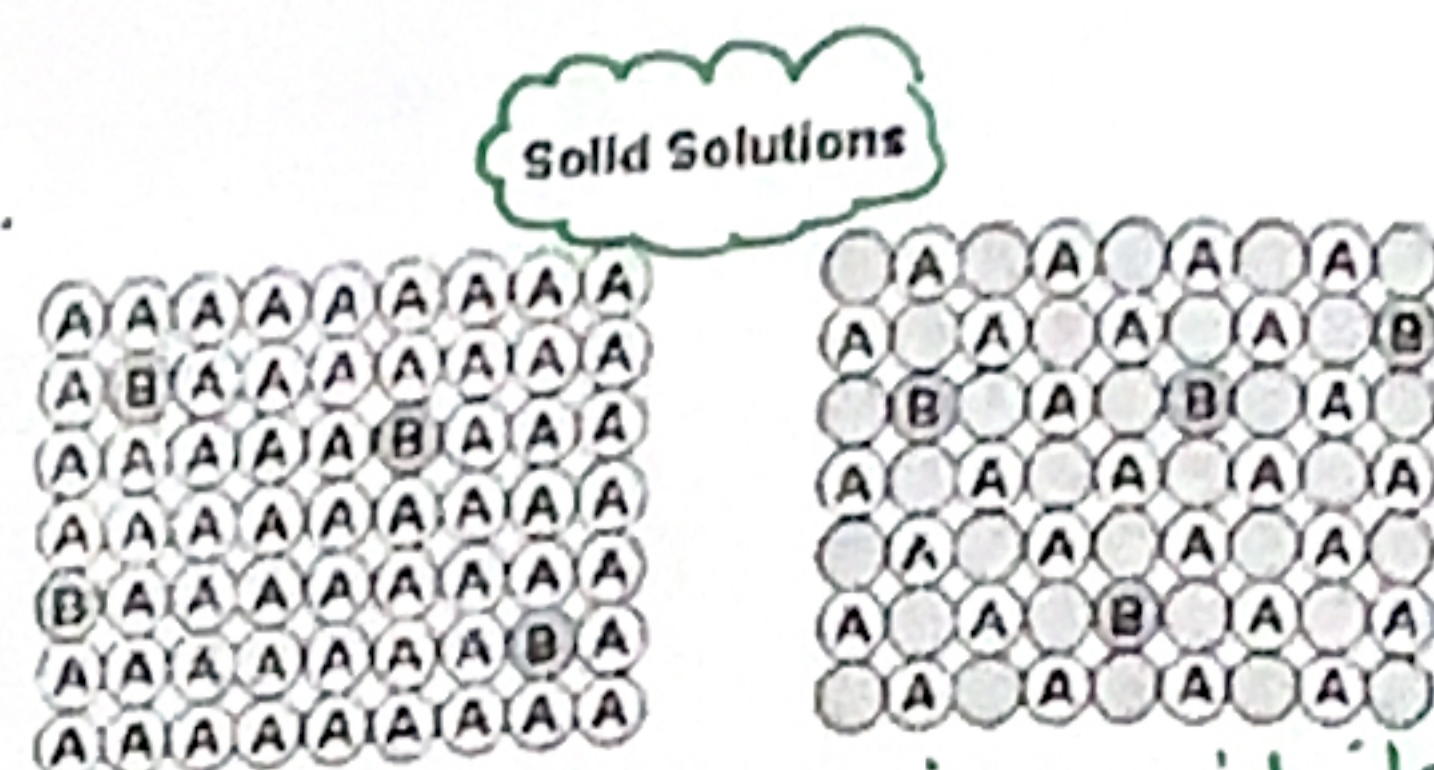
A solid solution, a term popularly used for metals, is a homogenous mixture of two different kinds of atoms in solid state and have a single crystal structure.



A solid solution is considered as a single phase.

Each polymorphic form constitutes a separate phase.

كل (Polymorph) شكل Phase متفرد عن الآخر



مداخلين ببعض → 2 metals
على المستوى الجزيئي (molecular level) يمكن ان يشكل
الفضائي لهم هو (Solid)

The Phase diagram

الرسمه التي توضح
(T + P) فقط

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, temperature, density, and concentration.

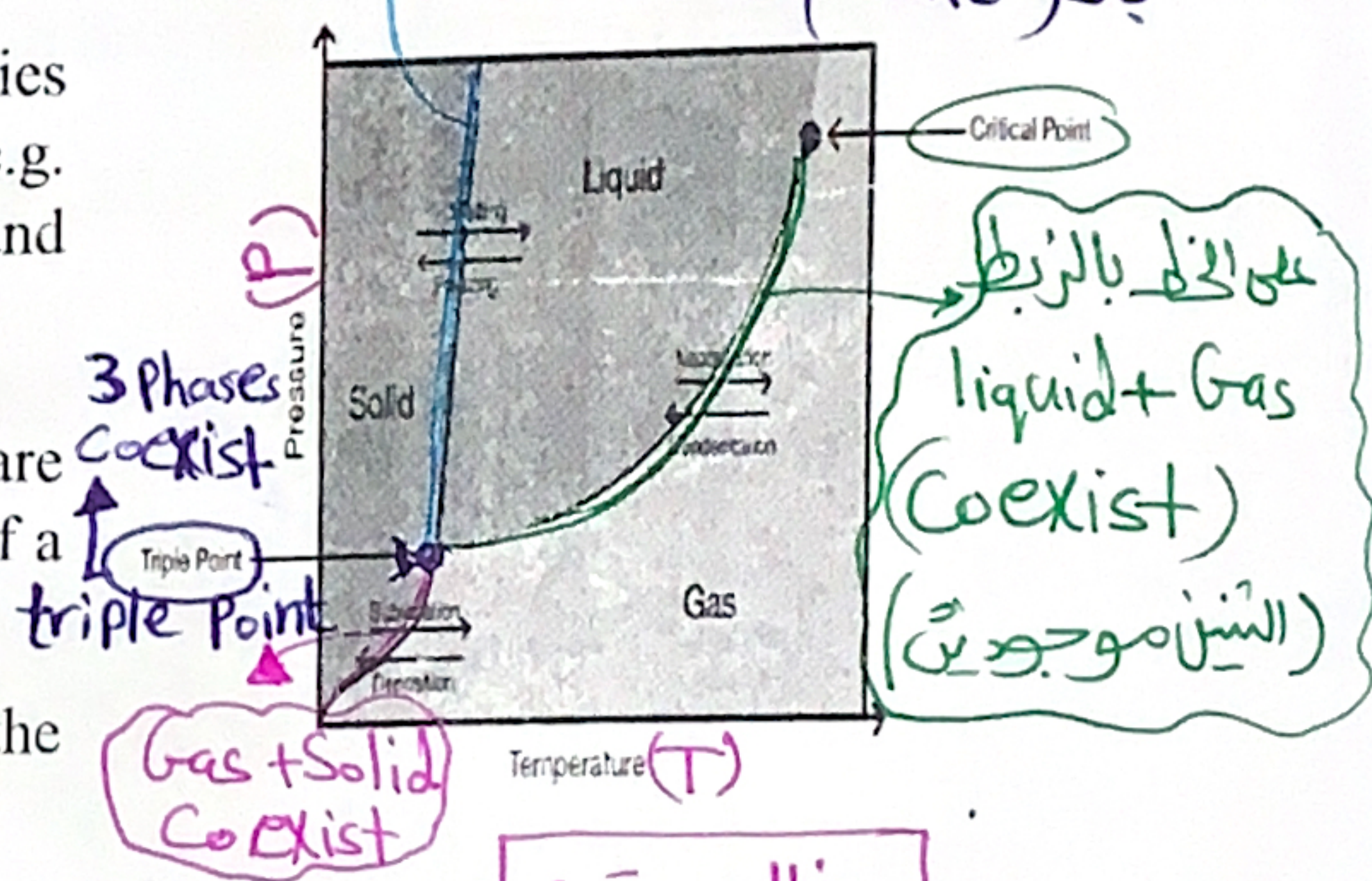
The simplest phase diagrams are (pressure-temperature) diagrams of a single substance.

The axes correspond to the (pressure and temperature).

