Lecture 22. *Chemical Potential*

- In this lecture, we will broaden our approach to thermodynamics where a system can exchange particles with its surrounding

- We will adapt our functions of state accordingly

$$\mu$$

Exchange of heat, work, what about particles?

- When writing the possible change in internal energy, we only considered heat and work being *transferred* in or out of a system

- What about a transfer of particles? (or simply a change in the number of particles?)

- We will introduce the *chemical potential* to account for this type of process (though it applies beyond chemical processes)

$$\mathrm{d}U = \text{đ}Q + \text{đ}W$$

Definition

The chemical potential μ is the amount of energy added to a system when an additional particle of a given type is added to it

$$+\mu\,\mathrm{d}N$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$

- It follows that $\quad \mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V}$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$

$$F = U - TS \qquad \Longrightarrow \qquad \mathrm{d}F \ = \ -p\mathrm{d}V - S\mathrm{d}T + \mu\mathrm{d}N$$

Meaning of the chemical potential

- The principle that explains what drives a system to reach equilibrium state is provided by the second law of thermodynamics

- It states that the system tends **to maximize entropy**

- Entropy is a function of state which can be seen as depending on U, V, and N

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

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{N,V} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{N,U} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,V} \mathrm{d}N$$

Remember: $\quad \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$

It follows: $\quad \mathrm{d}S = \dfrac{\mathrm{d}U}{T} + \dfrac{p\mathrm{d}V}{T} - \dfrac{\mu\mathrm{d}N}{T}$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{N,U} = \frac{p}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

Reminder: heat flow direction?

- Imagine two systems that can exchange heat between them (no work, no change in N)

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial U_1}\right)_{N,V} \mathrm{d}U_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{N,V} \mathrm{d}U_2$$

$$= \left(\frac{\partial S_1}{\partial U_1}\right)_{N,V} (-\mathrm{d}U) + \left(\frac{\partial S_2}{\partial U_2}\right)_{N,V} (\mathrm{d}U)$$

$$= \left(-\frac{1}{T_1} + \frac{1}{T_2}\right)\mathrm{d}U \geq 0$$

$$\boxed{\begin{array}{c} T_1 \\ U_1 \end{array}} \xrightarrow{\mathrm{d}U} \boxed{\begin{array}{c} T_2 \\ U_2 \end{array}}$$
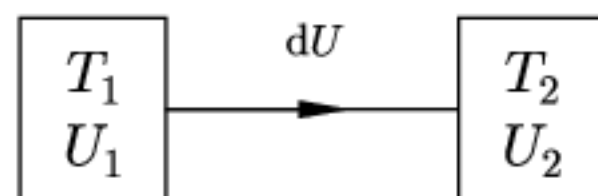
$$\Longrightarrow \quad \begin{array}{l} \mathrm{d}U > 0 \text{ if } T_1 > T_2 \\ \mathrm{d}U < 0 \text{ if } T_1 < T_2 \\ \mathrm{d}S = \mathrm{d}U = 0 \text{ if } T_1 = T_2 \end{array}$$

What about change in number of particles?

$$dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN_2$$

$$= \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} (-dN) + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} (dN)$$

$$= \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN \geq 0$$
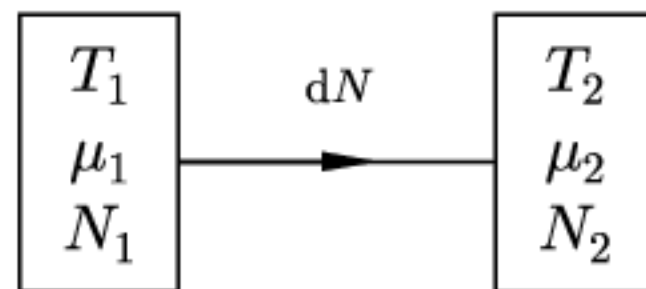
If the temperatures are equal:

- $dN > 0$ if $\mu_1 > \mu_2$

- $dN < 0$ if $\mu_1 < \mu_2$

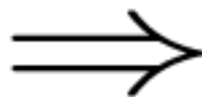- The system is at equilibrium when both chemical potentials are the same

Chemical potential of an ideal gas?

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

$$F = Nk_{\mathrm{B}}T[\ln(n\lambda_{\mathrm{th}}^3) - 1]$$

Previous lecture

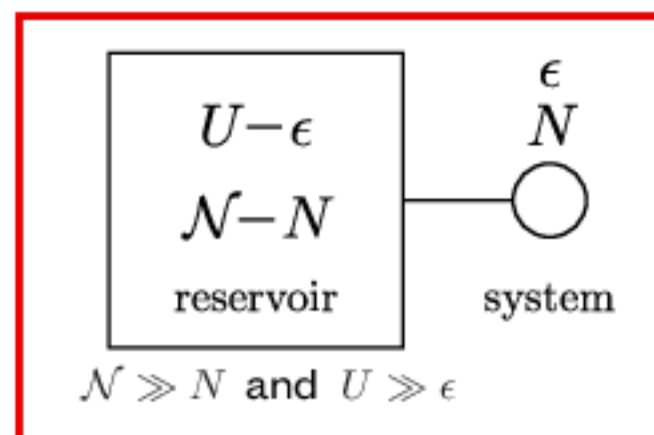$$\Longrightarrow$$

Grand partition function

$\mathcal{N} \gg N$ and $U \gg \epsilon$

- We will now generalize the definition of the PF to include the fact that the number of particles can change during a thermodynamical process

