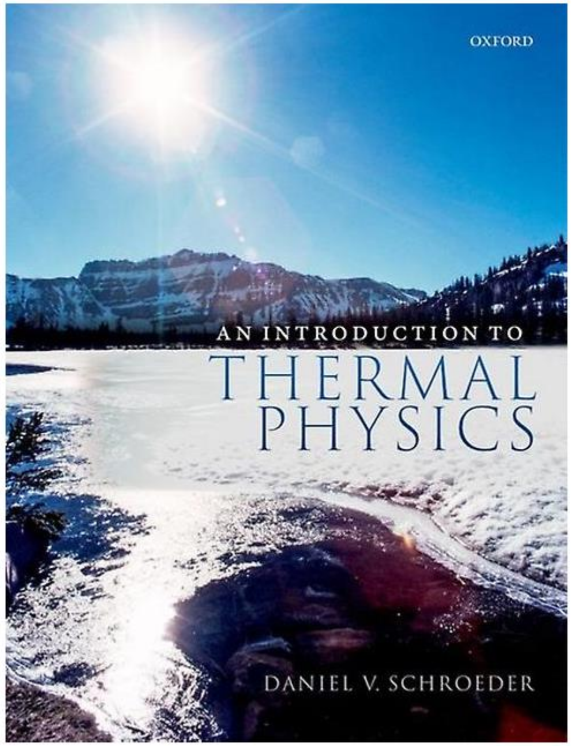
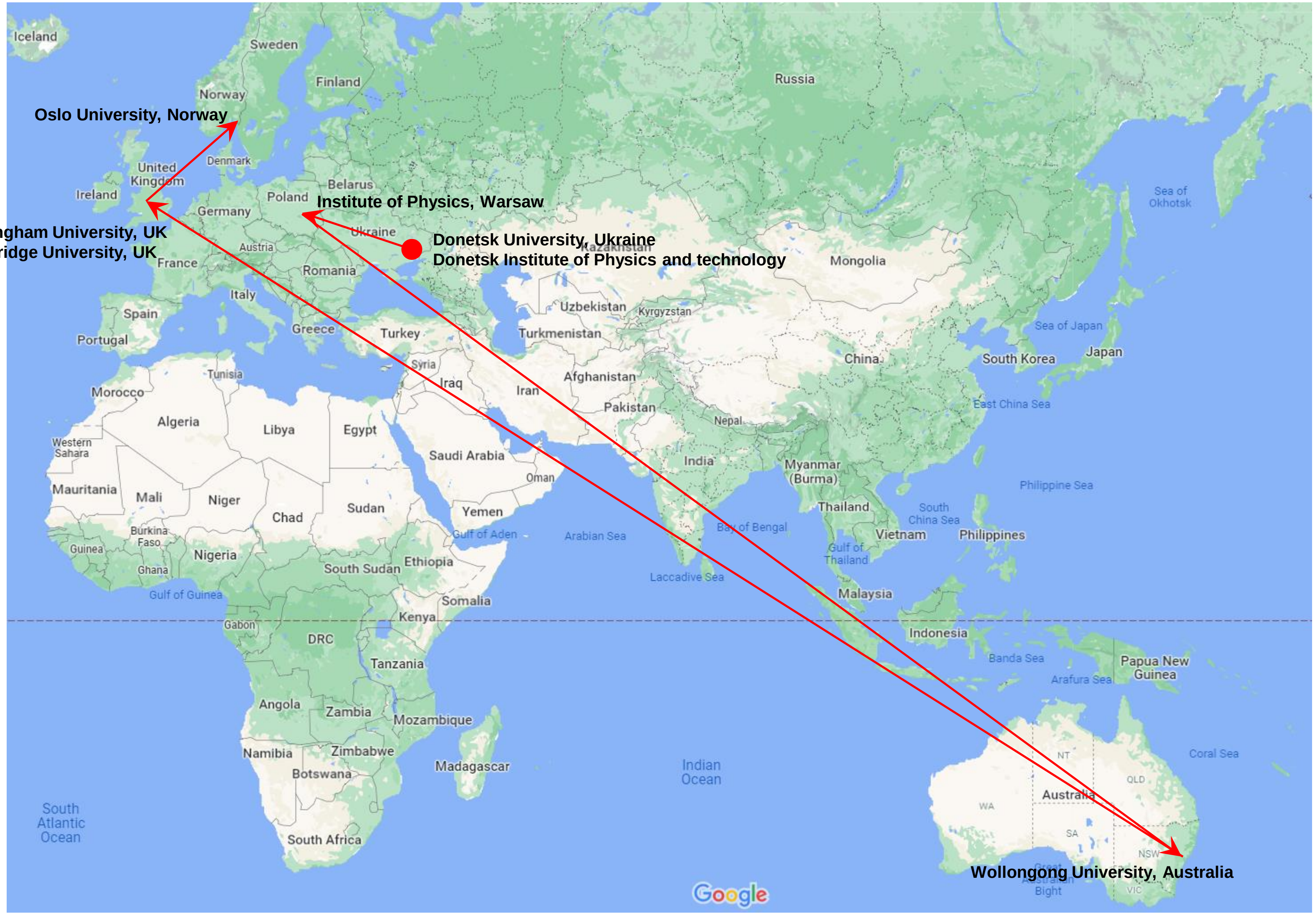
Free energies



UiO : University of Oslo

My odyssey



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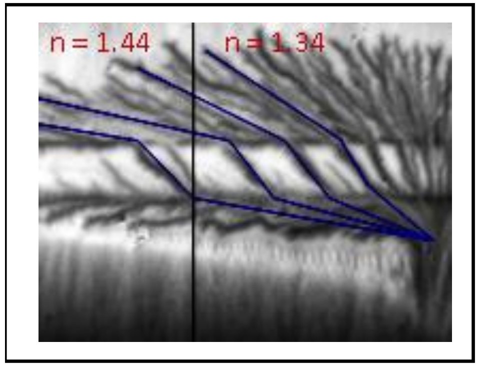
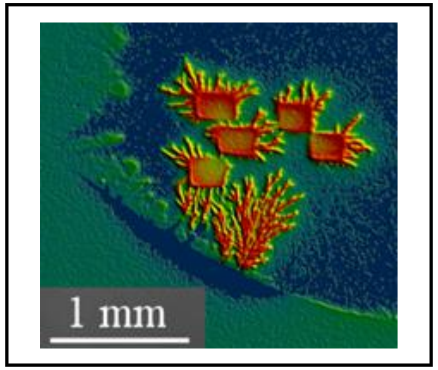
Advanced superconductivity

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)

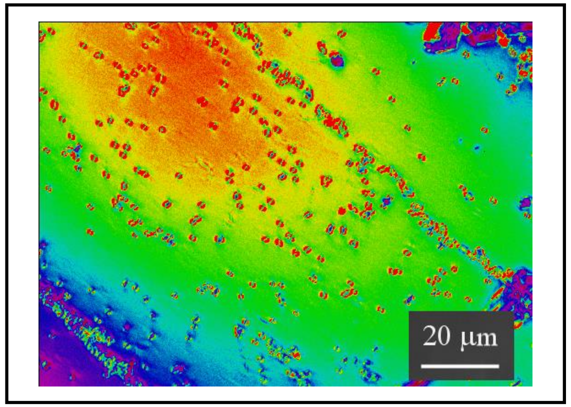
Magnetic Force Microscopy of Brain Microtubules (2021)

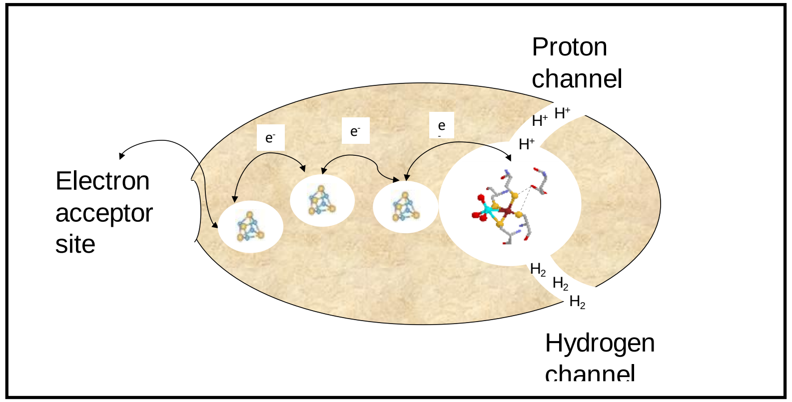
Room-temperature superconductivity in the brain