* أي نقطة على هذا الخط (liquid + solid) Coexist

Phase Diagram

الرسمه خاصة بال (water)



من الرسمه :

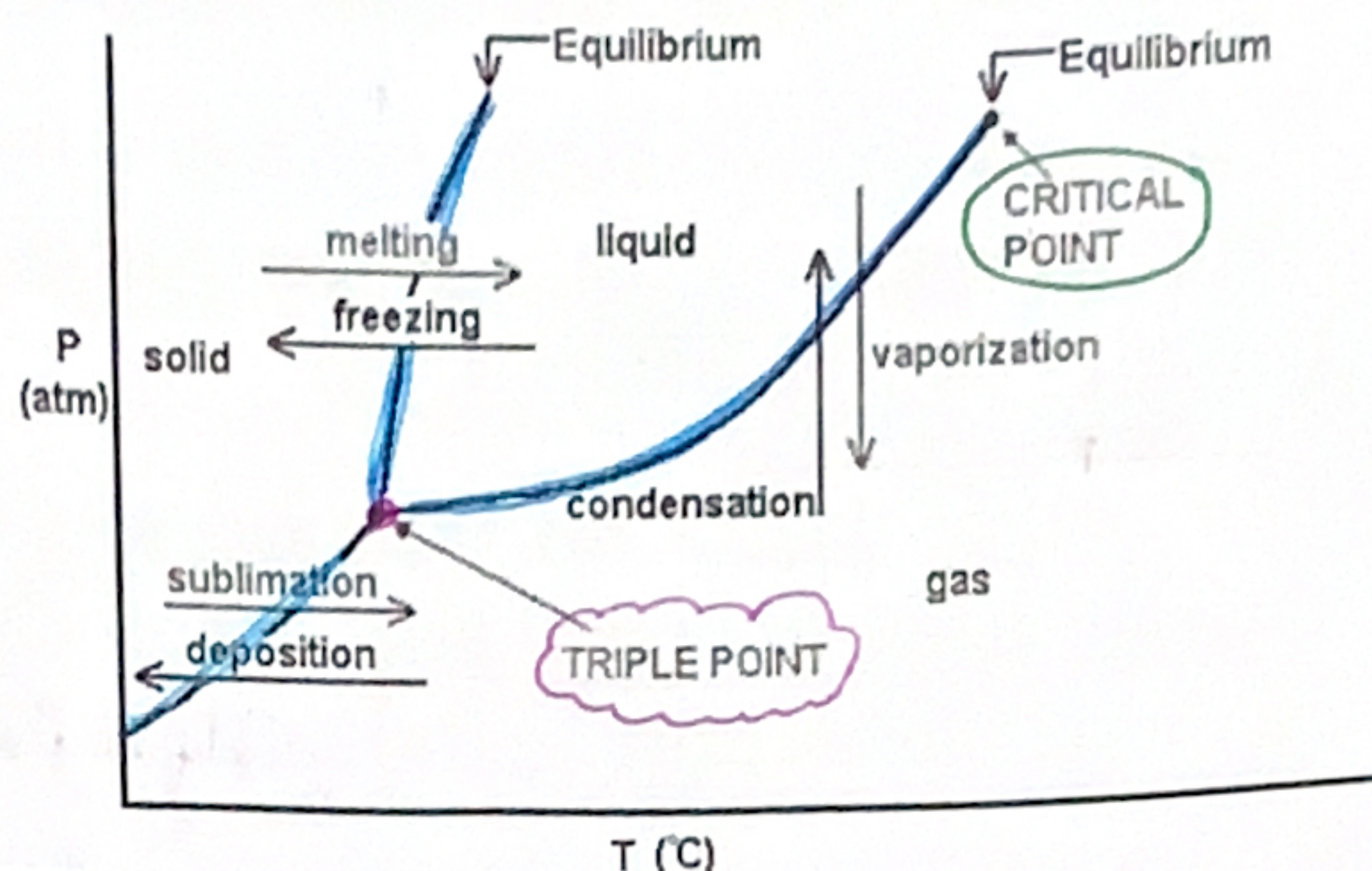
* على الجزء الذي (T) أقل وال (P) عالي
الحالة ← liquid

* على الجزء الذي (T) عالي وال (P) قليل
الحالة ← Gas

* التحول من Gas إلى Solid (deposition)
* التحول من liquid إلى Gas (Vaporization)
* التحول من Gas إلى liquid (Condensation)
* التحول من Solid إلى liquid (melting)
* التحول من liquid إلى Solid (Freezing)
* التحول من Solid إلى Gas (Sublimation)

The Phase diagram: One component system

- The lines in the phase diagram represent two phase systems, while the spaces between the lines represent one phase systems.
 أي نقطة على أي خط يكون فيها 2 Phases فقط
 أي نقطة على أي خط يكون فيها 1 Phase فقط
- 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)
 عند هذه النقطة ←



$$\text{density} = \frac{\text{mass}}{\text{Volume}}$$

Freeze الماء لـ Ice
يزيد حجمه ولما يزيد الحجم
بتقل الكثافة

$$D = \frac{m}{V}$$

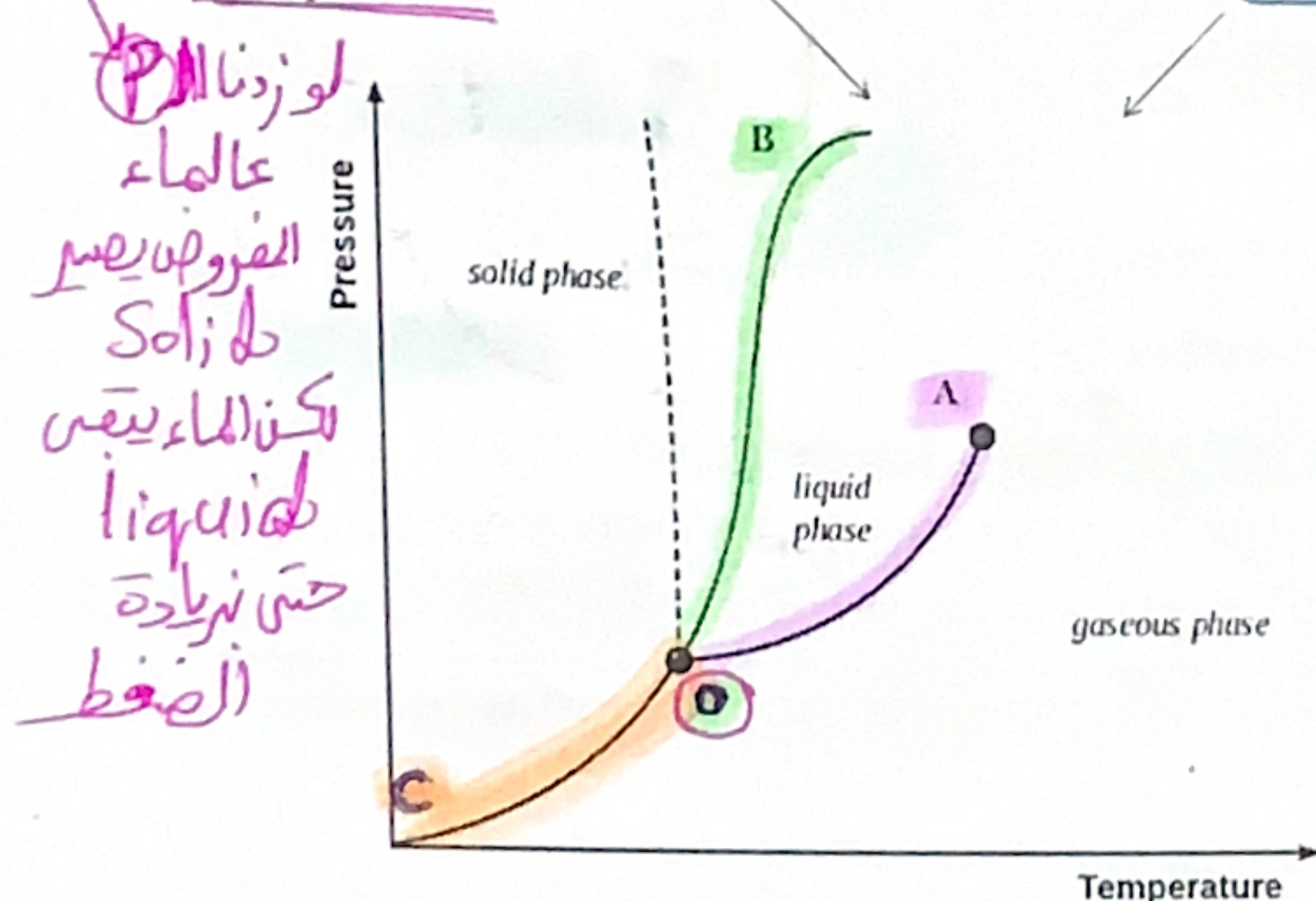
note
عكس باقي المواد
لما عملها (Freeze)
الحجم يقل وال (D) تزيد

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.

