Thermodynamics until now

- State variables and functions: $N, V, P, T, \mu, U, S, (H, F, G)$
- 1. law: $\Delta U = Q + W$
- 2. law: $\Delta S \geq 0$ for isolated system
- 3. law: $S \rightarrow$constant when $T \rightarrow 0$
- Equilibria
  - Thermal: $\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2} \Leftrightarrow$ $T_1 = T_2$
  - Mechanical: $\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2} \Leftrightarrow$ $P_1 = P_2$
  - Chemical: $\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} \Leftrightarrow$ $\mu_1 = \mu_2$
- Defined
  - Temperature: $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$
  - Pressure: $P \equiv T\left(\frac{\partial S}{\partial V}\right)_{N,U}$
  - Chemical potential: $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$
  - Heat Capacity: $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V}$

Thermodynamics until now

What can be measured?

- T: Equilibrium with thermometer or radiation
- V: Lengths^3
- P: Equilibrium with liquid columns, bent membranes...
- N: mass / weight
- Q: For known dissipation, f.ex: $\frac{dQ}{dT} = RI^2$
- W: $P\Delta V$
- U: 1. law
- C_V: $\Delta U/\Delta T$

Not directly measurable:

- S: Integration necessary: $\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT$
- μ: derivative of S

Thermodynamics until now

Extensive and intensive variables

- Extensiv: $\mathrm{E}(\alpha N) = \alpha E(N) \propto$ mass, N. F.ex.: N, V, U, S, C_V,mass
- Intensive: $I(\alpha N) = I(N)$. f.ex.: T, P, μ, ρ
- $E_1 I = E_2$, $E_1/E_2 = I$, $E_1 + E_2 = E_3$

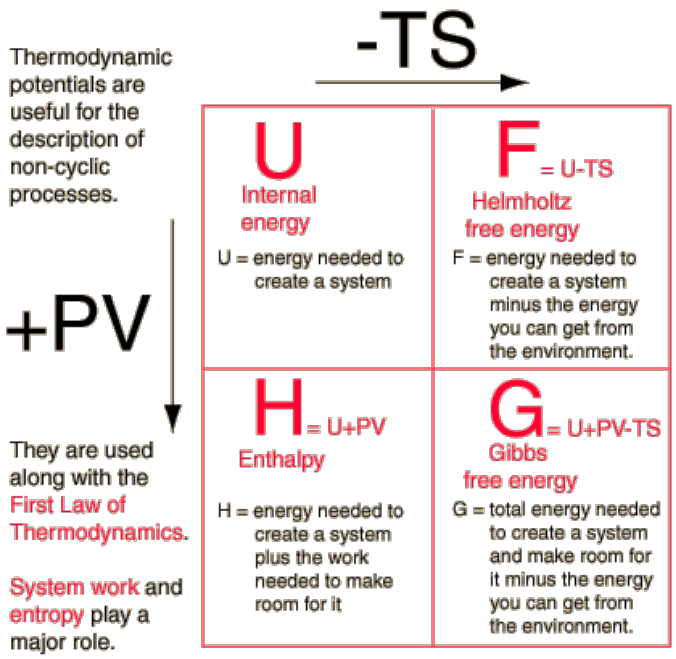
Thermodynamic identity: $dU = TdS - PdV + \mu dN$

Derived from: $dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN +$ definitions of T, P and μ

- until now: only (N,V,U) constant
- In experiments and reality (N, V, T), (N, P, T), (μ, V, T), (μ, P, T) are constant
- Therefore we need more thermodynamic potentials

Thermodynamic potentials

- Internal energy: $U = U(S, V, N)$
- Enthalpy: $H \equiv U + PV = H(S, P, N)$
- Helmholtz: $F \equiv U - TS = F(T, V, N)$
- Gibbs: $G \equiv U - TS + PV = G(T, P, N)$
- Grand: $\Phi \equiv U - TS - \mu N = \phi(V, T, \mu)$



Thermodynamic potentials and identities

Internal energy

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

Enthalpy

- $H \equiv U + PV$
- $dH = dU + PdV + VdP$
- Thermodynamic identity for H: $dH = TdS + VdP + \mu dN$
- $dH = \left(\frac{\partial H}{\partial S}\right)_{N,P} dS + \left(\frac{\partial H}{\partial P}\right)_{N,S} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN$
- $T = \left(\frac{\partial H}{\partial S}\right)_{N,P}$, $V = \left(\frac{\partial H}{\partial P}\right)_{N,S}$, $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$

