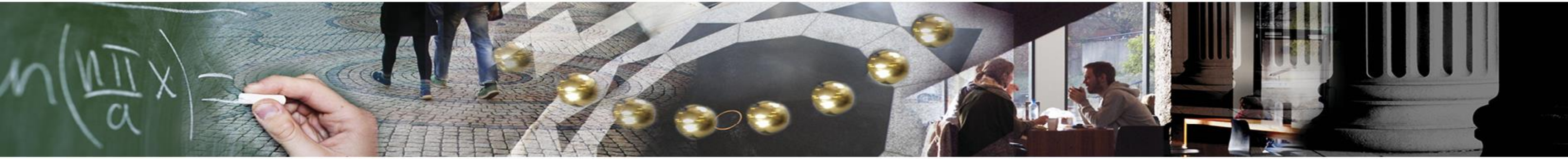
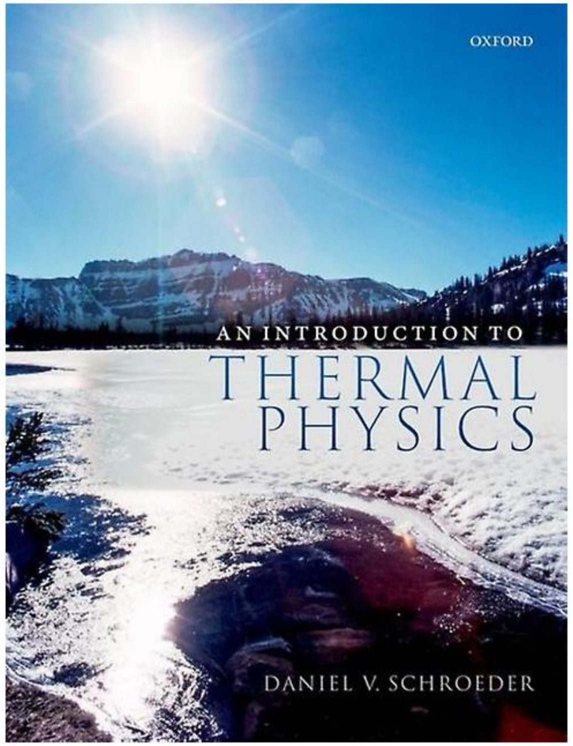


UiO : University of Oslo

Phase transitions of mixtures

DVS



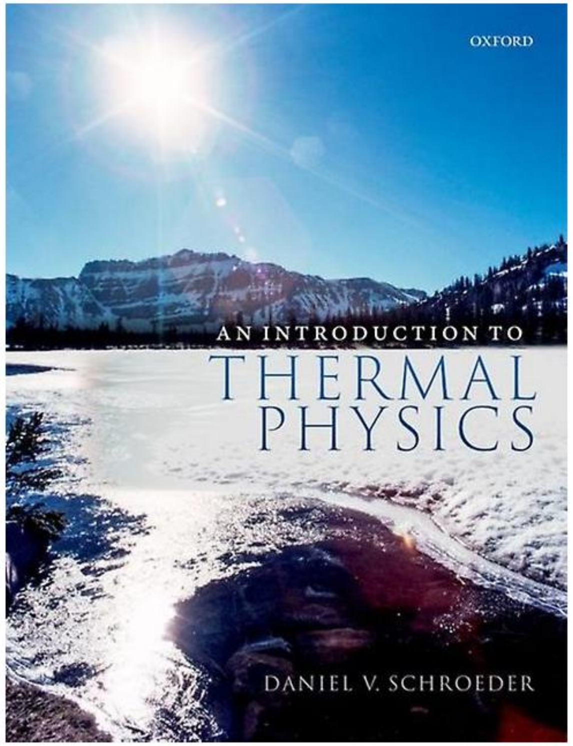
Tuesdays: Store fysiske auditorium

Wednesdays: Store fysiske auditorium

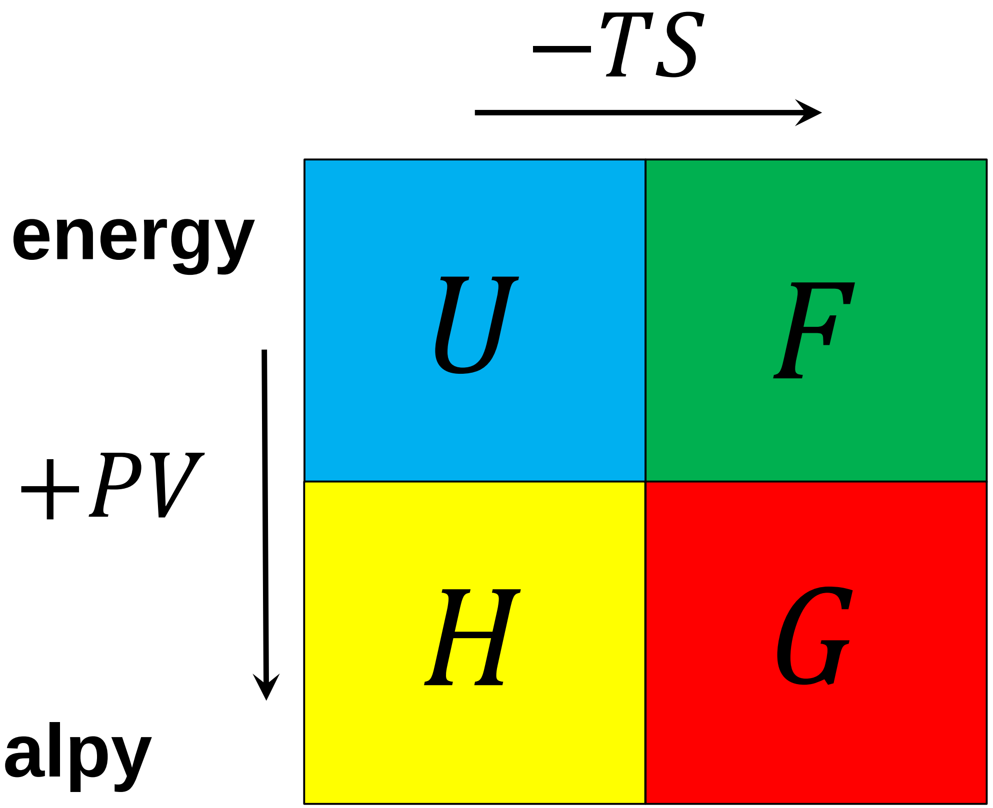
• Tuesday September 26	Free energies
• Wednesday October 4	Phase transitions of mixtures
• Tuesday October 31	Electron gas
• Tuesday November 7	Black body radiation
• Wednesday November 8	Specific heat

Tuesdays: 10:15 -12:00

Wednesdays: 12:15 -14:00



Thermodynamic potentials



Total energy

Enthalpy

$H\ = U + PV$

Helmholtz free energy

$F\ = U - TS$

Gibbs free energy

$G\ = U - TS + PV$

$G\ = H - TS$

By subtracting μN from $U, H, F,$ or G, one can obtain four new thermodynamic potentials. Of the four, the most useful is the grand free energy (or grand potential), $\Phi = U - TS - \mu N$.

Evaporation of liquid nitrogen

$$\Delta G = \Delta H - T\Delta S$$

Google

Element	**Nitrogen**
Molar Heat Capacity	20.8 J $K^{-1}mol^{-1}$
Standard Molar Entropy	153.3 J $K^{-1}mol^{-1}$
Enthalpy of Fusion	0.72 kJ mol^{-1}
Enthalpy of Vapourization	5.577 kJ mol^{-1}

1) Will evaporation happen at room temperature (25 °C)?
2) At what temperature evaporation becomes thermodynamically favourable?
3) How much heat would be taken from environment per 1mole of final gas?

Evaporation of liquid nitrogen

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1) Will evaporation happen at room temperature (25 °C)?

a) Yes b) No

2) At what temperature evaporation becomes thermodynamically favourable?

a) 36.4 K b) 72.8 K c) 77.4 K d) 299.4 K

3) How much heat would be taken from environment per 1mole of final gas?

a) 0 b) 45.7 kJ c) 40.1 kJ d) 40.7 kJ

Evaporation of liquid nitrogen

$$\Delta G \ = \Delta H - T\Delta S$$

	Element	Nitrogen
	Molar Heat Capacity	20.8 J $K^{-1}mol^{-1}$
ΔS	**Standard Molar Entropy**	153.3 J $K^{-1}mol^{-1}$
	Enthalpy of Fusion	0.72 kJ mol^{-1}
ΔH	**Enthalpy of Vapourization**	5.577 kJ mol^{-1}

298*0.1533 = 45.7 (kJ)

To heat 1 mole of water to 100 °C one needs 40.7 kJ.

$\Delta G \ = \Delta H - T\Delta S$ 5.577 - 0.1533*298 = -40,1064 (kJ mol^{-1}). Yes

$T = \Delta H/\Delta S$ 5.577/0.1533 = 36,4 (K)

$T = 2 * \Delta H/\Delta S$ 2*(5.577)/(0.1533) = 72,8 (K)

$\Delta G = 2 * \Delta H - T\Delta S$ (2*5.577) - 298*0.1533 = -34,5294 (kJ mol^{-1}) Yes

Evaporation of liquid nitrogen

$$\Delta G = \Delta H - T\Delta S$$

1) Will evaporation happen at room temperature (25 °C)?

a) Yes b) No

2) At what temperature evaporation becomes thermodynamically favourable?

a) 36.4 K b) 72.8 K c) 77.4 K d) 299.4 K

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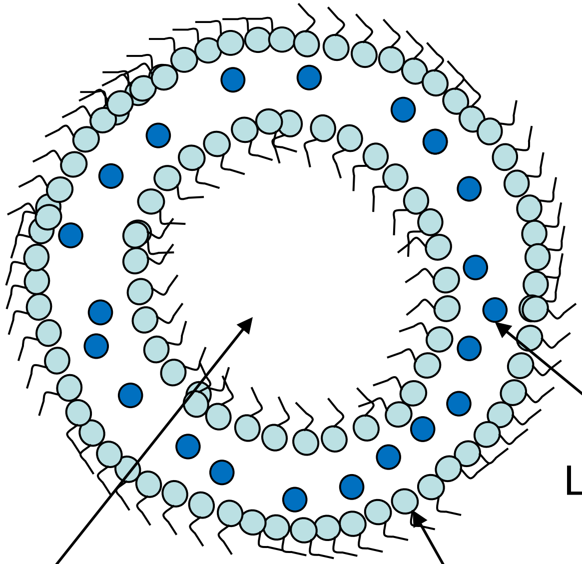
Soap-water mixture



Frozen soap bubble on snow at −7 ° C (19 ° F)

By Larry-pilot - Own work, CC BY 4.0, https://commons.wikimedia.org/w/index.php?curid=64273475

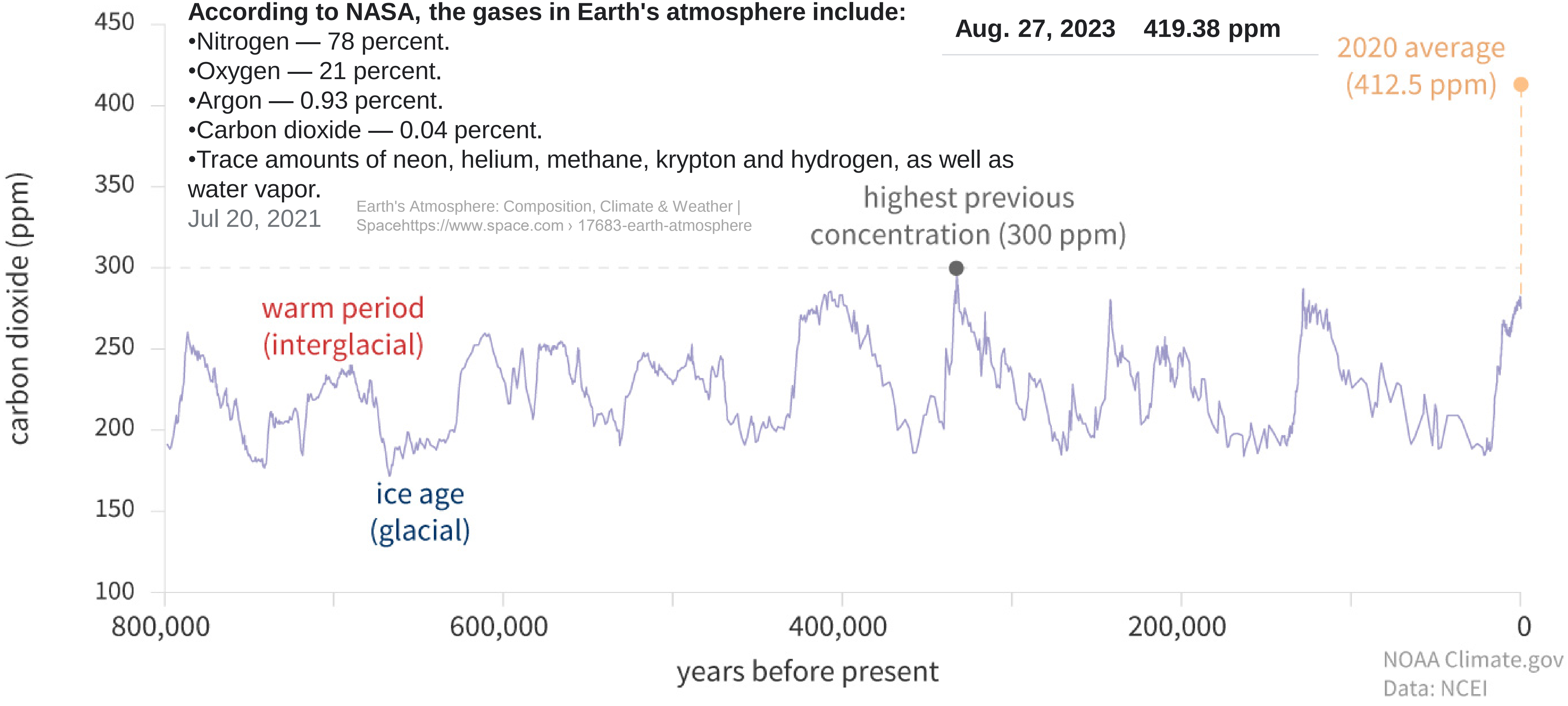
CARBON DIOXIDE OVER 800,000 YEARS

According to NASA, the gases in Earth's atmosphere include:

- Nitrogen — 78 percent.
- Oxygen — 21 percent.
- Argon — 0.93 percent.
- Carbon dioxide — 0.04 percent.
- Trace amounts of neon, helium, methane, krypton and hydrogen, as well as water vapor.