معظم المواد
عكس الماء



Curve OA: → liquid إلى غاز
vapor pressure curve

Curve OB: → liquid إلى Solid
Melting point curve

Curve OC: → Gas إلى Solid
Sublimation curve

The Phase diagram: One component system

- The **critical point** is the point on a phase diagram that indicates the critical temperature and pressure ($T_c + P_c$)

فوق
هو عند هاتى النقطة يكون
المادة حصة بفض النظر
عن كمية الضغط اللي بيديها
(ما بغير liquid)

The **critical temperature** T_c 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.

عند هاتى النقطة قد
ما نرفع الحرارة ما
يسحول ل Gas بظل
liquid

In the same way, the **critical pressure** P_c is the pressure above which the substance can no longer exist as a gas, no matter how high the temperature is.

- ScF** **Supercritical fluid** is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

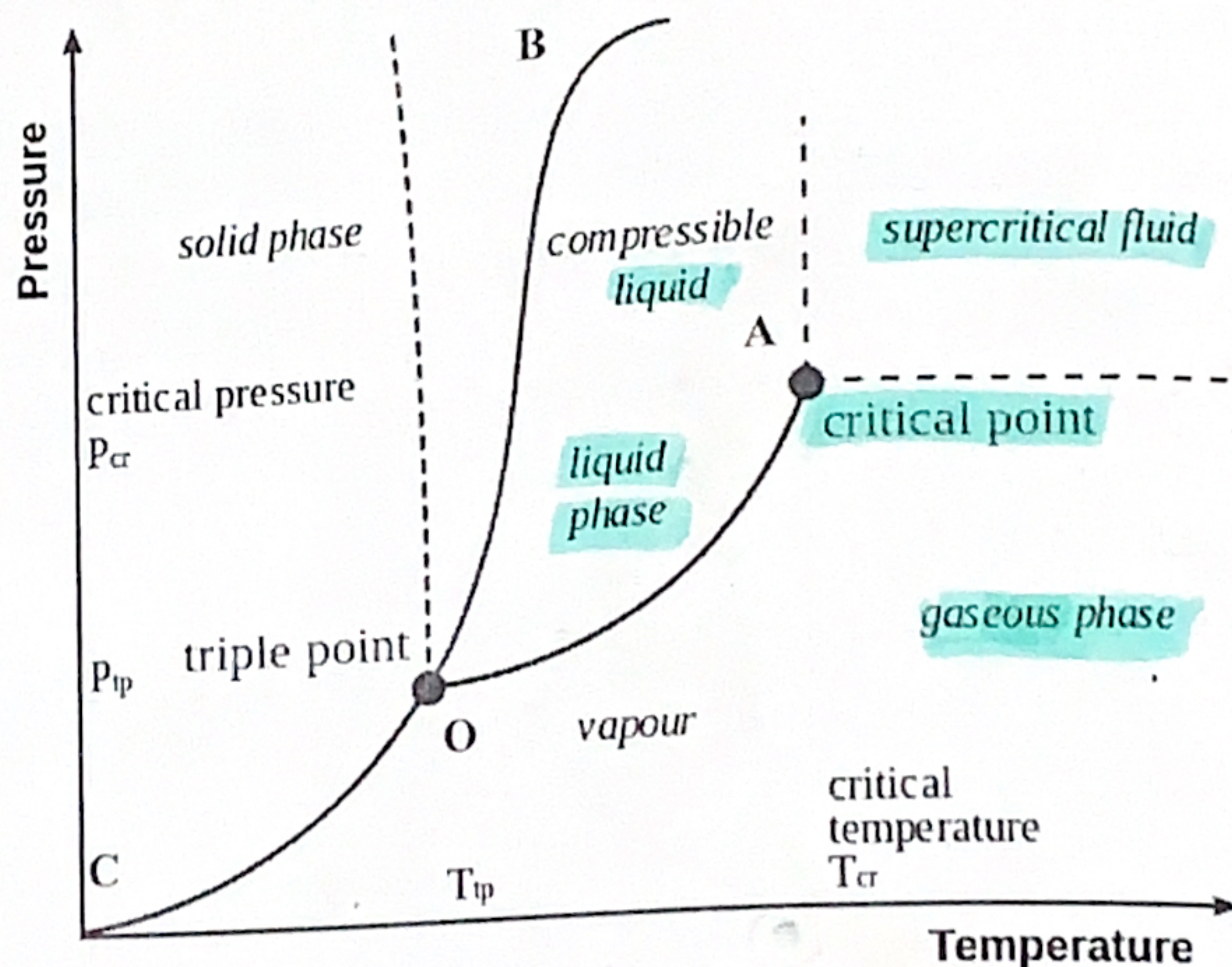
ما بتقدر تميز بينها liquid و gas
ألها خصائص التين ويتكون (One-Phase)
behave as a gas + liquid

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. استعمالات ال (Scf) بديل

- Supercritical fluids have the (viscosity) of a gas, but the densities and solvent power of a liquid, making SC fluids ideal for (extraction). سبب استعمل ال (Scf)
 (hexane, dichloromethane) → toxic
 يمكن Scf أقل Toxicity من ال (extraction)

الهدف منه اني احدد ال (Parameters)

لوصف حالة / مادة معينة

(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

يعني كم Parameter
 يحتاجه لوصف
 النظام
 (mixture)

Note: * لو لسا المادة واحدة
(3 components) ← بتتفكك → Solid
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \rightarrow \text{Gas}$
ولو تفككت كاملة وخلعت
 $\text{CaO} + \text{CO}_2$
(2 components)

The Gibbs phase rule

- What is the number of components in the following systems?
- Mixture of ice, liquid water, and water vapor

— One because the composition of all three phases is described by the chemical formula H_2O .

- Three-phase system CaCO_3 (Calcium Carbonate)

— Two, the composition of each phase can be expressed by a combination of any two of the chemical species present.

- What is the number of phases in the following systems?
- Liquid water, liquid ethyl alcohol, water vapor, and ethyl alcohol vapor

— Two, because gases are always miscible in all proportions. Moreover, water and ethyl alcohol are completely miscible.

ethyl alcohol vapor + water vapor
homogenous mixture ← (One Phase)

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 <i>bivariant</i> ($F = 2$) and lies anywhere within the area marked vapor, liquid, or solid in Figure 2-22. We must fix two variables, e.g., P_1 and T_1 , to define system D. → Univariant
Gas-liquid, liquid-solid, or gas-solid	2	$F = C - P + 2$ $= 1 - 2 + 2 = 1$	System is <i>univariant</i> ($F = 1$) 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 or T , to define system E.
Gas-liquid-solid	3	$F = C - P + 2$ $= 1 - 3 + 2 = 0$	System is <i>invariant</i> ($F = 0$) 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

Systems

- Bivariant
- Univariant
- Invariant

Phase Diagram بالأسطوانة بالـ
التي قبل

1 Phase لو أخذنا Solid مثلاً

لو أخذنا أي نقطة على أي خط (2 Phases)

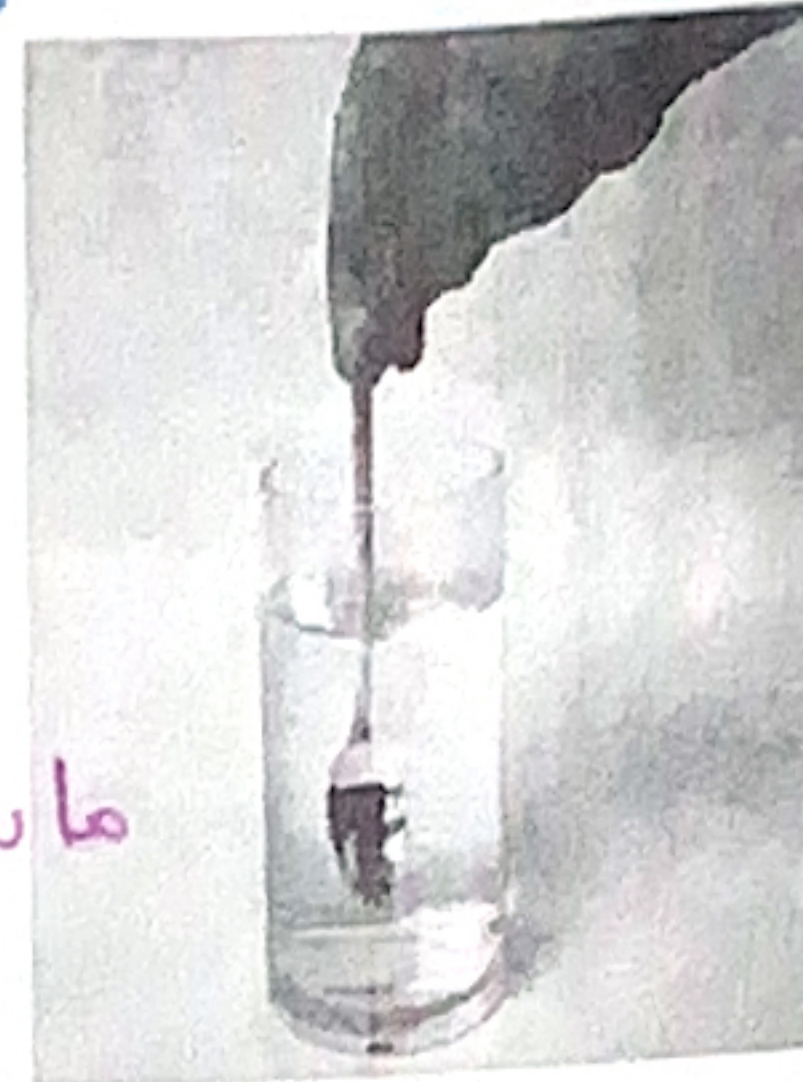
Triple Point نقطة التقاطع بين الخطوط الثلاثة

invariant ما لا متغيرات

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.