Thermodynamic potentials and identities

Internal energy

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

Helmholtz free energy

- $F \equiv U - TS$
- $dF = dU - TdS - SdT$
- Thermodynamic identity for F: $dF = -PdV - SdT + \mu dN$
- $dF = \left(\frac{\partial F}{\partial V}\right)_{N,T} dV + \left(\frac{\partial F}{\partial T}\right)_{N,V} dT + \left(\frac{\partial F}{\partial N}\right)_{V,T} dN$
- $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$, $S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$, $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

Thermodynamic potentials and identities

Internal energy

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

Gibbs free energy

- $G \equiv U + PV - TS = H - TS$
- $dG = dU + PdV + VdP - TdS - SdT$
- Thermodynamic identity for G: $dG = VdP - SdT + \mu dN$
- $dG = \left(\frac{\partial G}{\partial P}\right)_{N,T} dP + \left(\frac{\partial G}{\partial T}\right)_{N,P} dT + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$
- $V = \left(\frac{\partial G}{\partial P}\right)_{N,T}$, $S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$

Thermodynamic potentials and identities

Internal energy

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

Grand potential

- $\Phi \equiv U - TS - \mu N$
- $d\Phi = dU - TdS - SdT + \mu dN - \mu dN - Nd\mu$
- $dF = -PdV - SdT - Nd\mu$
- $d\Phi = \left(\frac{\partial \phi}{\partial V}\right)_{\mu,T} dV + \left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} dT + \left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T} d\mu$
- $P = -\left(\frac{\partial \Phi}{\partial V}\right)_{\mu,T}$, $S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V}$, $N = \left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T}$

Maxwells relations

Thermodynamic potentials have symmetry of second derivatives (with respect to their natural variables)

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

- $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$
- $-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$

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

- $\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$
- $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Likewise for $H(S, P)$ and $F(V, T)$
Also Maxwells relations for partial derivatives with respect to N and μ.

Interpretation and use of the potentials, "free energy"

The potentials represent the energy necessary to create the system from nothing, keeping the natural variables (of that potential) constant.

Or, conversely: The energy that is "free" to be used when the system is annihilated.

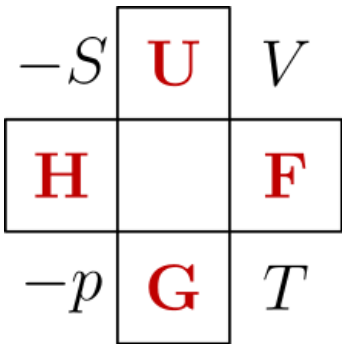
- V constant: U – energy to create a system
- P constant: H – energy to create a system and the work to make space for it
  - Normal conditions in a lab
  - Enthalpy of reaction, formation, melting, vaporization, mixing...
  - Measured and tabulated for most substances!
- T constant: F – energy to create a system minus the heat from the surroundings.
- P, T constant: G – energy to create a system and the work to make space for it minus the heat from the surroundings.
  - Measured and tabulated for many substances!
  - A process is spontaneous when the Gibbs free energy of the reactants is larger than that of the products.

2. law for other natural variables than (N,V,U)

When a system is not isolated the entropy of the surroundings (reservoir) must be accounted for: $dS_{tot} = dS + dS_R \geq 0$

- $dS_R = dU_R/T_R + P_R dV_R/T_R - \mu_R dN_R/T_R$ (TDI)
- (NVT) constant:
  - $dS_R = dU_R/T_R = -dU/T$ $T_R = T$, $dU_R = -dU$
  - $dS_{tot} = dS - dU/T = (TdS - dU)/T$
  - $dS_{tot} = -dF/T$
  - 2. law for (NVT) constant: $\Delta F \leq 0$
- (NPT) constant:
  - $dS_R = dU_R/T_R - P_R dV_R/T_R = -dU/T - PdV/T$
  - $T_R = T$, $P_R = P$ $dU_R = -dU$
  - $dS_{tot} = (TdS - dU - PdV)/T$
  - $dG = dU - TdS - SdT + PdV + VdP$, $dT = 0, dP = 0$
  - $dS_{tot} = -dG/T$
  - 2. law for (NPT) constant: $\Delta G \leq 0$
  - Spontaneous prosesses go from high to low Gibbs energy

The thermodynamic square (tricks for remembering)



- The natural variables of the potentials: nearest neighbours
  - U(S,V), H(S,P), F(V,T), G(P,T)
- Maxwells relations
  - Turn the square and make a U with the desired potential at the bottom.
  - The variables in the corners are now ordered as partial derivatives
  - G: $\frac{S}{P}, \frac{V}{T}$
  - Multiply with a minus sign on one side
  - $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$
- Thermodynamic identities
  - Choose potential (f.ex. U)
  - find the variable in the opposite corner ($dU = -Pd? + Td?$)
  - find differentials diagonaly in the opposite corner ($dU = -PdV + TdS$)
  - add μdN