Spontaneous Change

For a system in thermal equilibrium with its surroundings,

$$dS \geqslant \frac{\delta q}{T}$$ Clausius inequality

At constant volume:

$$dq_V = dU$$ no work

$$TdS - dU \geqslant 0$$

$$\left(dS\right)_{U,V} \geqslant 0$$ isolated system

$$\left(dU\right)_{S,V} \leqslant 0$$

At constant pressure:

$$dq_P = dH$$ PV work only

$$TdS - dH \geqslant 0$$

$$\left(dH\right)_{S,P} \leqslant 0$$

For convenience, define:

$$A = U - TS \qquad dA = dU - TdS - SdT$$

$$G = H - TS \qquad dG = dH - TdS - SdT$$

Then the conditions for spontaneous change become:

$$\left(dA\right)_{T,V} \leqslant 0 \qquad \left(dG\right)_{T,P} \leqslant 0$$

Helmholtz Energy *A*

Helmholtz energy; Helmholtz free energy; Helmholtz function; Maximum work function *A* for Arbeit

For spontaneous change at constant *T* and *V*

$$dA = dU - TdS \leqslant 0$$

Note that it is the *total* function *A* that tends to a minimum; this is *not* the same as minimizing *U* and maximizing *S*.

Maximum Work

Combine $dU = \delta q + \delta w$ and $TdS \geqslant \delta q$

$$\Rightarrow \quad dU \leqslant TdS + \delta w$$

equality for reversible change

Word done *by* the system

$$(-\delta w) \leqslant TdS - dU$$

$$(-\delta w)_{\text{max}} = TdS - \delta q_{\text{rev}} - \delta w_{\text{rev}} = -\delta w_{\text{rev}}$$

A system does maximum work when it is operating reversibly.

But $(dA)_T = dU - TdS = dU - \delta q_{\text{rev}} = \delta w_{\text{rev}}$

Therefore, for macroscopic changes

$$-w_{\text{max}} = -\Delta A = T\Delta S - \Delta U$$

constant *T*

(-*w*) can be more or less than Δ*U* according to the sign of Δ*S*.

For Δ*S* > 0, heat flows into the system to fuel the extra work.

Gibbs Energy *G*

Gibbs free energy, Gibbs function

- Very important in chemistry since it tells whether a particular reaction can proceed at a given *T* and *P*.

For spontaneous change,

$$(dG)_{T,P} \leqslant 0 \qquad\qquad \Delta G = G_{\text{products}} - G_{\text{reactants}} \leqslant 0$$

$\Delta G_{T,P}$ for reactions can be calculated from tabulated data

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$$

If ΔH is	and ΔS is	then ΔG	the reaction proceeds
-ve	+ve	< 0	at all temperatures
+ve	-ve	> 0	at no temperatures
-ve	-ve	…	if $T < \Delta H / \Delta S$
+ve	+e	…	if $T > \Delta H / \Delta S$

Maximum Work:

$$\begin{aligned}
(dG)_T &= dH - TdS \\
(dG)_{T,P} &= dU + PdV - TdS \\
&= \delta q_{\text{rev}} + \delta w_{\text{rev}} + PdV - TdS \\
&= \delta w_{\text{rev}} + PdV \\
&= \delta w_{\max}(\text{non-}PV)
\end{aligned}$$

