

Thermodynamic Potentials

We've seen H

$$H = U + PV$$

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

$$= TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

at constant pressure:

$$\Delta H = Q + W_{\text{non-PV}}$$

At const pressure, $\Delta H = \text{heat}$

$H = U + PV$ is the total energy
you could recover by annihilating
the system

This is a specific example of a
thermodynamic potential

- We can extend this idea

$$F \equiv U - TS$$

$$dF = dU - d(TS)$$

$$= TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

For a constant temp (and N) process

ΔF = mechanical work @ constant temp

Intuition:

$$F = U - TS$$

The total amount of work able to be extracted
from the system (we lose some of
it to entropy)

F is the "Helmholtz Free Energy"

- Free energy is a bad name

It's the "available" energy, since
some gets lost to waste heat

We've tried:

$$U + PV$$

$$U - TS$$

We could do:

$$U - \mu N$$

$$A = U - \mu N$$

$$dA = dU - d(\mu N)$$

$$= T dS - P dV + \mu dN - \mu dN - N d\mu$$

$$dA = T dS - P dV - N d\mu$$

Valid, but not useful

For a constant temp + pressure process:

Another useful potential is:

$$G = U - TS + PV$$

$$dG = TdS - PdV + \mu dN - TdS - SdT + PdV + VdP$$

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

Interpretation:

const T

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

$$\text{In general: } Q \leq T\Delta S$$

$$\Delta F \leq T\Delta S + W - T\Delta S$$

$$\boxed{\Delta F \leq W, \text{ const } T}$$

const P, T

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

$$\Delta G \leq T\Delta S + W - T\Delta S + P\Delta V$$

$$\Delta G \leq W + P\Delta V$$

$$\Delta G \leq -P\Delta V + W_{nonPV} + P\Delta V$$

$$\Delta G \leq W_{\text{nonPV}} \rightarrow \text{const } P, T$$

For example, electrical work

Example: Batteries

Chemical reactions release electrical energy /



$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S ; \text{ const } T$$

ΔG for this rxn is -394 kJ/mol

Electrical work produced is 394 kJ per mol
of Pb

- Note: ΔH is only -316 kJ/mol ; the other 78 kJ comes from heat absorbed from the environment

Our expressions for dF & dG give us some more interesting relationships

$$dF = -SdT - PdV + \mu dN$$

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

$$F = F(T, V, N)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$\text{so: } \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

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

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

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

Maxwell Relations

Consider: $dU = TdS - PdV + \mu dN$

We know:

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

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

What if I want

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} \right]_{S,N}$$

This is the same as:

$$\frac{\partial}{\partial S} \left[\left(\frac{\partial U}{\partial V}\right)_{S,N} \right]_{V,N}$$

$$f = f(x, y)$$

$$\frac{\partial}{\partial x} \frac{\partial}{\partial y} f = \frac{\partial}{\partial y} \frac{\partial}{\partial x} f$$

$$f = x^2 y^3$$

$$\begin{aligned} \frac{\partial}{\partial x} (3x^2 y^2) &= \frac{\partial}{\partial x} (2x y^3) \\ 6x y^2 &= 6x y^2 \end{aligned}$$

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

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

Maxwell Relation

$$dF = -SdT - PdV + \mu dN$$

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

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

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

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

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

Free Energy + Equilibrium

Second Law: Total entropy of Universe will increase

- For an isolated system, equilibrium is at S_{\max}
- What if our system isn't isolated?
It can exchange energy w/ environment

Assume environment is an infinite reservoir (its T doesn't change)

Then $\Delta S_{\text{tot}} = \Delta S + \Delta S_R$

$$dS_{\text{tot}} = dS + dS_R$$

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

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

$$dS_{\text{tot}} = dS + \frac{1}{T_R}dU_R + \frac{P_R}{T_R}dV_R - \frac{\mu_R}{T_R}dN_R$$

Assume V, N are fixed (exchange only heat)

$$\text{Then } dV = dV_R = 0$$

$$dN = dN_R = 0$$

$$dS_{\text{tot}} = dS + \frac{1}{T_R} dU_e$$

$$T_R = T, dU_e = -dU$$

$$\begin{aligned} dS_{\text{tot}} &= dS - \frac{1}{T} dU \\ &= -\frac{1}{T} (dU - T dS) = -\frac{1}{T} dF \end{aligned}$$

$$\Delta S_{\text{tot}} \propto -\Delta F$$

System will evolve towards minimal F

($-\Delta F$ pros are favored)

S_{tot} will increase

F_{sys} will decrease

- Similar to potential energy U

② const $T + V$, $\Delta F < 0$ indicates a spontaneous process

Similar for G

const P, T

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV$$

$$dS_{\text{tot}} = -\frac{1}{T} dG$$

Summary:

constant N and

$$U, V: \Delta S > 0$$

$$T, V: \Delta F < 0$$

$$P, T: \Delta G < 0$$

Intuition



$$F = U - TS \quad \begin{matrix} \text{Can exchange only} \\ \text{heat} \end{matrix}$$

at const T ,

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

$\Delta F < 0$ happens when the system loses energy + gains entropy

isothermal systems which don't do work try to minimize energy while maximizing entropy

