Plan for chapters 5, 6:

Chapter 5:

- I will cover just 5.1 for now.

- You should also look through section 5.3 and see the tables of relations for thermodynamic potentials.

Chapter 6:

- I will cover 6.1 through 6.4.

6.2: Helmholtz potential (Helmholtz free energy) and T,V,N situations. (Statistical mechanics: this is Canonical ensemble).

6.3: Enthalpy and U,P,N situations. Also I will cover throttling from this section.

6.4: Gibbs Potential (Gibbs Free energy) and T,P,N situations. Section title includes Chemical Reactions but my examples will be more focused on other problems addressed by Gibbs free energy.

Entropy maximization / energy minimization:

- Consider a *composite system*: self-contained but has 2+ parts joined by piston(s), or it is segregated into liquid/gas phases, etc.
- Entropy *must* look like the diagram shown (for normal systems with $T > 0$, $C > 0$). (hypersurface in the space of all extensive variables)
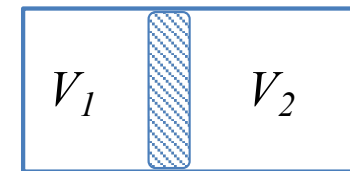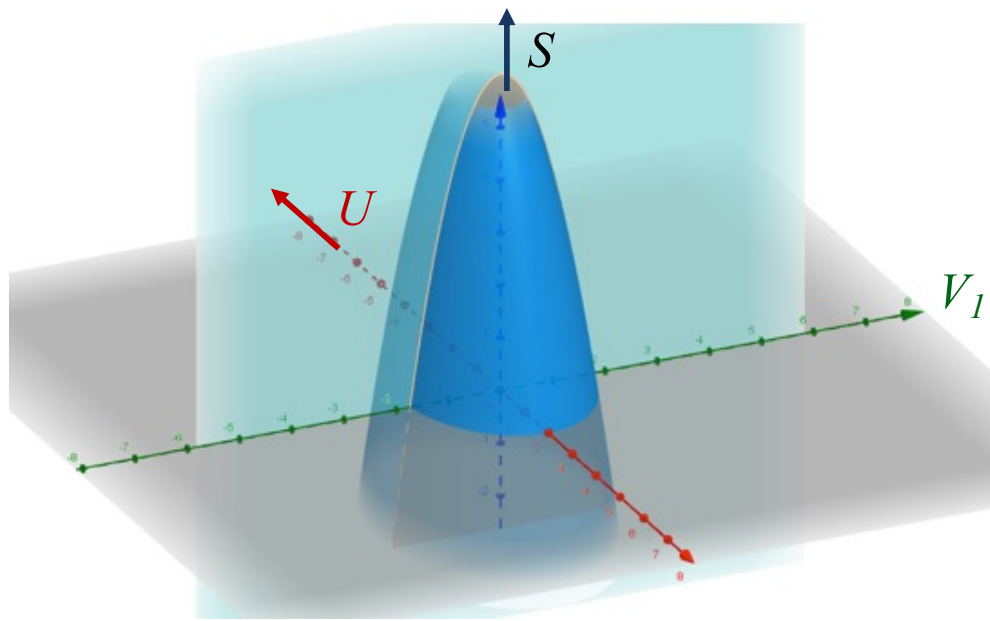
• For a given U, *S maximized* when internal variables reach equilibrium. ("microcanonical")
• *S keeps increasing* as U increases; negative curvature.

Entropy maximization / energy minimization:

