$$\boxed{\begin{aligned} Q &= \sum_r e^{-\beta E_r} \equiv e^{-\beta A} \\ S &= -k\sum_r p_r \ln p_r \end{aligned}}$$

$A(T, V$

$A = U - TS$

$$\langle E\rangle = U = \sum_r E_r p_r \Leftarrow$$

$$p_r = \frac{e^{-\beta E_r}}{Q} \Rightarrow \ln p_r = -\beta E_r - \ln Q$$

$$\Rightarrow E_r = -kT(\ln p_r + \ln Q)$$

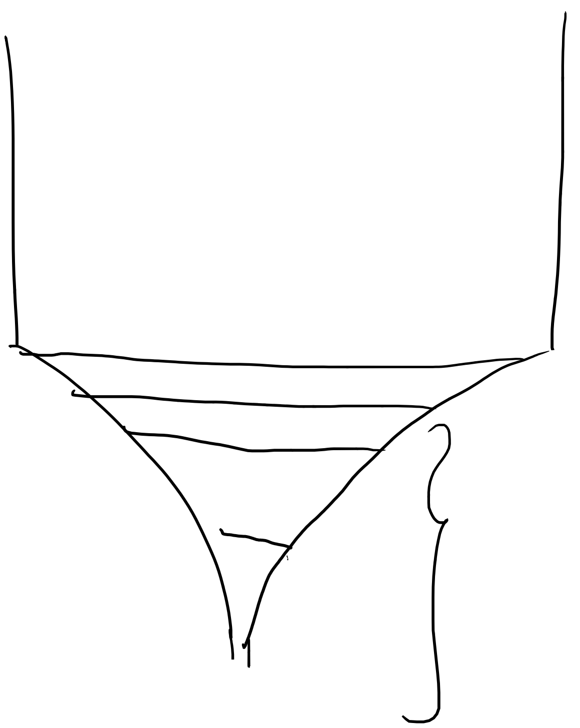
Hydrogen atom

$$\left.\begin{aligned} E_n = \frac{E_1}{n^2} \qquad E_1 = -13.7\,eV \end{aligned}\right\}$$

$$Q = \sum_{nlm} e^{-\beta E_n} = \left(\sum_{lm}\right) \sum_{n=1}^{\infty} e^{-\frac{\beta E_1}{n^2}}$$

$$\langle r\rangle \propto n^2$$

$$E_n \xrightarrow[n\to\infty]{} \frac{\hbar^2\pi^2}{2mL^2} n^2$$



$$U = \sum_r E_r p_r \Leftarrow$$

$$E_r = -kT(\ln p_r + \ln Q)$$

$$U = -kT \sum_r p_r \ln p_r + kT \ln Q \underbrace{\sum_r p_r}_{1}$$

$$\boxed{U = \underbrace{-kT \ln Q}_{A} \underbrace{- kT \sum_r p_r \ln p_r}_{TS}} = A + TS$$

$$A \stackrel{?}{=} -kT \ln Q$$

$$\underline{F \equiv -kT \ln Q} \Rightarrow \underline{dF = dA}$$

$$A(T, V) \qquad F(T, V)$$

$$dF = \underbrace{\left(\frac{\partial F}{\partial T}\right)_V}\, dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_T}\, dV$$

$$-P = \left(\frac{\partial A}{\partial V}\right)_T$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -kT \frac{1}{Q} \left(\frac{\partial Q}{\partial V}\right)_T$$

$$= -kT \frac{1}{Q} \frac{\partial}{\partial V_T} \sum_r e^{-\beta E_r}$$

$$= +kT \frac{1}{Q} \sum_r \left(+\beta \frac{dE_r}{dV} \right) e^{-\beta E_r}$$

$$= \sum_r (-P_r) p_r = -P = \left(\frac{\partial A}{\partial V}\right)_T$$

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T \Rightarrow \boxed{F = A + \varphi(T)}$$

$$F = -kT \ln Q$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -k \ln Q - kT \frac{1}{Q} \left(\frac{\partial}{\partial T}\right)_V \sum_r e^{-\beta E_r}$$

$$= -\cancel{k} \ln Q - \cancel{kT} \frac{1}{Q} \sum \frac{1}{kT^{\cancel{2}}} E_r \underline{e^{-\beta E_r}}$$

$$E_r = -kT (\ln p_r + \ln Q)$$

$$\left(\frac{\partial F}{\partial T}\right)_V = \cancel{-k \ln Q} + k \sum_r (\ln p_r + \cancel{\ln Q}) p_r$$

$$\left(\frac{\partial F}{\partial T}\right)_V = k \sum_r p_r \ln p_r$$

$$F = A + \varphi(T)$$

$$\left(\frac{\partial F}{\partial T}\right)_V = \underbrace{\left(\frac{\partial A}{\partial T}\right)_V}_{-S} + \varphi'(T) = k \sum_r p_r \ln p_r$$

$$\boxed{S = \underbrace{-k\sum_r p_r \ln p_r}_{S'} + \varphi'(T)}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{c_V/T}$$

$$S = S' + \phi(T)$$

$$dU = T\,dS - p\,dV$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV$$

$$\frac{d\phi}{dT} = \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{} - \left(\frac{\partial S'}{\partial V}\right)_T$$