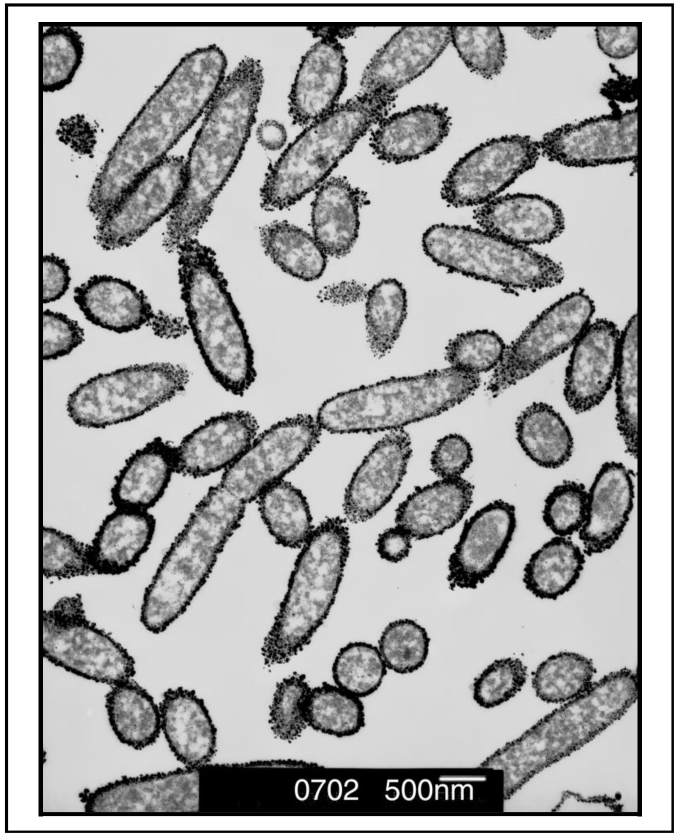
2022 IEEE 12th International Conference
Nanomaterials: Applications & Properties
Kraków, POLAND, Sep. 11-16, 2022

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

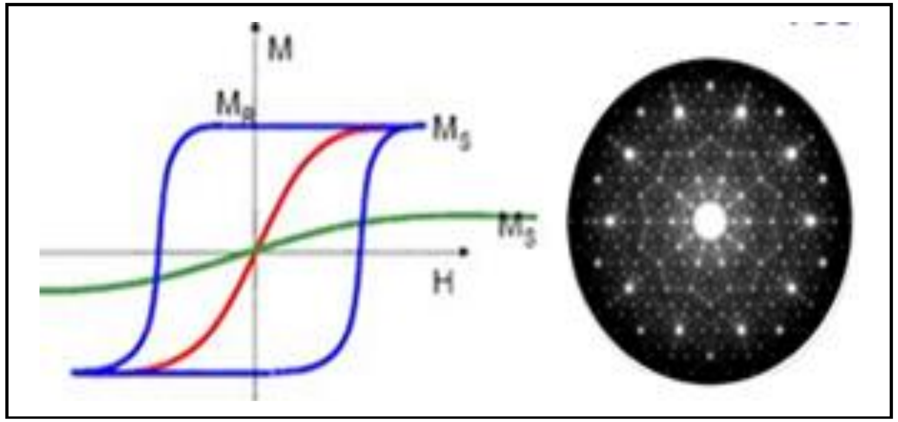


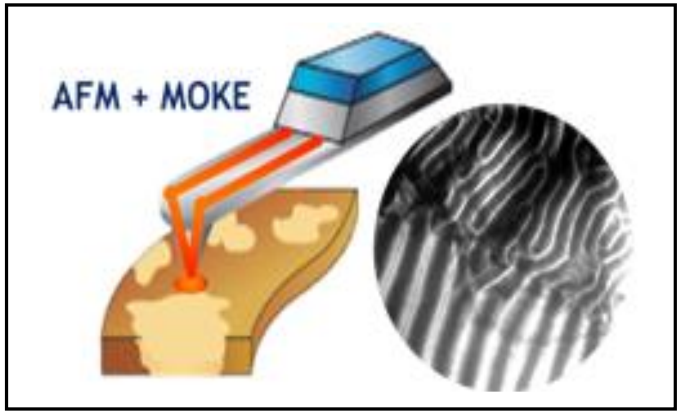


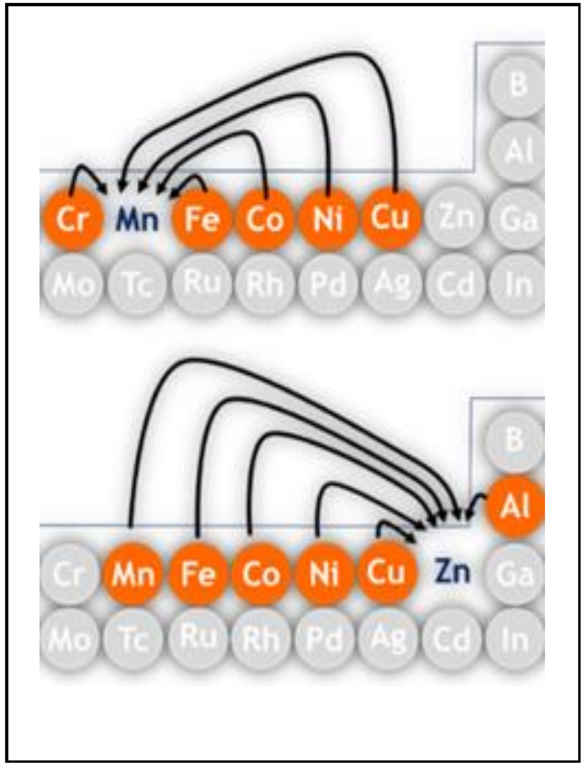


High entropy magnetic alloys for renewable electricity

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

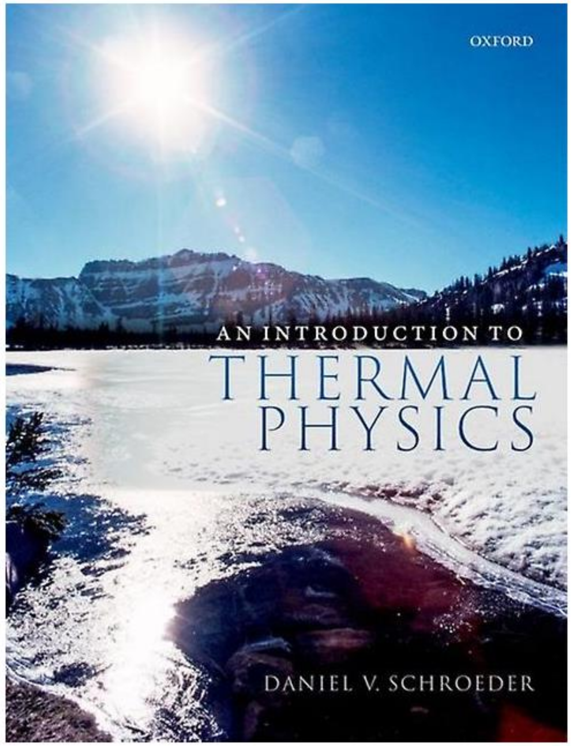






Store fysiske auditorium

• Wednesday September 28	Free energies
• Monday October 3	Phase transitions of mixtures
• Monday October 24	Chemical potential
• Monday October 31	Electron gas
• Wednesday November 2	Blackbody radiation



Wednesday: 10:15 -12:00; Monday: 14:15 -16:00

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.

U is total energy content of a system

$$\Delta U = Q + W$$

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

$$S = k \ln\Omega$$

k = 1.380649 × 10^{−23} J/K

Entropy **S** is the logarithm of multiplicity **Ω** or the number of ways of arranging **microstates** in the system.

For any system with *quadratic* degrees of freedom the multiplicity is $\boldsymbol{\Omega(U,V,N) = f(N)V^N U^{N*f/2}}$, where $N*f$ is the total number of degrees of freedom. Ω can be *VERY LARGE NUMBER*. For one mole of monoatomic gas: $\Omega = \boldsymbol{f(N)V^{6*10^{23}}U^{6*10^{23}*\frac{3}{2}}}$.

$$S = S_{max}$$

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

This is actually not the law, just strong statement.

The **second law** of thermodynamics

$S = k \ln\Omega$. Systems in equilibrium have the same temperature T.

