# L29: review

## chemical equilibrium

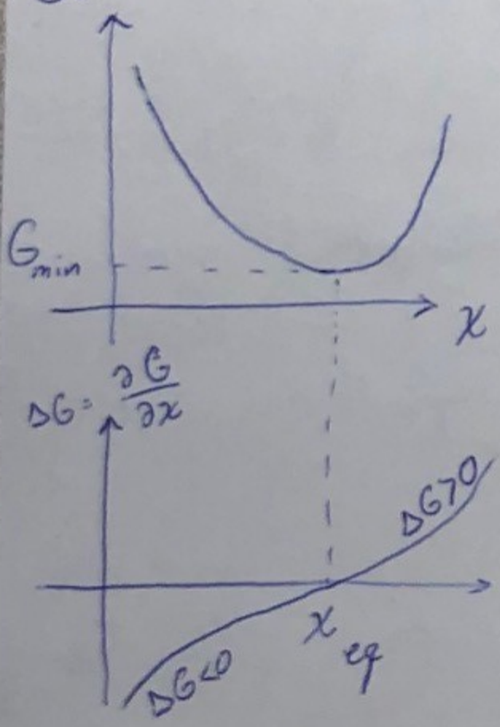
reaction: $\nu_1 X_1 + \nu_2 X_2 + \cdots \rightarrow \nu_3 X_3 + \nu_4 X_4 + \cdots$

e.g. $3H_2 + N_2 \rightarrow 2NH_3$; $\nu_1 = -3$, $\nu_2 = -1$

$\nu_3 = +2$

$n_i = n_i^0 + \nu_i \xi$ ($\xi$: progress coordinate (moles))

$n_i^0$: initial amount (moles)




$G(x) = \sum_i \mu_i n_i = \sum_i \mu_i (n_i^0 + \nu_i x) \Rightarrow$

$\Delta G = \frac{\partial G}{\partial x} = \sum_i \nu_i \mu_i^0 + T \sum_i \nu_i R \ln c_i$

because $S_i = S_i^0 - R \ln c_i \Rightarrow \mu_i = h_i - T s_i \approx h_i^0 - T s_i^0 + RT \ln c_i$ ($\mu_i^0$)

$\Delta G = \sum_i \nu_i \mu_i^0 + T \sum_i \nu_i R \ln c_i \Rightarrow$

($\sum_i \nu_i \mu_i^0 \rightarrow \Delta G^0$; $T \sum_i \nu_i R \ln c_i \rightarrow RT \ln Q$)

$\Delta G = \Delta G^0 + RT \ln Q$; $Q = \prod_i c_i^{\nu_i}$

$Q$: mass action coefficient.

At equilibrium:

$\Delta G = 0 = \Delta G^0 + RT \ln Q_{eq} \Rightarrow$

$$Q_{eq} \equiv K_{eq} = e^{-\Delta G^0/RT} = \frac{[X_3]^{\nu_3} \cdot [X_4]^{\nu_4} \cdots}{[X_1]^{\nu_1} \cdot [X_2]^{\nu_2} \cdots}$$

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Today: Could we calculate $K_{eq}$ ($\Delta G^0$) from the postulates?

1) Use CM or QM to calc $\varepsilon_j$ and $w_j$

2) Calc. $z_i$ for molecule $i$: $z_i = \sum_j w_j e^{-\varepsilon_j/RT}$ (single particle partition function)

3) Calc. $Z_i = \frac{z_i^{N_i}}{N_i!}$; $Z = \prod_i Z_i$ (bulk partition function)

4) $\mu_i^0 = -k_B T \frac{\partial \ln z}{\partial N_i} = -RT \frac{\partial \ln z}{\partial n_i}$ (next page)

why $\mu_i^\circ = -RT \frac{\partial \ln Z}{\partial n_i}$ ?

↳ Ans: $Z = e^{-\frac{E}{k_B T}} \Rightarrow F = -k_B T \ln Z$

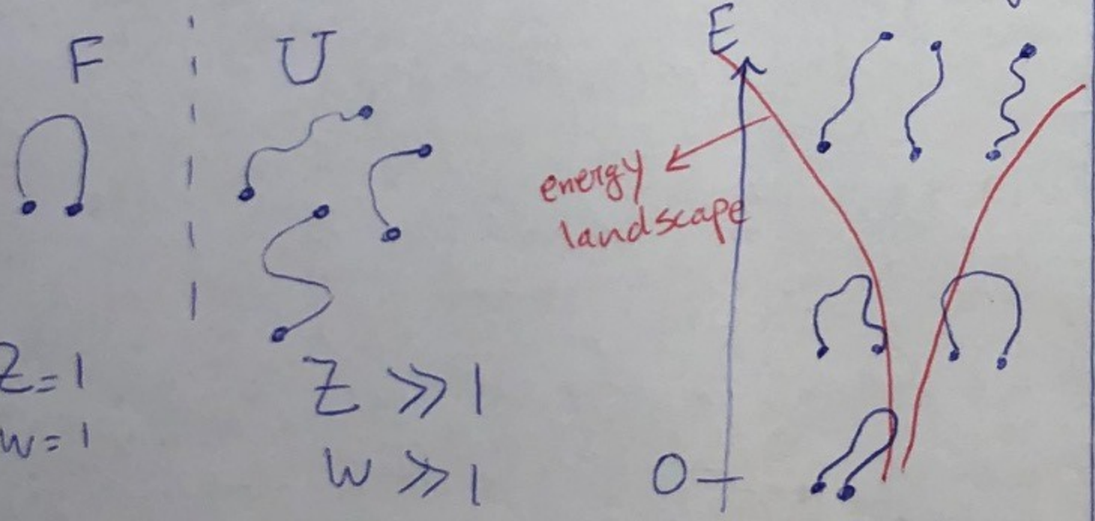
$F(T, V, n_i)$

$F = E - TS = -PV + \sum_i \mu_i n_i \Rightarrow \mu_i = \frac{\partial F}{\partial n_i}$

5) calc. $\Delta G^\circ = \sum_i \mu_i^\circ \cdot \nu_i$

6) $K_{eq} = e^{-\Delta G^\circ / RT}$ $\quad \Delta G^\circ : \frac{kJ}{mol}$

example: protein hairpin folding/unfolding




in the energy landscape of protein folding the depth denotes the energy of states and the width denotes the abundance of states in that given energy.

* Some of these states are "misfolded" as they cannot go to the folded state at the bottom of the energy funnel without breaking a favorable interaction, that is, without going uphill in the landscape.

↳ look up the demo on YouTube: "The journey" @ Protein Sonification