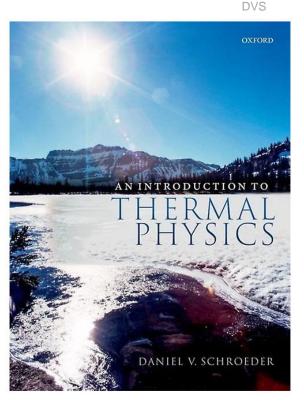


# Phase transitions of mixtures





Tuesdays: Store fysiske auditorium Wednesdays: Store fysiske lesesal

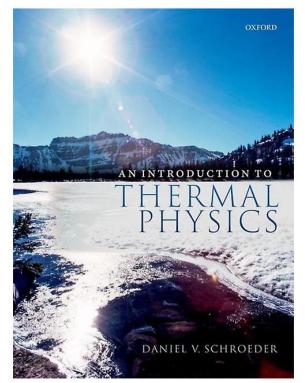
• Tuesday September 26

Free energies

- Wednesday October 4
- Tuesday October 31
- Tuesday November 7
- Wednesday November 8

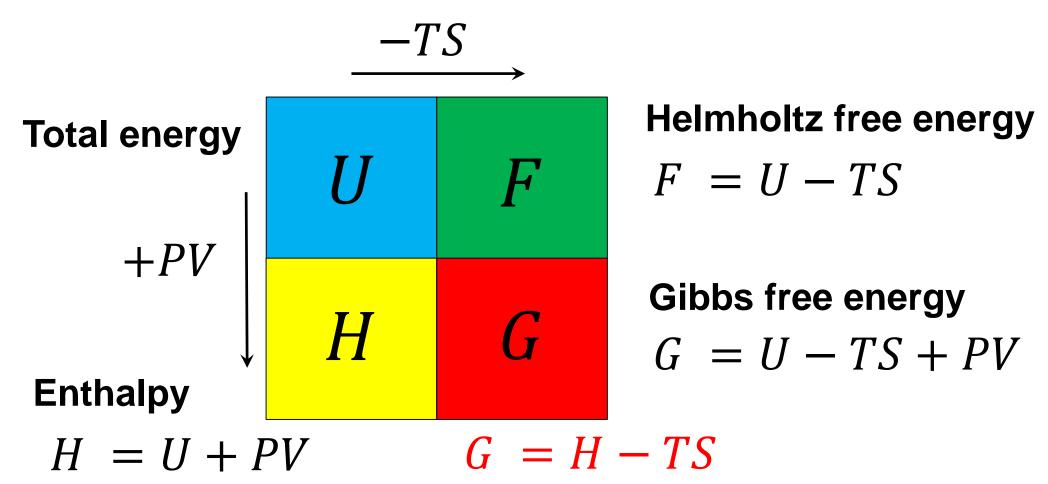
Tuesdays: 10:15 -12:00 Wednesdays: 12:15 -14:00

- Phase transitions of mixtures
- Electron gas
- Black body radiation
- Specific heat





# Thermodynamic potentials



By subtracting  $\mu N$  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),  $\Phi = U - TS - \mu N$ .

# Fuel Cell

$$H_2 O \leftarrow H_2 + \frac{1}{2} O_2$$

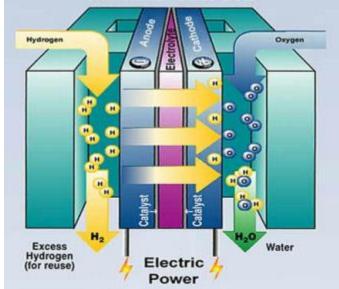
To heat 1 mole of water to 100 °C one needs 40.7 kJ.

4 kJ

237 kJ = 286 kJ - (298 K)(163 J/K).

 $S_{H20} = 70 \text{ J/K}; S_{H2} = 131 \text{ J/K}; S_{02} = 205 \text{ J/K}.$ 

Ideal hydrogen fuel cell has an "efficiency" of 83%, much better than any practical heat engine.



ttps://batteryuniversity.com/article/bu-210-how-does-the-fuel-cell-work

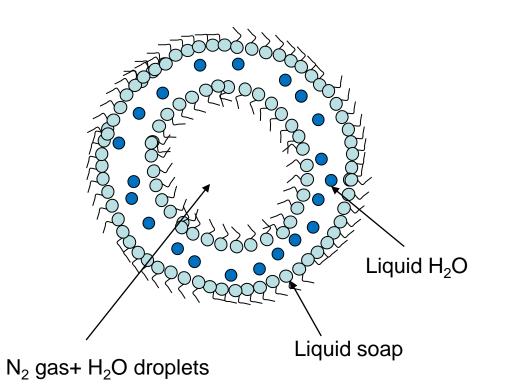
# Evaporation of liquid nitrogen $\Delta G = \Delta H - T \Delta S$

	Element	Nitrogen
	Molar Heat Capacity	20.8 J K <sup>-1</sup> mol <sup>-1</sup>
$\Delta S$	Standard Molar Entropy	153.3 J K <sup>-1</sup> mol <sup>-1</sup>
	Enthalpy of Fusion	0.72 kJ mol <sup>-1</sup>
$\Delta H$	Enthalpy of Vapourization	5.577 kJ mol <sup>-1</sup>

 $\Delta G = \Delta H - T \Delta S$  5.577 - 0.1533\*298 = -40,1064 (kJ mol<sup>-1</sup>). Yes

 $T = \Delta H / \Delta S \qquad 5.577 / 0.1533 = 36,4 \text{ (K)}$   $T = 2 * \Delta H / \Delta S \qquad 2^* (5.577) / (0.1533) = 72,8 \text{ (K)}$  $\Delta G = 2 * \Delta H - T \Delta S \qquad (2^* 5.577) - 298^* 0.1533 = -34,5294 \text{ (kJ mol}^{-1}) \text{ Yes}$ 

