Mass transfer and separation

Lecture 1

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Definition of mass transfer

*“**Mass Transfer** is the net movement of a component in a mixture from one location to another location where the component exists at a different concentration.” (J. D. Seader)*

“There is scarcely any chemical process which does not require a preliminary purification of raw materials or final separation of products from by-products, and for these the mass transfer operations are usually used.” *(Robert E. Treybal)*

Mass transfer is ***not***:

- The flow of a fluid through a pipe
- The flow of solids on a conveyor belt

Motivation

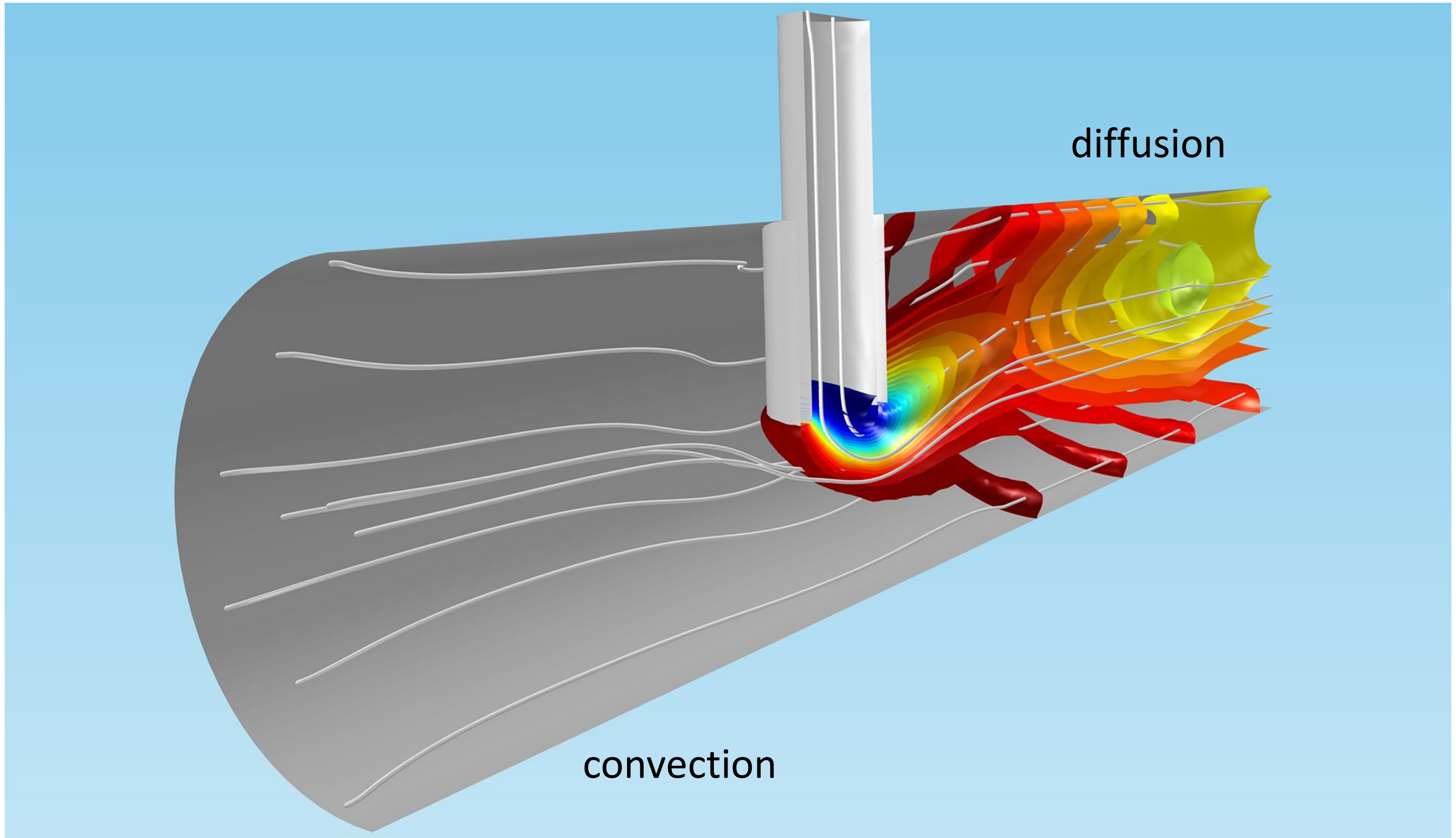
- Why is mass transfer interesting for the chemical engineer?
  - In many cases, the mass transfer of species takes place together with chemical reactions.
  - This implies that flux of a chemical species does not have to be conserved in a volume element, since chemical species may be produced or consumed in such an element.
  - The chemical reactions are sources or sinks in such flux balances.
- You would be designing a reactor in a chemical plant for instance, the understanding of the flux of reactants and products is essential.

Importance of mass transfer operations

- A major of the costs of a chemical plant are involved in its separation systems.
- For instance, distillation accounts for 90-95% of all industrial separations and approximately 40,000 distillation columns are in operation in the US alone, requiring around 40% of the total energy consumption in the US chemical process industries.
- This energy consumption is a major contributor to climate change.

Example: transport and reactions in a reactor

Convection:
larger separation between the concentration isosurfaces and takes place along the streamlines of the fluid flow, convection tends to eliminate concentration gradients along its main direction.



Diffusion:
perpendicular to the concentration isosurfaces, *i.e.* the reactions may cause a flux to the reaction site of the species that are consumed in the reaction.

Your teachers

- Dr Petra Ágota Szilágyi (1st half: mass transfer)
- Dr Stoyan Smoukov (2nd half: separation)

Schedule

- Week 1 (this one) – physical equilibria: phase diagrams, physical transformations
- Week 2 – mixtures, colligative properties / Coursework set
- Week 3 – motion of molecules: gases and liquids
- Week 4 – diffusion and mass transfer: condensed phase
- Week 5 – governing equations of mass transfer, diffusion in laminar boundary layer
- Week 6 – research week / test
- Week 7 – reading week
- Week 8 – tba
- Week 9 – tba
- Week 10 – tba
- Week 11 – tba / Coursework due
- Week 12 – tba

Assessment

- Research week – test: not compulsory! (for + 5% course work if above 70% and as long as course work mark does not exceed 100%)
- Course work (20%)
- Examination (80%)

Recommended literature

- Peter Atkins, Julio de Paula, Ronald Friedman; Physical Chemistry: Quanta, Matter, and Change (Oxford, 2nd Edition) (PAS)
- Koichi Asano; Mass Transfer: From Fundamental to Modern Industrial Applications (Wiley-VCH Verlag) (PAS)
- R. Byron Bird, Warren E. Stewai, Edwin N. Lightfoot; Transport Phenomena (John Wiley & Sons, 2nd Edition) (PAS)

Rules, rules, rules…

- Phones, laptops, *etc.* – only allowed if you need to use it for the lecture
- Speaking – be mindful of your fellow students, restrict it to group discussions
- Eating, drinking, *etc.* – be mindful of the rest of the class
- Contacting your lecturers: office hours, extra tutorials to be arranged by email, check your email before you send it (did you include everything, are you sending it to the right person, have you included address?)

Objectives

- Reminder - thermodynamics
- Physical equilibria
- Phase transformations, phase diagrams
- Physical transformations
- Chemical potential

Characteristics of mass transfer

- Modern transport phenomena - fundamental assumption: momentum, heat, and mass transfer are similar in nature.
- However, mass transfer - some specific issues that need to be addressed before any real approach to actual problems can be made.

Characteristics of mass transfer

- Phase equilibria - phase equilibrium determines an upper limit for mass transfer, whereas no such limitation exists for heat transfer.
- Mixture - momentum and heat transfer - pure fluids, ↔ mass transfer main targets: mixed systems of fluids; the simplest case is a binary system, and in most cases we have to deal with ternary or multi-component systems.
- Convective mass flux - mass fluxes are accompanied by convective mass fluxes, as will be discussed in detail in later sections, and can be expressed as the sum of the diffusional fluxes at the interface and the convective mass fluxes. In this respect, mass transfer is completely different from heat transfer, which is not associated with such accompanying fluxes.
- High mass flux - convective mass fluxes can also have a significant effect on the velocity and concentration distributions near the interface if the order of magnitude of the flux becomes considerable.
- Effect of latent heat - transfer of material is always accompanied by the energy transfer associated with the phase change; mass transfer is interrelated with heat transfer through the boundary conditions at the interface.

Reminder: thermodynamics

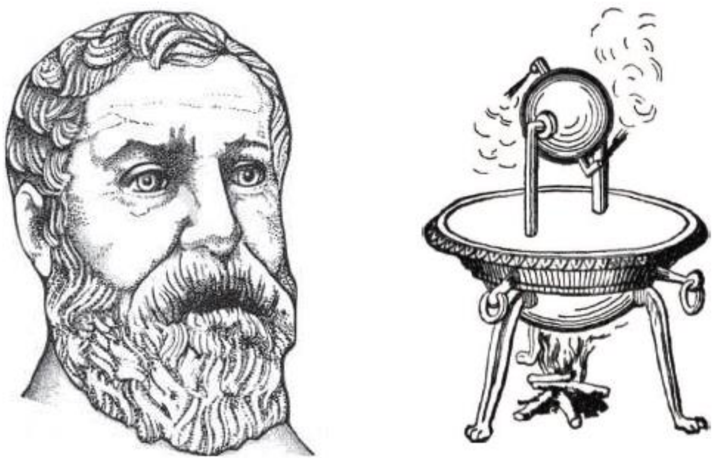
- θέρμη (*therme*): heat
- δύναμις (*dynamis*): power


Aristotle gives the first recorded use of the word “energy” his method of logic permeates classical thermodynamics.

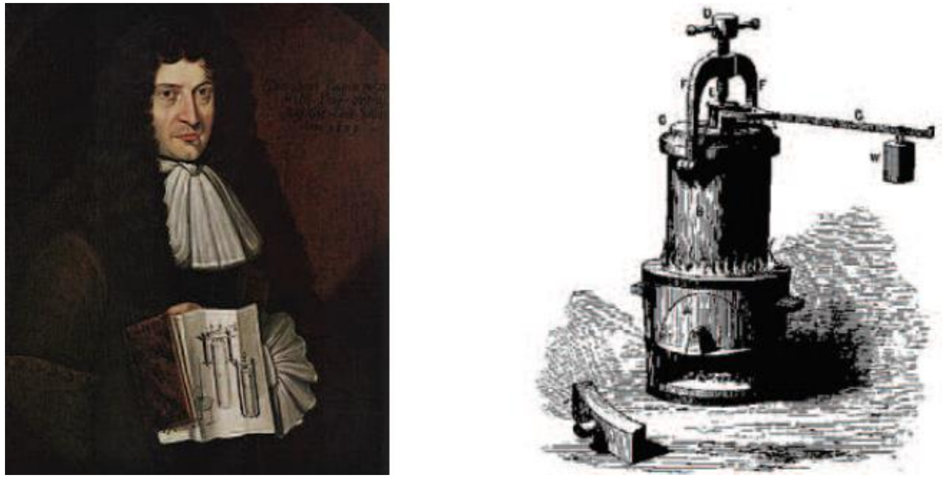

Gabrielle Emilie Le Tonnelier de Breteuil was the first to advance the notion of the kinetic energy being related to the square of velocity.


Thomas Young gave a more modern 1807 definition of (kinetic) energy.

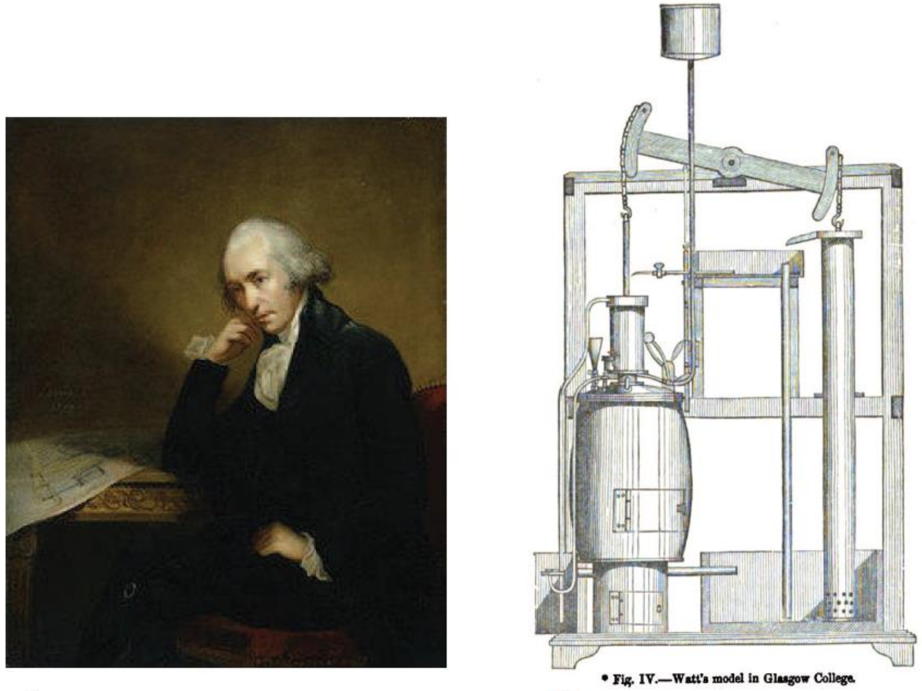
Devices through the classical approach of TD



Hero of Alexandria, device to convert heat into mechanical energy



Denis Papin (1647-1712) and his steam engine



a) b)

James Watt (1736-1819) and a sketch of one of Watt's steam engines

The effect of steam power, a contribution driven by engineers, on the development of the world remains remarkable.

