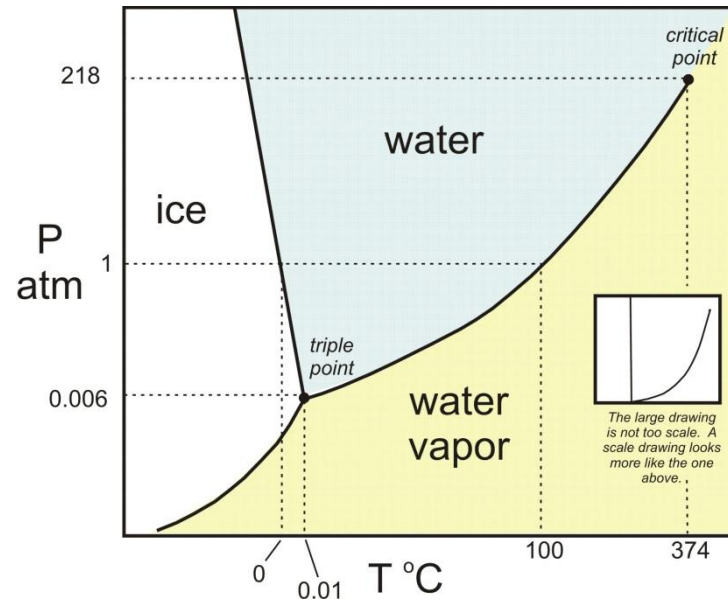


PHASE EQUILIBRIA

PHASE EQUILIBRIA

Phase equilibrium describes the way phases (such as solid, liquid and/or gas) co-exist at some temperatures and pressure, but interchange at others.



Energetic introduction to phase equilibria

Why does an ice cube melt in the mouth?

Further thermodynamic background: terminology

A **phase** is a component within a system, existing in a precisely defined physical state, e.g. gas, liquid, or a solid that has a single crystallographic form.

Concerning transitions between the two phases '1' and '2', Hess's Law states that $H(1 \rightarrow 2) = -1 \times H(2 \rightarrow 1)$.

PHASE CHANGES

Table 5.1 Summary of terms used to describe phase changes

Phase transition	Name of transition	Everyday examples
Solid \rightarrow gas	Sublimation	'Smoke' formed from dry ice
Solid \rightarrow liquid	Melting	Melting of snow or ice
Liquid \rightarrow gas	Boiling or vaporization	Steam formed by a kettle
Liquid \rightarrow solid	Freezing, solidification or fusion	Ice cubes formed in a fridge; hail
Gas \rightarrow liquid	Condensation or liquification	Formation of dew or rain
Gas \rightarrow solid	Condensation	Formation of frost

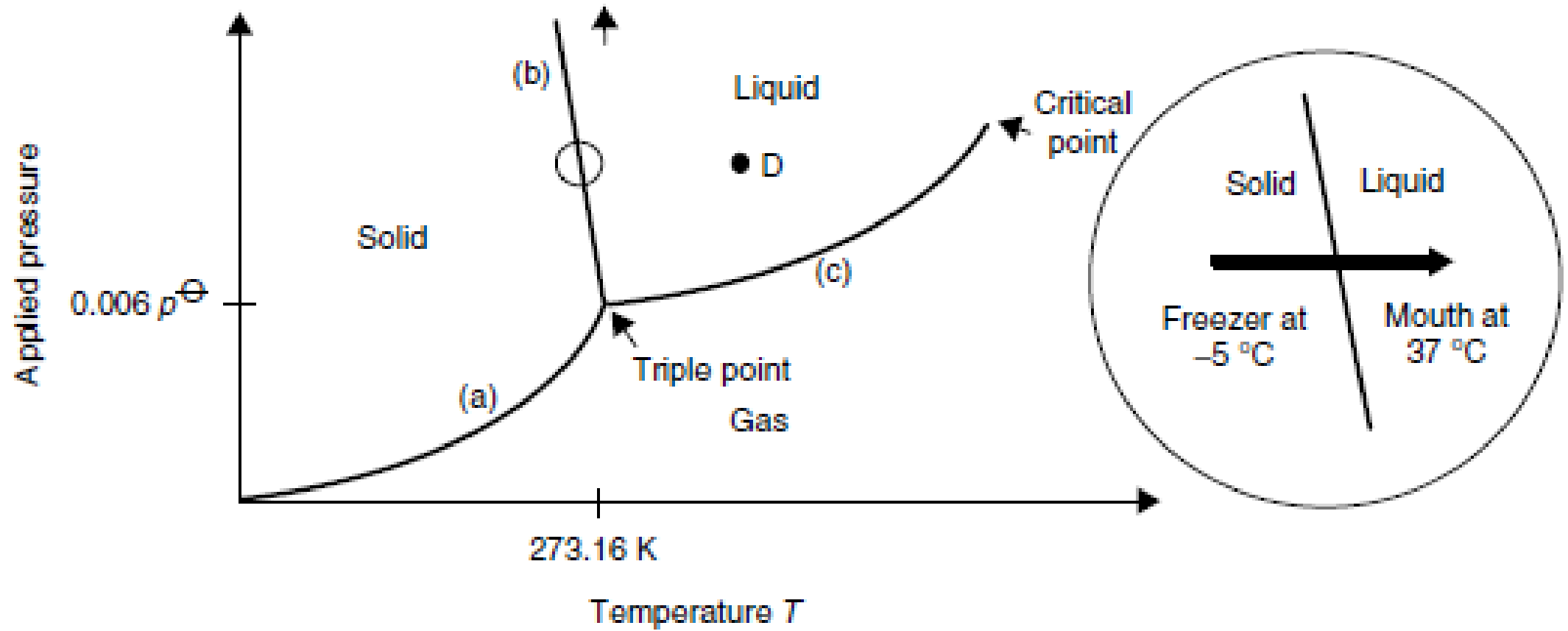
PHASE TERMINOLOGY

A ***phase diagram*** is a graph showing values of applied pressure and temperature at which equilibrium exists.

A ***phase boundary*** is a line on a phase diagram representing values of applied pressure and temperature at which equilibrium exists.

The ***triple point*** on a phase diagram represents the value of pressure and temperature at which *three* phases coexist at equilibrium.

A Sample Phase Diagram – H_2O



SPONTANEITY OF PHASE CHANGES

Why does water placed in the freezer become ice?

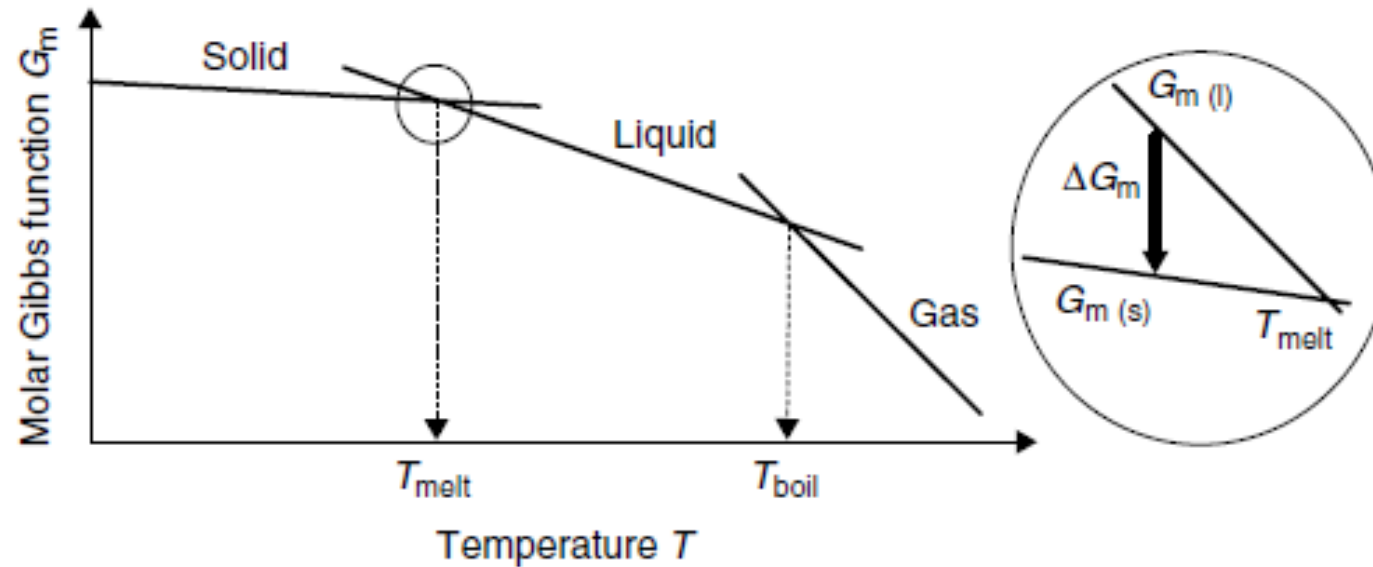


Figure 5.2 Graph of molar Gibbs function G_m as a function of temperature. *Inset:* at temperatures below $T_{(\text{melt})}$ the phase transition from liquid to solid involves a negative change in Gibbs function, so it is spontaneous

SOLID PHASE TRANSITIONS

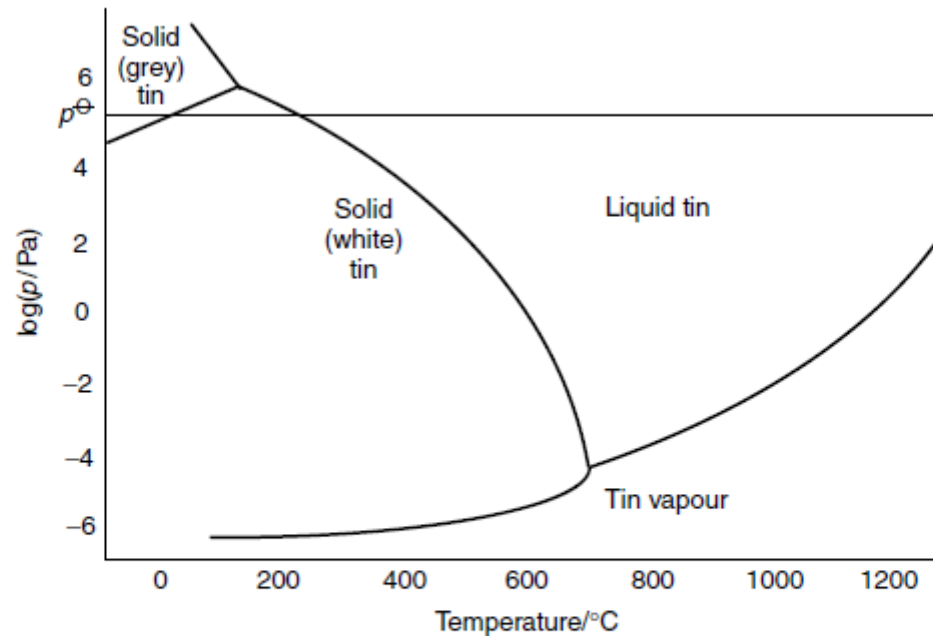
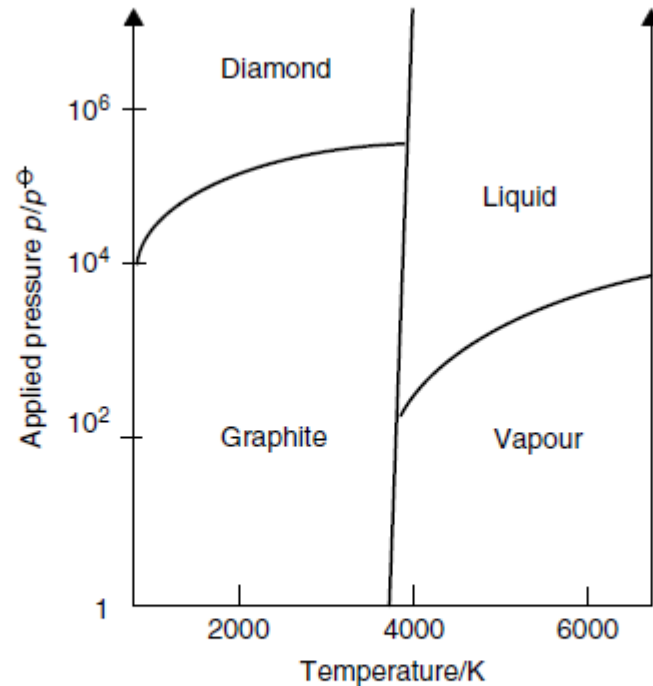


Figure 5.3 Phase diagram of tin computed from thermodynamic data, showing the transition from grey tin from white tin at temperatures below 13 $^{\circ}\text{C}$. Note the logarithmic y-axis. At p^{\ominus} , $T_{(\text{white} \rightarrow \text{grey})} = 13^{\circ}\text{C}$, and $T_{(\text{melt})} = 231.9^{\circ}\text{C}$. (Figure constructed from data published in *Tin and its Alloys and Compounds*, B. T. K. Barry and C. J. Thwaites, Ellis Horwood, Chichester, 1983)

the tin allotropes have very different densities ρ , so $\rho(\text{tin, grey}) = 5.8 \text{ gcm}^{-3}$ but $\rho(\text{tin, white}) = 7.3 \text{ gcm}^{-3}$.

KINETICS OF PHASE CHANGES



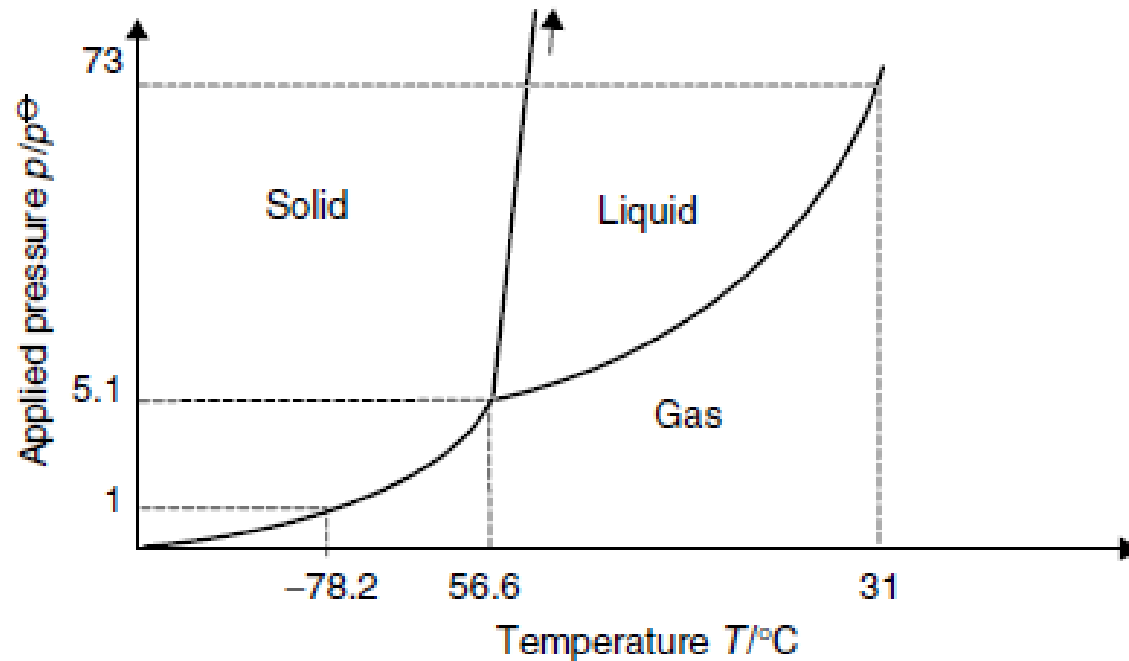
Phase transitions involving liquids and gases are generally fast!

Figure 5.4 The phase diagram of carbon showing the two solid-state extremes of diamond and graphite. Graphite is the thermodynamically stable form of carbon at room temperature and pressure, but the rate of the transition $C_{(\text{diamond})} \rightarrow C_{(\text{graphite})}$ is virtually infinitesimal

Pressure and temperature changes with a single-component system:

How is the 'Smoke' in horror films made?

The effect of temperature on phase change: sublimation



The Effect of Pressure on Phase Change:

How does freeze drying work?

Freeze-drying is a layman's description, and acknowledges that external conditions may alter the conditions of a phase change, i.e. the drying process (removal of water) occurs at a temperature lower than 100 °C.

