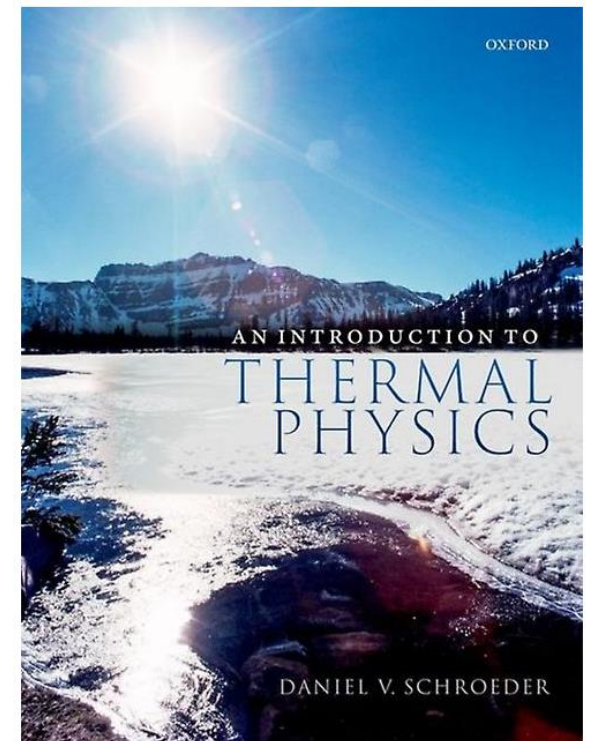
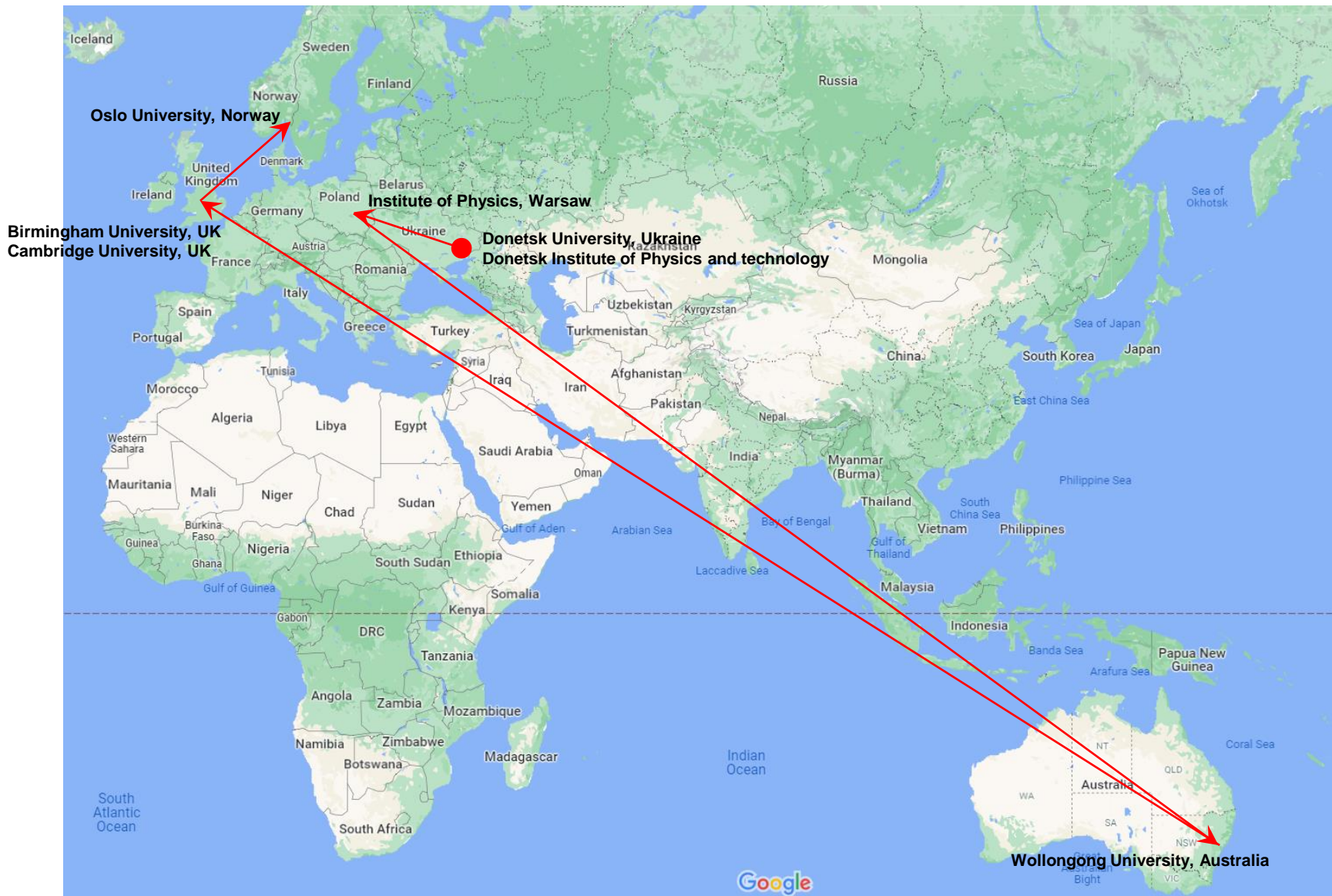


UiO • University of Oslo

Free energies



My odyssey



Prof. Pavlo Mikheenko
University of Oslo
Department of Physics
P.O.Box 1048, Blindern
0316 Oslo, Norway

Physics West
Room 404 (4th floor)
Phone: +47 228 57711/57471
Mobile: 94838864

Email pavlo.mikheenko@fys.uio.no
[http://www.mn.uio.no/fysikk/englis
h/people/aca/pavlom/index.html](http://www.mn.uio.no/fysikk/englis
h/people/aca/pavlom/index.html)

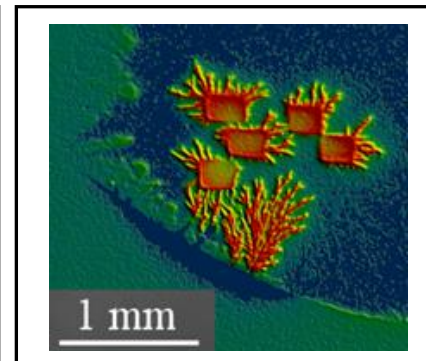
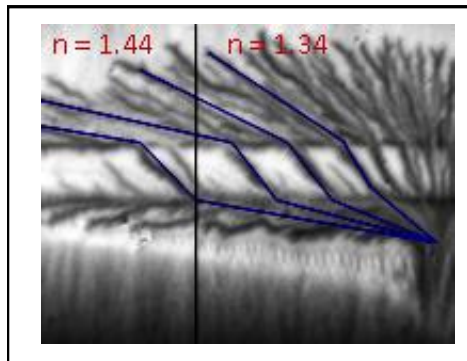
Advanced superconductivity

