

Free Energy and Equilibrium

kinetic definition of equilibrium position:

**the point at which rates of forward
and reverse reactions are equal**

thermodynamic definition :

the point of minimum free energy;

$$\Delta G = 0$$

The relationship between ΔG and ΔG°

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

reactants in their standard state completely changing into products in their standard state

as soon as the reaction starts the standard state condition no longer exists

$$\Delta G = \Delta H - T\Delta S$$

the absolute change in free energy change

The relationship between ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$\Delta G = 0$ at equilibrium

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The relationship between ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$\Delta G = 0$ at equilibrium

a large negative
value ΔG°

a large relative value for products
needed to make $(RT \ln Q)$
equivalent to ΔG°

$$0 = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The relationship between ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

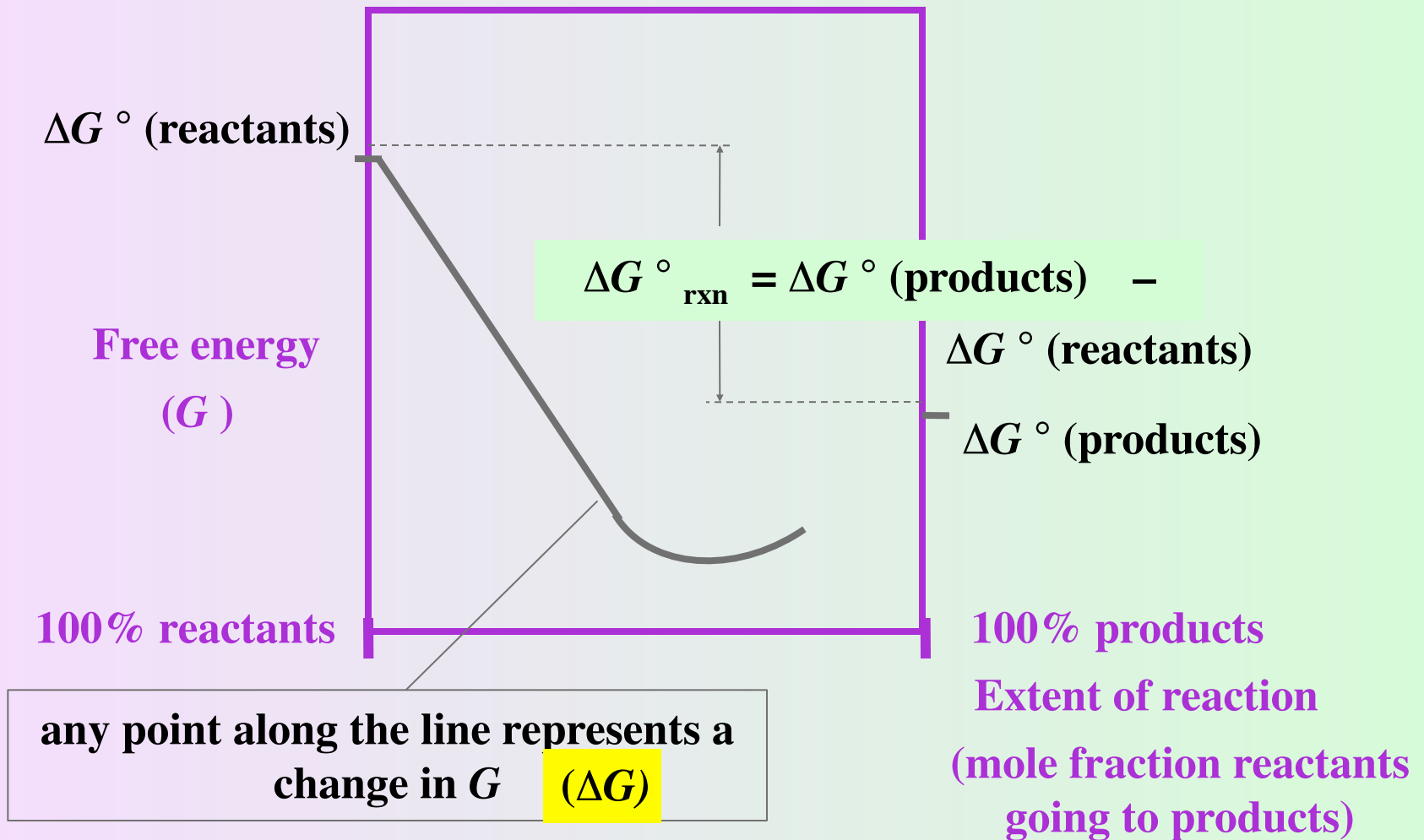
$\Delta G = 0$ at equilibrium

a large positive
value ΔG°

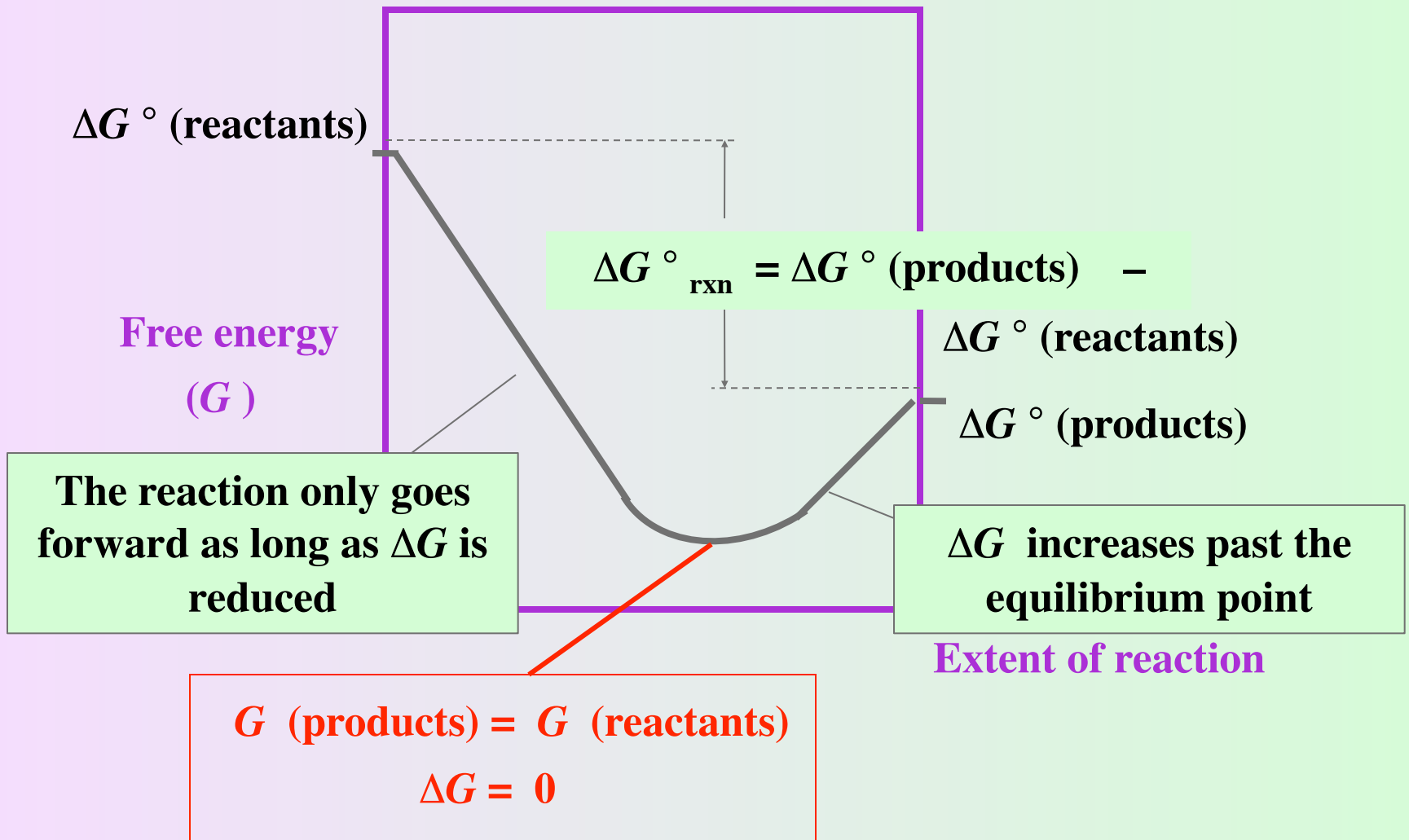
a small relative value for products
needed to make $(RT \ln Q)$
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$$0 = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

