Chemical Potential

- The extra energy from adding a particle $dU = TdS - PdV + \mu dN$
- The specific Gibbs $\mu = g$ for a pure substance.
- The quantity which drives particle flow.
- The quantity which defines chemical equilibrium

Chemistry:

- Instead of measuring a reaction "constant" $K(T, P)$ for every reaction.
- Measure $\mu(T, P)$ for each component

Entropy of mixing

"Ideal solution", the equivalent of an ideal gas

$$\mu(T, p_i) = g(T, p_i) = g_0(T, P_0) + RT \ln p_i / P_0$$

The specific entropy of each component in the mixture is then

$$s = -\left(\frac{\partial g}{\partial T}\right)_P = -R \ln x_i$$

From which the total entropy of the system is

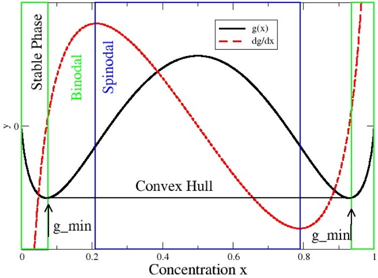
$$S = -\sum x_i s_i = -\sum x_i R \ln x_i$$

Two component solution

A & B interact $H = H_0 x_A x_B$

$G = H_0 x_A x_B + x_A RT \ln x_A + x_b RT \ln x_B$

n.b, μ_A depends on x_B

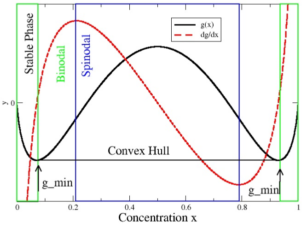


$$G = H_0 x_A (1 - x_A) + x_A RT \ln x_A + (1 - x_A) RT \ln(1 - x_A)$$

$$\left(\frac{dG}{dx_A}\right)_T = \frac{H_0}{RT}(1 - 2x_A) + \ln \frac{x_A}{1 - x_A} = 0$$

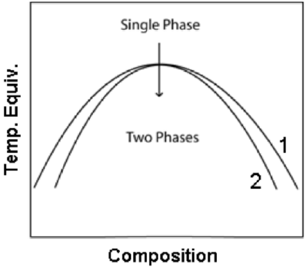
Binodal and Spinodal

$G = H_0 x_A(1 - x_A) + x_A RT \ln x_A + (1 - x_A)RT \ln(1 - x_A)$



At High T

- S dominates,
- system tends to ideal solution.
  Start out of equilibrium (Quench, stir)
- difference in μ causes atoms to move.



Spinodal $\frac{d^2g}{dx^2} < 0$ Spontaneous separation

Binodal $\frac{d^2g}{dx^2} > 0$ Nucleation and growth

A miscellany of applications.

The Second Law tell us to increase entropy.
And move towards lower chemical potential
It doesn't say how.

Ammonia Fountain

https://www.youtube.com/watch?v=gMqRxbv_IW8

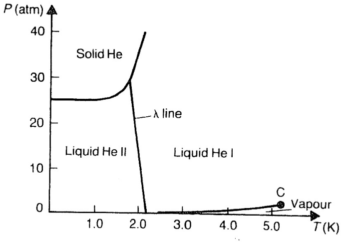
$$dg = dh - s.dT + v.dP + mg.dz$$

If $\Delta h < mg\Delta z$ (P,T constant) things move up.

Ammonia dissolves in water with large, negative Δh.

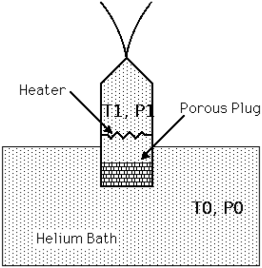
Helium II Fountain effect

https://www.youtube.com/watch?v=kCJ24176enM
https://www.youtube.com/watch?v=2Z6UJbwxBZI



- He II is a "mixture" of superfluid and "normal" He.
- Superfluid component: "all particles in ground state"
- So can add a particle to superfluid without changing S.
- "normal" He component has finite entropy.

Helium II Fountain effect



Two vessels of cold He ("system" + "bath")
Only superfluid flows through plug.
$\Delta Q = T\Delta S = 0$
Equilibrium: $\mu_1 = \mu_0$.

If "system" is heated ($T_1 > T_0$), equilibrium requires:

$$-s\ dT + v\ dp = 0 \Rightarrow dp/dT = s/v > 0$$

Thus heated "system" is at higher pressure than "bath".

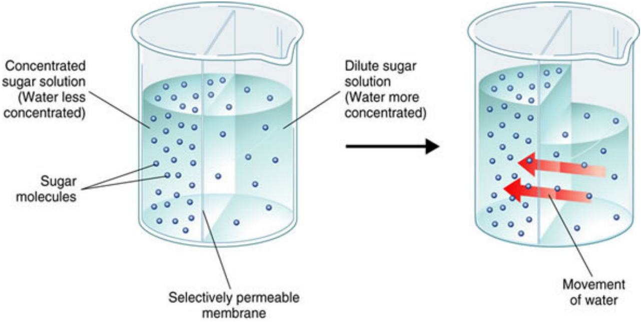
$$\Delta P = (s/v)\Delta T$$

This pressure difference is sufficient to generate a continuous fountain.