## Soap-water mixture



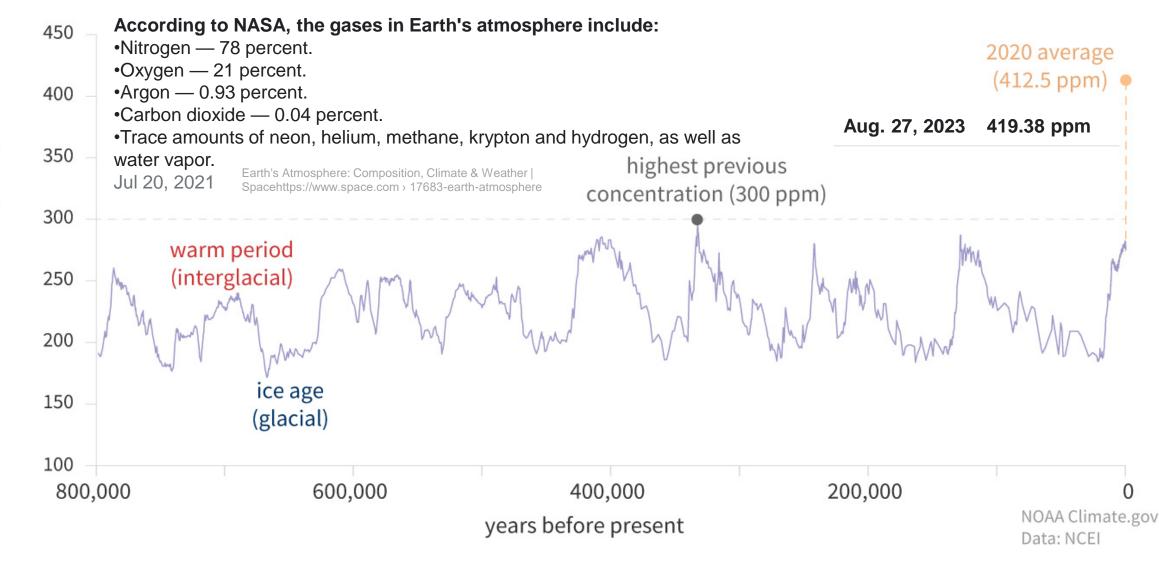


#### Frozen soap bubble on snow at –7 $^{\circ}$ C (19 $^{\circ}$ F)

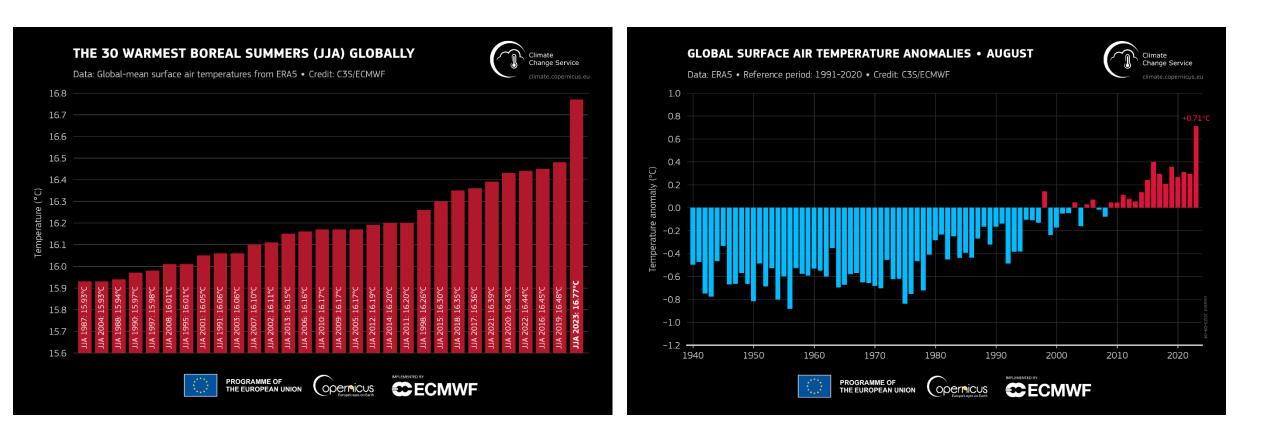
By Larry-pilot - Own work, CC BY 4.0, https://commons.wikimedia.org/w/index.php?curid=64273475

carbon dioxide (ppm)

#### CARBON DIOXIDE OVER 800,000 YEARS



# **Global warming**



Summer 2023: the hottest on record | Copernicus

8

#### Mixture of gases: physiological effects of CO<sub>2</sub> 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 rundown. 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.

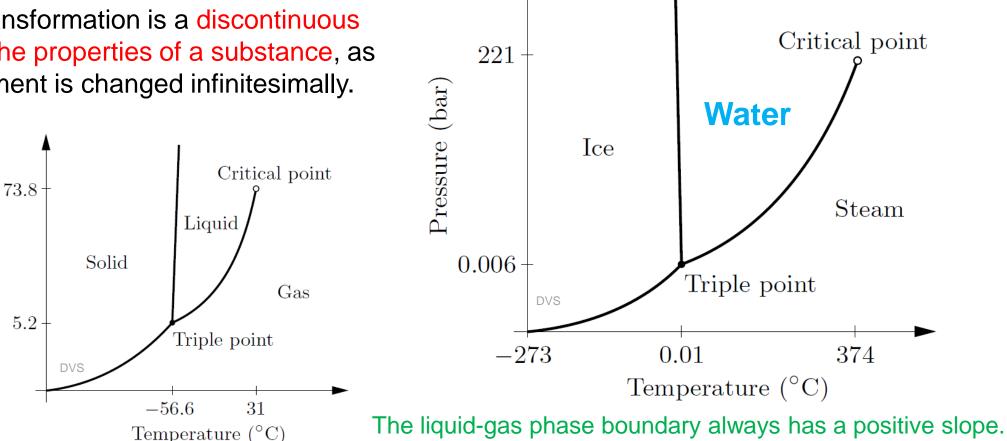
Pressure (bar)

 $CO_2$ 

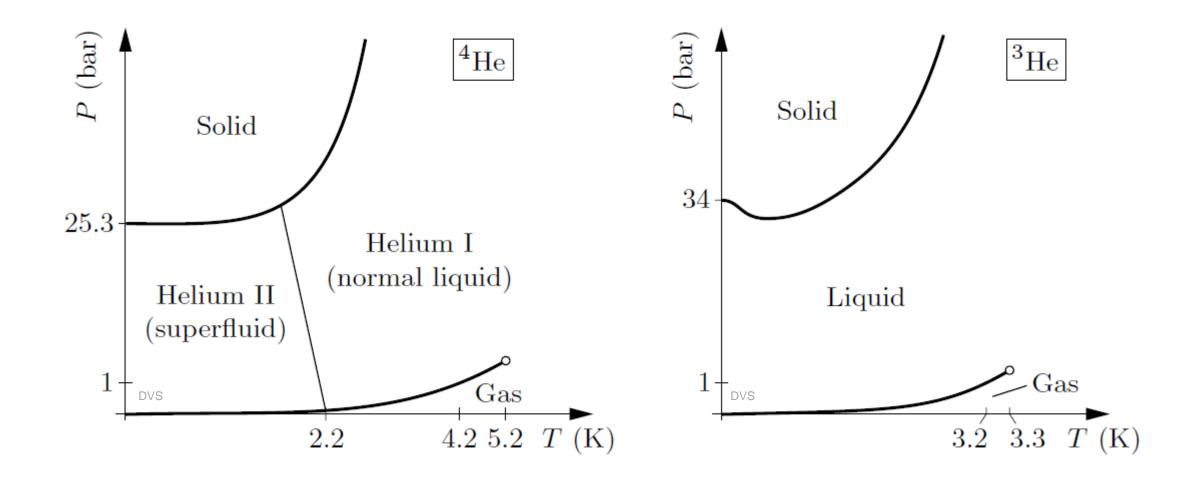
### Phase Diagrams of Pure Substances

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.

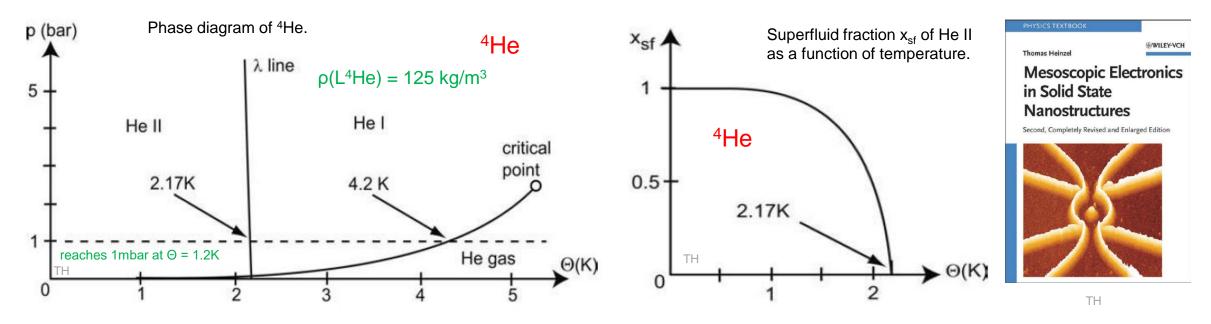
A phase transformation is a discontinuous change in the properties of a substance, as its environment is changed infinitesimally.