Basic concepts: definitions, and relationships

- Temperature (*T*)
  - Thermodynamic temperature is defined by the 3rd law of TD, in which the theoretically lowest temperature is the null or zero point. At this point, absolute zero, the particle constituents of matter have minimal motion and can become no colder.
- Internal energy (*U*)
  - The energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields.
- Work (*W*)
  - The energy transferred from one system to another without an accompanying transfer of entropy.
- Heat (*Q*)
  - A type of energy transfer in which energy flows from a warmer substance or object to a colder one.

$$Q=\Delta U+W$$

- Heat capacity (*C*)
  - The ratio of the heat added to (or removed from) an object to the resulting temperature change.

$$C=Q/\Delta T$$

Basic concepts: definitions, and relationships

- Enthalpy (*H*)
  - Enthalpy is a measurement of energy in a thermodynamic system. It is the thermodynamic quantity equivalent to the internal energy of the system plus the product of pressure and volume.

$$H=U+pV$$

- Entropy (*S*)
  - A quantitative measure of disorder or randomness in a system.

$$dU=TdS-pdV$$

- Gibbs energy (*G*)
  - A descriptor of the spontaneity of a reaction.

$$G=H-TS$$

- Chemical potential (μ)
  - A form of energy that can be absorbed or released during a chemical reaction or phase transition due to a change of the particle number of the given species.

$$dU=TdS-pdV+\sum_{i=1}^{n}\mu_i dN_i$$

The laws of TD

- **0th** If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other. (This law helps define the concept of temperature.)
- **1st** When energy passes, as work, as heat, or with matter, into or out from a system, the system's internal energy changes in accord with the law of conservation of energy. *i.e.* perpetual motion machines of the first kind (machines that produce work with no energy input) are impossible.
- **2nd** In a natural thermodynamic process, the sum of the entropies of the interacting thermodynamic systems increases. *i.e.* perpetual motion machines of the second kind (machines that spontaneously convert heat into work) are impossible.
- **3rd** The entropy of a system approaches a constant value as the temperature approaches absolute zero. With the exception of non-crystalline solids (glasses) the entropy of a system at absolute zero is typically close to zero, and is equal to the natural logarithm of the product of the quantum ground states.

Phase and equilibrium: definition

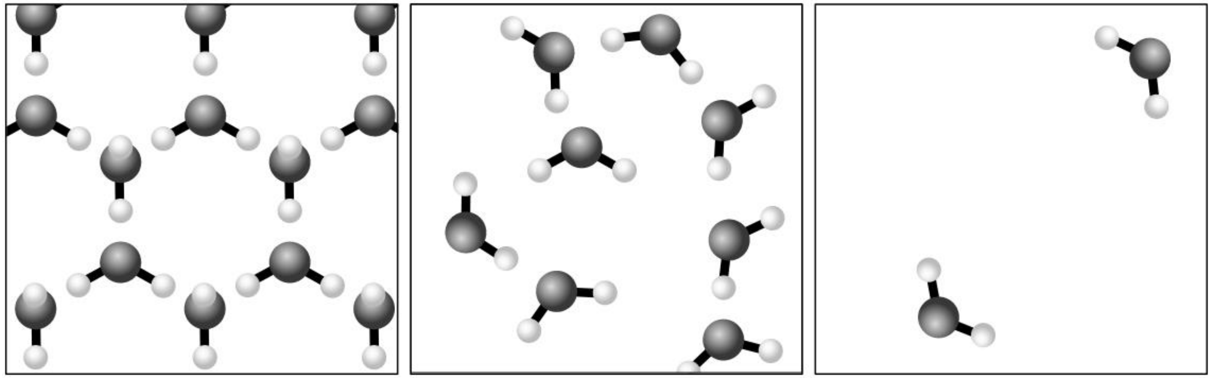
- Phase
  - is a region of space (a thermodynamic system), throughout which all physical properties of a material are essentially uniform.
    - *cf*. solid, liquid, gas, allotropes
- Phase transition
  - spontaneous conversion into another – occurs at a characteristic temperature/pressure.
    - *cf*. ice melts at 0 °C at atmospheric pressure
- Equilibrium
  - a state of a physical system in which it is in mechanical, chemical, and thermal equilibrium and in which there is therefore no tendency for spontaneous change.

Physical equilibria

- Includes phase transitions of pure materials and mixtures
- Insight into how one component may affect the properties of another
- Phase diagram summarises the equilibria between the various phases
  - They will be very helpful in the discussion of (fractional) distillation (of liquid mixtures)
- Ideal and real solutions

Phase transitions

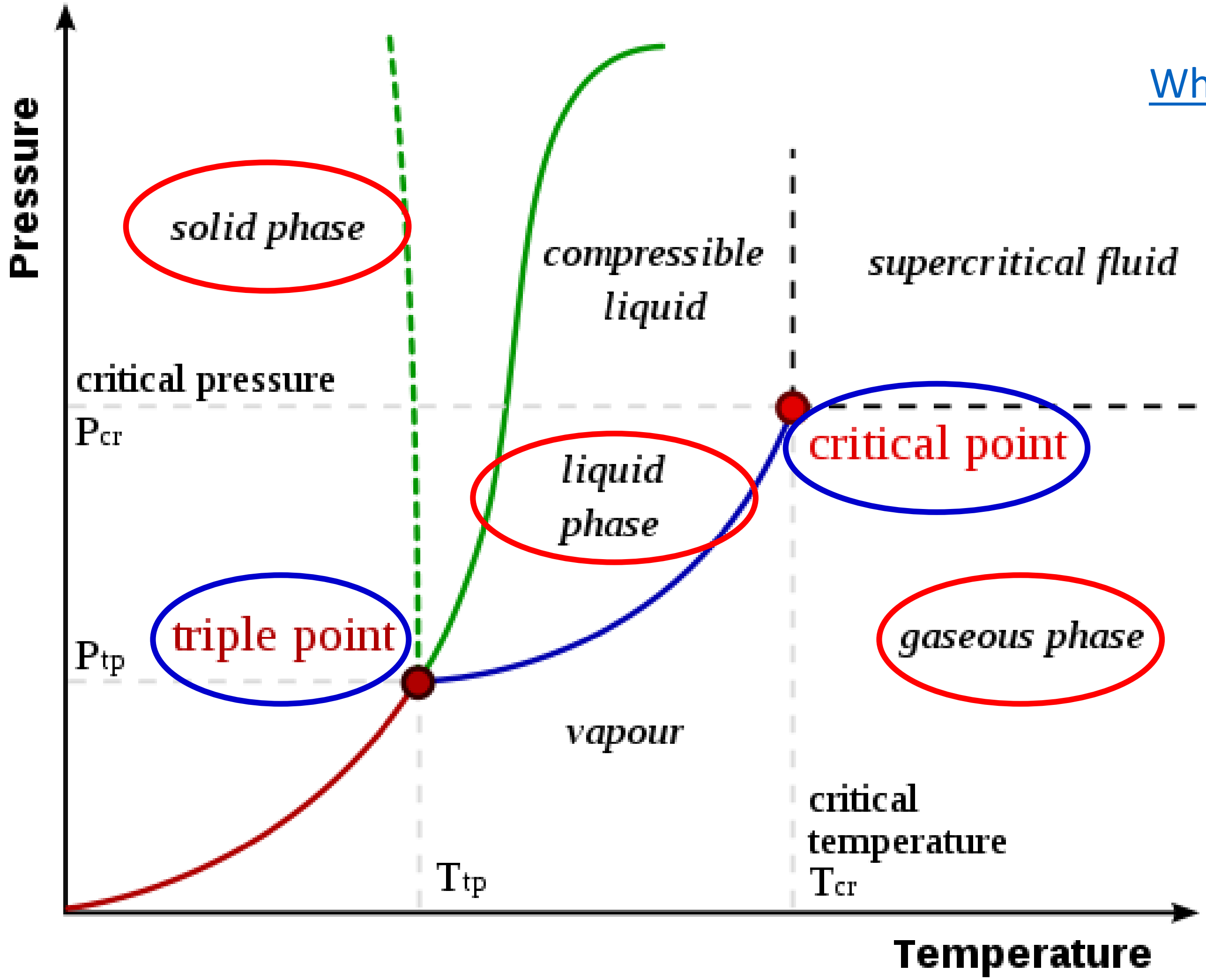
- Mass transfer is critical in phase transitions (think purification!)
- Occur widely in nature and industry
- As the macroscopic variables of a system change, its properties may abruptly change, often dramatically, *cf.* solid to a liquid, or liquid to a gas. These are examples of phase transitions.



Phase diagrams

- Definition: an empirically constructed diagram showing the regions of pressure and temperature at which its various phases are thermodynamically stable
- Note that for spontaneous processes $\Delta G<0$
- The lines separating the regions, called phase boundaries, show values of p and T at which 2 phases co-exist
- Similar properties diagrams can be constructed for mixtures

Phase diagram - example



What is a supercritical fluid?

Phase rule

- When two phases are in equilibrium their chemical potential is the same, the consequence of which is the phase rule
- It constrains the freedom to change the conditions while preserving equilibrium:

$$F=C-P+2$$

- F – variance; C – # components; P – # phases
- *constituent* – a chemical species that is present
- *component* – a chemically independent constituent of the system
- *variance* - # intensive variables that can be changed independently without disturbing the equilibrium

Question: constituents vs. components

- A mixture of ethanol and water has 2 constituents; a solution of salt has 3: water, Na^+ and Cl^-.
- How many constituents and components does water have after allowing for autoprotolysis?

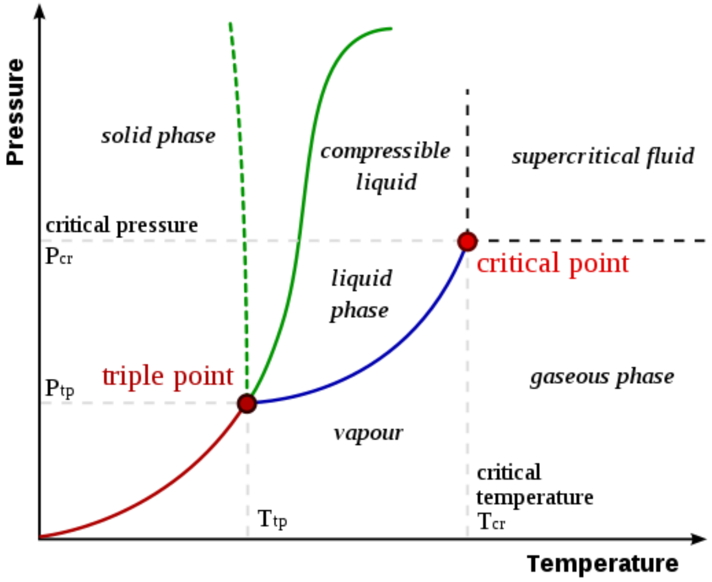
- $2\ H_2O \leftrightarrow H_3O^+ + OH^-$
- 3 constituents and 1 component (because of the above equilibrium the concentration of $H_2O \leftrightarrow H_3O^+ + OH^-$ cannot be modified independently.

Phase rule, single-component (*F*=3-*P*)

- Single-phase system (C=1, P=1): pressure and temperature may be changed independently without changing the phases → F=2
  - bivariant system, or degrees of freedom – 2.
- If the 2 phases are in equilibrium (C=1, P=2), the temperature or pressure can be changed at will but it is accompanied by a change in pressure (temperature) → F=1.
  - For 2 phases (α & β) in equilibrium $\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)$ – equation relating p and T, so only 1 of the variables is independent (think of x+y=2 then y=2-x so not independent).
  - Consequence: phase transitions, *cf.* freezing, along a line in the phase diagram
- For 3 phases in equilibrium: $\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)=\mu_J(\gamma;p,T)$ → F=0 (think of x+y=2 and 3x-y=4 just has 1 solution). (*cf.* triple point of H_2O)
- 4 phases cannot be in mutual equilibrium in a C=1 system. ($\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)=\mu_J(\gamma;p,T)=\mu_J(\delta;p,T)$: 3 equations for 2 unknowns)

One-component systems

- Consider liquid sample of a pure substance in a closed vessel
  - pressure of a vapour in equilibrium with the liquid: vapour pressure (p_{vap}) – liquid-vapour phase boundary in a phase diagram shows how vapour pressure varies with temperature
- Solid-vapour phase boundary – temperature variation of the sublimation vapour pressure