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T}; \qquad S_{Total} = S_1 + S_2.$$

For sub-systems with different temperatures, there will be spontaneous flow of heat from the sub-system with higher temperature to the sub-system with lower temperature until the temperatures will be equilibrated maximising the total entropy of the system.

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

The second law is not fundamental law of nature, but a rule that arises purely through the laws of probability and the mathematics of very large numbers.

None of the states is forbidden by fundamental laws. Some, however, are MUCH more probable than other.

The **third law** of thermodynamics

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

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$.

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

$$\boldsymbol{S_{T=0} = 0}$$

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

Henry's Bent's First Two Laws of Thermodynamics

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

2nd Law: You can't break even

Thermodynamic identity

$$dU = Q + W$$

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

$$\boldsymbol{dU = TdS - PdV}$$

Chemical potential: $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Chemical potential is the same for two systems when they are in diffusive equilibrium. Particles tend to flow from the system with higher μ into the system with lower μ.

Generalized thermodynamic identity:

$$\boldsymbol{dU = TdS - PdV + \mu dN}$$

The μdN term is sometimes referred to as "chemical work."

The **third law** of thermodynamics

$$S = k \ln\Omega.$$

$$dU = TdS - \cancel{PdV}$$

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}.$

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

$$\frac{dU}{dT} = T\frac{dS}{dT}$$

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

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

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

Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$$dU = TdS - PdV$$

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

Equipartition theorem: $U = Nf\frac{1}{2}kT$

Ideal gas: $PV = NkT$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{NfkT}{2}\right) = \frac{Nfk}{2}$$

$$C_P = C_V + Nk = C_V + nR$$

$$c_V = f\frac{R}{2}, \quad c_p = (f+2)\frac{R}{2}$$

Single-atom ideal gas

$$C_V = \frac{3}{2}Nk = \frac{3}{2}nR$$

$$c_p - c_V = R = 8.314\,4598(48)\ \mathrm{J/(K\cdot mol)}.$$

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Adiabatic compression

$$dU = \cancel{TdS} - PdV$$

Equipartition theorem: $U = Nf\frac{1}{2}kT$

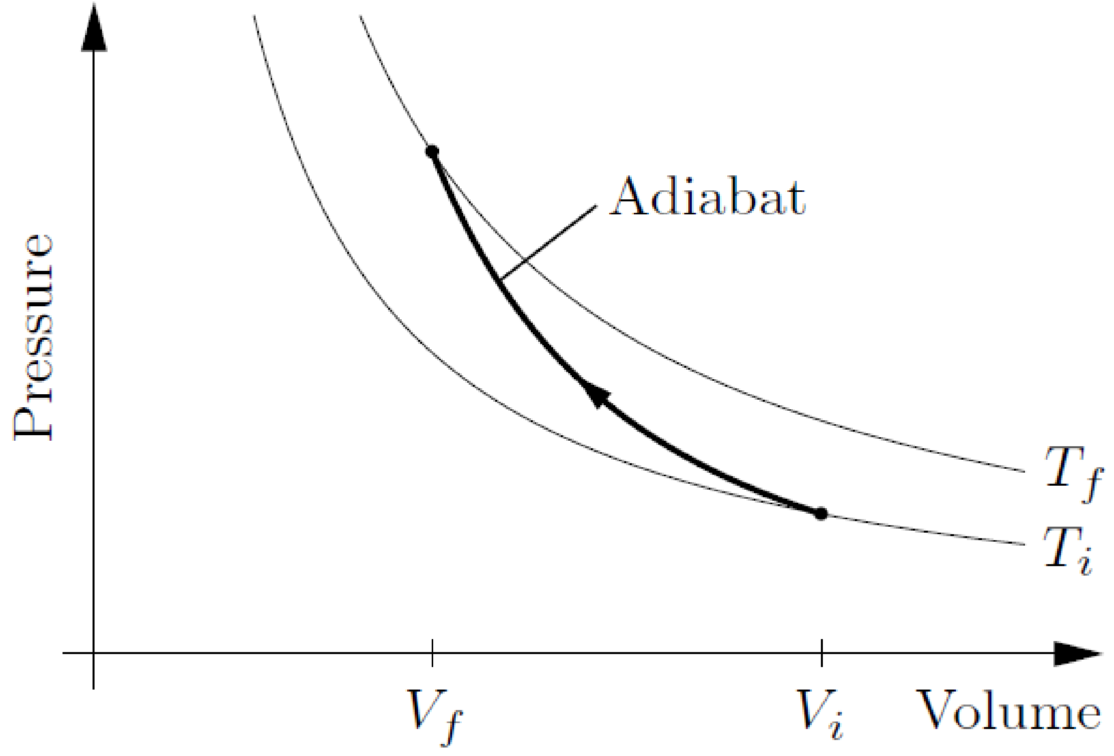
Ideal gas: $PV = NkT$

$$\frac{f}{2}\frac{dT}{T} = -\frac{dV}{V}$$

Integrating both sides:

$$\frac{f}{2}\ln\frac{T_f}{T_i} = -\ln\frac{V_f}{V_i} \qquad V_f\, T_f^{f/2} = V_i\, T_i^{f/2}$$

$$VT^{f/2} = \text{constant} \qquad V^\gamma P = \text{constant}$$



pV^γ, $TV^{\gamma-1}$, and $Tp^{1/\gamma-1}$ are constants.

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Propagation of sound

Speed of sound c depends on the density ρ of the gas and the **adiabatic** **compression modulus** *K*.

$$K = -V\frac{dp}{dV} = \gamma p \implies$$

$$c = \sqrt{\frac{K}{\rho}} = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{(f+2)p}{f\rho}}$$

From $\rho = m/V = nM_{\mathrm{mol}}/V$ and $pV = nRT$

$$c_{\mathrm{id}}(T) = \sqrt{\frac{(f+2)RT}{fM_{\mathrm{mol}}}}$$

Kundt's tube experiments

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

K1: contains argon or CO_2 at T = T_{room}
K2: contains air at T = T_{room}
K3: contains air at T ≃ 70 °C
K4: contains air at T ≃ 50 °C

pV^{γ}, $TV^{\gamma-1}$, and $Tp^{1/\gamma-1}$ are constants.

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Kundt's tube experiments

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

K1: contains argon or CO_2 at $T = T_{room}$

$c_{Exp} < c_{Theor}$ ($c_{id}(T)$)