#### Phase diagrams of helium



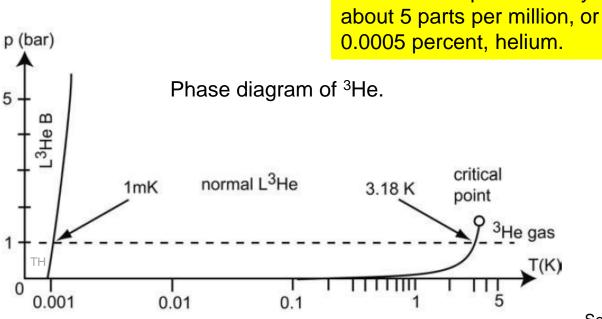
## Properties of liquid helium

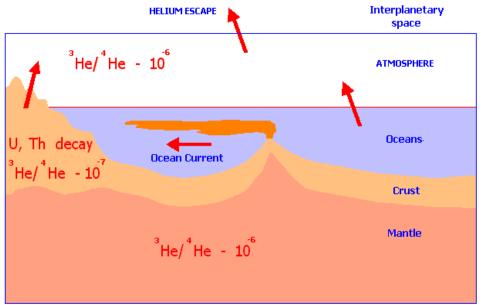


- Helium is the only element that remains liquid when cooled to the temperatures well below 1 mK. The latent heat that has to be absorbed when liquid helium is evaporated generates the cooling power.
- Helium comes in two isotopes, the boson <sup>4</sup>He and the fermion <sup>3</sup>He.
- Helium is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

## Properties of pure <sup>3</sup>He

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

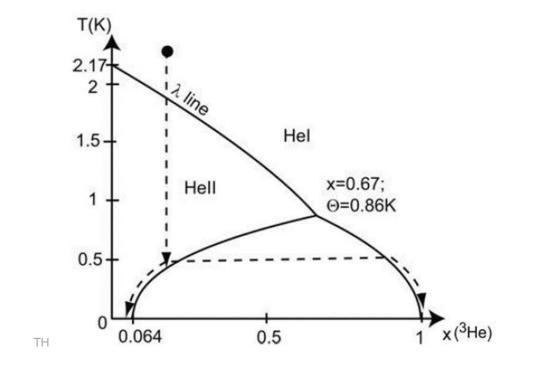




Seamounts release plumes of <sup>3</sup>He-rich water into the ocean. These helium plumes can be traced for thousands of kilometres http://www.threesology.org/3sxamples13.php

## The <sup>3</sup>He/<sup>4</sup>He mixture

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

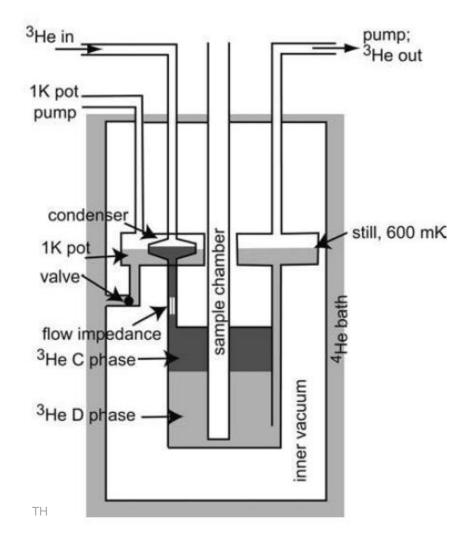


Phase separation is important for operation of dilution refrigerators.

Phase diagram of the <sup>3</sup>He/<sup>4</sup>He mixture vs. <sup>3</sup>He concentration

## <sup>3</sup>He/<sup>4</sup>He dilution refrigerator

- Since the dilute <sup>3</sup>He phase (D) can be thought of as the <sup>3</sup>He vapour of the <sup>3</sup>He-rich phase (C) with a significant vapour pressure even at T close to 0, pumping the <sup>3</sup>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 <sup>3</sup>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 <sup>3</sup>He is significant, while that of <sup>4</sup>He is negligible. The still therefore effectively distils <sup>3</sup>He from the D phase.
- <sup>3</sup>He is re-condensed in the "1K pot".



# Description of gas mixtures: basic mathematics G = U + PV - TS $S = k \ln \Omega$ $S_{total} = k \ln \Omega_{total} = k \ln (\Omega_A \Omega_B) = k \ln \Omega_A + k \ln \Omega_B = S_A + S_B.$ Stirling's approximation $N! \approx N^N e^{-N} \sqrt{2\pi N}$

#### Multiplicity and entropy of a monatomic ideal gas:

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} (\sqrt{2mU})^{3N-1} \qquad S = Nk \left[ \ln\left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2} \right]$$

O a aluum Tatma da la anuatiana

## **Entropy of Mixing**

#### Sackur-Tetrode equation:

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

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

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

DVS

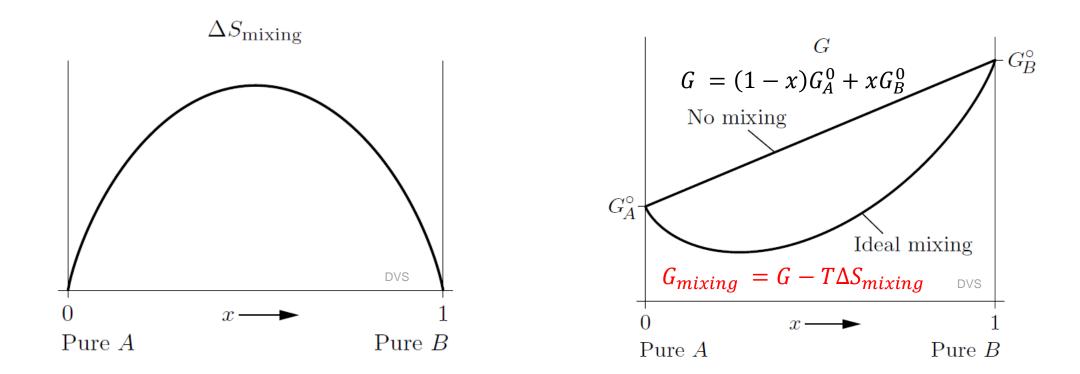
$$\Delta S_{mixing} = S_{mix} - S$$

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

## Ideal mixing

G = U - TS + PV

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



## Entropy of mixing

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

Per one mole:

$$\Delta S_{\text{mixing}} = -R \left[ x \ln x + (1-x) \ln(1-x) \right] \qquad \text{disc}$$

Nk = nR

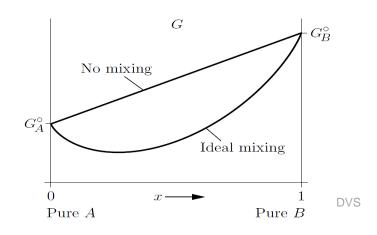
Boltzmann constantGas constant $k = 1.380649 \times 10^{-23} J/K$  $R = 8.3145 J/(mol \cdot K)$ 