Superconductivity for green economy

Live observation of magnetic flux distribution in superconductors

Fast developing thermomagnetic avalanches in superconducting films

Superconductivity in biological systems



Possible superconductivity in the brain (2019)

Nano superconductivity and quantum processing of information in living organisms (2020)

Superconductivity in Self-Assembled Microtubules (2023)

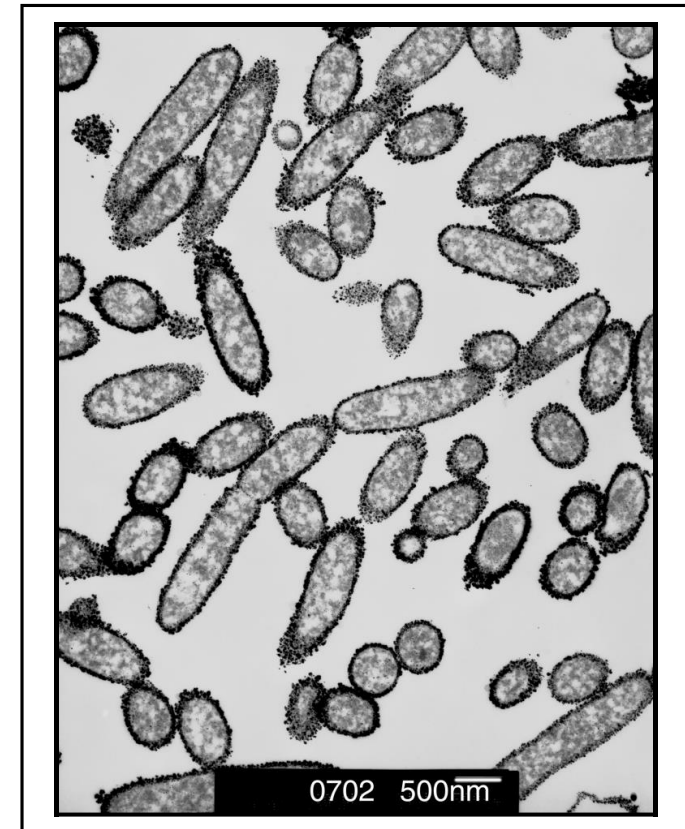
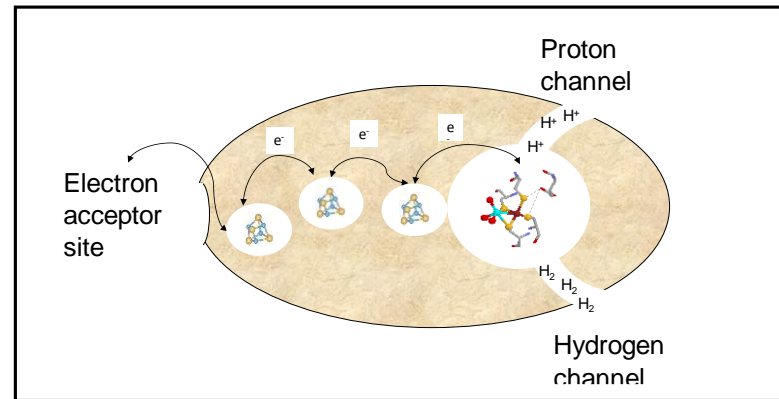
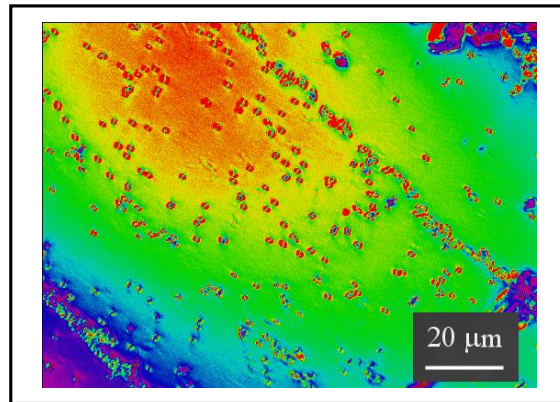
Biotechnology of magnetic nanoparticles

Ferromagnetic nanoparticles on surface of bacteria

Magneto-optical visualization of ferromagnetic nanoparticles

Magnetic force microscopy of bacteria-bound nanoparticles

Quantum mechanical applications of biologically derived nanoparticles



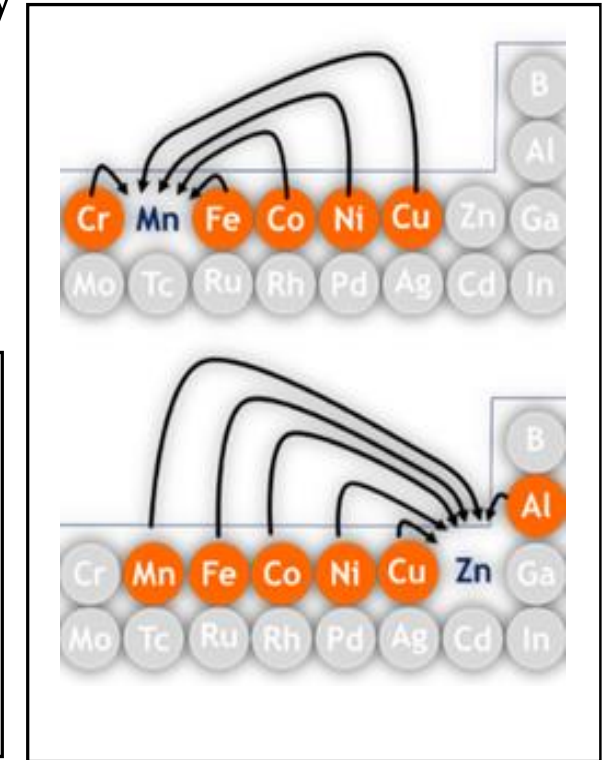
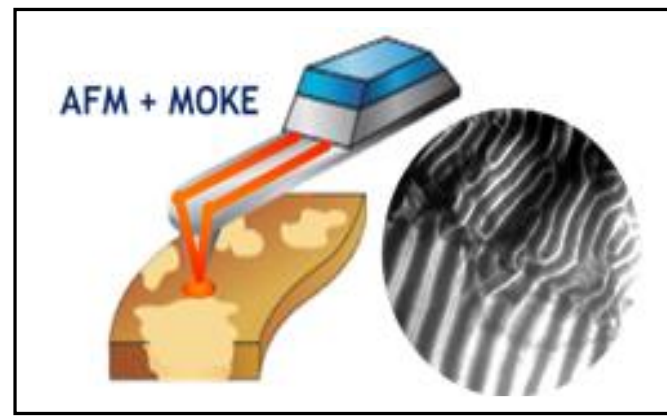
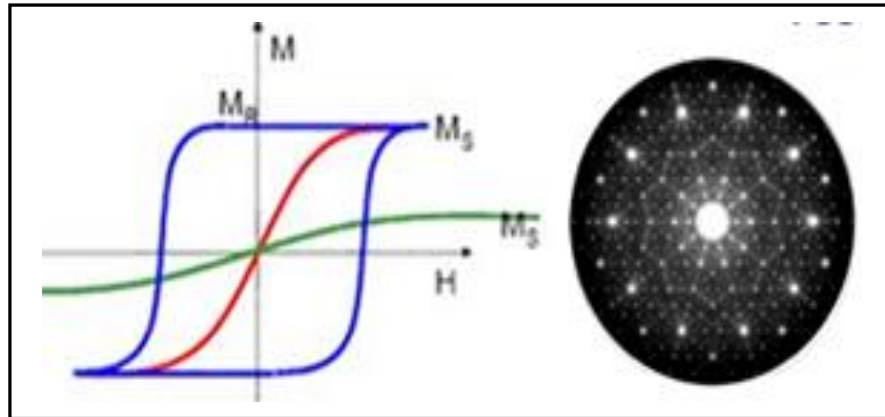
High entropy magnetic alloys for renewable electricity