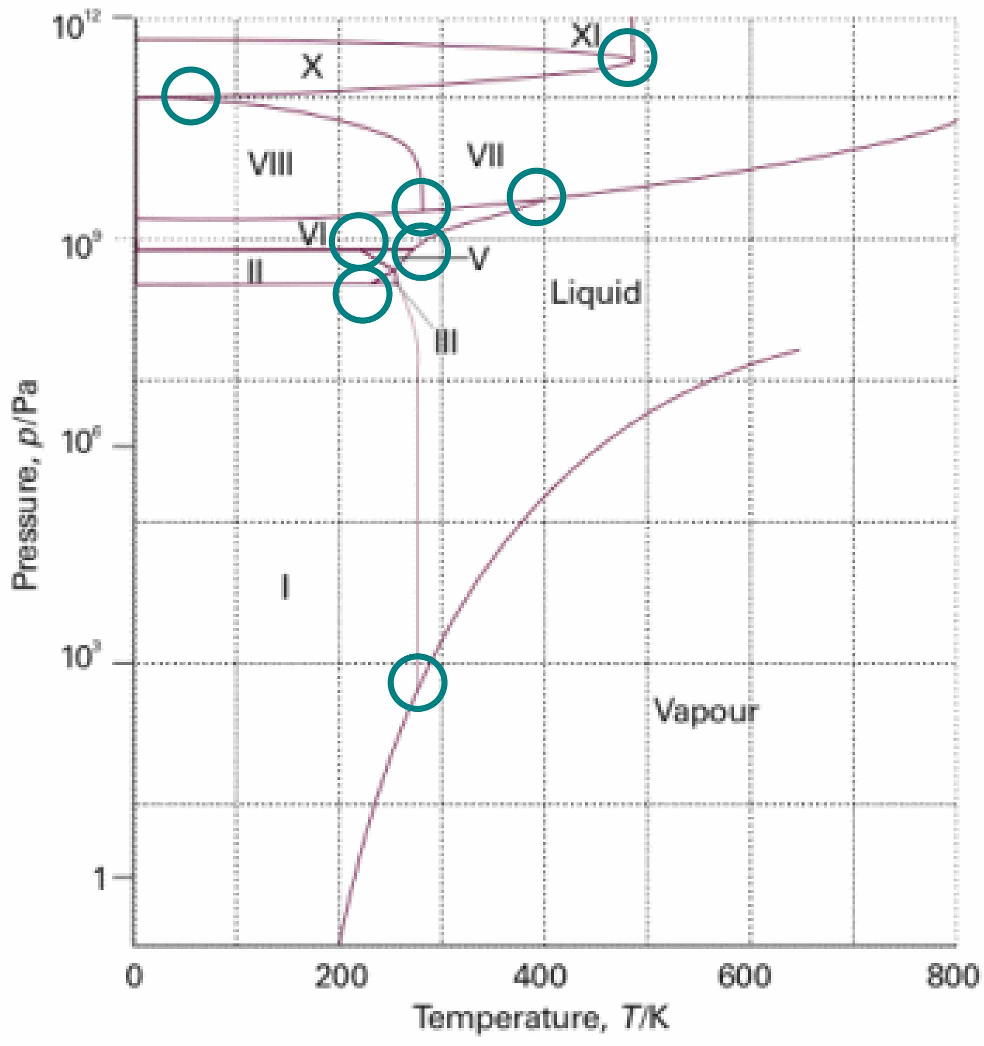


Phase characteristics

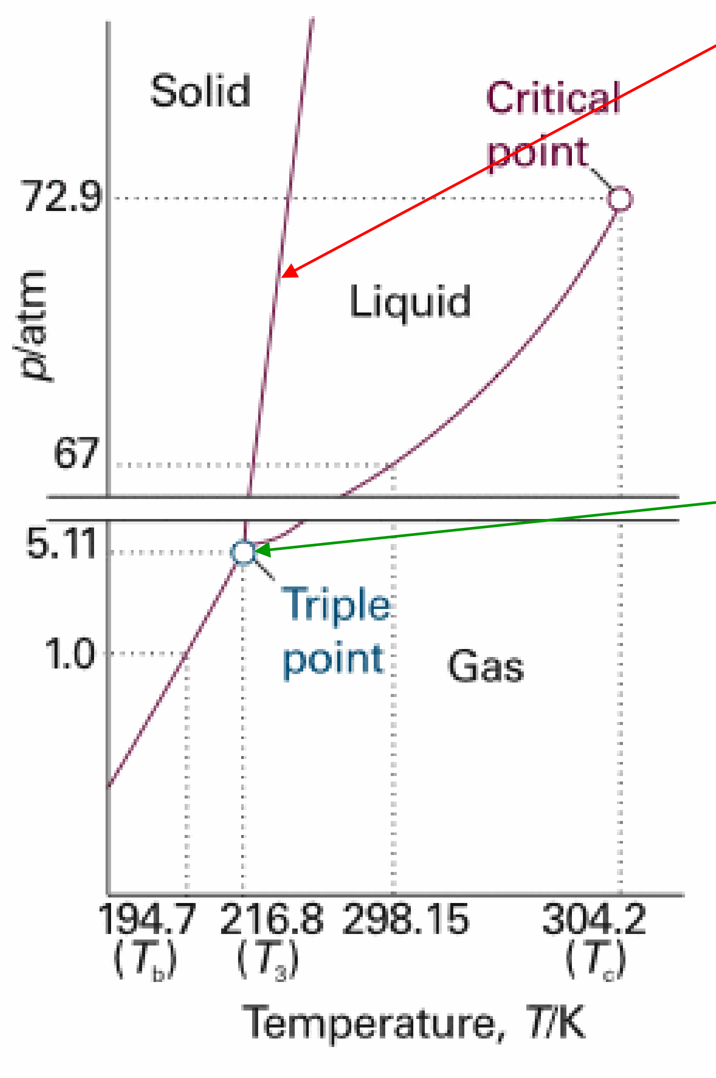
- Pure liquid heated in an open vessel: molecules may acquire enough kinetic energy to break free from their neighbours; at T at which $p_{vap}=p_{ext}$ vapour can form throughout the bulk of the liquid and expand freely into the surroundings – boiling
  - Temperature at which $p_{vap}=p_{ext}$ is called the boiling temperature (liquid-vapour phase boundary shows how the boiling temperature varies with pressure). At p=1 atm: normal boiling temperature T_b, at p=1 bar: standard boiling temperature.
- No boiling in partly filled, rigid, closed vessel, instead p_{vap} ↑ with ↑ T, whilst the density of liquid ↓. At some point $\rho_{vap}=\rho_{liq}$ and surface disappears, this is called critical temperature (T_c). The p_{vap} at this T is called critical pressure, p_c.
  - At and above this there is a single phase of supercritical fluid.
- T at which solid and liquid phases co-exist is called melting temperature (or freezing temperature).
  - At p=1 atm: normal freezing/melting temperature T_f, at p=1 bar: standard freezing temperature.
- Under 1 set of conditions 3 phases may co-exist in equilibrium – triple point (T_3), at which the 3 phase boundaries meet.
  - T_3 marks the lowest pressure at which the liquid and solid phases co-exist.

Triple points

- The triple point of water lies at 273.16 K & 611 Pa, and the 3 phases of water (ice, liquid and vapour) co-exist in equilibrium at no other combination of *T* and *p*. This invariance if the triple point was the basis of the Kelvin scale of temperature.
- How many T_3s are present in the full phase diagram for water?



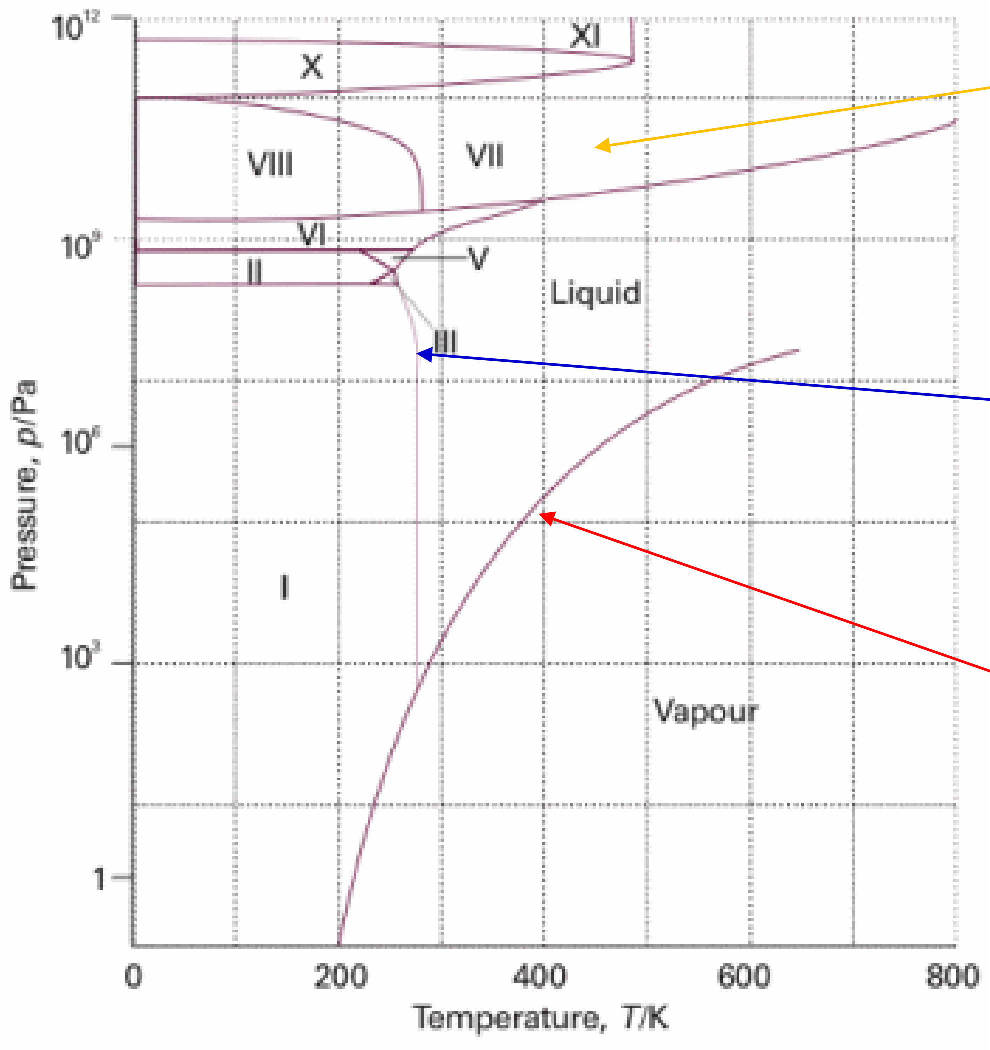
CO_2 phase diagram



positive slope: T_m ↑ when p ↑

Triple point lies above 1 atm
→ liquid cannot exist at atmospheric pressures
(dry ice)

H_2O phase diagram



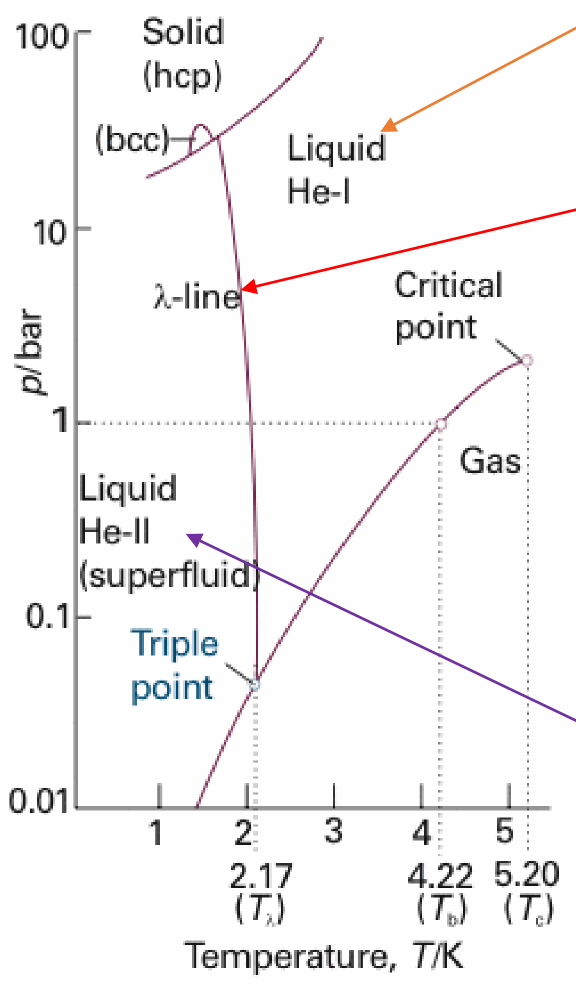
Many different solid phases (adaptability of the directional characteristics of hydrogen-bonding interactions)
Different polymorphs at different p – glaciers!!

Solid-liquid boundary
→ how T_m varies with p
→ up to 2 kbar: negative slope: almost unique property
T_m ↓ with p ↑ (V↓ on melting)

Liquid-vapour boundary
→ how p_{vap} varies with T
→ how T_b varies with p

He phase diagram

Solid He may only be obtained under applied pressure



‘Normal’ liquid

Apart from liquid crystals, He is the only material with liquid-liquid phase boundary

Solid and gas phases are never in equilibrium at low temperatures
Atoms are very light and vibrate with a large-amplitude motion

Superfluid: flows without viscosity
Quantum phenomenon; interatomic forces very weak
^{4}He – boson: Pauli exclusion principle does not apply (unrestricted # may occupy the same quantum state)
^{3}He – fermion: Pauli exclusion principle applies but it forms superfluid – in atom pairs.

Two-component systems

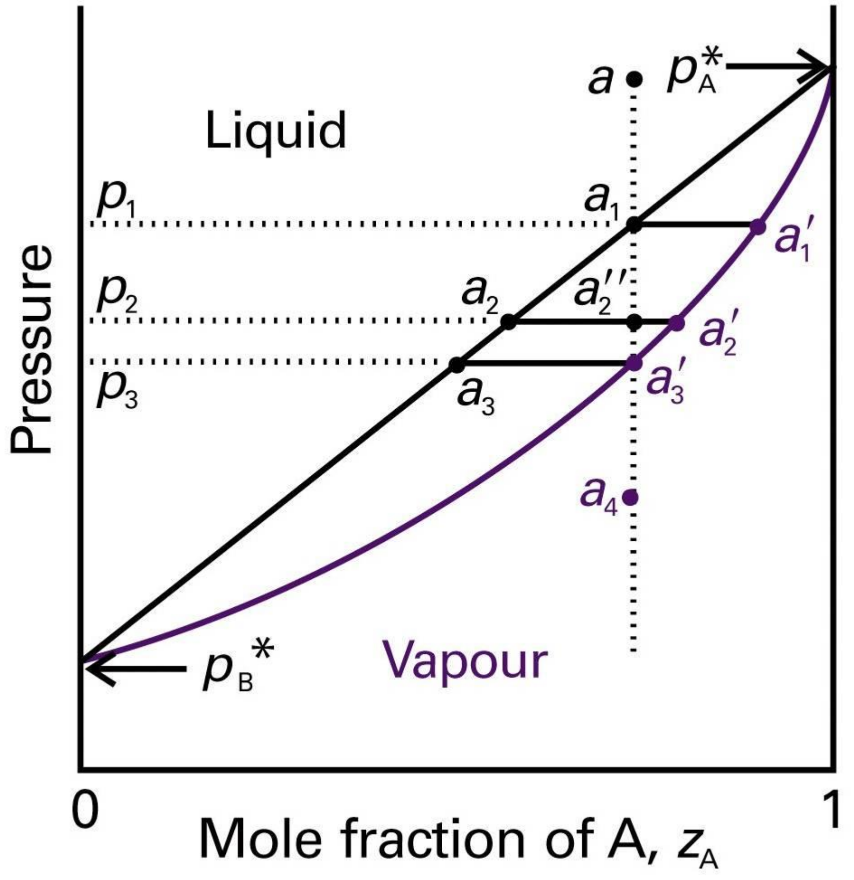
- Most phase diagrams of technological and chemical interest represent the phase stabilities of systems more than one component.
- A two-component phase diagram depicts the phases that are stable under the specified conditions of pressure and temperature.
- If 2 components are present in a mixture there are 3 variables to consider; pressure, temperature and composition (PCT).
  - One form of phase diagrams is a map of pressures and compositions at which each phase is stable at a given temperature.
  - Alternatively the pressure could be held constant and the phase diagram depicted in terms of temperature and composition.