FREEZE DRYING

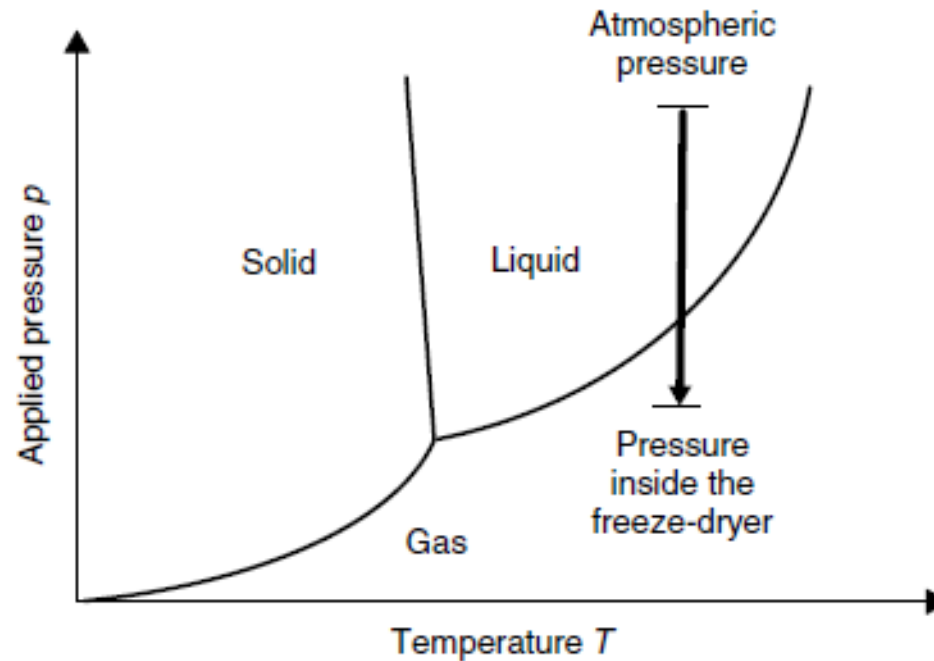


Figure 5.6 Freeze-drying works by decreasing the pressure, and causing a phase change; at higher pressure, the stable form of water is liquid, but the stable form at lower pressures is vapour. Consequently, water (as vapour) leaves a sample when placed in a vacuum or low-pressure chamber: we say the sample is ‘freeze-dried’

NOMOGRAPH

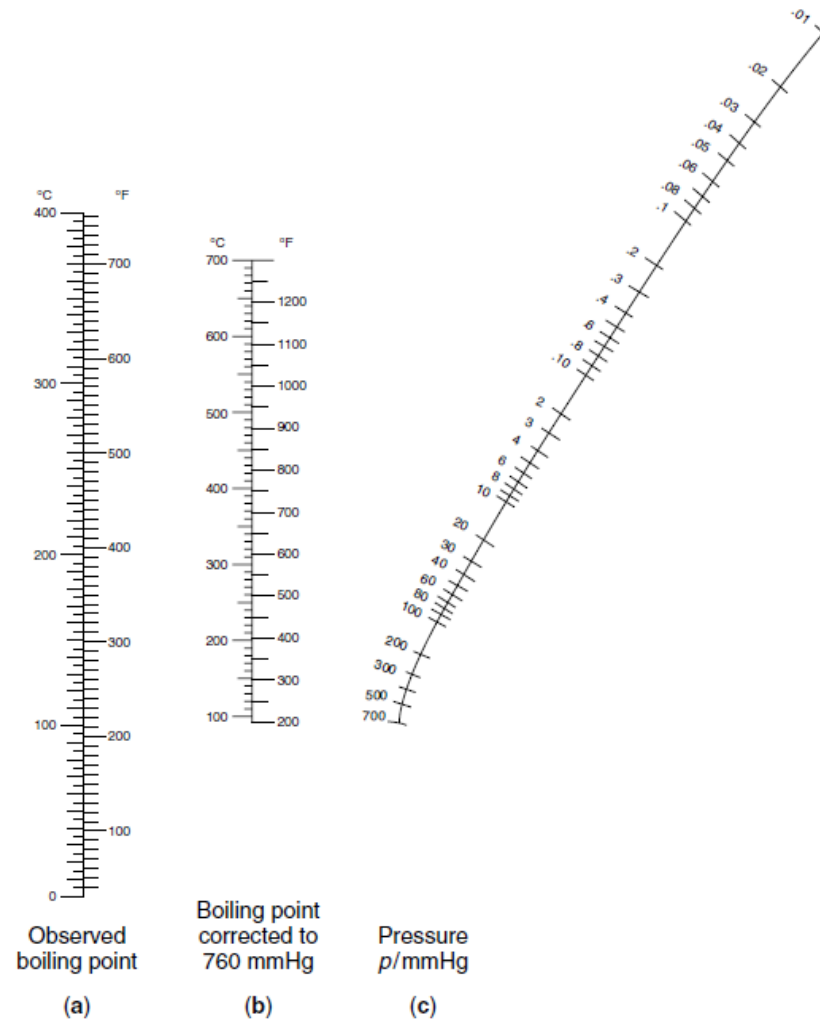


Figure 5.7 A typical nomograph for estimating the temperature at which a pure liquid boils when the pressure is decreased

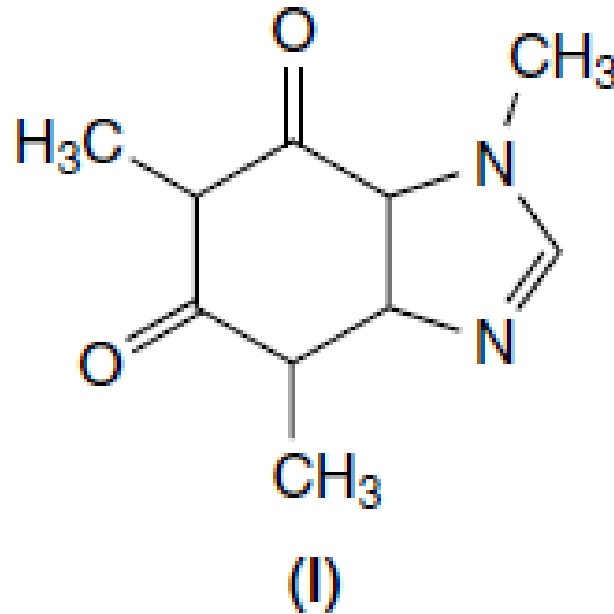
THERMODYNAMICS OF PHASE CHANGES

HOW DOES A ROTARY EVAPORATOR WORKS?

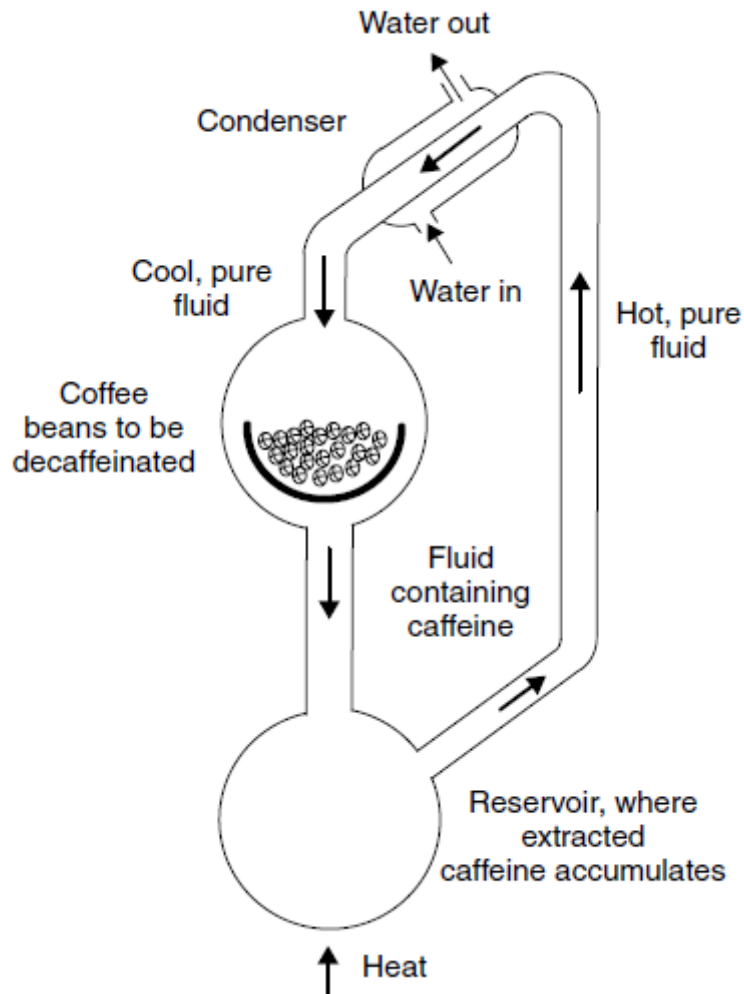


CRITICAL AND SUPERCRITICAL FLUIDS

How is coffee decaffeinated?



COFFEE DECAFFEINATED



The intensive properties of the liquid and gas (density, heat capacity, etc.) become equal at the *critical point*, which is the highest temperature and pressure at which both the liquid and gaseous phases of a given compound can coexist.

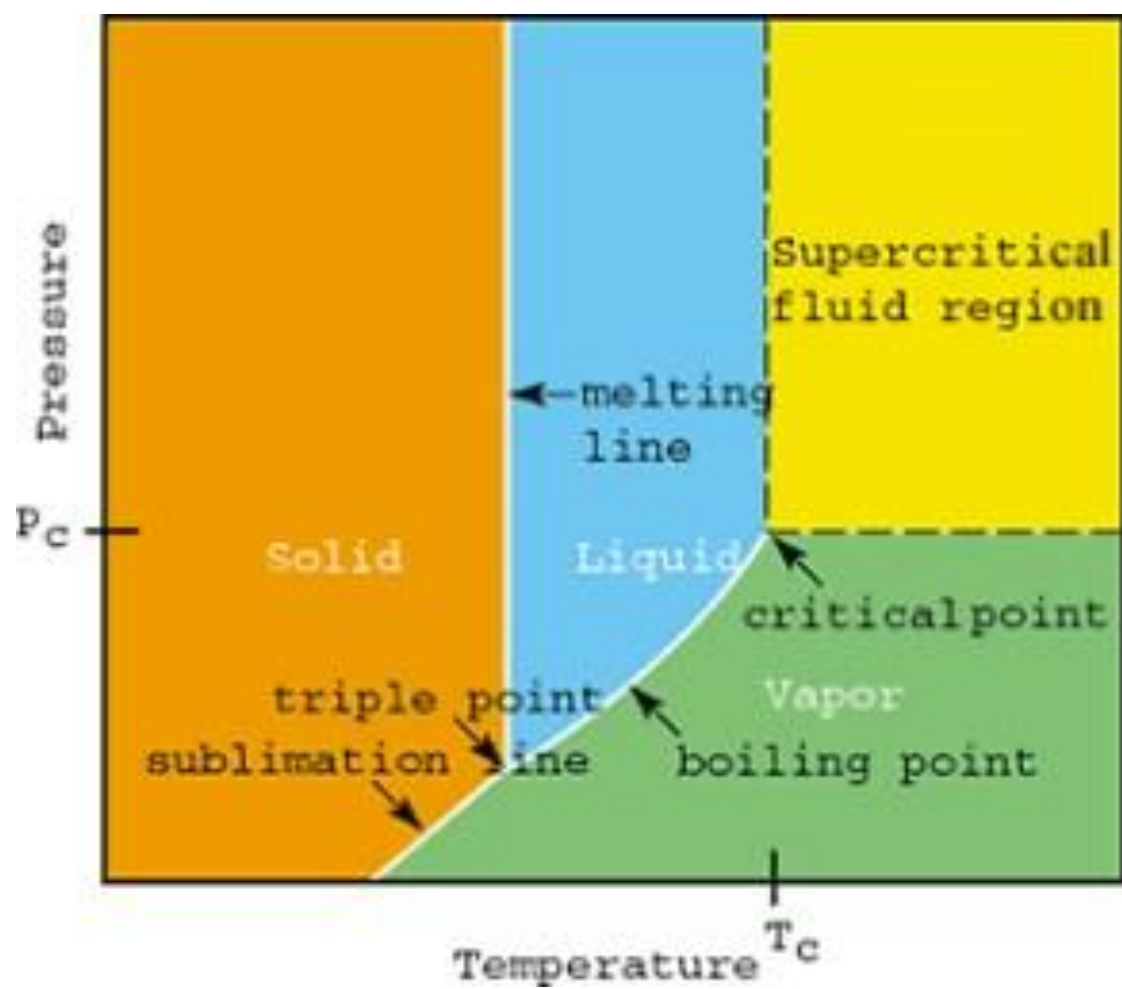


Table 5.2 Critical constants $T_{\text{(critical)}}$ and $p_{\text{(critical)}}$ for some common elements and bi-element compounds

Substance	$T_{\text{(critical)}}/\text{K}$	$p_{\text{(critical)}}/p^{\ominus}$
H ₂	33.2	12.97
He	5.3	2.29
O ₂	154.3	50.4
Cl ₂	417	77.1
CO ₂	304.16	73.9
SO ₂	430	78.7
H ₂ O	647.1	220.6
NH ₃	405.5	113.0

QUANTITATIVE ASPECTS OF P-T CHANGE

Why is ice so slippery?

The effect of p and T on the position of solid liquid equilibrium

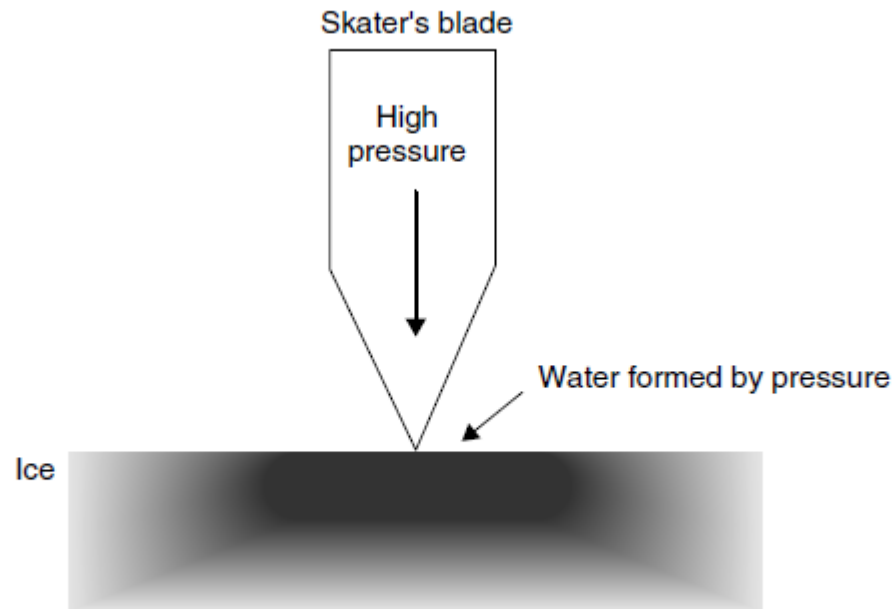


Figure 5.9 Skaters apply an enormous pressure beneath the blades of their skates. This pressure causes solid ice to melt and form liquid water

p - T Changes

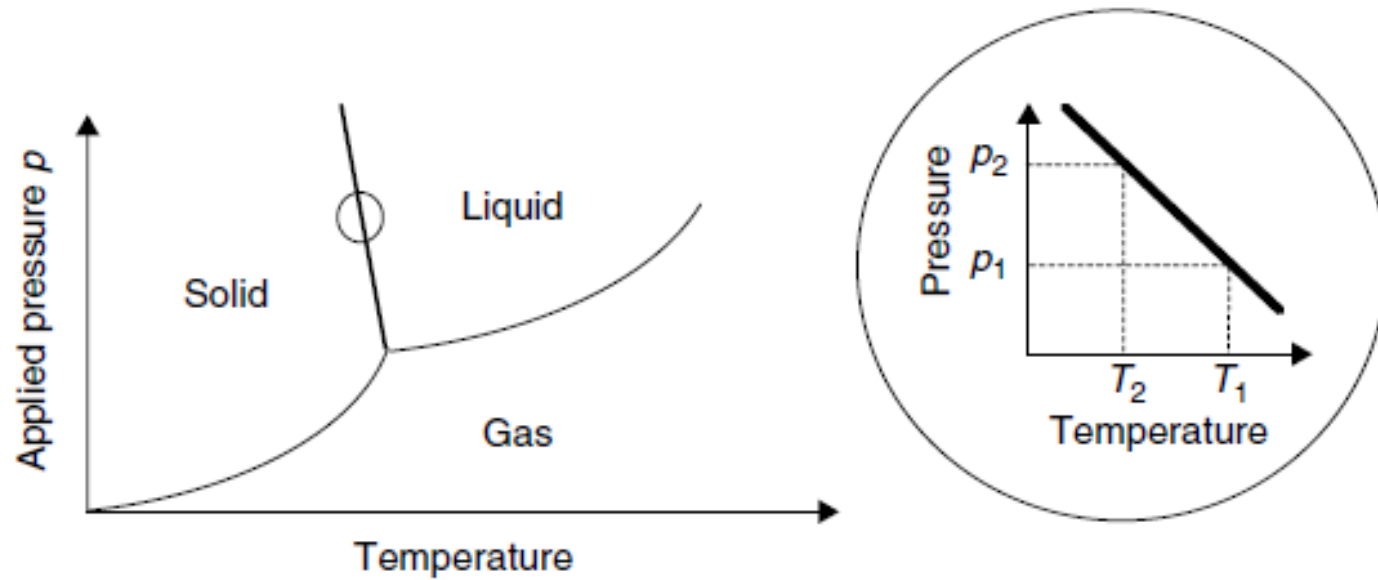


Figure 5.10 Phase diagram of water. *Inset:* applying a high pressure from p_1 (here p^\ominus) to p_2 causes the melting temperature of the ice to decrease from temperature T_1 (here 0°C) to T_2

P-T Quantitative Relationship

Clapeyron Equation:

$$\frac{dp}{dT} = \frac{\Delta H^{\ominus}}{T \Delta V}$$

SAMPLE PROBLEM:

Consider a car weighing 1000 kg (about 2200 lbs) parked on a sheet of ice at 273.15 K. Take the area under wheels in contact with the ice as 100 cm² i.e. 10⁻² m². What is the new melting temperature of the ice – call it $T(\text{final})$? Take $H_{\text{O}}(\text{melt}) = 6.0 \text{ kJ mol}^{-1}$ and water $V_{\text{m}}(\text{melt}) = -1.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

SAMPLE PROBLEM

Paraffin wax has a normal melting temperature $T(\text{melt})$ of 320 K. The temperature of equilibrium is raised by 1.2 K if the pressure is increased fivefold. Calculate V_m for the wax as it melts. Take $H(\text{melt}) = 8.064 \text{ kJ mol}^{-1}$.

TWO-COMPONENT SYSTEM

PHASE DIAGRAMS

- knowledge of the thermodynamics of simple mixtures to discuss the physical changes of mixtures when they are heated or cooled and when their compositions are changed.
- phase diagrams can be used to judge whether two substances are mutually miscible.

PHASE DIAGRAMS

- can equilibrium exist over a range of conditions or whether a system must be brought to a definite pressure, temperature and composition before equilibrium is established.
- phase diagrams are industrially and commercially important.

PHASE DIAGRAMS

- semiconductor, ceramics, steel and alloy industries rely heavily on phase diagrams to ensure uniformity of a product.
- phase diagrams are also the basis for separation procedures in the petroleum industry and the formulation of foods and cosmetic preparations.

