

More about entropy

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

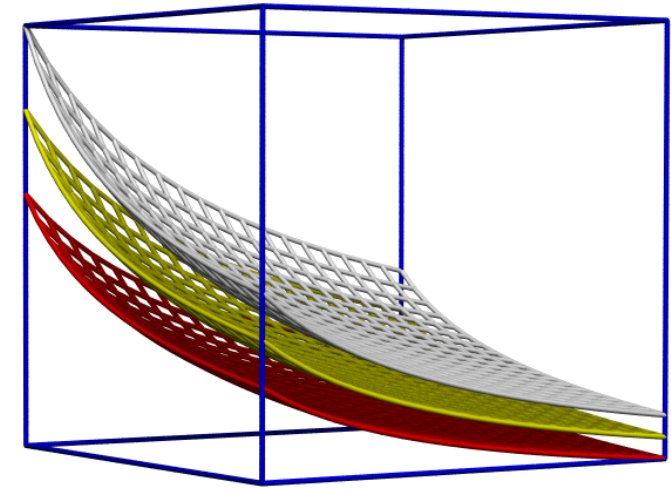
Energy dissipation (**irreversible** process: work \rightarrow energy) \Rightarrow surface \uparrow surface

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 $f dQ$ is a total differential; then $1/f \propto T$



credit: Wikipedia

Internal energy

$$U(S, V)$$

↓Gibbs eq.↓

$$dU = TdS - p dV$$

Enthalpy

$$H(S, p) = U + pV = U - \left(\frac{\partial U}{\partial V}\right) V \Rightarrow dH = TdS + Vdp$$

Helmholtz (free) energy (Helmholtz function, free (internal) energy)

$$F(T, V) = U - TS = U - \left(\frac{\partial U}{\partial S}\right) S \Rightarrow dF = -SdT - p dV$$

Often denoted by A

Gibbs (free) energy (Gibbs function, free enthalpy)

$$G(T, p) = H - TS = H - \left(\frac{\partial H}{\partial S}\right) S \Rightarrow dG = -SdT + Vdp$$

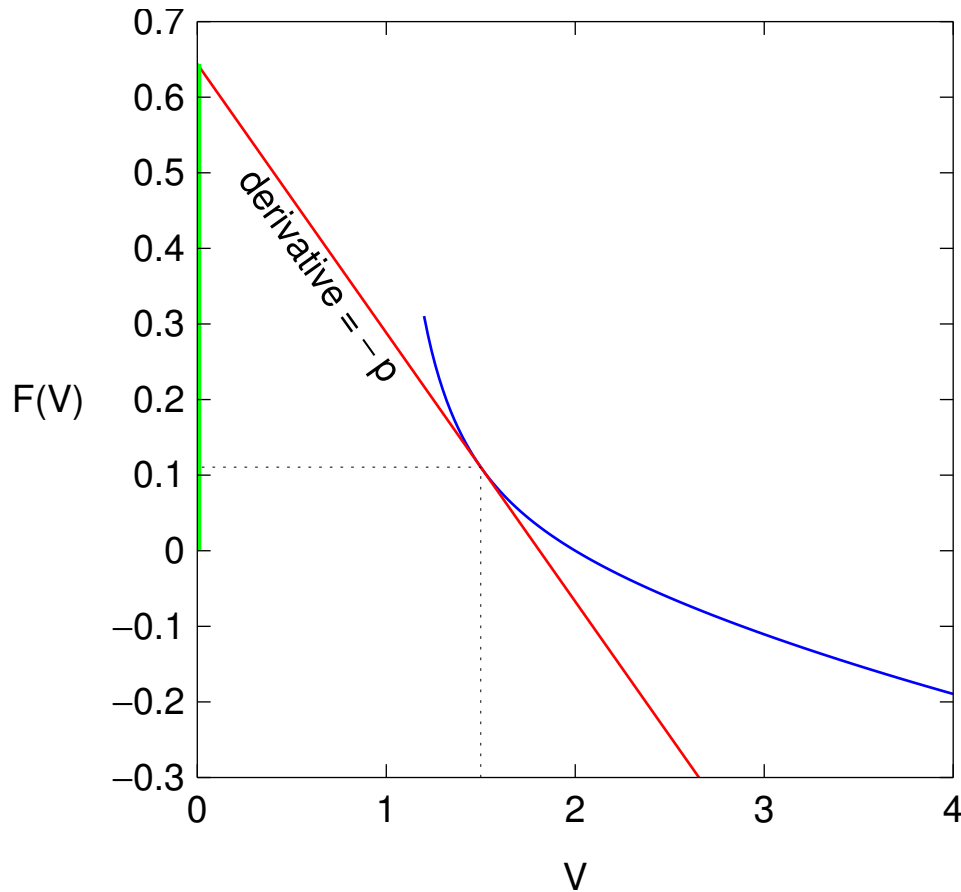
$$\text{Or: } G = F + pV = F - \left(\frac{\partial F}{\partial V}\right) V$$