Modern industry-based laser manufacturing of alloys

Unique multi-component approach

Advanced magnetic and structural characterization

New generation of soft magnetic materials for electrical applications



Tuesdays: Store fysiske auditorium

Wednesdays: Store fysiske auditorium

- Tuesday September 26
- Wednesday October 4
- Tuesday October 31
- Tuesday November 7
- Wednesday November 8

Tuesdays: 10:15 -12:00

Wednesdays: 12:15 -14:00

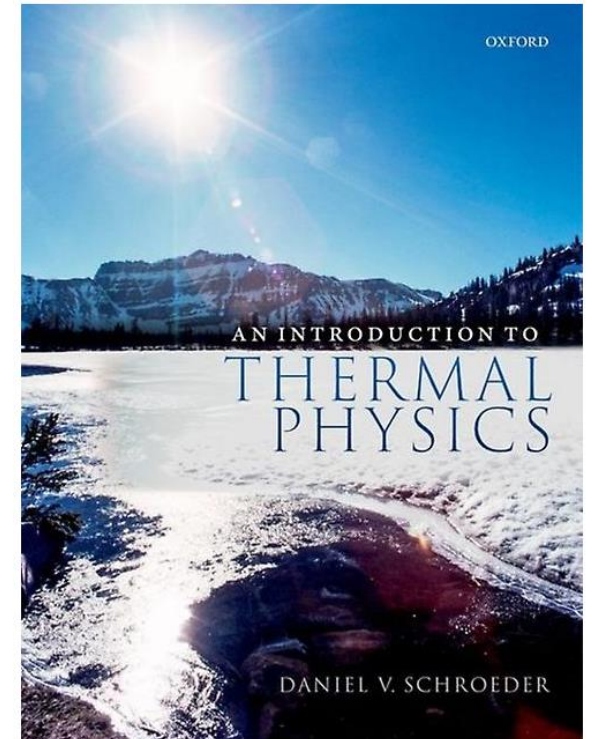
Free energies

Phase transitions of mixtures

Electron gas

Black body radiation

Specific heat



The **first law** of thermodynamics

Heat Q is *spontaneous* flow of energy from one object to another, caused by a *difference in temperature* between the objects.

Work W is any other transfer of energy into or out of a system.

Total energy of a system is **U** .

$$\Delta U = \Delta Q + \Delta W$$

The change in energy of a system equals the **heat added** plus the **work done on the system**.

This is the law of conservation of energy.

The **second law** of thermodynamics

Entropy **S** is proportional to the logarithm of **multiplicity** Ω , which is the number of ways of arranging **microstates** in the system.

$$S = k \ln \Omega$$

Boltzmann constant

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

Any large system in equilibrium will be found in the **macrostate** with the greatest entropy. Entropy **tends** to increase.

$$S = S_{\text{max}}$$

This is actually not the law, just strong statement.

The **third law** of thermodynamics

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T}$$

At **zero temperature**, a system should settle into its unique lowest-energy state with $\Omega = 1$ and $S = 0$.

$$**S_{T=0} = 0**$$

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \cdot \frac{\partial S}{\partial U \partial T} \equiv \frac{1}{T} \frac{\partial U}{\partial T} \quad \frac{\partial S}{\partial T} \equiv \frac{1}{T} \frac{\partial U}{\partial T} \quad S(T) = \int_0^T \frac{C_V(T)}{T} dT$

Heat capacity goes to zero as T goes to zero: $C_V \rightarrow 0$ as $T \rightarrow 0$.

Henry's Bent's Laws of Thermodynamics

1st Law: You can't win, you can only break even

2nd Law: You can't break even

3rd Law: You can't quit the game

Thermodynamic identity

$$dU = dQ + dW \quad \left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T}$$

Constant T and P

$$dU = TdS - PdV$$

$$\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V} \quad dU = TdS - PdV + \mu dN$$

Generalized thermodynamic identity:

The μdN term is sometimes referred to as “chemical work.”

Enthalpy

Keeping track of the compression-expansion work is difficult. We can agree to always take it into account.

Measuring change from a reference point.

$$dU = TdS - PdV \quad \longrightarrow \quad U = TS - PV$$

$$H = U + PV$$

$$H = TS$$

Enthalpy is free from the compression-expansion work.

$$W = -PV + W_{other}$$

$$H = TS + W_{other}$$

Enthalpy is not free from other work.

Helmholtz free energy

$$U = TS - PV$$

$$F = U - TS$$

$$F = -PV$$

Helmholtz free energy is free from heat.

$$W = -PV + W_{other}$$

$$F = -PV + W_{other}$$

Gibbs free energy

$$U = TS - PV$$

$$G = U - TS + PV$$

Gibbs free energy is free both from heat and compression - expansion work.