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

 $N_A k = R$ 

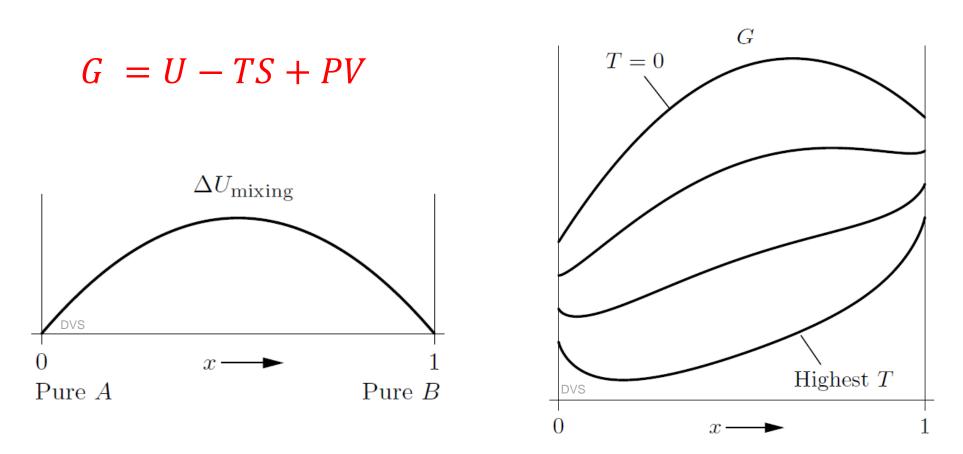
# Ideal mixing

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



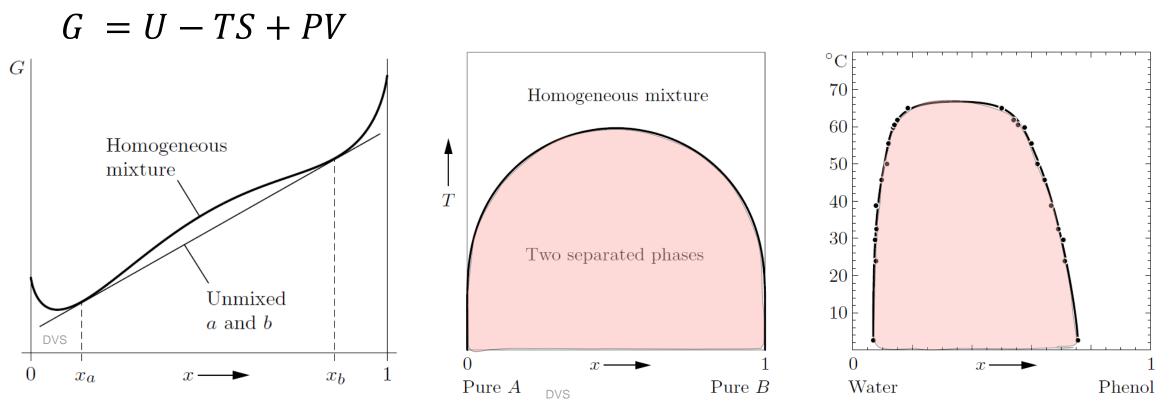
- Its derivative with respect to x goes to infinity at x = 0 and to minus infinity at x = 1.
- The graph of this expression therefore has a vertical slope at each endpoint.
- Because  $G_{mixing} < G$ , system will always be in the mixed state.





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

## Solubility gap



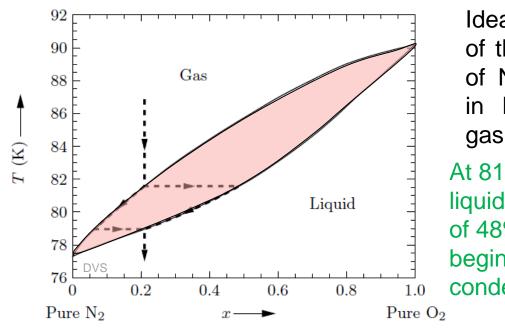
If the composition of the system lies between  $x_a$  and  $x_b$ , it will spontaneously separate into an A-rich phase of composition  $x_a$  and a B-rich phase of composition  $x_b$ . One says that the system has a solubility gap, or that the two phases are immiscible. Decreasing the temperature of this system widens the solubility gap.

#### Phase Changes in a Miscible Mixture

Air: 78% N<sub>2</sub> and 21% O<sub>2</sub>. Boiling temperature of O<sub>2</sub> ( $T_B$ ) is 90.2 K and boiling temperature of N<sub>2</sub> 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?

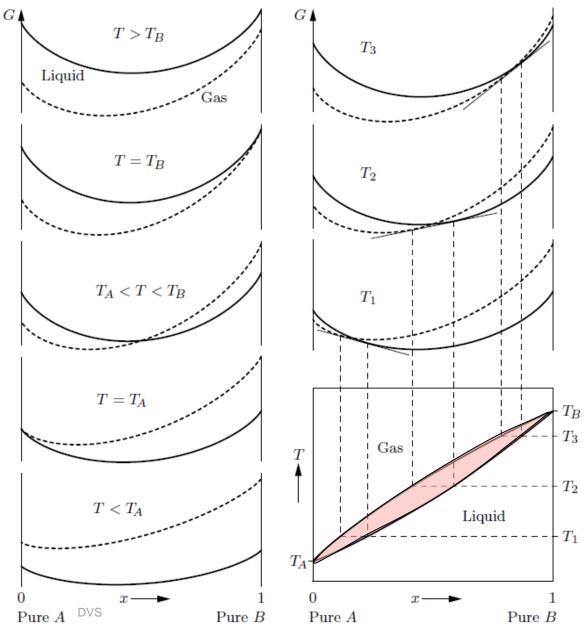
Answer is in Gibbs free energy of mixtures.

G = U - TS + PV

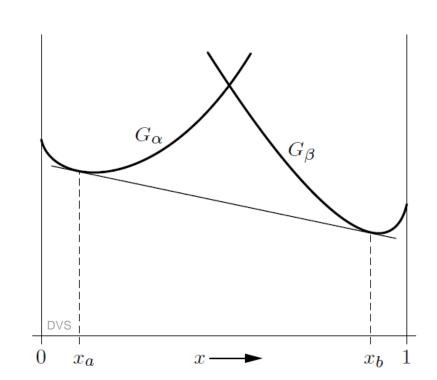


Ideal behavior of the mixture of  $N_2$  and  $O_2$ in liquid and gas states.

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



## Phase Changes of an Eutectic System

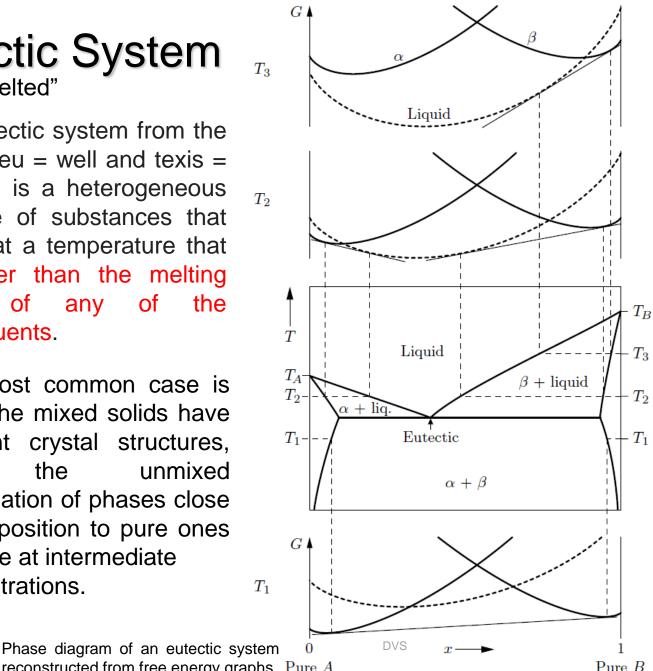


Free energy graphs for a mixture of two solids with different crystal structures:  $\alpha$  and  $\beta$ .

"easily melted"

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 of of point any the constituents.

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



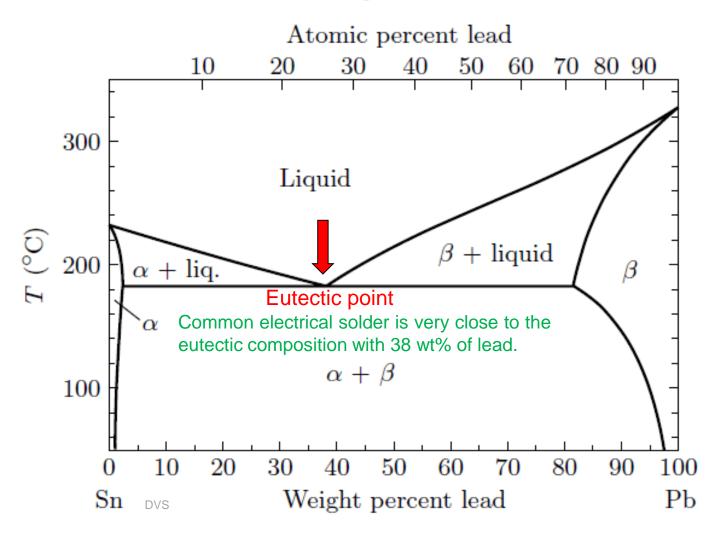
reconstructed from free energy graphs. Pure A

 $T_3$ 

 $T_2$ 

 $T_1$ 

#### **Example of an Eutectic System**



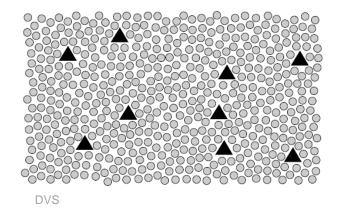
The eutectic point corresponds to a special composition at which the melting temperature is the lowest, lower than that of pure substances. A liquid near the eutectic composition remains stable at low temperatures because it has more mixing entropy than the unmixed combination of solids.