Jul 20, 2021 Earth's Atmosphere: Composition, Climate & Weather | Spacehttps://www.space.com › 17683-earth-atmosphere

Aug. 27, 2023 419.38 ppm

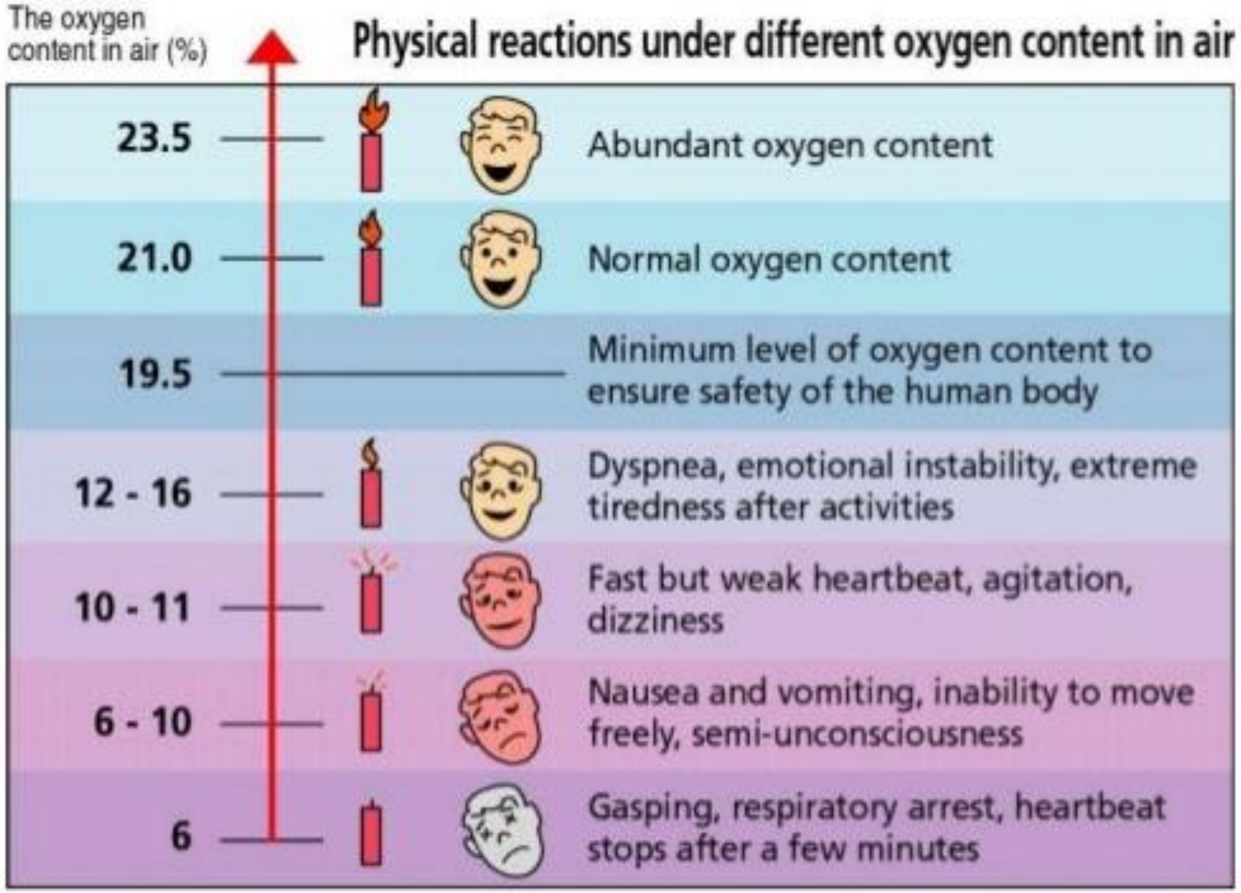


NOAA Climate.gov
Data: NCEI

Mixture of gases: physiological effects of CO_2 at various concentrations by volume

0.03%	Nothing happens, it is the normal carbon dioxide concentration in air.
0.5%	Lung ventilation increases by 5 percent, maximum safe working level.
1.0%	Feeling hot and clammy, lack of attention to details, fatigue, anxiety, clumsiness and loss of energy, 'jelly' legs.
2.0%	Lung ventilation increases by 50 percent, headache, loss of energy, feeling run-down. It may take up to several days for the body to return to normal.
3.0%	Lung ventilation increases by 100 percent, panting, headache, dizziness and possible vision disturbance such as speckled stars.
5 - 10%	Violent panting, fatigue to the point of exhaustion, severe headache, irreversible effects to health. Possible unconsciousness and death.
10 - 15%	Intolerable panting, severe headaches and rapid exhaustion. Unconsciousness and suffocation without warning. A burning paraffin candle is extinguished.
25% to 30%	Coma and convulsions within one minute of exposure. Certain death.

Physiological effect of O_2

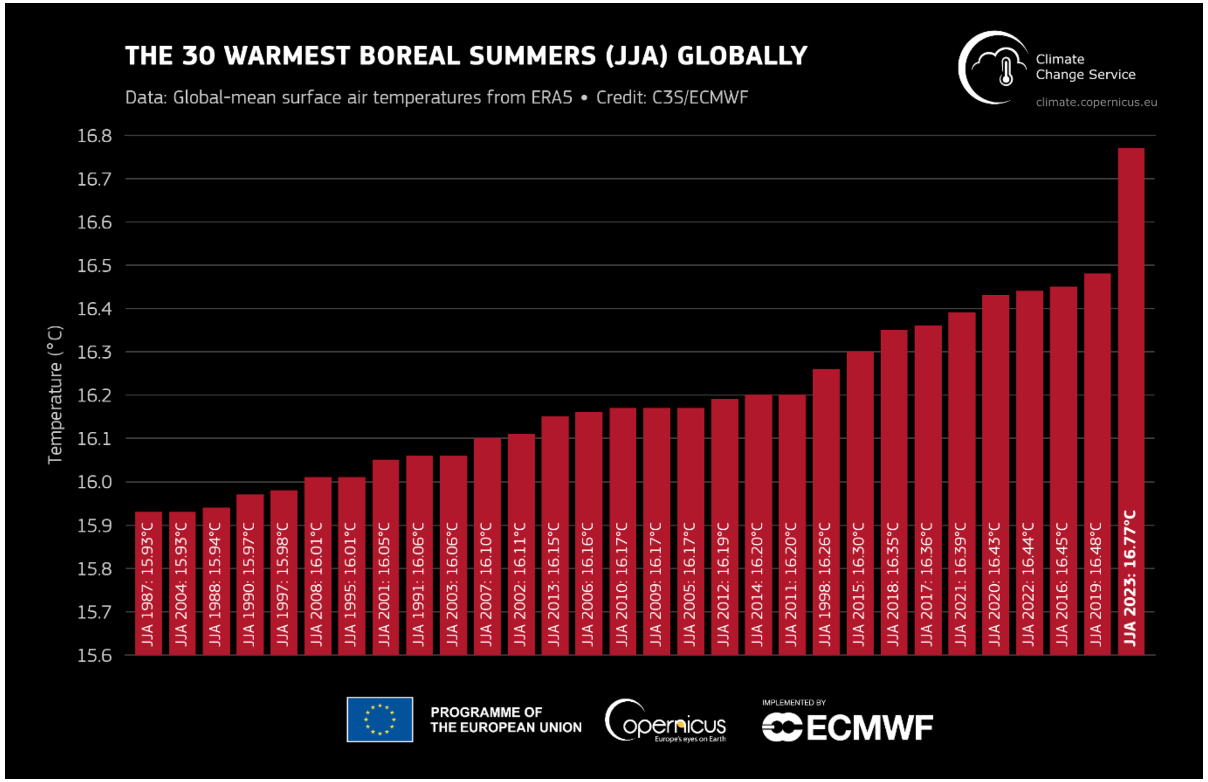


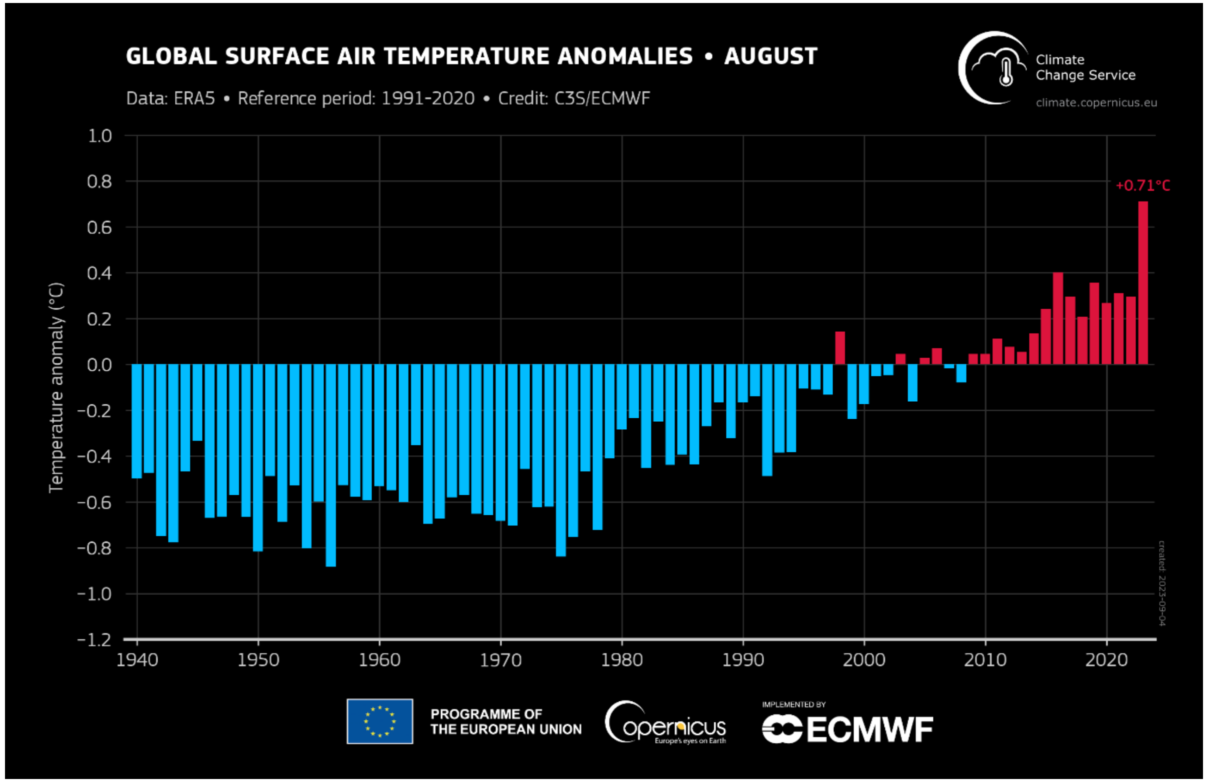
Physical reactions under different oxygen content in air

The oxygen content in air (%)	
23.5	Abundant oxygen content
21.0	Normal oxygen content
19.5	Minimum level of oxygen content to ensure safety of the human body
12 - 16	Dyspnea, emotional instability, extreme tiredness after activities
10 - 11	Fast but weak heartbeat, agitation, dizziness
6 - 10	Nausea and vomiting, inability to move freely, semi-unconsciousness
6	Gasping, respiratory arrest, heartbeat stops after a few minutes