avoid term “free energy” unless it is clear whether it is Gibbs or Helmholtz

only pressure-volume work

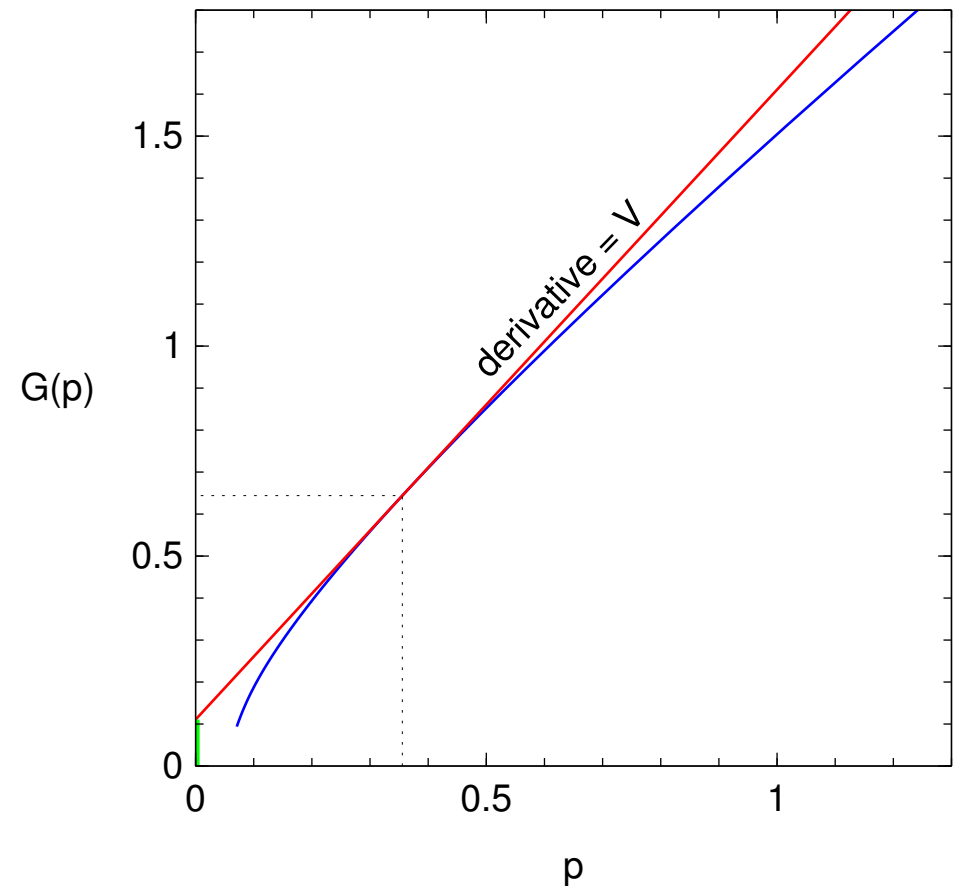
forward

$$G = F + pV = F - \left(\frac{\partial F}{\partial V} \right) V$$



backward

$$F = G - Vp = G - \left(\frac{\partial G}{\partial p} \right) p$$



The transf. is well-defined (gives one value) if $F(V)$ is convex. Then $G(p)$ is concave and there exists a back-transform.