DEFINITIONS

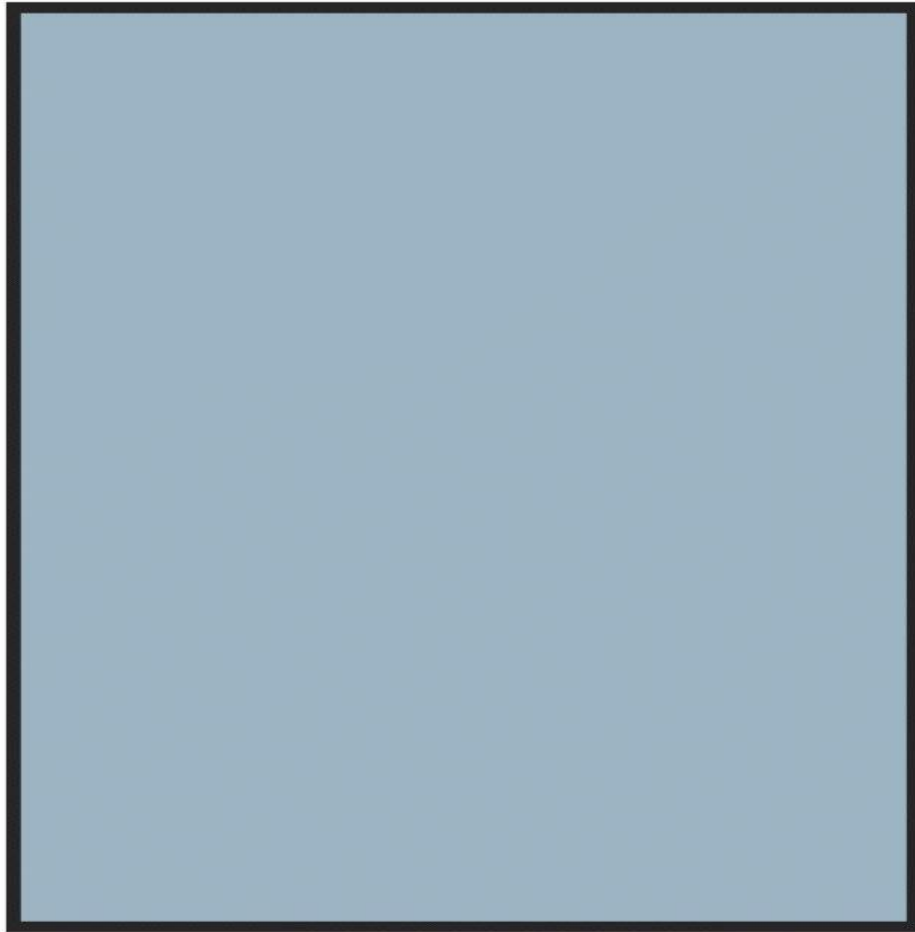
- A phase is a state of matter that is uniform throughout, not only in composition but also in physical state.
- A pure gas
- A gaseous mixture
- Two totally miscible liquids
- A crystal

DEFINITIONS

- A solution of sodium chloride
- Ice
- A slurry of ice and water

DEFINITIONS

- An alloy of two metals?



(a)



(b)

Figure 6-1
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DEFINITIONS

- an alloy of two metals is a two phase system if the metals are immiscible, but a single phase system if they are miscible.
- dispersion can be uniform on a macroscopic level, but not on a microscopic scale.
- dispersions are important in many advanced materials.

DEFINITIONS

- heat treatment cycles are used to achieve the precipitation of a fine dispersion of particles of one phase within a matrix formed by a saturated solid solution phase.
- the ability to control this microstructure resulting from phase equilibria makes it possible to tailor the mechanical properties of the materials.

DEFINITIONS

- A **constituent** of a system is a chemical species (an ion or a molecule) that is present.
- A mixture of water and ethanol has two constituents.
- A solution of sodium chloride has three constituents: Na^+ , Cl^- , H_2O .

DEFINITIONS

- a **component** is a chemically independent constituent of a system.
- the number of components in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system.

DEFINITIONS

- When no reaction takes place and there are no other constraints, the *number of components is the equal to the number of constituents*.
- Pure water is a one component system
- A mixture of ethanol and water is two component system.

DEFINITIONS

- an aqueous solution of sodium chloride is a two component system, because by charge balance, the number of Na^+ ions must be the same as the number of Cl^- ions.
- a system that consists of hydrogen, oxygen and water at room temperature has three components.

DEFINITIONS

- when a reaction can occur under the conditions prevailing in the system, we need to decide the minimum number of species that, after allowing for reactions in which one species is synthesized from others, can be used to specify the composition of all the phases.

DEFINITIONS

- $\text{CaCO}_{3(s)} \leftrightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$
- 3 phases
- 3 constituents
- To specify the composition of the gas phase, we need the species CO_2 , and to specify the composition of the solid phase on the right, we need the species CaO .

DEFINITIONS

- $\text{CaCO}_{3(s)} \leftrightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$
- We do not need an additional species to specify the composition of the phase on the right, because its identity (CaCO_3) can be expressed in terms of the other two constituents by making use of the stoichiometry of the reaction.
- 2 component system.

SAMPLE PROBLEM

How many components are present in a system in which ammonium chloride undergoes thermal decomposition?

The reaction is:



DEFINITIONS

- $\text{NH}_4\text{Cl}_{(s)} \leftrightarrow \text{NH}_{3(g)} + \text{HCl}_{(g)}$
- 2 phases
- 3 constituents
- 1 component

SAMPLE PROBLEM

- Give the number of components in the following systems: (a) water, allowing for its autoprotolysis, (b) aqueous acetic acid, (c) magnesium carbonate in equilibrium with its decomposition products.

DEFINITIONS

- The number of phases, P .
- The number of components, C .
- The variance of the system, F is the number of intensive variables (e.g. p and T) that can be changed independently without disturbing the number of phases in equilibrium.

PHASE RULE

- $F = C - P + 2$
- This is not an empirical rule based upon observations, it can be derived from chemical thermodynamics
- For a one component system $F = 3 - P$
- When only one phase is present, $F = 2$ and both p and T can be varied without changing the number of phases.

PHASE RULE

- When two phases are present, $F = 1$ which implies that pressure is not freely variable if the pressure is set. This is why at a given temperature a liquid has a characteristic vapor pressure.
- When three phases are present, $F = 0$. This special case occurs only at a definite temperature and pressure that is characteristic of the substance.

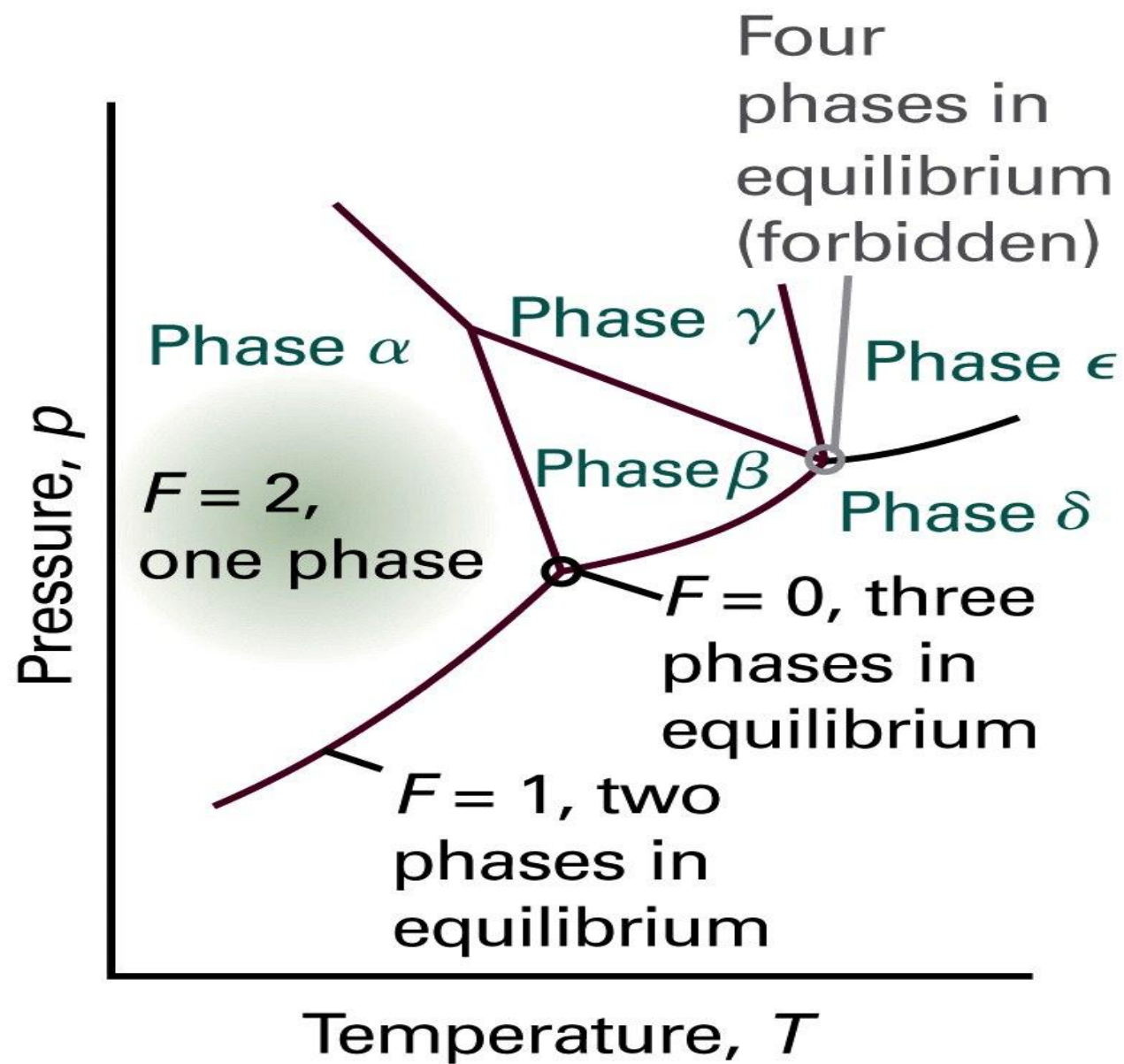


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EXPERIMENTAL PROCEDURE

- Thermal analysis – a sample is allowed to cool and its temperature is monitored. When a phase transition occurs, cooling may stop until the phase transition is complete and is easily observed on a thermogram.

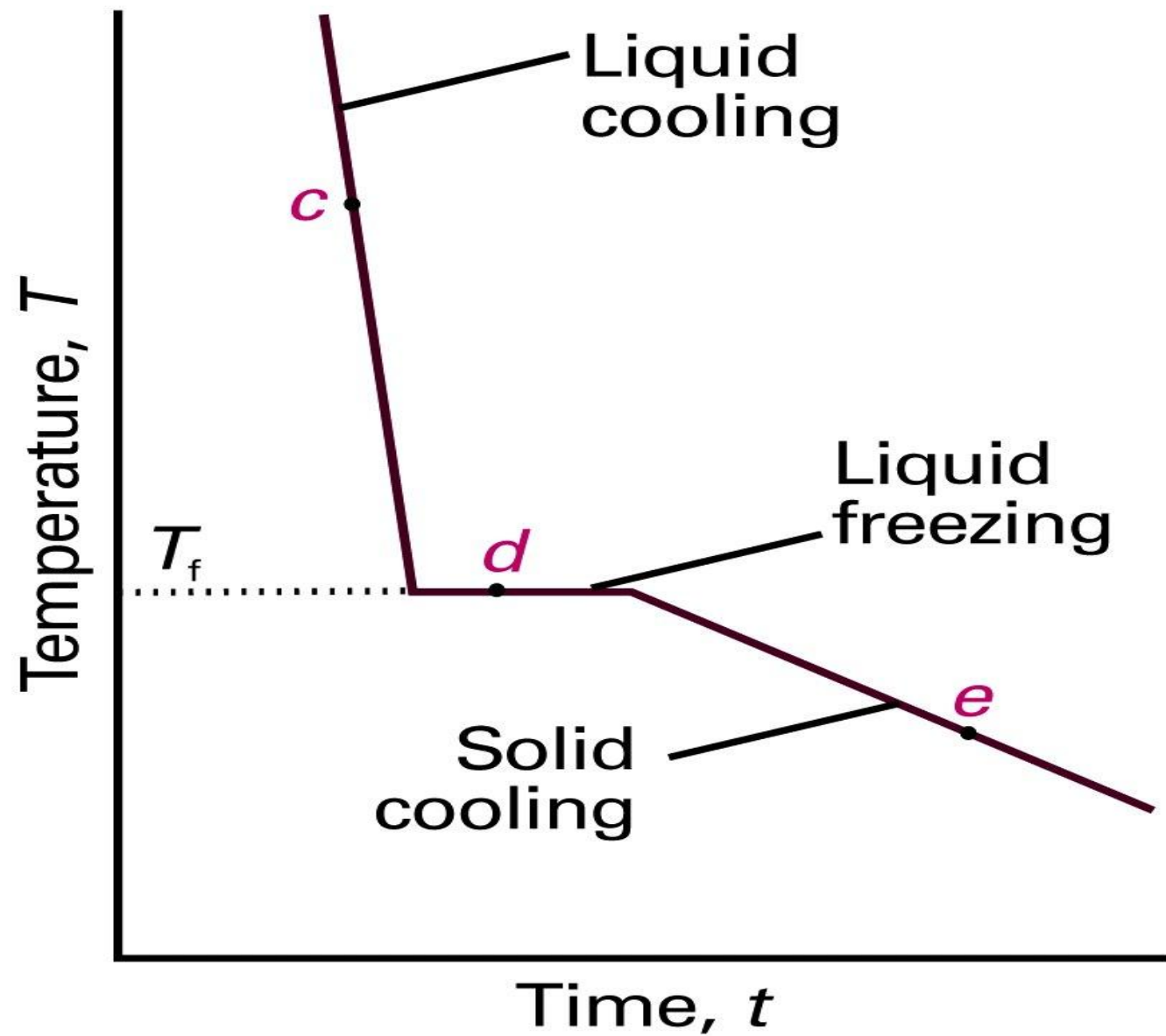


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EXPERIMENTAL PROCEDURES

- Modern work on phase transitions often deal with systems at very high pressures and more sophisticated detection properties must be adopted.
- A diamond anvil cell is capable of producing extremely high pressures.

PHASE RULE

- a sample is placed in a cavity between two gem-quality diamonds and then pressure is exerted by turning a screw. Pressures up to ~2 Mbar can be achieved.
- one application is the study the transition of covalent solids to metallic solids.

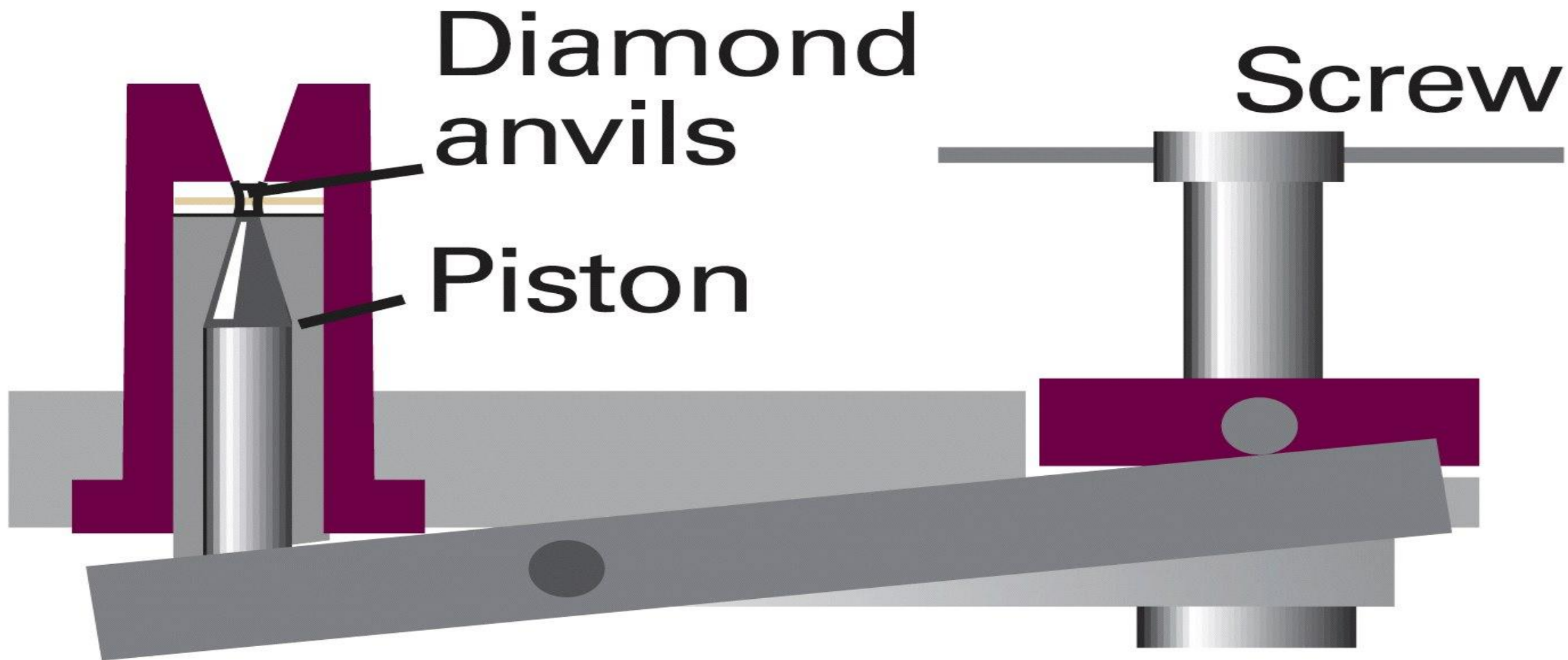


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EXPEIMENTAL PROCEDURES

- Iodine, I_2 , becomes metallic at ~ 200 kbar and makes a transition to a monatomic metallic solid at around 210 kbar.
- Relevant to the structure of material deep inside the earth and in the interiors of giant planets, where even hydrogen may be metallic.