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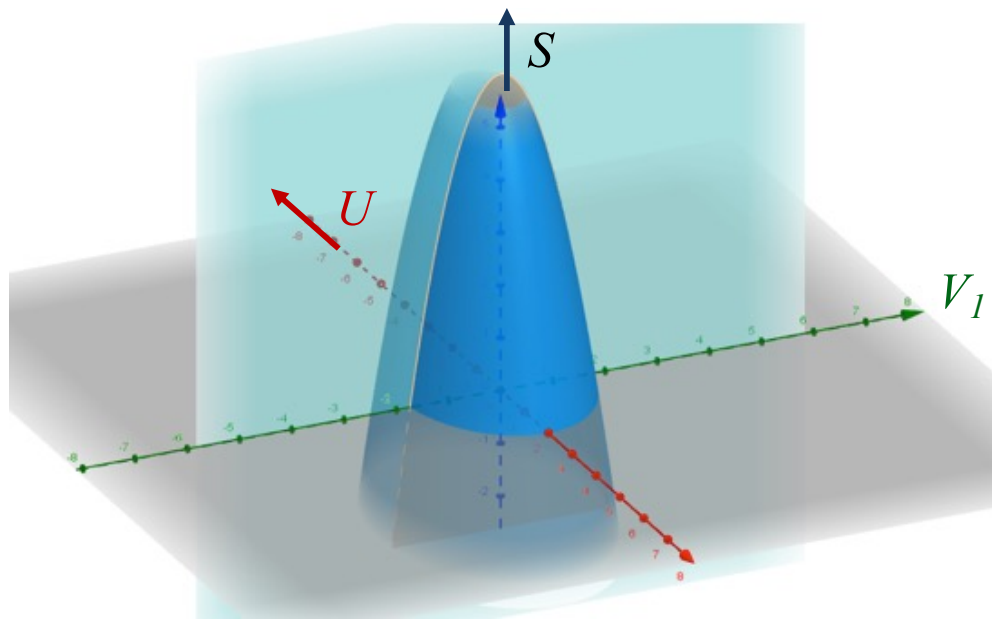
• For constant S (horizontal slice), we can see that for equilibrium conditions *U is minimized at constant S.*

Free Energy:

Helmholtz free energy defined: $F = U - TS$.

(or Helmholtz *potential*)

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

1) state variables: $F(T, V, N)$

Note not all are extensive variables, but F is extensive
So, is $F = -ST - PV + \mu N$ correct (Euler equation)?

2) Equilibrium: F minimization:
- **F is minimumized for constant T, V, N conditions**
- Important result: e.g. helps to understand phase changes, constant volume conditions
- *Canonical ensemble* I have defined before is the statistical formalism for this case.

3) Note that F is an energy state of a system, but U remains the *energy contained inside* a system. F can be considered the _available work at constant T_.

Maximum work theorem:

- Applies for *one-reservoir* problems
- Consider that system can perform work on external "reversible work system", W_{ext}. [Reversible means *no friction*; otherwise this is ordinary work as we have seen, idealized work we have been considering is reversible.]
- Question, what is maximum W_{ext} possible if a system goes from state 1 to state 2?
- Find: $W_{ext} \leq -\Delta U + T_{res}\Delta S$ "available work at constant T"
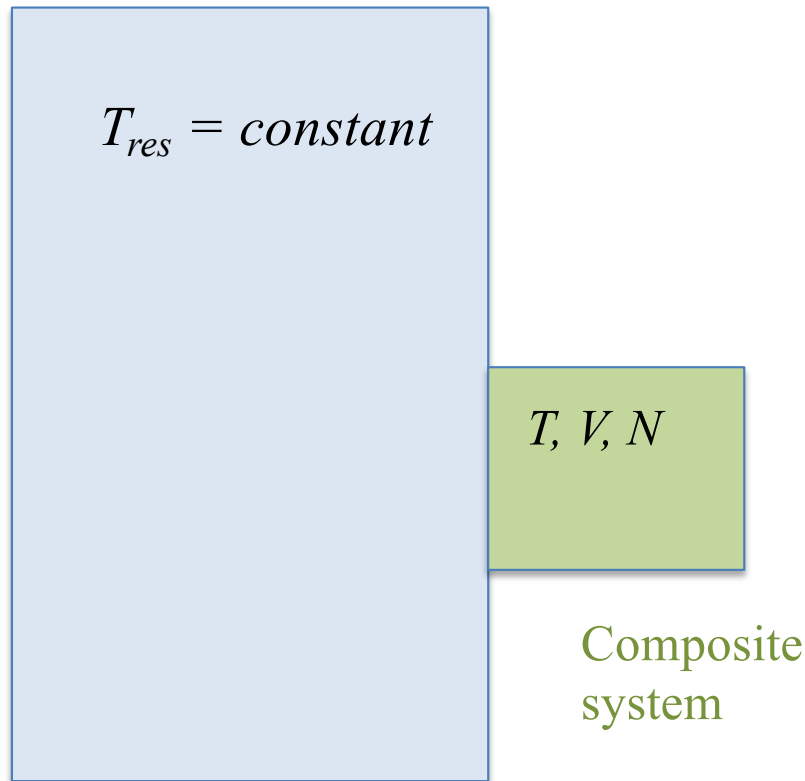- Maximum is <u>reversible</u> path from 1 to 2.