* يقتر ال Solid + liquid (2 Phase).
ويقال ال Vapor Phase
ما ال في تأشير عليه



- Systems containing liquids might be:

1. Completely immiscible (such as mercury and water) ما يختلط → الزيت مع الماء
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:

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

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

Three variables are required: temperature, pressure, and composition (بستنا ال P)

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

Phenol على حرارة الغرفة
يكون (Crystal) وغير ذائب
في الماء

Two component system containing liquid phases

(h) Upper consolute temperature = critical solution temperature

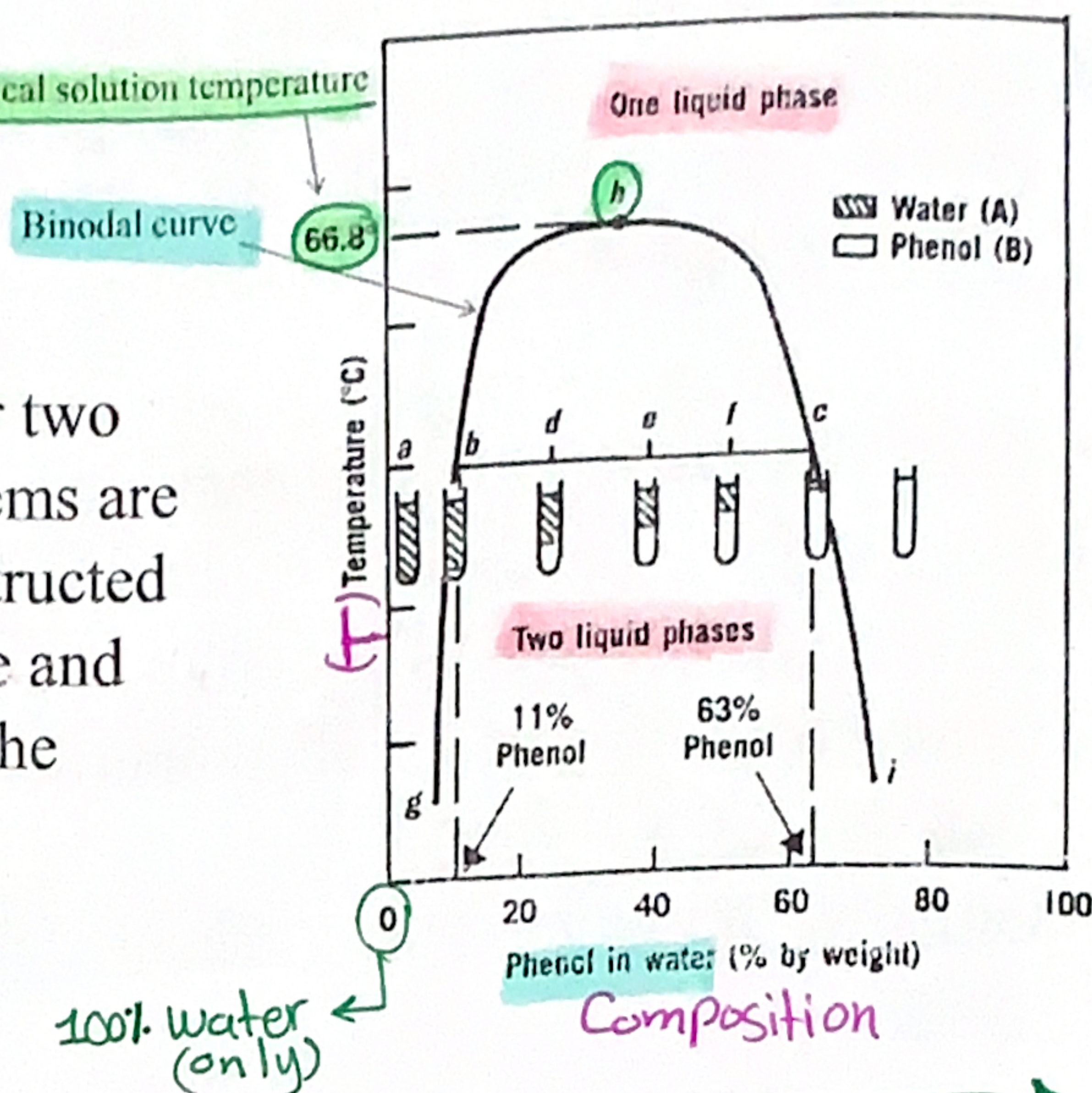
تحت الكيرف يكونوا
بغير أسوفهم (2 Phases)
بوضوح

لكن فوق الكيرف
above (66.8°C)

بمرور 1 Phase

وعلى الخط دائما
2 Phases exist.

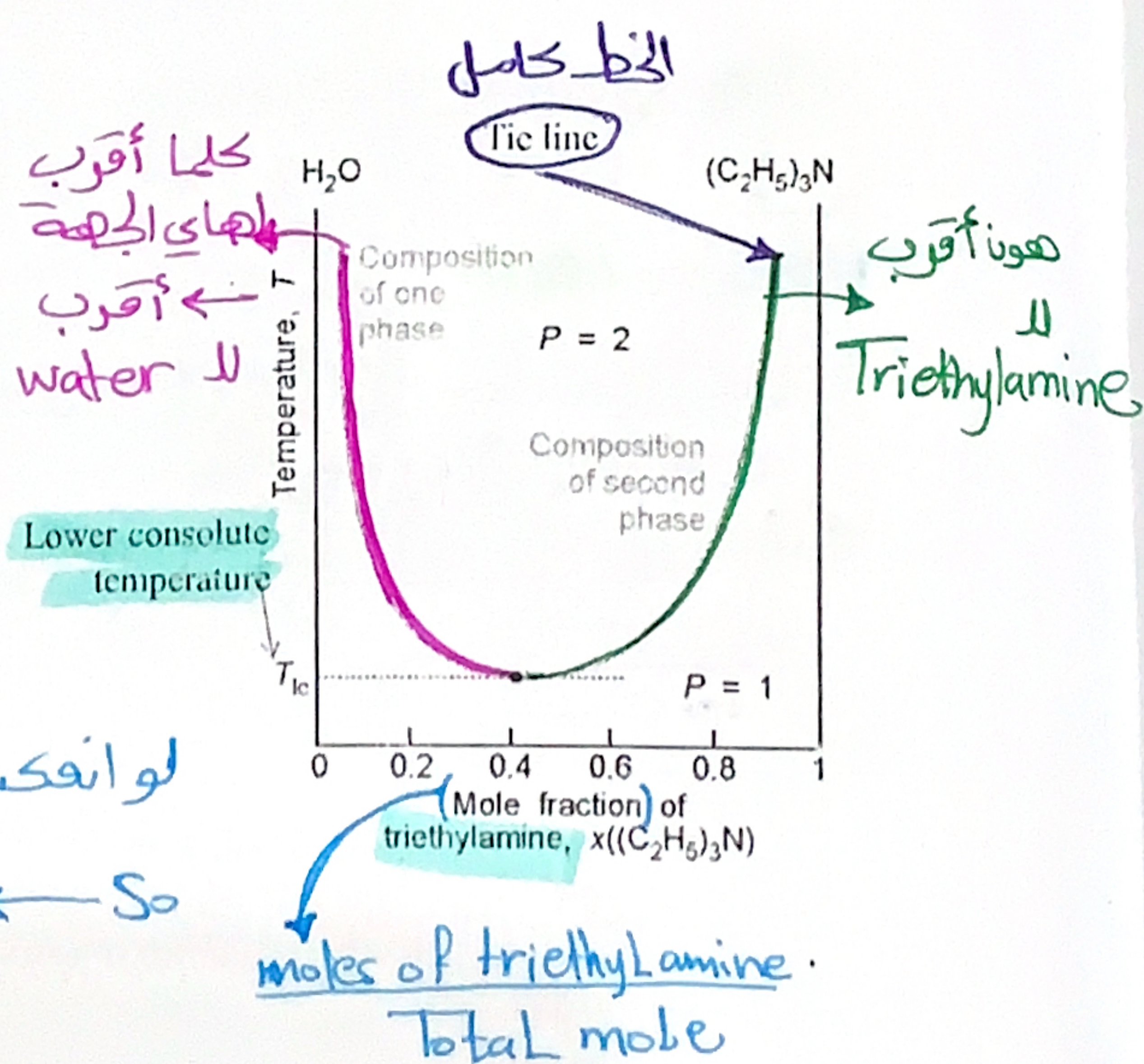
Phase diagrams for two component systems are commonly constructed with temperature and composition as the coordinates.



