UiO **: University of Oslo**

Invitation to answer Midterm evaluation form: https://nettskjema.no/a/289420

Chemical potential

3.5 Diffusive Equilibrium and Chemical Potential

5   Free Energy and Chemical Thermodynamics
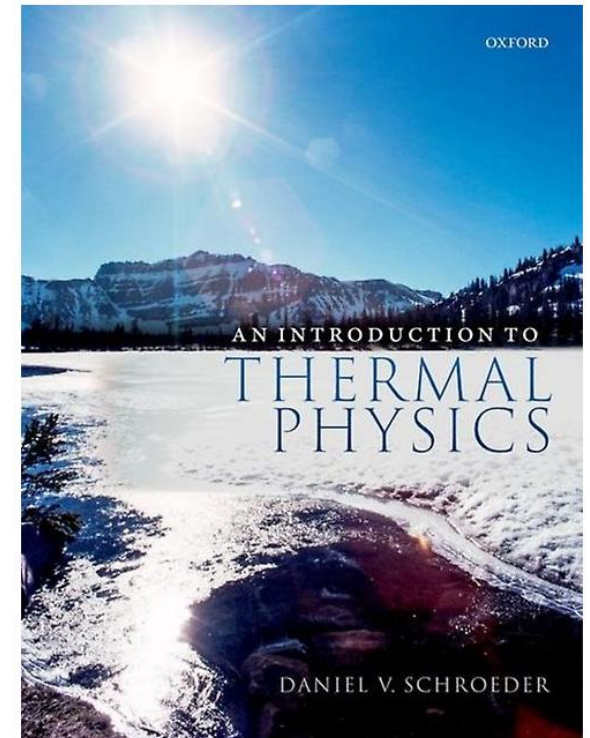
Thermodynamic potentials
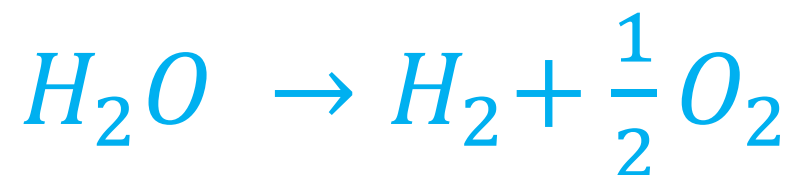
$$\boldsymbol{dU = TdS - PdV}$$

Thermodynamic identity

$$-TS \longrightarrow$$

Total energy

Helmholtz free energy

$$F = U - TS$$

$$+PV \downarrow$$

Gibbs free energy

$$G = U - TS + PV$$

U	F
H	G

Enthalpy

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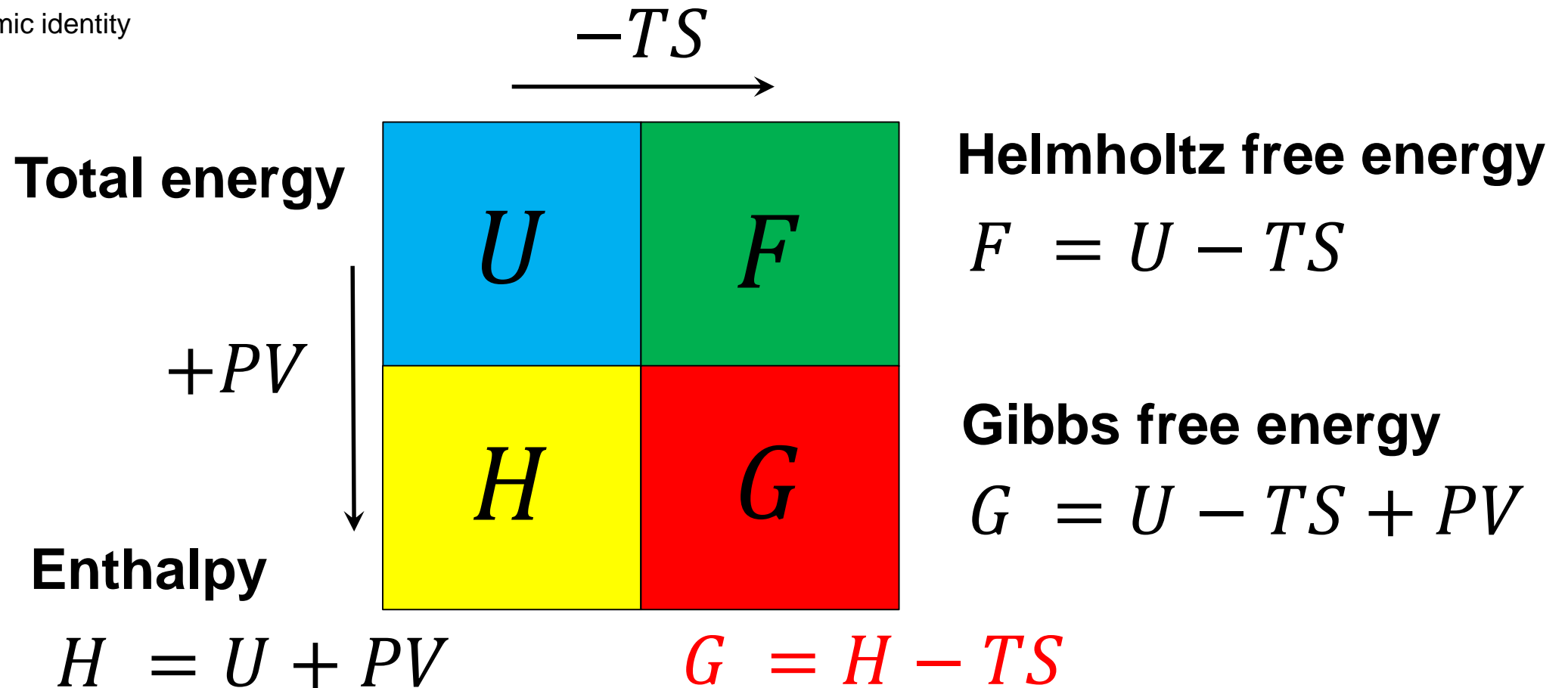
$$G = H - TS$$

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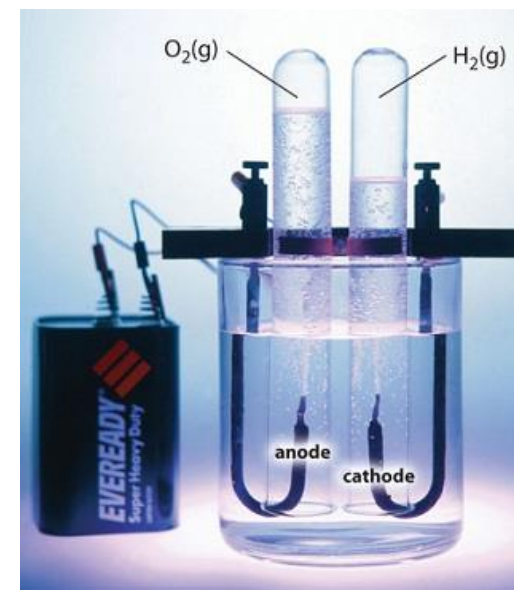
$$G = U - TS + PV = H - TS \qquad \Delta G = \Delta U - T\Delta S + P\Delta V$$

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.

Thermodynamic identity

$$\boldsymbol{dU} = \boldsymbol{Q} + \boldsymbol{W}$$

$$dU = TdS - PdV$$

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

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

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

Generalized thermodynamic identity:

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

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

Types of interactions

Electrolysis

49 kJ
Thermal energy

4 kJ
Mechanical energy

237 kJ
Electrochemical energy

Type of interaction	Exchanged quantity	Governing variable	Formula
thermal	energy	temperature	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

https://e-lyte-innovations.de/working-principle-lithium-ion-battery/

The electrochemical potential (ECP), $\bar{\mu}$, is a thermodynamic measure of chemical potential that does not omit the energy contribution of electrostatics: $\bar{\mu} = \mu + z\mathcal{F}\Phi$. Here z is valency of ion, $\mathcal{F}$ is Faraday constant in C/mol and Φ is local electrostatic potential, in V.

Onsager reciprocal relations

"Fourth law of thermodynamics"

- The Onsager reciprocal relations express the equality of certain ratios between flows and forces in thermodynamic systems out of equilibrium, but where a notion of **local equilibrium** exists.

- The temperature differences lead to heat flows from the warmer to the colder parts of a system, and a pressure differences lead to matter flow from high-pressure to low-pressure regions.

- It is remarkable that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow and pressure differences at constant temperature can cause heat flow.