What is the normal oxygen content of air? What level of oxygen in air is dangerous? and why ? - Quora

Global warming





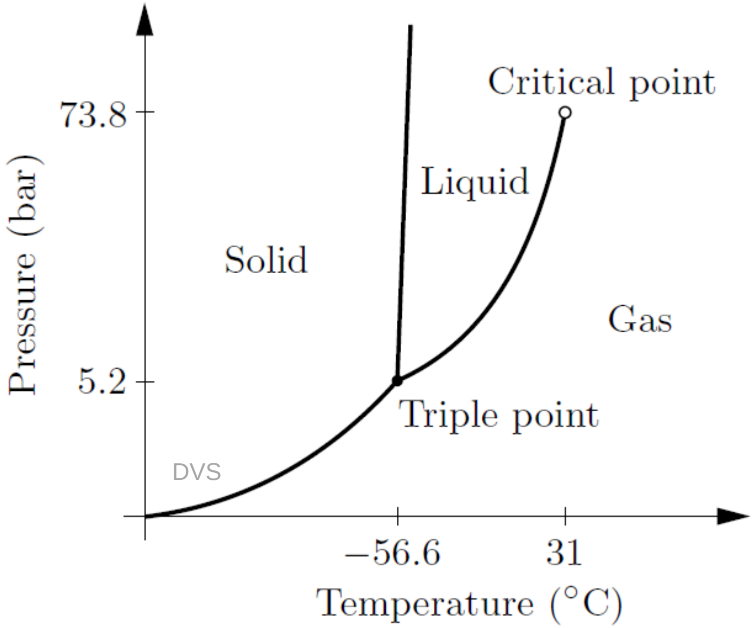
[Summer 2023: the hottest on record | Copernicus]

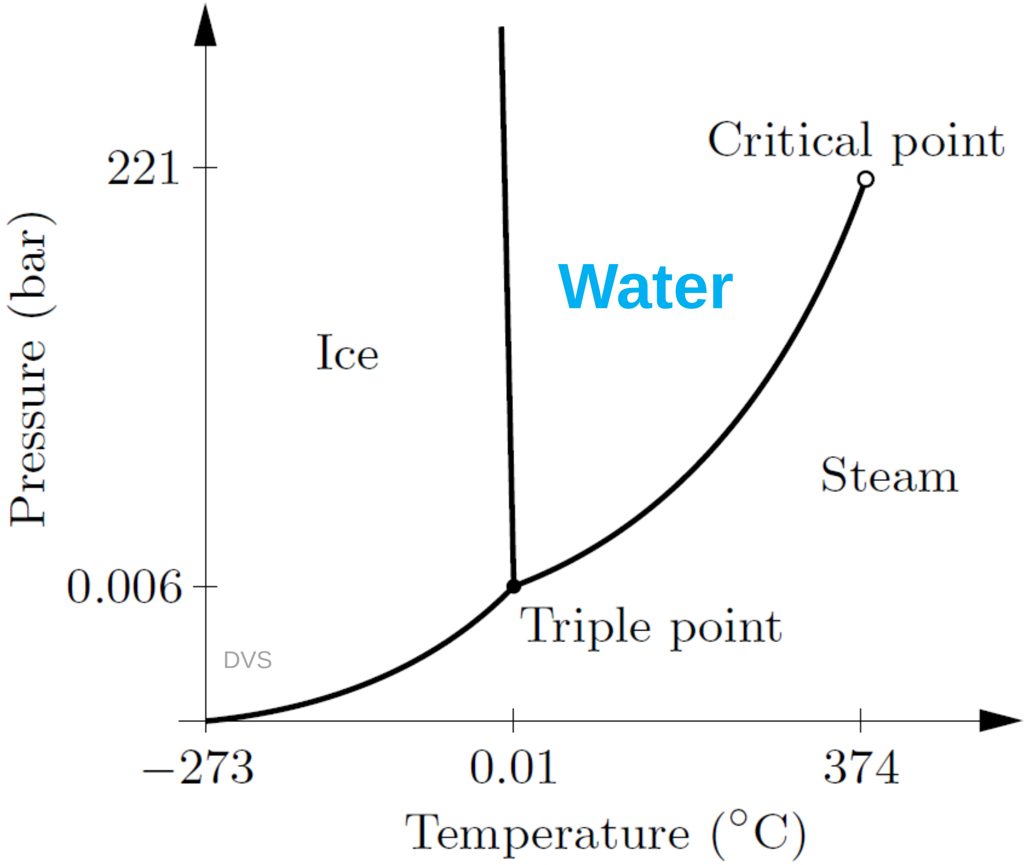
Phase Diagrams of Pure Substances

A graph showing the equilibrium phases as a function of temperature and pressure together with the lines of phase transformations is called a phase diagram.

A phase transformation is a discontinuous change in the properties of a substance, as its environment is changed infinitesimally.

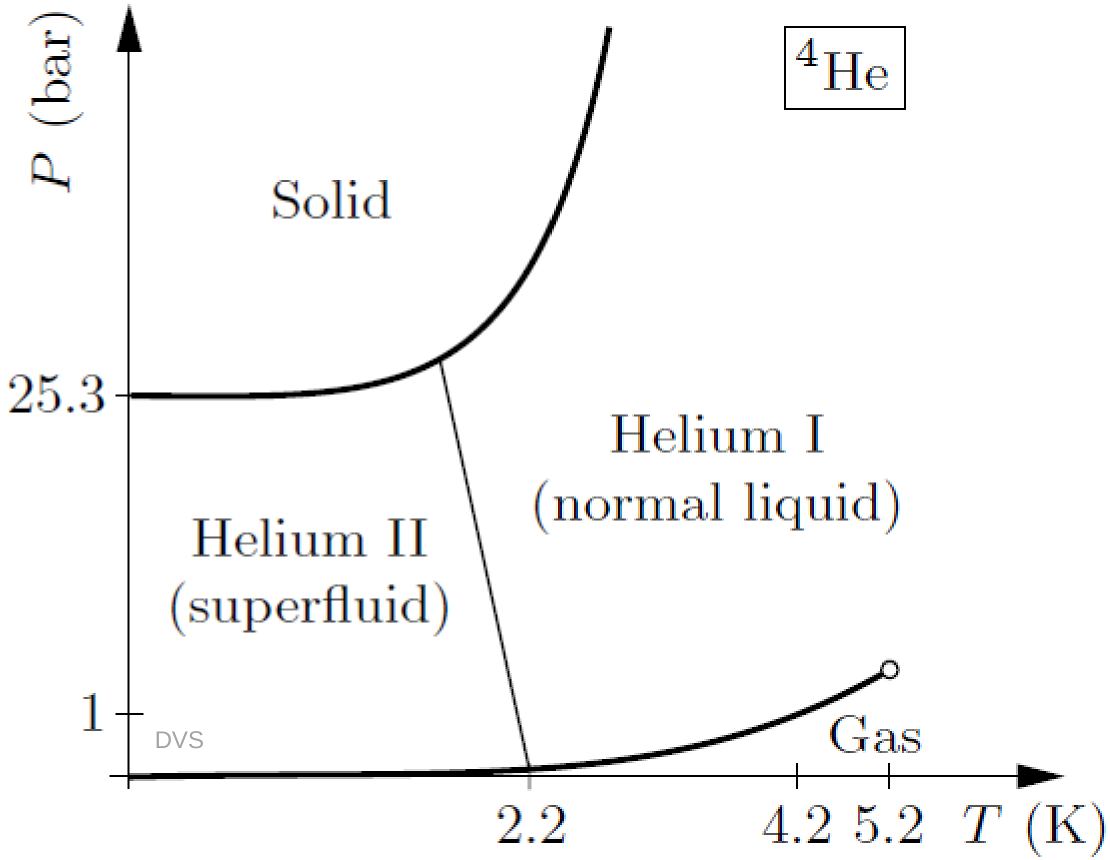
CO$_2$

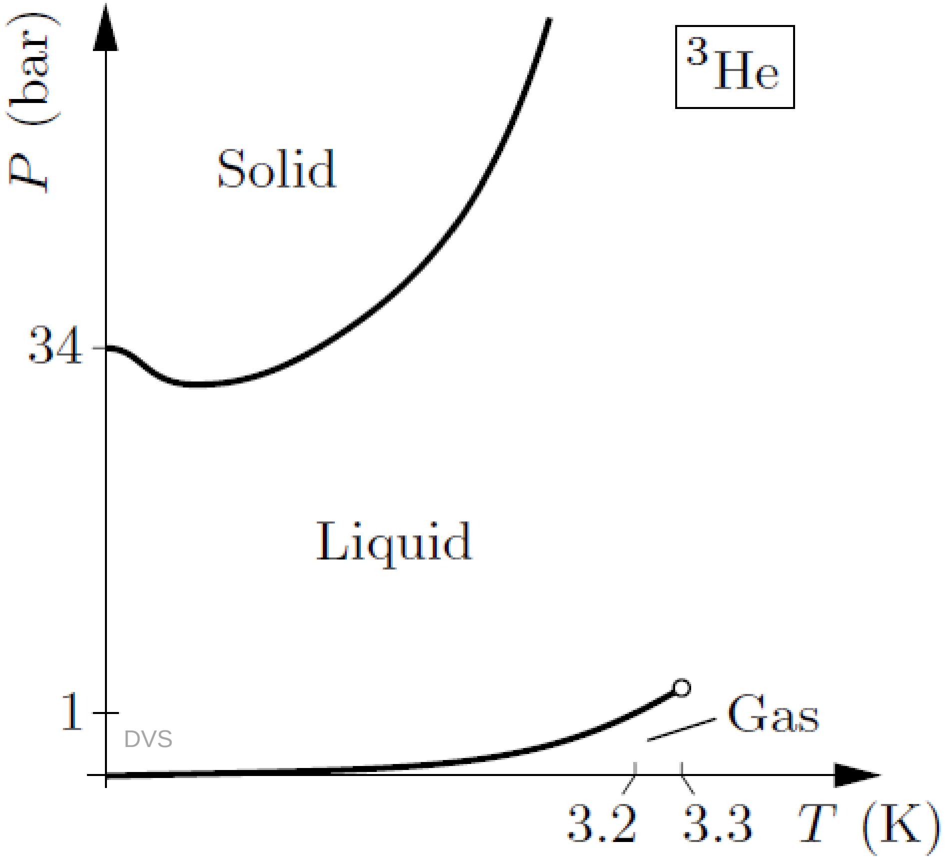




The liquid-gas phase boundary always has a positive slope.

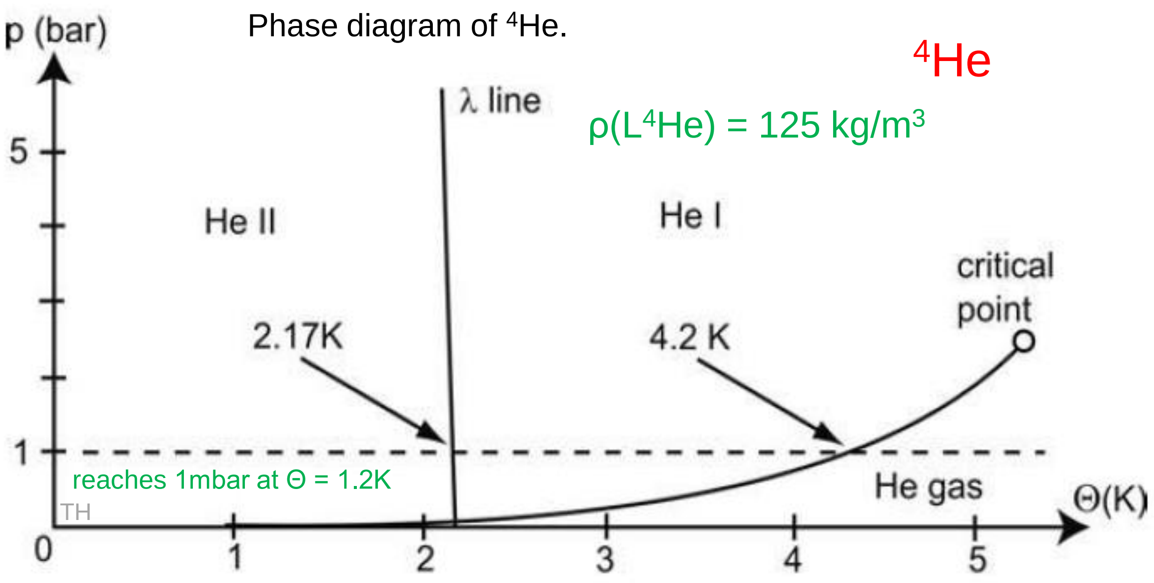
Phase diagrams of helium





Properties of liquid helium

- Helium is the only element that remains liquid when cooled to the temperatures well below 1 mK. The latent heat that has to be absorbed when liquid helium is evaporated generates the cooling power.
- Helium comes in two isotopes, the boson ^{4}He and the fermion ^{3}He.
- Helium is the only element for which the van der Waals energy is smaller than the kinetic energy of the atoms due to zero-point fluctuations.

