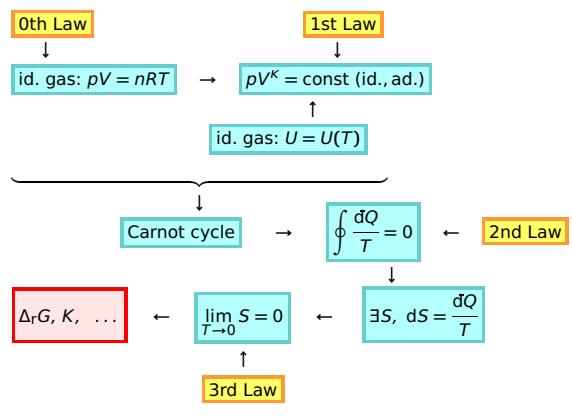
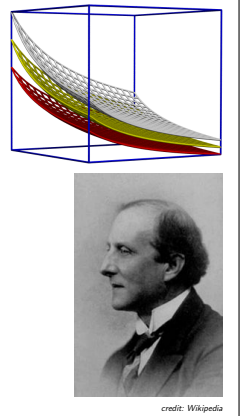


Overview of classical thermodynamics 1/16 col03



More about entropy [pic/entropy.sh] 2/16 col03

Consider a **reversible** adiabatic process ($dQ = 0$)
 In well-chosen variables (e.g., T, V, p) the system moves on a (hyper)surface
 Heat: surface \uparrow surface
 Cool: surface \downarrow surface
 Energy dissipation (**irreversible** process: work \rightarrow energy) \Rightarrow surface \uparrow surface
 Surfaces have constant entropy
 Entropy increases \uparrow in the direction of adding heat/energy dissipation
 Carathéodory: In every neighborhood of any state S of an adiabatically enclosed system there are states inaccessible from S .
 $\Rightarrow \exists$ function of empirical temperature so that $\int dQ$ is a total differential; then $1/f \propto T$

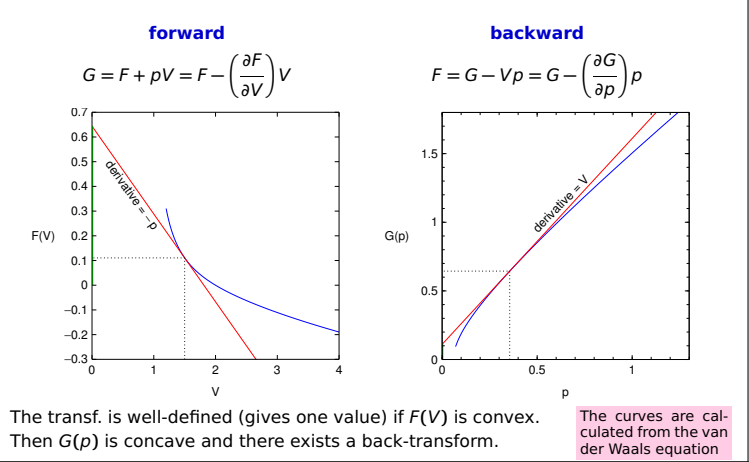


Helmholtz and Gibbs energies 3/16 col03

Internal energy $U(S, V)$ \downarrow Gibbs eq. $dU = TdS - pdV$
 Enthalpy $H(S, p) = U + pV = U - \left(\frac{\partial U}{\partial V}\right)_S V \Rightarrow dH = TdS + Vdp$
Helmholtz (free) energy (Helmholtz function, free (internal) energy)
 $F(T, V) = U - TS = U - \left(\frac{\partial U}{\partial S}\right)_V S \Rightarrow dF = -SdT - pdV$
 Often denoted by A
Gibbs (free) energy (Gibbs function, free enthalpy)
 $G(T, p) = H - TS = H - \left(\frac{\partial H}{\partial S}\right)_p S \Rightarrow dG = -SdT + Vdp$
 Or: $G = F + pV = F - \left(\frac{\partial F}{\partial V}\right)_T V$ avoid term "free energy" unless it is clear whether it is Gibbs or Helmholtz

only pressure-volume work

Mathematical context (Legendre transform) + 4/16 col03



Calculation of G 5/16 col03

Example—one phase transition.
 $G = H - TS$
 $H(T_2, p) = H(T_1, p) + \int_{T_1}^{T_2} C_p dT + \Delta_{fp} H + \int_{T_{fp}}^{T_2} C_p dT$
 $S(T_2, p) = S(T_1, p) + \int_{T_1}^{T_{fp}} \frac{C_p}{T} dT + \frac{\Delta_{fp} H}{T_{fp}} + \int_{T_{fp}}^{T_2} \frac{C_p}{T} dT$
 low T : $S(T_1, p) = \int_0^{\approx 15K} \frac{\text{const } T^3}{T} dT + \dots$
 $H(T, p_2) = H(T, p_1) + \int_{p_1}^{p_2} \left[V - T \left(\frac{\partial V}{\partial T}\right)_p \right] dp$
 $S(T, p_1) = S(T, p_2) - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_p dp$
 We can predict chemical equilibria from thermochemistry and EoS data!