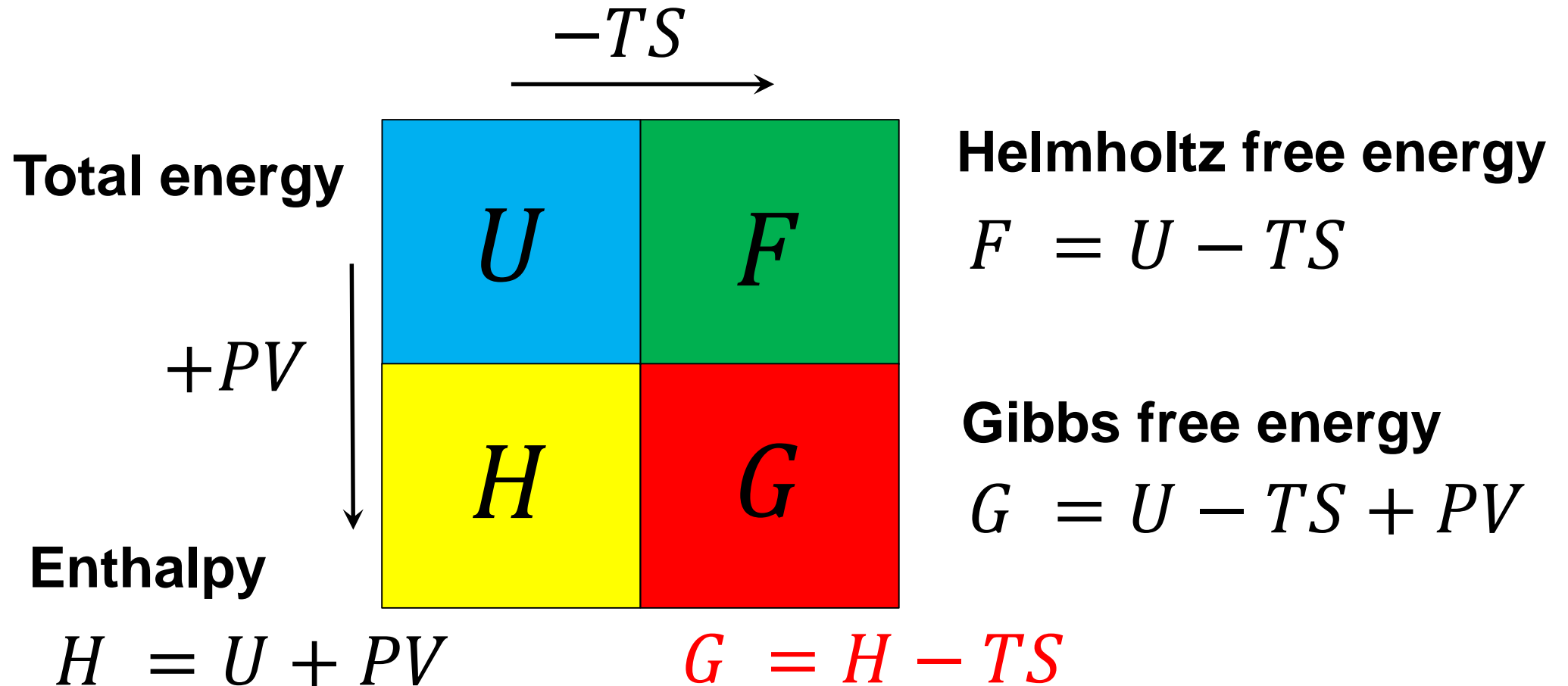


<https://www.domesticatedcompanion.com/magicians-biggest-tricks-explained/76/?xcmg=1>

$$W = -PV + W_{other}$$

$$\Delta G = W_{other}$$

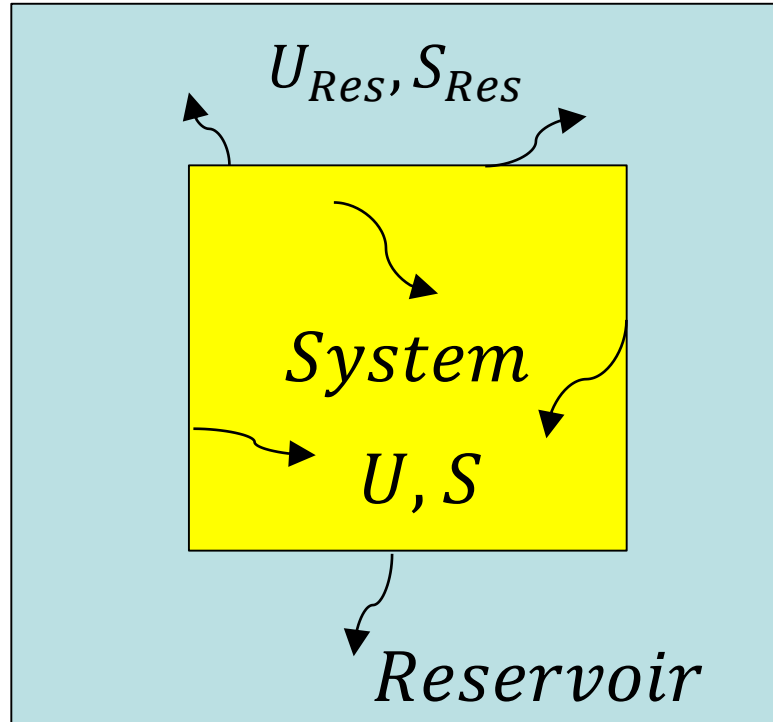
Thermodynamic potentials



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

System in contact with thermostat

The environment acts as a **reservoir** of energy (**thermostat**), large enough that it can absorb or release unlimited amounts of energy without changing its temperature.



$$dU = TdS - PdV$$

Constant volume

$$\begin{aligned} dS_{total} &= dS + \frac{1}{T} dU_{Res} \\ &= dS - \frac{1}{T} dU = -\frac{1}{T} (dU - TdS) \\ &= -\frac{1}{T} dF. \end{aligned}$$

At constant volume, the system will do whatever it can to minimize its Helmholtz free energy.

$$\begin{aligned} dS_{total} &= dS + \frac{1}{T} dU_{Res} + \frac{P}{T} dV_{Res} \\ &= dS - \frac{1}{T} dU - \frac{P}{T} dV = -\frac{1}{T} dG. \end{aligned}$$

At constant pressure, the system will do whatever it can to minimize its Gibbs free energy.

Driving system to equilibrium

- At constant **energy** and **volume**, **S tends to increase**.
- At constant **temperature** and **volume**, **F tends to decrease**.
- At constant **temperature** and **pressure**, **G tends to decrease**.

Gibbs energy and phase transformations

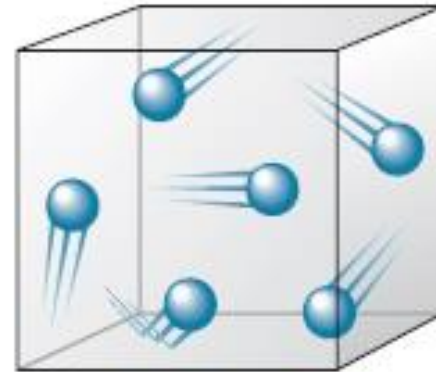
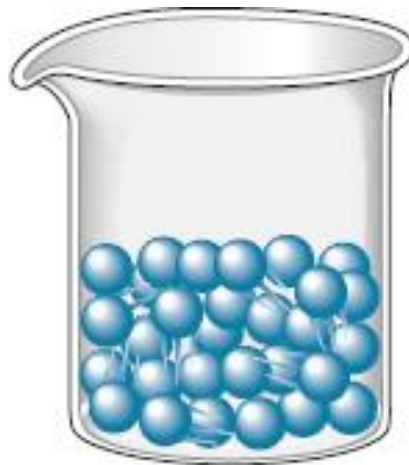
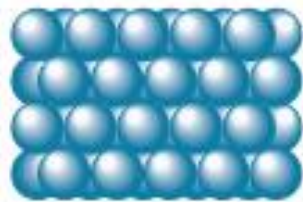
$$\Delta G = \Delta H - T\Delta S$$