Liquid-vapour systems

2 volatile liquids

Pressure-composition diagrams

- All points above the diagonal line – system under such high pressure that only liquid phase ∃
- All points below curve – such low pressure that only vapour phase ∃
- Points in between – 2 phases; liquid & vapour ∃
- Consider the effect of ↓ p in a liquid mixture in a.
  - The vertical line is called isopleth (gr. equal abundance)
- Until a_1 single liquid phase; at a_1 liquid exists in equilibrium with its vapour of composition a_1'.
  - The line joining the 2 points representing phases in equilibrium is called the tie line.



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Lever rule

- To use the phase diagram to find the relative amounts of 2 phases in equilibrium (α & β) in a 2-phase region; measure distances l_α and l_β along the horizontal tie line and then use the lever rule: $n_\alpha l_\alpha = n_\beta l_\beta$, where n_α and n_β are the amounts of phases α & β.
- **Justification:**

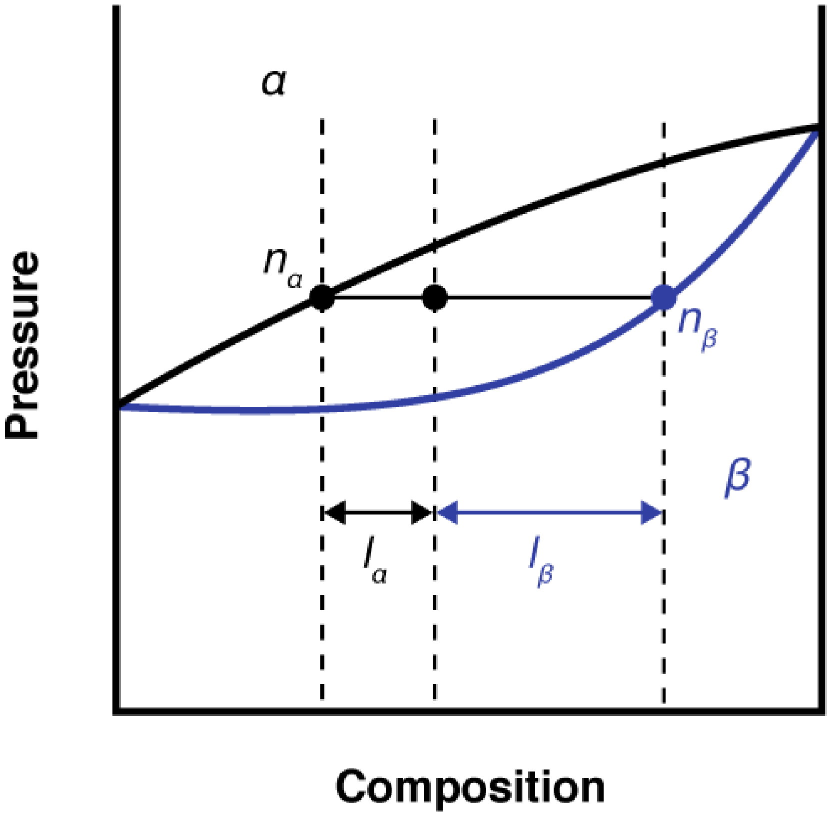
For component A

$n = n_\alpha + n_\beta$ (overall amount); overall amount of A $n x_A$, where x_A is the mole fraction of A in the mixture.

The amount of A in the 2 phases: (1) $n x_A = n_\alpha x_{A,\alpha} + n_\beta x_{A,\beta}$, where $x_{A,\alpha}$ is the mole fraction of A in phase α, and $x_{A,\beta}$ in phase β.

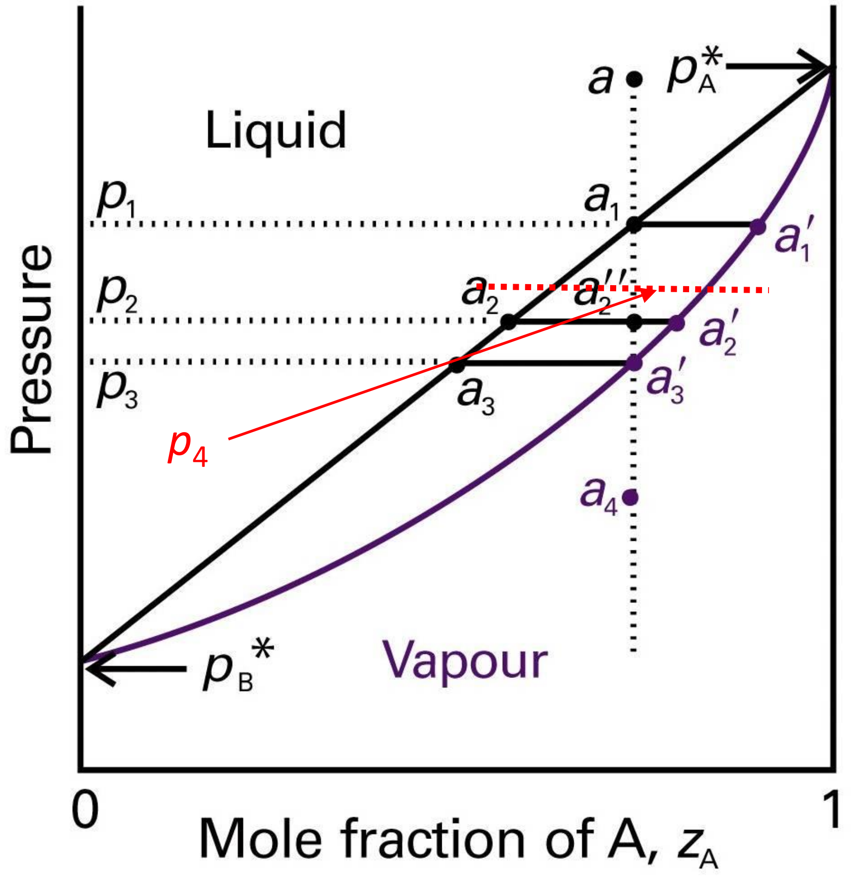
Also: (2) $n x_A = (n_\alpha + n_\beta) x_A = n_\alpha x_A + n_\beta x_A$

(1)=(2): $n_\alpha (x_{A,\alpha} - x_A) = n_\beta (x_A - x_{A,\beta}) = n_\alpha l_\alpha = n_\beta l_\beta$



Lever rule

- At p_1 the ratio l_{vap}/l_{liq} is almost infinite for this tie line so n_{liq}/n_{vap} is also almost infinite, and there is only a trace of vapour present.
- At p_2 the value of l_{vap}/l_{liq} is *ca.* 0.2 so n_{liq}/n_{vap} is also *ca.* 0.2 and the amount of liquid is 20% of the vapour.
- At p_3 the value of l_{vap}/l_{liq} is *ca.* 0 so n_{liq}/n_{vap} is also *ca.* 0, so there is only liquid present.
- What is the ratio of abundances of the two phases at p_4?



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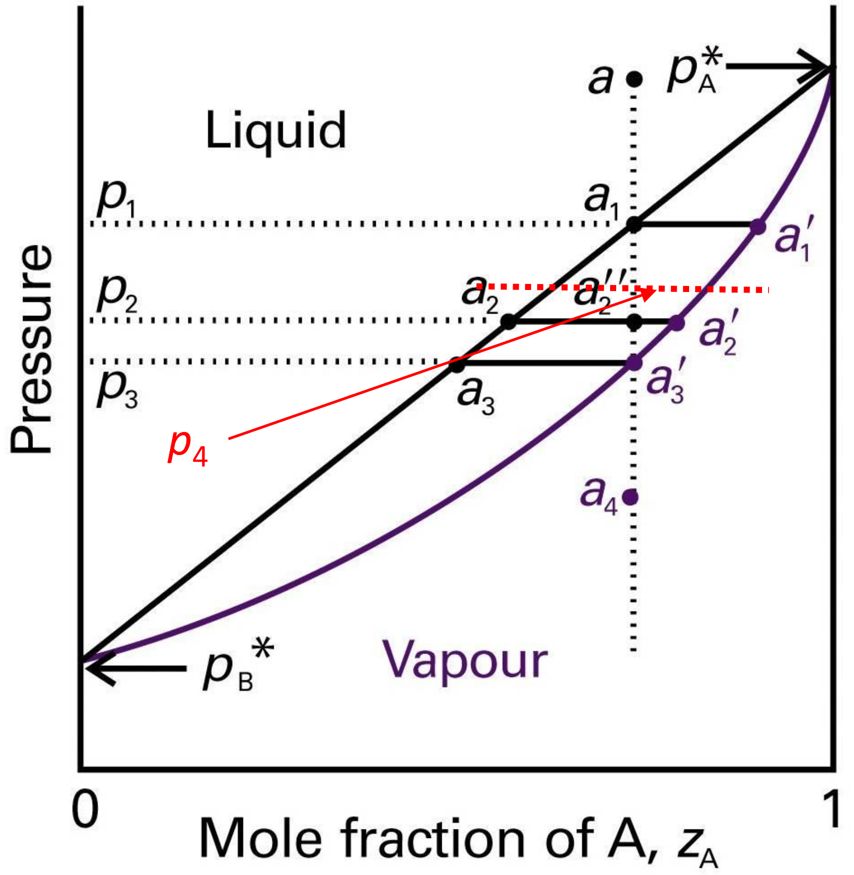
Answer

- $n_{vap}/n_{liq} \approx 0.5$



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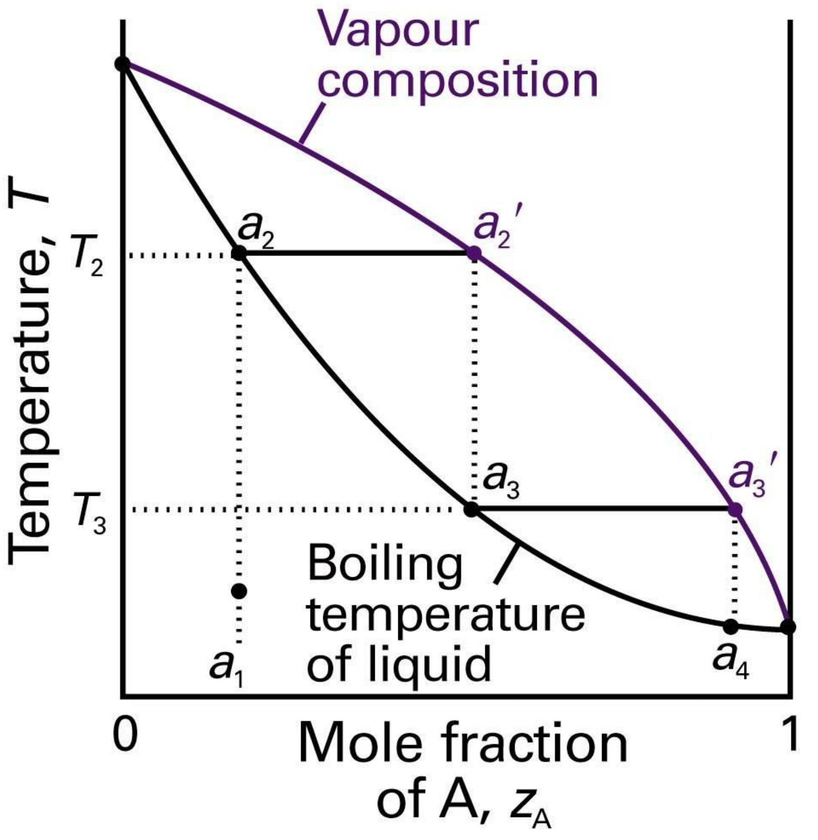
Liquid-vapour systems

Ideal mixture, ‘A’ more volatile

Temperature-composition diagrams

- Shows phases in equilibrium at various temperatures and fixed pressures.
- The liquid phase now lies in the lower part of PD, under such *T* that it contains only liquid.
- When a liquid of composition a_1 is heated to T_2 → starts boiling; liquid has composition a_2 (same as a_1) and vapour a_2'.
  - From the location of a_2' we can read out the vapour’s composition at the boiling point.
  - From the location of the tie line joining a_2 and a_2' we can read off the boiling temperature (T_2) of the original liquid mixture.