$$= \frac{p}{T} - - - -$$

$$S' = -k\sum p_r \ln p_r = -k\,\frac{\sum e^{-\beta E_r}}{Q}\left(-\beta E_r - \ln Q\right)$$

$$S' = \frac{1}{T}\,\frac{\sum E_r e^{-\beta E_r}}{Q} + k\ln\sum e^{-\beta E_r}$$

$$\left(\frac{\partial S'}{\partial V}\right)_T = \frac{1}{T}\left[\sum \overbrace{\left(\frac{dE_r}{dV}\right)}^{-p_r} p_r + \sum E_r(-\beta)\left(\frac{dE_r}{dV}\right)p_r\right]$$

$$-\cancel{k}\frac{1}{T}\frac{1}{Q}\sum + \frac{1}{\cancel{k}T}\overbrace{\left(\frac{dE_r}{dV}\right)}^{-p_r}e^{-\beta E_r}$$

$$\left\{-\frac{1}{T}\frac{\left(\sum E_r e^{-\beta E_r}\right)}{Q^2}\sum \quad (-\beta)\frac{\partial E_r}{\partial V}e^{-\beta E_r}\right.$$

$$\left(\frac{\partial S'}{\partial V}\right)_T = -\frac{1}{\cancel{T}}\cancel{P} + \frac{1}{T}\sum E_r(-\beta)\left(\frac{dE_r}{dV}\right)p_r + \cancel{\frac{P}{T}}$$

$$-\frac{1}{T}\left(\sum E_r p_r\right)(-\beta)\sum\left(\frac{dE_r}{dV}\right)p_r$$

$$\left(\frac{\partial S'}{\partial V}\right)_T = \frac{-\beta}{T}\left[\left\langle E_r\frac{dE_r}{dV}\right\rangle - \langle E_r\rangle\left\langle\frac{dE_r}{dV}\right\rangle\right]$$

$$\frac{d\phi}{dT} = \underbrace{\left(\frac{\partial S}{\partial V}\right)_T} - \left(\frac{\partial S'}{\partial V}\right)_T$$

$$= \frac{P}{T} + \frac{\beta}{T}\left\{\left\langle E_r\frac{dE_r}{dV}\right\rangle - \langle E_r\rangle\left\langle\frac{dE_r}{dV}\right\rangle\right]$$

$$\varphi(T) = F - A$$

$$d\varphi(T) = dF - dA$$

$$= \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$-\left(\frac{\partial A}{\partial T}\right)_V dT - \overbrace{\left(\frac{\partial F}{\partial V}\right)_T dV}$$

$$= \underbrace{\left[\left(\frac{\partial F}{\partial T}\right)_V - \left(\frac{\partial A}{\partial T}\right)_V\right]}dT$$

—— 0 ——

Grand Canonical Ensemble

$$q(\beta, \mu, \{E_{r,s}\}) = \ln \sum_{r=0,s}^{\infty} e^{-\beta(E_{r,s} - \mu N_r)}$$

$r = \{$ ~~# of~~ particles & their microstates$\}$

$$\begin{cases} r = \text{\# of particles} \\ s = \text{microstate} \end{cases}$$

$E_{r,s} = E(r,s)$

$N(r) = 0, 1, 2, \ldots$

$N(r) = r$

$r = 0, 1, 2, \ldots$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

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

$$\boxed{S = N \ln \left[\frac{V}{N} \left(\frac{E}{N}\right)^{s} C \right]}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = \ln [\quad] + \cdots \neq 0$$

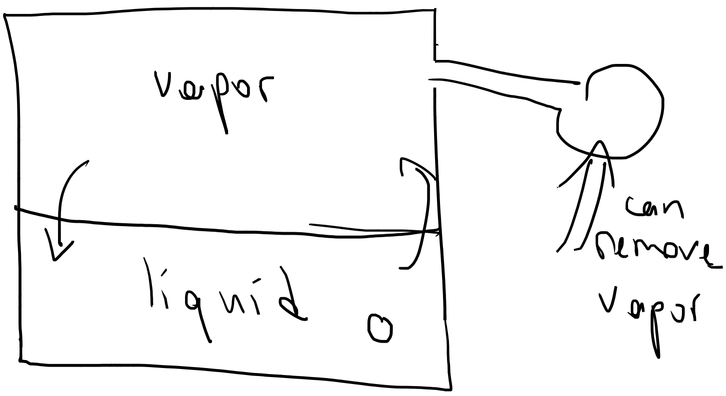
$$\left(\frac{\Delta E}{\Delta N}\right)_{S,V} = \mu \qquad dE = TdS - PdV + \mu dN$$

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

$$\frac{\partial}{\partial N}\Bigg|_{S,V}\left[S = N \ln\left[\frac{V}{N}\left(\frac{E}{N}\right)^{\delta} C\right]\right]$$

$$0 = \ln\left[\frac{V}{N}\left(\frac{E}{N}\right)^{\delta} C\right] + N\frac{\delta}{E}\overbrace{\left(\frac{\partial E}{\partial N}\right)_{S,V}}^{\mu} - N(\delta+1)\frac{1}{N}$$

$$\boxed{\mu = \frac{(\delta+1) - \ln\left[\frac{V}{N}\left(\frac{E}{N}\right)^{\delta} C\right]}{\frac{N\delta}{E}}}$$



boiling starts when

vapor pressure = external pressure