- We will consider the entropy as a function of U and N

- Taylor's series at first order (entropy of the reservoir):

$$S(U - \epsilon, \mathcal{N} - N) = S(U, \mathcal{N}) - \epsilon \left(\frac{\mathrm{d}S}{\mathrm{d}U} \right)_{\mathcal{N},V} - N \left(\frac{\mathrm{d}S}{\mathrm{d}\mathcal{N}} \right)_{U,V}$$

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

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

From previous <u>results</u>, we get:

$$S(U - \epsilon, \mathcal{N} - N) = S(U, \mathcal{N}) - \frac{1}{T}(\epsilon - \mu N)$$

$$S(U - \epsilon, \mathcal{N} - N) = S(U, \mathcal{N}) - \frac{1}{T}(\epsilon - \mu N)$$

$U - \epsilon$
$\mathcal{N} - N$
reservoir

ϵ
N
system

$\mathcal{N} \gg N$ and $U \gg \epsilon$

- Remember that the likelihood (probability P_i) of finding a system in a given macrostate is proportional to the number Ω of microstates in that macrostate.

- The entropy is proportional to the number of microstates

- The probability of finding the system with energy ϵ and N particles is:
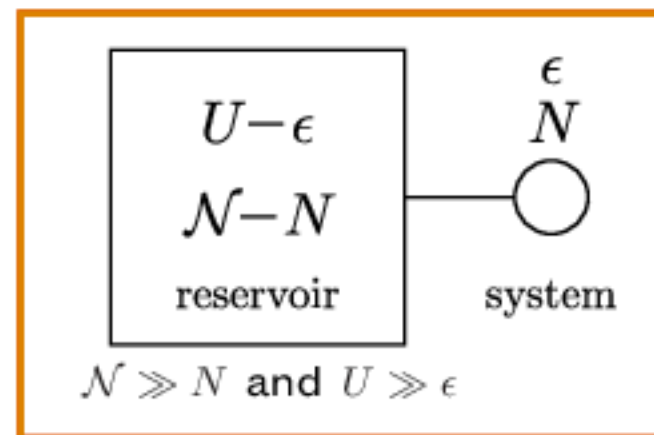
$$P_i \propto \Omega$$

$$P_i = \frac{\mathrm{e}^{\beta(\mu N_i - E_i)}}{\mathcal{Z}}$$

Relationship to thermodynamic quantities

$$N = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_\beta$$

$$U = \sum_i E_i P_i = - \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_\mu + \mu N$$

$$S = -k_B \sum_i P_i \ln P_i = \frac{U - \mu N + k_B T \ln \mathcal{Z}}{T}$$

Ensembles

- **Microcanonical ensemble**: ensemble of systems with same energy

  - The entropy is related to the number of microstates $S = k_{\mathrm{B}} \ln \Omega$ or $\Omega = \mathrm{e}^{\beta T S}$

- **Canonical ensemble:** ensemble of systems exchanging energy with a large heat reservoir

  - The Helmholtz function is $F = -k_{\mathrm{B}} T \ln Z$ or $Z = \mathrm{e}^{-\beta F}$

- **Grand canonical ensemble:** ensemble of systems that can exchange both energy and particles with a large reservoir (this fixes temperature and chemical potential)

  - The partition function is $\mathcal{Z} = \mathrm{e}^{-\beta \Phi_G}$ where we introduced the grand potential Φ_G

The grand potential $\quad \Phi_{\mathrm{G}} = -k_{\mathrm{B}} T \ln \mathcal{Z}$

$$S = \frac{U - \mu N + k_{\mathrm{B}} T \ln \mathcal{Z}}{T}$$

Chemical potential and Gibbs function

- If we scale a system by a factor λ, all the extensive variables will also be scaled by the same factor

$$U \to \lambda U, \qquad S \to \lambda S, \qquad V \to \lambda V, \qquad N \to \lambda N.$$

- And it follows, for the entropy:

$$\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$$

- Differentiating left and right with respect to λ

$$S = \frac{\partial S}{\partial(\lambda U)}\frac{\partial(\lambda U)}{\partial \lambda} + \frac{\partial S}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial S}{\partial(\lambda N)}\frac{\partial(\lambda N)}{\partial \lambda}$$

From previous <u>results</u>, we get:

$$S = \frac{U}{T} + \frac{pV}{T} - \frac{\mu N}{T} \qquad\qquad U - TS + pV = \mu N$$

$$\implies G = \mu N$$

$$\mu = \frac{G}{N}$$

The chemical potential can be thought of as the Gibbs function per particle

Also because

$$\Phi_{\mathrm{G}} = F - \mu N$$

$$F = U - TS$$

$$G = U - TS + pV$$

More than one type of particles

- Expanding to different types of particles: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$

- Likewise for the Helmholtz and Gibbs functions:

$$\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}N_i$$

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}N_i$$

- When pressure and temperature are kept constant, we have

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}N_i$$

- This is particularly important for chemical reactions

Particle number and conservation laws

- Imagine a constant V and constant T system that can have a varying number of particles

- The appropriate function of states is F

- The system will tend to *minimize* F with respect to the number of particles

$$\mathrm{d}F = \mathrm{d}U - S\mathrm{d}T - T\mathrm{d}S$$

- In other words, $\mu = 0$

Imagine that the number of particles is a conserved quantity (e.g. electrons)