يليش أنفص من الماء
وأضيف (Phenol) بنفس الكمية
(يحفظ على الحجم)
عند النقطة C كمية ال (Phenol)
أكبر من النقطة B

Two component system containing liquid phases

Other liquid mixtures show no Upper Consolute Temperature but lower Consolute Temperature.



لو انفكت الرجة بتسير (Lower Consolute) بدل (Upper)

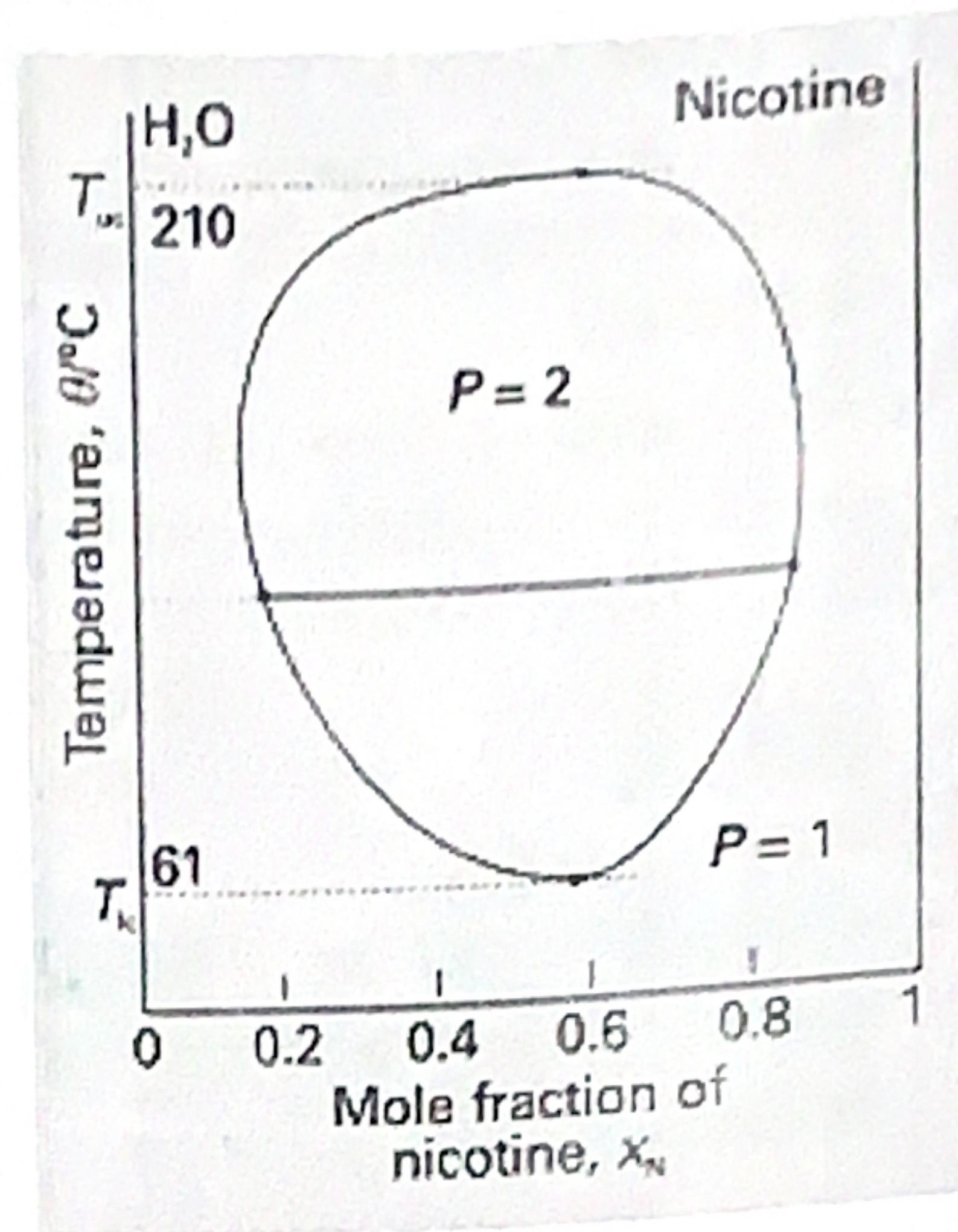
Only one Phase ← Below Curve ← So

(2 Phases) ← ودخل الكيرف عند

(2 Phases) ← وعلى كل

Two component system containing liquid phases

Other liquid mixtures show both upper and Lower Consolute Temperatures.



* داخل الـ (Curve) وعلى
الـ (Curve) بالزبط يكون
عنا ← 2 Phases

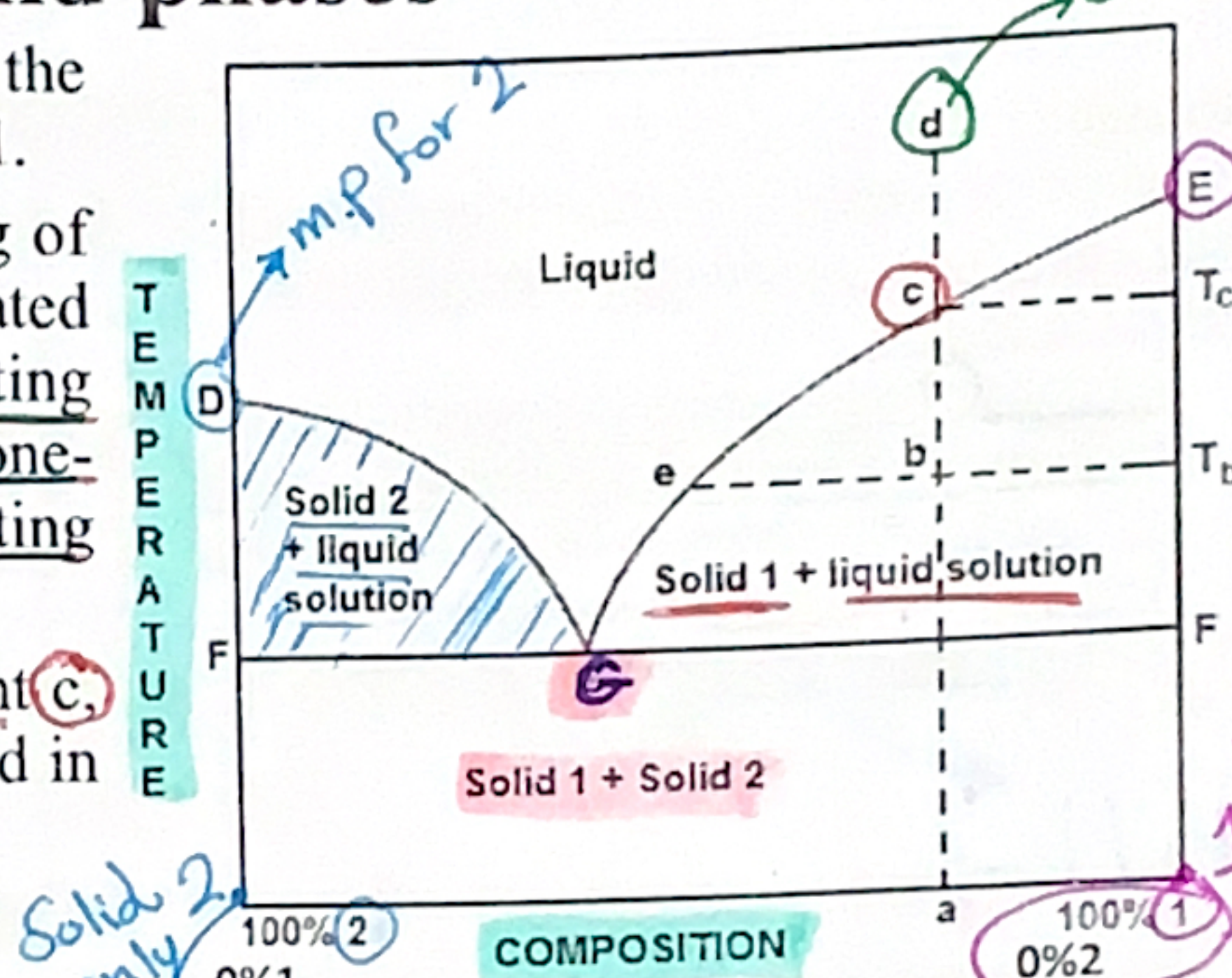
* خارج الـ (Curve) عندي
(One-Phase)

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).

