

# Thermodynamic Potentials

$U$  internal energy

$H$  enthalpy  $H = U + PV$

$F$  Helmholtz free energy  $F = U - TS$

$G$  Gibbs free energy  $G = H - TS$

Each has their own set of "natural variables"

$$dU = T dS - P dV + \mu dN$$

$S, V, N$  are natural variables of  $U$   
the independent parameters

$$U(S, V, N)$$

$$T(S, V, N)$$

$$P(S, V, N) \quad \mu(S, V, N)$$

$$H = U + PV$$

$$dH = dU + d(PV)$$

$$= (T dS - \cancel{P dV} + \mu dN) + (\cancel{P dV} + V dP)$$

$$dH = T dS + V dP + \mu dN$$

$S, P, N$  are natural variables of  $H$

Legendre transformation!

flip variables  
 $P \& V$ ,  
and changed sign

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$$F = U - TS$$

$$dF = -S dT - P dV + \mu dN$$

natural variables

$T, V, N$

$$dG = -S dT + V dP + \mu dN$$

$T, P, N$

Only one of each conjugate variable ( $S \& T$ ,  $V \& P$ ,  $\mu \& N$ )  
is a natural variable at any one time.

e.g.  $\left( \frac{\partial G}{\partial P} \right)_{T, N} = V$

$G$  & its natural variables

$$dG = V dP$$

$$\left( \frac{\partial T}{\partial P} \right)_{G, N} = \frac{V}{S}$$

$$0 = -S dT + V dP$$

Your choice of thermodynamic potential may depend on which parameters you can control

eg. in a lab,  $T$  may be easier to regulate than  $S$

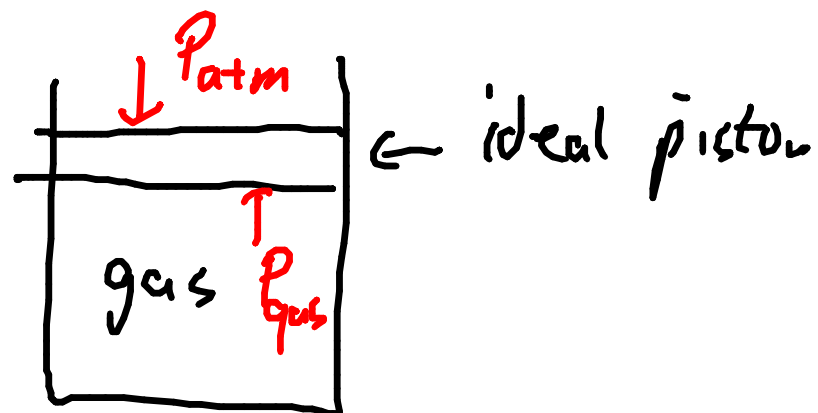
$$F : T, V, N$$

eg. a gas in a sealed box has constant Volume

$$G : T, P, N$$

eg. any system in equilibrium with atmospheric pressure  
- any solid or liquid with large changes in  $T$

- for a gas



Derivatives refer to experiments

$$\left( \frac{\partial G}{\partial T} \right)_{P, N}$$

"If I heat up a system at constant pressure how does Gibbs Free Energy change?"

At constant  $T$ ,

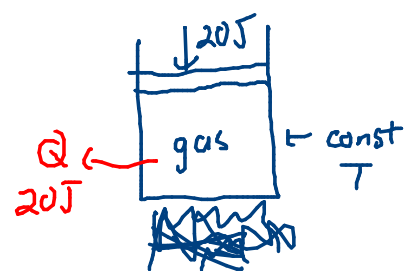
$$F = U - TS$$

$$\Delta F = \Delta U - T\Delta S$$

$$= Q + W - T\Delta S$$

if quasistatic,  
 $Q = T\Delta S$

$$\Delta F = W \rightarrow F \text{ is only affected by work, not by heat, at constant temperature}$$



I do 20J of work on piston, I know  $F$  increases by 20J.  $U$  is probably constant b/c  $T$  is. So  $Q$  flows out

"probably" because system  
- might not obey eq. thm  
-  $f$  might change

if not quasistatic

$$Q \leq T\Delta S$$

$$\Delta F \leq W$$

At constant  $T$  &  $P$ ,

$$G = H - TS = U + PV - TS$$

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

$$= (\cancel{Q} + \cancel{W_c} + W_{\text{other}}) + \cancel{P\Delta V} - \cancel{T\Delta S}$$

quasistatic

$$\Delta G = W_{\text{other}}$$

non-quasistatic

$$\Delta G \leq W_{\text{other}}$$

← electrical  
friction  
microwave oven, etc.

For ideal gas, this is rather restrictive condition ( $T, P$  const)

but during chemical process (eg.  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ )

in equilibrium with the air

you can have interesting things happen at constant  $T$  &  $P$ ,

&  $F$  &  $G$  become important.