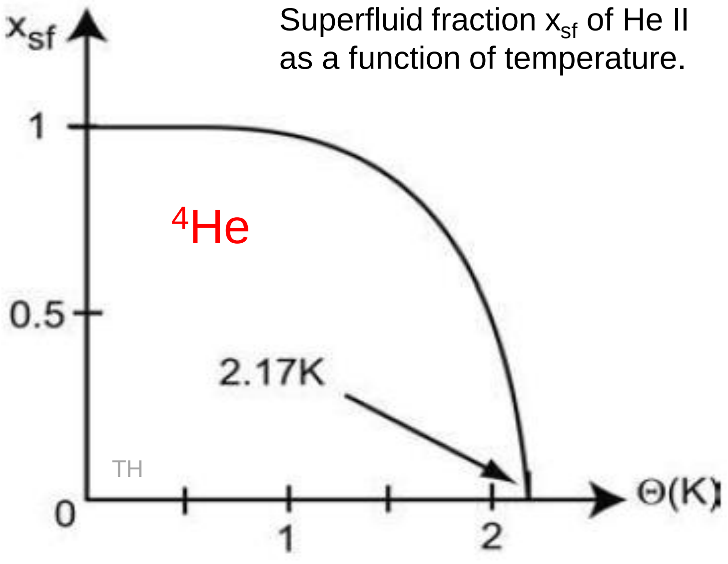

Phase diagram of ^{4}He.

^{4}He

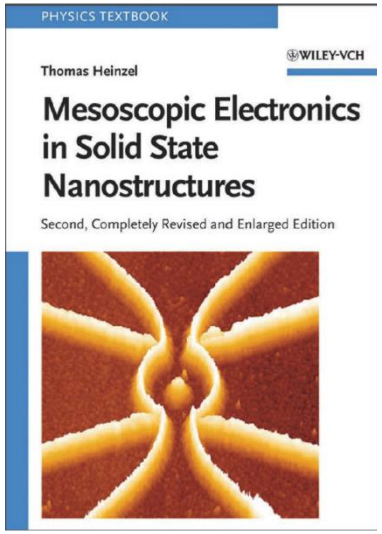
$\rho(L^4He) = 125\ kg/m^3$

reaches 1mbar at $\Theta = 1.2K$

https://www.youtube.com/watch?v=2Z6UJbwxBZI


Superfluid fraction x_{sf} of He II as a function of temperature.

^{4}He


PHYSICS TEXTBOOK

WILEY-VCH

Thomas Heinzel

Mesoscopic Electronics in Solid State Nanostructures

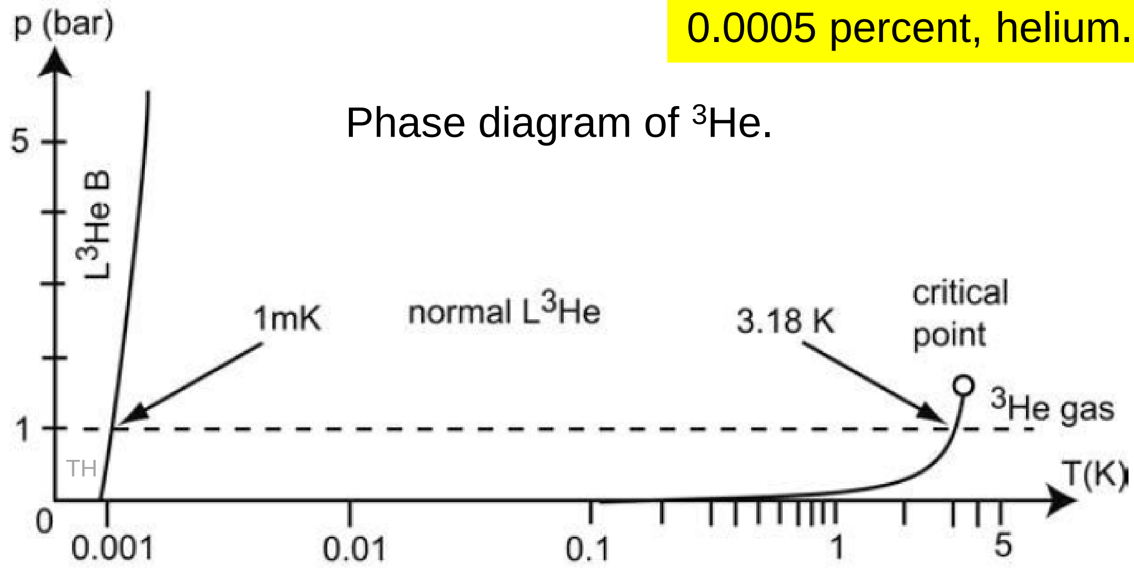
Second, Completely Revised and Enlarged Edition

TH

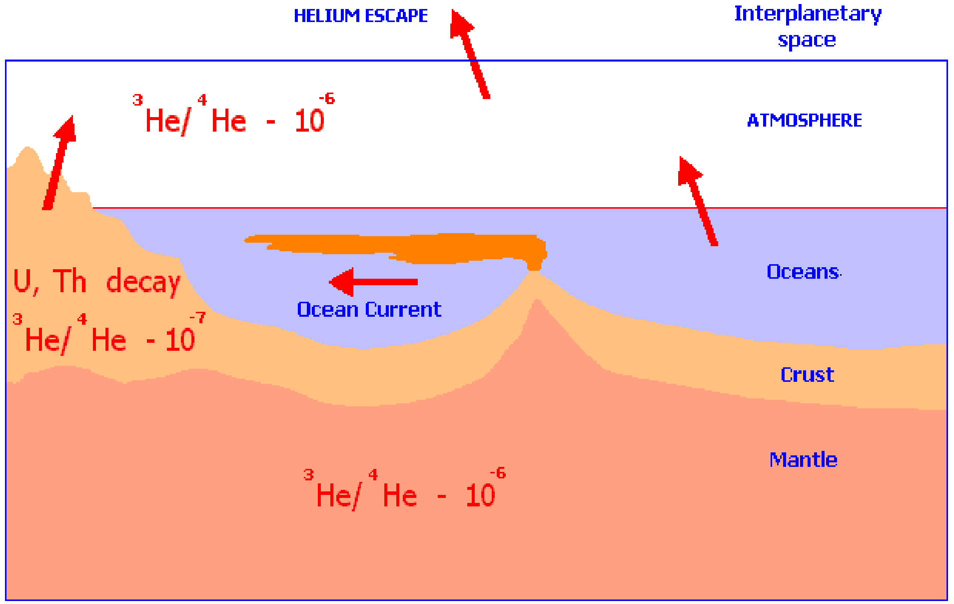
Properties of pure ^{3}He

- The density of L^{3}He is $\rho(^3\text{He}) = 59\ \text{kg/m}^3$. At atmospheric pressure, it liquefies at $\Theta = 3.19$ K. It is near-to-completely absent on Earth.
- The vapour pressure is higher (at identical temperatures) than in L^{4}He. Pressure drops to 10^{-3} mbar at about $\Theta = 270$mK.
- ^{3}He atoms are fermions, and the liquid can be approximated by a Fermi gas.
- For $\Theta < 2$mK, the ^{3}He atoms form Cooper pairs and undergo a Bose–Einstein condensation into superfluid ^{3}He.

Earth's atmosphere is only about 5 parts per million, or 0.0005 percent, helium.



Phase diagram of ^{3}He.

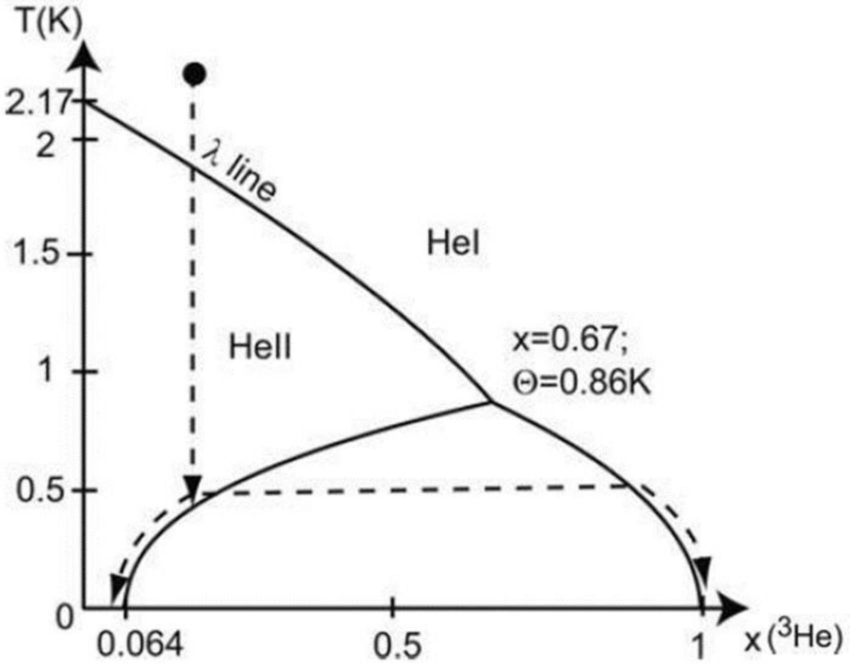


Seamounts release plumes of ^{3}He-rich water into the ocean. These helium plumes can be traced for thousands of kilometres

http://www.threesology.org/3sxamples13.php

The ^{3}He/^{4}He mixture

- For temperatures below 860 mK, an important phase separation into a dilute ^{3}He-poor phase (D) and a ^{3}He-rich phase (C) takes place.
- The ^{3}He dissolved in ^{4}He is a dilute Fermi gas with an effective mass ≈ 2.4m(^{3}He). ^{3}He atoms move in ^{4}He without friction.
- The chemical potential of the C-phase is somewhat higher than that, of a single ^{3}He atom in ^{4}He. Hence, ^{3}He atoms will go into ^{4}He until the chemical potentials have aligned.



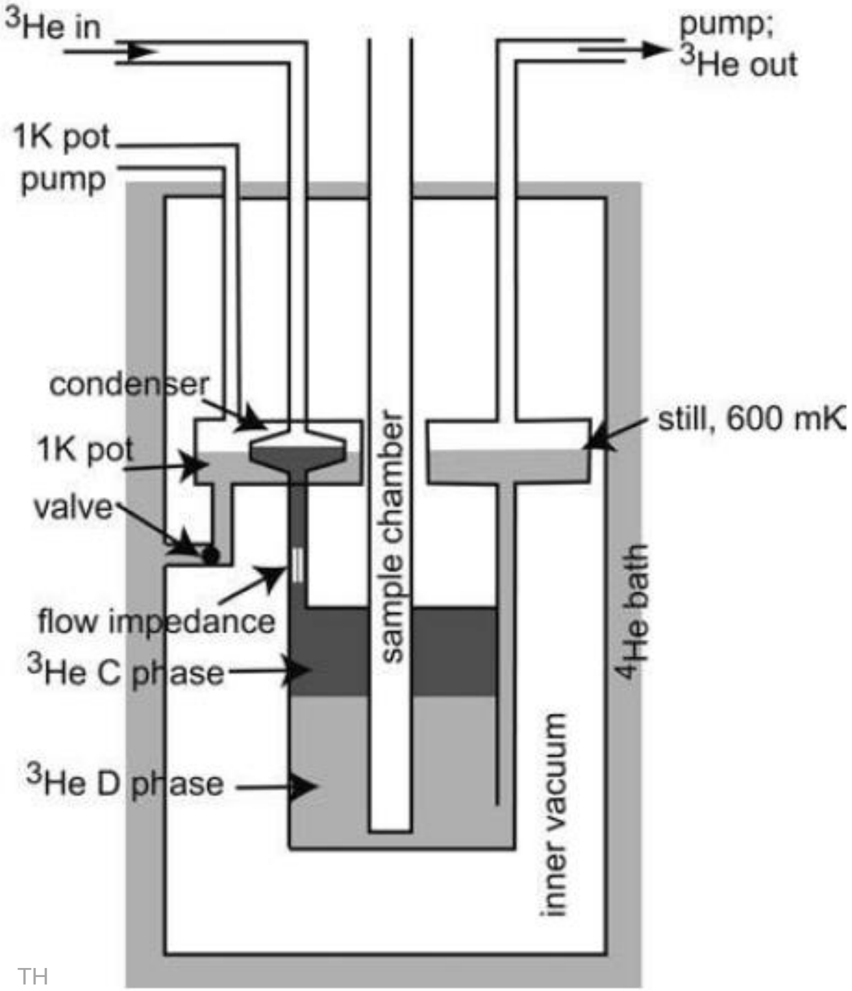
Phase separation is important for operation of dilution refrigerators.