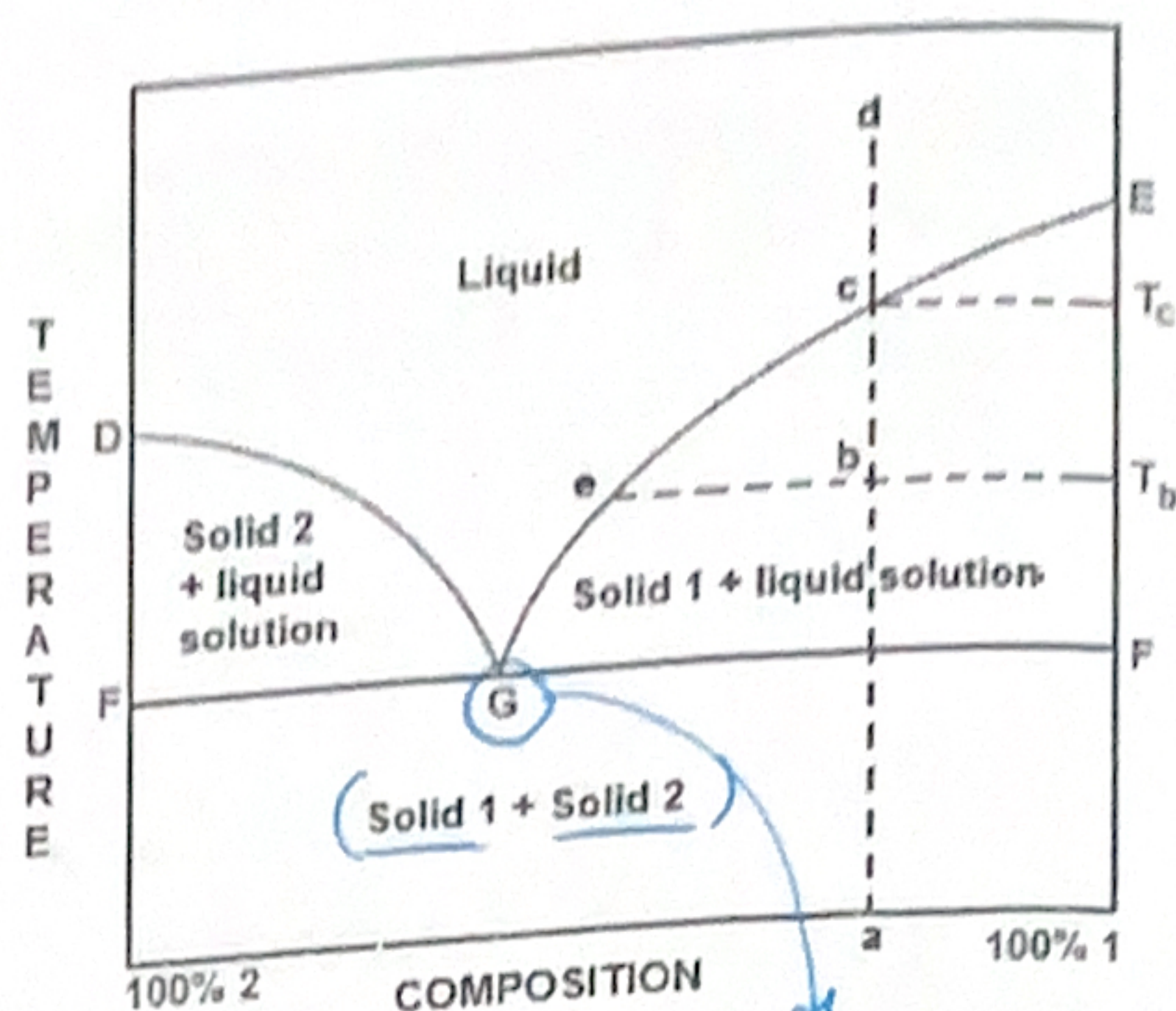


مادة واحدة فقط
مع السكر نحو المين
المادة الأخرى تزداد

انفس سوحيات ان
المادة الاولى اخف
والاخرى بقية
لوحدها

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.



نزلنا عن الم.ط. للصلب
(Solid)

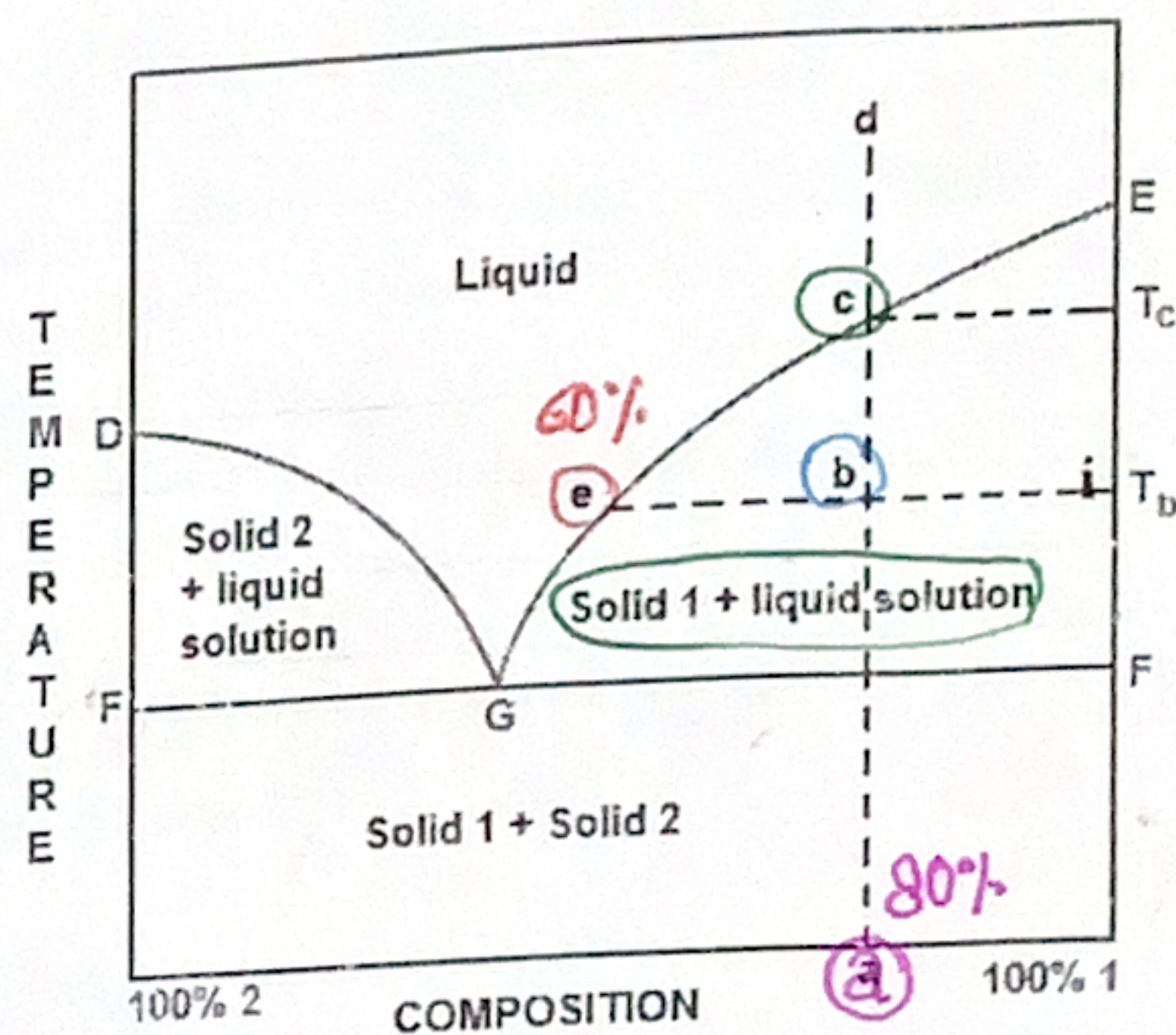
* لو رفعنا الحرارة أكثر من **G** (above G)
يسخن بال (Liquid)
على temperature أقل من الم.ط. (m.p.)
For 2 Solids

Example:

Suppose we prepare a mixture of containing 80% of 1 (point a) and the temperature was raised to point d.