- Even more surprising is that the heat flow per unit of pressure difference and the density (matter) flow per unit of temperature difference are equal.

- This equality was shown to be necessary by Lars Onsager using statistical mechanics as a consequence of the time reversibility of microscopic dynamics.

- The theory developed by Onsager is much more general than this example and capable of treating more than two thermodynamic forces.

Lars Onsager
1903 -1976
Born in Oslo, graduated from Frogner School. **Nobel Prize in Chemistry 1968** for the Onsager reciprocal relations.

M is mass

$$dU = TdS - PdV + \mu dM$$

Diffusive equilibrium and chemical potential

When two systems are in thermal equilibrium, their temperatures are the same. When they're in mechanical equilibrium, their pressures are the same. What quantity is the same when they're in diffusive equilibrium?

DVS
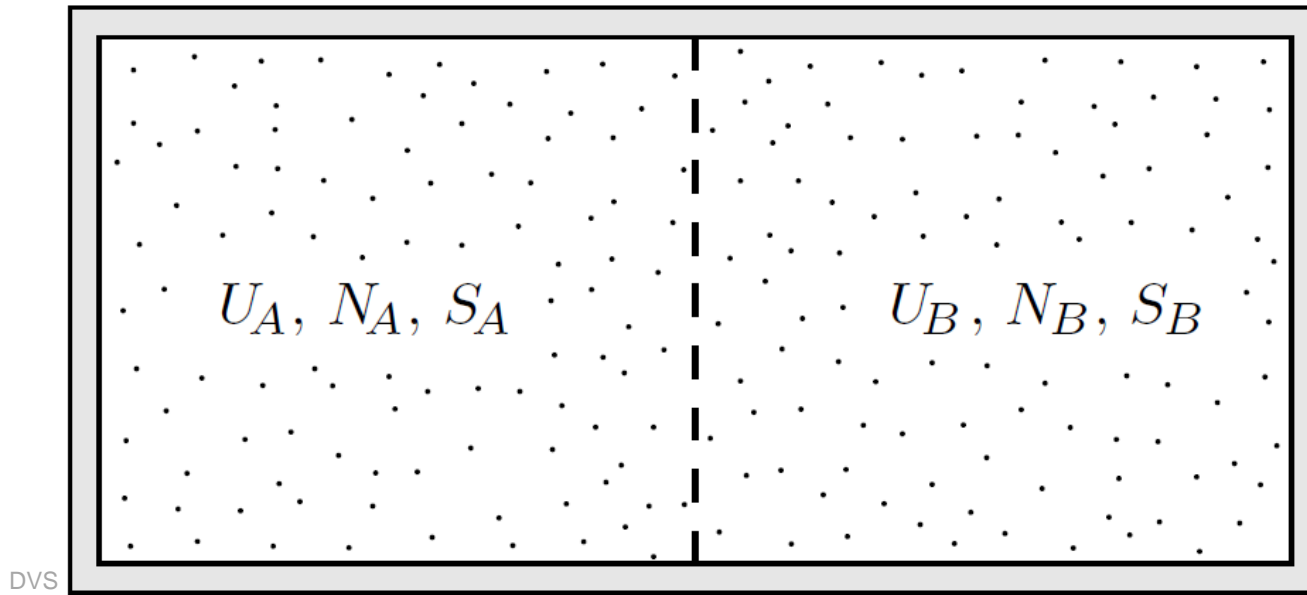
An example of two systems that can exchange both energy and particles with total energy and number of particles fixed. **At equilibrium, the total entropy is at a maximum.**

$$\left(\frac{\partial S_{total}}{\partial U_A}\right)_{N_A,N_B} = 0 \qquad \left(\frac{\partial S_{total}}{\partial N_A}\right)_{U_A,U_B} = 0$$

$$\frac{\partial S_{total}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

$$\frac{\partial S_A}{\partial U_A} = -\frac{\partial S_B}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad \left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T}$$

At equilibrium:

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad\qquad \frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

Constant T

What parameter is constant here?

The diagram shows a box divided by a dashed line with U_A, N_A, S_A on the left and U_B, N_B, S_B on the right.

Diffusive equilibrium and chemical potential

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$-T\frac{\partial S_A}{\partial N_A} = -T\frac{\partial S_B}{\partial N_B}$$

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

μ is chemical potential. In equilibrium, $\mu_A = \mu_B$.

μ is parameter, which is constant in diffusive equilibrium.

If two systems are not in diffusive equilibrium, then the one with the larger value of $\partial S / \partial N$ will tend to gain particles, since it will thereby gain more entropy than the other loses. Because of the minus sign, this system has the smaller value of μ. Therefore, particles tend to flow from the system with higher μ into the system with lower μ .

Generalized thermodynamic identity

Let us change U by dU, V by dV, and N by dN
and see what will happen with S:

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

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

$$dS = \frac{dU}{T} + \frac{PdV}{T} - \frac{\mu dN}{T}$$

$$TdS = dU + PdV - \mu dN$$

$$dU = TdS - PdV + \mu dN$$

Link with Gibbs free energy

$$dU = TdS - PdV + \mu dN$$

Generalized thermodynamic identity

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

$$dG = dU - TdS + PdV = \mu dN \qquad \mu = \left(\dfrac{\partial G}{\partial N}\right)_{T,P}$$

The chemical potential of a species in a mixture is defined as the rate of change of Gibbs free energy of a thermodynamic system with respect to the change in the number of atoms or molecules of the species that are added to the system.

$$dU = TdS - PdV + \sum \mu_i dN_i$$

The $\mu_i dN_i$ terms are sometimes referred to as "chemical works".

Chemical potential: different formulas

$$dU = TdS - PdV + \mu dN$$

Fixed U and V: $\qquad \mu = -T\left(\dfrac{\partial S}{\partial N}\right)_{U,V}$

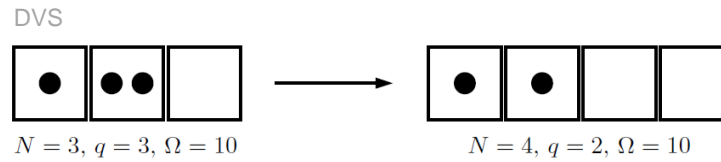Fixed U and S: $\qquad \mu = P\left(\dfrac{\partial V}{\partial N}\right)_{U,S}$

Fixed V and S: $\qquad \mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V}$

Chemical potential is the amount by which a system's energy changes when one adds one particle and keeps the entropy and volume fixed. μ has units of energy.

Chemical potential: examples

a) Fixed V and S: $\quad \mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V}$

DVS

$N = 3, q = 3, \Omega = 10 \longrightarrow N = 4, q = 2, \Omega = 10$

Small Einstein solid with three oscillators and three units of energy ε, adding 4th oscillator: $k \ln 10 \longrightarrow k \ln 20$. One unit of energy is necessary to remove $\quad \mu = -\epsilon/1 = -\epsilon$.

y = ln(x)
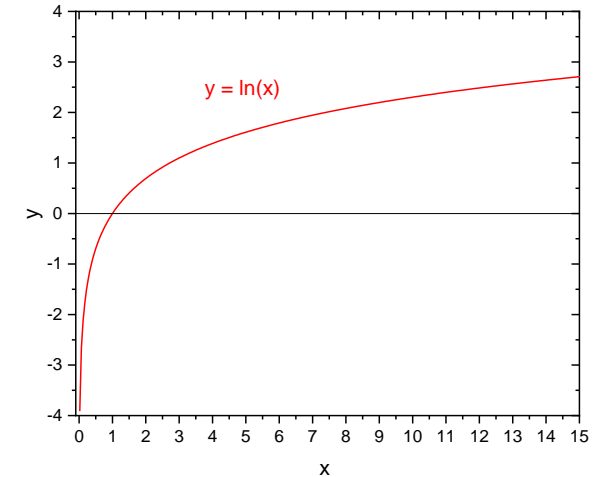
b) Ideal gas, Sackur-Tetrode equation: $\quad S = Nk\left[\ln\left(\dfrac{V}{N}\left(\dfrac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \dfrac{5}{2}\right]$ $\qquad \mu \equiv -T\left(\dfrac{\partial S}{\partial N}\right)_{U,V}$

$$\mu = -kT\ln\left[\dfrac{V}{N}\left(\dfrac{2\pi mkT}{h^2}\right)^{3/2}\right].$$

For He at ambient conditions, μ = -0.32 eV.

1 eV = 1.60218e-19 J.

Increasing the density of particles in a system always increases its chemical potential.

Normally, to hold the entropy (or multiplicity) fixed, you must remove some energy as you add a particle, so μ is negative. However, it could be positive.