F, G and work—reversible processes 6/16 col03

$dU = TdS + dW$
 $dF = -SdT + dW \Rightarrow dF = dW [T]$
Change of the Helmholtz energy at const. $T =$ work
 $dW = -pdV + dW_{\text{other than pressure-volume}}$
 $dG = -SdT + Vdp + dW_{\text{other than pressure-volume}} = dW_{\text{other than pressure-volume}} [T, p]$
Change of the Gibbs energy at const. $T, p =$ work other than pressure-volume
 Interpretation of terms $F = U - TS$ ($G = H - TS$)
 ● **low temperature** \Rightarrow the influence of **energy** (enthalpy) $>$ of entropy
 ● **high temperature** \Rightarrow the influence of **entropy** $>$ energy (enthalpy)

Irreversible processes 7/16 col03

heating: $T = T_{\text{out}}$, $dQ > 0$, $T > T_{\text{in}}$
 $\Rightarrow dS \approx \frac{dQ}{T_{\text{in}}} > \frac{dQ}{T}$
cooling: $dQ < 0$, $T < T_{\text{in}}$
 $\Rightarrow dS \approx \frac{dQ}{T_{\text{in}}} > \frac{dQ}{T}$
 $dS > \frac{dQ}{T}$
dissipation of energy by friction: $p = p_{\text{out}}$, $dQ_{\text{dis}} > 0$
 pressure-volume work only
 $dW = p_{\text{in}}(-dV) + dQ_{\text{dis}}$
 always $dQ_{\text{dis}} > 0$ (loss)
 $dS \approx \frac{dQ_{\text{dis}}}{T} > 0$
 $dU = dQ + dW < TdS - pdV$ (irrev.) $\rightarrow dG < -SdT + Vdp$ (irrev.)
 $dU < 0$ ($[S, V]$, irrev.) $\rightarrow dG < 0$ ($[T, p]$, irrev.)
The Gibbs energy of a closed system at constant T, p spontaneously (via irreversible processes) decreases. In equilibrium it reaches a minimum.

Chemical potential 8/16 col03

id. gas/mixture: compounds do not interact
 $G = H - TS \rightarrow \Delta_{\text{mix}} S_m = -R \sum_i x_i \ln x_i, \Delta_{\text{mix}} H_m = 0$
 $\mu_i^{\text{id}} = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_{j \neq i}} = \mu_i^* + RT \ln x_i$
 Chemical potential μ_i of compound i (w.r.t a standard state) = reversible work needed to transform 1 mole of the compound (from the standard state) to the given state = "ability to perform this work"
Example. How much energy is needed to obtain 1 m³ of fresh water from sea water (3.5 wt.% NaCl, 300 K)?
 $\Delta_{\text{mix}} S_m = 0$

Activity and the chemical potential

9/16
col03

General definition:

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$

⊖ = plimsoll

● for substance i in a standard state it holds $a_i = 1$

Standard state overview:

$$\begin{aligned} a_i^\circ &= \frac{p_i}{p^{\text{st}}} \gamma^\circ = \frac{x_i p}{p^{\text{st}}} \gamma^\circ & p_i \rightarrow 0 \\ a_i^* &= x_i \gamma_i^* & x_i \rightarrow 1 \\ a_i^{[x]} &= x_i \gamma_i^{[x]} & x_i \rightarrow 0 \\ a_i^{[c]} &= \frac{c_i}{c^{\text{st}}} \gamma_i^{[c]} & c_i \rightarrow 0 \\ a_i^{[m]} &= \frac{m_i}{m^{\text{st}}} \gamma_i^{[m]} & m_i \rightarrow 0 \end{aligned}$$

In the respective limit $\gamma^\circ = 1$

γ° is called a fugacity coefficient, usu. denoted ϕ or ν

Chemical equilibrium—balance

10/16
col03

General reaction:

$$0 = \sum_{i=1}^k \nu_i R_i \quad \nu_i < 0 \text{ (reactants)}, \nu_i > 0 \text{ (products)}$$

Balance in the amount of substance:

$$n_i = n_{i,0} + \nu_i \xi$$

ξ = extent of reaction; units [ξ] = mol

Let 1=key compound = first to be consumed ($n_1 = 0$) ($\Rightarrow \xi = \xi_{\text{max}}$).