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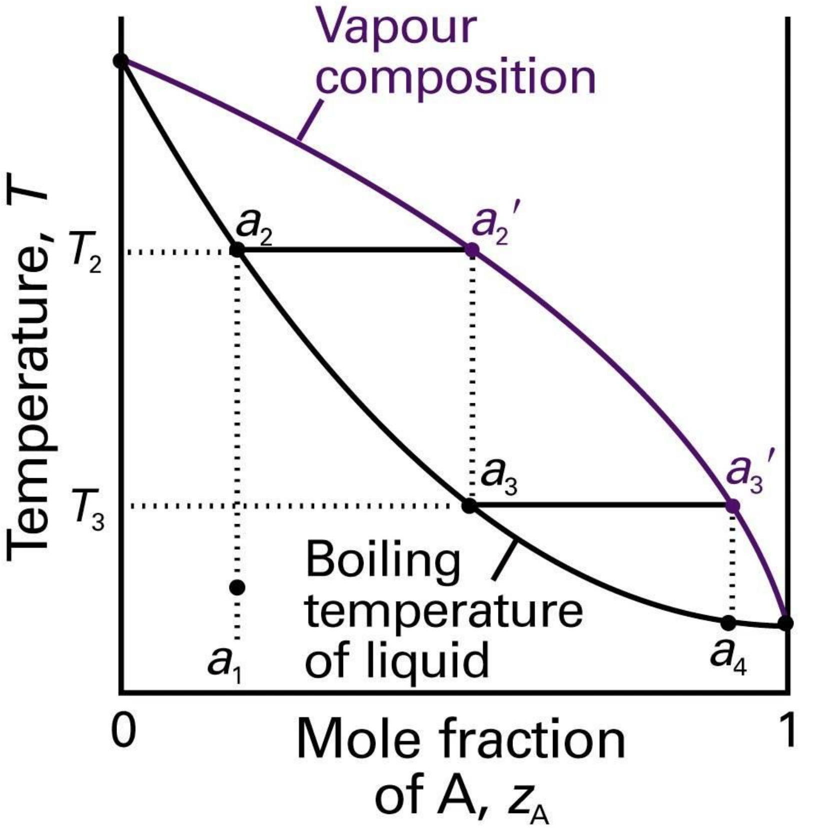
Liquid-vapour systems

- In a simple distillation the vapour is withdrawn and condensed – separate a volatile liquid from a non-volatile solution or solid.
- In fractional distillation the boiling and condensation cycle is repeated successively – separate volatile liquids.
- Follow the changes occurring during the heating of composition a_3; the mixture boils at T_3 yielding vapour composition of a_4, the cycle may be repeated until almost pure A is obtained.



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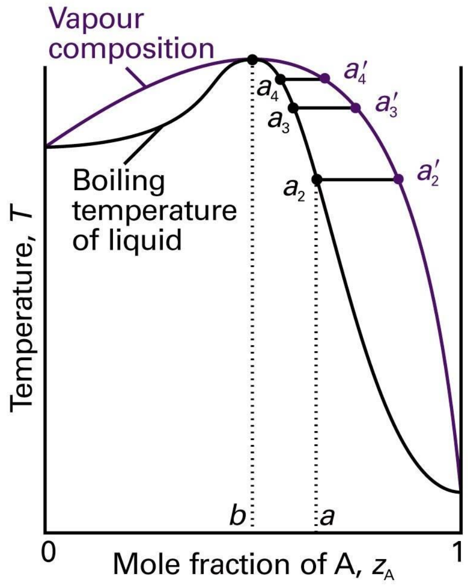
Extrema in the phase diagram

Maximum

- Favourable interactions between A and B molecules, stabilise liquid.
  - (we'll see more for Raoult's law)

cf. nitric acid/water



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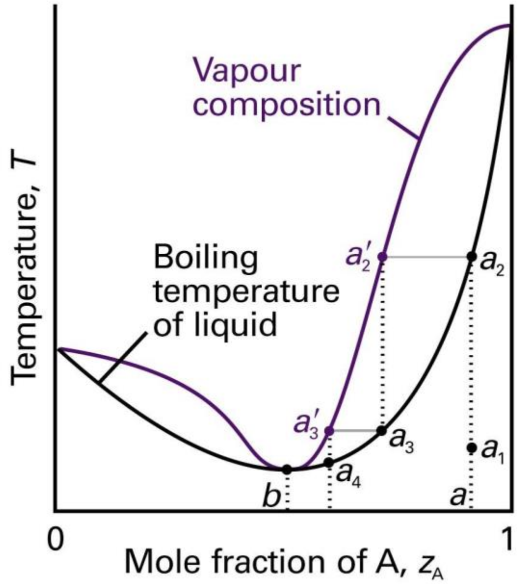
Minimum

- Mixture is destabilised vis-à-vis ideal solution; A-B interactions unfavourable.

cf. ethanol/water



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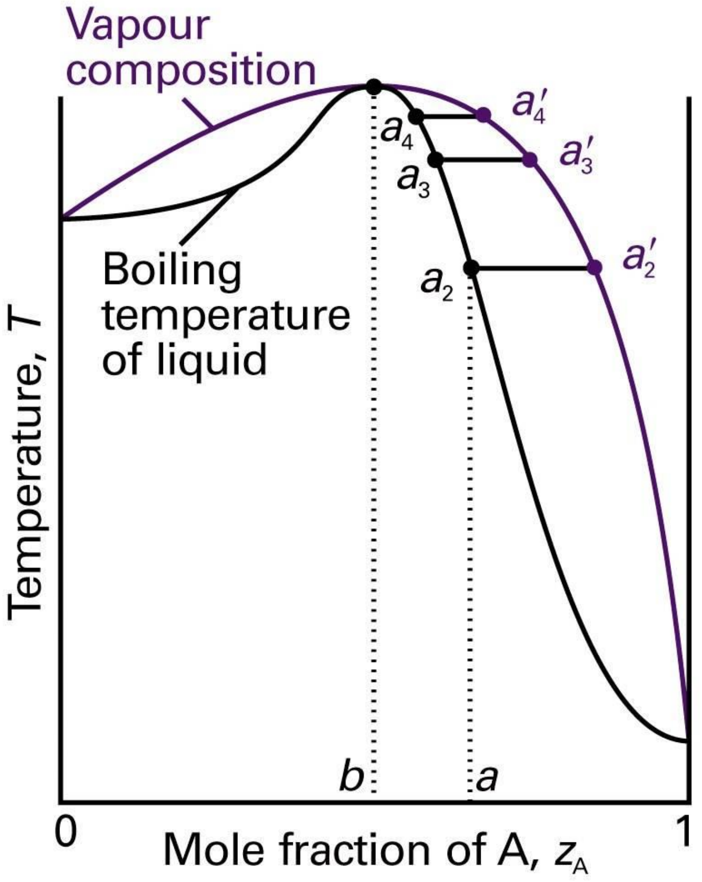
Azeotropes

- When evaporation occurs without the change of composition, the mixture is said to be an azeotrope (gr. ‘boiling without changing’).
- When the azeotropic composition is reached distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid.
- *Cf.* hydrochloric acid/water 80% at 108.6 °C.

Azeotropes

- Suppose we start with a mixture of composition of a_1.
    - The mixture boils at a_2 to give a vapour composition of a'_2.
    - This vapour condenses to a liquid of the same composition (a_3).
    - It reaches equilibrium with its vapour at a'_3, which condenses to give a liquid of the same composition, now a_4.
    - The distillation shifts the composition to the azeotropic composition but not beyond.
- Consider a liquid of a composition on the left of the maximum. Show that repeated distillations will also result in the formation of an azeotrope.



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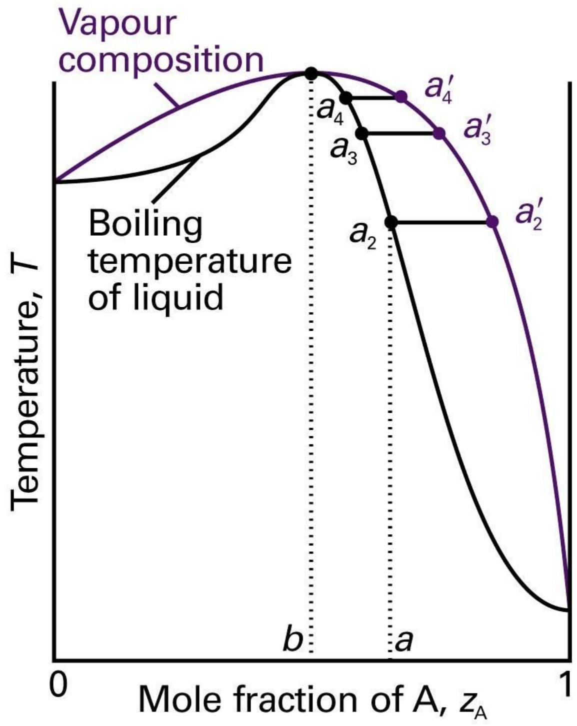
Answer

- It is an azeotrope as evaporation proceeds, the composition of the remaining liquid shifts towards A as B is drawn off.



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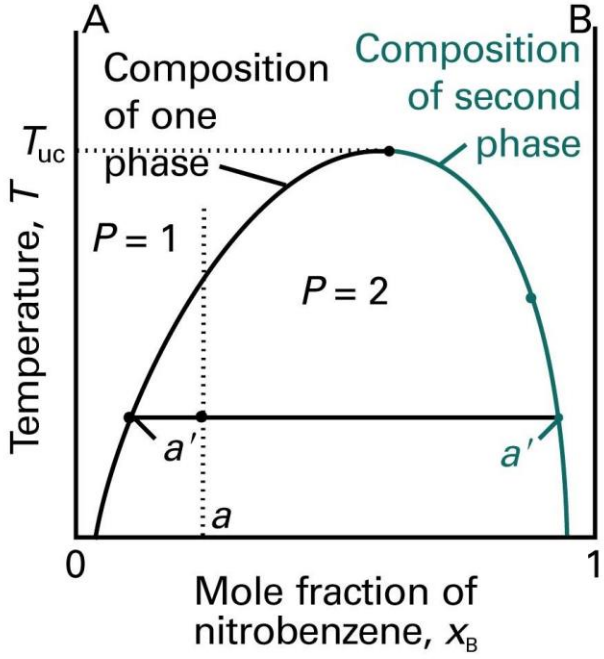
Liquid-liquid systems

- Pairs of partially miscible liquids, which do not mix in all proportions at all temperatures, *cf.* hexane and nitrobenzene.
- ! small amount of B is added to A at T'.
- Dissolves completely – 1 phase.
- When more B is added at some point no more is dissolved – A saturated with B + minor phase of B saturated with A (*a*' and *a*', respectively).
  - Relative compositions given by the lever rule.
- When more B is added, at some point B can dissolve all A → single phase.
- The compositions of the two phases at equilibrium vary with temperature, *cf.* hexane/nitrobenzene miscibility ↑ with *T* ↑.



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Liquid-liquid systems

- The upper critical solution temperature (T_{uc}) is the highest temperature at which phase separation occurs.
  - This temperature exists because the greater thermal motion overcomes any potential disadvantage of the molecules being close.
  - *Cf.* nitrobenzene/hexane
- The lower critical solution temperature (T_{lc}), below which they mix in all proportions
  - They may form a weak complex, which break up at higher T.
  - *Cf.* water/triethylamine

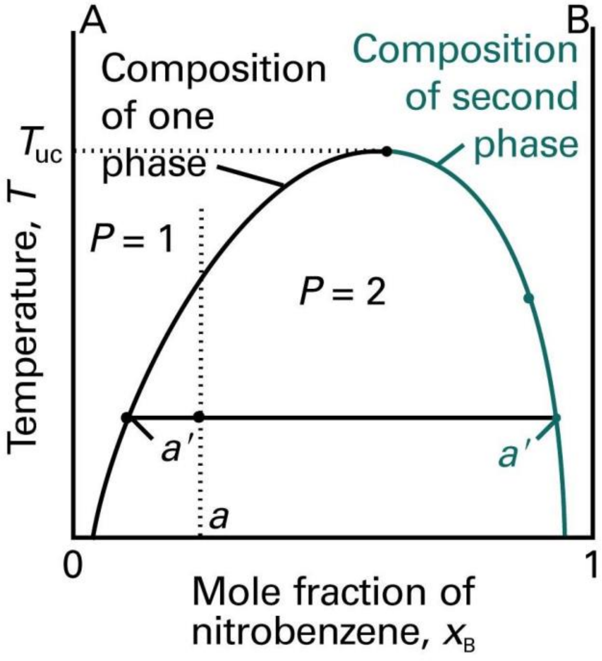

Figure 6-19
Atkins Physical Chemistry, Eighth Edition
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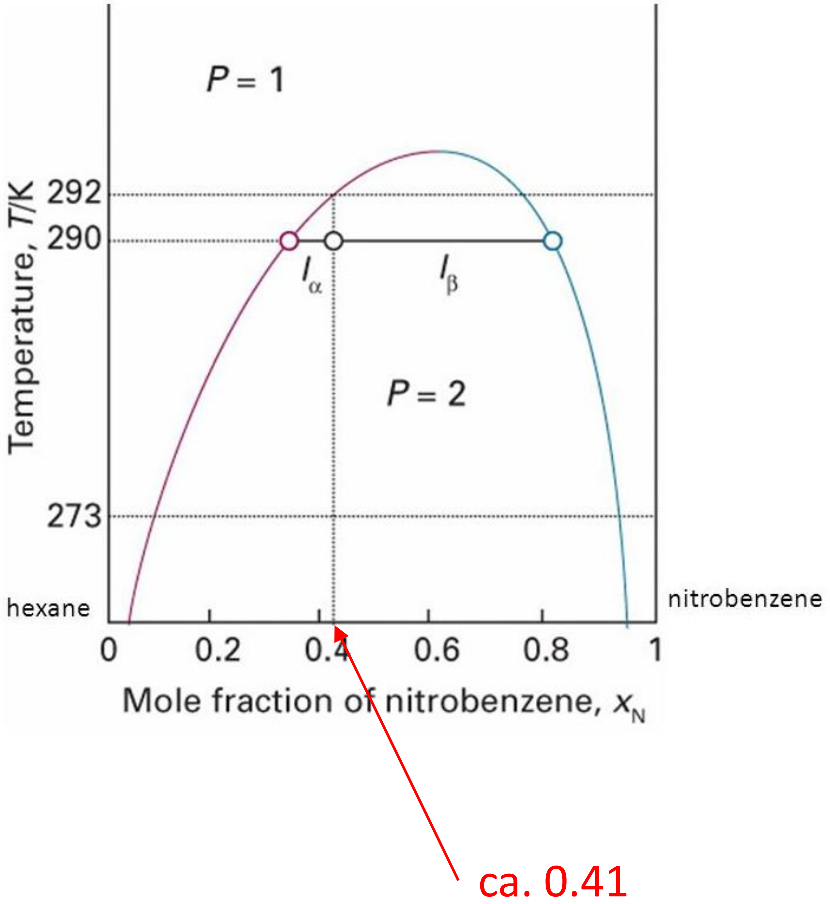
Liquid-liquid phase diagram