Quantum volume and length

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right].$$

$$\vartheta_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi m kT}}\right)^3$$

$$\frac{h}{\sqrt{2\pi m kT}} \xrightarrow{\quad} \frac{h}{\sqrt{2\pi m \epsilon}} \xrightarrow{\epsilon = \frac{p^2}{2m}} \frac{h}{p\sqrt{\pi}} \xrightarrow{p = \frac{\hbar h}{2\pi}} \frac{2\pi}{\hbar\sqrt{\pi}} \xrightarrow{\frac{2\pi}{\hbar} = \lambda_{dB}} \frac{\lambda_{dB}}{\sqrt{\pi}}$$

- For the air we breathe, the average distance between molecules is about 3 nm while the average de Broglie wavelength is less than 0.02 nm, so condition $\frac{V}{\vartheta_Q N} \gg 1$ is satisfied.

- For an electron at room temperature, because of low mass, the quantum volume is $\vartheta_Q = (4.3 \text{ nm})^3$, while the volume per conduction electron is roughly the volume of an atom, $(0.2 \text{ nm})^3$. Therefore, electron gas in metals at ambient conditions is quantum gas, for which $\frac{V}{\vartheta_Q N} \ll 1$.


$y = \ln(x)$
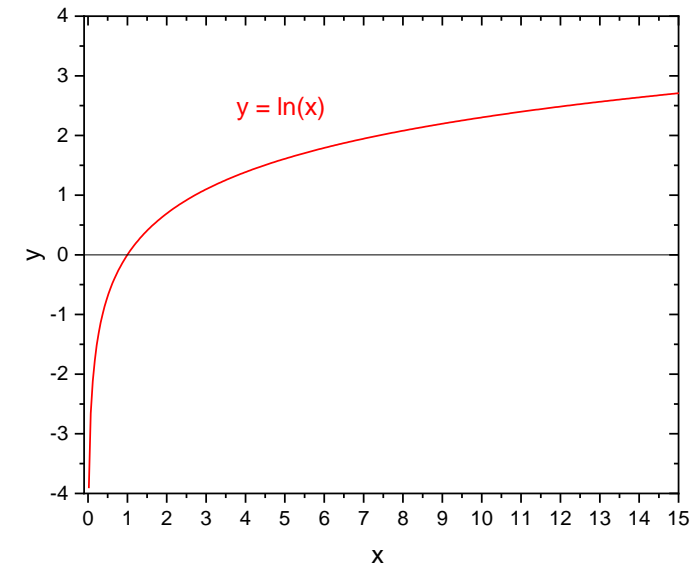
Dilute solutions

DVS
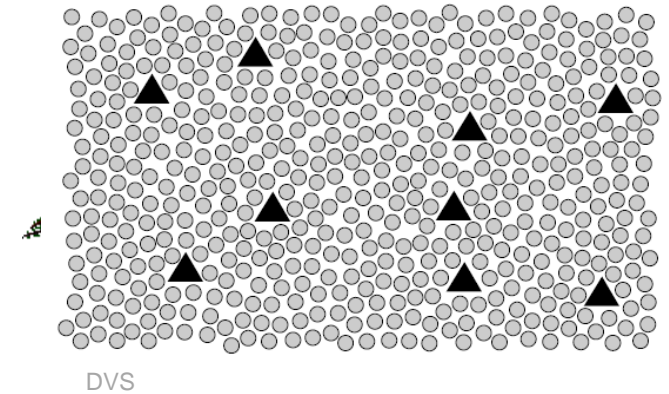
- A dilute solution is a mixture, in which one component (the solvent) is dominant or primary and the other component (the solute) is minor or secondary.

- 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.

Dilute solutions

The key for understanding behavior of dilute solutions is deriving chemical potentials of the solvent and solute.
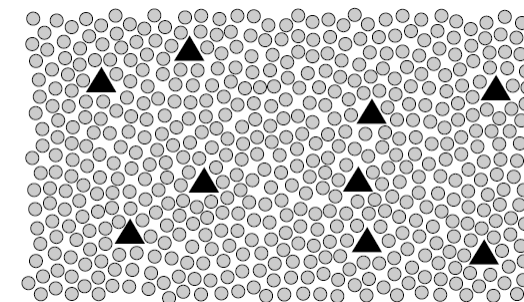
DVS

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} \qquad \mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A}$$

$$G = N_A \mu_0 (T,P) \quad \text{(pure solvent)} \qquad dG = dU + PdV - TdS$$
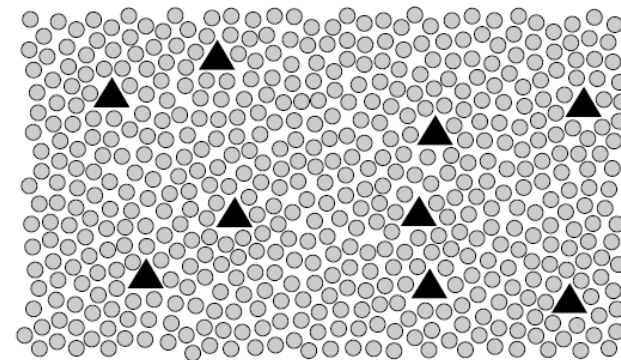
$$(N_A - \text{independent})$$

Both dU and PdV depend only on how the *B* molecule interacts with its immediate neighbors, regardless of how many other A molecules are present.

Adding one B molecule: $$dG = f(T,P) - kTlnN_A \qquad\qquad N_B \ll N_A$$

Adding two B molecules: $$dG = 2f(T,P) - 2kTlnN_A + kTln2$$

Dilute solutions

Adding two B molecules: $dG = 2f(T,P) - 2kTlnN_A + kTln2$

Adding N B molecules:

Stirling's approximation $\quad N! \approx N^N e^{-N}\sqrt{2\pi N} \qquad lnN! \approx N(lnN - 1)$

$$G = N_A\mu_0(T,P) + N_Bf(T,P) - N_BkTlnN_A + N_BkTlnN_B - N_B kT$$

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} \qquad\qquad \mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A}$$

solvent $\qquad\qquad\qquad\qquad\qquad$ solute

$$\mu_A = \mu_0(T,P) - \frac{kTN_B}{N_A} \qquad\qquad \mu_B = f'(T,P) + kTln\left(\frac{N_B}{N_A}\right)$$

- Adding more solute reduces the chemical potential of A and increases the chemical potential of B.
- Both chemical potentials depend on N_B/N_A only.

Osmotic pressure

Equation for solvent: $\mu_A = \mu_0(T,P) - \dfrac{kTN_B}{N_A}$

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

When the pressure is just right to stop the osmotic flow, the chemical potential of the solvent must be the same on both sides of the membrane.
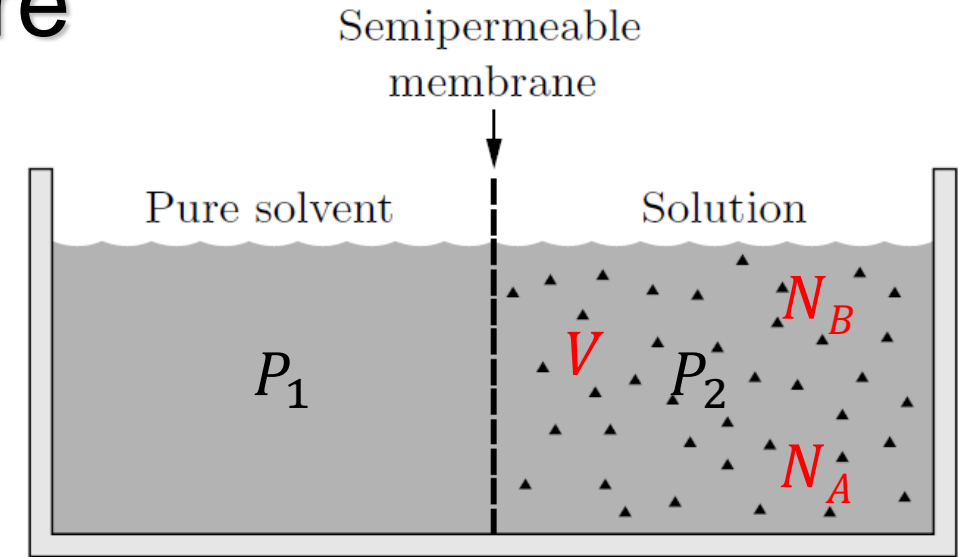
$$\mu_0(T,P_1) = \mu_0(T,P_2) - \frac{kTN_B}{N_A}$$

$$\mu_0(T,P_2) \approx \mu_0(T,P_1) + (P_2 - P_1)\frac{\partial \mu_0}{\partial P}$$

$$(P_2 - P_1)\frac{\partial \mu_0}{\partial P} = \frac{kTN_B}{N_A}$$

Chemical potential of a pure substance is just the Gibbs free energy per particle, *G/N*. Since ∂G/∂P = V (at constant T and N):

$$\frac{\partial \mu_0}{\partial P} = \frac{V}{N_A}$$

Van't Hoff's Formula: $(P_2 - P_1) = \dfrac{N_B kT}{V} = \dfrac{n_B RT}{V}$

Semipermeable membrane

Pure solvent   Solution

P_1 V P_2 N_B N_A

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.