Free Energy:

■ **_F_ minimum for constant _T, V, N_ conditions**

$$F = U - TS = -PV + \mu N$$

Heat bath:
So large its temperature can't change

$T_{res} = constant$

_T, V, N_

Composite
system

- We already know equilibrium *temperatures* equal (maximizing total entropy)
- Here considering further changes happen in composite system (Piston can move, phase change, crystals form…)

Free Energies:

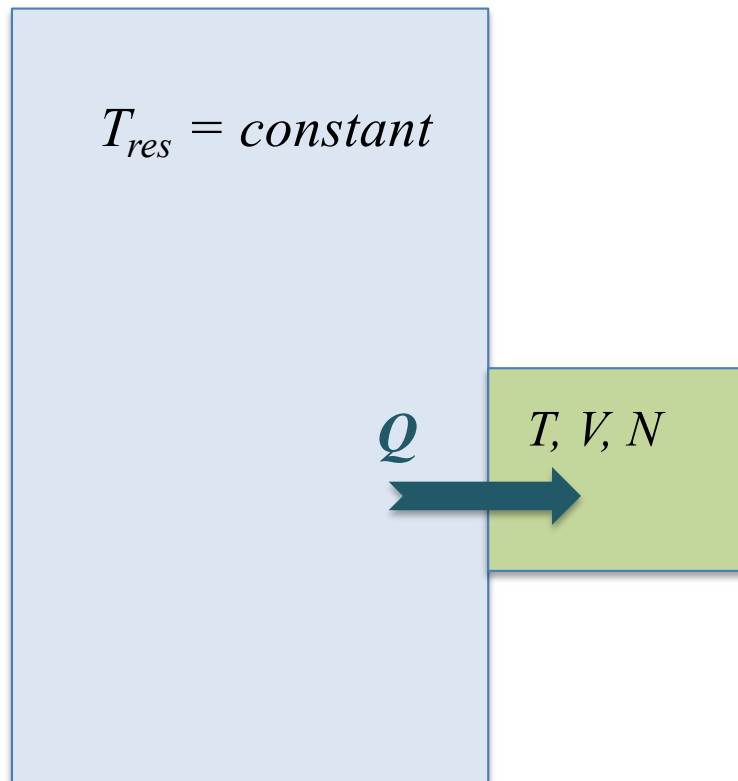- **F minimum for constant T, V, N conditions**

(system: no subscripts)

$$\Delta S_{tot} = \Delta S - \frac{Q}{T_{res}} \geq 0 \qquad \text{global entropy}$$

Same as:

$$\frac{T\Delta S - \Delta U}{T} \geq 0 \qquad \text{Equilibrium: equal temperatures}$$

$T_{res} = constant$

Q $\qquad T, V, N$

Free Energies: ▪ *F* **minimum for constant** *T, V, N* **conditions**

(system: no subscripts)

$$\Delta S_{tot} = \Delta S - \frac{Q}{T_{res}} \geq 0$$

maximized

Minimized once equilibrium is reached

$$\frac{\boxed{T\Delta S} - \boxed{\Delta U}}{T} \geq 0$$

$$\frac{-\Delta F}{T} \geq 0$$

$T_{res} = constant$

Q *T, V, N*

Free Energies:

- **F minimum for constant T, V, N conditions**

(system: no subscripts)

$$\Delta S_{tot} = \Delta S - \frac{Q}{T_{res}} \geq 0$$

Canonical Ensemble:
closed system in contact with heat bath. "NVT ensemble"

Minimized once equilibrium is reached

maximized

$$\frac{\boxed{T\Delta S} - \boxed{\Delta U}}{T} \geq 0$$

$T_{res} = constant$

$$\frac{-\Delta F}{T} \geq 0$$

Q T, V, N

F = Free energy
<u>minimized</u> by internal processes at constant T.