Phase diagram of the ^{3}He/^{4}He mixture vs. ^{3}He concentration

^{3}He/^{4}He dilution refrigerator

- Since the dilute ^{3}He phase (D) can be thought of as the ^{3}He vapour of the ^{3}He-rich phase (C) with a significant vapour pressure even at T close to 0, pumping the ^{3}He atoms out of the D is able to reduce T down to 1 mK.
- C phase has a smaller density than D and the “liquid” is floating on top of the “gas”.

- Pumping the ^{3}He atoms out of the D phase pulls the corresponding effective latent heat out of the mixture.
- The D phase is connected through a tube with the still heated to about 600 mK. At this temperature, the vapour pressure of ^{3}He is significant, while that of ^{4}He is negligible. The still therefore effectively distils ^{3}He from the D phase.
- ^{3}He is re-condensed in the “1K pot”.



TH

Essential components of a ^{3}He/^{4}He dilution refrigerator.

Description of gas mixtures: basic mathematics

$$G = U + PV - TS$$

$$\mathrm{S} = \mathrm{k}\ \ln\Omega$$

$$\mathrm{S}_{\mathrm{total}} = \mathrm{k}\ \ln\Omega_{\mathrm{total}} = \mathrm{k}\ \ln(\Omega_{\mathrm{A}}\,\Omega_{\mathrm{B}}) = \mathrm{k}\ \ln\Omega_{\mathrm{A}} + \mathrm{k}\ \ln\Omega_{\mathrm{B}} = \mathrm{S}_{\mathrm{A}} + \mathrm{S}_{\mathrm{B}}.$$

Stirling's approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

Multiplicity and entropy of a monatomic ideal gas:

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}(\sqrt{2mU})^{3N-1}$$

Sackur-Tetrode equation:

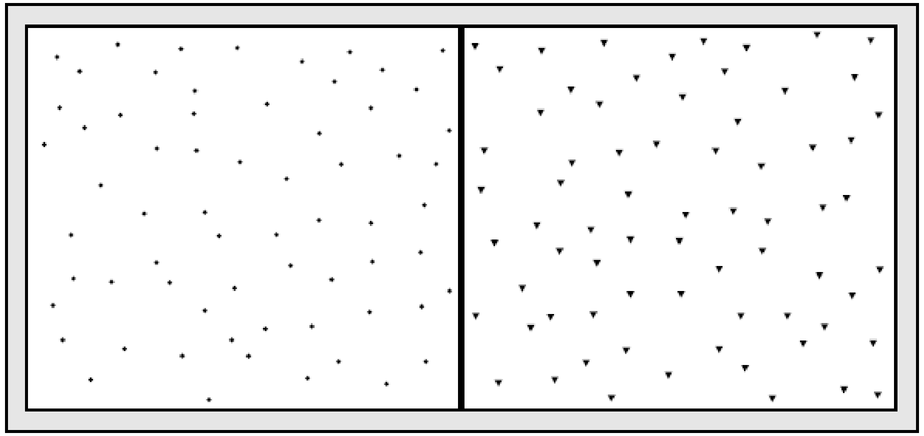
$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

Entropy of mixing

Sackur-Tetrode equation:

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

$$S_{total} = S_{helium} + S_{argon}$$



After removing partition:

$$\Delta S_A = Nkln\frac{V_f}{V_i} = Nk\ln 2$$

DVS

p.80 Chapter 2

$$\Delta S = \Delta S_A + \Delta S_B = 2Nkln\frac{V_f}{V_i} = 2Nk\ln 2$$

Entropy of the mixing of two monoatomic gases of equal volume: $\Delta S = 2Nk\ln 2$

Entropy of variable concentration mixing

Sackur-Tetrode equation:

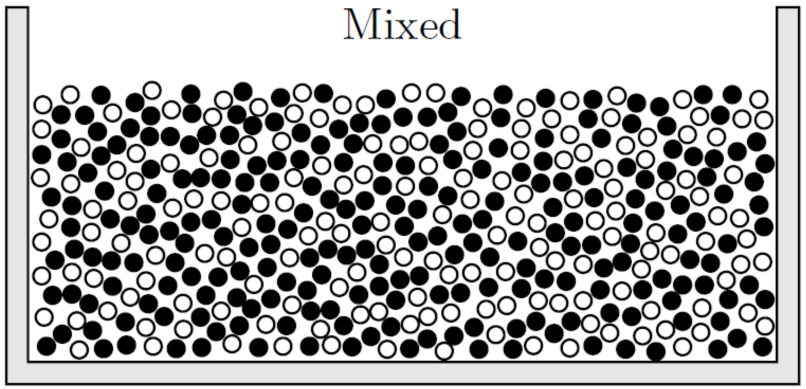
$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

$$N_A = xN \qquad N_B = (1-x)N$$

$$S_{mix} = S_A + S_B$$

$$\Delta S_{mixing} = S_{mix} - S$$

$$\boxed{\Delta S_{mixing} = -Nk[x\, lnx + (1-x)ln(1-x)]}$$

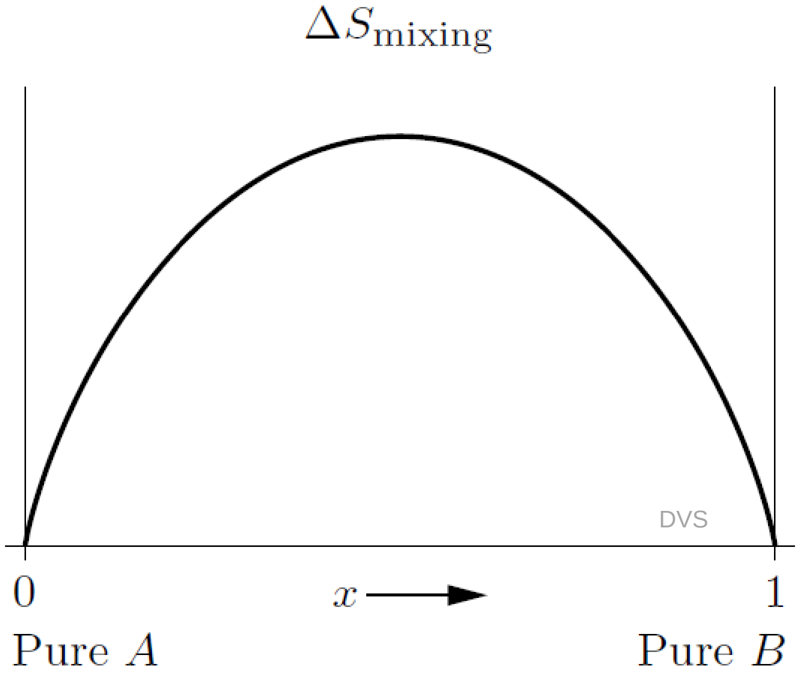


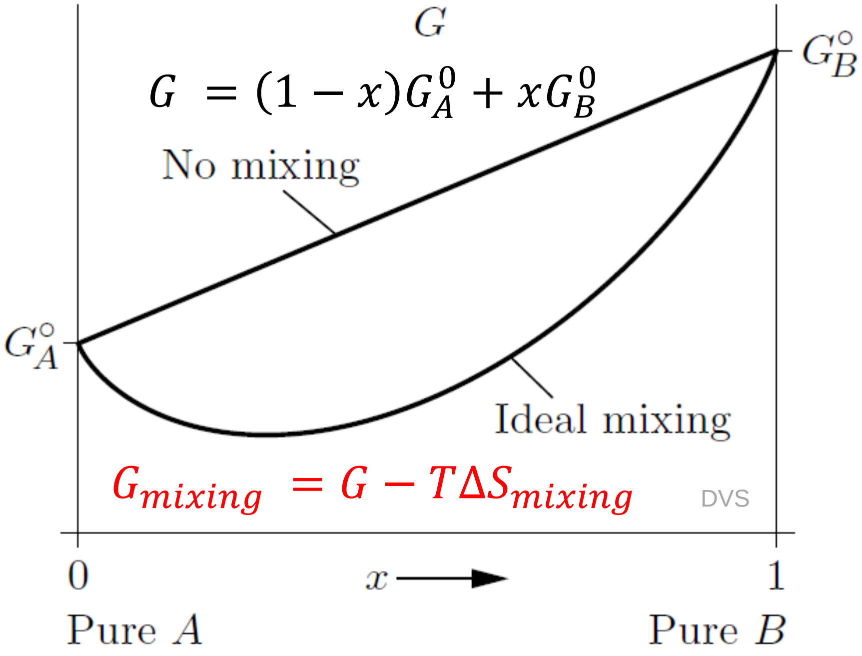
DVS

Ideal mixing

$$G \;= U - TS + PV$$

$$\Delta S_{mixing} = -Nk[x\,lnx + (1-x)ln(1-x)]$$





Entropy of mixing

$$\Delta S_{mixing} = -Nk[x\, lnx + (1-x)ln(1-x)]$$

Per one mole: $$\Delta S_{\mathrm{mixing}} = -R\left[x \ln x + (1-x)\ln(1-x)\right]$$ DVS

$$Nk = nR$$

Boltzmann constant

$$k = 1.380649 \times 10^{-23}\, J/K$$

Gas constant

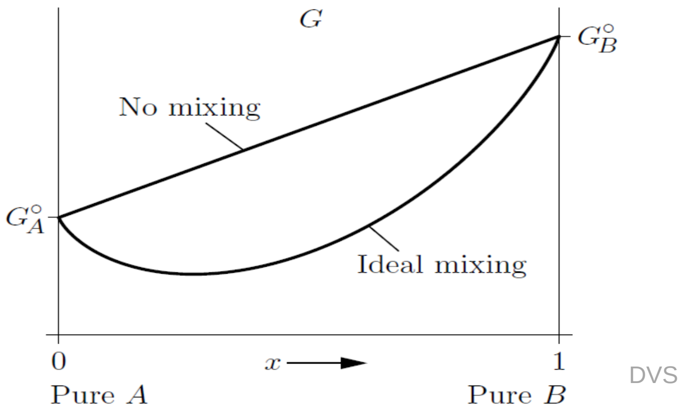
$$R = 8.3145\, J/(mol \cdot K)$$

Avogadro number

$$N_A = 6.022\, 10^{23}\, 1/mol$$

$$N_A k = R$$

Ideal mixing



- There is minimum in the function $G_{mixing}(x)$.

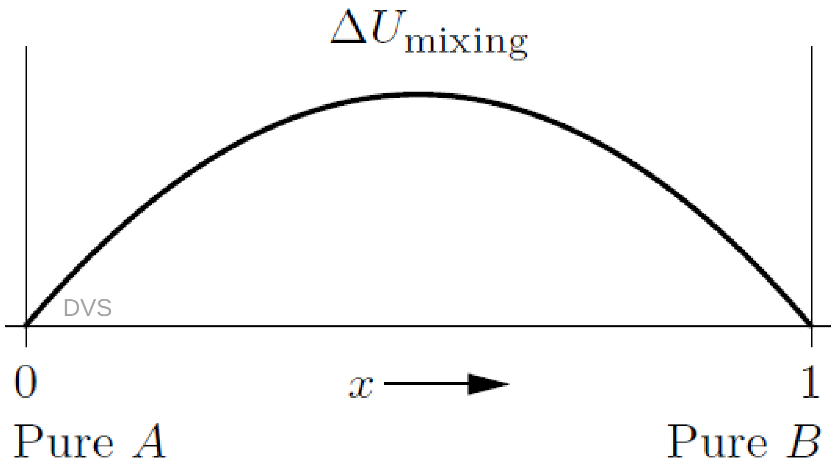
- Its derivative with respect to x goes to infinity at x = 1 and to minus infinity at $x = 0$.

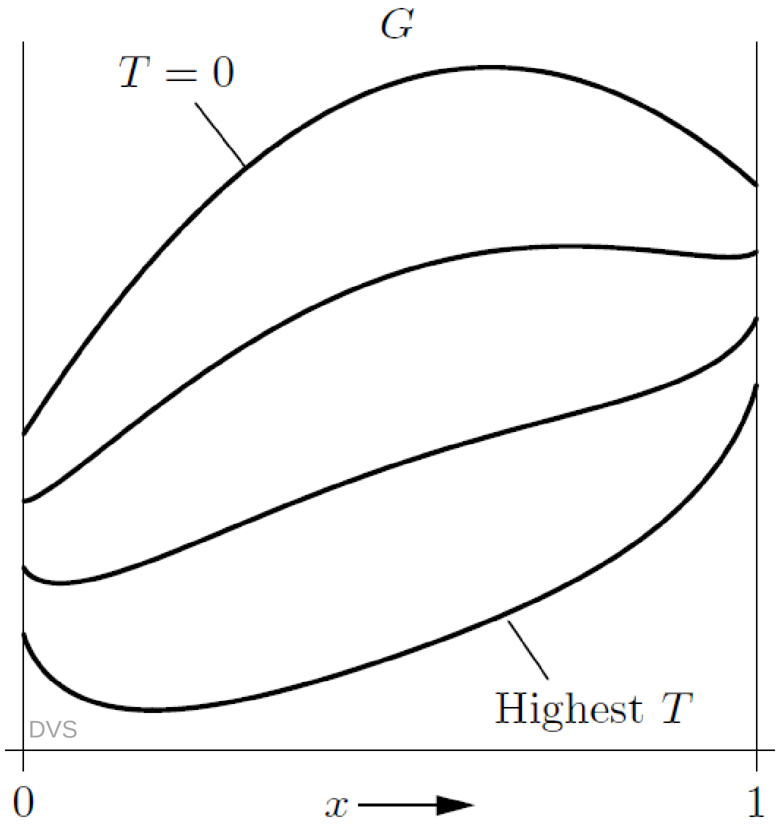
- The graph of this expression therefore has a vertical slope at each endpoint.