The system can gain energy spontaneously, as long as $T\Delta S > \Delta U$

Now:

$$G = U + PV - TS$$

System can exchange heat + Volume

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{Const } T, P$$

System minimizes $U + PV$ while increasing S

Example: Falling object

- During fall, $\Delta U = 0$ (potential is converted to kinetic)
- When object lands, extra energy is transferred to surroundings as heat, sound

This lowers U of the object

- It also lowers S of the object
- Not all energy will leave object
- Energy transfer until $\Delta U + T\Delta S$ balance

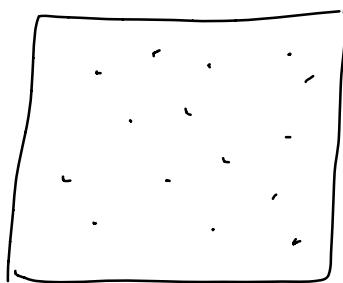
Extensive vs Intensive

We've discussed many different variables now:-

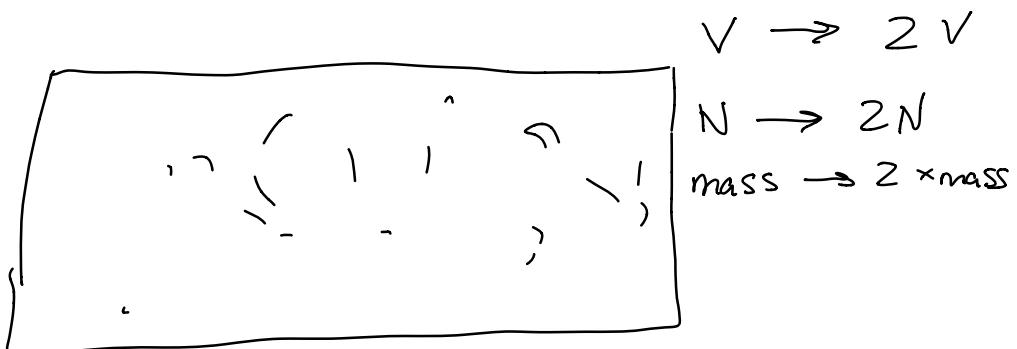
$U, V, N, S, T, P, \mu, H, F, G, \dots$

One useful way to organize:

If I change the amount of matter/size in my system, which variables change with it?



$P, T, V, U, \text{etc..}$



$$U? \quad U \approx \frac{1}{2}mv^2 \times N$$

$$U \rightarrow zU$$

$$S \rightarrow zS$$

$$\rho \text{ (density)} \quad \rho = \frac{m}{v} \rightarrow \frac{zm}{zv} = \rho$$

$$\rho \rightarrow \rho$$

$$T? \quad T \sim \frac{U}{N} \rightarrow \frac{zu}{zn} = \frac{u}{n}$$

$$T \rightarrow T$$

$$P? \quad P \sim \frac{N\tau}{v} = \frac{ZN(\tau)}{Zv} = \frac{Z\tau}{v} = \varphi$$

$$P \rightarrow \varphi$$

$$U \rightarrow U$$

Additive: V, N, S, U, mass

Non Additive: T, P, S, μ

$$F = U - TS \rightarrow zU - zTS \rightarrow zF$$

F, G, H are additive

Extensive: V, N, S, U, H, F, G

Intensive: T, P, μ, S

$$\frac{(E_{ext})}{(E_{ext})} \rightarrow (int) \quad \frac{m}{V} \rightarrow S$$

$$(E_{ext})(int) \rightarrow (ext) \quad V \cdot g \rightarrow m$$

$$(E_{ext})(E_{ext}) \rightarrow ? \quad V \cdot V = V^2$$

$$(E_{ext}) + (E_{ext}) \rightarrow (ext)$$

$$(E_{ext}) + (int) \rightarrow ?$$

$$V + \frac{V}{N} \rightarrow ?$$

Consider:

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

Suppose I go from $N \rightarrow zN$
while T, P don't change

$$\mu \rightarrow \mu$$

$$G \rightarrow zG$$

$$N \rightarrow zN \quad \frac{\Delta G}{\Delta N} = \frac{G}{z} = \mu$$

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

$$G = N\mu$$

μ : is the Gibbs energy per particle

$G = \max$ non-PV work

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

Ideal Gas: $T \propto \frac{U}{N}$ total E per particle

$$\mu = \frac{G}{N} \quad \begin{matrix} \text{total available non-PV work} \\ \text{per particle} \end{matrix}$$