Chemical Potential

- So far we have been dealing with fixed numbers of particles. But in actuallity the number of particles can fluctuate through microscopic reactions, e.g.

$$2H_2 + O_2 \rightarrow 2H_2O$$

We should be able to predict the mean abundances. In addition some particles are not conserved at all

$$e^+ + e^- \leftrightarrow \gamma + \gamma$$

Themodynamics Definition

$$dU = TdS - pdV + \mu\, dN$$

↑ energy required to add an additional particle to the system

So

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

Think "salinity" of salt water. If the concentration is high the chemical potential is also high. It is some what analogous to temperature

We can still change variables

$$F = U - TS$$

So

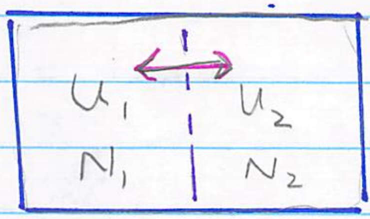
$$dF = -S\,dT - p\,dV + \mu\,dN$$

And thus we have also:

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

Equilibration

- Given two different systems exchanging energy and particles, when will they come to equilibrium?

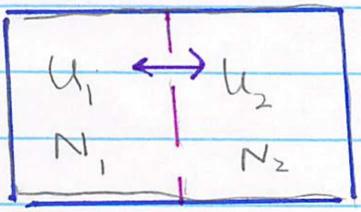


- Answer: the two systems will equilibrate when they have the same temperature and chemical potential.

- First note that

$$dU = T\,dS - p\,dV + \mu\,dN$$

or $$\boxed{dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN}$$



- The number of configurations of system 1 is $\Omega_1(U_1,N_1)$ and $\Omega_2(U_2,N_2)$ for system 2. The total number of configurations is

$$\Omega_{TOT} = \Omega_1(E_1,N_1)\,\Omega_2(E_2,N_2)$$

Then

$$\ln \Omega_{TOT} = \ln \Omega_1 + \ln \Omega_2$$

- or

$$\boxed{S_{TOT} = S_1(U_1,N_1) + S_2(U_2,N_2)}$$

The combined system will evolve to maximize the total number of configuations

$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1}\frac{dU_1}{dt} + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1}\frac{dN_1}{dt} + \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2}\frac{dU_2}{dt} + \left(\frac{\partial S}{\partial N_2}\right)_{U_2}\frac{dN_2}{dt}$$

Now since:

$$U_1 + U_2 = U \longleftarrow \text{Total energy}$$

$$N_1 + N_2 = N \swarrow \text{constant, total \#}$$

And so, $\dfrac{dN_1}{dt} = -\dfrac{dN_2}{dt}$

- We find using: $dS = {}^{1}\!/_{T}\, dU - {}^{\mu}\!/_{T}\, dN$ (V fixed)

$$\left(\frac{\partial S}{\partial U}\right)_N = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_U = \frac{\mu}{T}$$

We find demanding that entropy increase:

$$\boxed{\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\frac{dN_1}{dt} \geq 0}$$

- Thus if system I is hotter than 2, we have $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0$ and $\frac{dE_1}{dt} < 0$. That is system #1 looses energy.

- If system one has higher chemical potential (e.g. saltier), then $\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} > 0$ and $\frac{dN_1}{dt}$ will decrease, i.e. system 1 will lose particles.

- The two systems equilibrate when $\frac{dS_{TOT}}{dt} = 0$ or:

$$T_1 = T_2 \quad \text{and} \quad \mu_1 = \mu_2$$

Comparison of Temperature and μ

Note

$$\boxed{dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN}$$

$$\frac{1}{T} \longleftrightarrow U$$

If $1/T$ is large
You are very hungry for energy

$$-\frac{\mu}{T} \longleftrightarrow N$$

If $-\mu/T$ is large, you are very hungry for particles. In an ideal gas the concentration is very low, we are very hungry for more particles and μ/T will be very negative

The Gibbs-Duhem Relation & μ for ideal gas

- Let's look at

$$dU = T\,dS - p\,dV + \mu\,dN$$

Then $G = U - TS + Vp$, So

$$dG = -S\,dT + V\,dp + \mu\,dN$$

- Now if I double the size of system the Temperature and pressure remain fixed (and μ), but N and G double so we must have

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

Or

$$\boxed{U - TS + pV = \mu N}$$

- We can also prove it like this: (you may wish to skip this proof)

$U(S, V, N)$ ← U is a function of the extensive variables S, V, N

Increasing the system size by a factor λ

$$S \to \lambda S, \quad V \to \lambda V, \quad N \to \lambda N$$

The energy also increases

So

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

Differentiating with respect to λ, ie taking $d/d\lambda$ of the result

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

Now setting $\lambda = 1$, and using, $dU = T\,dS - p\,dV + \mu\,dN$, implying that $\partial U/\partial S = T$ and $\partial U/\partial N = \mu$ etc gives

$$\boxed{U = TS - pV + \mu N}$$

This is the Gibbs-Duhem relation again

The chemical Potential of an ideal gas

Note $G = F + pV = \mu N$ and we know F for an ideal gas

$$G = -NkT \ln\left(\frac{eV_N}{\lambda^3}\right) + NkT = \mu N$$

with $\ln e = 1$ find:

$$\mu = -kT \ln\left(\frac{V_N}{\lambda^3}\right)$$

In terms of the density, $V_N = V/N = 1/n$, we find

$$\boxed{\mu = kT \ln(n\lambda^3)}$$

Sometimes $1/\lambda^3$ is called the quantum density, wich is a very large density, when the debroglie wavelengths overlap. So we have

$$\boxed{n = n_Q e^{\mu/T} \qquad \text{with} \qquad n_Q \equiv \frac{(2\pi mkT)^{3/2}}{h^3},}$$

Since the density is normally much lower than the quantum density, we normally have that μ/T is a large negative number