K2: contains air at $T = T_{room}$

$c_{Exp} \approx c_{Theor}$

K3: contains air at $T \simeq 70$ °C

$c_{Exp} > c_{Theor}$

K4: contains air at $T \simeq 50$ °C

$c_{Exp} \geq c_{Theor}$

$$c_{\mathrm{id}}(T) = \sqrt{\frac{(f+2)RT}{f M_{\mathrm{mol}}}}$$

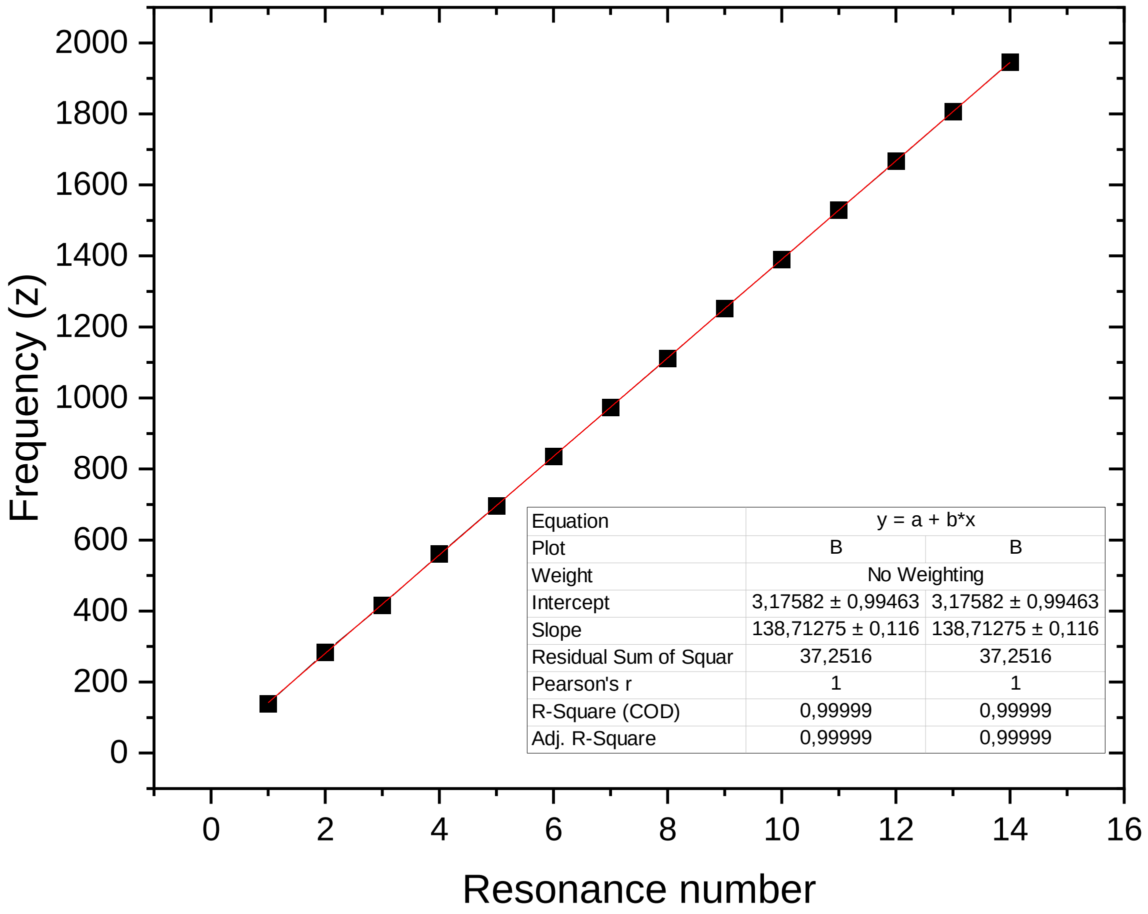
$$Z = \frac{pV}{nkT} = 1 + B\rho + C\rho^2 + \ldots,$$

Negative B signifies that the attractive interactions between the molecules dominate.

Linear regression

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

Origin:

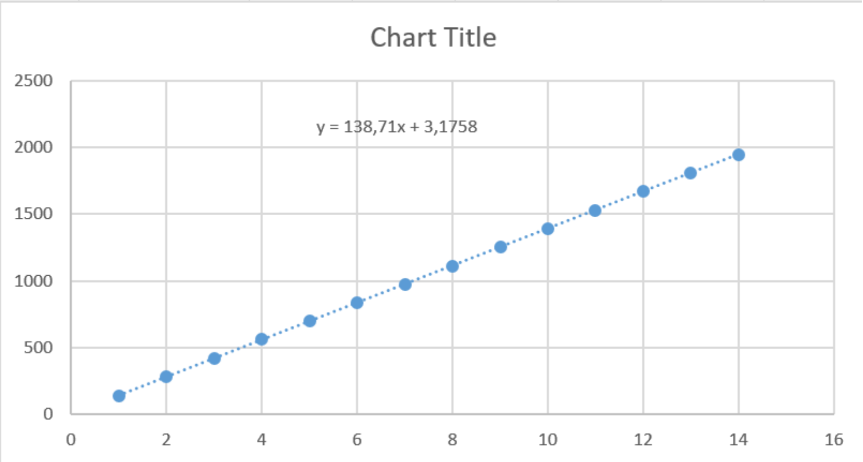


Equation	y = a + b*x	
Plot	B	B
Weight	No Weighting	
Intercept	3,17582 ± 0,99463	3,17582 ± 0,99463
Slope	138,71275 ± 0,116	138,71275 ± 0,116
Residual Sum of Squar	37,2516	37,2516
Pearson's r	1	1
R-Square (COD)	0,99999	0,99999
Adj. R-Square	0,99999	0,99999

Excel:

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	ower 95,0%	pper 95,0
Intercept	3,17582418	0,994626832	3,192981	0,007733	1,008718	5,34293	1,008718	5,34293
X Variable	138,712747	0,116812997	1187,477	8,57E-32	138,4582	138,9673	138,4582	138,9673

Column1	Column2
1	139
2	284,1
3	416,7
4	560,7
5	697
6	835,8
7	974
8	1112
9	1252
10	1390
11	1529
12	1667
13	1806
14	1946



Piton:

x = [1, 2, 3, . . . , n]

y = [ν_1, ν_2, ν_3, . . . , ν_n]

```
from scipy import stats
stats.linregress(x, y)
```

K1: contains argon or CO_2 at $T = T_{room}$
K2: contains air at $T = T_{room}$
K3: contains air at $T \simeq 70$ °C
K4: contains air at $T \simeq 50$ °C

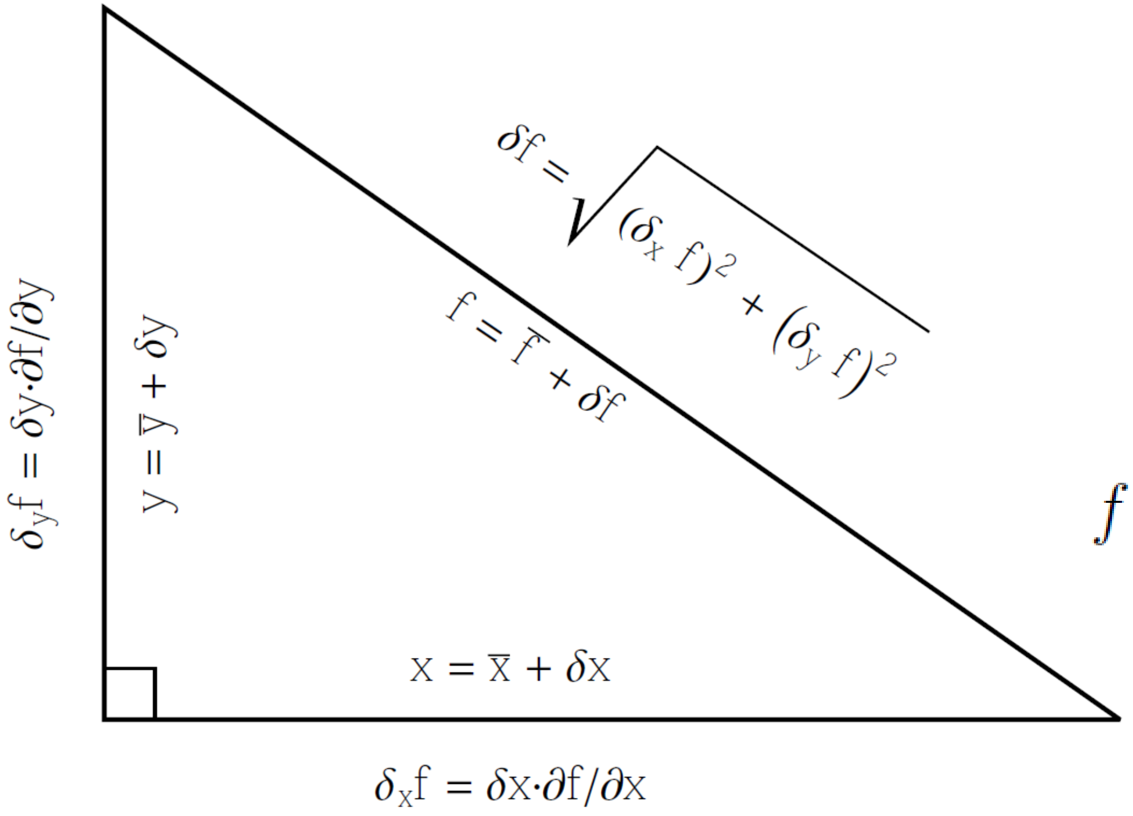
K1: L = 1243 ± 1.5 mm
K2: L = 1243 ± 1.5 mm
K3: L = 1244 ± 1.5 mm
K4: L = 1244 ± 1.5 mm

Estimation of error

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

$$c = 2La$$

$$f(x,y) = xy \implies \frac{\delta f}{f} = \sqrt{\left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2}$$



Enthalpy

Consider number of particles fixed.

Constant-pressure processes occur quite often. Keeping track of the compression-expansion work is difficult. To avoid this, instead of talking about the energy content, we can agree to always add in the work needed to make room for it, which is product of pressure and volume.

$$dU = TdS - PdV \qquad U = TS - PV$$

$$dU = Q + W \qquad H = U + PV$$

Enthalpy H is the total energy needed to create the system out of nothing and put it into the environment.

$$W = -PV + W_{other} \qquad H = TS + W_{other}$$

Enthalpy is free from the compression-expansion work (but not from other work).