- The number of electrons is conserved, and the only way to reduce the number is through annihilation with a positron (and anti-electron), creating a photon γ

$$e^- + e^+ \rightleftharpoons \gamma$$

- Imagine a box with N_- electrons and N_+ positrons

- Conservation law imposes that $N = N_- - N_+$ is a conserved quantity

$$\left(\frac{\partial F}{\partial N_-} \right)_{V,T,N} = 0$$

- The minimization problem has the additional constraint on N
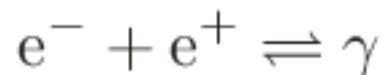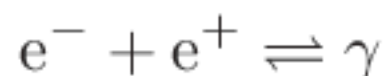
The Helmholtz function is due to electrons and positrons

$$e^- + e^+ \rightleftharpoons \gamma$$

$$\left(\frac{\partial F}{\partial N_-}\right)_{V,T,N_+} + \left(\frac{\partial F}{\partial N_+}\right)_{V,T,N_-} \frac{dN_+}{dN_-} = 0$$

We also remember that $\quad \left(\frac{\partial F}{\partial N_-}\right)_{V,T,N_+} = \mu_-$ and $\left(\frac{\partial F}{\partial N_+}\right)_{V,T,N_-} = \mu_+$ and $\frac{dN_-}{dN_+} = 1$

Thus: $\quad \mu_+ + \mu_- = 0$

*photon has zero chemical potential due to lack of conservation law

Chemical reactions

- What is the equilibrium position of a chemical reaction?

Chemical potential of an ideal gas

$$\mu = k_{\mathrm{B}} T \ln(n \lambda_{\mathrm{th}}^3)$$

$$\mu = k_{\mathrm{B}} T \ln\left(\frac{\lambda_{\mathrm{th}}^3}{k_{\mathrm{B}} T}\right) + k_{\mathrm{B}} T \ln p \qquad p = n k_{\mathrm{B}} T$$

We define standard temperature and pressure as:

$$T^{\ominus} = 298\mathrm{K}$$

$$A \rightleftharpoons B$$

The reaction is possible both forwards and backwards

Partial pressures of A and B, p_A and p_B

Equilibrium constant: $K = \dfrac{p_{\mathrm{B}}}{p_{\mathrm{A}}}$ $K \ll 1$ Backwards, mostly A

Change in Gibbs function: $\mathrm{d}G = \mu_{\mathrm{A}}\, \mathrm{d}N_{\mathrm{A}} + \mu_{\mathrm{B}}\, \mathrm{d}N_{\mathrm{B}}$

Because A changes into B or *vice versa*

$$\mathrm{d}G = (\mu_{\mathrm{B}} - \mu_{\mathrm{A}})\, \mathrm{d}N_{\mathrm{B}}$$

We know chemical potential is Gibbs function per particle***

Molar Gibbs function: $\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^{\ominus} + RT \ln \dfrac{p_{\mathrm{B}}}{p_{\mathrm{A}}}$

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln \frac{p_B}{p_A}$$

$$A \rightleftharpoons B$$
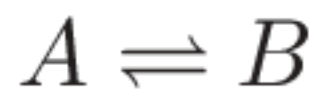
$$K = \frac{p_B}{p_A}$$

Molar chemical potential of the two species

$\Delta_r G < 0$ $\qquad A \rightarrow B$ $\quad$ Occurs spontaneously

$\Delta_r G > 0$ $\qquad B \rightarrow A$ $\quad$ Occurs spontaneously
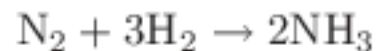
$\Delta_r G = 0$ $\qquad$ Equilibrium $\quad \ln K = -\dfrac{\Delta_r G}{RT}$

p reactants and *q* products

$$\sum_{j=1}^{p} (-\nu_j) A_j \rightarrow \sum_{j=p+1}^{p+q} (+\nu_j) A_j$$

Negative coefficients for reactants and positive coefficients for products.

> **Example**
>
> $N_2 + 3H_2 \rightarrow 2NH_3$
>
> $\nu_1 = -1, \qquad \nu_2 = -3, \qquad \nu_3 = 2$

At equilibrium, the Gibbs function is minimized

$$\sum_{j=1}^{p+q} \mu_j \, dN_j = 0 \qquad \longrightarrow \qquad \sum_{j=1}^{p+q} \nu_j \mu_j = 0.$$

The reaction is balanced and the changes are proportional to the coefficients of the reaction!

Example
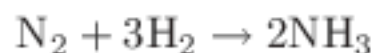
$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$\nu_1 = -1, \qquad \nu_2 = -3, \qquad \nu_3 = 2$$

$$-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$$

Equilibrium constant

$$K = \prod_{j=1}^{p+q} \left(\frac{p_j}{p^{\ominus}} \right)^{\nu_j}$$

<div>

Example
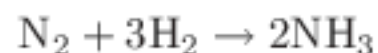
$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$

$$\nu_1 = -1, \qquad \nu_2 = -3, \qquad \nu_3 = 2$$

$$-\mu_{\text{N}_2} - 3\mu_{\text{H}_2} + 2\mu_{\text{NH}_3} = 0$$

$$K = \frac{(p_{\text{NH}_3}/p^{\ominus})^2}{(p_{\text{N}_2}/p^{\ominus})(p_{\text{H}_2}/p^{\ominus})^3} = \frac{p_{\text{NH}_3}^2 \, p^{\ominus \, 2}}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

</div>

Equilibrium

$$K = \prod_{j=1}^{p+q} \left(\frac{p_j}{p} \right)^{\nu_j}$$

$$\sum_{j=1}^{p+q} \nu_j \mu_j = 0 \quad \longrightarrow \quad \sum_{j=1}^{p+q} \nu_j \left(\mu_j + RT \ln \frac{p_j}{p^{\ominus}} \right) = 0$$

$$\longrightarrow \quad \Delta_{\mathrm{r}} G = \sum_{j=1}^{p+q} \nu_j \mu_j$$

$$\Delta_{\mathrm{r}} G + RT \sum_{j=1}^{p+q} \nu_j \ln \frac{p_j}{p} = 0 \quad \longrightarrow \quad \Delta_{\mathrm{r}} G + RT \ln K = 0$$

$$\boxed{\ln K = -\frac{\Delta_{\mathrm{r}} G}{RT}}$$

$$\ln K = -\frac{\Delta_r G}{RT} \longrightarrow \frac{d \ln K}{dT} = -\frac{1}{R}\frac{d(\Delta_r G\ /T)}{dT} \longrightarrow \boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2}}$$