TWO COMPONENT SYSTEM

- When two components are present in a system,
 $C = 2$, so $F = 4 - P$.
- If the temperature is constant, the remaining variance is $F' = 3 - P$.
- F' indicates that one of the degrees of freedom has been discarded – in this case the temperature.
- The two remaining degrees of freedom are the pressure and the composition

TWO COMPONENT SYSTEM

- The partial vapor pressure of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's Law:

$$p_A = x_A p_A^* \quad p_B = x_B p_B^*$$

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = x_A p_A^* + (1 - x_A) p_B^*$$

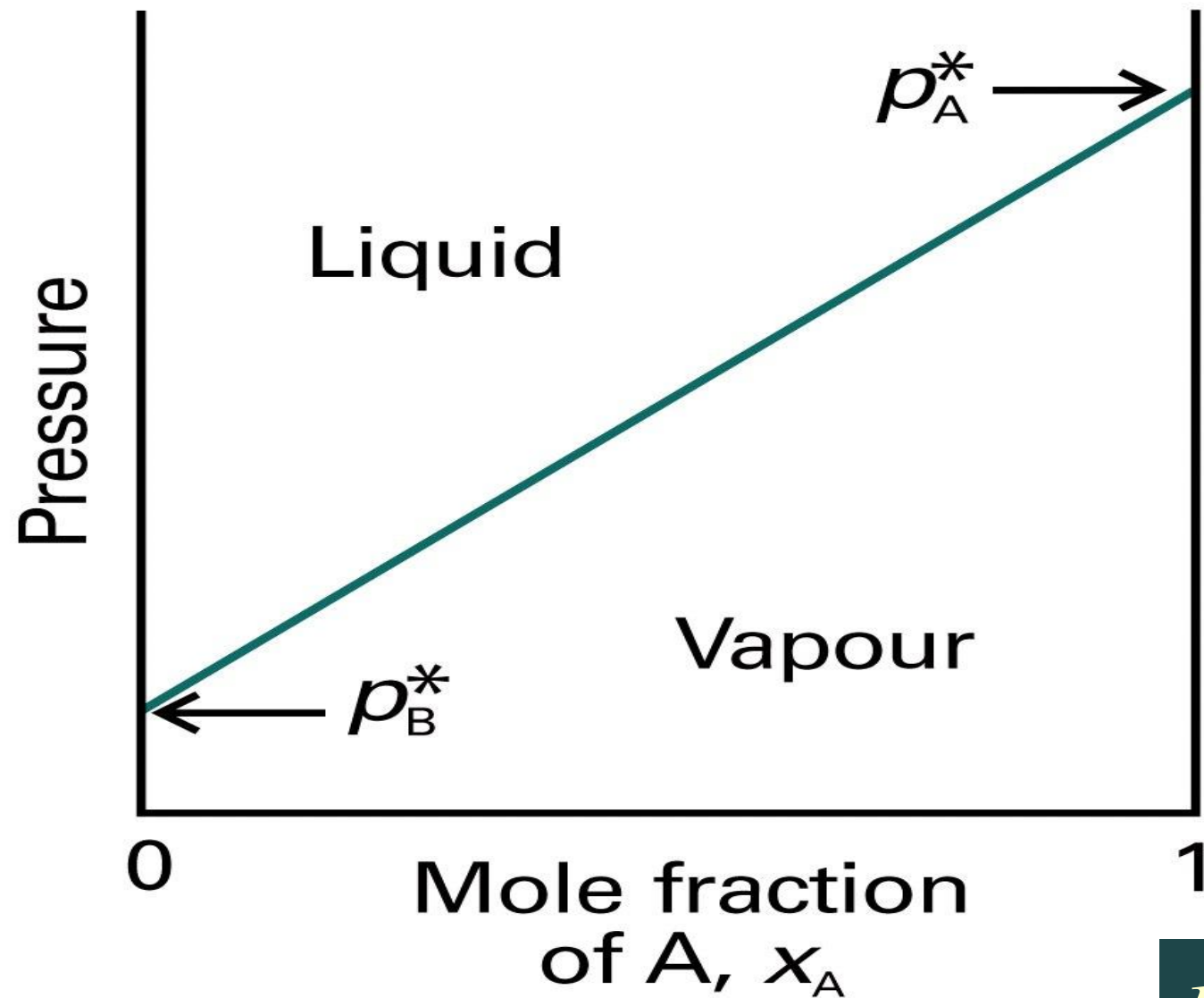
$$p = x_A p_A^* + p_B^* - x_A p_B^*$$

$$p = p_B^* + (p_A^* - p_B^*) x_A$$

TWO COMPONENT SYSTEM

$$p = p_B^* + (p_A^* - p_B^*)x_A$$

- This expression shows that the total vapor pressure (at a fixed temperature) changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1.



$$p = p_B^* + (p_A^* - p_B^*)x_A$$

Figure 6-6
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TWO COMPONENT SYSTEM

- The compositions of the liquid vapor that are in mutual equilibrium are not necessarily the same. The more volatile the component, the higher amount of that substance should be in the vapor.
- y_A and y_B are the mole fractions of A and B in the gas.

$$y_A = \frac{p_A}{p} \quad y_B = \frac{p_B}{p}$$

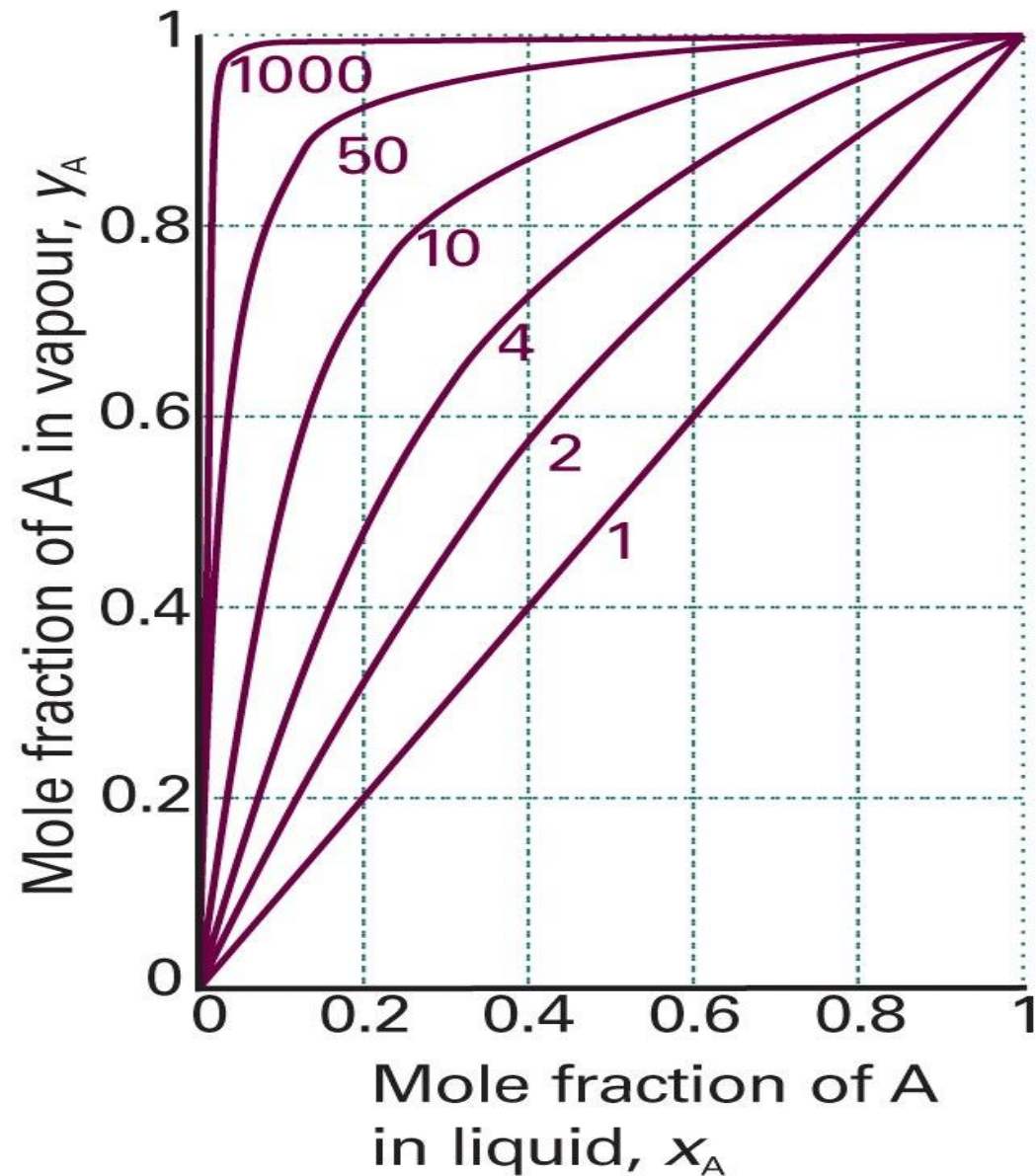
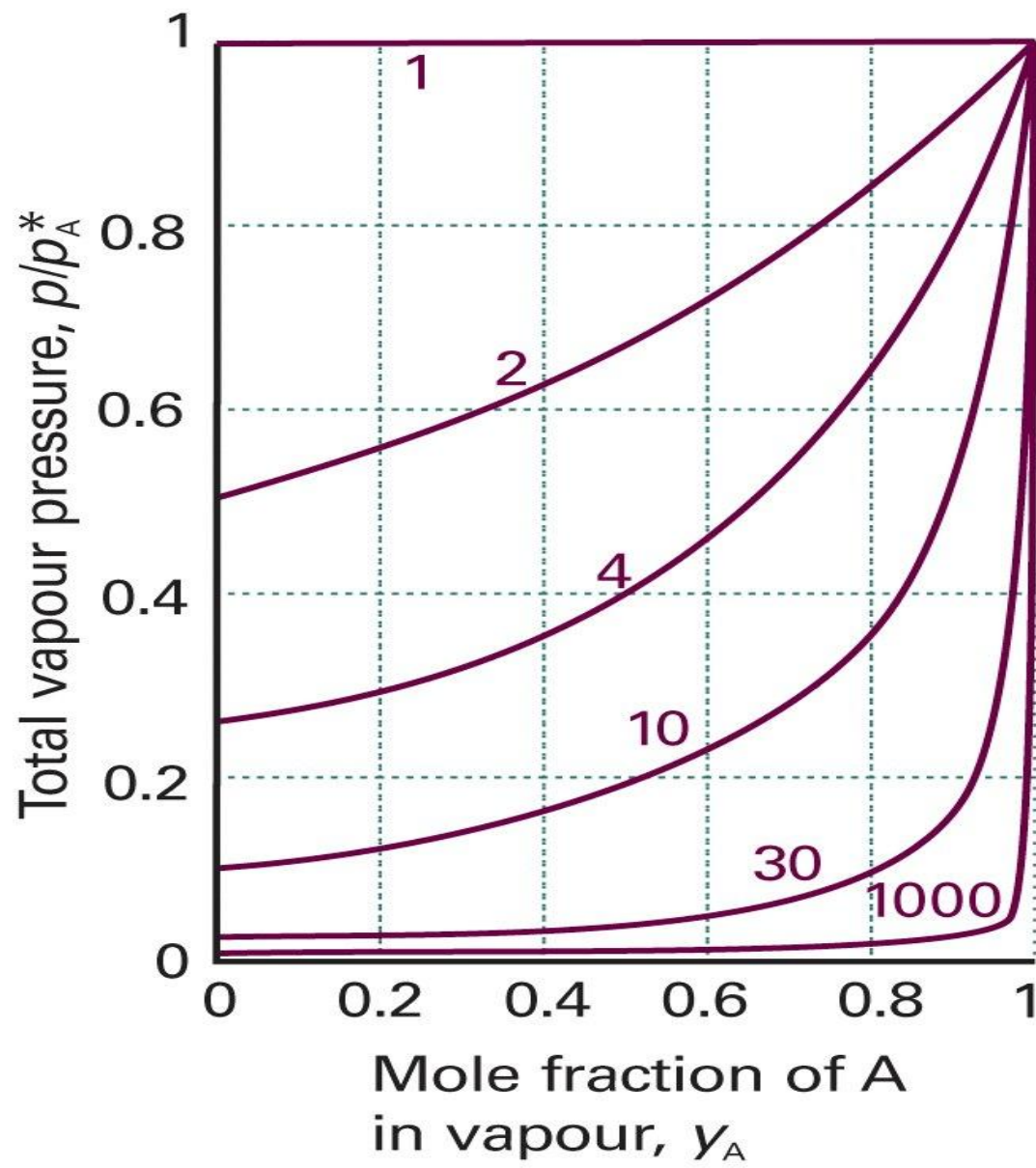


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$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p_B + (p_A^* - p_B^*)x_A}$$

$$y_B = 1 - y_A$$

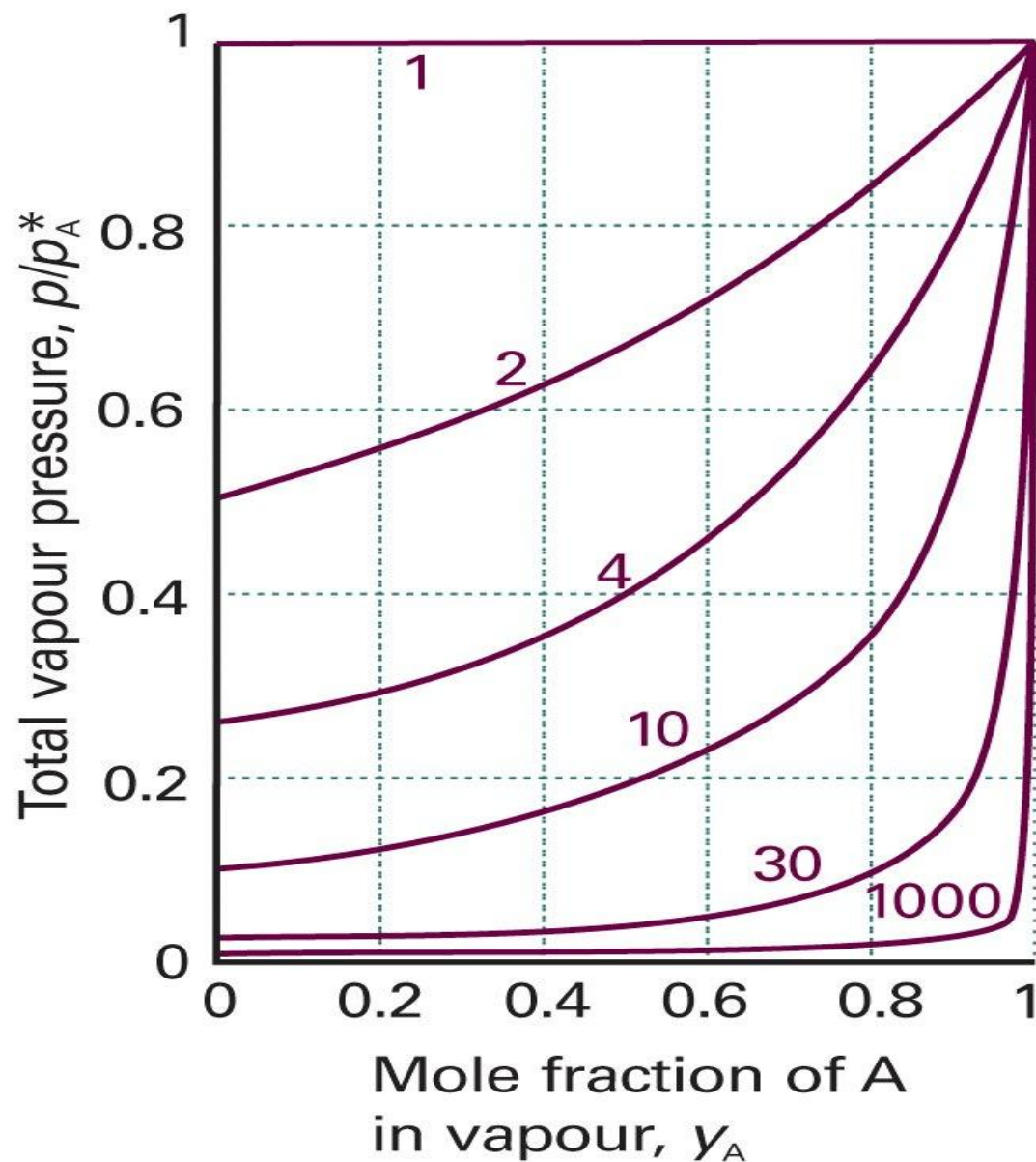
$$\frac{p_A^*}{p_B^*}$$



$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$$

$$\frac{p_A^*}{p_B^*}$$

Figure 6-8
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$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$$

$$\frac{p}{p_A^*} = \frac{p_B^*}{p_A^*} \text{ when } y_A \text{ is zero}$$

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TWO COMPONENT SYSTEM

- If we are interested in distillation, both vapor and liquid compositions are of equal interest.
- So it makes sense to present data showing both the dependence of vapor and liquid composition upon mole fraction.