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

Phase diagram for the mixture of tin and lead.

## **Dilute solutions**

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

- 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  $OH^-$  in water) ions is  $10^{-7}$ .

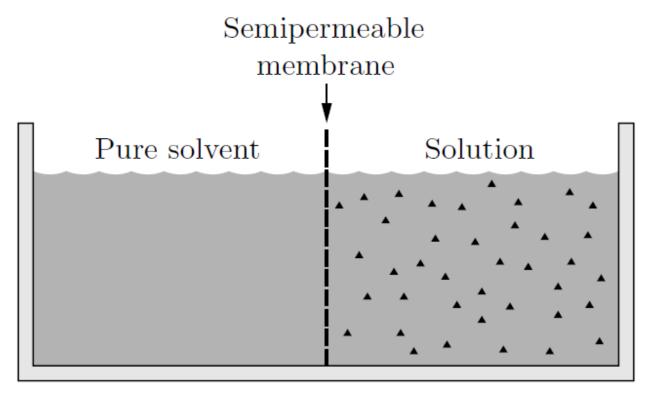
When the pH is less than 7 (indicating a higher H+ concentration) we say the solution is **acidic**, while when the pH is greater than 7 (indicating a lower H+ concentration) we say the solution is **basic**.

## **Osmotic pressure**

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

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:



DVS

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

### 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:

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

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

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

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

 $(P_2 - P_1) = 6.9 \ bar$ 

Seawater has a salt concentration of about 35 kg/m<sup>3</sup>, corresponding to an osmotic pressure of about  $27 \times 10^5$  Pa (27 bar). This pressure value corresponds to the pressure exerted by a water column of 270 m high.

For 1 m<sup>3</sup> of pure water:  $U = PV = 27 \times 10^5 \text{ Pa} \times 1 \text{ m}^3 = 2.7 \text{ MJ} (0.75 \text{ kWh})$ 

In Norway, electric power consumption (kWh per capita) is  $\approx 66$  kWh per day.

#### This is an amount of energy needed to lift 1 m<sup>3</sup> of water (1000 kg) to a height of about 270 m.

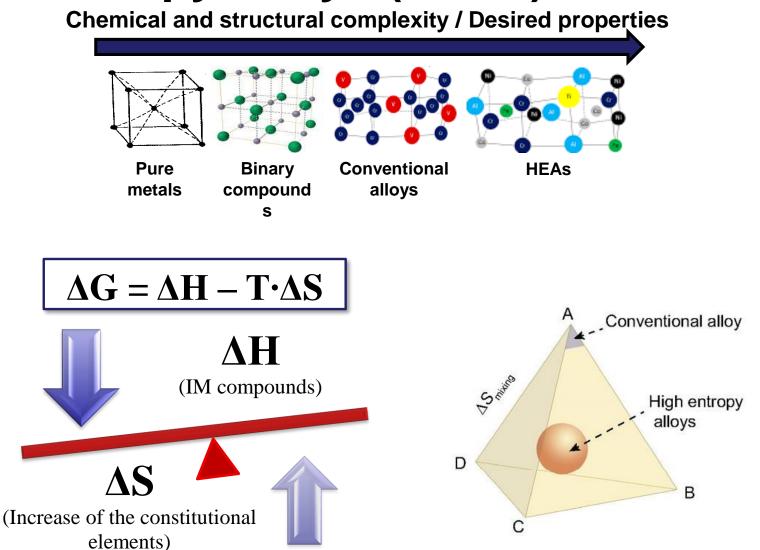
For NaCl the maximum solubility is about 360 kg/m<sup>3</sup>. Then, in principle, extracted osmotic energy could be one order of magnitude higher.

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

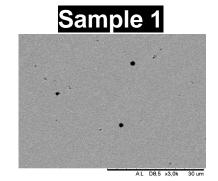
## **Mixtures in High Entropy Alloys (HEAs)**

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

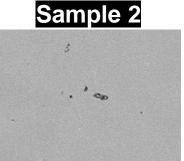
Project "<u>MAGNIFICENT -</u> <u>Additively manufactured</u> <u>magnetic high entropy</u> <u>alloys for renewable</u> <u>electricity</u>", funded by the Research Council of Norway (pr. nr 287979) within the Nano2021 Program



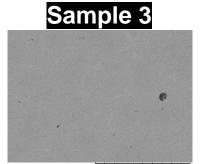
#### SEM evidence of spinodal decomposition

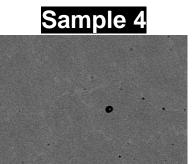


Sample 10



AL D10,0x3,0k

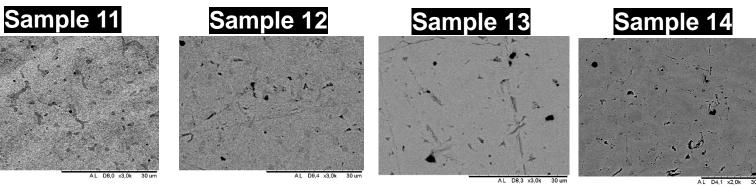




AL D11,1 x3,0k

AL D9,5 x3,0k

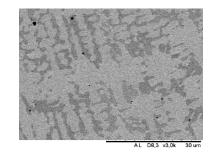
Sample 5 Sample 6 Sample 7 Sample 9 Sample 8 AL D9.4 x4.0k AL D9.2 x3.0k AL D8,5 x3,0k 30 um AL D8,3 x3,0k AL D8,4 x3,0k 30 un



30 un

AL D9,5 x3,0k

#### **Spinodal decomposition**



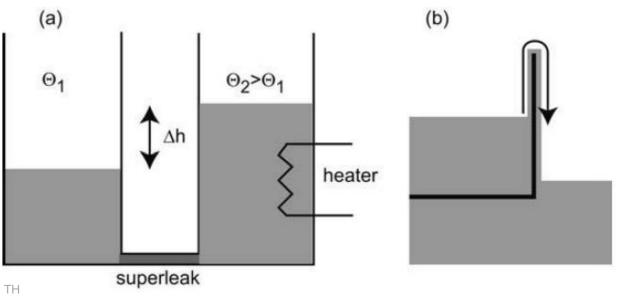
- Spinodal decomposition occurs when one thermodynamic phase spontaneously (i.e., without nucleation) separates into two phases. Decomposition occurs in the absence of nucleation because certain fluctuations in the system reduce the **free energy**. As a result, the phase change occurs immediately.
- 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.

# 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.

## Properties of superfluid helium

- The superfluid helium has zero entropy and zero viscosity, which means, for example, that there is no flow resistivity. The thermal conductivity of the superfluid is in theory infinitely large.
- In He II, the thermal conductivity is very large, and evaporation takes place at the surface only. Hence, He II is perfectly quiet, even if it boils off.
- Phase transition to superfluid helium is a Bose–Einstein condensation process.
- Superfluid helium displays phenomenon of superleak.
- Superfluid He tends to creep over any wall and shows extreme adhesion to surfaces and "complete wetting" effect.



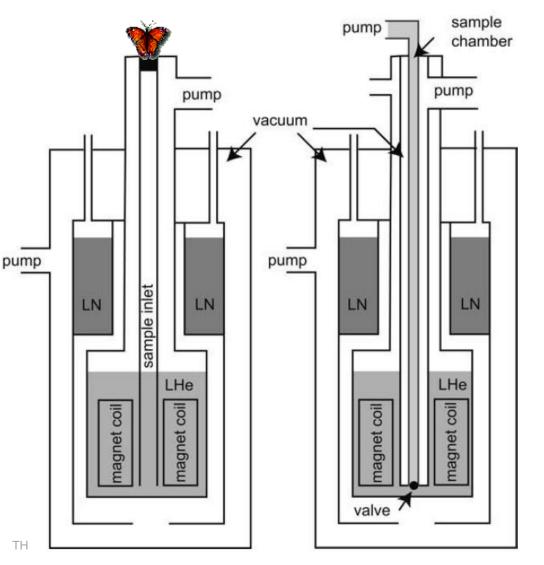
(a) Sketch of a He II osmotic cell. (b) Superfluid film creeping across a wall.