If you are lost in the sea, is it wise to drink sea water?

The osmotic pressure difference is like the pressure of an ideal gas of the solute.

Examples of osmotic pressure

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

Gas constant
$$R = 8.3145 \frac{J}{mol \cdot K}$$

In biological cell, there are about 200 water molecules for each molecule of something else.

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

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

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

The difference of pressure being in water:
$$(P_2 - P_1) = 6.9 \; bar$$

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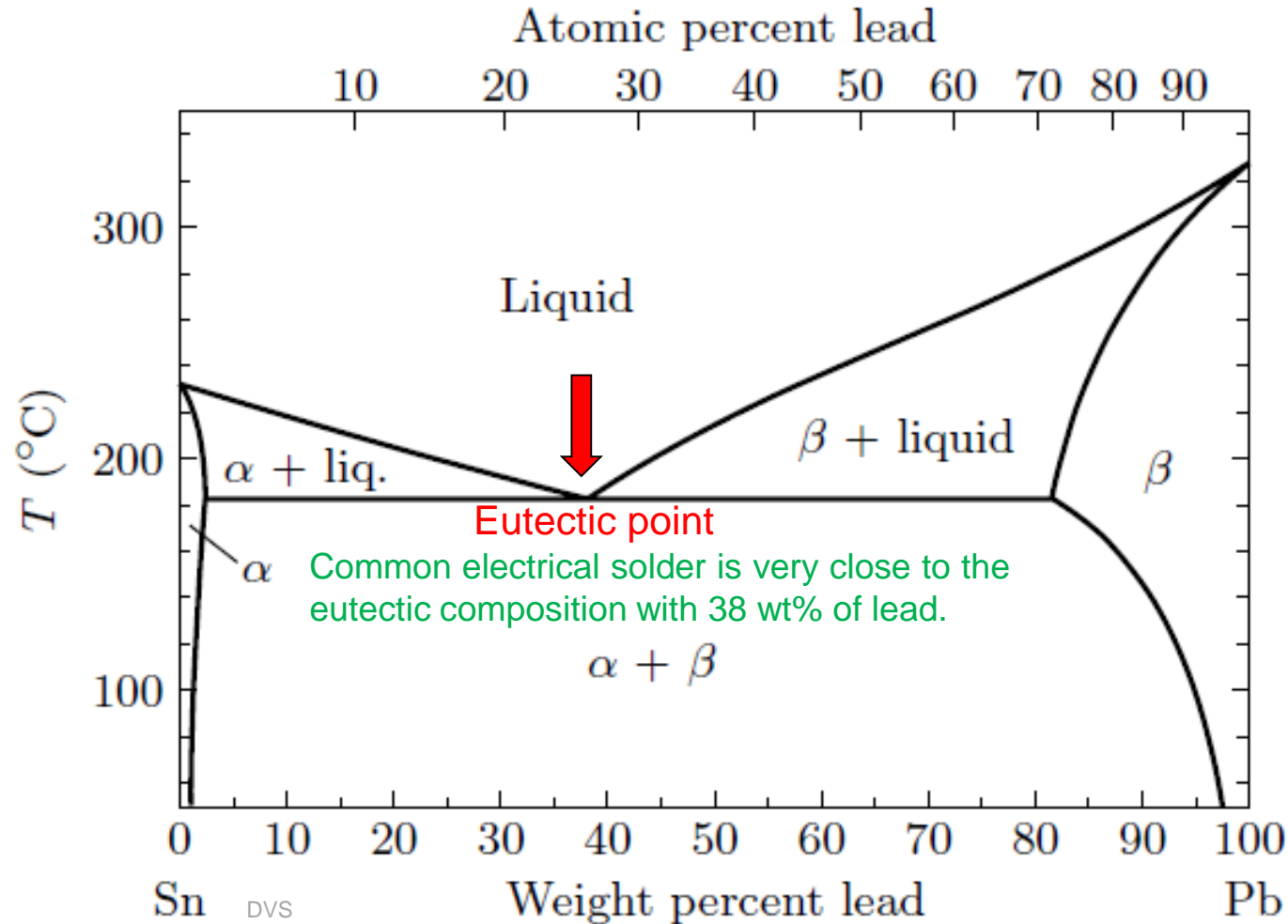
For 1 m³ of pure water: $U = PV = 27 \times 10^5 \text{ Pa} \times 1 \text{ m}^3 = 2.7 \text{ MJ } (0.75 \text{ kWh})$

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

Example of an Eutectic System

Eutectic point

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

Phase diagram for the mixture of tin and lead.

Boiling and freezing points of mixtures

$$\mu_A = \mu_0 (T, P) - \frac{kTN_B}{N_A}$$

Eutectic behavior of liquids:

- Water + table salt can remain a liquid at temperatures as low as −21°C at the eutectic composition of 23% NaCl by weight.

- A coolant used in automobile engines, a mixture of water and ethylene glycol (HOCH2CH2OH) can remain liquid at −49°C at the eutectic composition of 56% of ethylene glycol by volume.

- Using concept of chemical potential and its equality in different phases during phase transformations, it is possible to quantify change in boiling and freezing points for the dilute solutions.

Boiling and freezing points of a dilute solution

$$\mu_{A,liq}(T,P) = \mu_{A,gas}(T,P) \qquad \mu_A = \mu_0(T,P) - \frac{kTN_B}{N_A}$$

For pure solvent: $\qquad \mu_0(T_0,P) = \mu_{A,gas}(T_0,P) \qquad \frac{\partial \mu}{\partial T} = \frac{\partial G}{N \partial T} = \frac{S}{N} \qquad \frac{L}{T_0} = S_{gas} - S_{liq}$

$$\mu_0(T_0,P) + (T-T_0)\frac{\partial \mu_0}{\partial T} - \frac{N_B kT}{N_A} = \mu_{gas}(T_0,P) + (T-T_0)\frac{\partial \mu_{gas}}{\partial T}$$

$$T - T_0 = \frac{N_B kT_0^2}{L} = \frac{n_B RT_0^2}{L}$$

L is the latent heat of vaporization.

For boiling temperature of seawater, $T - T_0 = 0.6 \, K$

Change of pressure above the solution

$$\mu_A = \mu_0(T, P) - \frac{kTN_B}{N_A}$$

$$\mu_{A,liq}(T, P) = \mu_{A,gas}(T, P) \qquad \text{For pure solvent:} \qquad \mu_0(T, P_0) = \mu_{A,gas}(T, P_0)$$

$$\mu_0(T, P_0) + (P - P_0)\frac{\partial \mu_0}{\partial P} - \frac{N_B kT}{N_A} = \mu_{\text{gas}}(T, P_0) + (P - P_0)\frac{\partial \mu_{\text{gas}}}{\partial P}$$

$$\frac{\Delta P}{P_0} = \frac{N_B}{N_A} \qquad \text{or} \qquad \frac{P}{P_0} = 1 - \frac{N_B}{N_A} \qquad \frac{\partial \mu}{\partial P} = \frac{V}{N}$$

This is **Raoult's law**: the vapor pressure is reduced by a fraction equal to the ratio of the numbers of solute and solvent molecules. For seawater: $\frac{\Delta P}{P_0}$ = −0.022.

- The presence of a solute reduces the tendency of a solvent to evaporate.
- Both change in pressure and boiling temperature are small for the dilute solution.
- Freezing temperature is reduced in the solution.
- Dilute solution effects depend only on the amount of solute, not on what the solute is.

