

Notes:

Homework:

- I will take volunteers for #3, 4, 5 for Thursday.

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.

Recall, thermodynamic potentials:

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

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

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

Equilibrium conditions: minimization for *composite systems*

- F minimum for constant T, V, N conditions $F(T, V, N)$
- G minimum for constant T, P, N conditions $G(T, P, N)$
- H minimum for constant S, P, N conditions $H(S, P, N)$

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

(or, Helmholtz *potential*)

Alternative form $F = -PV + \mu N$
(from Euler relation)

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

- **F is minimized for constant T, V, N conditions**
- **ΔF is the available work at constant T .**

(recall, showed maximum work theorem similarity)

Summary:

or $\sum_i \mu_i dN_i$ as before

Internal energy (or Entropy):

$$S, V, N$$

$$dU = TdS - PdV + \mu dN \quad U(S, V, N)$$

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

$$S = k \ln \Omega \text{ maximized}$$

Enthalpy: $H = U + PV$.

$$H(S, P, N)$$

$$dH = TdS + VdP + \mu dN$$

$$S, P, N$$

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

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

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

$$T, V, N$$

Canonical ensemble

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

$$G(T, P, N)$$

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

$$T, P, N$$

isobaric ensemble

Grand Potential:

$$\Phi = U - TS - \mu N.$$

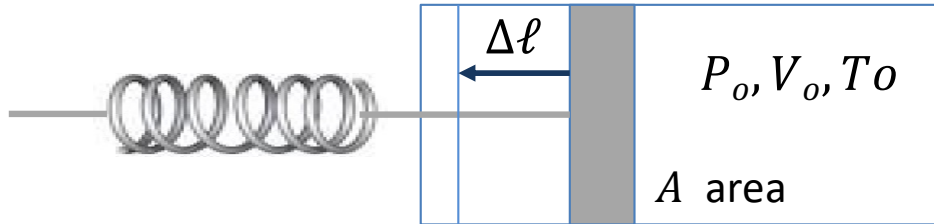
$$\Phi(T, V, \mu)$$

Grand canonical ensemble: useful for Bose or Fermi statistics

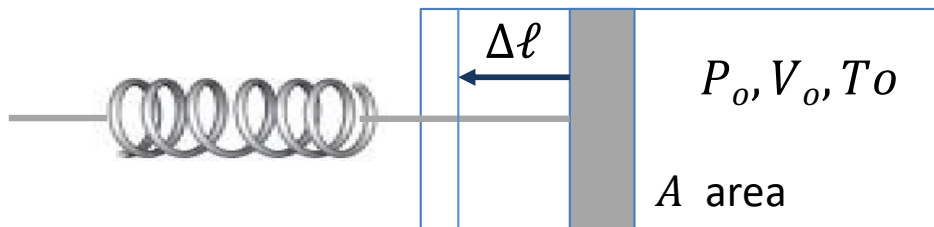
$$T, V, \mu$$

(see section 5.3)

ΔF is the available work at constant T :



Adiabatic, $W_{ext} = -\Delta U$



Contacting thermal bath, $W_{ext} = -\Delta F$

Example: Calculate work for ideal gas case?

Enthalpy: $H = U + PV$.

Alternative form $H = TS + \mu N$
(from Euler relation)

Differential: $dH = TdS + VdP + \mu dN$

- **H is minimized for constant S, P, N conditions**
(showed last time)
- **ΔH is the available heat at constant P & N , for a given change of conditions.**

Example: *Enthalpy of formation* tables, for substances relative to constituent elements (see last section, ch. 6)

Enthalpy: $H = U + PV$.

Alternative form $H = TS + \mu N$
(from Euler relation)

Differential: $dH = TdS + VdP + \mu dN$

- **H is minimized for constant S, P, N conditions**

(showed last time)

- **ΔH is the available heat at constant P & N , for a**

given change of conditions.

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Example: *Enthalpy of formation* tables, for substances relative to constituent elements (see last section, ch. 6)

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Alternative form $G = \mu N$
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Differential: $dG = SdT + VdP + \mu dN$