Helmholtz free energy

$$dU = TdS - PdV$$

$$U = TS - PV$$

$$\Delta U = Q + W$$

$$F = U - TS$$

$$TS \approx Q$$

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

$$\Delta F \cong -PV + W_{other}$$

Helmholtz free energy is the total energy needed to create the system, minus the heat you can get from an environment at temperature T. In other words, F is the energy that must be provided as work, if you're creating the system out of nothing.

Helmholtz free energy is free from heat.

Gibbs free energy

$$U = TS - PV$$

$$\Delta U = Q + W$$

$$G = U - TS + PV$$

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

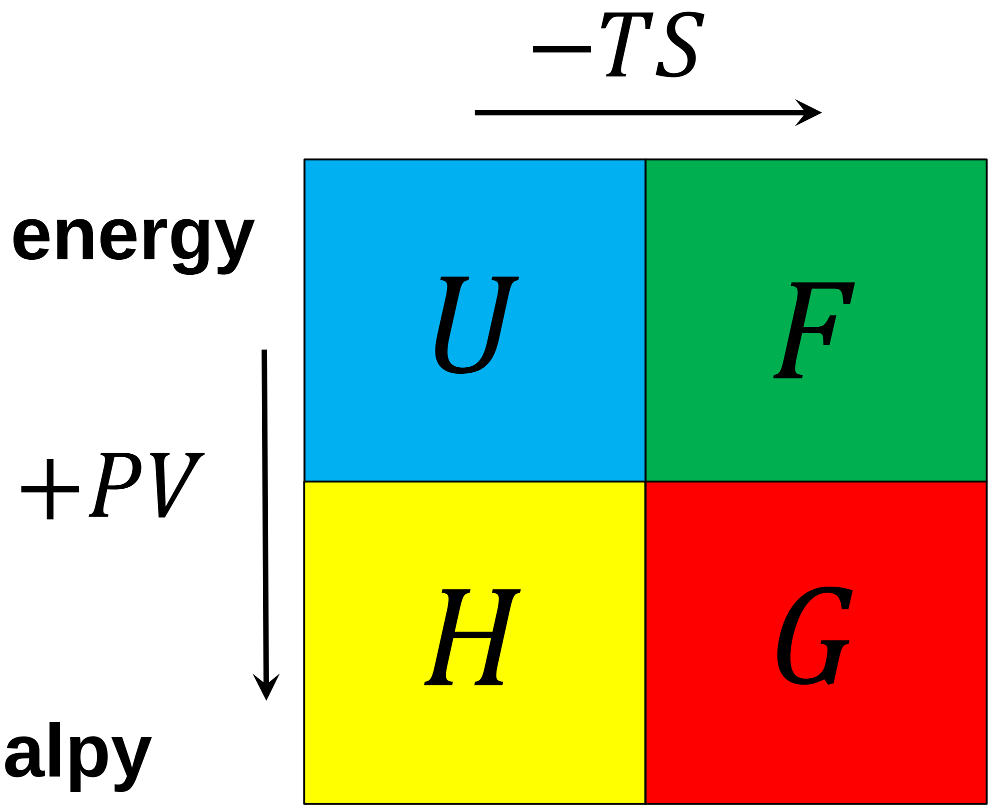
G is just the system's energy, minus the heat term plus the atmospheric work term.

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

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

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

Thermodynamic potentials



Total energy

Enthalpy

$$H = U + PV$$

Helmholtz free energy

$$F = U - TS$$

Gibbs free energy

$$G = U - TS + PV$$

$$G = H - TS$$

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

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

Electrolysis

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

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

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

4 kJ

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

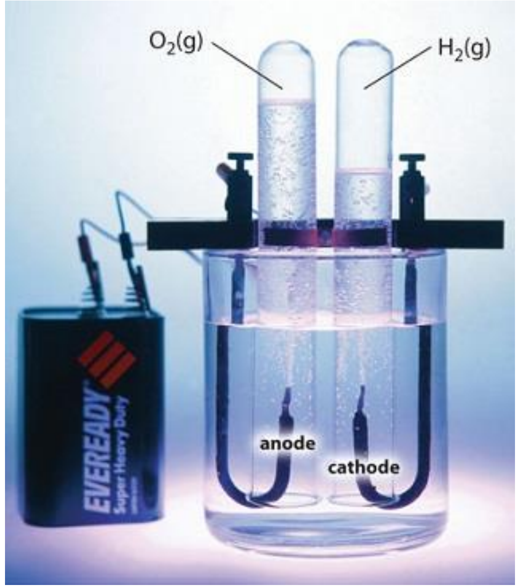
49 kJ

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

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

$$S_{H2O} = 70\ J/K;\ S_{H2} = 131\ J/K;\ S_{O2} = 205\ J/K.$$

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



https://chem.libretexts.org/Courses/University_of_California_Davis/UCD_Chem_002CH/Text/UNIT_II%3A_ELECTRO-CHEMISTRY/17.7%3A_A_Deeper_Look%3A_Electrolysis_of_Water_and_Aqueous_Solutions

Fuel Cell

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

$$H_2O \leftarrow H_2 + \frac{1}{2} O_2$$

4 kJ

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

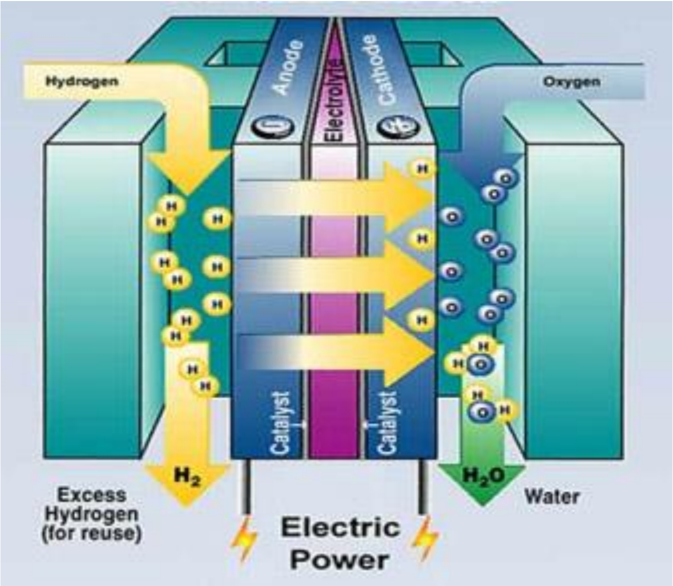
49 kJ

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

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

$S_{H2O} = 70\ J/K$; $S_{H2} = 131\ J/K$; $S_{O2} = 205\ J/K$.

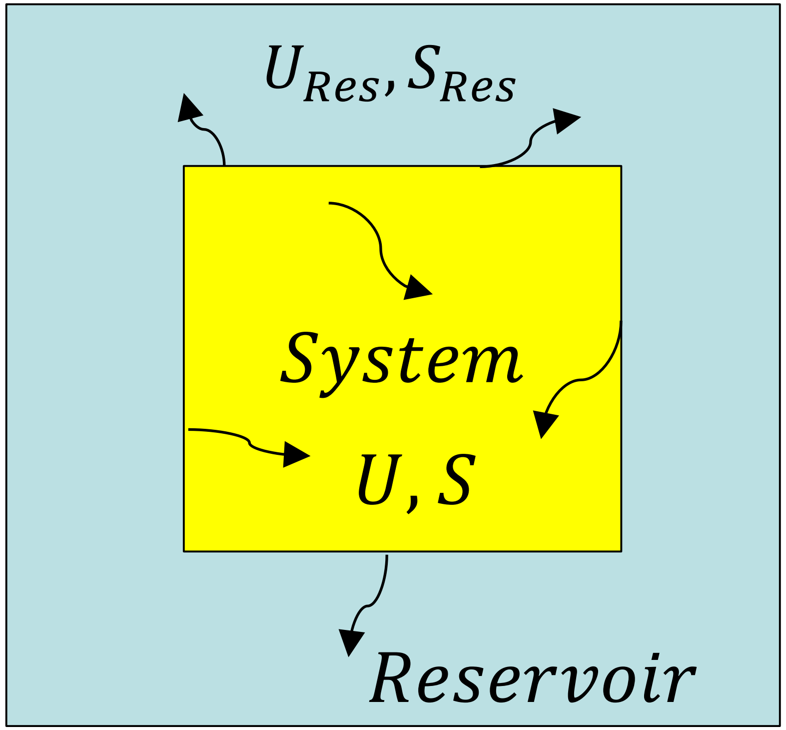
Ideal hydrogen fuel cell has an "efficiency" of 83%, much better than any practical heat engine.