Chemical equilibrium


$$H_2O \leftrightarrow H^+ + OH^-$$
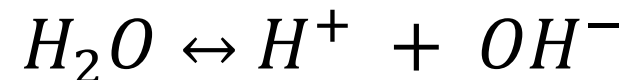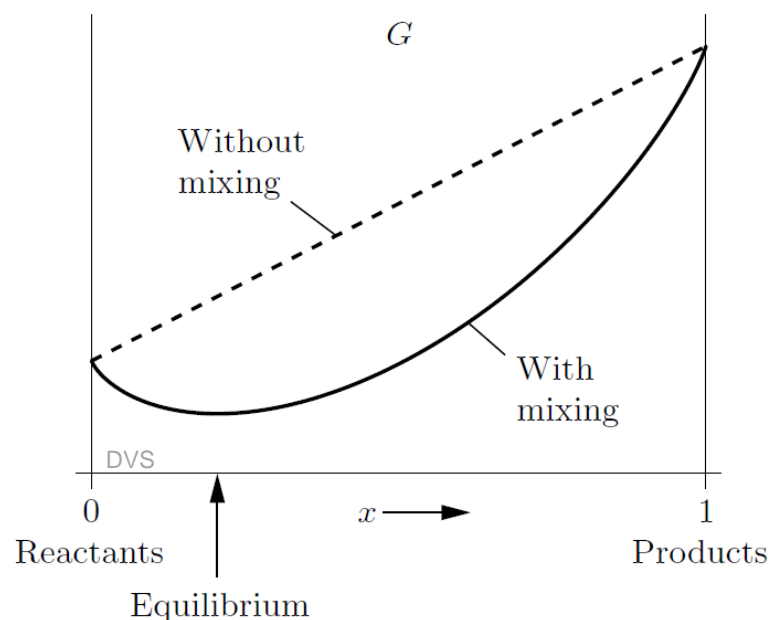
The derivative $\frac{dG}{dx}$ is infinite at the endpoints $x = 0$ and $x = 1$ of the diagram. No matter how great the energy difference between the reactants and the products, the equilibrium point (the minimum of G) will lie below the line without mixing. At equilibrium, system will stay at concentration with minimal G:

$$dG = \sum_i \mu_i dN_i = 0 \quad \text{at fixed temperature and pressure.}$$

$$dN_{H_2O} = dN_{H^+} + dN_{OH^-} \implies \mu_{H_2O} = \mu_{H^+} + \mu_{OH^-}$$

In equilibrium, the balance of chemical potentials is the same as in the reaction equation, with the names of the chemical species replaced by their chemical potentials.

$$N_2 + 3H_2 = 2NH_3 \implies \mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$$
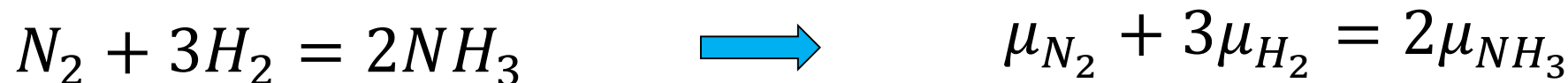
Chemical equilibrium in water

Chemical reactions are hardly ever go to completion. An example is dissociation of water into H^+ and OH^- ions:

$$H_2O \leftrightarrow H^+ + OH^-$$
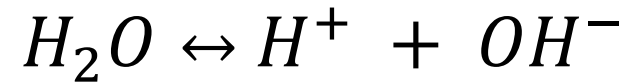
- The pH of a solution is defined as minus the base-10 logarithm of the molality m of H^+ ions:

$$\mathbf{pH} \equiv -\log_{10} m_{H+} \qquad m = \frac{Number\ of\ moles\ of\ solute}{Number\ of\ kilograms\ of\ solvent} \qquad m \propto \frac{N_B}{N_A}$$
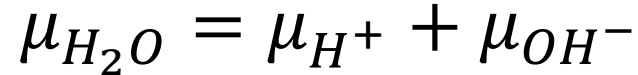
For pH = 7, number of H^+ (and OH^- in water) ions is 10^{-7}.

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**.

Breaking few molecules apart into ions lowers the Gibbs free energy, because the entropy increases substantially. At higher temperature this entropy will contribute more to G, so there will be more ions.

Dissociation of water

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

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-}$$

solvent

solute

$$m \propto \frac{N_B}{N_A}$$

$$\mu_A = \mu_0\,(T,P) - \frac{kTN_B}{N_A}$$

$$\mu_B = f'(T,P) + kTln\left(\frac{N_B}{N_A}\right)$$

Deviation of μ_{H_2O} from its value for pure water is negligible.

$$\mu^{\circ}_{H_2O} = \mu^{\circ}_{H^+} + kTlnm_{H^+} + \mu^{\circ}_{OH^-} + kTlnm_{OH^-}$$

Each μ° represents the chemical potential of the substance in its standard state — pure liquid for H_2O and a concentration of one mole per kilogram solvent for the ions.

$$RT\,ln(m_{H^+}m_{OH^-}) = -N_A\left(\mu^{\circ}_{H^+} + \mu^{\circ}_{OH^-} - \mu^{\circ}_{H_2O}\right) = -\Delta G^{\circ}$$

$$m_{H^+}m_{OH^-} = e^{-\frac{\Delta G^{\circ}}{RT}} = K \qquad K \text{ is equilibrium constant.} \qquad \text{pH} = 7$$
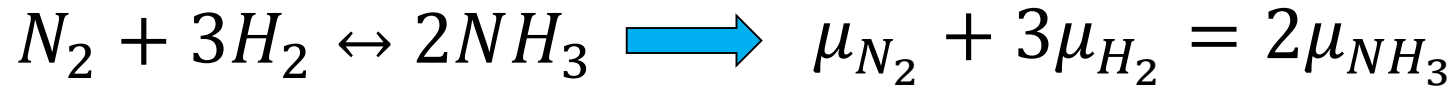
$$\Delta G^{\circ} = 79.9\,\frac{kJ}{mol} \qquad R = 8.31\,\frac{J}{mol\,K} \qquad m_{H^+}m_{OH^-} = 10^{-14} \qquad m_{H^+} = m_{OH^-} = 10^{-7}$$

Fixation of nitrogen

$$\frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N} = kT/P$$

$$\mu(T, P) - \mu(T, P^\circ) = kT\ln(P/P^\circ).$$

$$\mu(T, P) = \mu^\circ(T) + kT\ln(P/P^\circ).$$

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \implies \mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$$

$$\mu_{N_2}^\circ + kT\ln\left(\frac{P_{N_2}}{P^\circ}\right) + 3\mu_{H_2}^\circ + 3kT\ln\left(\frac{P_{H_2}}{P^\circ}\right) = 2\mu_{NH_3}^\circ + 2kT\ln\left(\frac{P_{NH_3}}{P^\circ}\right)$$

$$\frac{P_{NH_3}^2\left(P^\circ\right)^2}{P_{N_2}P_{H_2}^3} = e^{-\frac{\Delta G^\circ}{RT}} = K \qquad \Delta G^\circ = -32.9\,\frac{kJ}{mol}$$

Industrial process at 500 °C and pressure around 400 bar was developed in the early 20th century by the German chemist Fritz Haber.

- If the gases are initially in equilibrium and more nitrogen or hydrogen is added, some of it will have to react to form ammonia in order to maintain equilibrium.

- If ammonia is added, some of it will have to convert to nitrogen and hydrogen.

- If the partial pressure of both the hydrogen and the nitrogen is doubled, the partial pressure of the ammonia must quadruple.

- Increasing the total pressure favors the production of more ammonia.

- However, rate of reaction is low. High temperature, high pressure and catalyst (iron-molybdenum) is necessary.

Oxygen Dissolving in Water

The dissolution of oxygen in water can be treated as a chemical reaction with its own equilibrium constant.

$$\mu_{gas} = \mu_{solute} \qquad \mu = \mu° + kT\ln m$$

$$\overset{°}{\mu_{gas}} + kT\ln\frac{P}{P°} = \overset{°}{\mu_{solute}} + kT\ln m$$

Multiplying by Avogadro's number:

$$\frac{mP°}{P} = e^{-\frac{\Delta G°}{RT}} \qquad \Delta G° = 16.4\,\frac{kJ}{mol}$$

$$\frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N} = kT/P$$

$$\mu(T,P) - \mu(T,P°) = kT\ln(P/P°).$$

$$\mu(T,P) = \mu°(T) + kT\ln(P/P°).$$

m is the molality of the dissolved oxygen in moles per kilogram of water

Henry's law: the ratio of the amount of dissolved oxygen to the amount in the adjacent gas is a constant at any given temperature and total pressure.

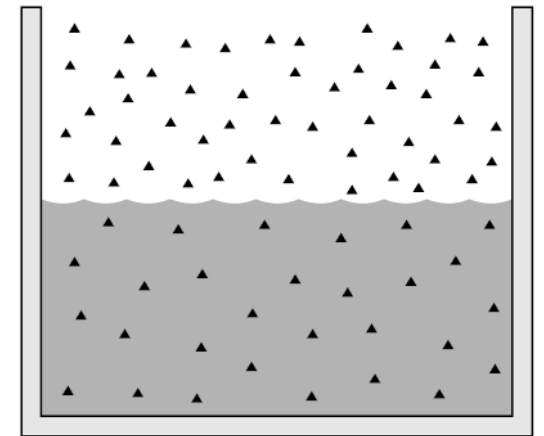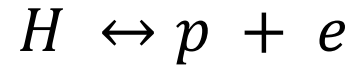For oxygen in water at room temperature, $e^{-\frac{\Delta G°}{RT}} = \frac{1}{750}$.