## <sup>4</sup>He cryostats

- In a cryostat, He is isolated from the environment by a vacuum jacket. LHe container is made of a material with a poor thermal conductivity, such as glass or stainless steel.
- Main types of <sup>4</sup>He cryostats are bath cryostat and gas flow cryostat.
- In a bath cryostat temperature is reduced by pumping.
- He vapour pressure p drops exponentially as temperature Θ decreases:

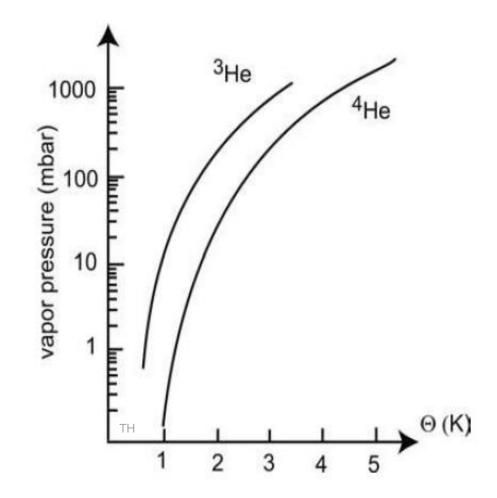
 $p(\Theta) = p_0 \exp(-L/k_B\Theta).$ 

- Low pressure and high pumping speed is necessary to reach low temperatures.  $\Theta \sim 1.2$ K at p = 1mbar.
- Continuous variation of temperature between 1.2 K and room temperature is possible in a gas flow cryostat.

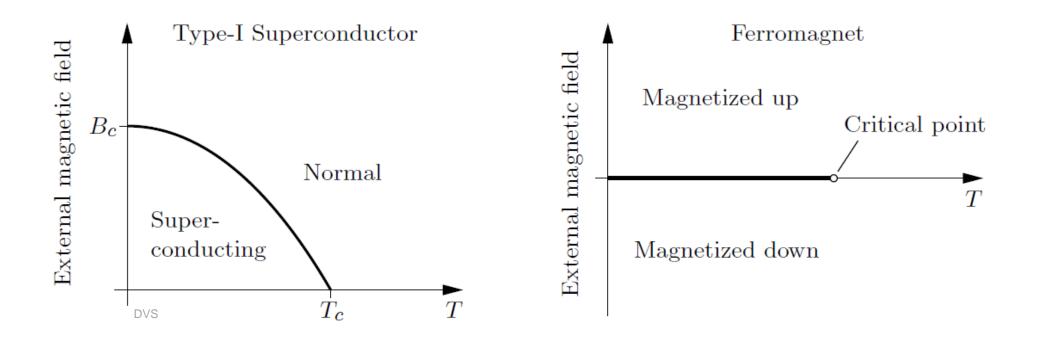


#### <sup>3</sup>He cryostats

- Below 1 K, the vapour pressure of <sup>3</sup>He is much higher than that of <sup>4</sup>He. Temperatures down to about 270 mK can be reached by pumping L<sup>3</sup>He.
- <sup>4</sup>He is used for a precooling stage.
- <sup>3</sup>He is kept in a closed cycle.
- Evaporated <sup>3</sup>He gas can be condensed by a small, pumped <sup>4</sup>He pot, which is connected to the <sup>4</sup>He bath via a needle valve, such that its temperature stays well below 3.2K.
- Some cryostats are equipped with a continuous flow option, where, the pumped <sup>3</sup>He is immediately re-condensed.
- With somewhat higher base temperature, measurement period becomes unlimited.

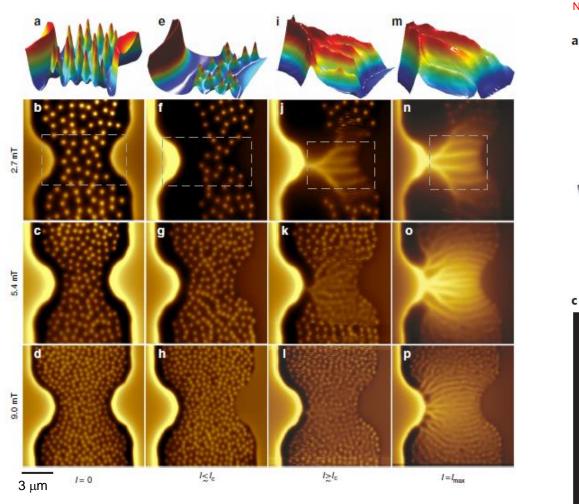


## Other phase diagrams

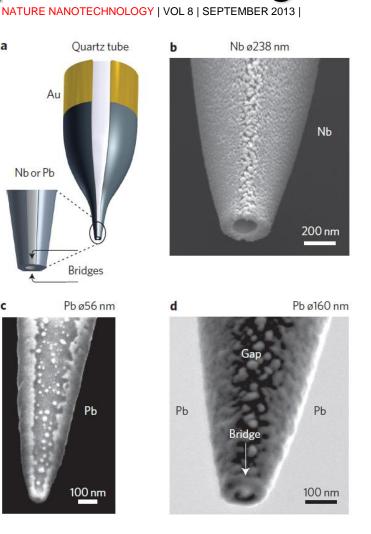


Phase diagrams for two magnetic systems: type-I superconductor (tin, mercury or lead) and a ferromagnet such as iron, which has magnetized phases pointing either up or down, depending on the direction of the applied field.

### UiO : University of Oslo Imaging of super-fast dynamics and flow instabilities of superconducting vortices



Magnetic imaging of stationary and fast moving vortices in Pb film at 4.2 K.

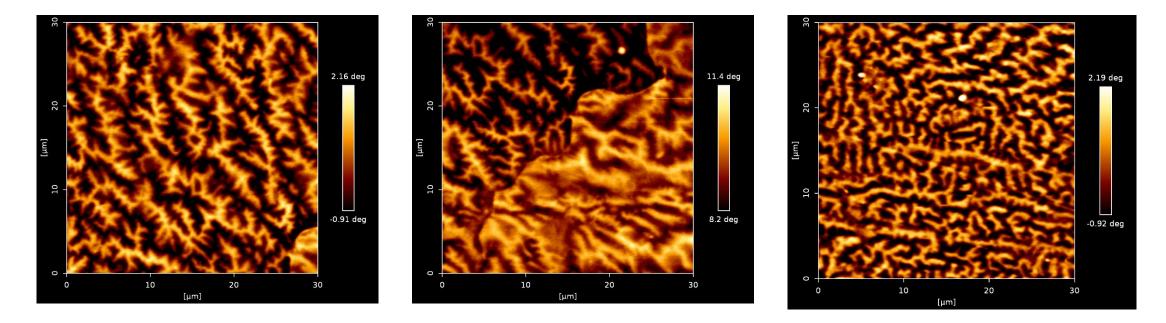


SEM images of SOT devices.

Department of Condensed Matter Weizmann Institute of Physics, Science, Rehovot 7610001, Israel, The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel. Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium, Département de Physique, Université de Liège, B-4000 Sart Tilman, Belgium, Departments of Physics and Electrical Engineering, University of Colorado Denver, Denver, Colorado 80217, USA, Verkin Institute for Low Temperature Physics & Engineering, Ukrainian Academy of Sciences, Kharkov 61103, Ukraine, Department of Physics, Old Dominion University, Norfolk, Virginia 23529-0116, USA.

### **Domain structure and Magnetic Force Microscopy**

The domain structure of a material is the one which minimizes the Gibbs free energy of the material.