Examples:

$\vec{B}$
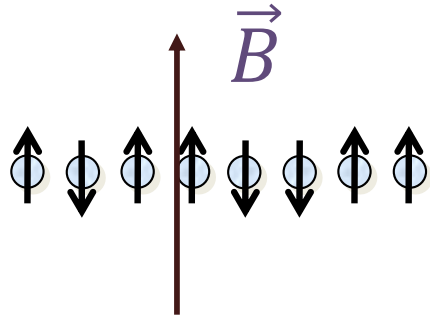
Paramagnet in B field at constant T.

$F = U - TS$

liquid

solid

T
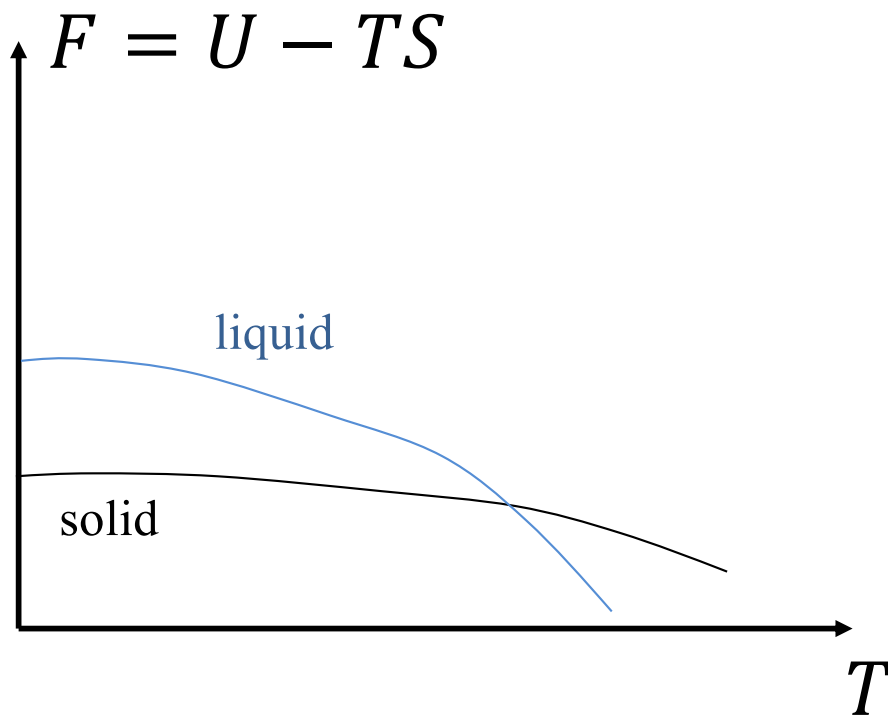
Material with liquid-solid transformation at fixed T in rigid container (constant-V)

Thermodynamic potentials:

Helmholtz free energy: $F = U - TS.$ $\quad dF = -SdT - PdV + \mu dN$

Gibbs free energy: $\quad G = U - TS + PV, \quad dG = -SdT + VdP + \mu dN$
$$(= H - TS).$$

Enthalpy: $\quad H = U + PV \quad\quad dH = TdS + VdP + \mu dN$

Equilibrium conditions: minimization:
- F minimum for constant T, V, N conditions $\quad F(T,V,N)$
- G minimum for constant T, P, N conditions $\quad G(T,P,N)$
- H minimum for constant S, P, N conditions $\quad H(S,P,N)$

Thermodynamic potentials/ensembles:

Internal energy (or Entropy):

$$dU = TdS - PdV + \mu dN \qquad \boxed{U(S,V,N)}$$

$$\boxed{S, V, N}$$

Closed system, well-defined energy (or e.g. $U \pm \Delta$):
"Microcanonical ensemble"

$$S = kln\Omega \underline{\text{ maximized}}$$

Enthalpy: $H = U + PV$.

$$\boxed{H(S,P,N)} \qquad dH = TdS + VdP + \mu dN$$

$$\boxed{S, P, N}$$

Gibbs introduced ~1902

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

$$\boxed{F(T,V,N)} \qquad dF = -SdT - PdV + \mu dN$$

$$\boxed{T, V, N}$$

Canonical ensemble

Gibbs free energy: $\qquad G = U - TS + PV$.

$$\boxed{G(T,P,N)} \qquad dG = -SdT + VdP + \mu dN$$

$$\boxed{T, P, N}$$

isobaric ensemble

or $\sum_i \mu_i dN_i$ as before

Free Energies: *T, P, N* **conditions:**

$$\Delta S_{tot} = \Delta S - \frac{Q}{T_{res}} \geq 0 \quad \underline{\text{global}} \atop \underline{\text{entropy}}$$

Same as:

$$\frac{T\Delta S - \Delta U - \Delta(PV)}{T} \geq 0$$

$-Q$ (1st law).