In spite of this small amount, each liter of water contains the equivalent of about 7 cm^3 of pure oxygen, enough for fish to breathe.

DVS

Ionization of hydrogen

It is an important reaction in stars such as our sun.

$$H \leftrightarrow p + e$$

Equilibrium condition:
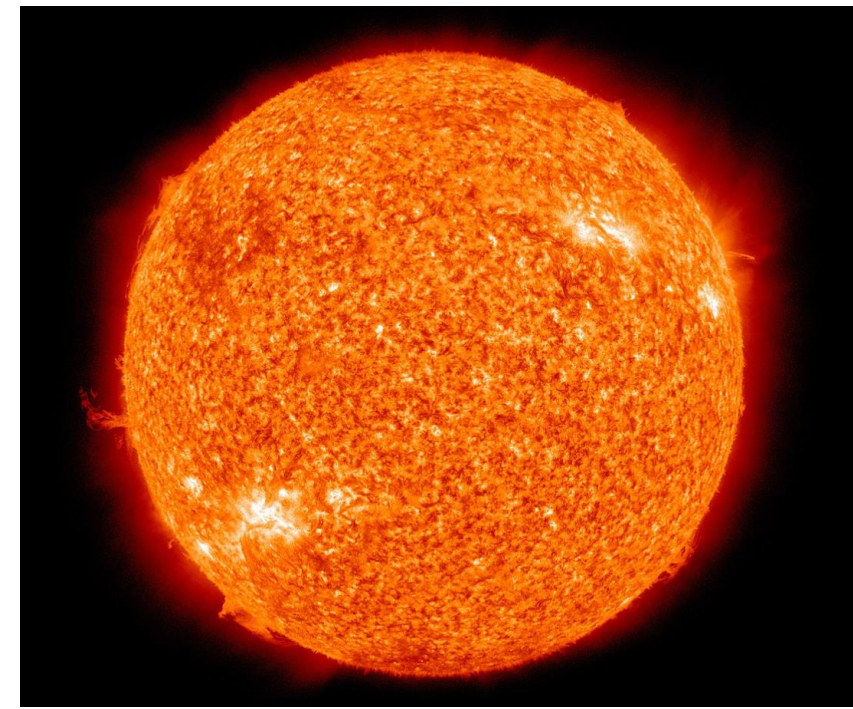
$$kT \, ln\left(\frac{P^{\circ}P_H}{P_p P_e}\right) = \mu_H^{\circ} - \mu_p^{\circ} - \mu_e^{\circ}$$

Multiplicity of a monatomic ideal gas:

Stirling's approximation

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

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

Sackur-Tetrode equation:

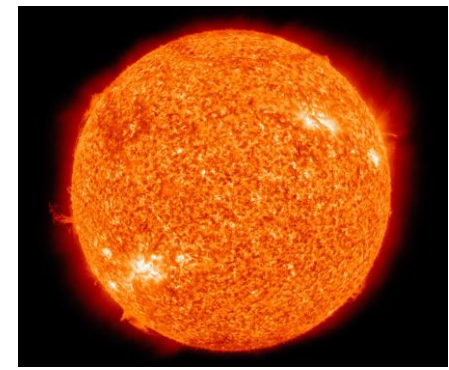$$S = Nk\left[ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right]$$

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

Ionization of hydrogen

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

Monatomic ideal gas:

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

$$\mu = -kT\ ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] = -kT\ ln\left[\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]$$

$$kT\ ln\left(\frac{P^\circ P_H}{P_p P_e}\right) = \mu_H^\circ - \mu_p^\circ - \mu_e^\circ$$

If to take into account ionization energy, $I = 13.6\ eV$ that is necessary to put in to convert H to $p + e$, it will shift μ_H° by 13.6 eV.

$$\mu_H^\circ = -kT\ ln\left[\frac{kT}{P^\circ}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - I$$

For μ_p° and μ_e° equations are the same, but without I.

Taking into account that $m_H \approx m_p$:

At the surface of the sun, the temperature is about 5800 K,
$\frac{P_e}{kT} \approx 2 \times 10^{19}\ \frac{1}{m^3}$, then $\frac{P_p}{P_H} = 8\ 10^{-5}$.

On the surface of the sun, in spite of very high temperature, less than one hydrogen atom per 10,000 is ionized.

$$\frac{P_p}{P_H} = \frac{kT}{P_e}\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{I}{kT}}$$
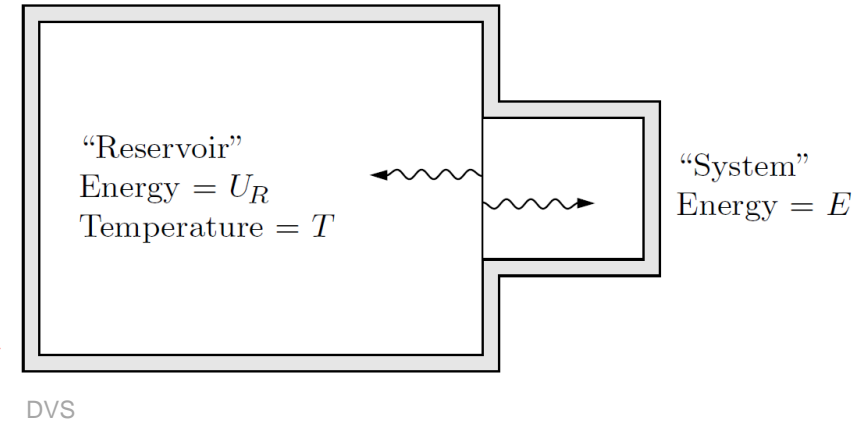
Saha equation

Boltzmann statistics

Boltzmann statistics calculates probability of the system in the contact with reservoir having energy E. This probability is proportional to multiplicity of reservoir:

$$P(E) = C\Omega_R \ (E)$$

"Reservoir"
Energy $= U_R$
Temperature $= T$

"System"
Energy $= E$

$$\Omega(E) = A\Omega_R \ (0) \quad \textcolor{red}{S_R(E) = \ k \ln\Omega_R(0) + klnA}$$

DVS

$$\Delta S_R = \ klnA \qquad \Delta U \ = T\Delta S \textcolor{magenta}{- P\Delta V + \mu\Delta N}$$

$$\textcolor{red}{P(s) = \frac{1}{Z}e^{-\frac{E(s)}{kT}}}$$

$$E \ = -\Delta U_R = -T\Delta S_R \qquad \Delta S_R = -\frac{E}{T}$$

$$\textcolor{red}{Z = \sum_s e^{-\frac{E(s)}{kT}}}$$

$$A = \boxed{\colorbox{yellow}{$e^{-E/kT}$}} \qquad P(E) = AC\Omega_R \ (0)$$

Boltzmann distribution

$$A \text{ is Boltzmann factor } e^{-\frac{E}{kT}} \qquad P(E) = e^{-E/kT}C\Omega_R \ (0) = \frac{1}{Z}e^{-E/kT}.$$