- Because $G_{mixing} < G$, **system will always be in the mixed state**.

Mixing with increase of energy

$$G = U - TS + PV$$

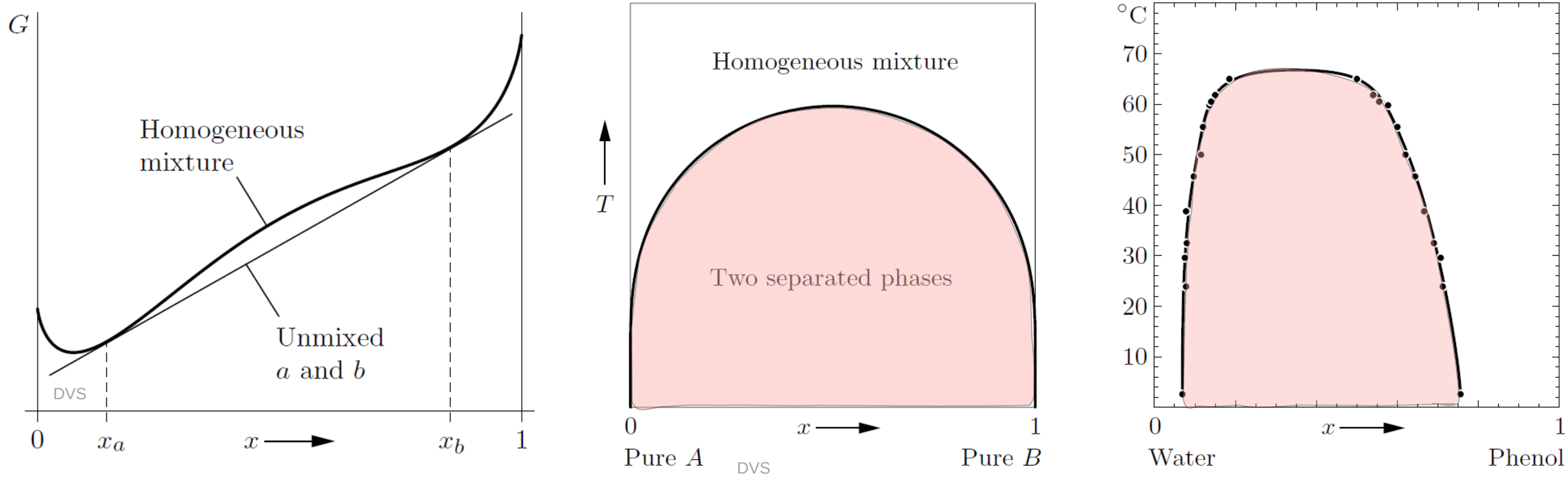




Mixing A and B can often increase the energy of the system. The concave-down free energy function indicates an unstable mixture.

Spontaneous separation

$$G = U - TS + PV$$



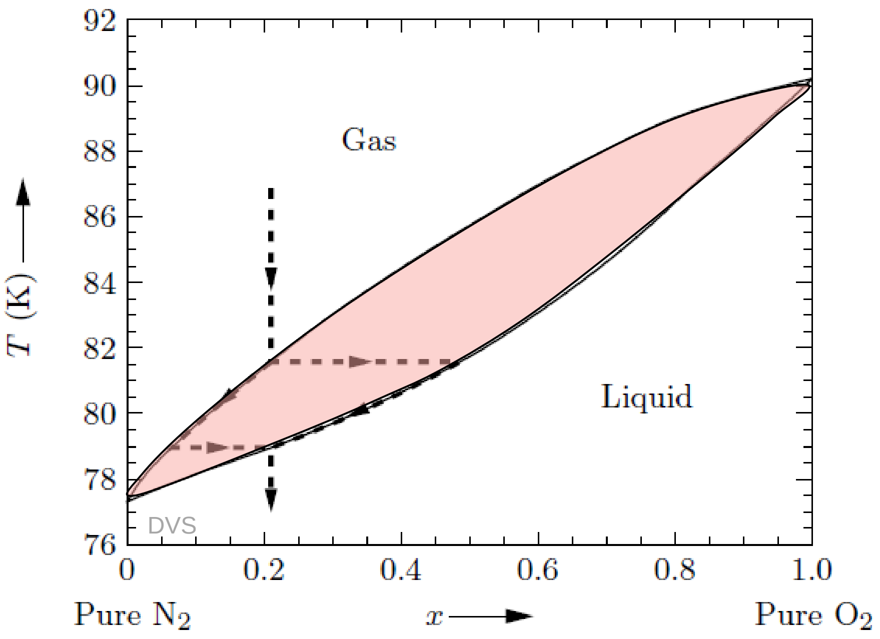
If the composition of the system lies between x_a and x_b, it will spontaneously separate into an A-rich phase of composition x_a and a B-rich phase of composition x_b.

Solubility gap

Air: 78% N_2 and 21% O_2. Boiling temperature of O_2 (T_B) is 90.2 K and boiling temperature of N_2 is 77.3 K (T_A) . But transition into the liquid state does not happen in two steps: at 90.2 and 77.3 K. It starts at 81.6 K only. Why?

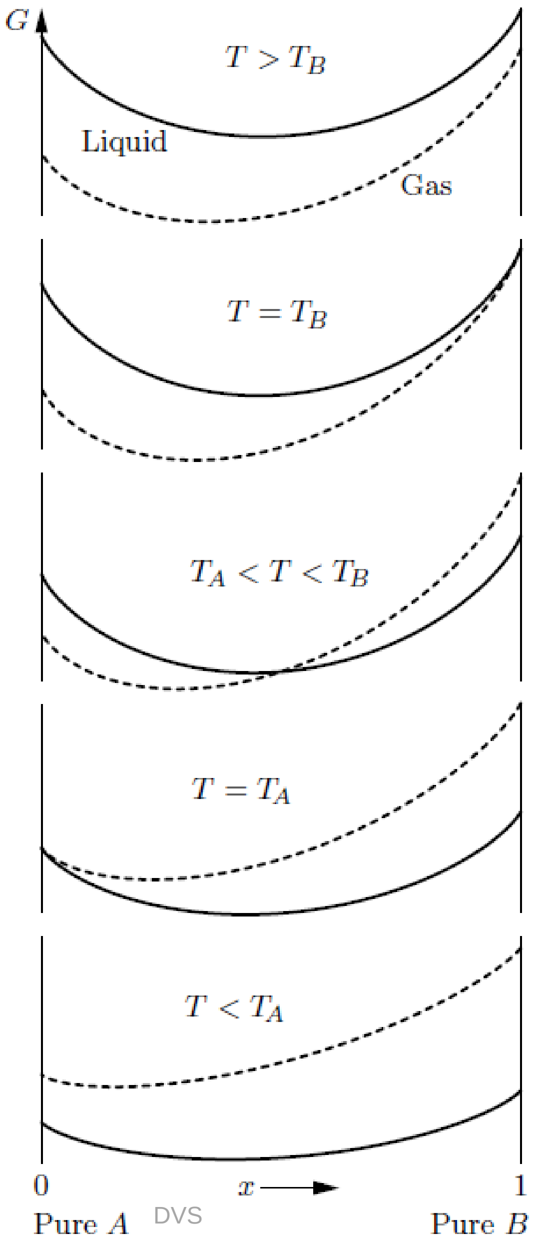
Answer is in Gibbs free energy of mixtures.

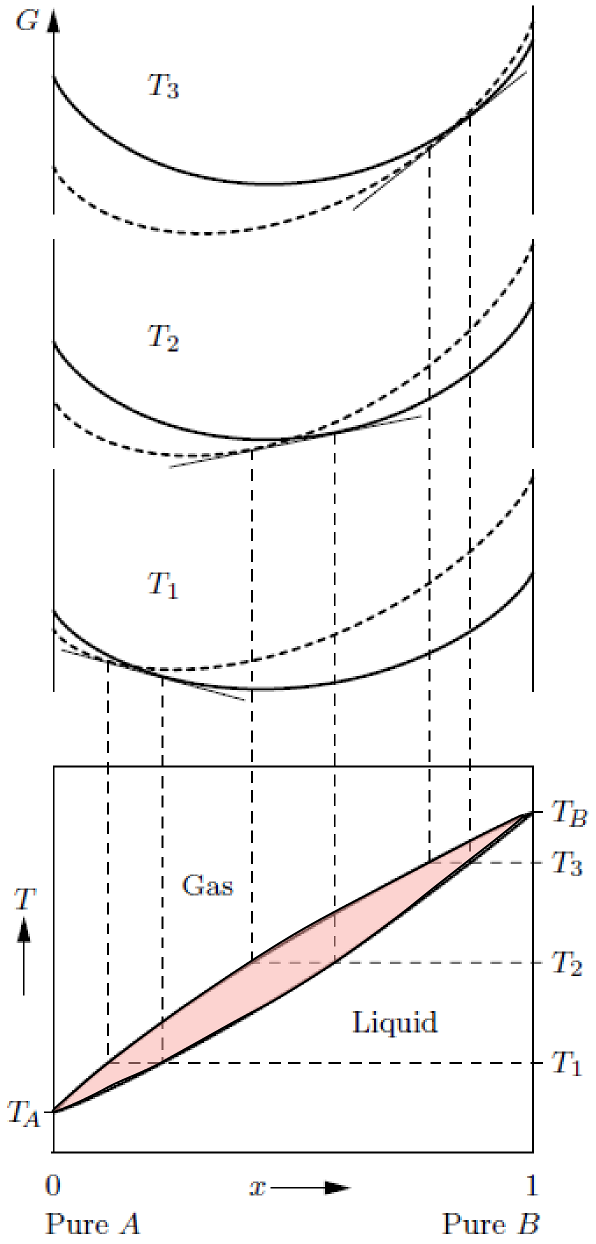
$$G = U - TS + PV$$



Ideal behavior of the mixture of N_2 and O_2 in liquid and gas states.

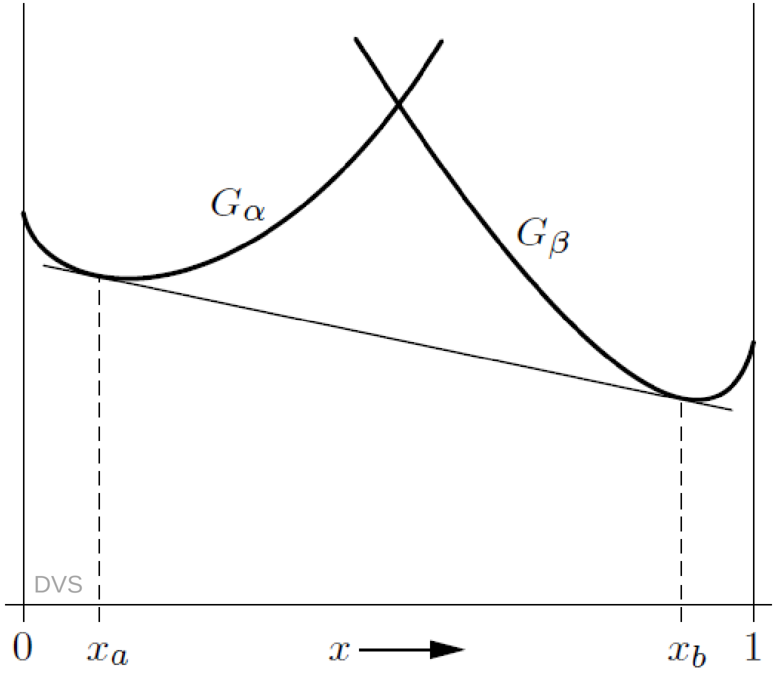
At 81.6 K, a liquid consisting of 48% oxygen begins to condense.