$$\Delta w_{\max}(\text{non-}PV) = \Delta G$$

constant *T*, *P*

Basic Thermodynamic Relations 1

Laws

$$dU = \delta q - PdV \qquad \ldots(1)$$

$$dS = \delta q_{\text{rev}} / T \qquad \ldots(2)$$

Definitions

$$H = U + PV \qquad \ldots(3)$$

$$A = U - TS \qquad \ldots(4)$$

$$G = H - TS \qquad \ldots(5)$$

Fundamental Equations

$$dU = TdS - PdV \qquad \ldots(6)$$

$$dH = TdS + VdP \qquad \ldots(7)$$

$$dA = -SdT - PdV \qquad \ldots(8)$$

$$dG = -SdT + VdP \qquad \ldots(9)$$

Partial Differentials

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

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

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

Basic Thermodynamic Relations 2

Maxwell Relations

From (6) $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots(10)$$

From (7) $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \ldots(11)$$

From (8) $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(12)$$

From (9) $$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(13)$$

Thermodynamic Equation of State

$$dU = TdS - PdV \qquad \ldots(6)$$

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

Substituting (12) $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$$

How Free Energy Depends on *T*

$$G = H - TS \qquad \ldots(1)$$ definition

$$\Delta G = \Delta H - T\Delta S \qquad \ldots(2)$$ constant T

$$dG = VdP - SdT \qquad \ldots(3)$$ fundamental eqn.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G-H}{T}$$ from (1)

$$\therefore \quad \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T} \qquad \ldots(4)$$

But $$\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} \qquad \ldots(5)$$

Gibbs-Helmholtz Equation

$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

substitute (4) in (5)

alternative form:

$$\left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H$$

By applying the Gibbs-Helmholtz equation to both reactants and products of a chemical reaction,

$$\Rightarrow \quad \left(\frac{\partial (\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

How Free Energy Depends on *P*

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

For solids and liquids *V* does not change much with *P*, so

$$G_2(T) \approx G_1(T) + V(P_2 - P_1)$$

For a perfect gas $V = \frac{nRT}{P}$

$$\Delta G_T = nRT \ln(P_2 / P_1)$$

$$G = G^\circ(T) + nRT \ln(P / P^\circ)$$

where *G*° is the standard free energy defined at *P*°=1 bar

The chemical potential for a pure substance is the molar Gibbs energy:

$$\mu = \bar{G} = \frac{G}{n}$$

∴ For a perfect gas

$$\mu = \mu^\circ + RT \ln(P / P^\circ)$$

The Chemical Potential

So far, our thermodynamic relations apply to closed systems. However, *G*, *U*, *H*, etc. are extensive properties.

Partial molar quantities are used to describe quantities which depend on composition.

$$\bar{J}_i = \left(\frac{\partial J}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad J = U, H, S, A, G, V$$

$$J = \sum_i n_i \bar{J}_i$$

In general
$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\ldots} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\ldots} dT$$

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} dn_2 + \ldots$$

Chemical Potential
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

Fundamental Equations
$$dU = TdS - PdV + \sum \mu_i dn_i$$

$$dH = TdS + VdP + \sum \mu_i dn_i$$

etc.

$$\Rightarrow \quad \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,S} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T}$$

Free Energy of Mixing 1

Consider the mixing of two *ideal* gases A and B at constant *T* and *P*.

Before: $$G_1 = n_A\mu_A(\text{pure}) + n_B\mu_B(\text{pure})$$

where $$\mu_A(\text{pure}) = \mu_A^\circ + RT\ln(P/P_0)$$

After mixing: $$\begin{aligned} G_A &= n_A\left\{\mu_A^\circ + RT\ln(p_A/P_0)\right\} \\ &= n_A\left\{\mu_A^\circ + RT\ln(P/P_0) + RT\ln\chi_A\right\} \\ &= n_A\mu_A(\text{pure}) + n_A RT\ln\chi_A \end{aligned}$$

negative

$$G_2 = G_A + G_B < G_1$$

Change: $$\begin{aligned} \Delta G_{\text{mix}} &= G_2 - G_1 \\ &= n_A RT\ln\chi_A + n_B RT\ln\chi_B \\ &= nRT\left(\chi_A\ln\chi_A + \chi_B\ln\chi_B\right) \end{aligned}$$

$$\Delta G_{\text{mix}} = nRT\left(\chi_A\ln\chi_A + \chi_B\ln\chi_B\right)$$

$\Delta G_{\text{mix}} < 0$ Mixing is spontaneous.