Using <u>Gibbs-Helmholtz</u> relation

Exothermic reaction under standard conditions: $\Delta_r H\ < 0$

It follow that K **decreases** as T increases

"fewer products"

Endothermic reaction under standard conditions: $\Delta_r H\ > 0$

It follow that K **increases** as T increases

"more products"

This justifies

Le Chatelier's principle: a system at equilibrium, when subjected to a disturbance, responds in such a way as to minimize that disturbance.

van 't Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_r H}{RT^2}$$

→

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -\frac{\Delta_r H^{\ominus}}{R}$$

Slope

$-\Delta_r H^{\ominus}/R$

$\ln K$

$1/T$
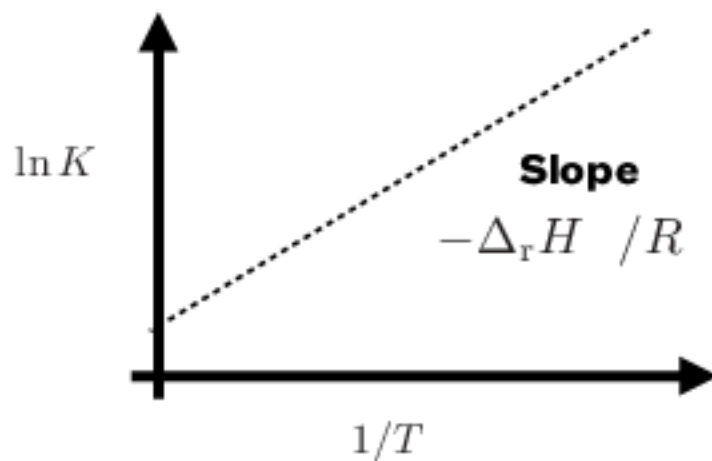
Example: molecular hydrogen dissociation

$$H_2 \rightarrow H \cdot + H \cdot$$
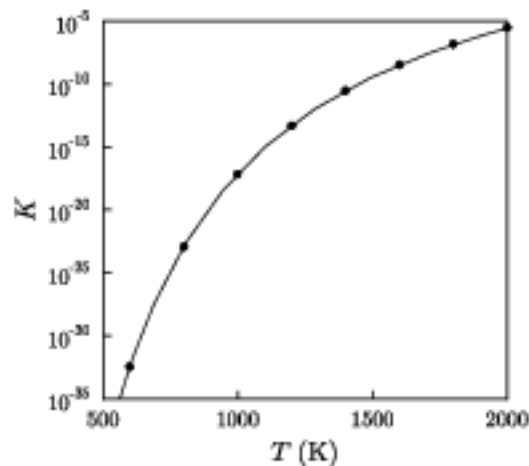
Very small K, reaction leans on the left heavily
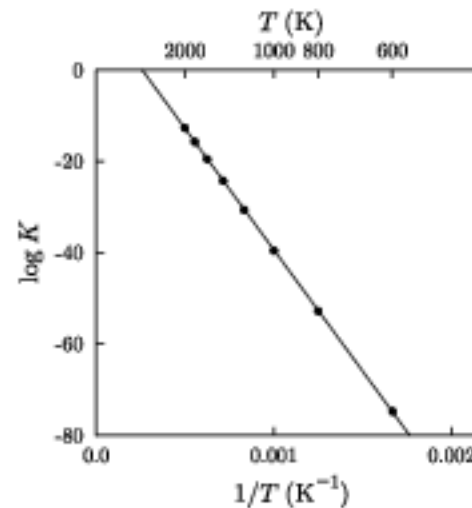
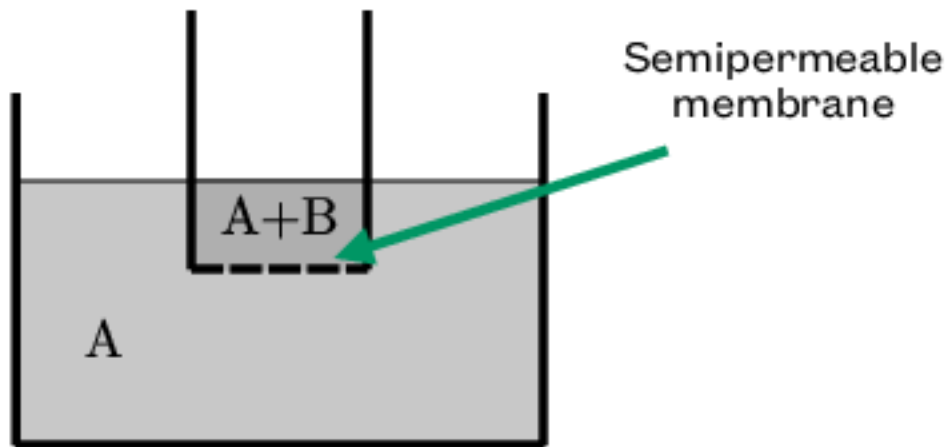$\Delta H^{\ominus}$ is about 440 kJ/mol (endothermic)

Entropic force

Differences in chemical potential can drive the flow from one reservoir to another

This drive is due to entropy (the system finds the most *likely* macrostate to maximize S

This drive can be described as an ***entropic force*** (because it is due to entropy, not energy)