Osmosis: Chemical potential and ergodicity

semipermeable membrane between regions A and B

some particles can flow e.g. water not sugar.
$\mu^w_A = \mu^w_B$; $\mu^s_A \neq \mu^s_B$;



Simple case - noninteracting molecules $\mu^w \propto p^W$, so $p^W_A = p^W_B$
Total pressure: sum of partial pressure $P = \sum_i p_i$
If A also contains sugar: its *total* pressure is higher by p^s_B.

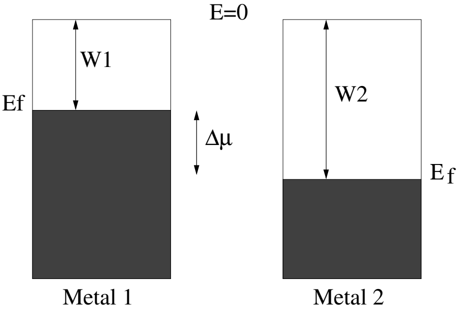
If water and sugar interact, Raoult's Law fails u^w depends on sugar concentration.
If sugar/water attract $\Delta u^W < 0$, so for $\Delta g^W = 0$ must have $\Delta p^W = 0$,

Too much solvent outside a cell reverses flow of water

Take a slug, add salt...

Electrons and Fermi Energy

In a metal, electrons occupy energy states up to the "Fermi Level".

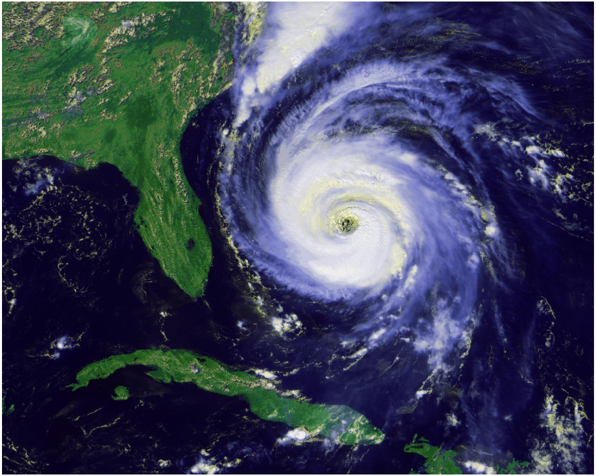


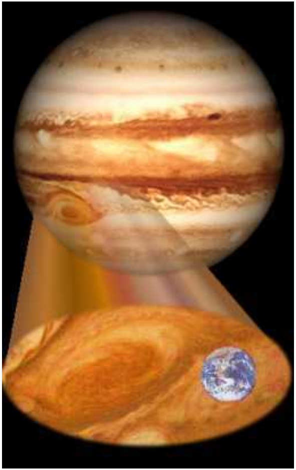
Adding an electron: $\mu = E_F$.
Placing two metals together means E_F must be the same.
E=0 $\implies$ Electron at infinity.
But ...
Work functions, ϵ_W are different.
Electrons must flow to equalise E_F

$$V = (W_1 - W_2)/e$$

a "pile" forms a battery.

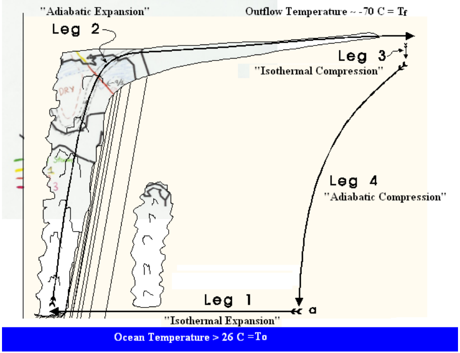
On earth, as it is in heaven





Hurricanes

A hurricane is a self assembling heat engine.
The hot reservoir is the ocean surface ($T_h \approx 300K$),
The cold reservoir is the top of the atmosphere, ($T_c \approx 200K$)
Work is done creating winds.



It approximates to a Carnot cycle.

Isothermal expansion - air spirals towards the eye. (+ absorb water)
Adiabatic expansion Hot air rises to (low P).
Isothermal compression Water vapour condenses and falls as rain, releasing latent heat.
Adiabatic compression In theory, air drops back to sea level.

In a *thermoelectric* material

- μ_e depends on temperature.
- If a temperature gradient is applied,
- electrons or holes flow from hot to cold.

A *thermoelectric heat engine*

- two *thermoelectric* materials:
- electrons flow from hot to cold, around a circuit doing work.
- No moving parts.
- Efficiency reduced by flow of heat.