The curves are calculated from the van der Waals equation

Example—one phase transition.

$$H(T_2, p) = H(T_1, p) + \int_{T_1}^{T_{\text{fp}}} C_p dT + \Delta_{\text{fp}}H + \int_{T_{\text{fp}}}^{T_2} C_p dT$$

$$S(T_2, p) = S(T_1, p) + \int_{T_1}^{T_{\text{fp}}} \frac{C_p}{T} dT + \frac{\Delta_{\text{fp}}H}{T_{\text{fp}}} + \int_{T_{\text{fp}}}^{T_2} \frac{C_p}{T} dT$$

low T : $S(T_1, p) = \int_0^{\approx 15\text{K}} \frac{\text{const } T^3}{T} dT + \dots$

$$H(T, p_2) = H(T, p_1) + \int_{p_1}^{p_2} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

$$S(T, p_1) = S(T, p_2) - \int_{p_1}^{p_2} \left(\frac{\partial v}{\partial T} \right)_p dp$$

$G = H - TS$

We can predict chemical equilibria from thermochemistry and EoS data!

$$dU = TdS + \delta W$$

$$dF = -SdT + \delta W \Rightarrow dF = \delta W \quad [T]$$

Change of the Helmholtz energy at const. T = work

$$\delta W = -p dV + \delta W_{\text{other than pressure-volume}}$$

$$\begin{aligned} dG &= -SdT + Vdp + \delta W_{\text{other than pressure-volume}} \\ &= \delta W_{\text{other than pressure-volume}} \quad [T, p] \end{aligned}$$

Change of the Gibbs energy at const. T, p
= work other than pressure-volume

Interpretation of terms $F = U - TS$ ($G = H - TS$)

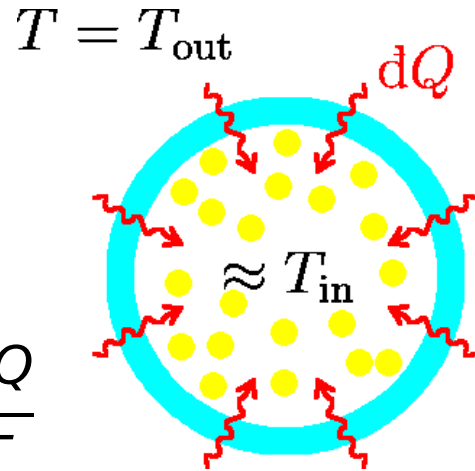
- **low temperature** \Rightarrow the influence of **energy** (enthalpy) $>$ of entropy
- **high temperature** \Rightarrow the influence of **entropy** $>$ energy (enthalpy)

heating:

$$dQ > 0$$

$$T > T_{in}$$

$$\Rightarrow dS \approx \frac{dQ}{T_{in}} > \frac{dQ}{T}$$

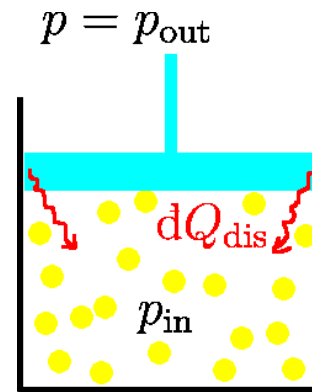


cooling:

$$dQ < 0, T < T_{in} \Rightarrow dS \approx \frac{dQ}{T_{in}} > \frac{dQ}{T}$$

$$dS > \frac{dQ}{T}$$

dissipation of energy by friction:



pressure-volume work only

$$dW = p_{in}(-dV) + dQ_{dis}$$

always $dQ_{dis} > 0$ (loss)

$$dS \approx \frac{dQ_{dis}}{T} > 0$$

$$dU = dQ + dW < TdS - p dV \text{ (irrev.)}$$

$$dU < 0 \text{ } ([S, V], \text{ irrev.})$$



$$dG < -SdT + Vdp \text{ (irrev.)}$$

$$dG < 0 \text{ } ([T, p], \text{ irrev.})$$



The Gibbs energy of a closed system at constant T, p spontaneously (via irreversible processes) decreases. In equilibrium it reaches a minimum.

id. gas/mixture: compounds do not interact



$$G = H - TS$$

→

$$\Delta_{\text{mix}} S_m = -R \sum_i x_i \ln x_i, \quad \Delta_{\text{mix}} H_m = 0$$



$$\mu_i^{\text{id}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} = \mu_i^\bullet + RT \ln x_i$$

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)?

$$> 3.1 \text{ MJ} = 0.85 \text{ kWh}$$

General definition:

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

\ominus = plimsoll

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

Standard state overview:

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

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

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

General reaction:

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

Balance in the amount of substance:

start
↙

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

ξ = **extent of reaction**; units $[\xi] = \text{mol}$

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

Degree of reaction:

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

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

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**

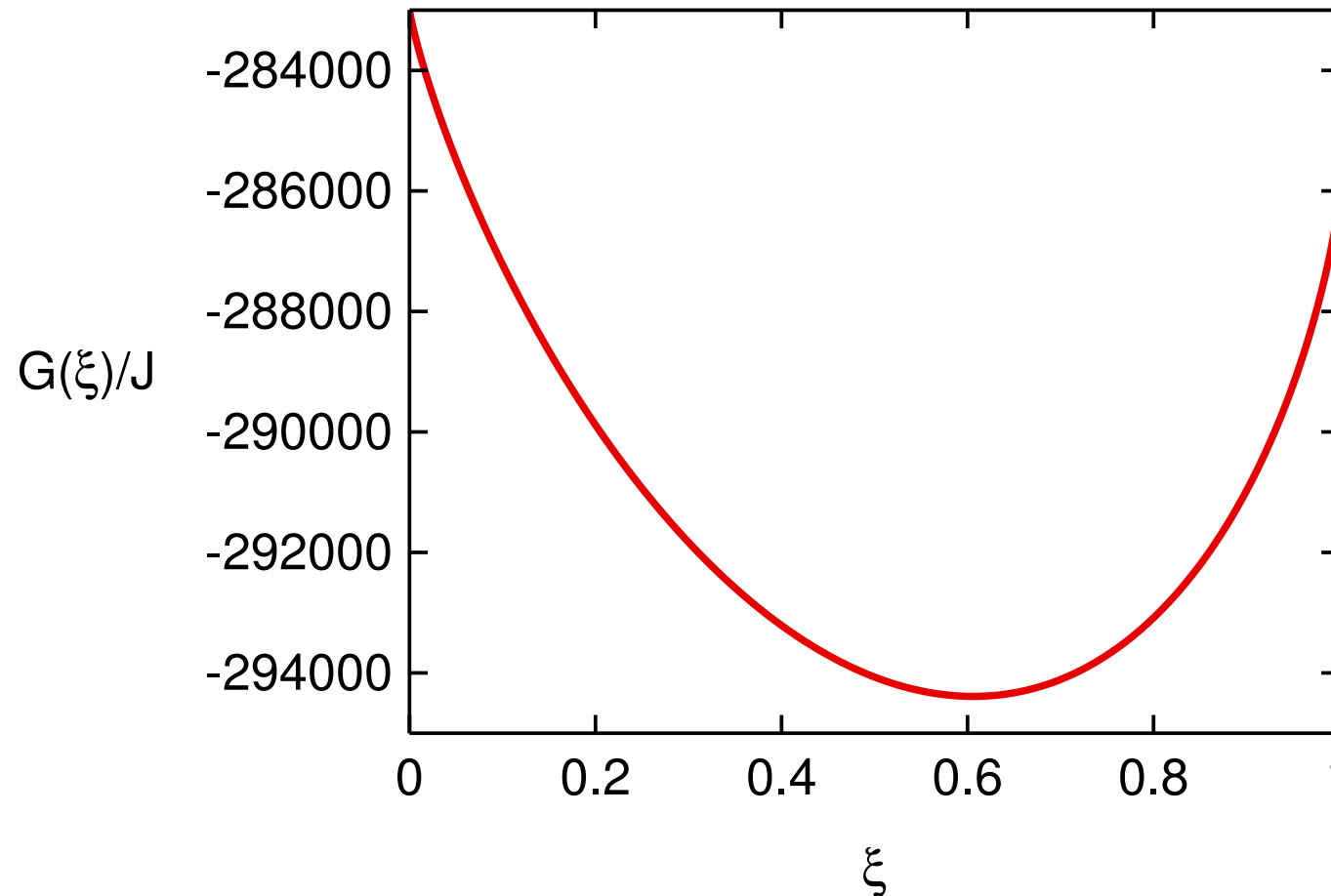
$\Delta_r G_m$	direction of reaction	name of reaction
< 0	\longrightarrow	exergonic
$= 0$	equilibrium	isoergonic
> 0	\longleftarrow	endergonic