Transition to Gibbs statistics

Boltzmann statistics calculates probability of the system in the contact with reservoir having energy E. This probability is proportional to multiplicity of reservoir:

$$P(E) = C\Omega_R\ (E)$$

$$\Omega(E) = A\Omega_R\ (0) \quad {\color{red}S_R(E) =\ k\ln\Omega_R(0) + klnA}$$

$$\Delta S_R =\ klnA \qquad \Delta U\ = T\Delta S {\color{magenta}- P\Delta V} {\color{green}+ \mu\Delta N}$$
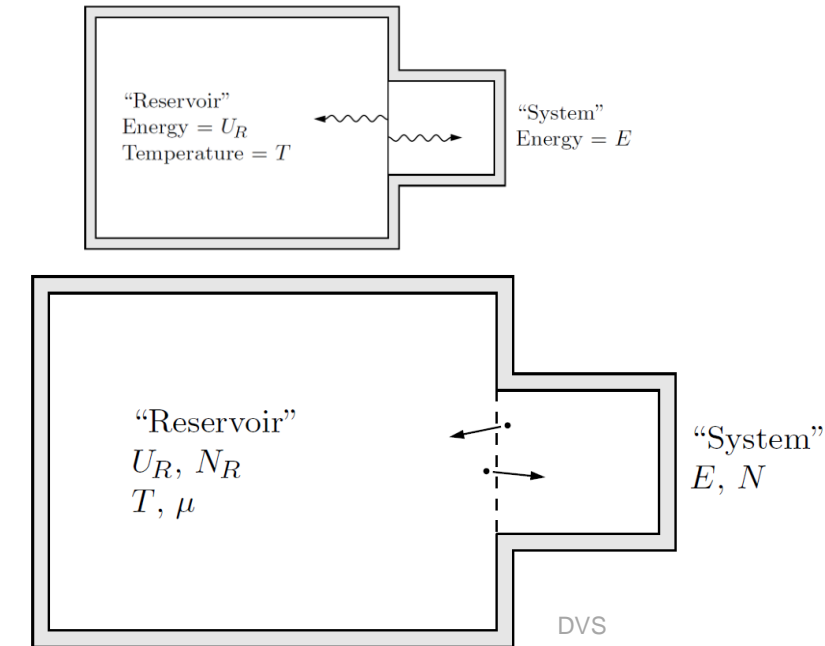
$$E\ = -\Delta U_R = -T\Delta S_R - \mu\Delta N_R \qquad \Delta S_R = -\frac{E - \mu N}{T}$$

$$A = \boxed{e^{-(E-\mu N)/kT}} \qquad \mathcal{P}(E) = AC\Omega_R\ (0)$$

Gibbs distribution

$$A \text{ is Gibbs factor } e^{-\frac{E-\mu N}{kT}} \quad {\color{green}\mathcal{P}(E) = e^{-(E-\mu N)/kT}C\Omega_R\ (0) = \frac{1}{Z}e^{-(E-\mu N)/kT}}.$$

Grand canonical ensemble

Gibbs factor

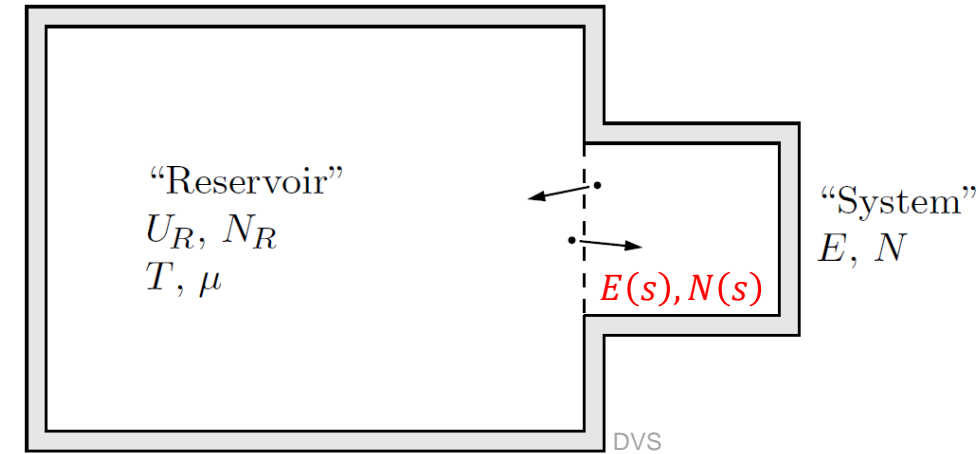$$e^{-\frac{E(s)-\mu N(s)}{kT}}$$

Probability distribution

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-\frac{E(s)-\mu N(s)}{kT}}$$

$\mathcal{Z}$ is the grand partition function

$$\mathcal{Z} = \sum_{s} e^{-\frac{E(s)-\mu N(s)}{kT}}$$

If more than one type of particle is present in the system, then the μN term in equations becomes a sum over species of $\mu_i N_i$.

"Reservoir" U_R, N_R T, μ

"System" E, N

$E(s), N(s)$

DVS

The grand partition function for this single-site occupation by oxygen of hemoglobin site. It has just two terms:

$$\mathcal{Z} = 1 + e^{-\frac{\epsilon-\mu}{kT}}$$

ϵ = −0.7 eV μ = −0.6 eV

$$\mathcal{Z} = 1 + e^{\frac{0.1\ eV}{kT}} \approx 41$$

The probability of site occupation is
40/(40+1) = 98%.

With CO 100 times less abundant, it drops to 25%.

Grand canonical ensemble allows exchange of both energy and particles and has well defined chemical potential μ.

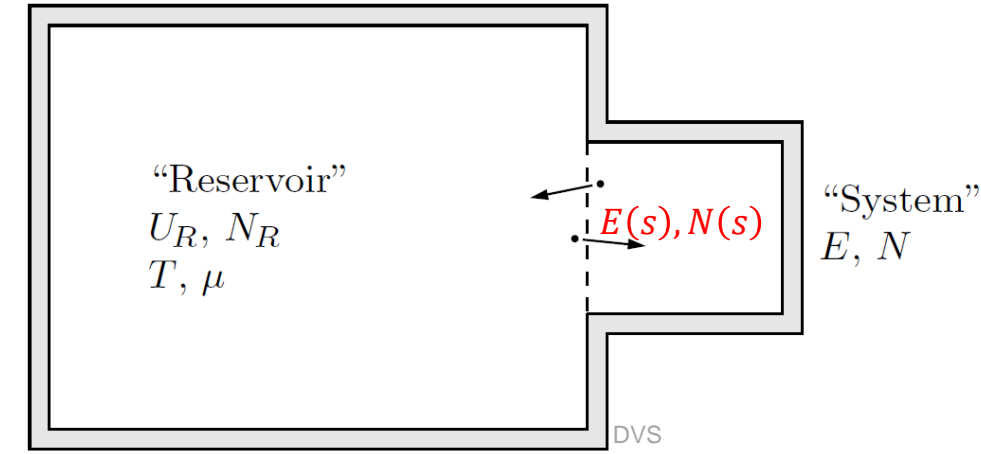# Grand canonical distribution for quantum particles

Gibbs factor

$$e^{-\frac{E(s)-\mu N(s)}{kT}}$$

Probability distribution

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-\frac{E(s)-\mu N(s)}{kT}}$$

Grand partition function

$$\mathcal{Z} = \sum_{s} e^{-\frac{E(s)-\mu N(s)}{kT}}$$

"Reservoir"
$U_R,\ N_R$
$T,\ \mu$

$E(s), N(s)$

"System"
$E,\ N$

DVS

Bose - Einstein distribution

$$\bar{n}_{BE} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} - 1} \quad (\epsilon = hf)$$

Fermi-Dirac distribution

$$\bar{n}_{FD} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1}$$

Planck distribution

$$\bar{n} = \frac{1}{e^{\frac{hf}{kT}} - 1}$$

Number of photons

Planck distribution is Bose - Einstein distribution with chemical potential equal to zero. This comes from the fact that photons can be created or destroyed in any quantity. Their total number is not conserved. If one imposes μ by grand canonical distribution, this can only be done with μ = 0.

The chemical potential for a gas of photons in a box is zero.

Comparison of distributions

$$F = -kT\ln(Z)$$

$$\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

For the Boltzmann distribution: $\quad P(s) = \dfrac{1}{Z_1} e^{-\frac{\epsilon}{kT}} \qquad \mu = -kT\ln\left(\dfrac{Z_1}{N}\right)$

$$Z = \frac{Z_1{}^N}{N!} = \frac{Z_1{}^N}{N!}$$

$$\bar{n}_{Boltzmann} = \frac{1}{Z_1} N e^{-\frac{\epsilon}{kT}} = e^{-\frac{\epsilon}{kT}} e^{\frac{\mu}{kT}} = e^{-\frac{(\epsilon-\mu)}{kT}}$$