Entropic force

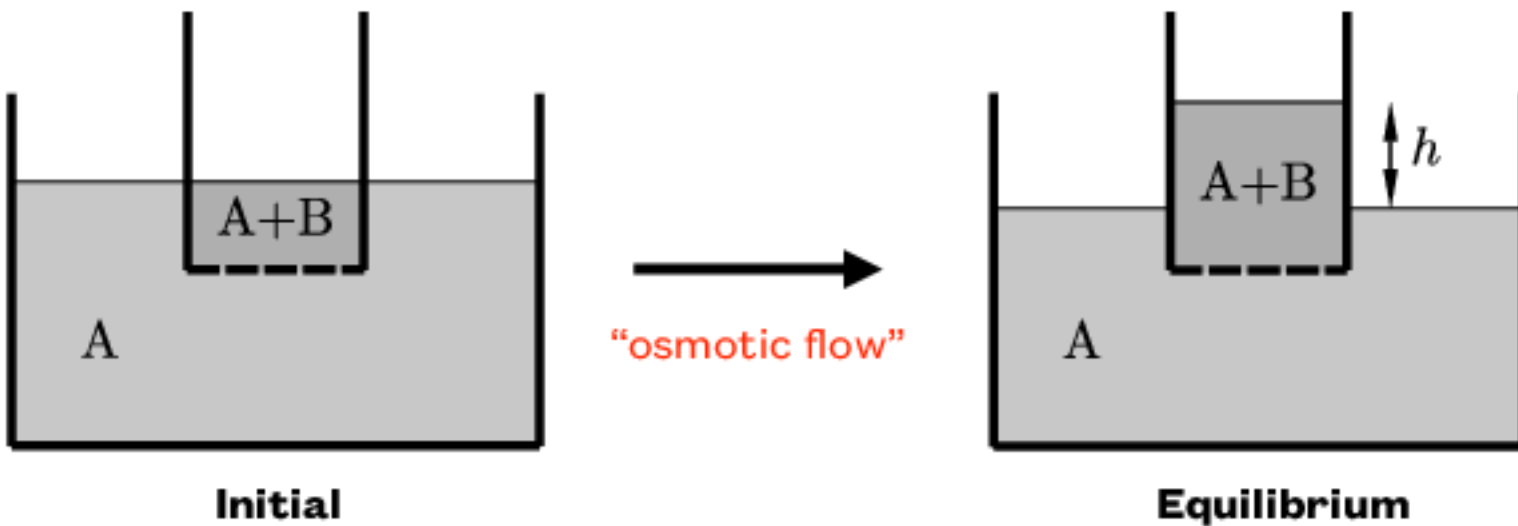$$T_1 \quad \mu_1 \quad N_1 \qquad \mathrm{d}N \qquad T_2 \quad \mu_2 \quad N_2$$

$$\mathrm{d}S = \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \mathrm{d}N \geq 0$$

$$T_1 \quad U_1 \qquad \mathrm{d}U \qquad T_2 \quad U_2$$

$$\mathrm{d}S = \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) \mathrm{d}U \geq 0$$

Example: Osmosis

Semipermeable
membrane

A+B

A
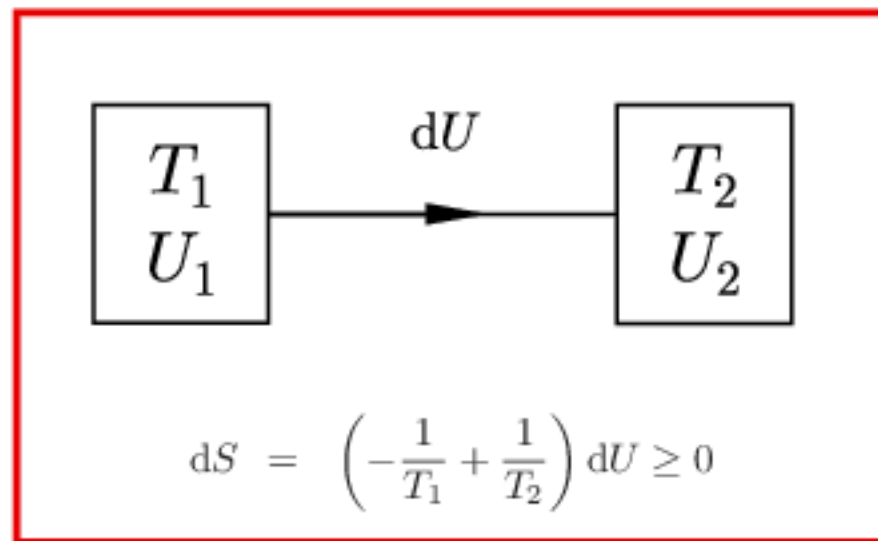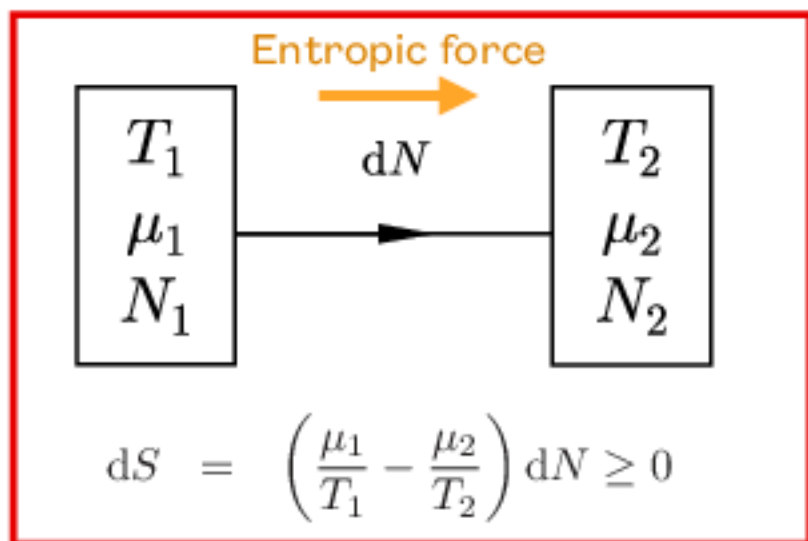
Initially: A surrounds a solution of B in A