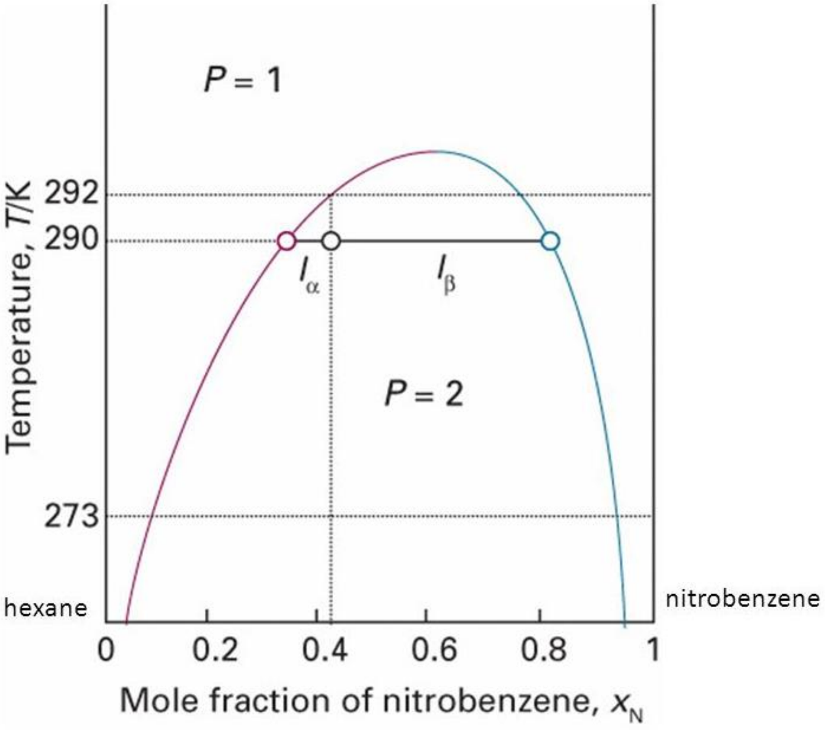
- A mixture of 50 g of hexane (0.58 mol) and 50 g of nitrobenzene (0.41 mol) was prepared at 290 K.
- What are the compositions of the phases and in what proportion do they occur?
- To what temperature must the sample be heated in order to obtain a single phase?
- Reminder: the compositions of phases in equilibrium are given by the points where the tie line representing the temperature intersects the boundary, in accordance with the lever rule: $n_\alpha l_\alpha = n_\beta l_\beta$



ca. 0.41

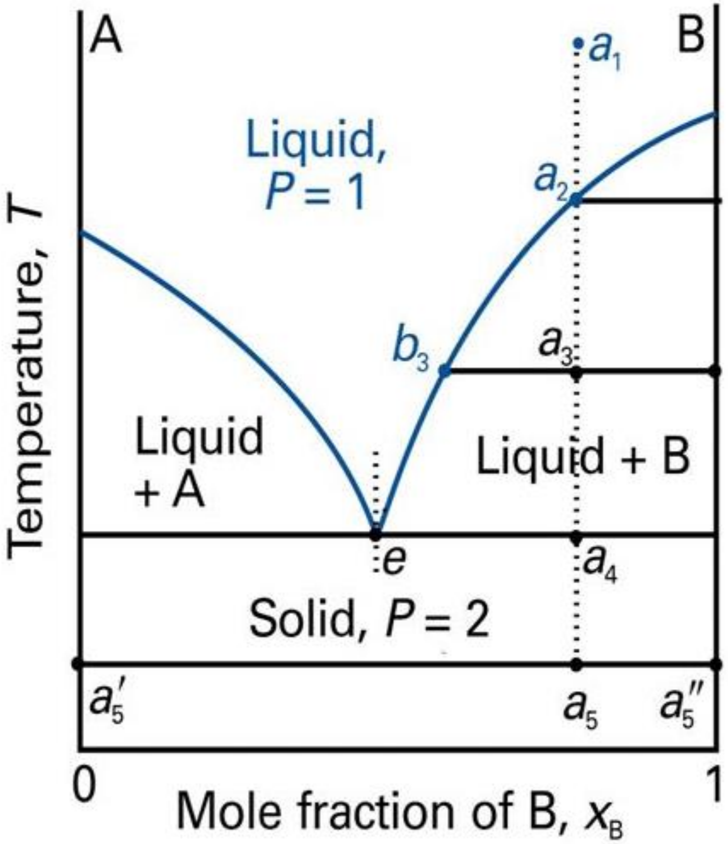
Answer

- The point at $x_{\text{nitrobenzene}}$=0.41, T= 290 K occurs in a two-phase region.
- The horizontal tie line cuts the boundary at *ca.* $x_{\text{nitrobenzene}}$=0.35 and $x_{\text{nitrobenzene}}$=0.83.
- According to the lever rule the ratio of amounts in each phase equals the ratio of the distances l_α and l_β: $\frac{n_\beta}{n_\alpha} = \frac{l_\alpha}{l_\beta} = \frac{0.83-0.41}{0.41-0.35} = \frac{0.42}{0.06} = 7.$
- Heating the sample to 292 K takes it to the single-phase region.



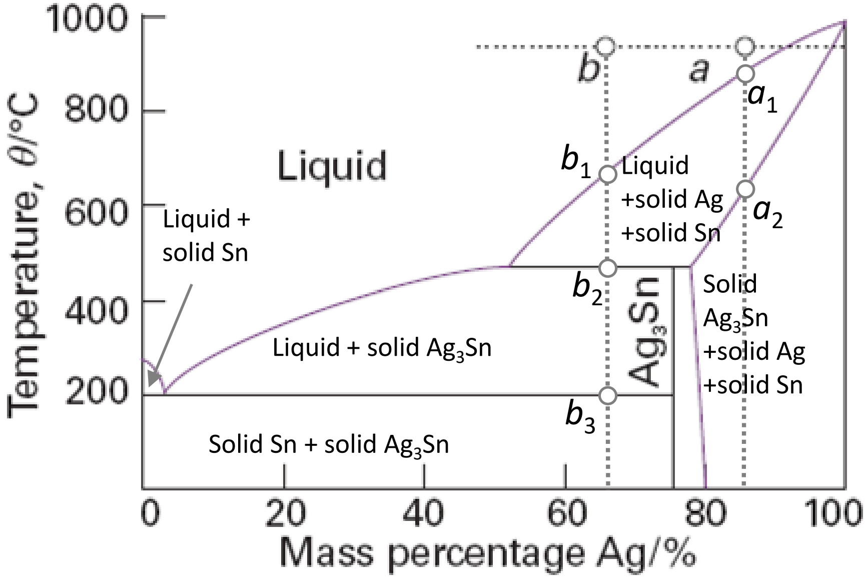
Liquid-solid systems

- Consider a 2-component system;
- $a_1 \rightarrow a_2$. The system enters the two-phase region labelled 'liquid + B'. Pure solid B begins to crash out from solution and the remaining liquid becomes richer in A.
- $a_2 \rightarrow a_3$. More of the solid forms, relative amount of solid and liquid are given by the lever rule (*ca.* 50-50). The liquid phase is richer in A than before, its composition is given by b_3.
- $a_3 \rightarrow a_4$. less liquid than in a_3, composition given by *e*. System freezes in two-phase system of pure A and pure B.
- The isopleth e corresponds to the eutectic composition, the mixture with the lowest melting point (gr. 'easily melted')
  - A liquid with the eutectic composition freezes at a single temperature without previously depositing solid A and B.
  - A solid with the eutectic composition melts without change of composition.
  - Solutions of composition to the right of e deposit B as they cool, and solutions to the left deposit A.
  - Only the eutectic mixture (apart from pure A and pure B) solidifies at a single definite temperature.



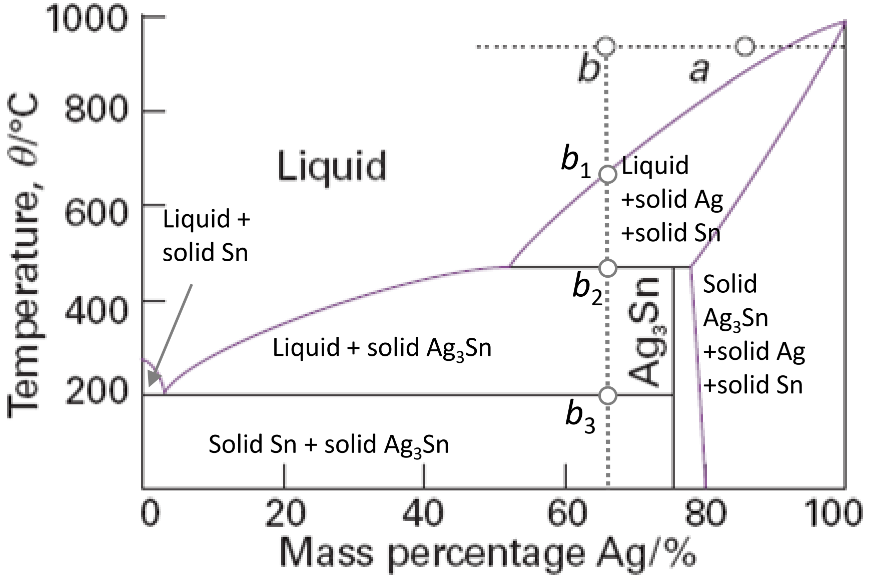
Binary phase diagram

- When a liquid of composition *a* is cooled, solid silver with dissolved tin begins to precipitate at a_1 and the sample solidifies completely at a_2.
- Describe what happens when the sample of composition *b* is cooled.