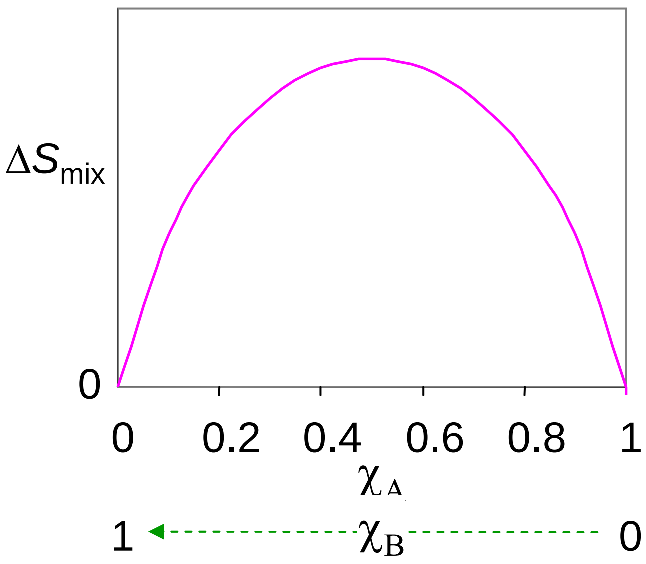
Entropy of Mixing $$\Delta S_{\text{mix}} = -\left(\partial\Delta G_{\text{mix}}/\partial T\right)_{P,n_i} = -nR\sum\chi_i\ln\chi_i$$

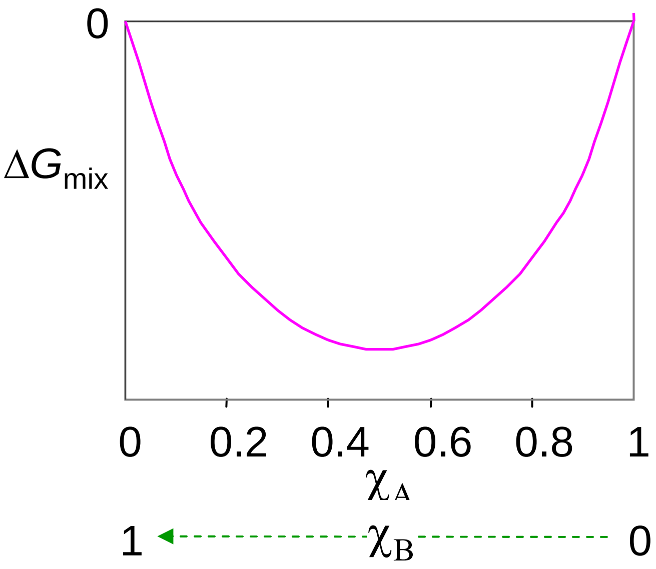
Enthalpy of Mixing $$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}} = 0$$

Similarly, $\Delta U_{\text{mix}} = \Delta V_{\text{mix}} = 0$ for ideal gases and solutions

Free Energy of Mixing 2

For a binary system, ΔG_{mix} is at its minimum and ΔS_{mix} at its maximum when $\chi_{\text{A}} = \chi_{\text{B}} = 0.5$



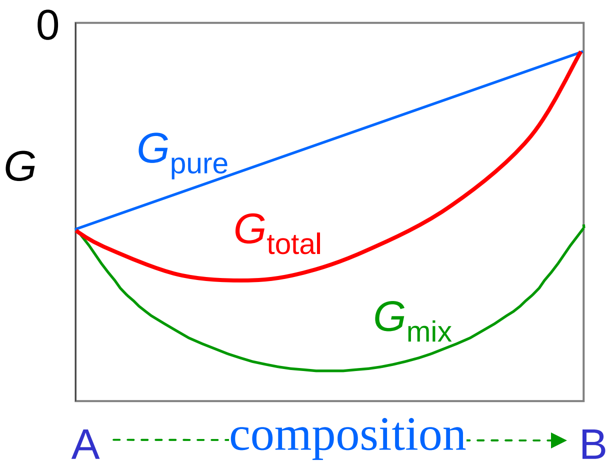


Equilibrium and Mixing:

Consider an equilibrium between two ideal gases $\text{A} \rightleftharpoons \text{B}$

$$G = G_{\text{A}}(\text{pure}) + G_{\text{B}}(\text{pure}) + \Delta G_{\text{mix}}$$

$$= n\left(\chi_{\text{A}}\mu_{\text{A}} + \chi_{\text{B}}\mu_{\text{B}}\right) + nRT\left(\chi_{\text{A}}\ln\chi_{\text{A}} + \chi_{\text{B}}\ln\chi_{\text{B}}\right)$$



The equilibrium composition is determined by the minimum in G_{total}.