**Semipermeable
membrane**

- - - - - -

Let small molecules
through, not large ones

Osmotic pressure: $\Pi = \rho_{\text{solution}} g h$

This is the pressure to stop the rise of the column of solution

Importance of osmosis

It is osmosis that is responsible for giving cells their internal pressure.

It provides the structural stability of many plants

Water is absorbed into a plant's cells and provides **turgor pressure**.

Water in the ground seems to be "sucked up" from the roots up to the top of the plant: the water flows upwards because it is driven by osmotic pressure.
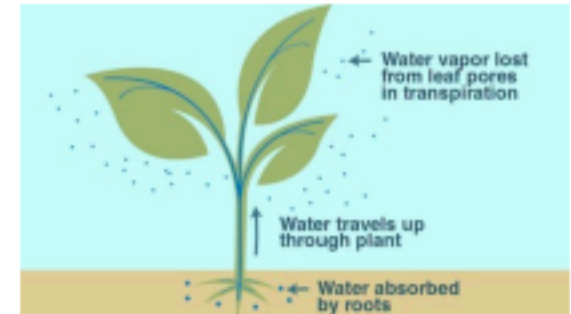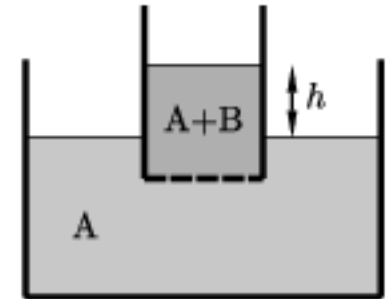

(Image credit: NASA/JPL-Caltech)

The water draws small nutrients from the soil with it as it flows up into the plant, and some water evaporates from the leaves (**transpiration**), and provides the plant with cooling.

Failure to water a plant results in wilting because the turgor pressure falls; wilting can also be produced by watering with salty water, which would cause osmotic flow of water out of the plant.

Osmosis in fish

Freshwater and **saltwater** fish are adapted for their respective environments and can be harmed by placing them in water with the wrong salinity, precisely because this upsets the osmotic balance of their cells.

Amoebae swimming in fresh water have to contend with fluid continually passing through their cell's wall, and need a pump (the contractile **vacuole** to discharge water periodically and prevent bursting.

https://www.britannica.com/animal/fish/Excretory-organs
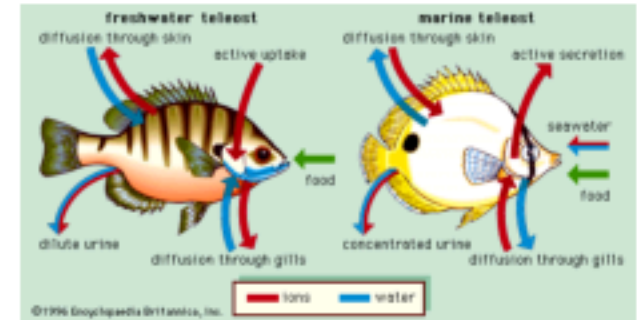
Osmosis in blood cells

Even our own blood cells are adapted for a particular osmotic pressure.

In blood transfusions and intravenous feeding it is important that the liquid injected is **isotonic** with blood;

if it is too concentrated (higher osmotic pressure than blood), it is said to be **hypertonic** and will draw water out of the blood cells, causing them to shrivel;

if it is too diluted (lower osmotic pressure than blood), it is said to be **hypotonic** and water will flow into the blood cells, causing them to burst.

Hypertonic   **Isotonic**   **Hypotonic**

https://en.wikipedia.org/
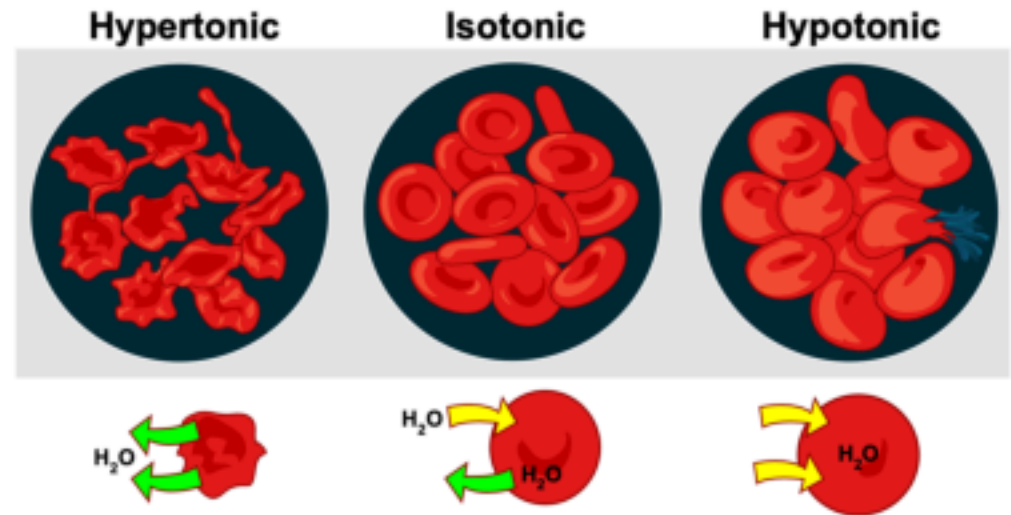
Origin of osmotic pressure