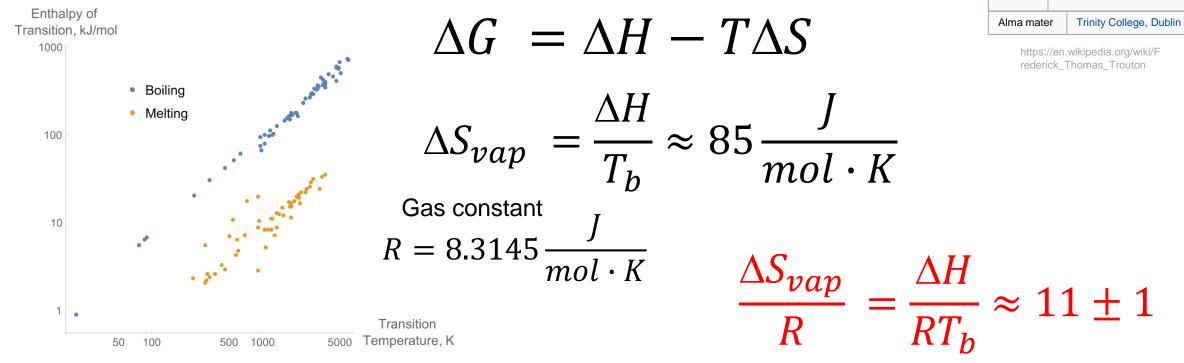


Examples of magnetic domains in FeNiCoAl<sub>x</sub>Mn<sub>x</sub>

## Trouton's rule

The enthalpy of vaporization  $\Delta H_{vap}$  is the latent heat of vaporization or simply heat of evaporation.

Trouton's rule states that the entropy of vaporization  $\Delta S_{vap}$  is almost the same value, about 85–88 J/(K·mol), for various kinds of liquids at their boiling points T<sub>b</sub>.  $\Delta S_{vap}$  is defined as the ratio between the enthalpy of vaporization and the boiling temperature. It is named after Frederick Thomas Trouton.



Mgibby5 CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=38532289

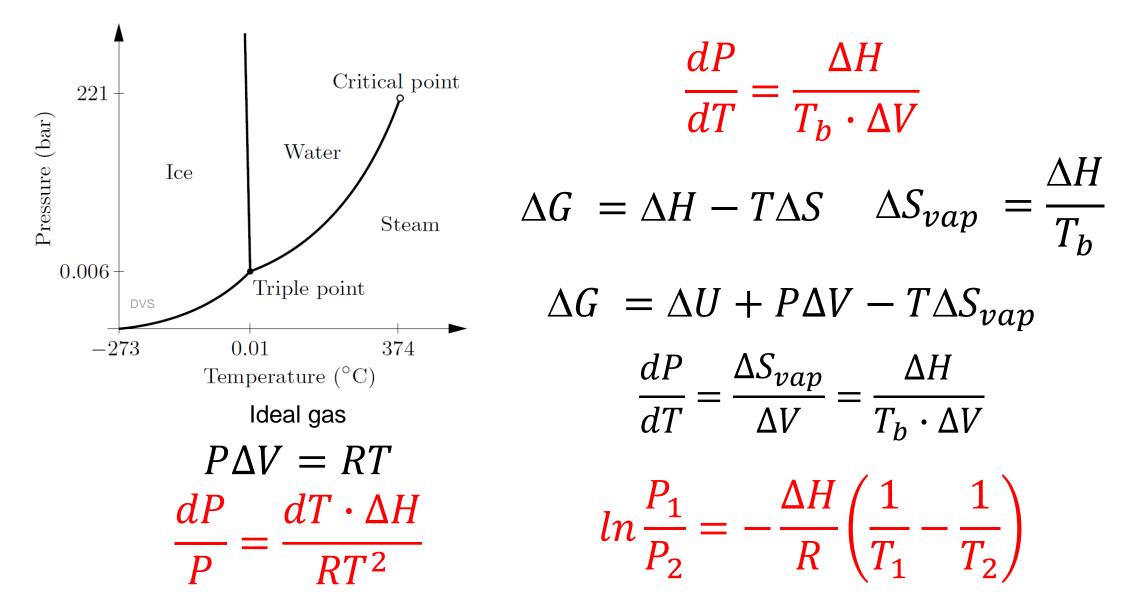


**Frederick Thomas Trouton** 

24 November 1863 Dublin

Born

## **Clausius-Clapeyron relation**



### Magnetic Force Microscopy (MFM)

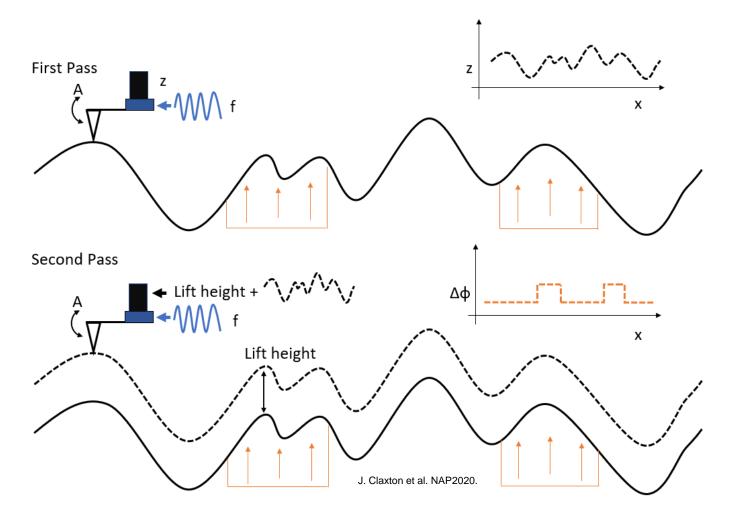
- Scanning probe technique
- Measures probe-sample interaction using magnetic tips

### A tool for measuring magnetic properties of High Entropy Alloys

Image Source: jpk.com



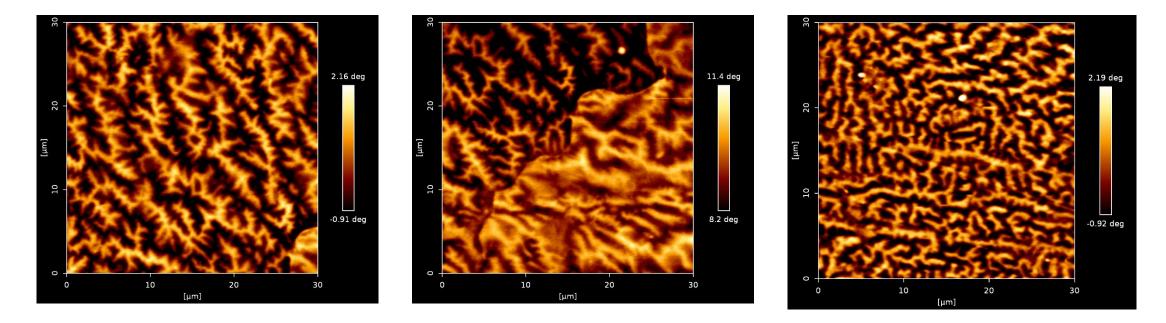
### **Two Pass Technique**



Magnetic material

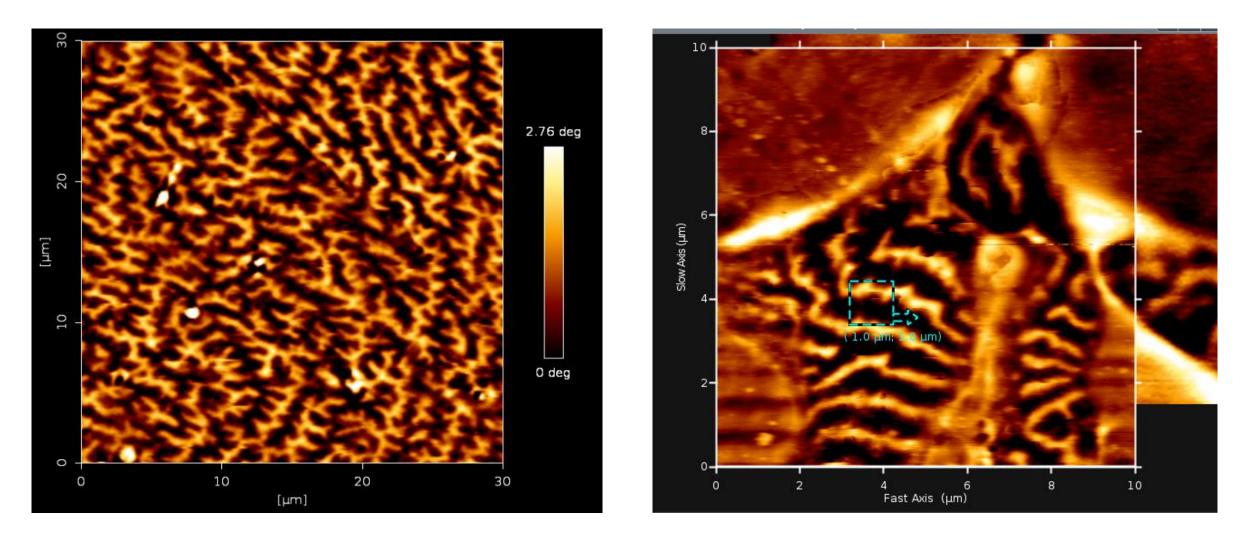
### **Domain structure and Magnetic Force Microscopy**

The domain structure of a material is the one which minimizes the Gibbs free energy of the material.