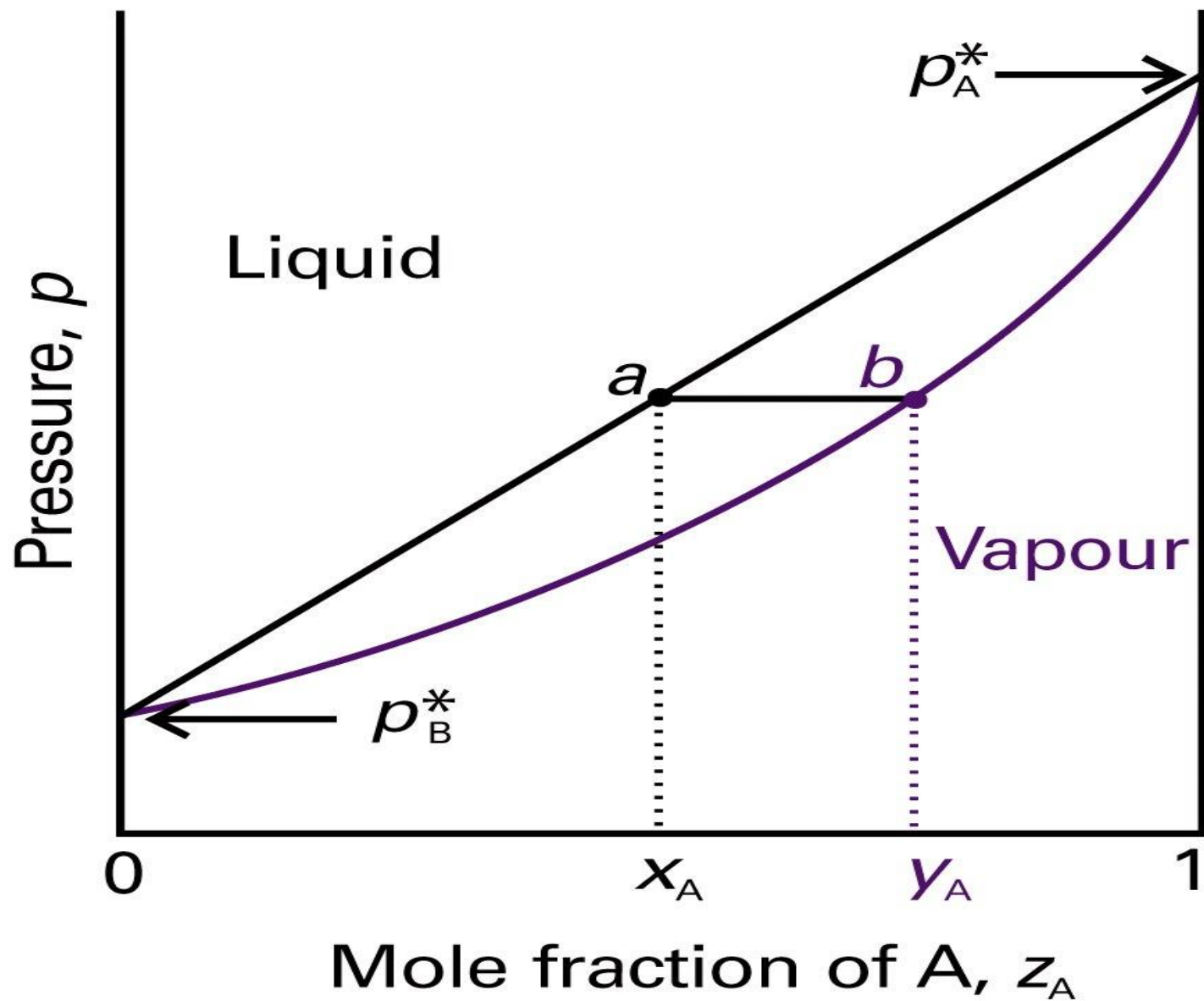


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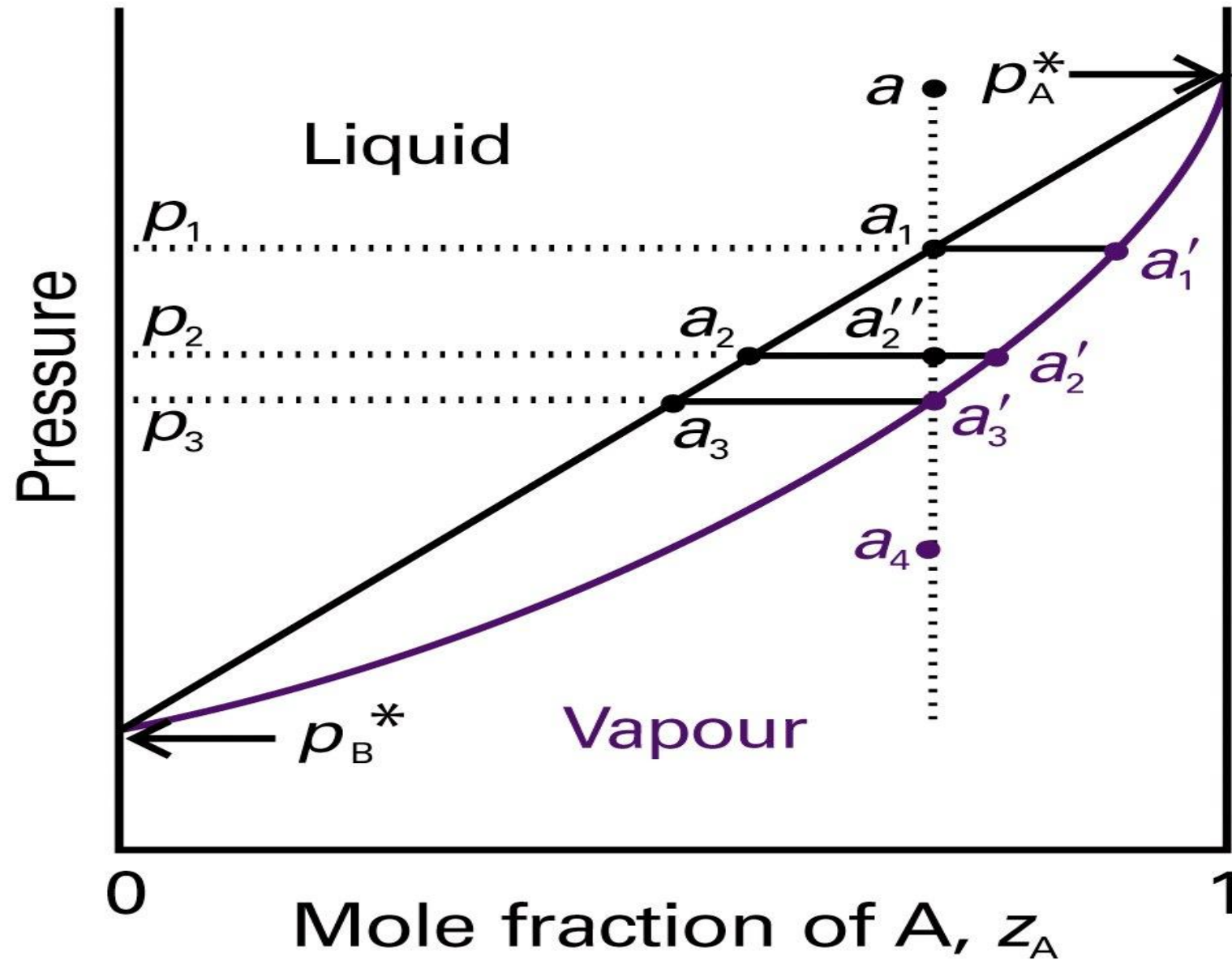


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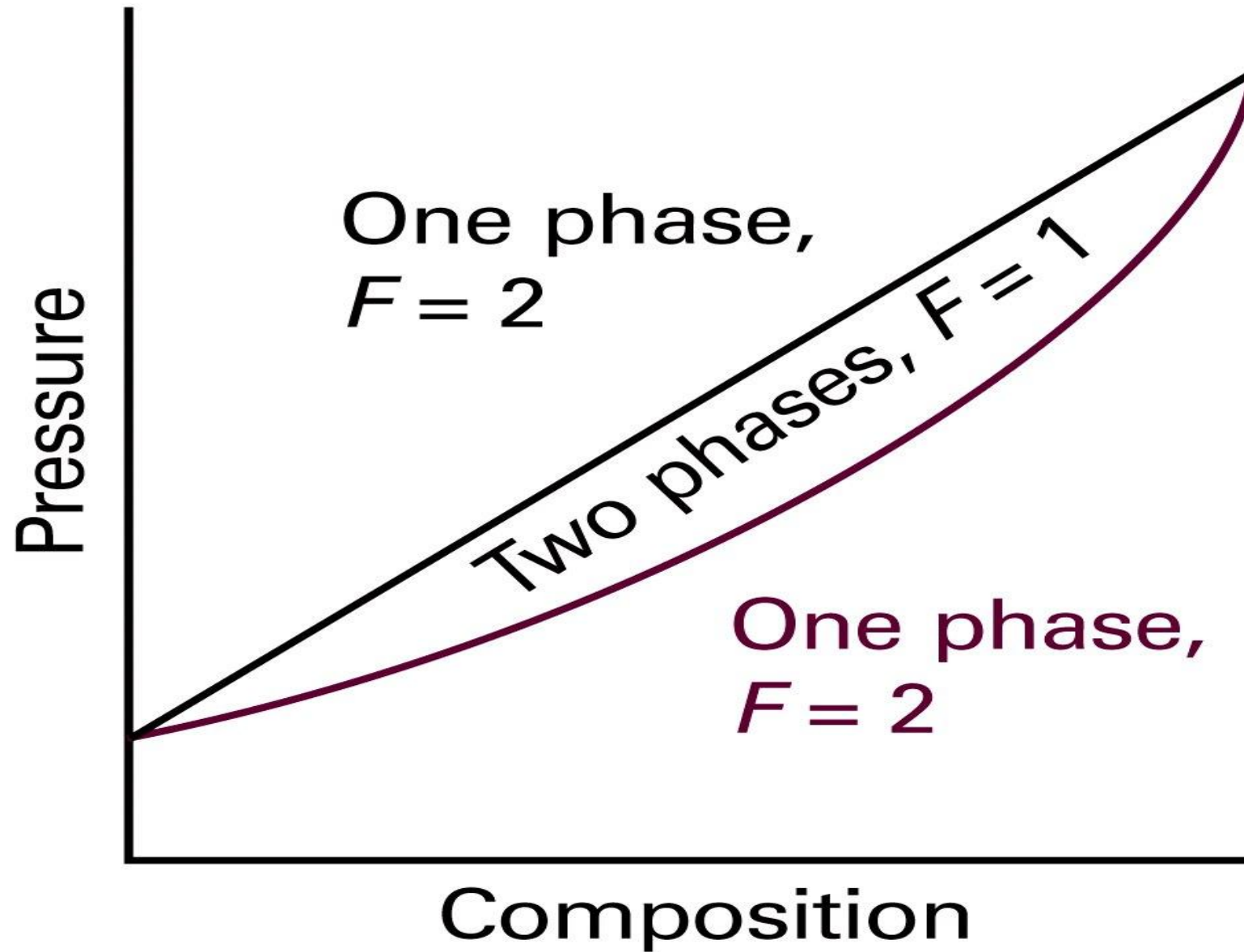


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LEVER RULE

- A point in the two-phase of a phase diagram indicates not only qualitatively that both liquid and vapor present, but represents quantitatively the relative amounts of each.
- To find the relative amounts of two phases α and β that are in equilibrium, we measure the distances l_α and l_β along the horizontal tie line, and then use the lever rule.

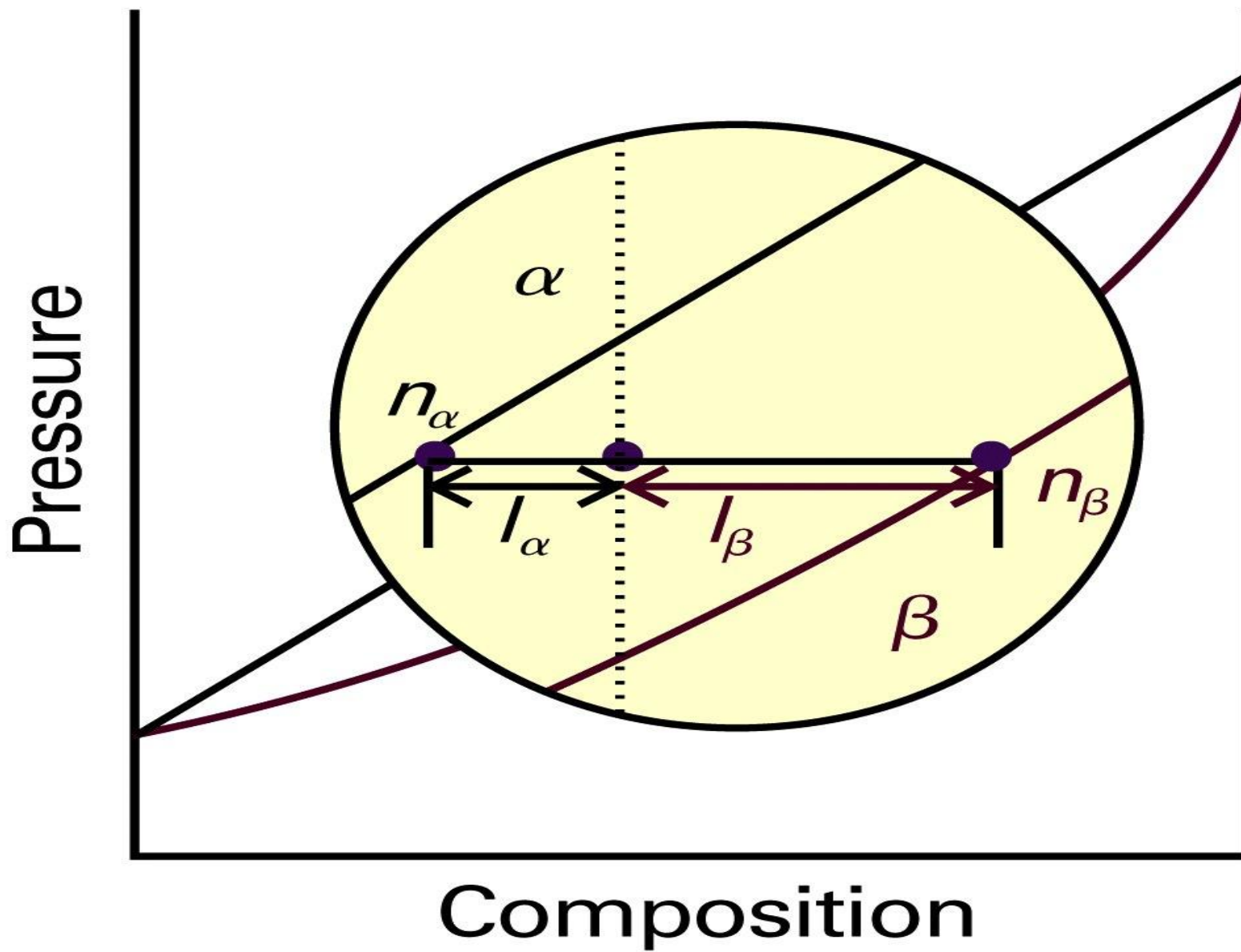


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LEVER RULE

$$n_{\alpha}l_{\alpha} = n_{\beta}l_{\beta}$$

$$\frac{n_{\alpha}}{n_{\beta}} = \frac{l_{\beta}}{l_{\alpha}}$$

- Where n_{α} is the amount of phase α and n_{β} is the amount of phase β .

TEMPERATURE COMPOSITION DIAGRAMS

- To discuss distillation we need a temperature-composition diagram instead of a pressure-composition diagram.
- Such a diagram shows composition at different temperatures at a constant pressure (typically 1 atm).

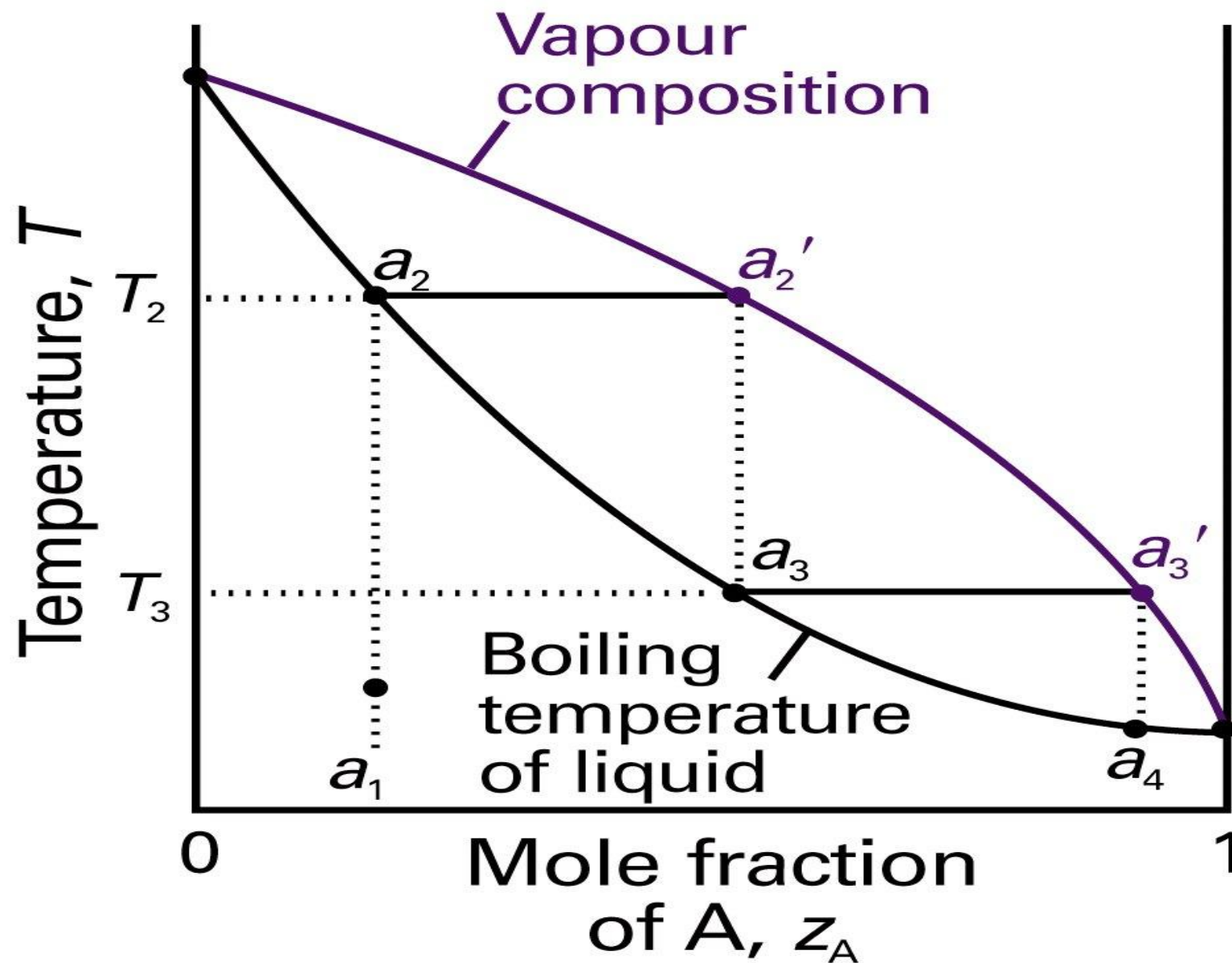


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TEMPERATURE COMPOSITION DIAGRAMS

- In a simple distillation the vapor is withdrawn and condensed. This technique is used to separate a volatile liquid from a non-volatile solute or solid.
- In a fractional distillation, the boiling and condensation cycle is repeated successively. This technique is used to separate volatile liquids.

TEMPERATURE COMPOSITION DIAGRAMS

- The efficiency of a fractionating column is expressed in terms of the number of theoretical plates, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate.