- The origin is the tendency to maximize entropy

- In other words, to find the state with the largest number of microstates

- The system tries to equalize pressure on both sides of the membrane

(a)

p p

OSMOSIS

pure solvent   solution

(b)

p $p+\Pi$

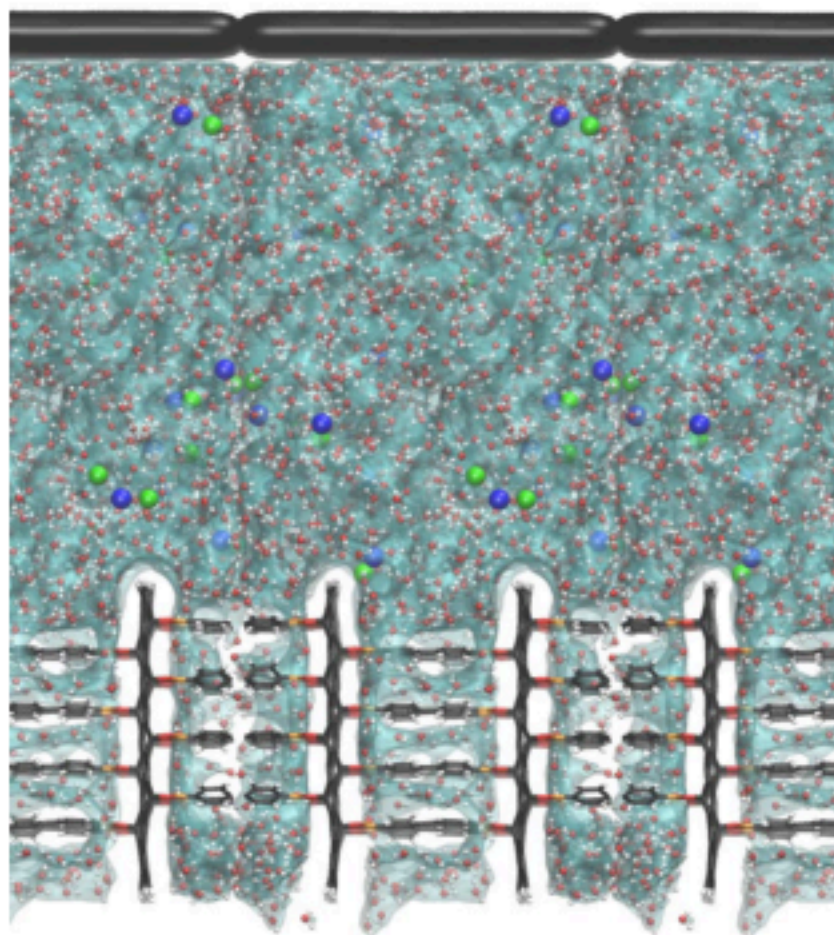$\mu_A^*(p)$ $\mu_A(p+\Pi)$

pure solvent   solution
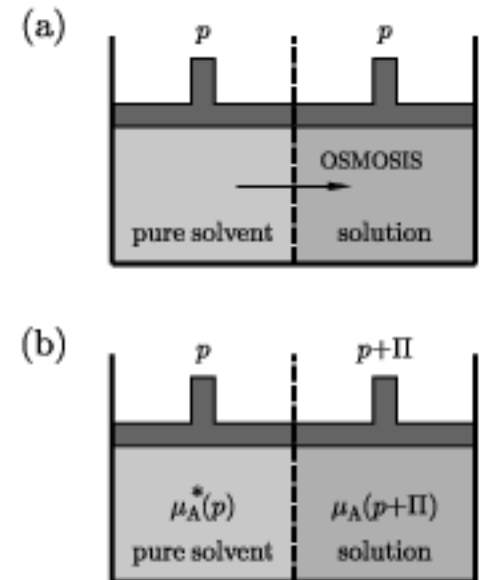
Reverse osmosis

- We apply a pressure *above* the osmotic pressure, thus driving ions from the solution to the pure solvent

- There are applications in filtration and desalination processes
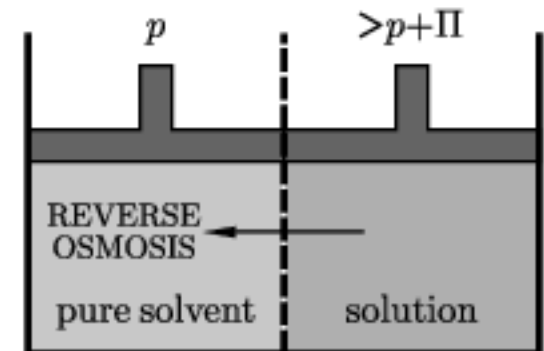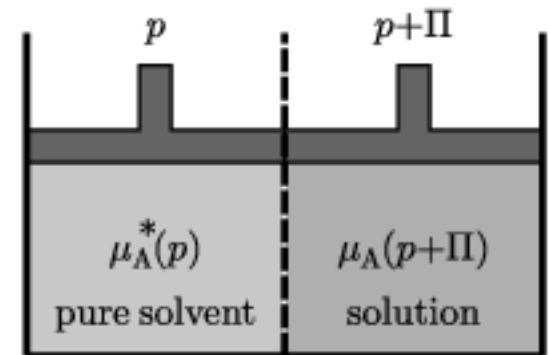
A Nicolaï, BG Sumpter, V Meunier;
Physical Chemistry Chemical Physics 16 (18), 8646-8654 (2014)

Another example of entropic force

- When a rubber band is stretch by a weight down and it is heated, it's entropic increase, and the rubber band *contract*, thus lifting the weight.