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

System in contact with thermostat

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



$$dU = TdS - PdV$$

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

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

Under the conditions of fixed T, V , and N, increase in the total entropy of the system plus reservoir is equivalent to a decrease in the Helmholtz free energy of the system.

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

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**

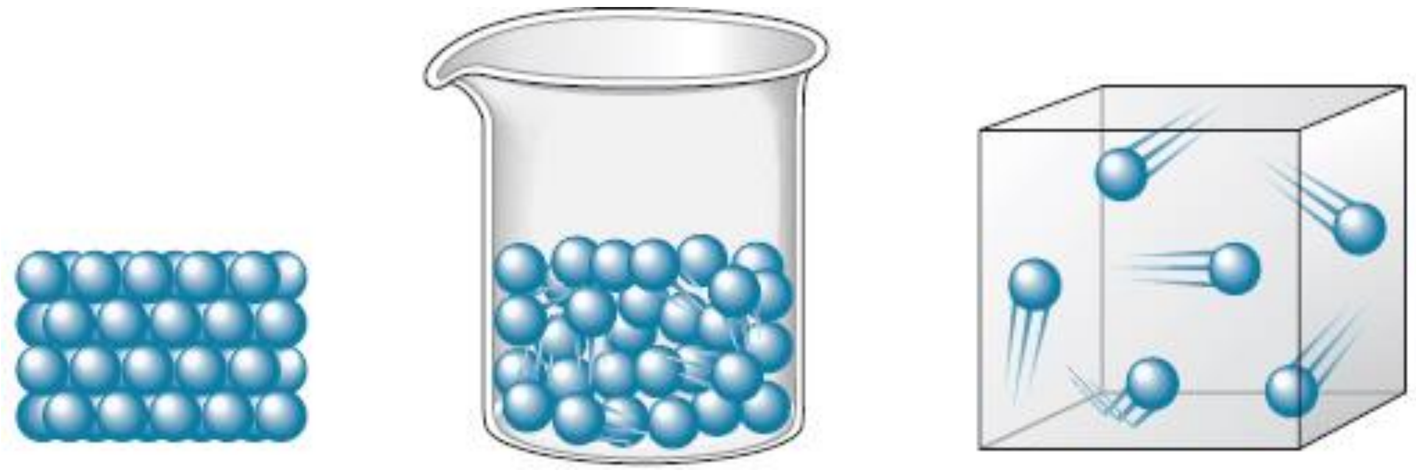
- The criterion takes into account **enthalpy**, **entropy**, and **temperature**

- 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

$S_{solid} < S_{liquid} << S_{gas}$



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 taken from environment per 1mole of final gas?

Evaporation of liquid nitrogen

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

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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)?

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}

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

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

$\Delta G = 2 * \Delta H - T\Delta S$ (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

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

Spontaneity of phase transformations

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

Value of ΔH	***Value of TΔS***	***Value of ΔG***	***Spontaneity***
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 TΔS (works at low temperatures)
Positive	Positive	Negative or positive	Spontaneous if the absolute value of TΔS 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.

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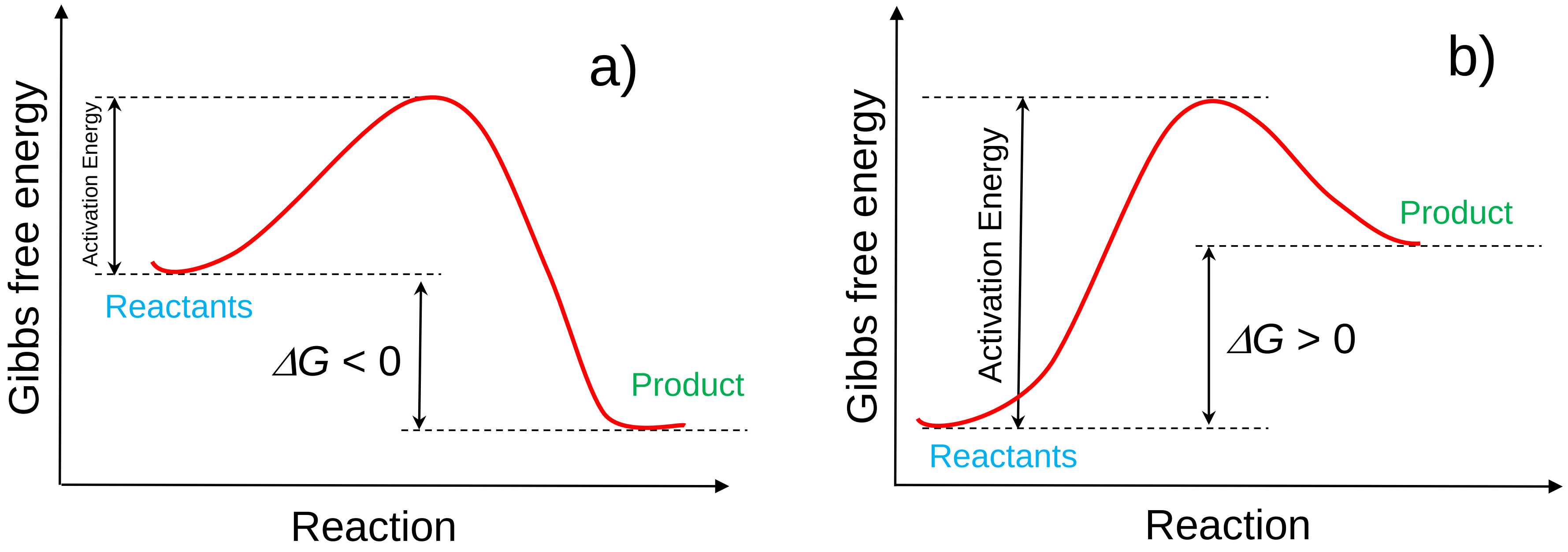
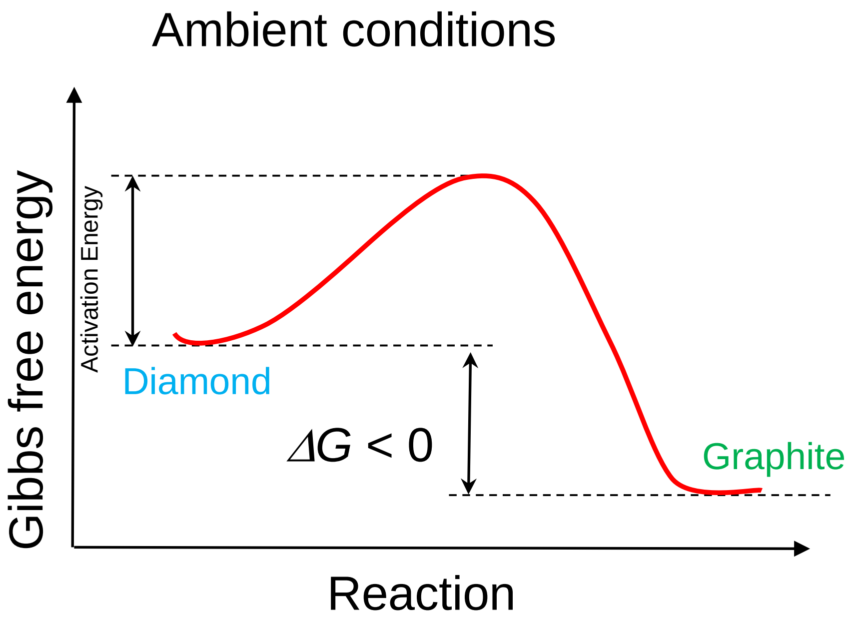
A barrier for phase transformation