- ΔG determines whether a process is spontaneous (happens by itself) or not
 - **If ΔG is negative, process is spontaneous**
- The criterion takes into account **enthalpy**, **entropy**, and **temperature**
- The name honors Josiah Gibbs a physics professor at Yale University during the late 1800's who was developing modern thermodynamics

Positional Entropy

- The probability of occurrence of a particular state depends on the number of ways (microstates) in which that arrangement can be achieved

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$



Spontaneity of phase transformations

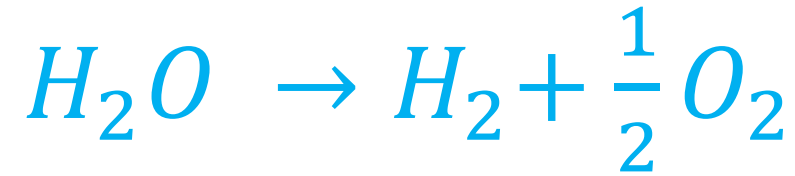
$$\Delta G = \Delta H - T\Delta S$$

<i>Value of ΔH</i>	<i>Value of $T\Delta S$</i>	<i>Value of ΔG</i>	<i>Spontaneity</i>
Negative	Positive	Negative	Spontaneous
Positive	Negative	Positive	Nonspontaneous
Negative	Negative	Negative or positive	Spontaneous if the absolute value of ΔH is greater than the absolute value of $T\Delta S$ (works at low temperatures)
Positive	Positive	Negative or positive	Spontaneous if the absolute value of $T\Delta S$ is greater than the absolute value of ΔH (works at high temperatures)

Spontaneity of phase transformations depend on value of ΔG . Transformation is spontaneous if ΔG is negative and nonspontaneous if it is positive.

Electrolysis

One mole of water is taken, or the number of grams equal to the sum of all atomic masses in the substance.



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

4 kJ

$$G = U - TS + PV = H - TS \quad \Delta G = \Delta U - T\Delta S + P\Delta V$$

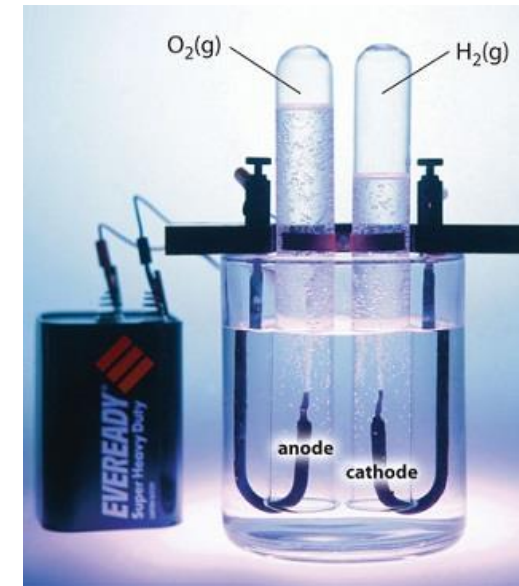
$$\Delta G = \Delta H - T\Delta S$$

$$237 \text{ kJ} = 286 \text{ kJ} - (298 \text{ K})(163 \text{ J/K}).$$

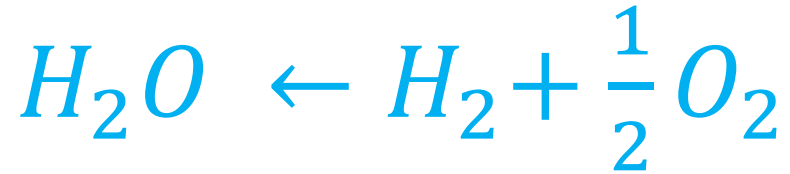
$$S_{H_2O} = 70 \text{ J/K}; S_{H_2} = 131 \text{ J/K}; S_{O_2} = 205 \text{ J/K}.$$

$$131 + (205/2) - 70 = 163 \text{ (J/K)}$$

The amount of energy that must enter as electrical work is the difference between 286 and 49, that is, **237 kJ**.