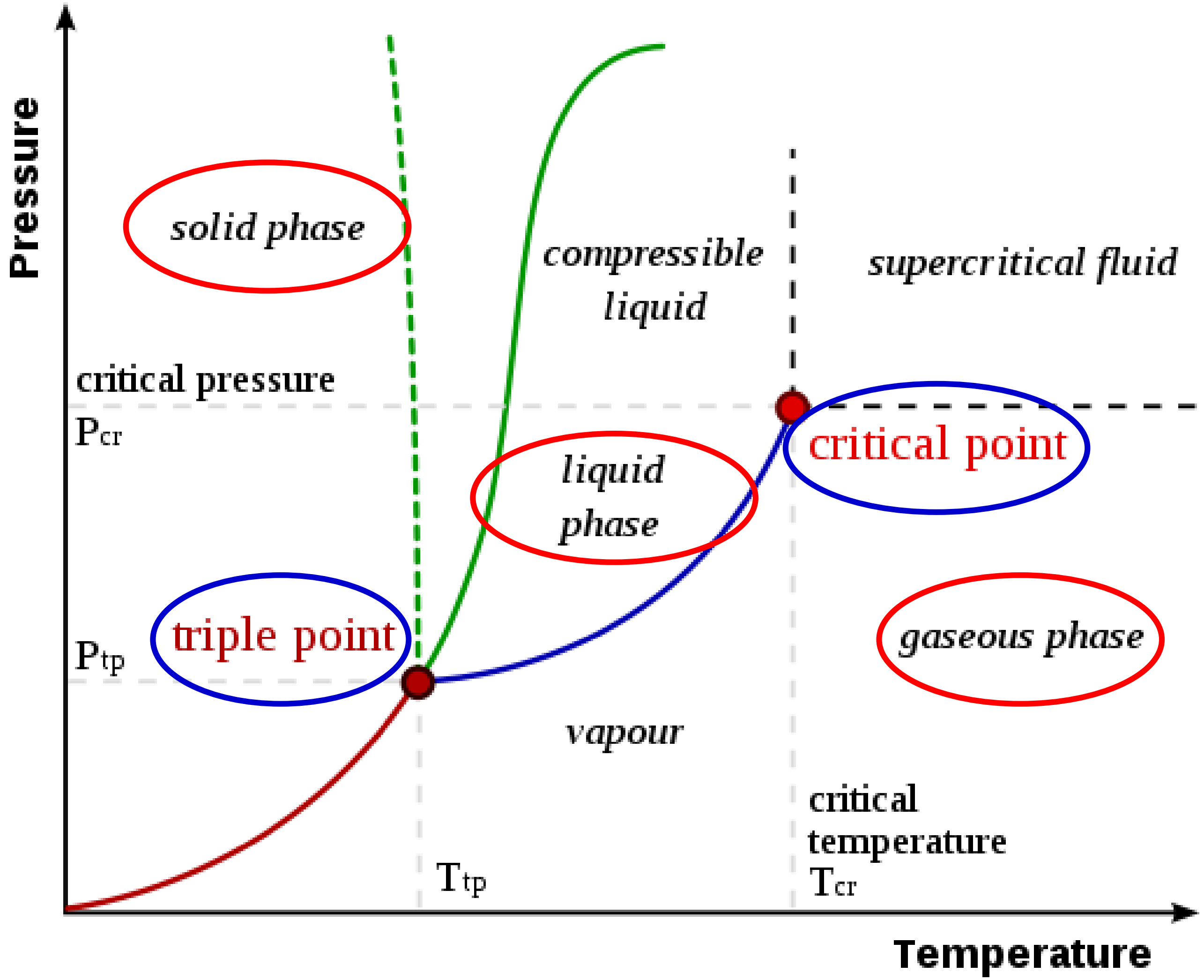


Answer

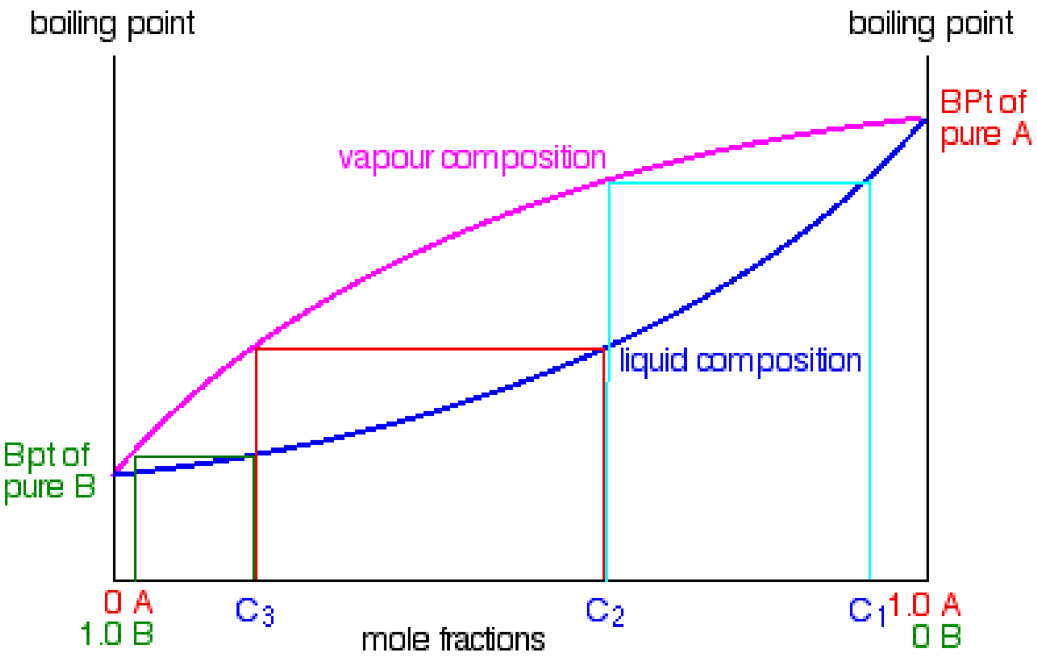
- Solid Ag with dissolved Sn begins to precipitate at b_1, and the liquid becomes richer in Sn as the temperature falls further.
- At b_2, solid Ag_3Sn begins to precipitate, and the liquid becomes richer in Sn.
- At b_3, the system has its eutectic composition (a solid solution of Sn and Ag_3Sn) and it freezes without further change in composition.



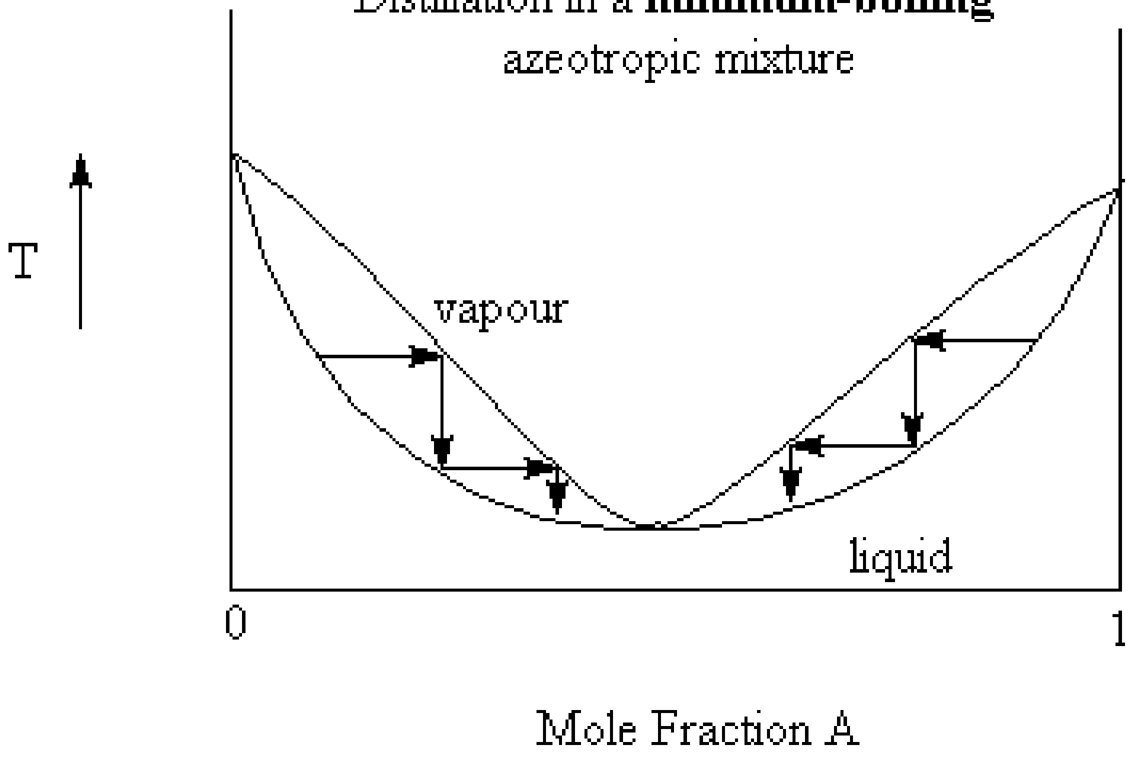
Phase diagram - example

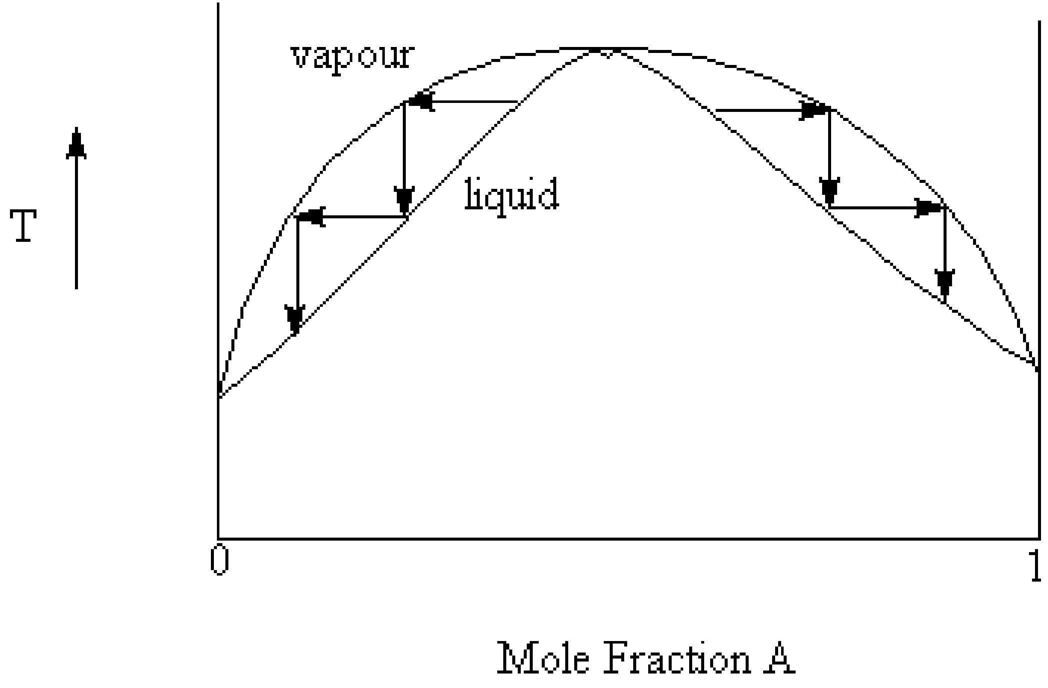


Fractional distillation



Azeotropes


Distillation in a **minimum-boiling** azeotropic mixture

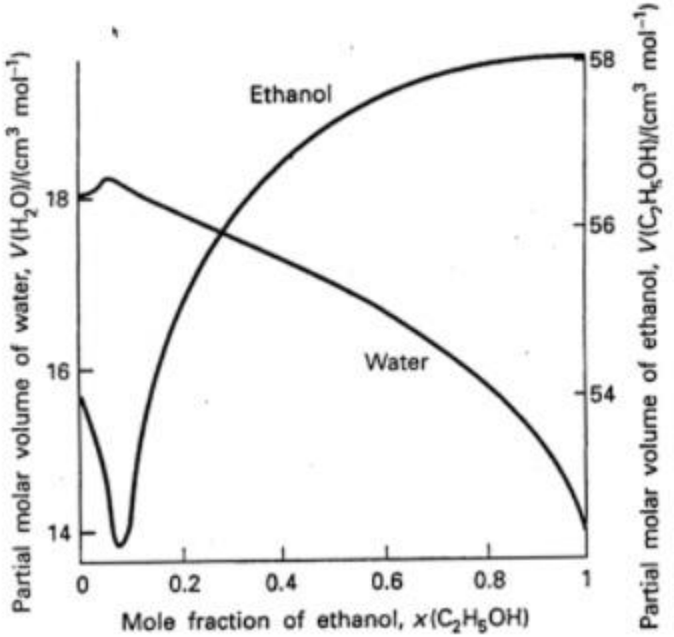

Distillation in a **maximum-boiling** azeotropic mixture

Physical transformations

- The chemical potential is the central unifying property for discussing the TD criteria of equilibria.
- The chemical potentials of a substance are the same in all the phases in which it exists at equilibrium.
- Reminder: $dG = Vdp - SdT + \sum_{i=1}^{n} \mu_i dn_i$

Partial molar quantities: volume

- The contribution of component of a mixture makes to the total volume of the sample.
- Imagine adding 1 mol of H_2O to an amount of water.
    - This corresponds to a 18 cm^3 mol^{-1} increase
- If we add the same amount of H_2O to a large amount of ethanol the volume increase is only 14 cm^3.
    - The volume occupied by a given number of H_2O MQs depends on their surroundings (H-bonding)
- The partial molar volume of H_2O in ethanol is 14 cm^3 mol^{-1}.
- The partial molar volumes of the components of a mixture vary with composition – as the MQs' surrounding change also (and forces acting on the MQs)



Partial molar volume

- $V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n\prime}$ definition of partial molar volume of substance J, *n*' signifies the amount of all other substances in the mixture.
- On the addition of dn_A of A and dn_B of B the total volume of a mixture changes by $dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$
- Provided the relative compositions are held constant as the amounts of A and B are increased the partial molar volumes are both constant so $V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B = V_A n_A + V_B n_B$
- Molar volumes are always positive but partial molar volumes need not be, *cf.* addition of $MgSO_4$ in a large volume of water -1.4 cm^3 mol^{-1}.
  - Hydration of ions

Partial molar quantities: Gibbs energy

- The concept of partial molar quantity may be extended to any extensive state function.
- A system consisting of several J components each of which contributes to the total Gibbs energy, we may introduce the partial molar Gibbs energy of each component.
- $\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n\prime}$, is also called the chemical potential, where n’ signifies that the abundance of all the other species in the mixture is held constant.
- For a 1-component system $\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} = \left(\frac{\partial (nG_m)}{\partial n}\right)_{p,T} = G_m$.
- Just like the partial molar volume, the chemical potential of a component in a mixture varies with composition.
- The total Gibbs energy of a mixture $G = \sum_J n_J \mu_J$. According the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture.

Chemical potential

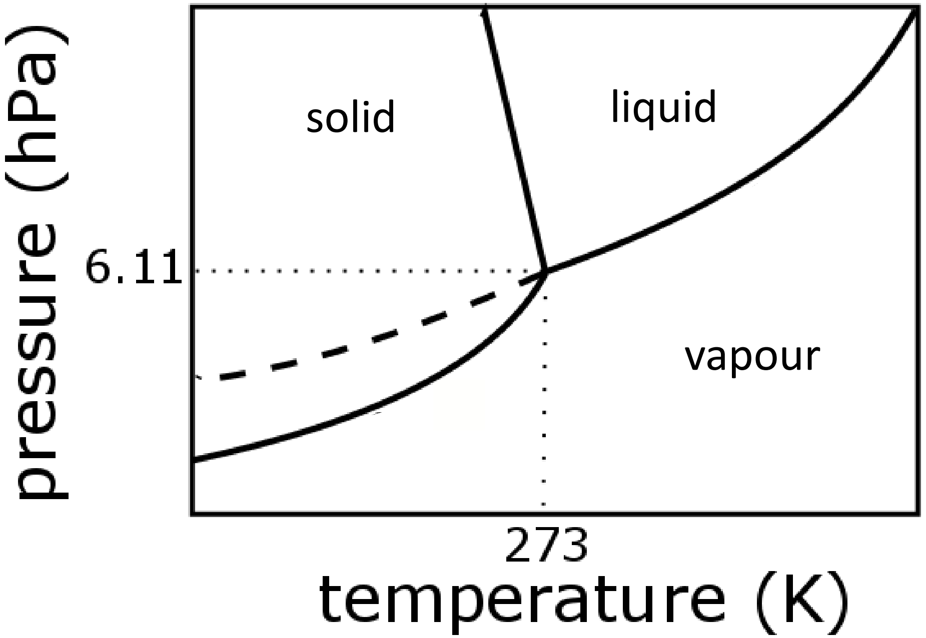
- It is the measure of the potential that a substance has for producing change in a system.
- Gibbs energy: $dG = Vdp - SdT + \sum_J \mu_J dn_J$ - fundamental equation of the chemical thermodynamics.
- At constant pressure and temperature $dG_{p,T} = \sum_J \mu_J dn_J$.
- According to the Gibbs-Duhem equation $\sum_J n_J d\, \mu_J = 0$ at constant temperature and pressure, *i.e.* in a binary mixture if the μ of a component increases that of the other one must increase; $d\mu_B = -\frac{n_A}{n_B} d\mu_A$.