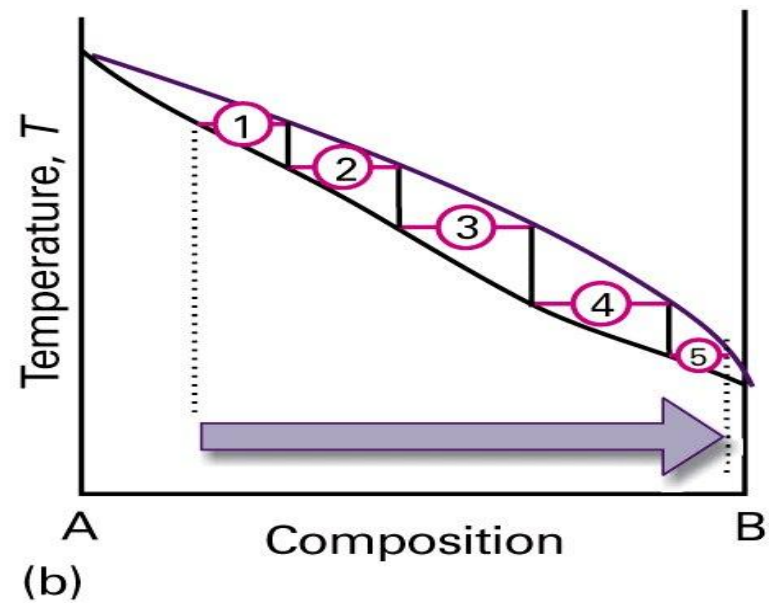
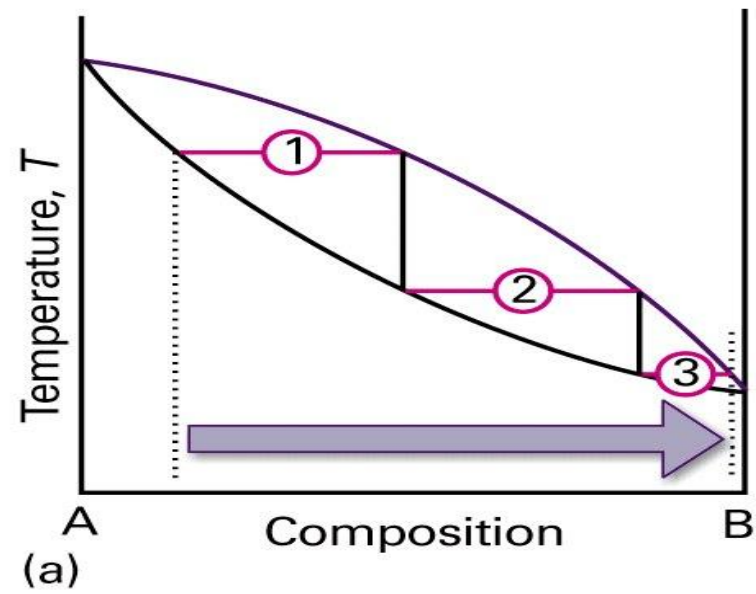


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AZEOTROPES

- Although many liquids have temperature-composition phase diagrams resembling the ideal version, a number of important liquids deviate from ideality.
- If a maximum occurs in the phase diagram, favorable interactions between A and B molecules stabilize the liquid.

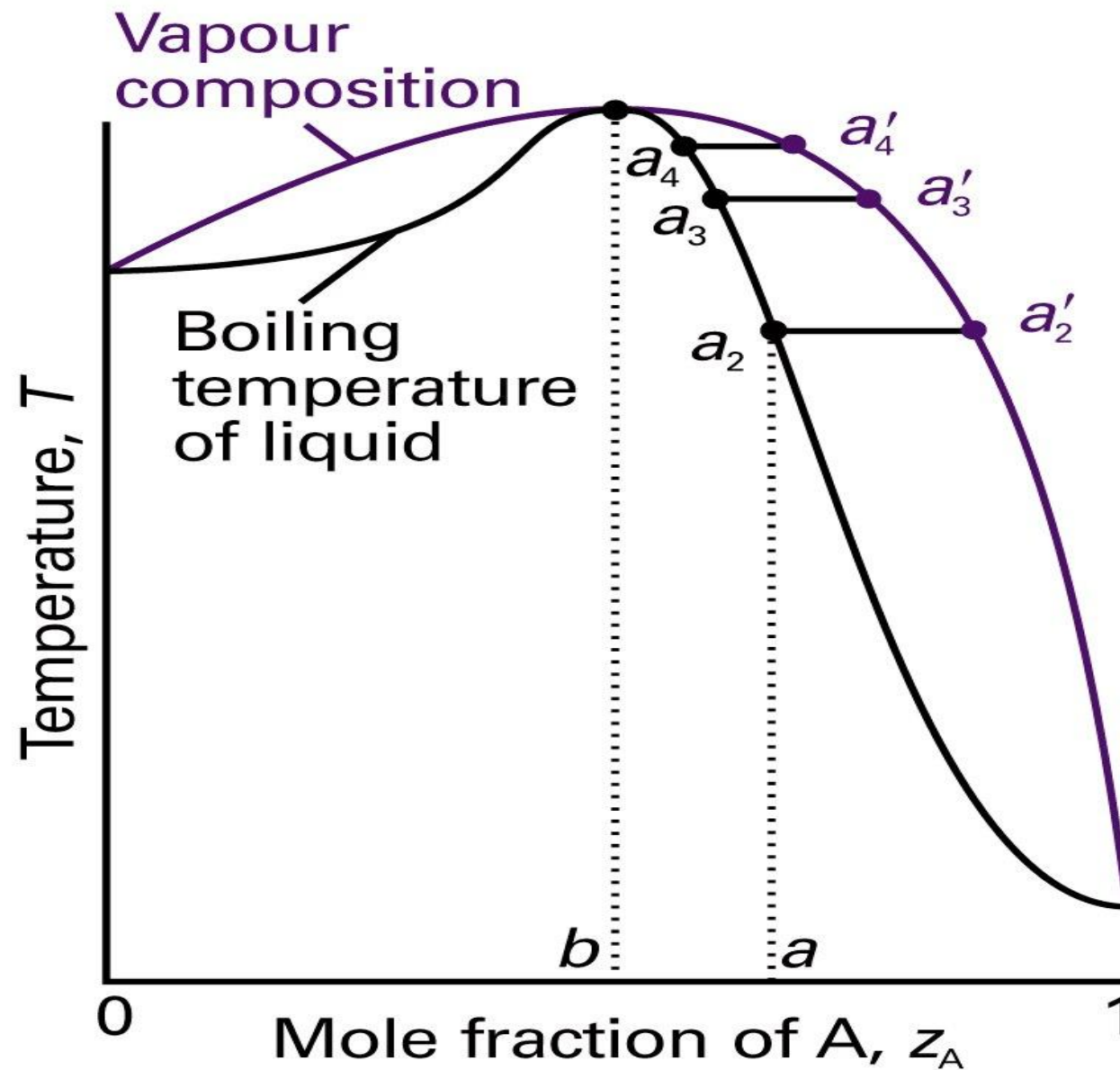


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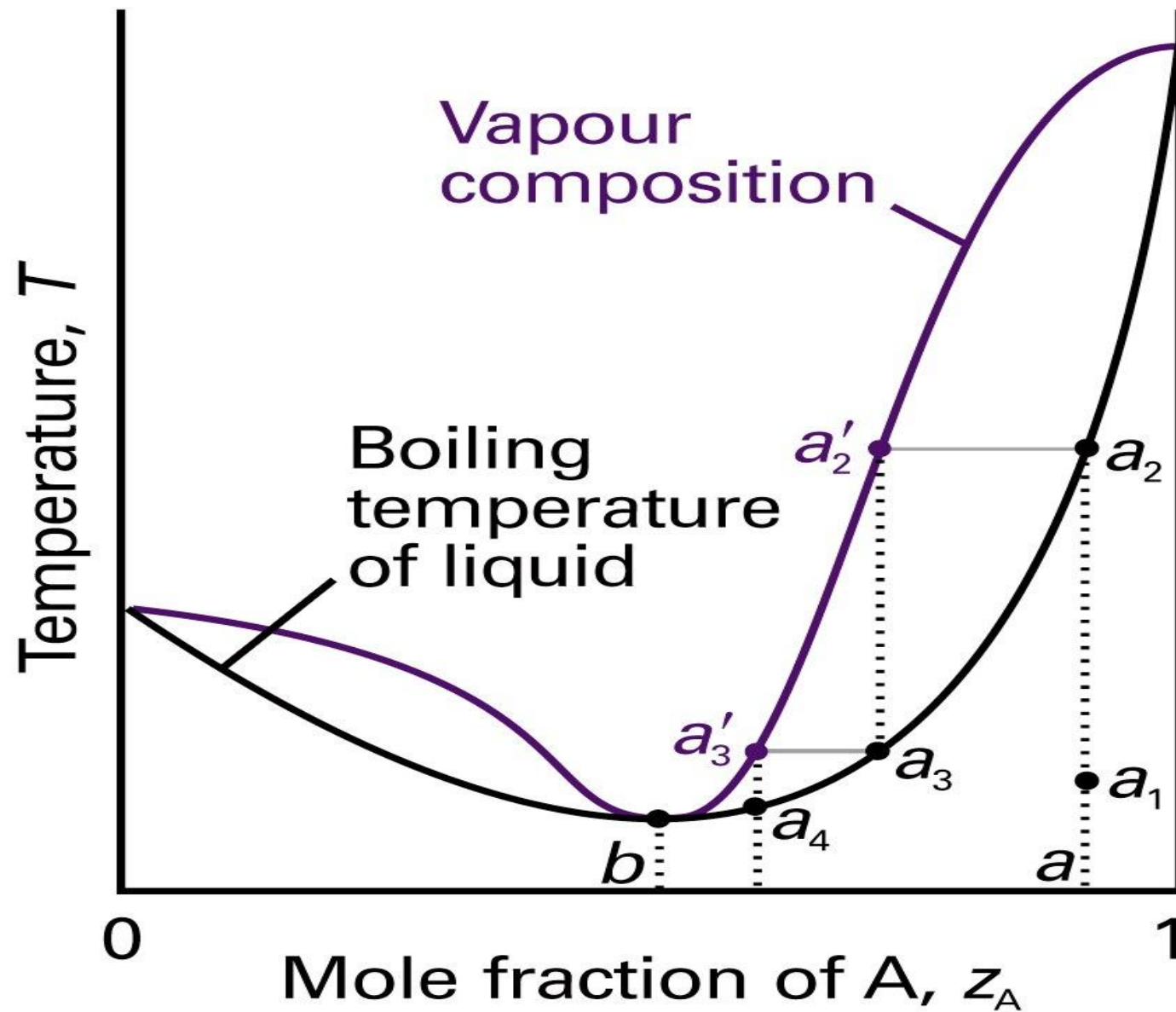


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AZEOTROPES

- An azeotrope is a mixture of two (or more) miscible liquids that when boiled produce the same composition in the vapor phase as that is present in the original mixture.

LIQUID-LIQUID PHASE DIAGRAMS

- Let's consider the distillation of two immiscible liquids, such as octane and water.
- The system can be considered as the joint distillation of the separated components.
- Total vapor pressure $p = p_A^* + p_B^*$
- Mixture boils when $p = 1 \text{ atm}$, and so the mixture boils at a lower temperature than either component would alone.

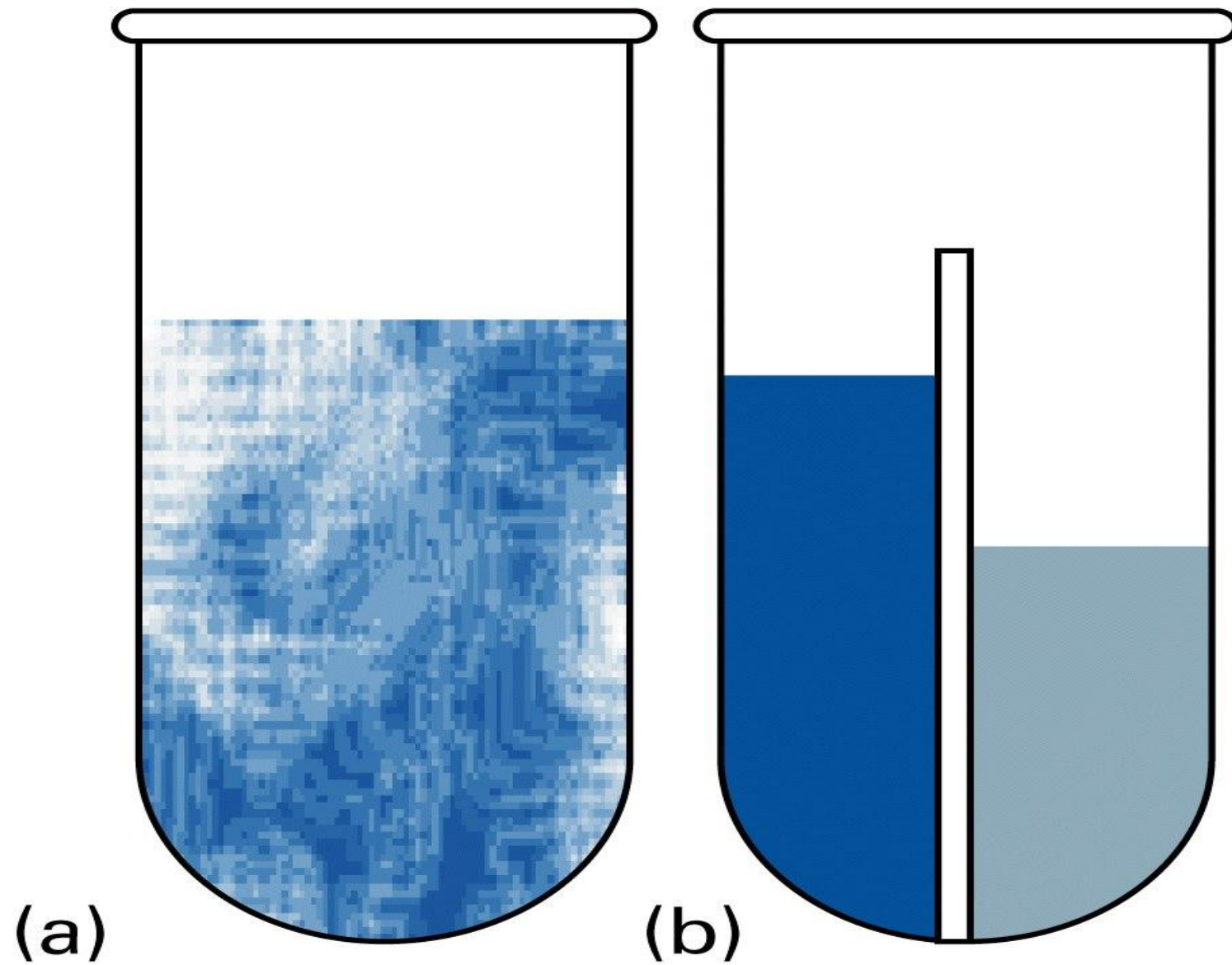


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LIQUID-LIQUID PHASE DIAGRAMS

- Let's consider temperature-composition diagrams for systems that consist of pairs of partially miscible liquids.
- Partially miscible liquids are liquids that do not mix at all proportions at all temperatures.

PHASE SEPARATION

- Suppose a small amount of liquids B is added to another liquid A at a temperature T' .
- If it dissolves completely the binary mixture is a single phase.
- As more B is added, A becomes saturated in B and no more B dissolves \rightarrow 2 phases.
- Most abundant phase is A saturated with B.
- Minor phase is B saturated with A.

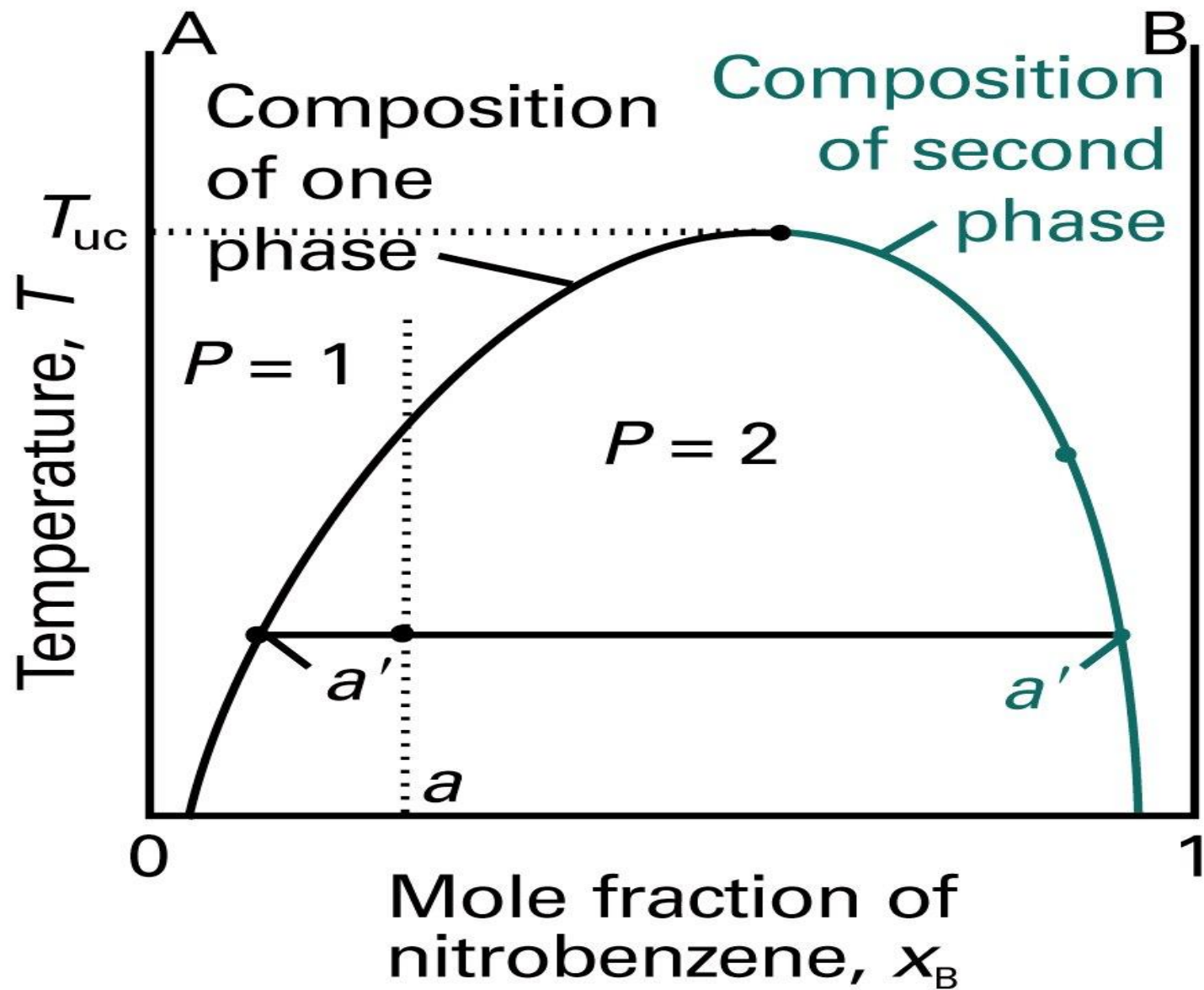


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PHASE SEPARATION

- The relative abundance of each phase is given by the lever rule.
- As the amount of B increases the composition of each phase stays the same, but the amount of each changes with the lever rule.
- Eventually a point is reached when so much B is present that it can dissolve all the A, and system reverts to a single phase.