Fuel Cell



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

4 kJ

$$G = U - TS + PV = H - TS$$

$$\Delta G = \Delta U - T\Delta S + P\Delta V$$

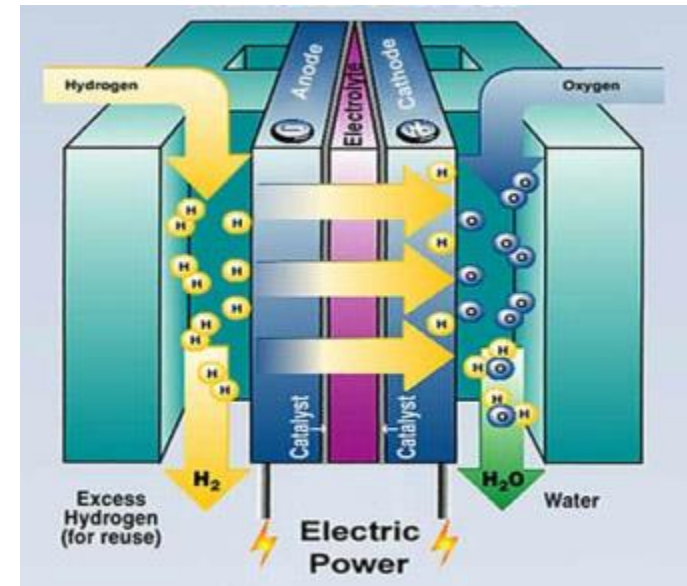
$$\Delta G = \Delta H - T\Delta S$$

$$237 \text{ kJ} = 286 \text{ kJ} - (298 \text{ K})(163 \text{ J/K}).$$

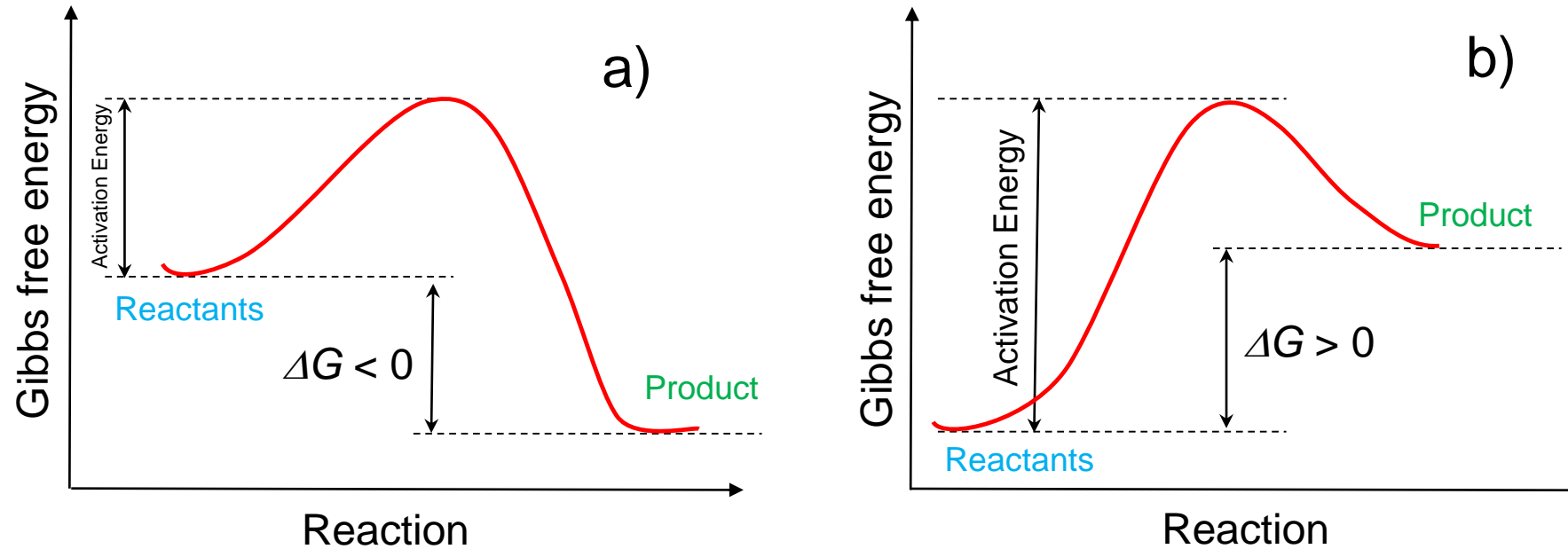
$$S_{H_2O} = 70 \text{ J/K}; S_{H_2} = 131 \text{ J/K}; S_{O_2} = 205 \text{ J/K}.$$

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

$$\frac{237}{286} = 0.83$$

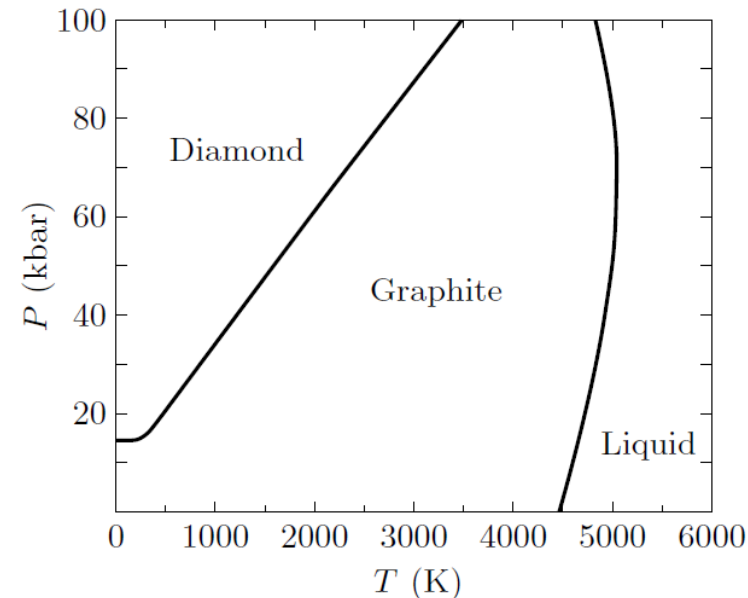
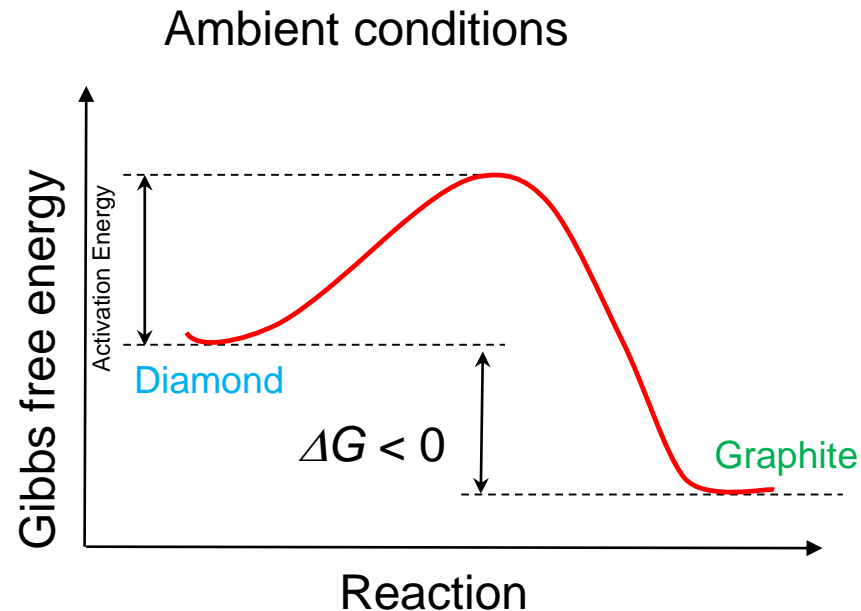


A barrier for phase transformation



- a) Spontaneous reaction is that in which product has a lower free energy (G) than the reactants ($\Delta G < 0$)
- b) Nonspontaneous reaction is that in which reactants have a higher free energy than the product ($\Delta G > 0$)

Graphite and diamond



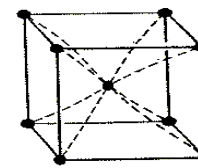
Under standard conditions, graphite is more stable than diamond because the **Gibbs free energy of a mole of diamond is on 2900 J greater than the Gibbs free energy of a mole of graphite**. However, the temperature required to quickly convert diamond to graphite is quite high: about 1500 °C. The first synthesis of diamond from graphite was **achieved at 1800 K and 60 kbar**. Natural diamonds form at similar temperatures and pressures at depths of **100–200 km below earth's surface**.

High Entropy Alloys (HEAs) – Basic Concept

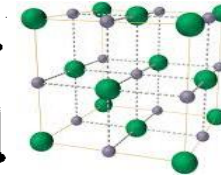
High Entropy Alloys (HEAs): Alloys that contain at least 5 principal elements, each having an atomic percentage between 5 - 35 at.%.