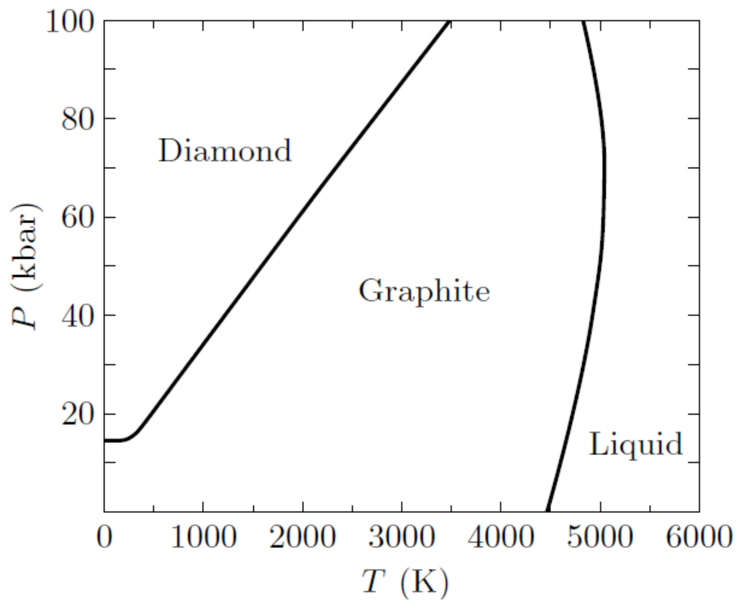


a) Spontaneous reaction in which product has a lower free energy (G) than the reactants ($\Delta G < 0$)

b) Nonspontaneous reaction in which reactants have a higher free energy than the product ($\Delta G > 0$)

Graphite and diamond



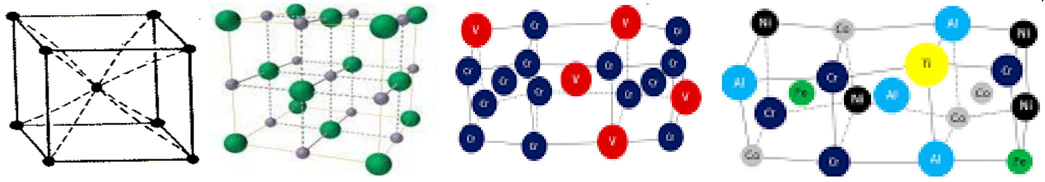


Under standard conditions, graphite is more stable than diamond because the Gibbs free energy of a mole of diamond is on 2900 J greater than the Gibbs free energy of a mole of graphite. However, the temperature required to quickly convert diamond to graphite is quite high: about 1500 °C. The first synthesis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

High Entropy Alloys (HEAs) – Basic Concept

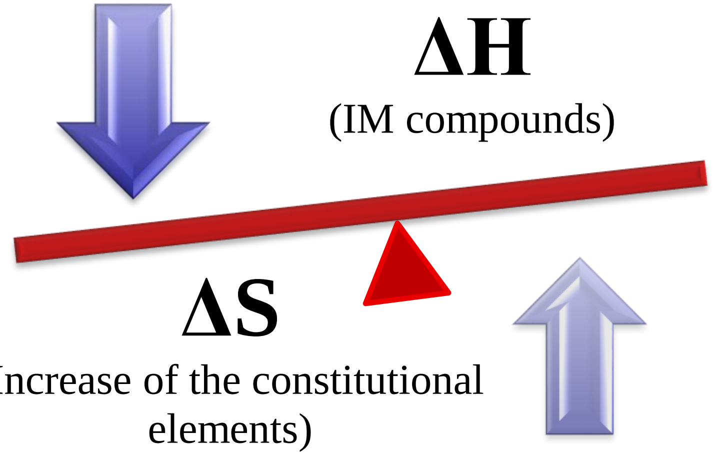
<u>**H**igh **E**ntropy **A**lloys (HEAs)</u>**:** Alloys that contain at least 5 principal elements, each having an atomic percentage between 5 - 35 at.%.

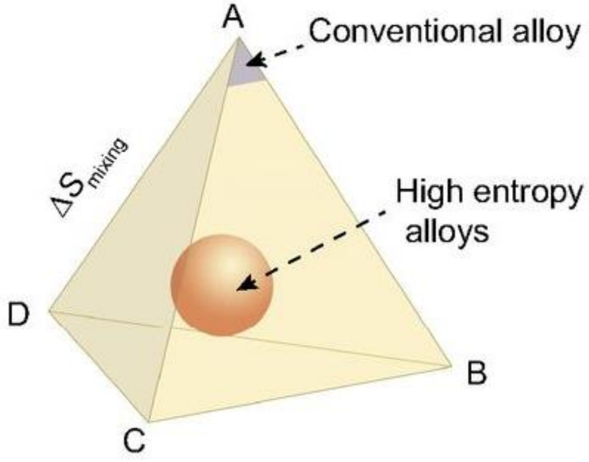
Chemical and structural complexity / Desired properties



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

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

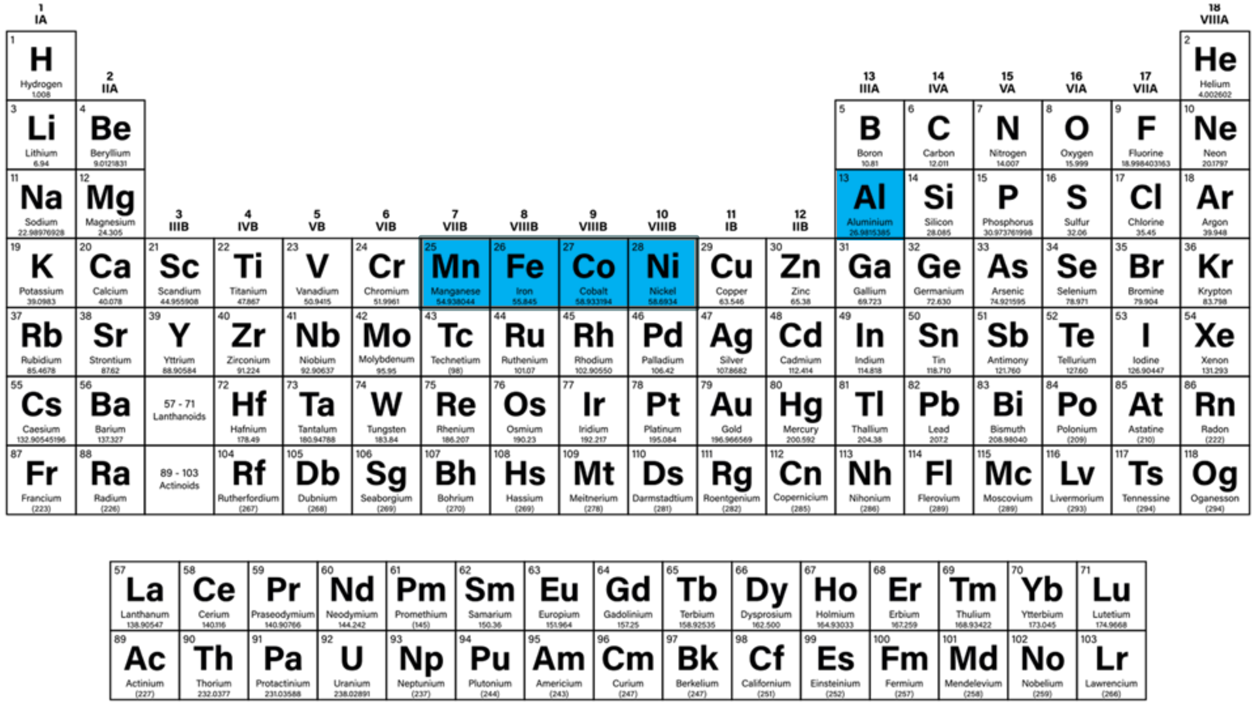




High-entropy alloys (HEAs) and $FeNiCoAl_xMn_x$

$FeCoNiAl_xMn_x$

- Soft magnetic system



HEAs:

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

Phase Formation modelling

Structure	Model	Wyckoff sites			ΔH_{form} (meV)				ΔS_{conf} (meV/K)				ΔH_{form} - T ΔS_{conf} (meV) @1000 K			
		a	b	c	A	B (dendrite)	B (interd.)	C	A	B (dendrite)	B (interd.)	C	A	B (dendrite)	B (interd.)	C
BCC		Al Co Fe Mn Ni			178	19	94	2	0.137	0.129	0.135	0.120	41	-110	-41	-118
B2	M1	Al Mn	Co Fe Ni		38	-	-	-	0.077	-	-	-	-39	-	-	-
	M2	Al Co Ni	Co Fe Mn Ni		135	0	88	2	0.093	0.089	0.105	0.091	42	-89	-17	-89
	M3	Al Co Fe Mn Ni	Co Fe Mn Ni		125	22	78	13	0.118	0.125	0.124	0.116	7	-103	-46	-103
$L2_1$	M1	Al	Mn	Co Fe Ni	0	-	-	-	0.047	-	-	-	-47	-	-	-
	M2	Al	Fe Mn	Co Fe Mn Ni	26	-	-	-	0.071	-	-	-	-45	-	-	-
	M3	Al Co Ni	Fe Mn	Co Fe Mn Ni	-	6	12	0	-	0.086	0.076	0.077	-	-80	-64	-77
	M4	Al Mn	Co Fe Mn Ni	Al Co Fe Ni	-	-	0	-	-	-	0.059	-	-	-	-59	-
FCC		Al Co Fe Mn Ni			161	1	82	13	0.137	0.129	0.135	0.120	24	-128	-53	-107

Electronic-scale calculations based on density functional theory (DFT) were performed with the Vienna Ab initio Simulation Package (VASP), where a generalized gradient approximation was employed. Solid-solution structures were simulated with special quasi-random structures (SQS) consisting of 48 atoms, generated with the temperature-dependent effective potential (TDEP) software. Five different SQS candidates were tested for each composition and model.