SAMPLE PROBLEM

A mixture of 50 g of hexane (0.59 mol C_6H_{14}) and 50 g of nitrobenzene (0.41 mol $\text{C}_6\text{H}_5\text{NO}_2$) was prepared at 290 K. What are the compositions of the phases, and in what proportions do they occur? To what temperature must the sample be heated in order to obtain a single phase?

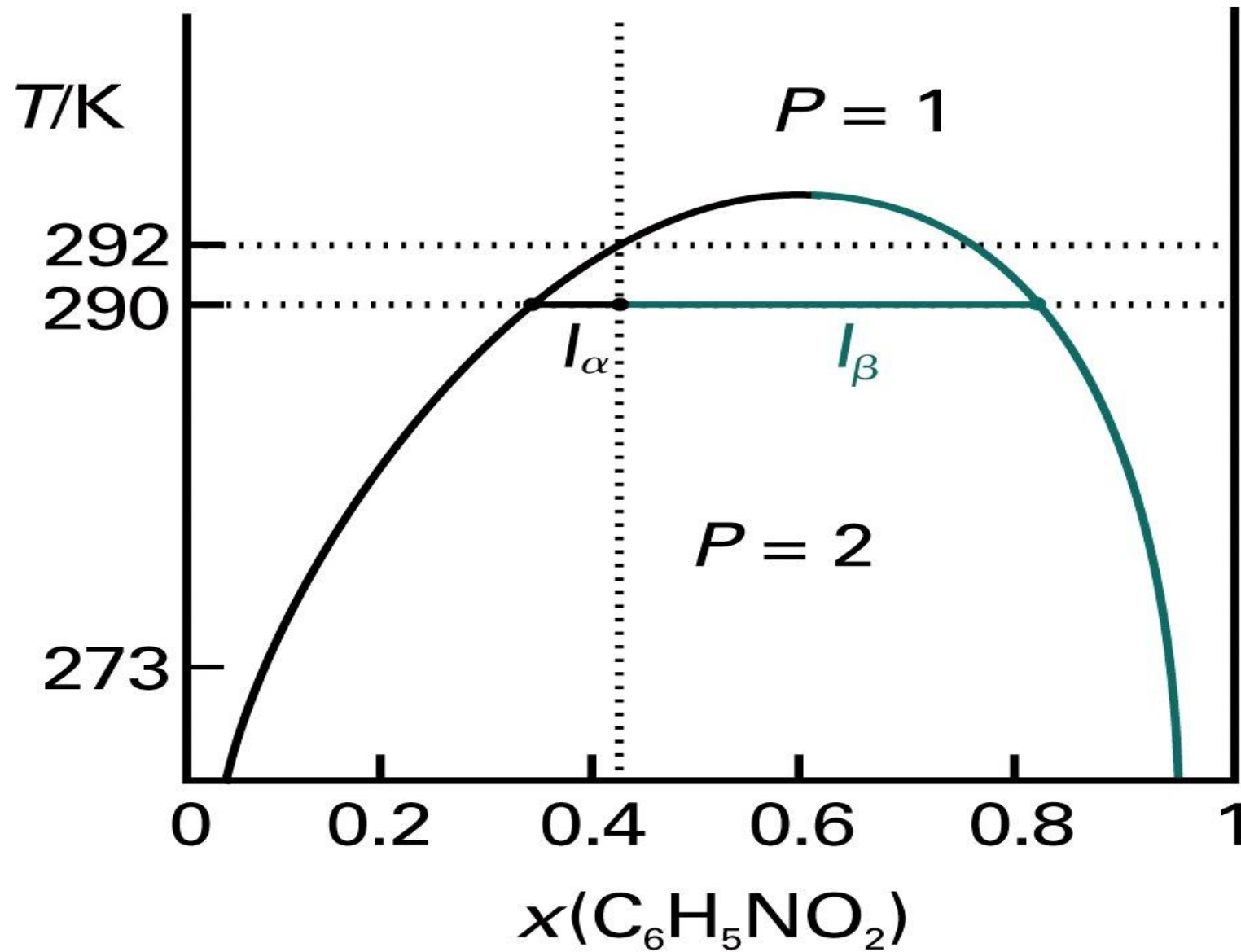


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CRITICAL SOLUTION TEMPERATURES

- The upper critical solution temperature, T_{uc} is the highest temperature at which phase separation occurs.
- Above the critical temperature the two components are fully miscible.
- On the molecular level, this can be interpreted as the kinetic energy of each molecule overcoming molecular interactions that want molecules of one type to come close together.

Critical solution temperatures

- Some systems show a lower critical solution temperature, T_{lc} .
- Below this temperature the two components mix in all proportions and above which they form two phases.
- An example is water and triethylamine.

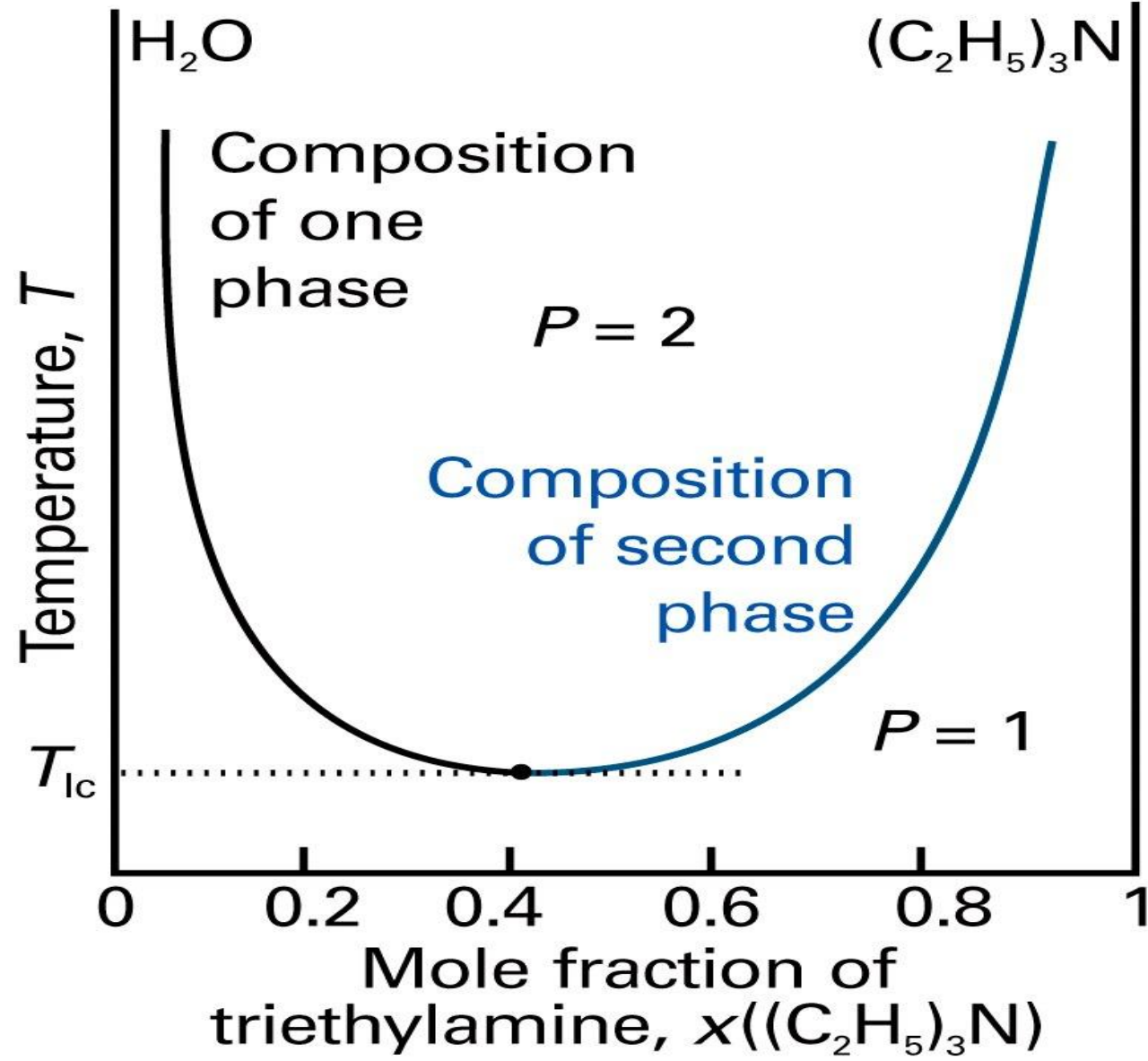


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CRITICAL SOLUTION TEMPERATURES

- The molecular reason for this is that water and triethylamine form a weak molecular complex. At higher temperatures the complexes break up and the two components are less miscible.
- Some systems have upper and lower critical solution temperatures.

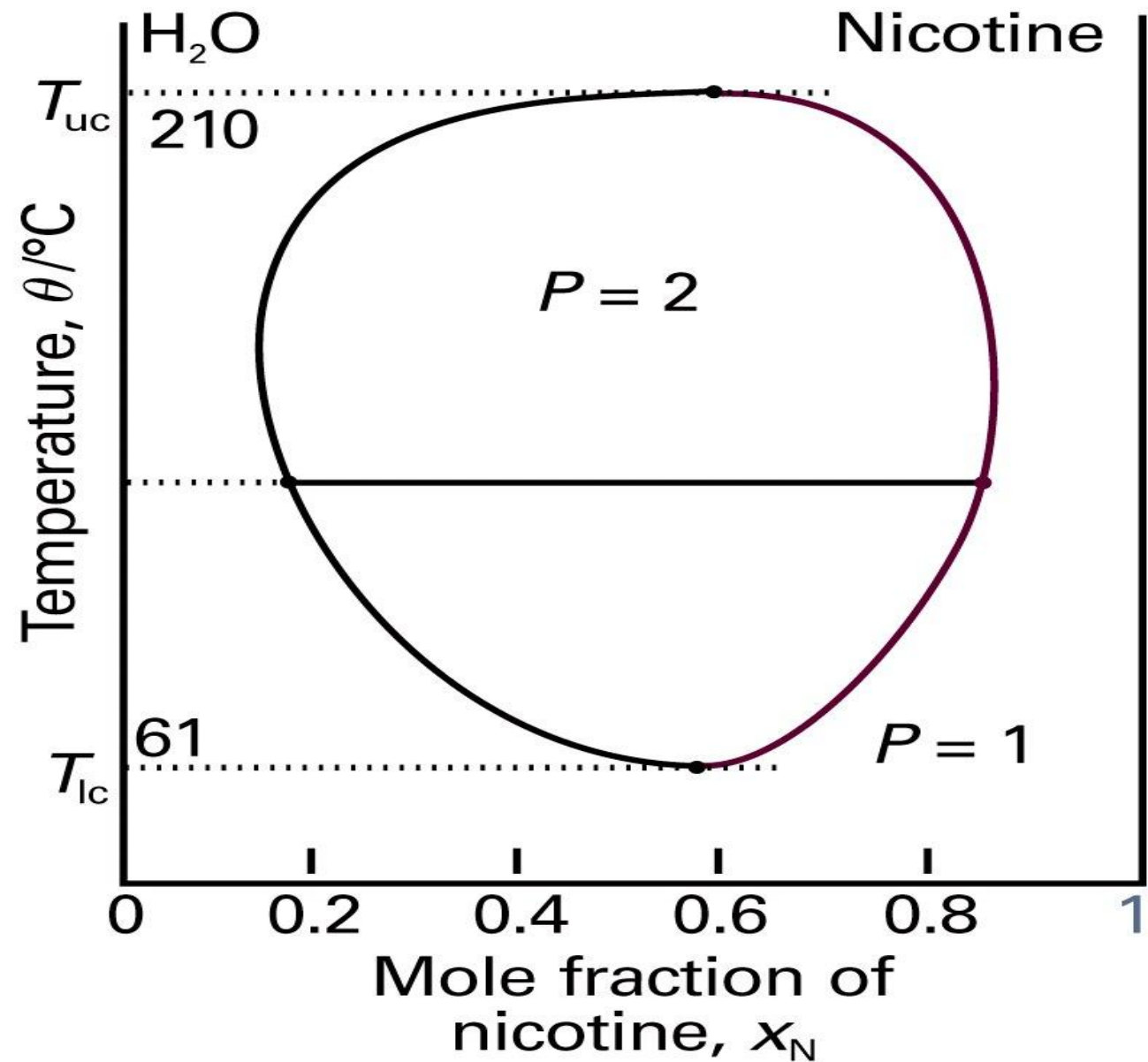


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DISTILLATION OF PARTIALLY MISCIBLE LIQUIDS

- What happens when you distill partially miscible liquids?
- A pair of liquids that are partially miscible often form a low-boiling azeotrope.
- Two possibilities can exist: one in which the liquid become fully miscible before they boil; the other in which boiling occurs before mixing is complete.

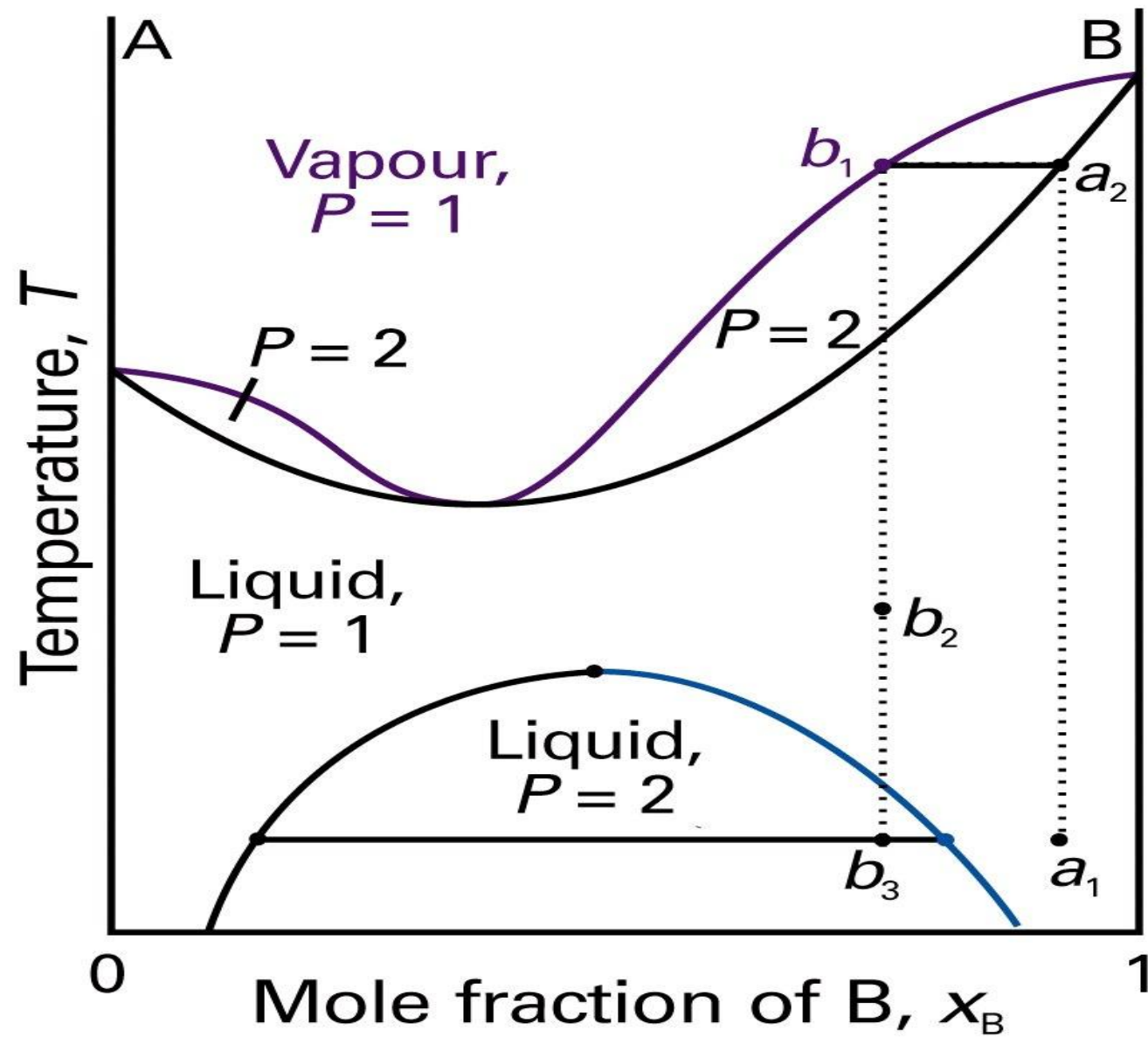


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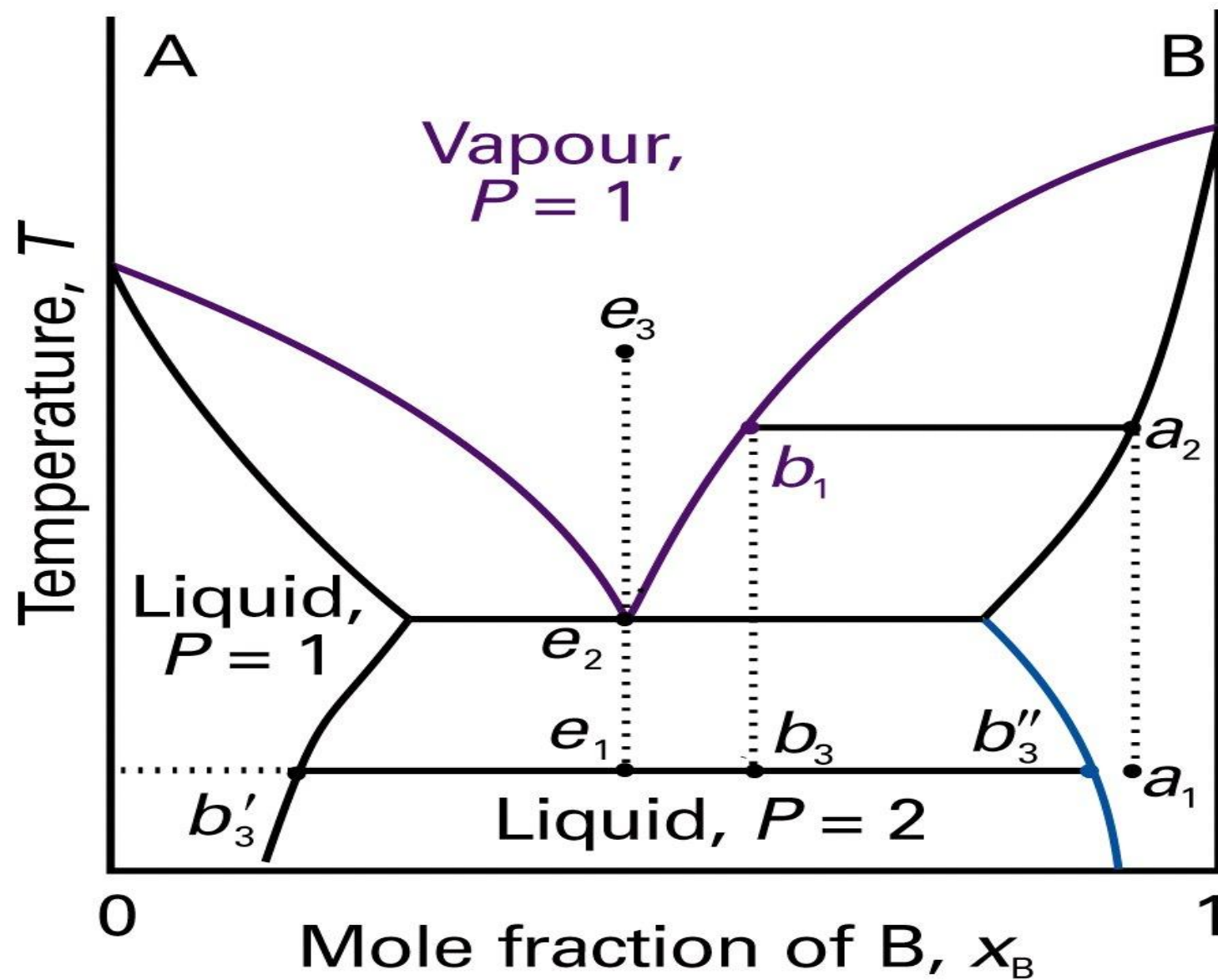


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LIQUID-SOLID PHASE DIAGRAMS

- The knowledge of temperature-composition diagrams for solid mixtures guides the design of important industrial processes, such as the manufacture of liquid crystal displays and semiconductors.