- This is because there are many more configurations of the band when it is contracted (molecular origin)

stretch

entropy *decreases*
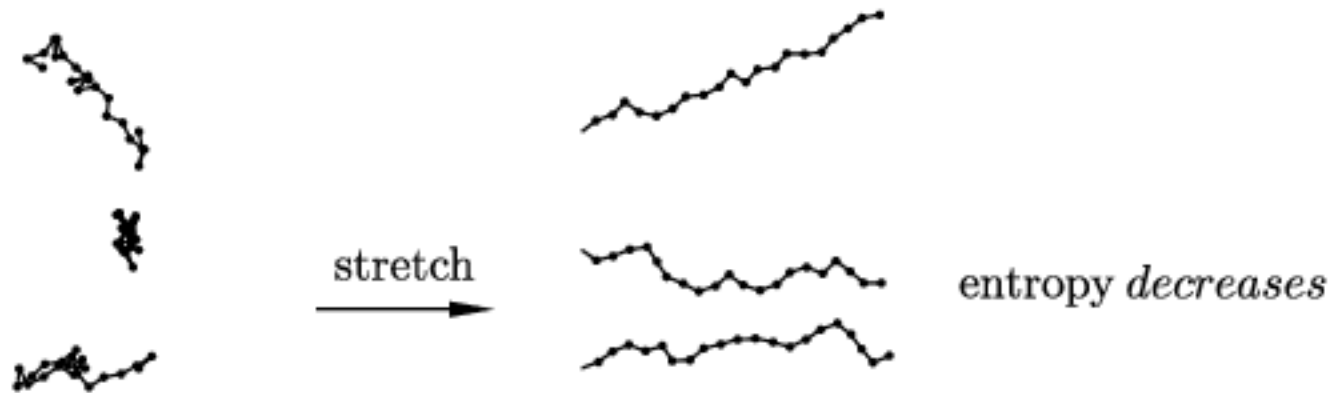
Worked example: chemical potential of a solvent A with a solute B

$$\mu_A^{(g)*} = \mu_A + RT \ln \frac{p_A^*}{p}$$

This is for a gas (g) and a pure substance (*)

(chemical potential *per mole*)

$$\mu_A^{(\ell)*} = \mu_A + RT \ln \frac{p_A^*}{p}$$

Liquid in equilibrium with the gas

mole fraction of A: number of moles of A over total number of moles

If we mix B into liquid A, the mole fraction of A (x_A) is less than 1

The chemical potentials of A in the gas and liquid are still equal but the gas has different vapor pressure p_A

$$\mu_A^{(\ell)} = \mu_A^{(g)} = \mu_A + RT \ln \frac{p_A}{p} \quad \longrightarrow \quad \mu_A^{(\ell)} = \mu_A^{(\ell)*} + RT \ln \frac{p_A}{p_A^*}$$

$$p_A = x_a p_A^* \text{ (Raoult's law)} \quad \longrightarrow \quad \mu_A^{(g)} = \mu_A^{(\ell)} = \mu_A^{(\ell)*} + RT \ln x_A$$

The chemical potential of A has decreased

Quantitative analysis of osmosis

Consider the equilibrium between pure solvent A held at constant pressure p and the solution with contains a small number of B molecules in solvent A, held at pressure $p + \Pi$
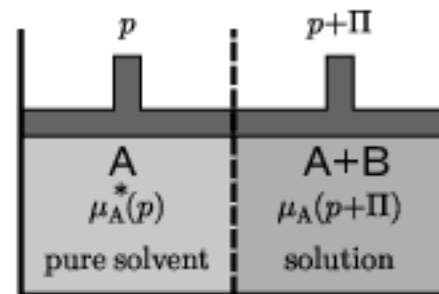
The semipermeable membrane does not allow B molecules to pass through

Equilibrium is establishes when the chemical potentials are the same on both sides:

$$\mu_A^*(p) = \mu_A(p + \Pi) \longrightarrow \mu_A^*(p) = \mu_A^*(p + \Pi) + RT \ln x_A$$

How does chemical potential vary with pressure?

$$(\partial G / \partial p)_T = V \qquad\qquad \mu_A^*(p + \Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_A \, dp$$

$$\mu_A^*(p) = \mu_A^*(p) + \Pi V_A + RT \ln x_A$$

$$\Pi V_\mathrm{A} = -RT \ln x_\mathrm{A}$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \frac{x^5}{5} - \cdots$$

Summary

- An extra term is introduced into the combined first and second laws to give $dU = TdS - pdV + \mu dN$, to allow for cases in which the number of particles can vary; μ is the chemical potential, which can be expressed as $\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$; it is also the Gibbs function per particle.

- For a system that can exchange particles with its surroundings, the chemical potential plays a similar role in particle exchange as temperature does in heat exchange.

- The grand partition function $\mathcal{Z}$ is given by $\mathcal{Z} = \sum_i e^{\beta(\mu N_i - E_i)}$

- The grand potential is $\Phi_G = -k_B T \ln \mathcal{Z} = U - TS - \mu N = -pV$

- $\mu = 0$ for particles with no conservation law.

- For a chemical reaction $dG = \sum \mu_j dN_j = 0$ and hence $\sum \nu_j \mu_j = 0$

- The equilibrium constant K can be written as $\ln K = -\Delta_r G^\ominus / RT$

- The temperature dependence of K follows $d \ln K / dT = \Delta_r H^\ominus / RT^2$