Phase Changes of an Eutectic System

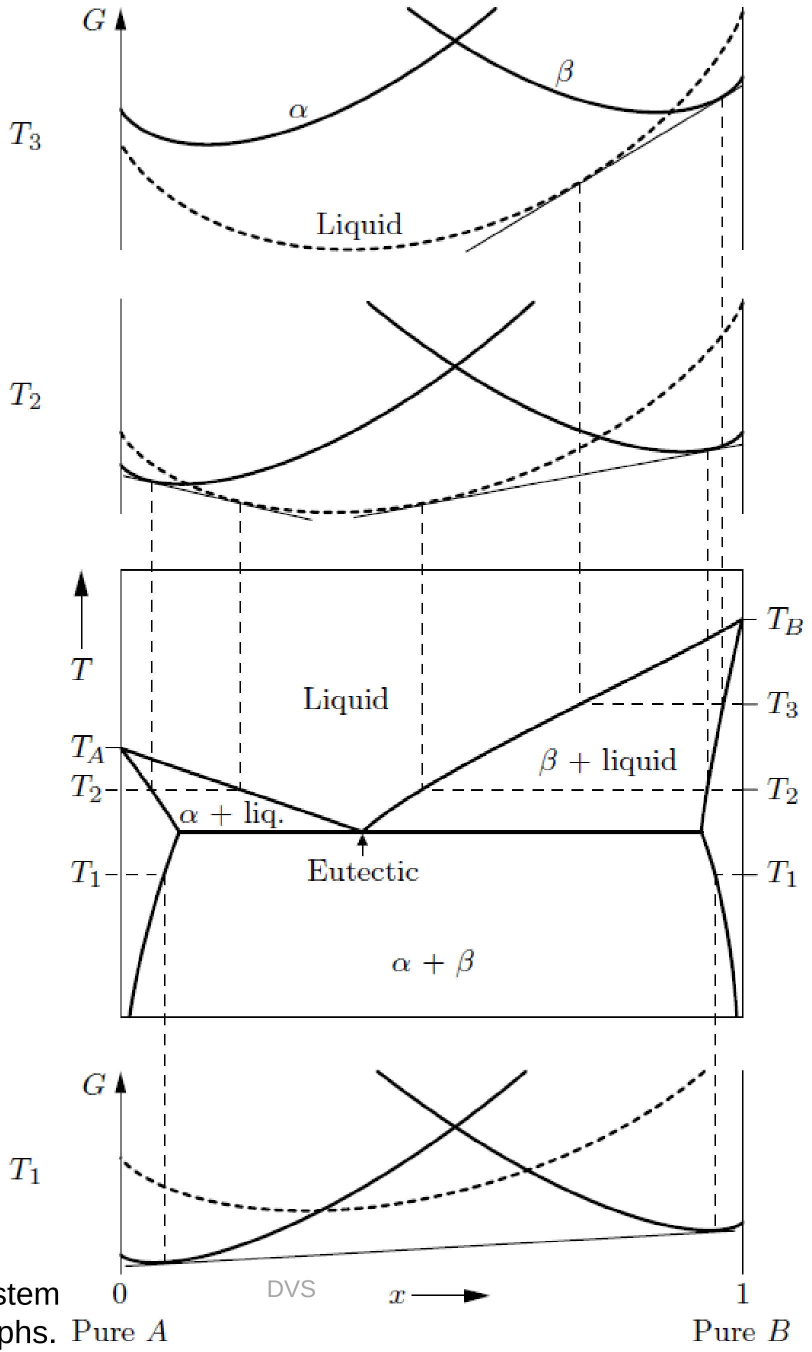
"easily melted"



Free energy graphs for a mixture of two solids with different crystal structures: α and β.

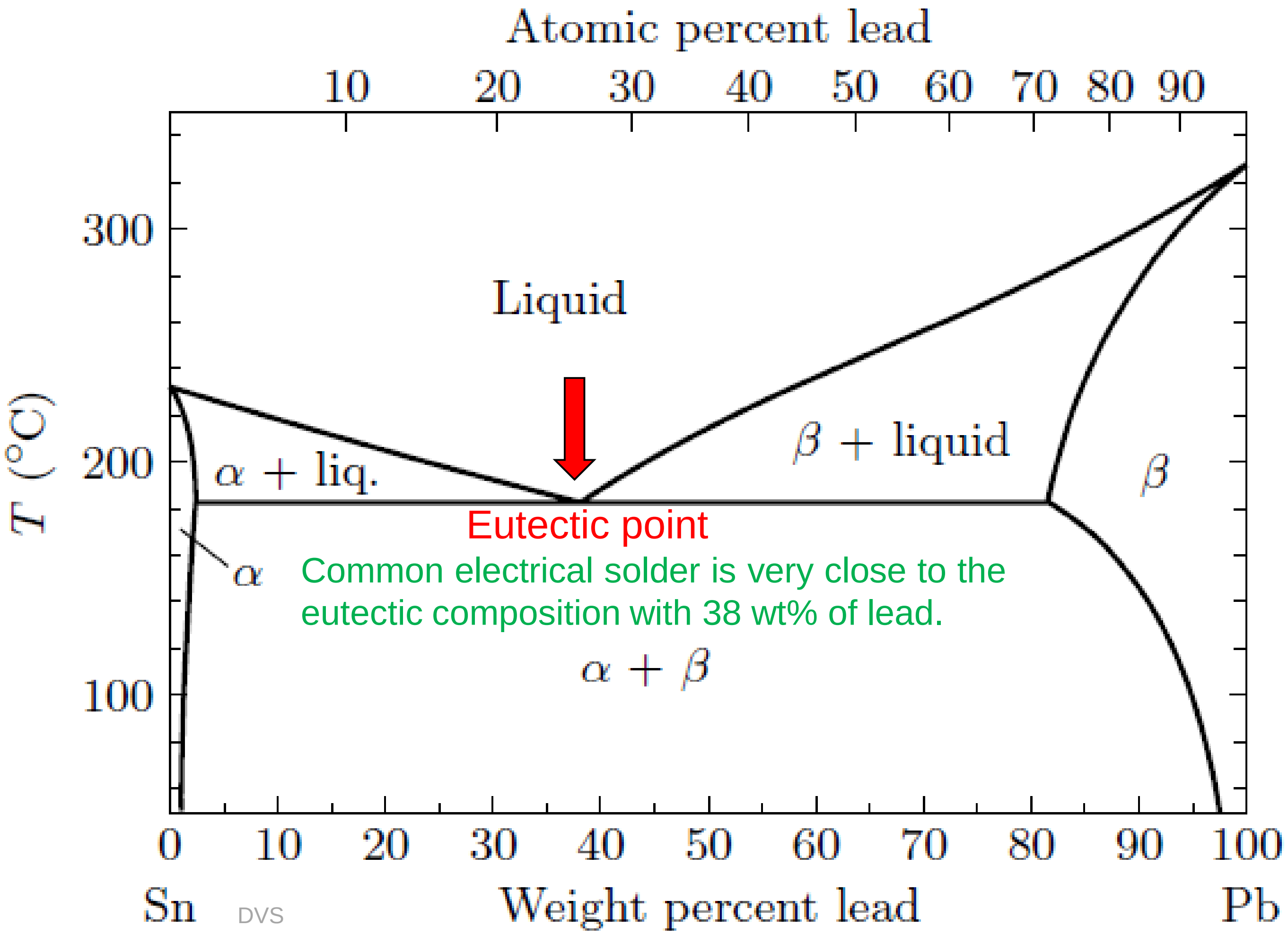
An eutectic system from the Greek eu = well and texis = melting is a heterogeneous mixture of substances that melts at a temperature that is lower than the melting point of any of the constituents.

The most common case is when the mixed solids have different crystal structures, and the unmixed combination of phases close in composition to pure ones is stable at intermediate concentrations.



Phase diagram of an eutectic system reconstructed from free energy graphs.

Example of an Eutectic System



Eutectic point

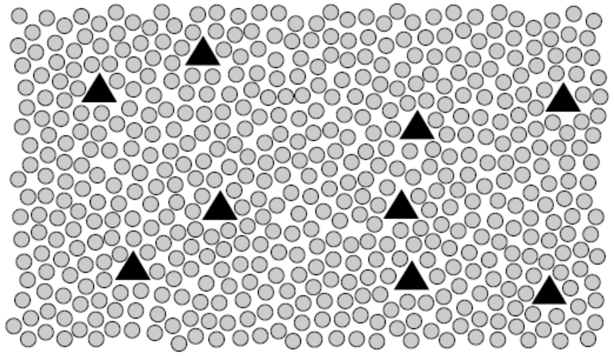
Common electrical solder is very close to the eutectic composition with 38 wt% of lead.

Phase diagram for the mixture of tin and lead.

The eutectic point corresponds to a special composition at which the melting temperature is the lowest, lower than that of pure substances. A liquid near the eutectic composition remains stable at low temperatures because it has more mixing entropy than the unmixed combination of solids.

There is an unmixed combination of Sn-rich and Pb-rich phases in the solid solution.

Dilute solutions



DVS

Is sea water a dilute solution?
Is pure water a dilute solutions?

- A dilute solution is a mixture, in which one component (the solvent) is dominant or primary and the other component (the solute) is minor or secondary.
- There could be several solute components an a solvent.
- The solute molecules are much less abundant than the solvent molecules.
- The solute molecules are "always" surrounded by solvent molecules and rarely interact directly with other solute molecules.
- The solute in a dilute solution behaves like an ideal gas.

Molality and molarity

Molality $m = \dfrac{Number\ of\ moles\ of\ solute}{Number\ of\ kilograms\ of\ solvent}$

- Molality is the number of moles of solute per number of kilogram of solution.
- Molality is dimensionless unit.
- Molarity is the number of moles of solute per number of liters of solution.
- Molality and molarity are different parameters, but for dilute solutions in water, the two are almost identical.
- The pH of a solution is defined as minus the base-10 logarithm of the molality of H^+ ions:

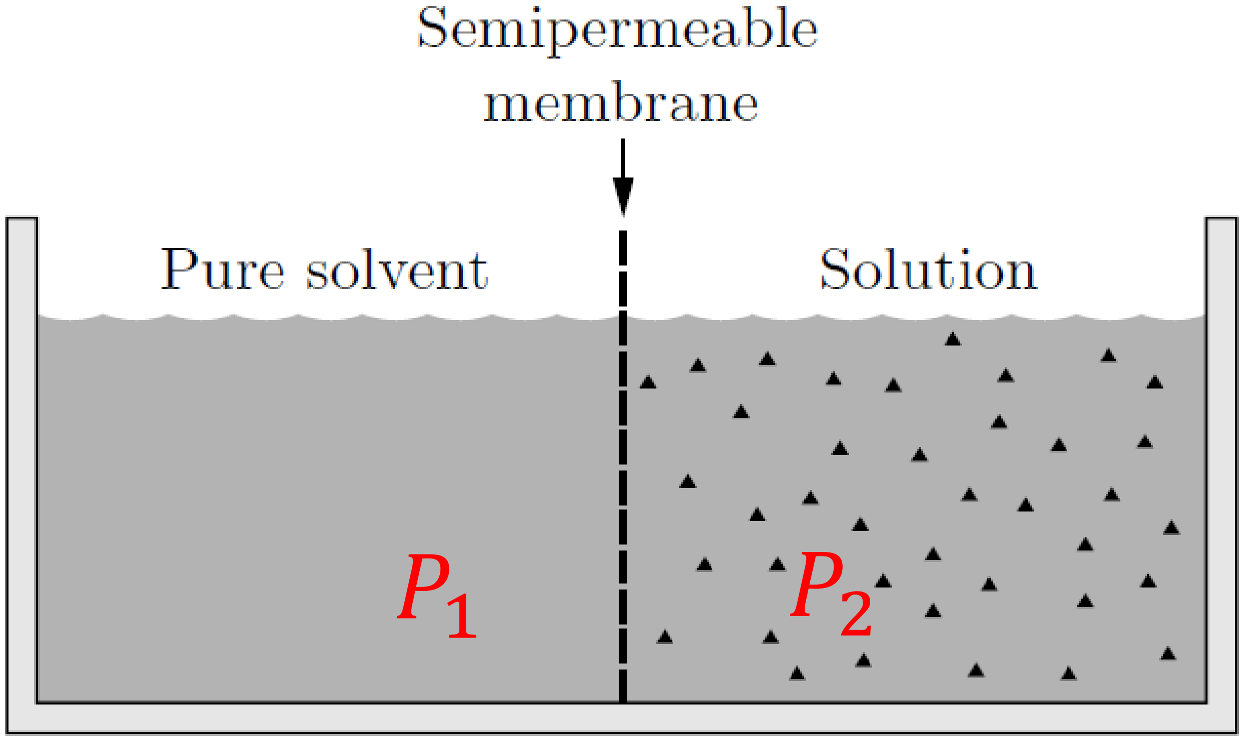
$$\mathbf{pH} \equiv -\log_{10} m_{H+}$$

For pH = 7, number of H^+ (and OH^-) moles per kilogram of solvent is 10^{-7}.

When the pH is less than 7 (indicating a higher H+ concentration) we say the solution is **acidic**, while when the pH is greater than 7 (indicating a lower H+ concentration) we say the solution is **basic**.

Osmotic pressure

The solvent molecules will spontaneously flow from the pure solvent into the solution. This flow of molecules is called osmosis.