- At point **c** solid 1 starts to separate out to form solid 1 phase and mixture liquid phase
- At point **b** the system is composed of liquid 1 in 2 (point **e** (60%)) and pure solid 1 (**i**)
- The **W** ratio of **e** to **i** = $(100-80)/(80-60)$
 $=20/20=1$

i-b / b-e



← يعني نسبة ال Solid 1 في mixture of liquid
تساوي (1) عند نقطة (B)

Two component system containing solid and liquid phases

- Examples of such systems: *mixture of 2 Phases (Solid + liquid) :*
 - 1- Salol-thymol
 - 2- Salol-camphor
 - 3- Acetaminophen-propyphenazone
- Importance of the phase diagram *الهدف منه*
 - Determine the composition at any temperature
- يحدد بالنسبة والسأب كم نسبة
ال (Solid phase) إلى ال (Liquid phase)
- مثل ال - ال سابق -*

Phase equilibria in three-component systems

For three component systems:

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

$$\textcircled{P \geq 1} \Rightarrow F \leq 4$$

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

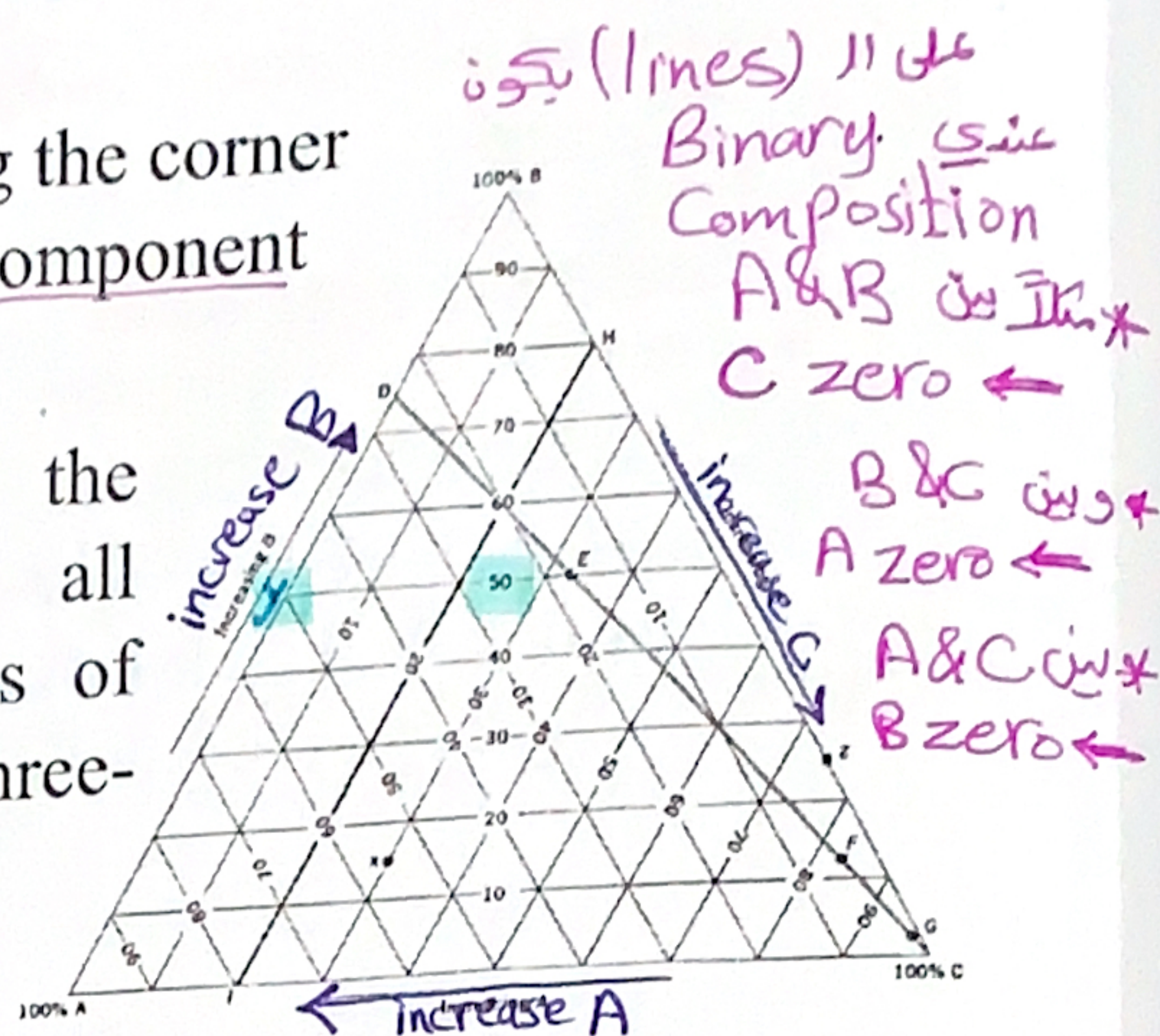
If the ^{isotherm} temperature and pressure are both fixed then, only two compositions are required

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

لو أخذت نقطة على line مثلا $\leftarrow y \leftarrow$ نسبتها 50 يعني (A 50% / B 50%)
 لو أخذت نقطة بعد ال y (فوقها) $\leftarrow$ نسبتها 60 يعني (A 40% / B 60%)
 $\leftarrow$ النسبة الأكبر لـ B لأنها بوجه نحو تزايد B (الأعلى)
 مهم كيف نقرأ ال Corner من الداخل (انظر الأرقام بالداخل)

Rules relating to triangular diagram

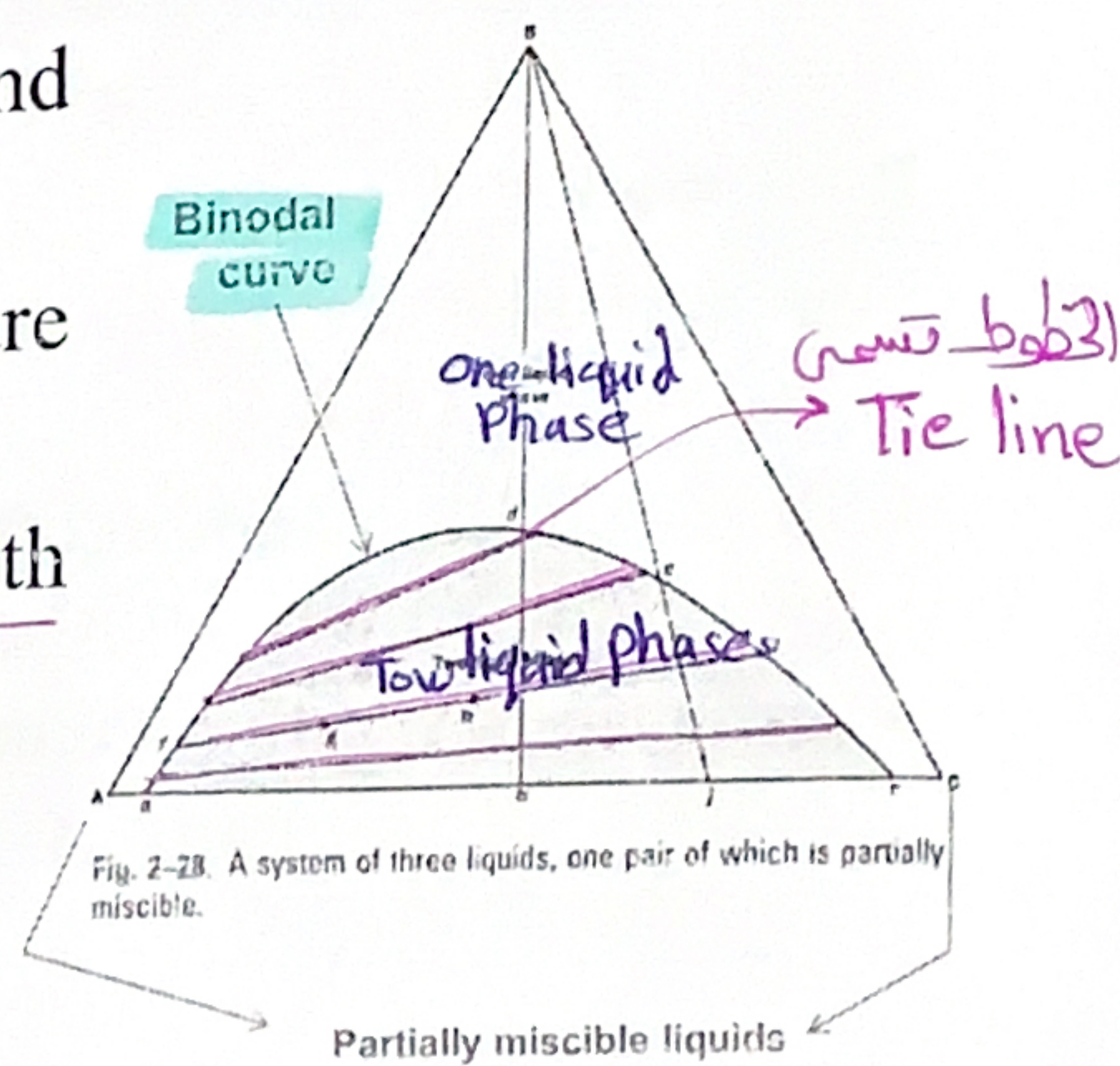
- Each of the three corners represent 100% by weight of one component.
- The three lines joining the corner points represent two component mixture.
- The area within the triangle represent all possible combinations of A, B, and C to give three-component system