$$\ln N! \approx N(\ln N - 1)$$

$$\bar{n}_{Boltzmann} = e^{-\frac{(\epsilon-\mu)}{kT}} \qquad \bar{n}_{FD} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1} \qquad \bar{n}_{BE} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} - 1}$$
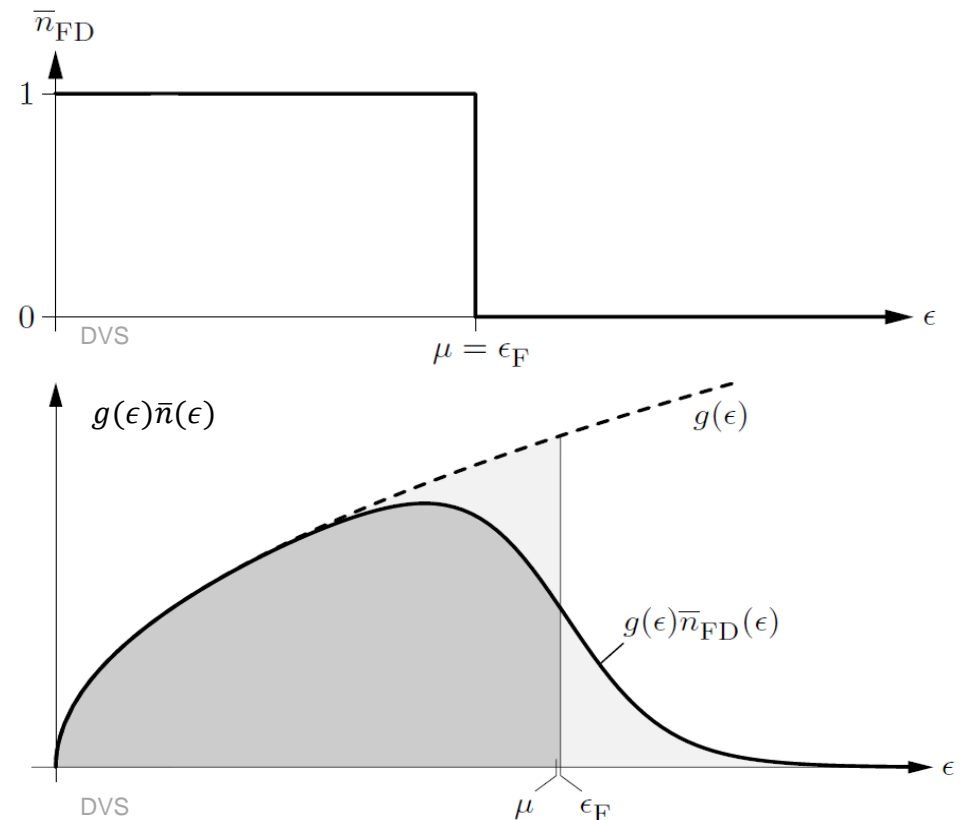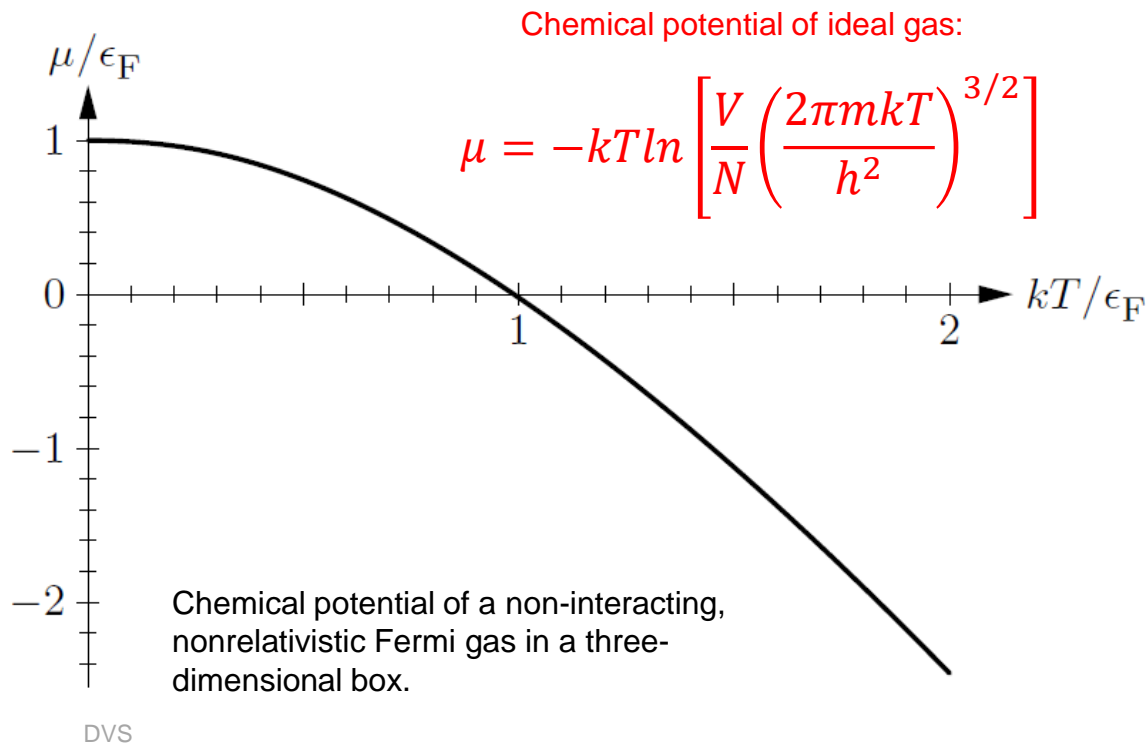
When $\varepsilon \gg \mu$, the exponent is very large, one can neglect the 1 in the denominator of Fermi-Dirac and Bose-Einstein distributions, and both are reduced to the Boltzmann distribution. The precise condition for the three distributions to agree is: $\epsilon - \mu \gg kT$.

To apply the distributions to any particular system, one needs to know what the energies of all the states are.

Boltzmann

Bose-Einstein

Fermi-Dirac

$\overline{n}$

μ $\quad \mu + kT$

ϵ

DVS
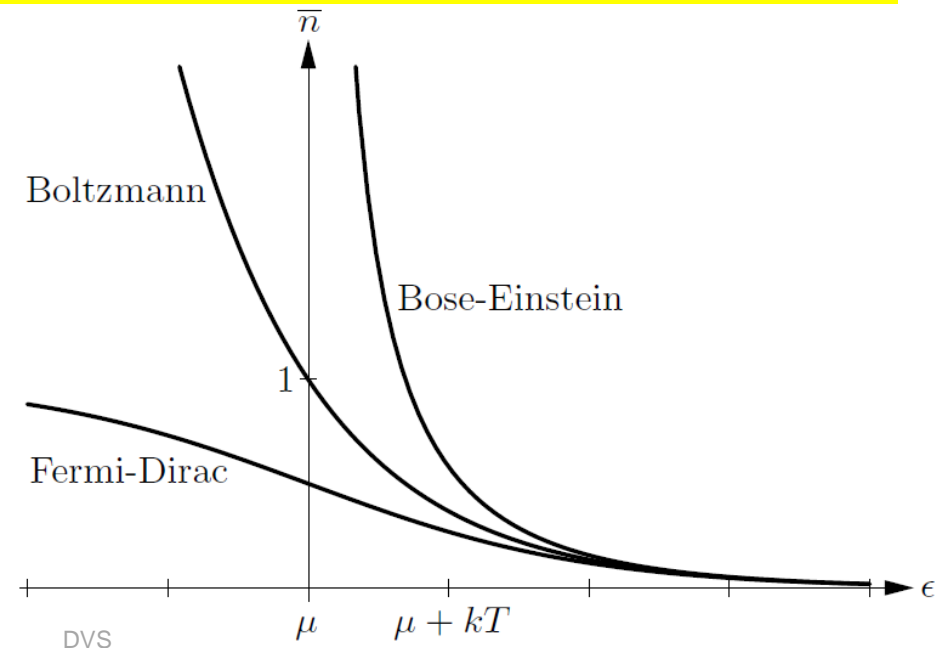
Chemical potential of degenerate Fermi gas

- The chemical potential for fermions is the point where the probability of a state being occupied is exactly 1/2. At $T = 0$, $\mu = \epsilon_F$.

- The chemical potential decreases with increase of T.

- At high temperatures μ becomes negative and approaches the form for an ordinary gas obeying Boltzmann statistics.

Chemical potential of ideal gas:

$$\mu = -kTln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

Chemical potential of a non-interacting, nonrelativistic Fermi gas in a three-dimensional box.

Summary

- Chemical potential is important parameter, which deals with interaction between thermodynamic systems allowing exchange of particles.

- Chemical potential comes from first principles as partial derivative of entropy with respect to number of particles $\left(\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}\right)$ at constant volume and total energy.

- There are several other definitions of μ, among them $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$. At constant volume and entropy, μ is the change of total energy when one particles is added to the system $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$. μ has units of energy.

- μ is constant in the diffusive equilibrium. Its value is negative for ideal gas or other non-dense systems with negligible probability for particles to occupy the same energy state.

- Chemical potential is a powerful tool allowing to solve in a simple way a range of problems like Osmotic pressure and change of boiling or freezing temperature in the mixtures.

- Chemical potential is a convenient parameter to describe chemical equilibrium and the processes of dissociation of water, fixation of nitrogen, ionization of hydrogen and many other.

- Chemical potential is main tool in grand canonical ensemble and statistics of quantum particles.