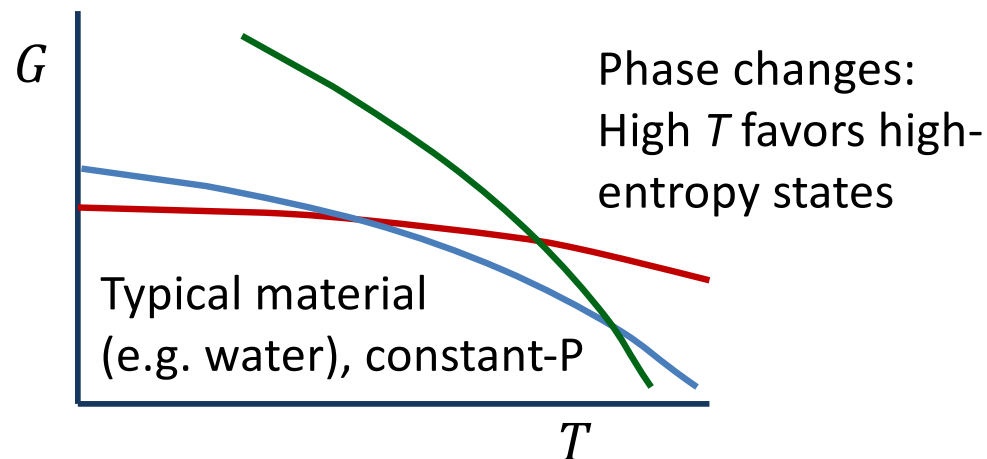
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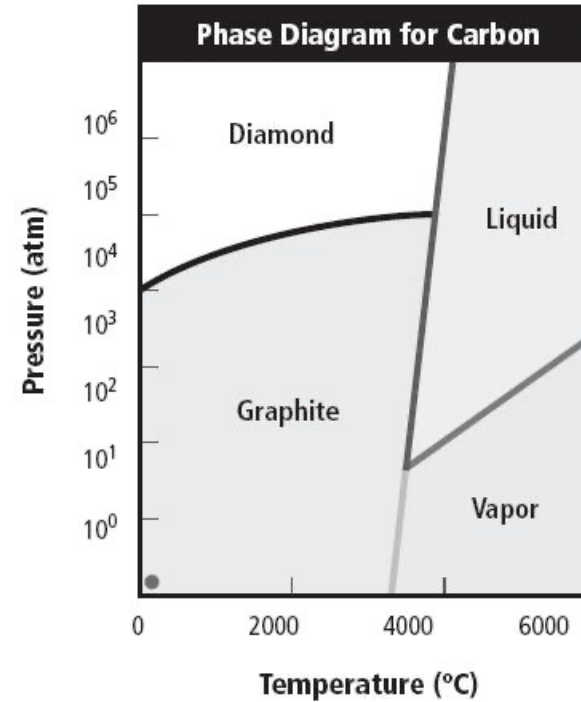
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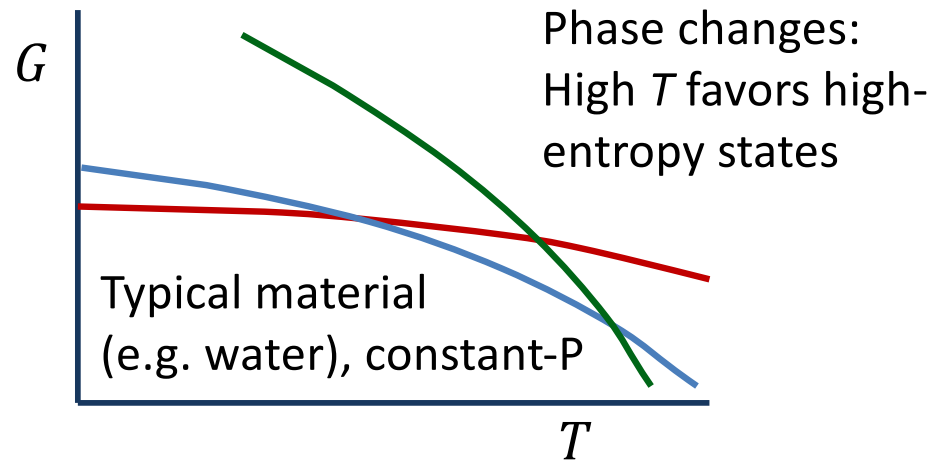


Typical experimental
conditions

Gibbs Free energy:



- **G is minimized for constant T, P, N conditions**



Gibbs Free energy: $G = U - TS + PV$.

Alternative form $G = \mu N$
(from Euler relation)

Differential: $dG = SdT + VdP + \mu dN$

- **G is minimized for constant T, P, N conditions**

Gibbs Free energy vs. Chemical potential:
 $\mu = G$ per atom.

Multicomponent system:

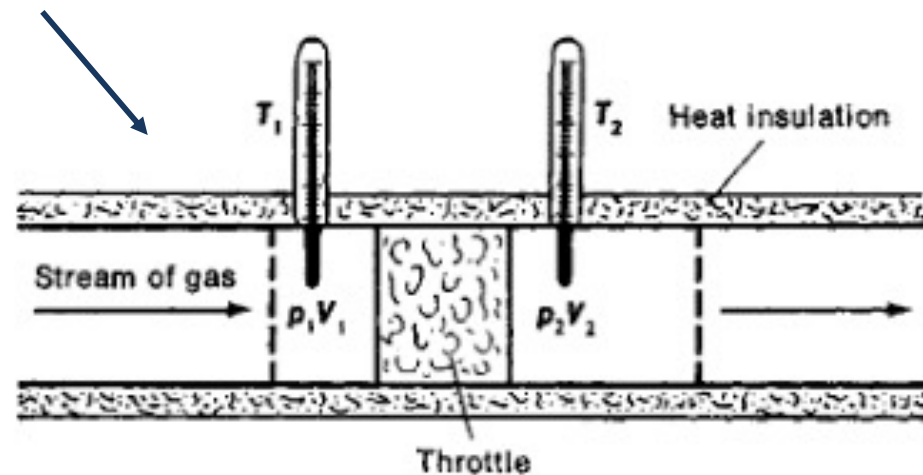
$$G = \mu_1 N_1 + \mu_2 N_2 + \dots$$

Enthalpy: $H = U + PV.$ \longrightarrow $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$ General result

- H simplifies constant-pressure processes
- useful for chemical reactions

Also solved by enthalpy method: **Joule-Thomson expansion** can show, constant-enthalpy process.

Temperature change expected for ideal gas?



Joule-Thomson process:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

Joule-Thomson coefficient:

Temperature change in constant-enthalpy process.

$$\left(\frac{\partial T}{\partial P} \right)_H \left(\frac{\partial H}{\partial T} \right)_P \left(\frac{\partial P}{\partial H} \right)_T = -1$$

C_P

use

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial t} \right)_y \left(\frac{\partial t}{\partial y} \right)_z + \left(\frac{\partial x}{\partial y} \right)_t$$

Joule-Thomson process:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

Joule-Thomson coefficient:

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C_P

$$V + T \left(\frac{\partial S}{\partial P} \right)_T = V - TV\alpha$$

$$\mu_{JT} = \frac{V(T\alpha - 1)}{C_P}$$

Cooling with
P decrease