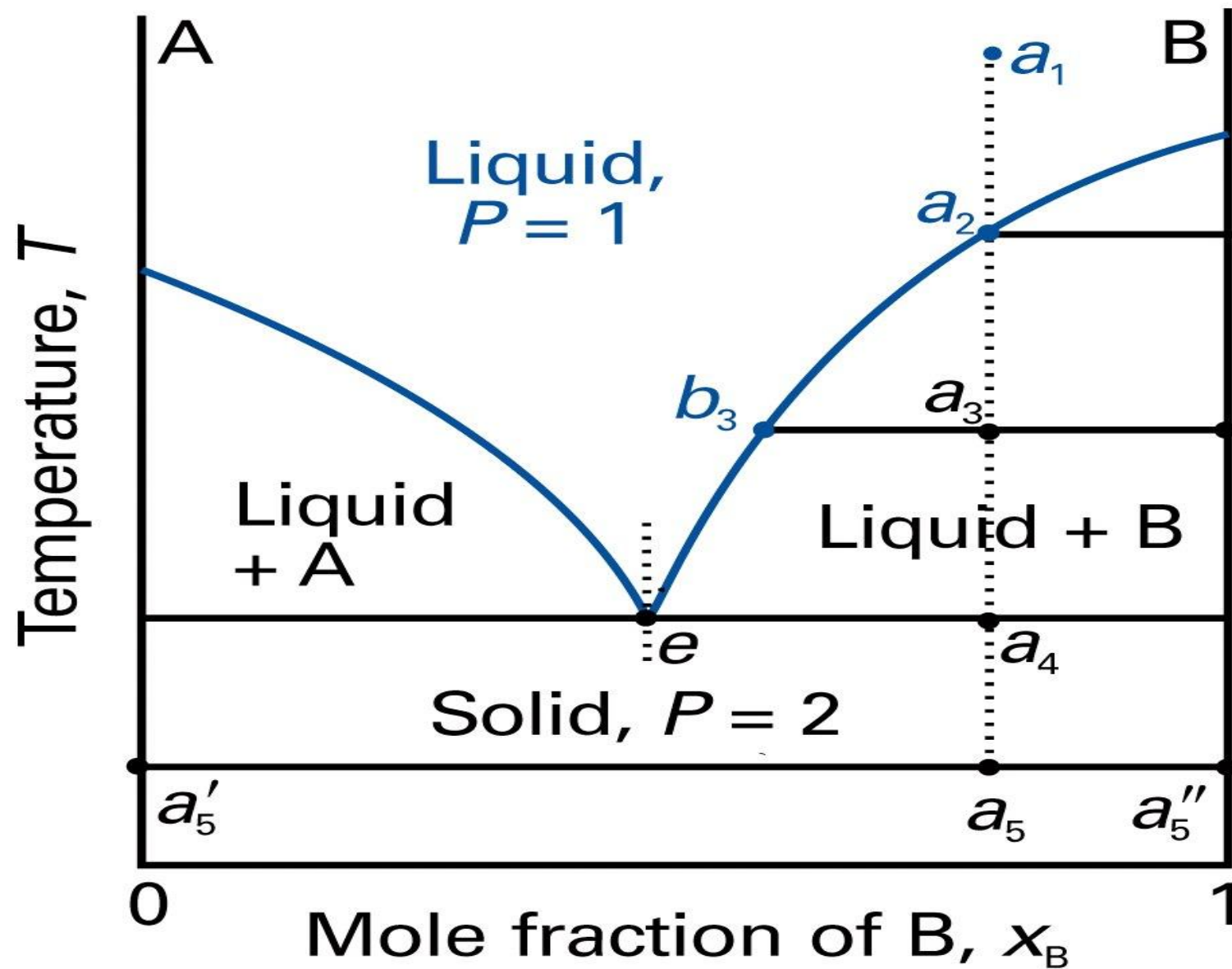


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EUTECTICS

- The isopleth at e corresponds to the eutectic composition, the mixture with the lowest melting point.
- A liquid with a eutectic composition freezes at a single temperature without depositing solid A or B.
- A solid with the eutectic composition melts without any change of composition at the lowest temperature of any mixture.

EUTECTICS

- Solder – 67% tin and 33% lead by mass melts at 183 °C.
- 23% NaCl and 77% H₂O by mass forms a eutectic mixture which melts at -21.1 °C. Above this temperature the mixture melts.

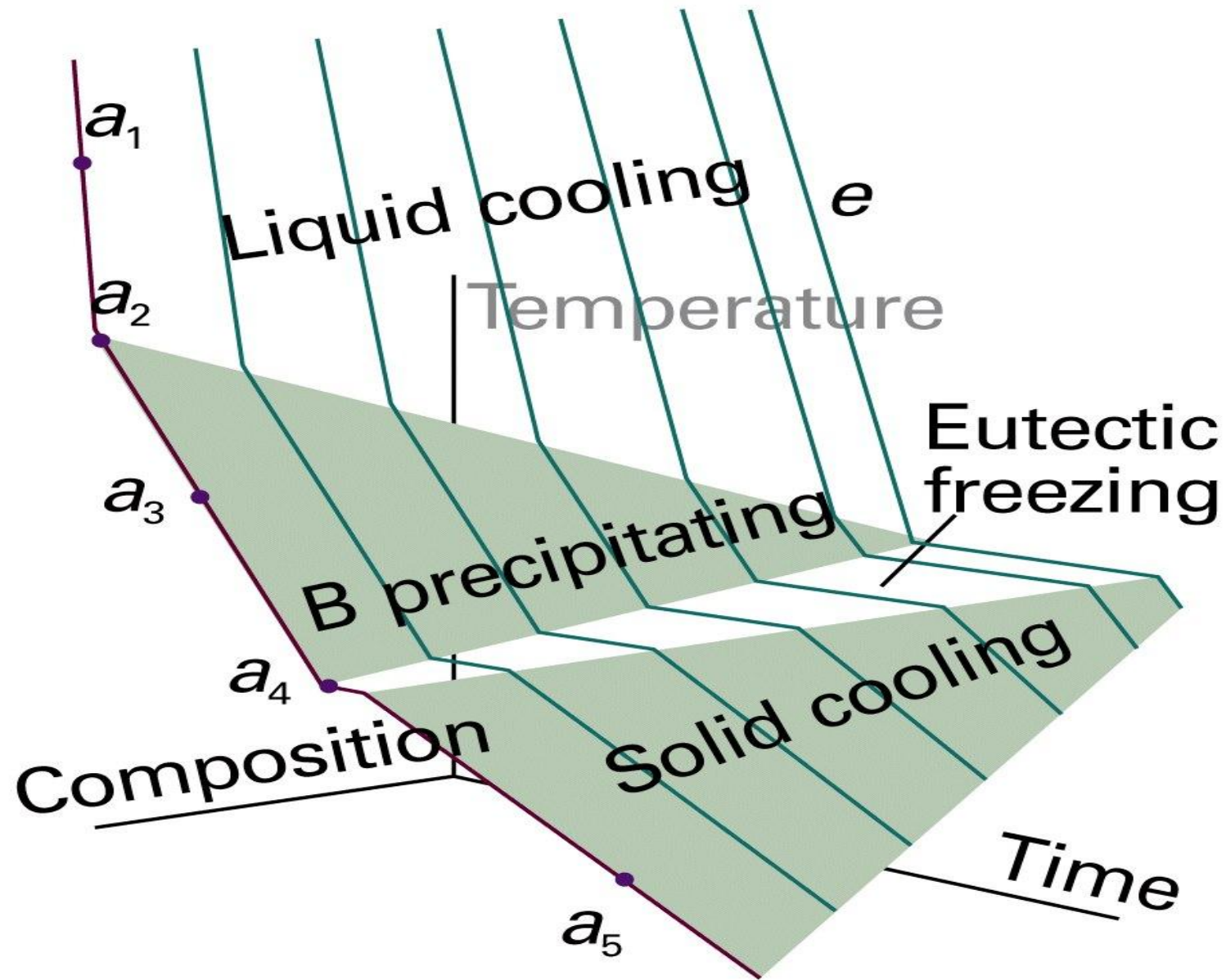


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REACTING SYSTEMS

- Many binary mixtures react produce compounds.
- Gallium arsenide is a technologically important example – semiconductor.
- $\text{Ga} + \text{As} \leftrightarrow \text{GaAs}$

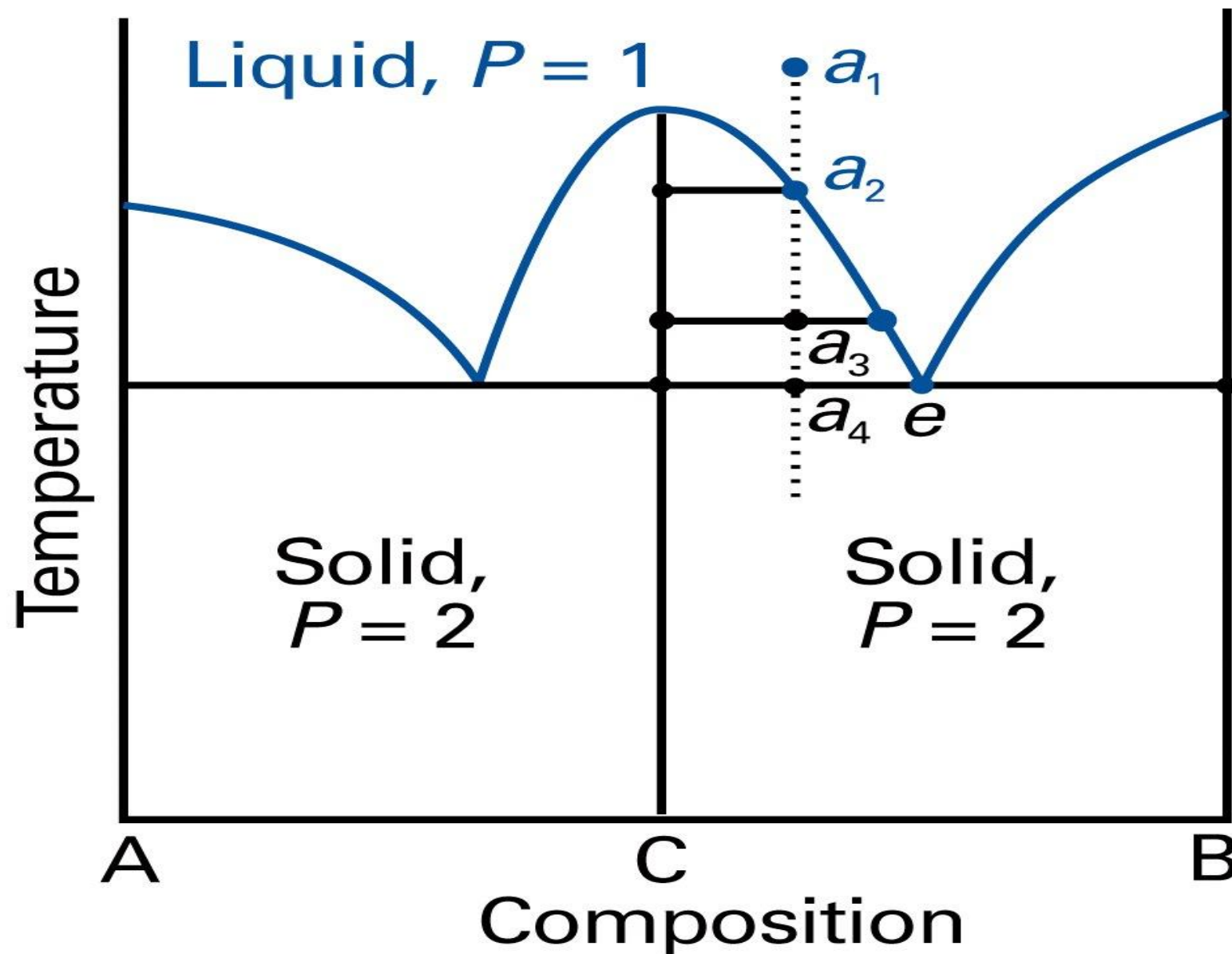


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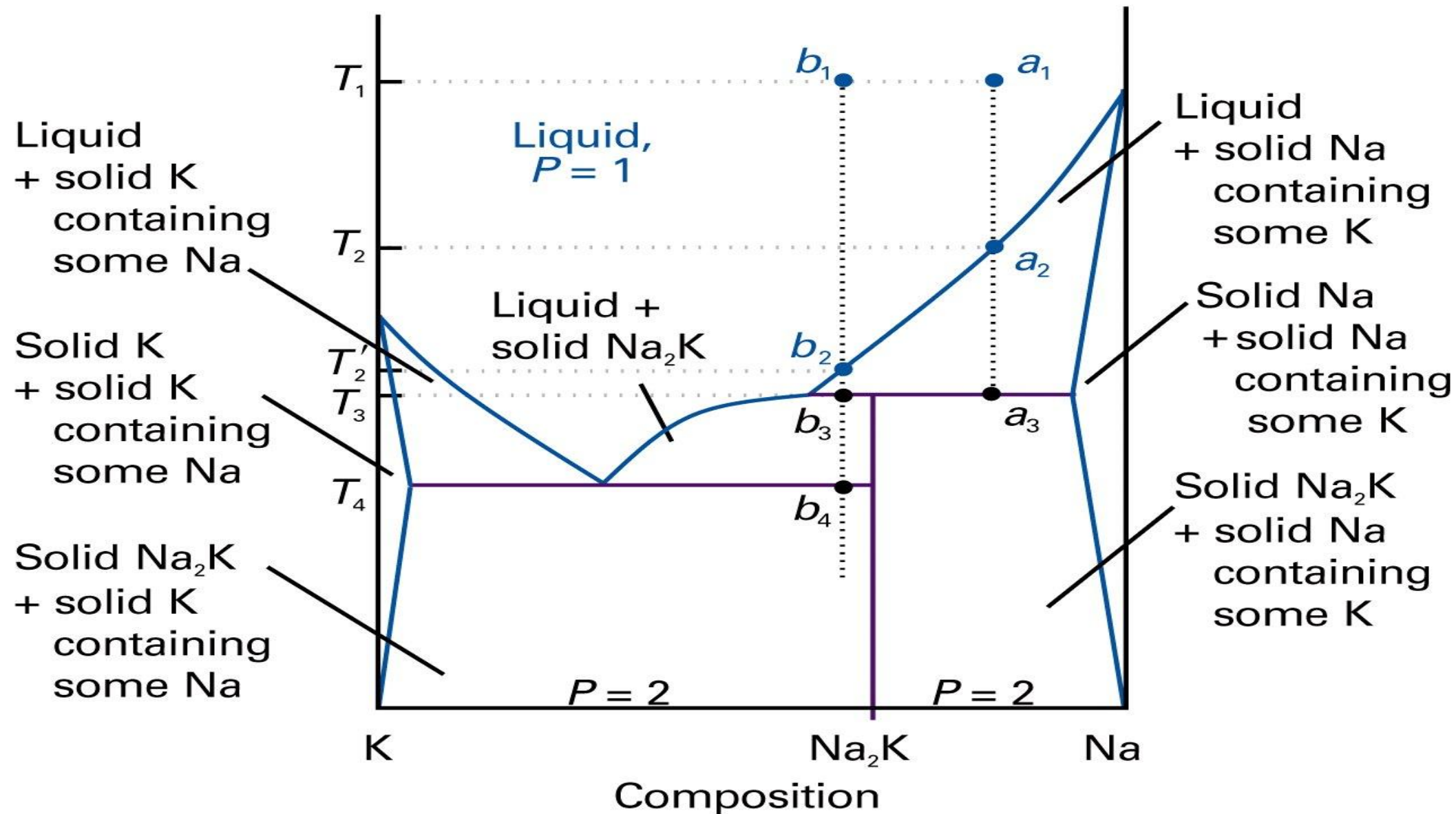


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