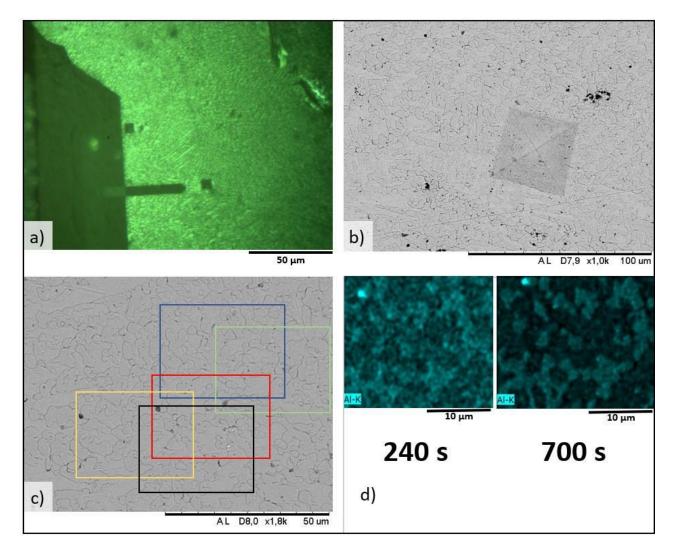


Examples of magnetic domains in FeNiCoAl<sub>x</sub>Mn<sub>x</sub>

# **MFM Results**

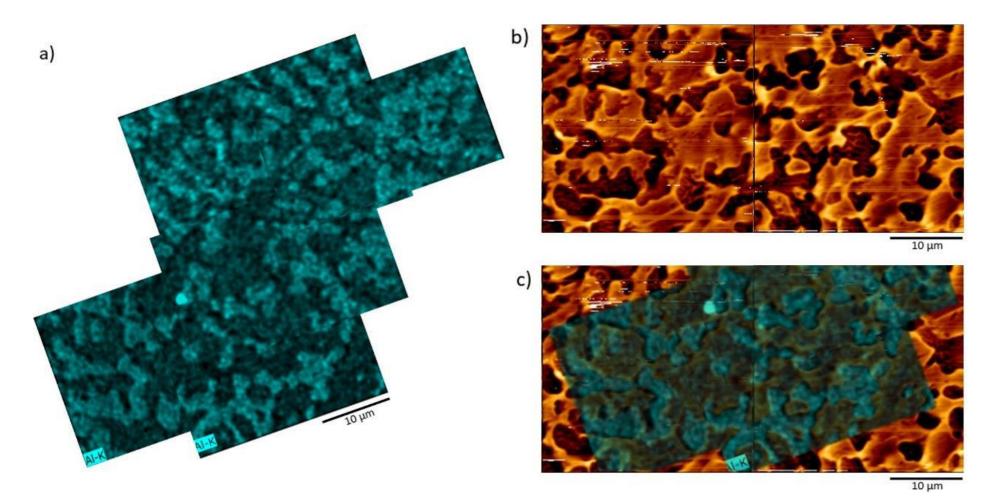


## MFM and SEM measurements



a) Optical image from MFM showing the cantilever next to an indentation mark. b) An SEM image of the corresponding indentation mark. c) The area of each recorded EDS map surrounded by rectangular frames of different colour. d) Two AI EDS maps of the same area, but with different times of acquisition.

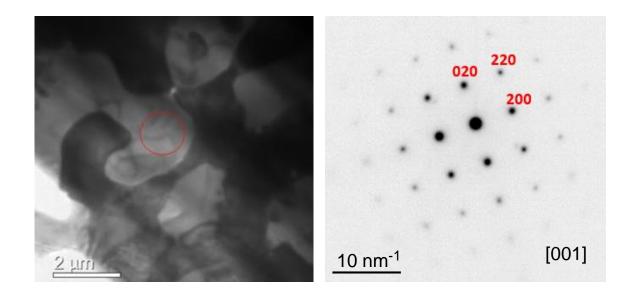
# Correlation in MFM and SEM measurements



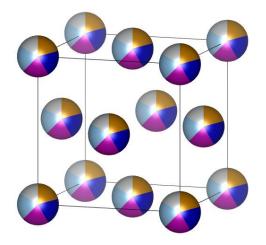
a) AI elemental map from EDS, b) MFM map from the same region as the AI elemental map and c) MFM map overlaid with the elemental map, having 30 % transparency.

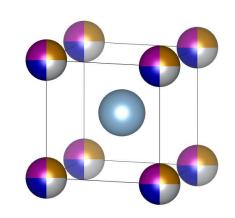
### **Crystal structure determination with TEM**

### Selected Area Diffraction (SAD)







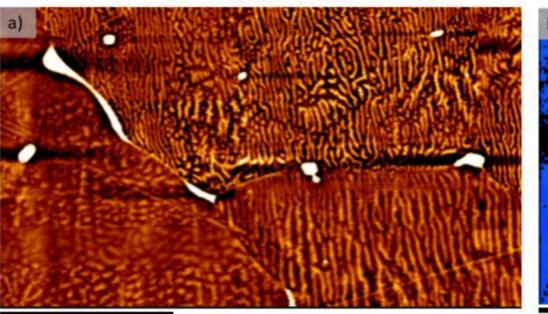


a = 0.36 nm

a = 0.29 nm



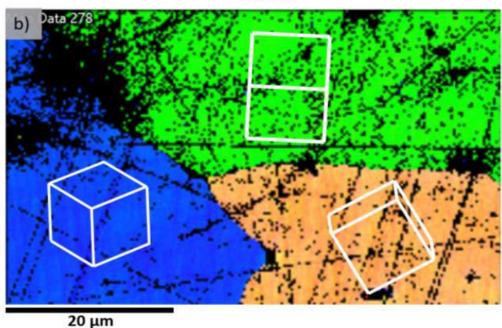
# Correlation in MFM and EBSD measurements



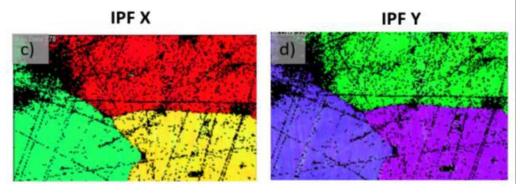
MFM

#### 20 µm

a) MFM map b) IPF in z-direction from EBSD for same region as the MFM map, with illustrations of the crystal orientations c) IPF x-direction d) IPF y-direction. e)-i) are the elemental EDS maps for Al, Ni, Co, Fe and Mn, respectively, for the same region as MFM and EBSD above. j) is the combined EDS map with all colours together and SEM image in the background.



IPF Z



### Free energies in van der Waals fluid

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

$$G = -NkT\ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$$

$$G = F + PV$$
  $F = G - PV$ 

$$F = -NkT \left( \ln \left( \frac{n_Q(V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V}$$
$$n_Q(T) = \left( \frac{2\pi mkT}{h^2} \right)^{3/2}$$