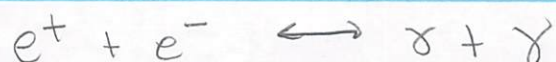# Chemical Potential

- 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.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

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

$$e^+ + e^- \longleftrightarrow \gamma + \gamma$$

Thermodynamics 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 somewhat analogous to temperature
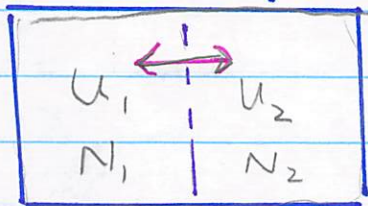
We can still change variables

$$F = U - TS$$

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?

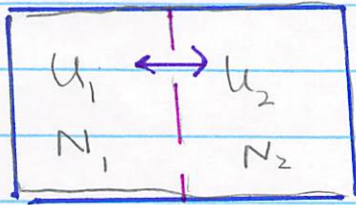$$
\begin{array}{c|c}
U_1 & U_2 \\
N_1 & N_2
\end{array}
$$

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

• 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

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

Now since: $\quad U_1 + U_2 = U \quad \leftarrow$ Total energy

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

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

- We find using: $dS = \frac{1}{T} dU - \frac{\mu}{T} dN$ (V fixed)

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

We find demanding that entropy increase:

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

- Thus if system 1 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:

$$T_1 = T_2 \qquad and \qquad \mu_1 = \mu_2$$

The Gibbs-Duhem Relation & μ for ideal gas

- Let's look at

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

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

$$dG = -SdT + Vdp + \mu dN$$

- 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)

$$U(S, V, N) \leftarrow U \text{ is a function of the extensive variables } S, V, N$$

Increasing the system size by a factor λ

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

The energy also increases

So

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

Differentiating both sides w.r.t. λ yields

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

Now set $\lambda = 1$ (it holds at all λ) and use:

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

So

$$U(S, V, N) = TS - pV + \mu N$$

$\underline{\mu \text{ for an ideal gas:}}$

- $G = F + pV$ ← this is Gibbs Duhem

  Now:

  $$F = -k_B T \ln Z \qquad p = \frac{NkT}{V}$$

  ↑ we derived this earlier

  $$= N k_B T \left(\ln(n\lambda_{th}^3) - 1 \right)$$
  from F

  $$+ \; N k_B T$$
  from pV

  $$G = N k_B T \ln(n\lambda_{th}^3)$$

So

$$\boxed{\mu = \frac{G}{N} = k_B T \ln(n\lambda_{th}^3)}$$

note $e^{\mu/k_B T} = n\lambda_{th}^3$

Since $n\lambda_{th}^3 \ll 1$ we have μ/kT negative