Thermodynamic criterion of equilibrium

- At equilibrium, the chemical potential of a substance is the same throughout the sample, regardless of the number of phases.
- When 2 phases of a many-component mixture are in equilibrium the chemical potential of each component is the same in every phase.
- ! A system with μ_1 of one component at one location and μ_2 at another. The locations may be in the same or in different phases.
- When an amount of dn of the substance is transferred from one location to the other. The Gibbs energy of the system changes by $-\mu_1 \mathrm{d}n$ when material is removed from location 1 and $+\mu_2 \mathrm{d}n$ when it is added to location 2.
- The overall change is $\mathrm{d}G= -\mu_1 \mathrm{d}n + \mu_2 \mathrm{d}n= (\mu_2-\mu_1)\mathrm{d}n$.
- If $\mu_1>\mu_2$ then $\mathrm{d}G<0$, *i.e.* the process is spontaneous. Therefore only when $\mu_1=\mu_2$ is the system in equilibrium so no spontaneous processes may occur.

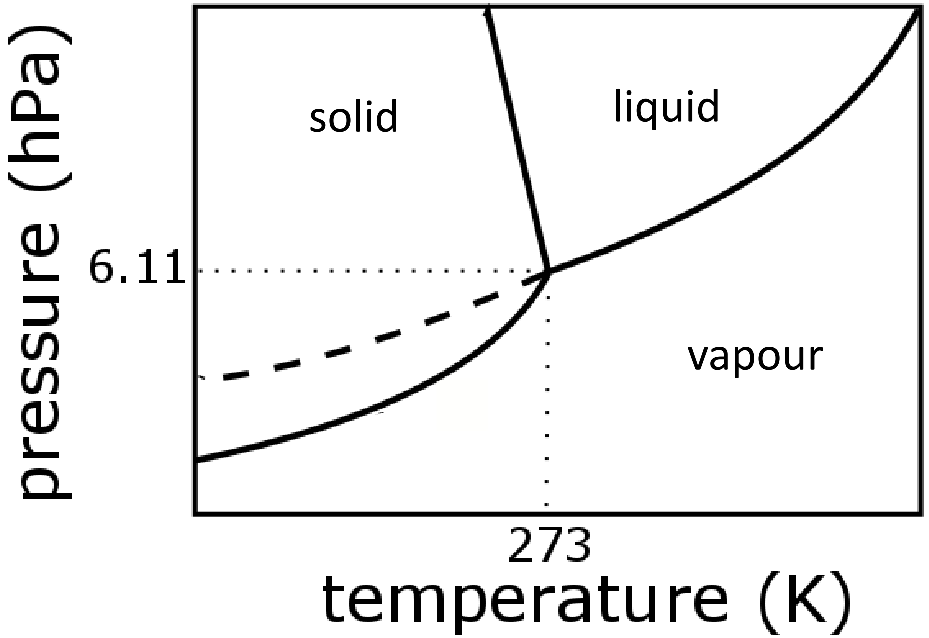
Phase equilibria

- What is the relation between the chemical potential of the phases of water at 273.16 K and 611 Pa?



Answer

- Triple point $\mu_{water}(s)=\mu_{water}(g)=\mu_{water}(l)$



The response of μ to the conditions: *T*

- Temperature dependence of the Gibbs energy: $\left(\frac{\partial G}{\partial T}\right)_p = -S$
- As μ of a pure substance is its molar Gibbs energy: $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_M$, the temperature dependence of μ.
- As *T* ↑ μ ↓.
- The *G* is the difference between the total energy and that stored ‘chaotically’, and the latter ↑w *T*.

μ dependence on T

- The molar entropy of water vapour at 25 °C is 189 J K^{-1} mol^{-1}.

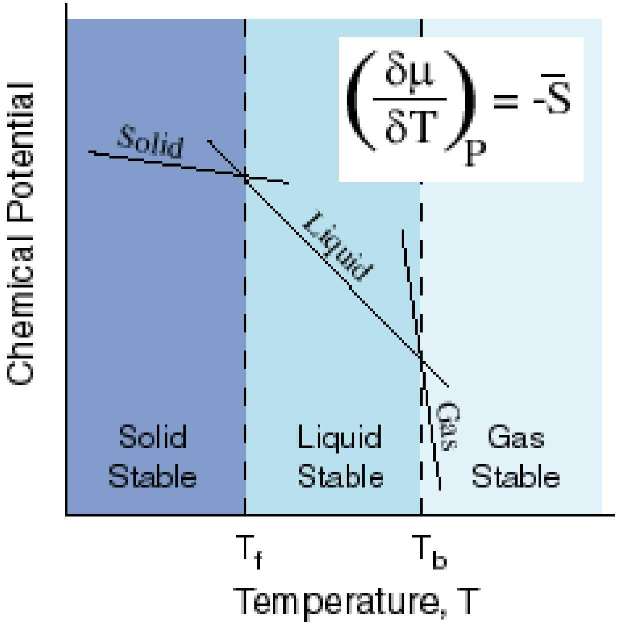
How would an 1 K increase of temperature affect the chemical potential of pure water?

Answer

- $(\partial \mu / \partial T)_p = -189 \text{ J K}^{-1} \text{ mol}^{-1}$
- So the 1 K increase of temperature decreases μ by 189 J mol^{-1}

μ as a function of T

- $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_M$: slope of the plot of μ vs T is steeper for gases than for liquids as $S_m(g)>S_m(l)$.
- Slope of μ(l) results in its falling below μ(s) when T is high enough, and the liquid becomes the stable phase *i.e.* the solid melts.

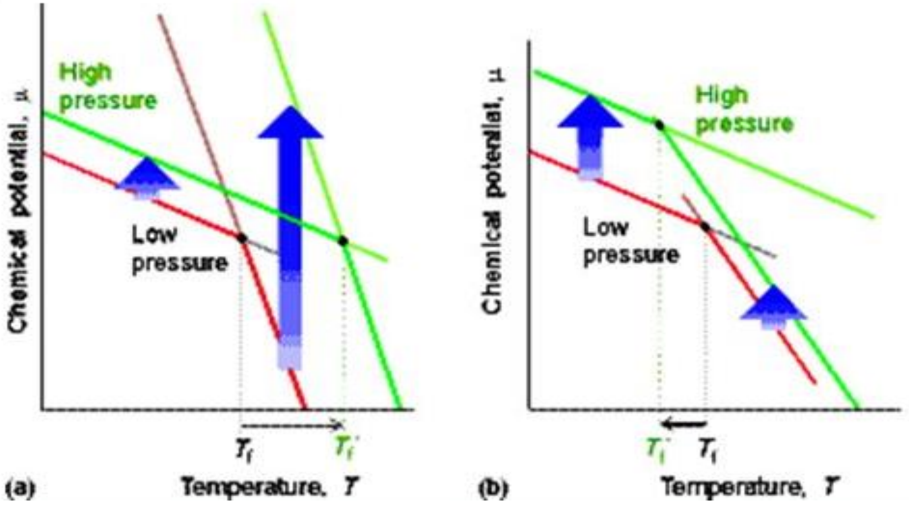


The response of μ to the conditions: p

- Most substances melt at a higher T when subjected to p. As if p is preventing the formation of the less dense liquid.
- A notable exception is water and ice, why?
  - The density of ice is lower, therefore it freezes at ↓T with ↑p.

- $\left(\frac{\partial \mu}{\partial p}\right)_T = V_M$, from ($\left(\frac{\partial G}{\partial p}\right)_T = V$). Slope equals V_m.
  - Typically $V_m(l)>V_m(s)$

$V_m(l)>V_m(s)$
↑p ↑μ as $V_m>0$
T_f ↑



$V_m(l)<V_m(s)$
↑p ↑μ(l) + than μ(s)
T_f↓

μ dependence on p

- The molar volume of water vapour at 25 °C, treated as perfect gas, is 25 $dm^3\ mol^{-1}$, corresponding to $2.5 \times 10^{-2}\ m^3\ mol^{-1}$.

How would an 1.0 bar increase in pressure affect the chemical potential of pure water?

Answer

- $(\partial\mu/\partial p)_T$ = 2.5*10^{-2} m^3 mol^{-1}
- So the 1 K increase of temperature increases μ by $\delta\mu$ = (2.5*10^{-2} m^3 mol^{-1})*(1.0*10^5 Pa) = 2.5*10^3 Pa m^3 mol^{-1} = 2.5 kJ mol^{-1}

The structure of 1-component phase diagrams

- Precise locations of phase boundaries in a 1-component PD may be found through the fact that when 2 phases are in equilibrium, their μ must be equal; $\mu(\alpha;p,T)=\mu(\beta;p,T)$.
- By solving this equation for p in terms of T we get the Clapeyron equation: $\frac{dp}{dT}=\frac{\Delta_{trs}S}{\Delta_{trs}V}$, where $\Delta_{\mathrm{trs}}S=S_{\mathrm{m}}(\beta)-S_{\mathrm{m}}(\alpha)$, idem for V.

2-phase boundaries

- Melting/fusion is accompanied by $\Delta_{\text{fus}}H$ molar enthalpy change at T, with $\Delta_{\text{fus}}H/T = \Delta_{\text{fus}}S$.
  - Clapeyron equation becomes: $\frac{dp}{dT} = \frac{\Delta_{fus}S}{\Delta_{fus}V}$ on the solid-liquid boundary.
  - This usually positive (ext. H_2O for example) and small.
- Vaporisation is accompanied by $\Delta_{\text{vap}}H$ molar enthalpy change at T, with $\Delta_{\text{vap}}H/T = \Delta_{\text{vap}}S$.
  - Clapeyron equation becomes: $\frac{dp}{dT} = \frac{\Delta_{vap}S}{\Delta_{vap}V}$ on the liquid-vapour boundary.
  - This is usually positive and large.
  - Boiling temperature is more responsive to pressure than melting temperature.
- For sublimation:
  - Clapeyron equation becomes: $\frac{dp}{dT} = \frac{\Delta_{sub}S}{T\Delta_{sub}V}$ on the solid-vapour boundary.

Clausius-Clapeyron

- A $V_m(g) >> V_m(l)$ or $V_m(s)$, $\Delta_{vap}V \approx V_m(g)$ or $\Delta_{sub}V \approx V_m(g)$.
- If the gas behaves perfectly, $V_m(g) = RT/p$.
- Clapeyron eq. will be $\frac{dp}{dT} \approx \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$ or $\frac{dp}{dT} \approx \frac{p\Delta_{sub}H}{RT^2}$.
- As $dp/p = d\ln p$, the above rearranges into the Clausius-Clapeyron eq.:

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

- Used to understand the location and shape of the liquid-vapour or solid-vapour boundaries of single component phase diagrams.
- As T_{boil} is the T at which $p_{vap} = p_{ext}$, Clausius-Clapeyron may be interpreted as an expression for ΔT_{boil} as a function of p.

Estimating boiling *T*

- The vapour pressure of dichloromethane at 24.1 °C is 53.3 kPa and its enthalpy of vaporisation is 28.7 kJ mol^{-1}.
- Estimate its boiling temperature when the external pressure is 80.0 kPa.
- Clue: we need to determine *T* where $p_{\mathrm{vap}}=p_{\mathrm{ext}}$.
- For this the Clausius-Clapeyron equation ($\frac{d\ln p}{dT}=\frac{\Delta_{vap}H}{RT^2}$) has to be converted into an expression for p_{vap} at 2 *T*s by integration assuming that $\Delta_{\mathrm{vap}}H$ is independent of *T*, and solve it for the *T* at which $p_{\mathrm{vap}}=p_{\mathrm{ext}}$.
- The integration of $\frac{d\ln p}{dT}=\frac{\Delta_{vap}H}{RT^2}$ gives $\int_{\ln p_1}^{\ln p_2}\mathrm{d}\ln p=\int_{T_1}^{T_2}\frac{\Delta_{vap}H}{RT^2}\mathrm{d}T=\frac{\Delta_{vap}H}{R}\int_{T_1}^{T_2}\frac{\mathrm{d}T}{T^2}$

Answer

- $\ln \frac{p_2}{p_1} = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- Rearrange to find T_2 at p_2 vapour: $T_2 \frac{\Delta_{vap}H/R}{\frac{\Delta_{vap}H}{RT_1} - \ln\left(\frac{p_2}{p_1}\right)} = \frac{T_1}{1 - \left(\frac{RT_1}{\Delta_{vap}H}\right) - \ln\left(\frac{p_2}{p_1}\right)}$
- From the data T_1=297.3 K; $\Delta_{vap}H$=28.7 kJ mol^{-1}; p_1=53.3 kPa; p_2=80.0 kPa: $T_2 \frac{297.3\ \mathrm{K}}{1 - \left(\frac{8.3145\ \mathrm{JK^{-1}mol^{-1}} * 297.3\ \mathrm{K}}{2.87 * 10^4\ \mathrm{J\ mol^{-1}}}\right) - \ln\left(\frac{80.0\ \mathrm{kPa}}{53.3\ \mathrm{kPa}}\right)} = 308$ K, *i.e.* 35 °C.

Any questions?