Probing the structural evolution and its impact on magnetic properties of FeCoNi(AlMn)$_x$ high-entropy alloy at the nanoscale

C. Baziotiᵃ,*, O.M. Løvvik[b], A. Poulia[a], P.A. Carvalho[b], A.Azar[b], P. Mikheenko[a], S. Diplas[b], A.E. Gunnæs[a]

Samples 1-14: $FeNiCoAl_xMn_x$ (0.05<x<3.08)

Sample 1: $FeNiCoAl_{3.08}Mn_{3.08}$

Sample 2: $FeNiCoAl_{1.28}Mn_{1.28}$

Sample 3: $FeNiCoAl_{0.9}Mn_{0.9}$

Sample 4: $FeNiCoAl_{0.72}Mn_{0.72}$

Sample 5: $FeNiCoAl_{0.57}Mn_{0.57}$

Sample 6: $FeNiCoAl_{0.39}Mn_{0.39}$

Sample 7: $FeNiCoAl_{0.32}Mn_{0.32}$

Sample 8: $FeNiCoAl_{0.29}Mn_{0.29}$

Sample 9: $FeNiCoAl_{0.28}Mn_{0.28}$

Sample 10: $FeNiCoAl_{0.24}Mn_{0.24}$

Sample 11: $FeNiCoAl_{0.2}Mn_{0.2}$

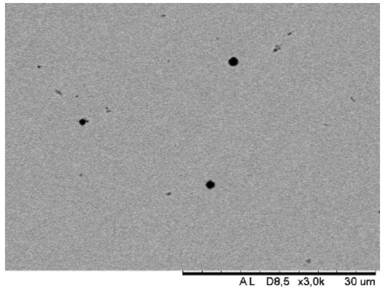
Sample 12: $FeNiCoAl_{0.19}Mn_{0.19}$

Sample 13: $FeNiCoAl_{0.08}Mn_{0.08}$

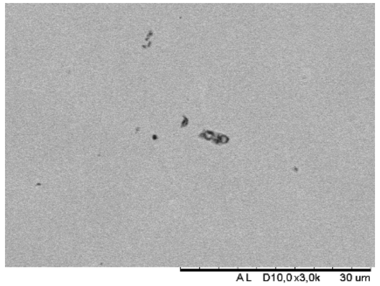
Sample 14: $FeNiCoAl_{0.05}Mn_{0.05}$

SEM evidence of spinodal decomposition

Sample 1



Sample 2



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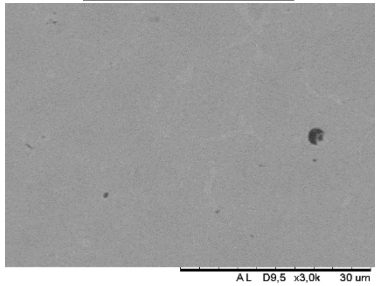

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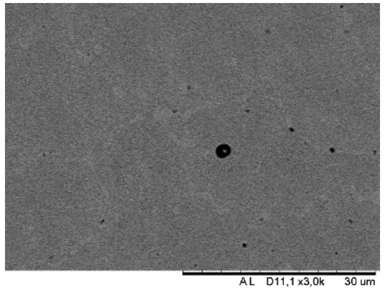

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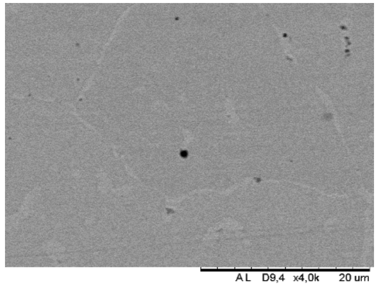

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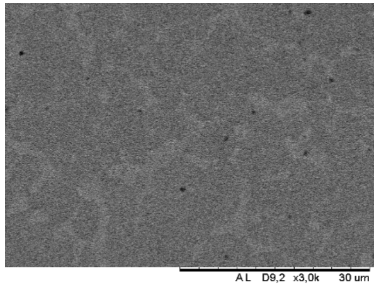

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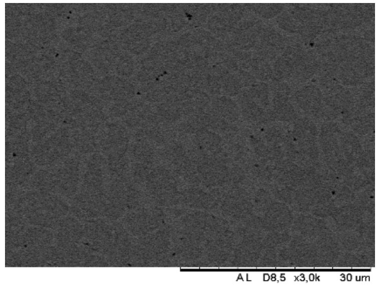
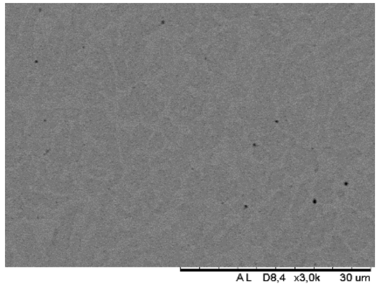
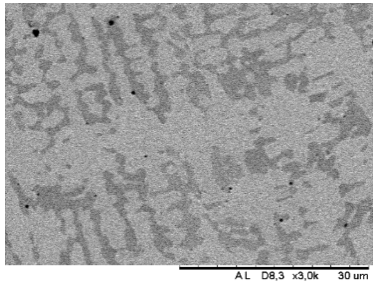


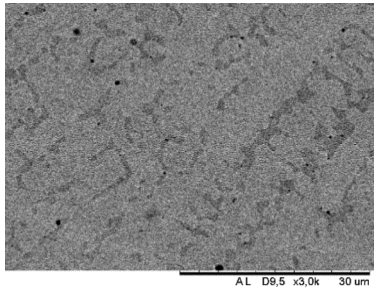
Sample 8



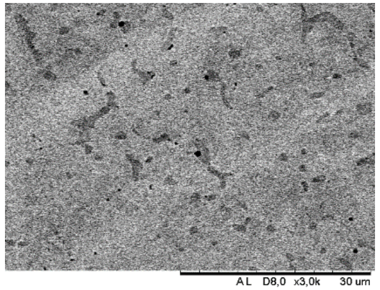
Sample 9



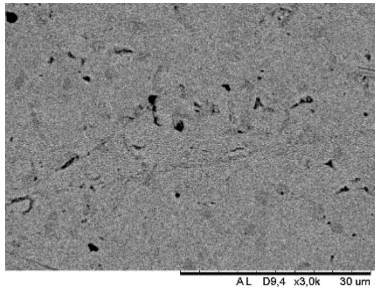
Sample 10



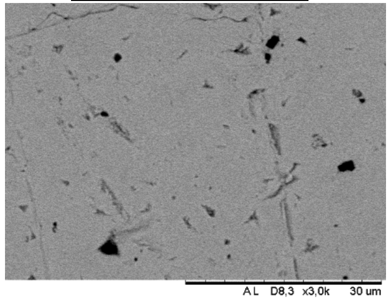
Sample 11



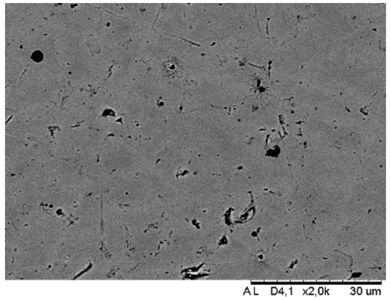
Sample 12



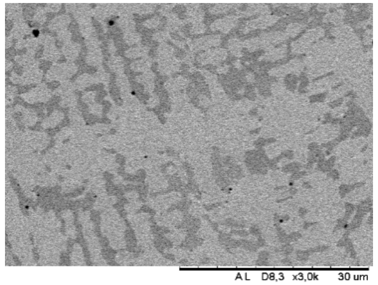
Sample 13



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

- 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.