DVS

Examples of semipermeable membranes: membranes surrounding plant or animal cells, which are permeable to water and small molecules but not to larger molecules, and the membranes that are used in industry for the desalination of seawater.

The osmotic pressure is described by Van't Hoff's Formula:

$$(P_2 - P_1) = \frac{kTN_B}{V} = \frac{RTn_B}{V}$$

N_B is number of molecules of solute

Examples of osmotic pressure

Van’t Hoff’s Formula: $$(P_2 - P_1) = \frac{kTN_B}{V} = \frac{RTn_B}{V}$$

In biological cell, there are about 200 water molecules for each molecule of something else. The difference of pressure being in water:

$$\frac{n_B}{V} = \left(\frac{1}{200}\right)\left(\frac{1\ \mathrm{mol}}{18\ \mathrm{cm}^3}\right)\left(\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3 = 278\ \mathrm{mol/m}^3$$

$$\frac{n_B}{V} = 278\ \frac{mol}{m^3}$$

$$(P_2 - P_1) = 6.9\ bar$$

$$(278\ \mathrm{mol/m}^3)(8.3\ \mathrm{J/mol{\cdot}K})(300\ \mathrm{K}) = 6.9 \times 10^5\ \mathrm{N/m}^2$$

An animal cell membrane would burst, but plant cells can withstand such a pressure.

Seawater has a salt concentration of about 35 kg/m³, corresponding to an osmotic pressure of about 27×10^5 Pa (27 bar). This pressure value corresponds to the pressure exerted by a water column of 270 m high.

For 1 m³ of pure water: $U = PV = 27 \times 10^5\ \mathrm{Pa} \times 1\ \mathrm{m}^3 = 2.7\ \mathrm{MJ}\ (0.75\ \mathrm{kWh})$

In Norway, electric power consumption (kWh per capita) is ≈66 kWh per day.

This is an amount of energy needed to lift 1 m³ of water (1000 kg) to a height of about 270 m.

For NaCl the maximum solubility is about 360 kg/m³. Then, in principle, extracted osmotic energy could be one order of magnitude higher.

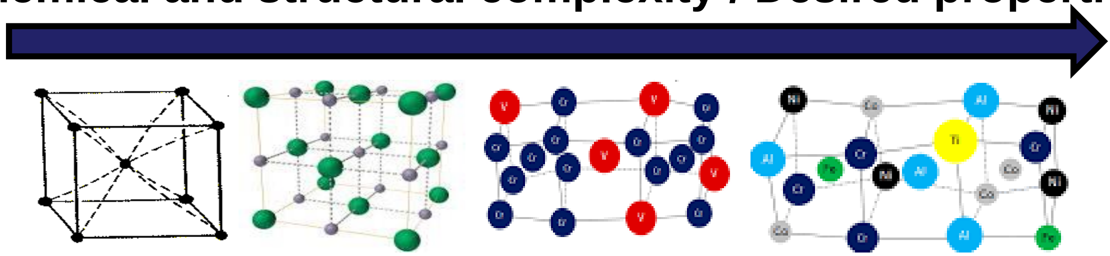
https://www.sciencedirect.com/topics/engineering/salinity-gradient-power

Mixtures in High Entropy Alloys (HEAs)

High Entropy Alloys (HEAs): Alloys that contain at least 5 principal elements, each having an atomic percentage between 5 - 35 at.%.

Project “**MAGNIFICENT - Additively manufactured magnetic high entropy alloys for renewable electricity**”, funded by the Research Council of Norway (pr. nr 287979) within the Nano2021 Program

Chemical and structural complexity / Desired properties



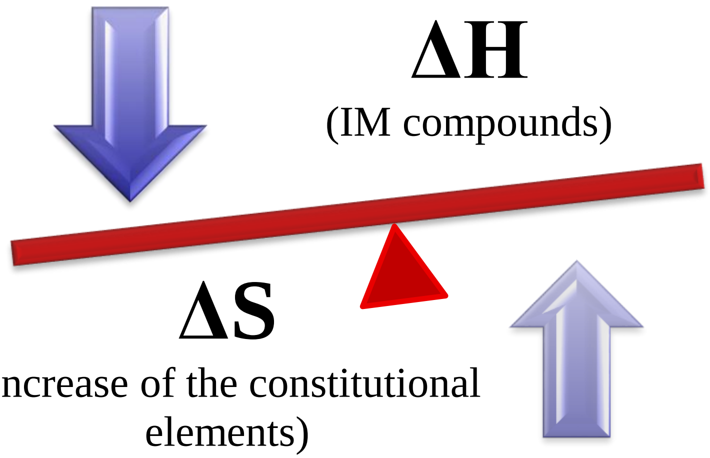
Pure metals

Binary compounds

Conventional alloys

HEAs

$$\boxed{\Delta G = \Delta H - T\cdot\Delta S}$$

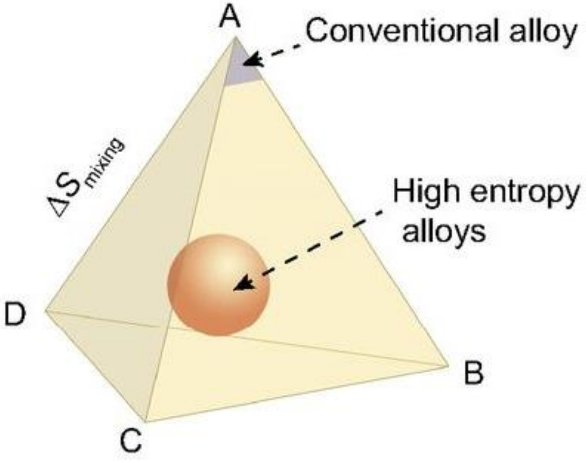


ΔH

(IM compounds)

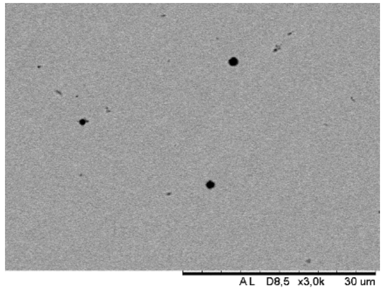
ΔS

(Increase of the constitutional elements)



SEM evidence of spinodal decomposition

Sample 1



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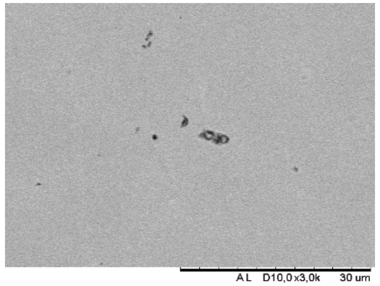
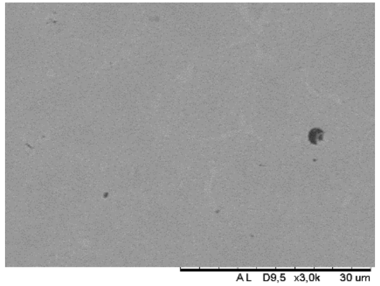


Sample 3



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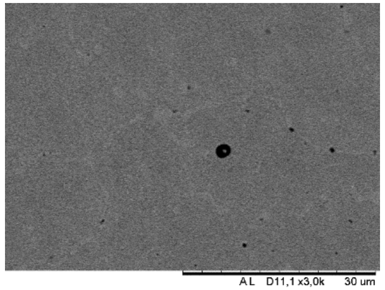
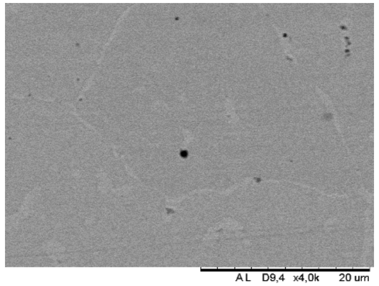


Sample 5



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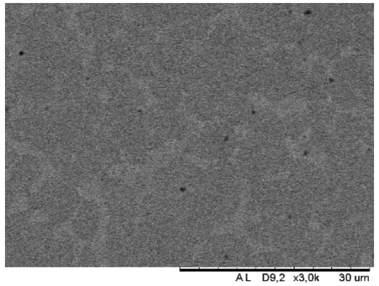

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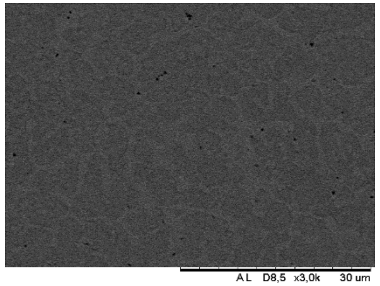

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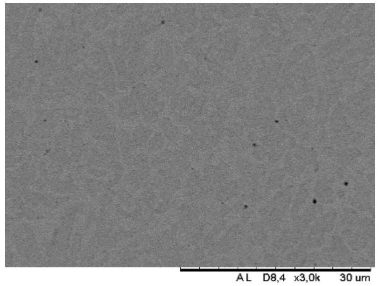

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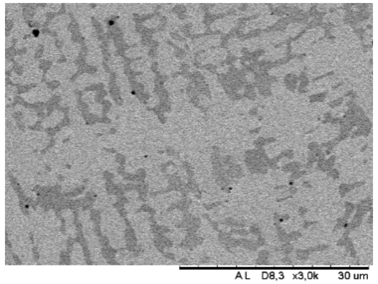
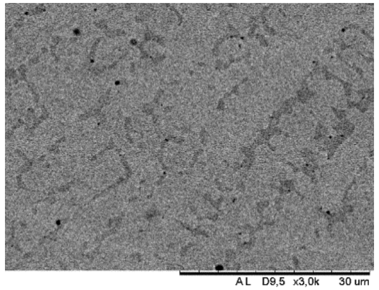
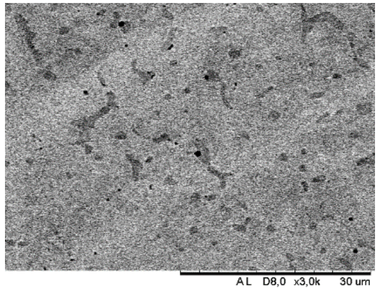


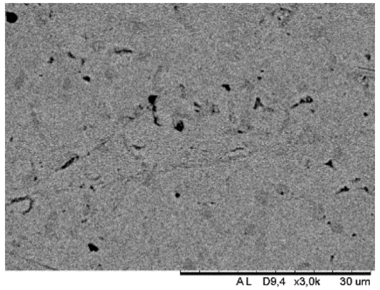
Sample 10



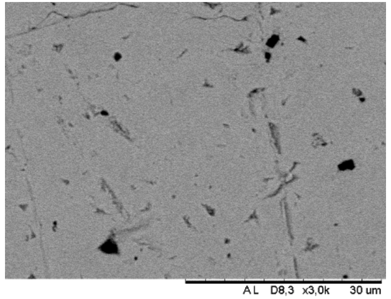
Sample 11



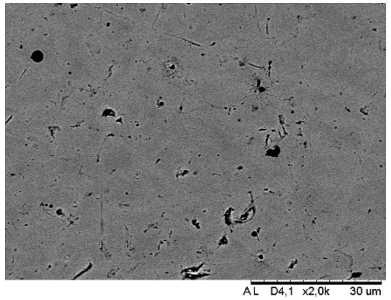
Sample 12



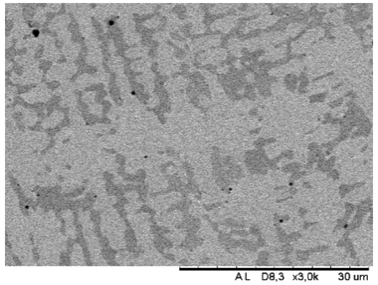
Sample 13



Sample 14



Spinodal decomposition



- Spinodal decomposition occurs when one thermodynamic phase spontaneously (i.e., without nucleation) separates into two phases. Decomposition occurs in the absence of nucleation because certain fluctuations in the system reduce the **free energy**. As a result, the phase change occurs immediately.
- Spinodal decomposition is observed, for example, in mixtures of metals. When the two phases emerge in approximately equal proportion (each occupying about the same volume or area), they form characteristic intertwined structures that gradually coarsen.
- Spinodal decomposition occurs when a homogenous phase becomes thermodynamically unstable. An unstable phase lies at a maximum in free energy.

https://en.wikipedia.org/wiki/Spinodal_decomposition

Summary

- Mixtures of phases are common in physics and the mixing strongly influences phase transitions of pure phases.
- It is the entropy of mixing that influence phase transitions.
- Key for understanding phase transitions in mixtures is in concentration dependence of Gibbs free energy.
- The entropy of mixing, together with the increase of total energy, leads to appearance of solubility gap in the phase diagram of the mixture.
- The solubility gap leads to the split of homogeneous mixture into co-existing phases.
- A dilute solution is an important type of mixtures, in which the solute molecules are much less abundant than the solvent molecules.
- A contact of a dilute solution with solvent through a membrane blocking solute molecules leads to the phenomenon of osmotic pressure.
- The unique properties of mixtures are intensively used in the modern science and technology.