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

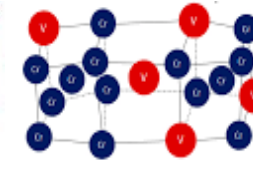
Chemical and structural complexity / Desired properties



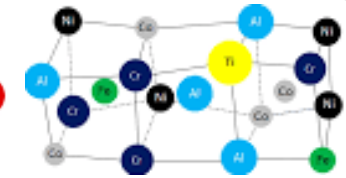
Pure metals



Binary compound
s



Conventional alloys



HEAs

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

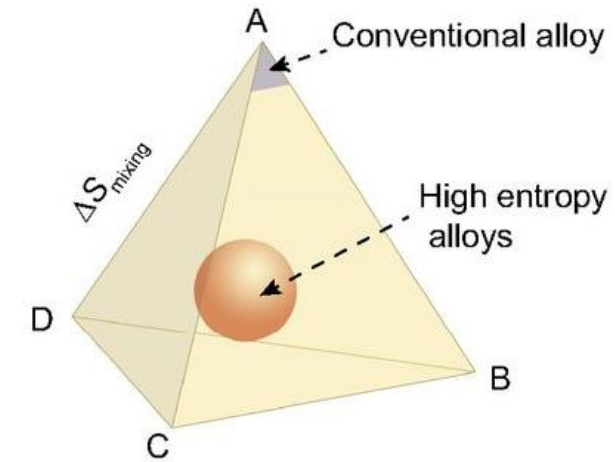


ΔH
(IM compounds)



ΔS

(Increase of the constitutional elements)



High-entropy alloys (HEAs) and FeNiCoAl_xMn_x



- Soft magnetic system

1 IA										2 IIA										13 IIIA										14 IVA										15 VA										16 VIA										17 VIIA										18 VIIIA																																																																																																																																																																																																																																																													
1	H																	2	He																																																																																																																																																																																																																																																																																																																
3	Li																	4	Be																																																																																																																																																																																																																																																																																																																
11	Na																	12	Mg																																																																																																																																																																																																																																																																																																																
19	K																	20	Ca																	21	Sc																	22	Ti																	23	V																	24	Cr																	25	Mn																	26	Fe																	27	Co																	28	Ni																	29	Cu																	30	Zn																	31	Ga																	32	Ge																	33	As																	34	Se																	35	Br																	36	Kr																
37	Rb																	38	Sr																	39	Y																	40	Zr																	41	Nb																	42	Mo																	43	Tc																	44	Ru																	45	Rh																	46	Pd																	47	Ag																	48	Cd																	49	In																	50	Sn																	51	Sb																	52	Te																	53	I																	54	Xe																
55	Cs																	56	Ba																	57 - 71	Lanthanoids																	72	Hf																	73	Ta																	74	W																	75	Re																	76	Os																	77	Ir																	78	Pt																	79	Au																	80	Hg																	81	Tl																	82	Pb																	83	Bi																	84	Po																	85	At																	86	Rn																
87	Fr																	88	Ra																	89 - 103	Actinoids																	104	Rf																	105	Db																	106	Sg																	107	Bh																	108	Hs																	109	Mt																	110	Ds																	111	Rg																	112	Cn																	113	Nh																	114	Fl																	115	Mc																	116	Lv																	117	Ts																	118	Og																

57	La																	58	Ce																	59	Pr																	60	Nd																	61	Pm																	62	Sm																	63	Eu																	64	Gd																	65	Tb																	66	Dy																	67	Ho																	68	Er																	69	Tm																	70	Yb																	71	Lu																
89	Ac																	90	Th																	91	Pa																	92	U																	93	Np																	94	Pu																	95	Am																	96	Cm																	97	Bk																	98	Cf																	99	Es																	100	Fm																	101	Md																	102	No																	103	Lr																

HEAs:

- Have typically five or more principal elements in solid solution
- Are materials with a mixture of properties from all constituent elements

Samples 1-14: $\text{FeNiCoAl}_x\text{Mn}_x$ ($0.05 < x < 3.08$)

Sample 1: $\text{FeNiCoAl}_{3.08}\text{Mn}_{3.08}$

Sample 2: $\text{FeNiCoAl}_{1.28}\text{Mn}_{1.28}$

Sample 3: $\text{FeNiCoAl}_{0.9}\text{Mn}_{0.9}$

Sample 4: $\text{FeNiCoAl}_{0.72}\text{Mn}_{0.72}$

Sample 5: $\text{FeNiCoAl}_{0.57}\text{Mn}_{0.57}$

Sample 6: $\text{FeNiCoAl}_{0.39}\text{Mn}_{0.39}$

Sample 7: $\text{FeNiCoAl}_{0.32}\text{Mn}_{0.32}$

Sample 8: $\text{FeNiCoAl}_{0.29}\text{Mn}_{0.29}$

Sample 9: $\text{FeNiCoAl}_{0.28}\text{Mn}_{0.28}$

Sample 10: $\text{FeNiCoAl}_{0.24}\text{Mn}_{0.24}$

Sample 11: $\text{FeNiCoAl}_{0.2}\text{Mn}_{0.2}$

Sample 12: $\text{FeNiCoAl}_{0.19}\text{Mn}_{0.19}$

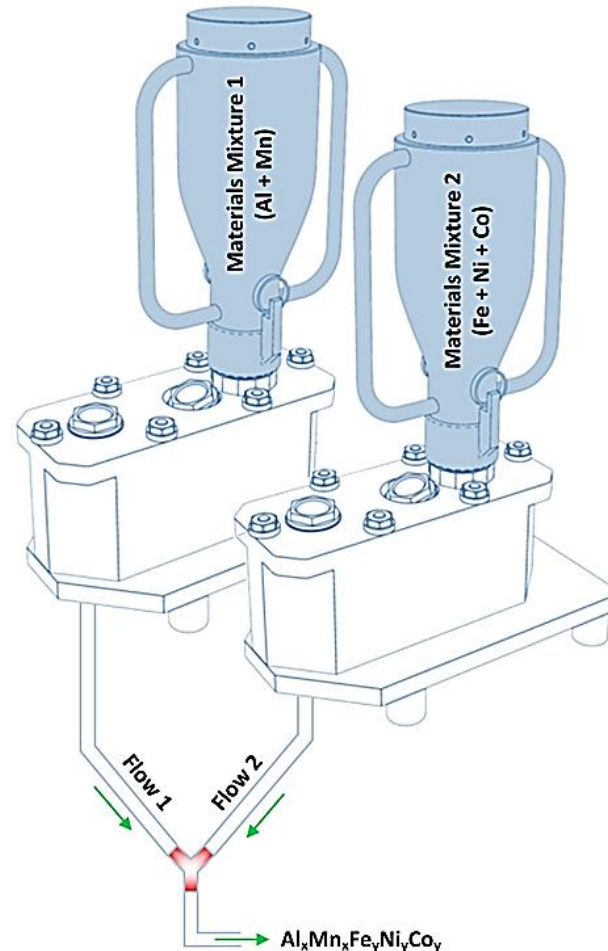
Sample 13: $\text{FeNiCoAl}_{0.08}\text{Mn}_{0.08}$

Sample 14: $\text{FeNiCoAl}_{0.05}\text{Mn}_{0.05}$

Processing Method

Laser Metal Deposition (LMD)

LMD is an **additive manufacturing technology (AM)** that is also referred as Laser Engineering Net Shaping (LENS). It is a sub-category of a generic AM technology called Directed Energy Deposition (DED)