$T_{res} = constant$

Reservoir
supplies
heat

Q
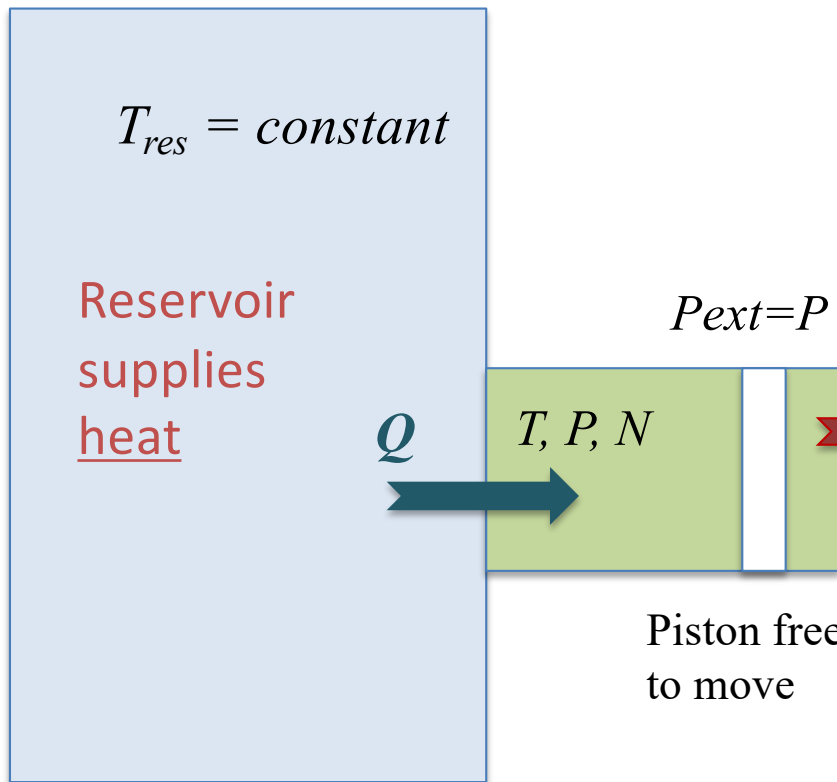
T, P, N

$Pext=P$

Reservoir
supplies
work

Piston free
to move
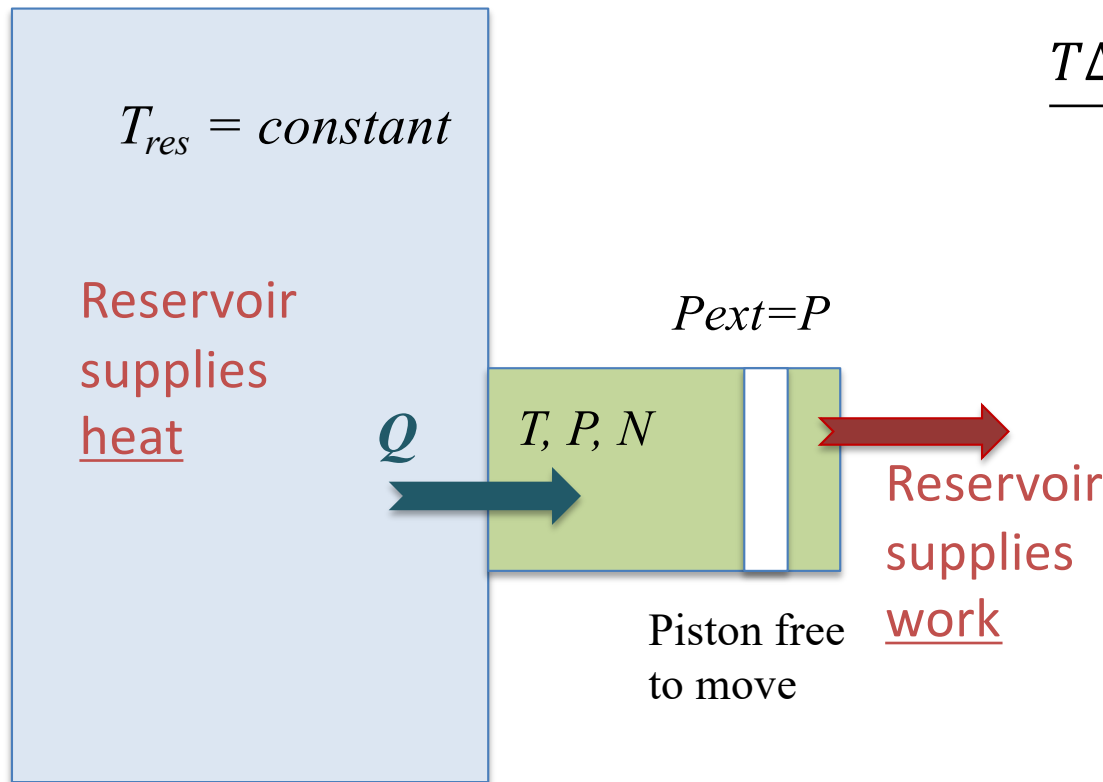
Free Energies: *T, P, N* **conditions:**

