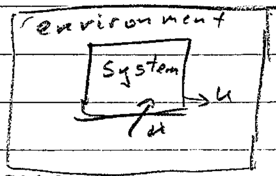
5.2 Free energy and interaction with environment

Environment – huge and acts as reservoir of energy

Want to account for the environment without having to explicity redo calculation of system + environment everytime.

For example



constant T, V, N
energy can go in/out
system and environment at same T

$$dS_{TOT} = \overbrace{dS}^{\text{system}} + \overbrace{dS_R}^{\text{reservoir}}$$

If only energy travels in/out
$dS_R = dU_R / T_R = -dU/T$

$$\Rightarrow dS_{TOT} = dS - \frac{1}{T} dU$$
$$= -\frac{1}{T}(dU - TdS)$$
$$= -dF/T$$

But... $dF = dU - TdS - S\cancelto{0}{dT}$

$\Rightarrow$ Under condition of fixed T, V, N $\quad dS_{TOT} = -\frac{dF}{T}$

One way to think about this is only worry about the system but system goes to state that maximizes Helmholtz Free Energy

If the volume can change but changes are done at constant P, T

$$dS_R = \frac{dU_R}{T_R} + \frac{P_R}{T_R} dV = -\frac{dU}{T} - \frac{P}{T} dV$$

$$\Rightarrow dS_{TOT} = dS - \frac{dU}{T} - \frac{P}{T} dV = -\frac{1}{T}(dU - TdS + PdV)$$
$$= -dG/T$$

$\Rightarrow$ under condition of fixed T, P, N $\quad dS_{TOT} = -\frac{dG}{T}$

Summary, if you only look at the system
At constant U, V, N ; system evolves to maximum S.
At constant T, V, N , " " -" minimize F!
At constant T, P, N , " " " minimize G!

Remember, this is a shortcut for saying system plus environment evolves to maximize S_{TOT}.

Prob 5.18 Free energy (KE + PE) should evolve to minimum

In important relation is between Gibbs' Free energy and chemical pot.

$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \Rightarrow G = N \cdot \mu$!! why $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \not\Rightarrow F = N\mu$

or $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \not\Rightarrow S = -N\frac{\mu}{T}$

Because adding particles at const T, P
does not change μ.

Can use $G = N\mu$ to derive μ for ideal gas

$\left(\frac{\partial \mu}{\partial P}\right) = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N} = k_B T/P \Rightarrow \mu(T,P) - \mu(T,P_0) = k_B T \ln\left(\frac{P}{P_0}\right)$

$\Rightarrow \mu(T,P) = \mu_0(T) + k_B T \ln(P/P_0)$ P_0 = ref pressure (1 atm for example)

$\Rightarrow \mu_0(298\,K)$ can be found using $\Delta G/N$ from tables 404-5!

Find ΔG for H_2 at 298 K and 3 atm (1 mole)

$\Delta G = N\mu(T,P) = N\mu_0(298K) + N k_B T \ln(3)$

$= \Delta G_{Table} + 8.31\frac{J}{K}\, 298\,K \ln 3 = \overset{0\,kJ}{\Delta G_{Table}} + 2.7\,kJ$