* بكل Corner (زاوية) يكون عندى مادة وحدة والباقي صفر $\rightarrow$

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



على الخط $\leftarrow$ Binary
 جوا الخط $\leftarrow$ Ternary

Ternary systems with one pair of partially miscible liquids

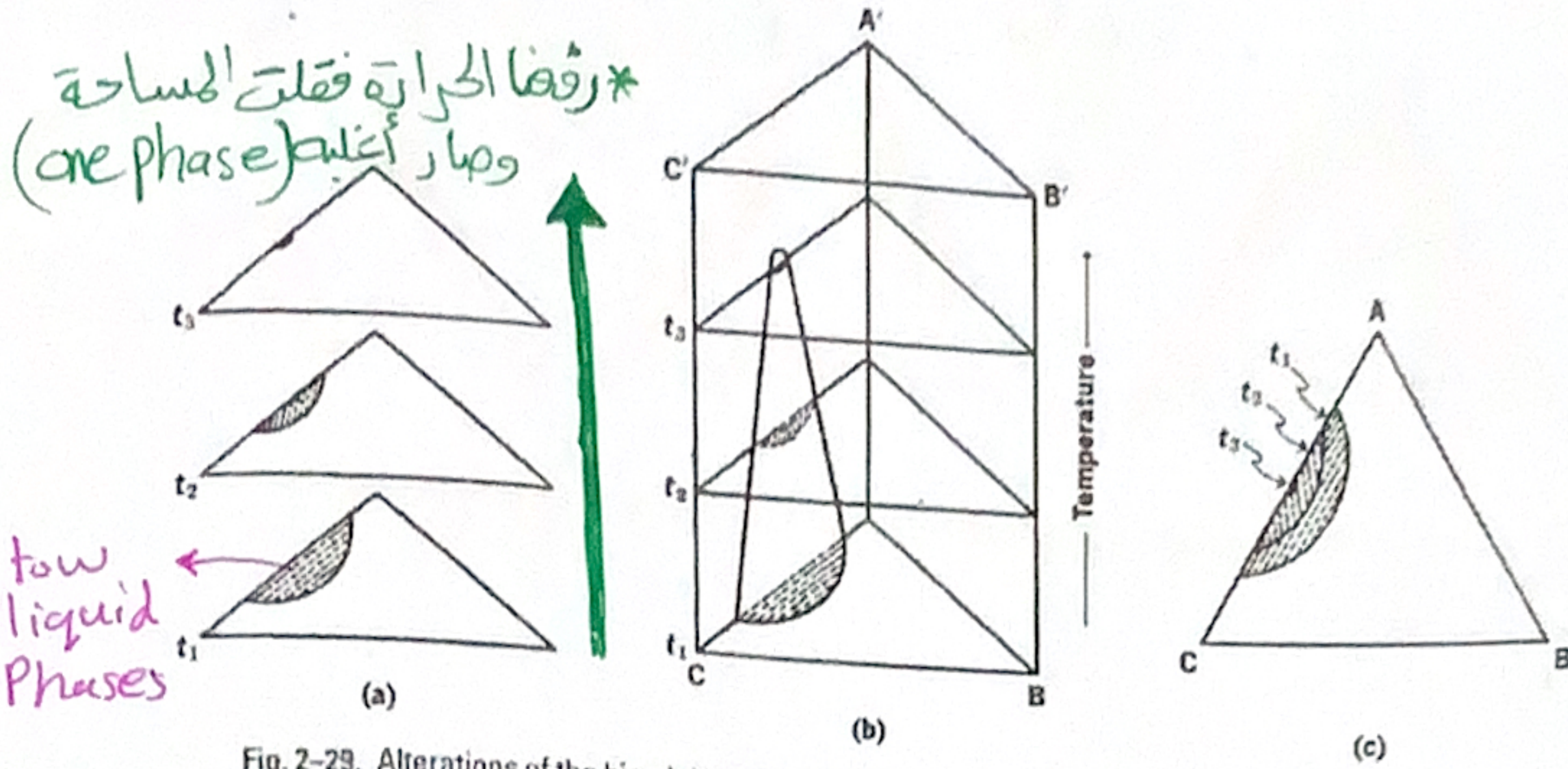


Fig. 2-29. Alterations of the binodal curves with changes in temperature. (a) Curves on the triangular diagrams at temperatures t_1 , t_2 , and t_3 . (b) The three-dimensional arrangement of the diagrams in the order of increasing temperature. (c) The view one would obtain by looking down from the top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

Ternary systems with two or three pairs of partially miscible liquids

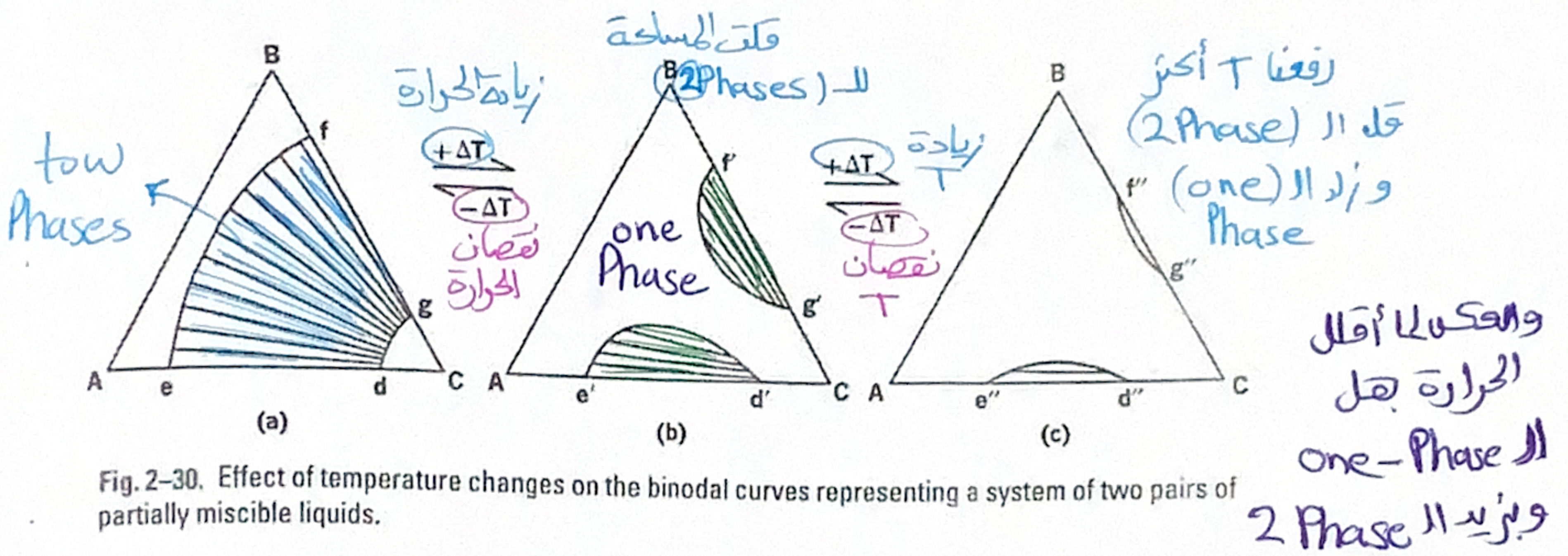


Fig. 2-30. Effect of temperature changes on the binodal curves representing a system of two pairs of partially miscible liquids.