Gibbs free energy
(Gibbs potential)
minimized

$$\Delta S_{tot} = \Delta S - \frac{Q}{T_{res}} \geq 0 \quad \underline{\text{global}} \text{ entropy}$$

$T_{res} = constant$

Reservoir
supplies
<u>heat</u>

Q

$Pext=P$

T, P, N

Reservoir
supplies
<u>work</u>

Piston free
to move

$$\frac{T\Delta S - \Delta U - \Delta(PV)}{T} \geq 0$$

$$\Delta G \leq 0$$

G minimized, at
equilibrium

Enthalpy minimization: *S, P, N* **conditions:**

$$dU + PdV = đQ \leq TdS \qquad \longrightarrow \qquad dU \leq TdS - PdV$$

Const. *S, V*: this is <u>energy minimization principle</u>

Pext=P

S, P, N

Piston free to move

Pressure reservoir supplies work, adiabatic conditions
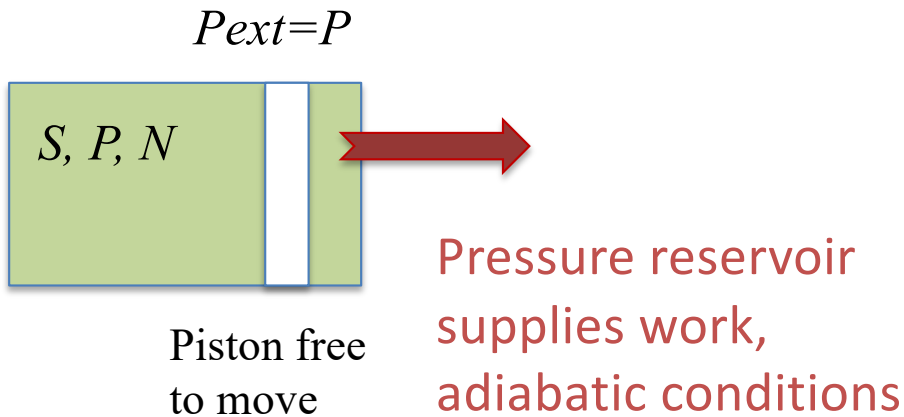
Enthalpy minimization: *S, P, N* **conditions:**

$$dU + PdV = \bar{d}Q \leq TdS \quad \longrightarrow \quad dU \leq TdS - PdV$$

Const. *S, V*: this is
<u>energy minimization
principle</u>

$$dH \leq TdS - VdP$$

Pext=P

S, P, N	
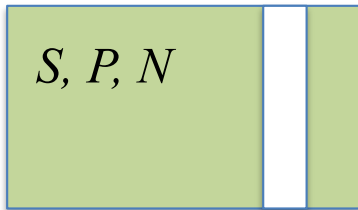
Piston free
to move

$$dH \leq 0, \text{ for } S, P, N$$
held constant