Reaction Equilibrium 1

Consider $\mathrm{A} \rightleftharpoons \mathrm{B}$

Suppose an amount *dx* of A turns into B.

Then $(dG)_{T,P} = \mu_{\mathrm{A}} dn_{\mathrm{A}} + \mu_{\mathrm{B}} dn_{\mathrm{B}} = -\mu_{\mathrm{A}} dx + \mu_{\mathrm{B}} dx$

$$\Rightarrow \quad \left(\frac{\partial G}{\partial x}\right)_{T,P} = \mu_{\mathrm{B}} - \mu_{\mathrm{A}}$$

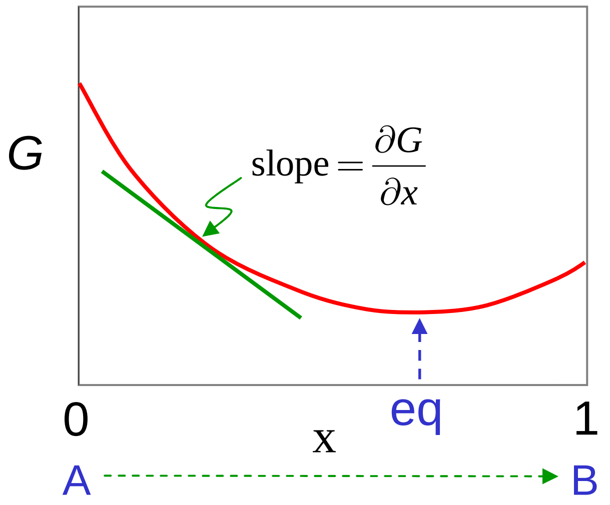
μ_A and μ_B depend on composition, and therefore change during the reaction.

If $\mu_A > \mu_B$ the reaction proceeds from A → B.

If $\mu_A < \mu_B$ the reaction proceeds from B → A.

At equilibrium

$$\mu_{\mathrm{A}} = \mu_{\mathrm{B}}$$



$$\mu_{\mathrm{A}}^{\circ} + RT\ln\left(p_{\mathrm{A}}^{\mathrm{eq}} / P^{\circ}\right) = \mu_{\mathrm{B}}^{\circ} + RT\ln\left(p_{\mathrm{B}}^{\mathrm{eq}} / P^{\circ}\right)$$

$$RT\ln\left(p_{\mathrm{A}}^{\mathrm{eq}} / p_{\mathrm{B}}^{\mathrm{eq}}\right) = \mu_{\mathrm{B}}^{\circ} - \mu_{\mathrm{A}}^{\circ} = \Delta\overline{G}_{\mathrm{rxn}}^{\circ}$$

$$\frac{p_{\mathrm{B}}^{\mathrm{eq}}}{p_{\mathrm{A}}^{\mathrm{eq}}} = \exp\left(-\Delta\overline{G}_{\mathrm{rxn}}^{\circ} / RT\right)$$

Reaction Equilibrium 2

A reaction such as 2A + 3B → C + 2D can be written as

$$0 = -2A - 3B + C + 2D$$

or completely generally as $0 = \sum_i \nu_i \mathrm{R}_i = 0$

Then $$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \nu_i \mu_i$$

and at equilibrium, $\sum_i \nu_i \mu_i = 0$

$$\sum_i \left(\nu_i \mu_i^\circ + \nu_i RT \ln \frac{p_\mathrm{i}^\mathrm{eq}}{P^\circ} \right) = 0$$

$$\Delta \bar{G}^\circ_\mathrm{rxn} + RT \ln \left[\prod_i \left(\frac{p_i}{P^\circ} \right)_\mathrm{eq}^{\nu_i} \right] = 0$$

$$\Delta \bar{G}^\circ_\mathrm{rxn} = -RT \ln K$$

$$K = \prod_i \left(\frac{p_i}{P^\circ} \right)_\mathrm{eq}^{\nu_i}$$