Powder feeding

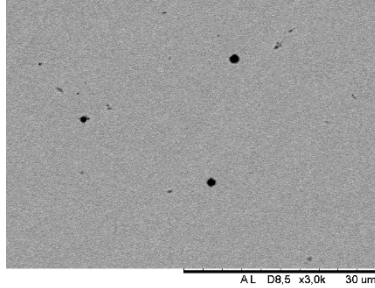


Produced alloy compositions

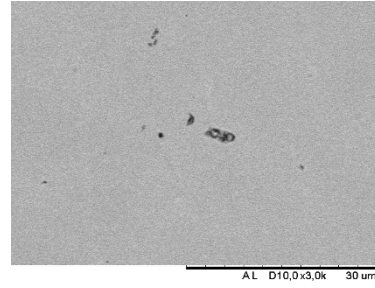
Sample code	Element content (at.%)
S-A	Fe _{28.1} Co _{28.1} Ni _{28.1} Al _{7.8} Mn _{7.8}
S-B	Fe _{28.8} Co _{28.8} Ni _{28.8} Al _{6.8} Mn _{6.8}
S-C	Fe _{29.4} Co _{29.4} Ni _{29.4} Al _{5.9} Mn _{5.9}
S-D	Fe _{29.6} Co _{29.6} Ni _{29.6} Al _{5.6} Mn _{5.6}
S-E	Fe _{31.6} Co _{31.6} Ni _{31.6} Al _{2.6} Mn _{2.6}
S-F	Fe _{32.3} Co _{32.3} Ni _{32.3} Al _{1.6} Mn _{1.6}

SEM evidence of spinodal decomposition

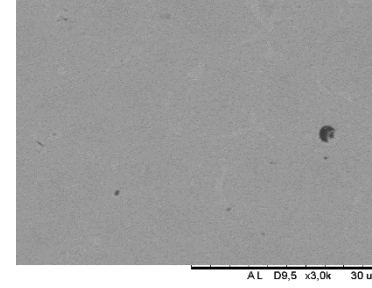
Sample 1



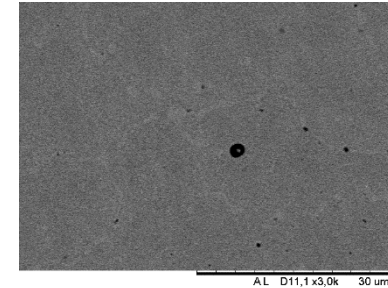
Sample 2



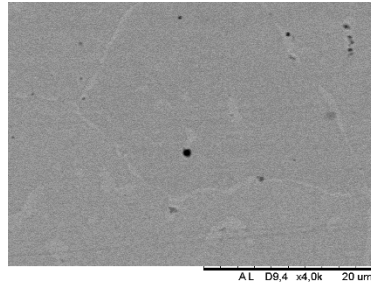
Sample 3



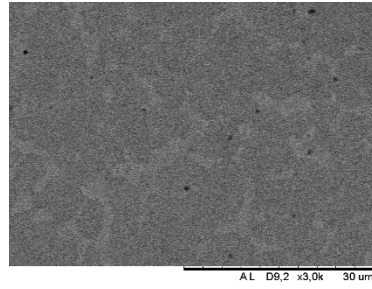
Sample 4



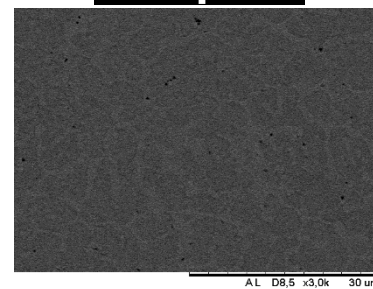
Sample 5



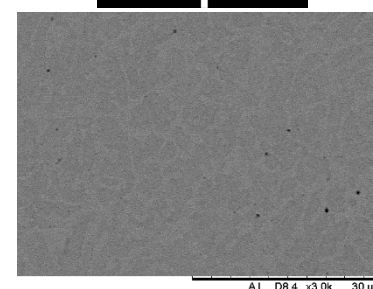
Sample 6



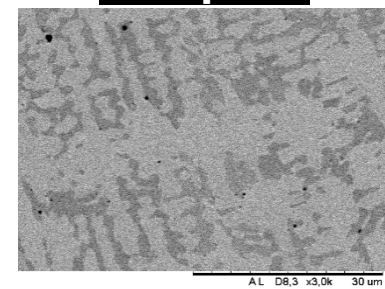
Sample 7



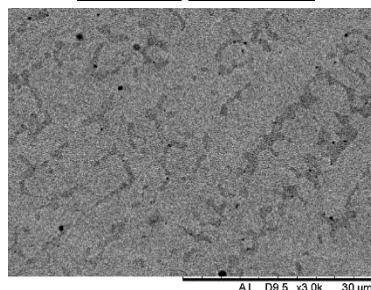
Sample 8



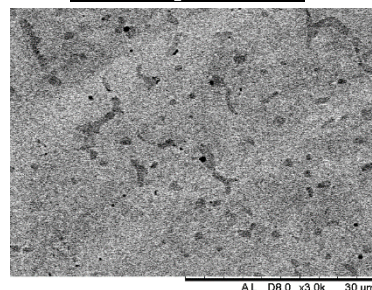
Sample 9



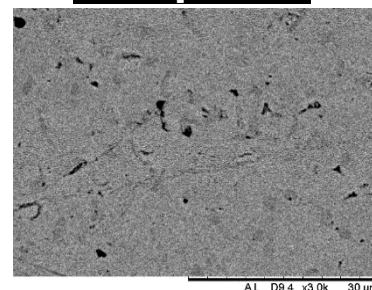
Sample 10



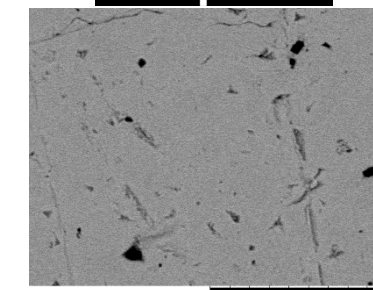
Sample 11



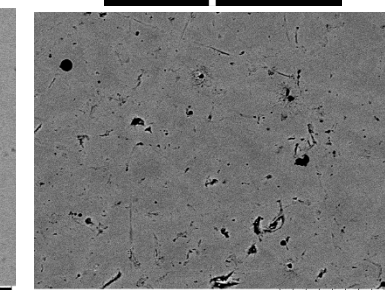
Sample 12



Sample 13



Sample 14



Summary

- There are two free energies: **Helmholtz free energy** (F) and **Gibbs free energy** (G).
- Helmholtz free energy is **free from heat**.
- Gibbs free energy is **free from heat and compression – expansion work**.
- At constant temperature and volume, **F tends to decrease**.
- At constant temperature and pressure, **G tends to decrease**.
- Gibbs free energy is key parameter for calculation of **energy balance** in chemical reactions.
- Gibbs free energy allows to find out if a reaction is **spontaneous** or not.
- Gibbs free energy is primary parameter behind cutting-edge research, for example, in field of **high-entropy alloys**.