Degree of reaction:

$$\alpha = \frac{n_{1,0} - n_1}{n_{1,0}} = -\frac{\nu_1 \xi}{n_{1,0}} = \frac{\xi}{\xi_{\text{max}}}$$

Equilibrium and G

11/16
col03

At $[T, p]$ we look for the minimum of

$$G(n_1, \dots, n_k) = \sum_{i=1}^k n_i \mu_i$$

where

$$n_1 = n_{1,0} + \nu_1 \xi, \dots, n_k = n_{k,0} + \nu_k \xi$$

in interval $\xi \in [\xi_{\text{min}}, \xi_{\text{max}}]$ (in homogeneous systems: in $\xi \in (\xi_{\text{min}}, \xi_{\text{max}})$)

NB: $\mu_i = \mu_i(n_1, \dots, n_k)$

Minimum condition:

$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{i=1}^k \nu_i \mu_i \equiv \Delta_r G_m = 0$$

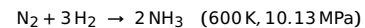
$\Delta_r G_m$ = reaction Gibbs energy

$\Delta_r G_m$	direction of reaction	name of reaction
< 0	→	exergonic
= 0		isoergonic
> 0	←	endergonic

Exergy (availability, available energy) = maximum work a system may deliver upon transition to equilibrium

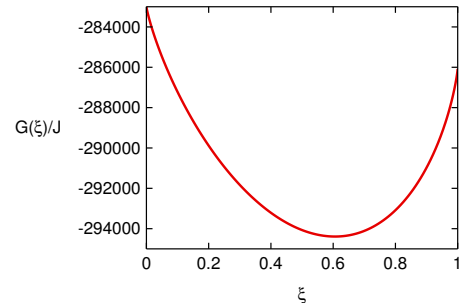
Example G(ξ)

12/16
col03



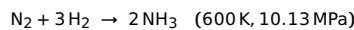
Initial composition: $n_{\text{N}_2,0} = 1 \text{ mol}$, $n_{\text{H}_2,0} = 3 \text{ mol}$, $n_{\text{NH}_3,0} = 0 \text{ mol}$

$$G(\xi) = n_{\text{NH}_3} \mu_{\text{NH}_3} + n_{\text{H}_2} \mu_{\text{H}_2} + n_{\text{N}_2} \mu_{\text{N}_2} = 2\xi \mu_{\text{NH}_3} + (3 - 3\xi) \mu_{\text{H}_2} + (1 - \xi) \mu_{\text{N}_2}$$



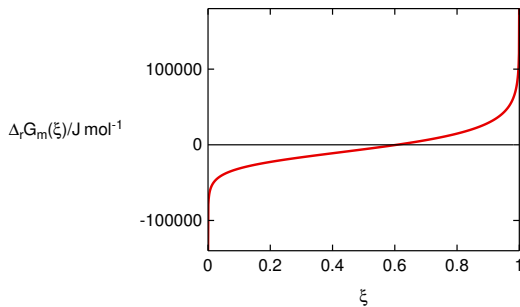
Example $\Delta_r G_m(\xi)$

13/16
col03



Initial composition: $n_{\text{N}_2,0} = 1 \text{ mol}$, $n_{\text{H}_2,0} = 3 \text{ mol}$, $n_{\text{NH}_3,0} = 0 \text{ mol}$

$$\Delta_r G_m(\xi) = \nu_{\text{NH}_3} \mu_{\text{NH}_3} + \nu_{\text{H}_2} \mu_{\text{H}_2} + \nu_{\text{N}_2} \mu_{\text{N}_2} = 2\mu_{\text{NH}_3} - 3\mu_{\text{H}_2} - \mu_{\text{N}_2}$$



Equilibrium constant

14/16
col03

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$

$$\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln \prod_{i=1}^k a_i^{\nu_i} \quad \text{in equilibrium} = 0$$

Definition of the equilibrium constant*:

$$K = \exp\left(-\frac{\Delta_r G_m^\ominus}{RT}\right)$$

⇒ equilibrium condition:

$$K = \frac{\prod_{i=1}^k a_i^{\nu_i}}{\left(\text{products}\right)} \quad \left(\text{reactants}\right)$$

● greater K : more products (→)

● smaller K : more reactants (←)

*According to IUPAC gold book, this K is "standard" or "thermodynamic" equilibrium constant. Just "equilibrium constant" may be based on concentrations, fugacities, or molalities and may have dimension.

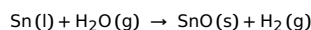
Direction of a reaction

15/16
col03

$$\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln \prod_{i=1}^k a_i^{\nu_i}$$

$\Delta_r G_m$	direction of a reaction
negative	→
zero	equilibrium
positive	←

Example. The equilibrium constant of reaction



is 0.435 at $T = 928 \text{ K}$. Mixture of $\text{H}_2\text{O} + \text{H}_2$ contains 65 mol. % of water vapor. Is tin oxidized or reduced?

$$\text{reduced} \Leftarrow \xi = 0.213 = \frac{\mu_{\text{H}_2}}{\mu_{\text{H}_2\text{O}}}$$

Temperature dependence of K

16/16
col03

$$\left(\frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2} \Rightarrow \frac{d(\Delta_r G_m^\ominus/T)}{dT} = -\frac{\Delta_r H_m^\ominus}{T^2}$$

⇒ (van 't Hoff)

$$\frac{d \ln K}{dT} = \frac{\Delta_r H_m^\ominus}{RT^2}$$

$\Delta_r H_m^\ominus$	higher $T \Rightarrow K$	equilibrium shifted to
negative (exothermic)	decreases	←
positive (endothermic)	increases	→

Le Chatelier(-Braun) principle: Any change in status quo prompts an opposing reaction in the responding system.

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, the equilibrium shifts to counteract the imposed change and a new equilibrium is established.