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



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

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

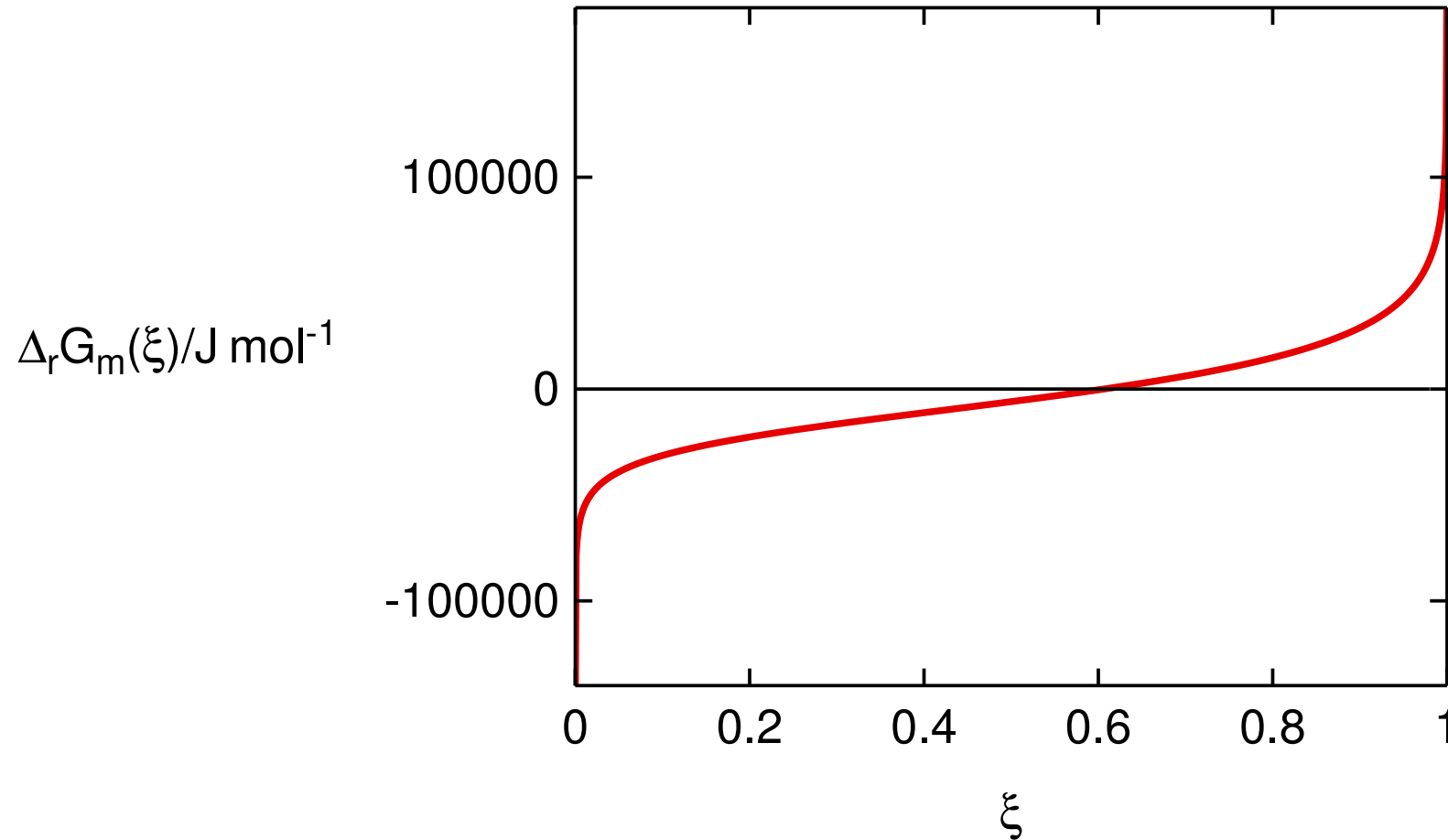


Example $\Delta_r G_m(\xi)$



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

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



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

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

Definition of the equilibrium constant*:

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

⇒ equilibrium condition:

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

● 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.

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

$\Delta_r G_m$	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?

$$\frac{\Delta_r G_m}{RT} = 0.213 \Rightarrow \text{reduced}$$

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

⇒ (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.