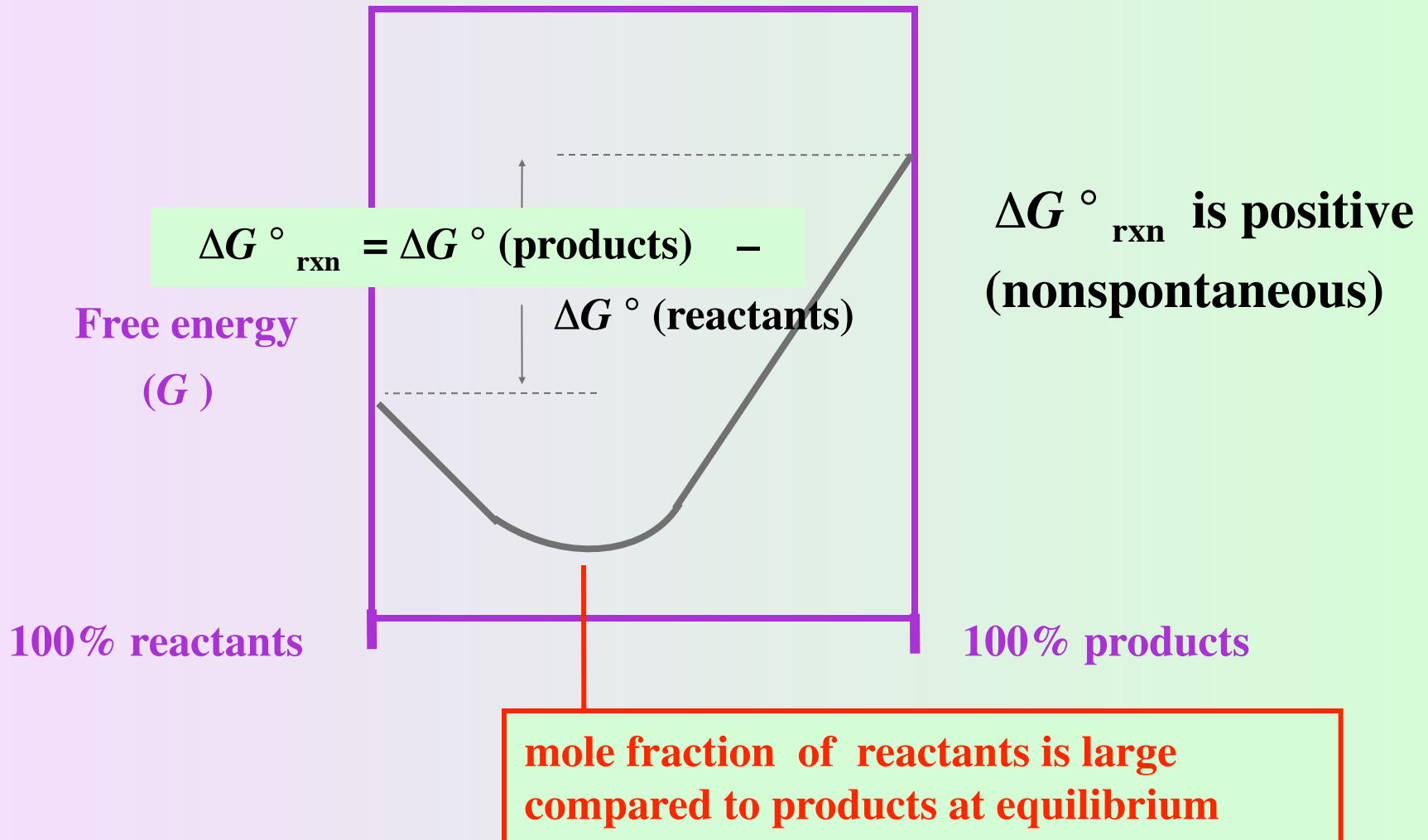
The relationship between ΔG and ΔG°



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The relationship between ΔG and ΔG°



The relationship between ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

at equilibrium: $\Delta G = 0$ and $Q = K$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

Example

$\Delta G^\circ = -33.2 \text{ kJ}$ for the reaction:



Is the reaction going forward in the direction written under these conditions?

$P(\text{NH}_3) = 12.9 \text{ atm}$, $P(\text{N}_2) = 0.87 \text{ atm}$, and $P(\text{H}_2) = 0.25 \text{ atm}$?

Example



$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = -33.2 \text{ kJ} + (8.314 \text{ J/mol K}) (298\text{K}) \ln \frac{P^2(\text{NH}_3)}{P(\text{N}_2) P^3(\text{H}_2)}$$

Example



$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = -33.2 \text{ kJ} + (8.314 \text{ J/mol K}) (298\text{K}) \ln \frac{(12.9)^2}{(0.87) (0.25)^3}$$

$$\Delta G = -33200 \text{ J} + 23000 \text{ J} = -9900 \text{ J}$$

Reaction is not at equilibrium; the direction is to the right

Applications

calculate the equilibrium constants from tables of standard free energies of formation

$$\Delta G^\circ = -RT \ln K$$

K

K_a

K_{sp}

Example

Calculate the equilibrium constant (K_p) for the reaction shown at 25°C .



$$\Delta G^\circ_f = 2\text{mol} (163.4 \text{ kJ/mol})$$

$$3\text{mol} (0 \text{ kJ/mol})$$

$$\Delta G^\circ = -326.8 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K$$

Example

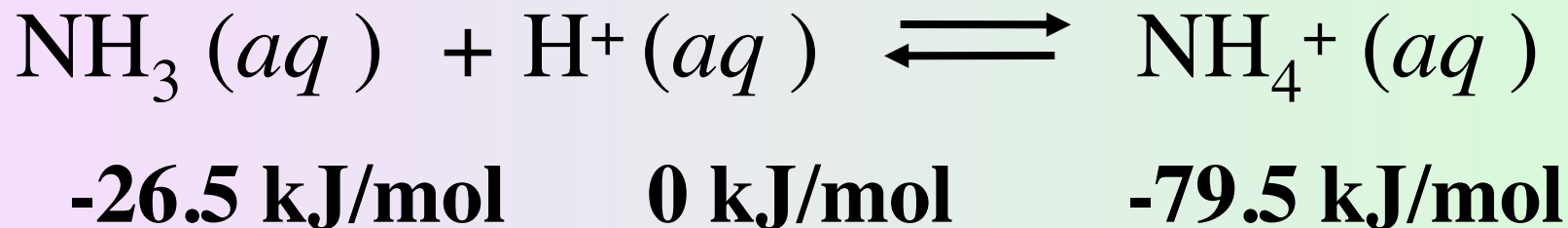
$$\Delta G^\circ = -RT \ln K$$

$$-326800 \text{ J/mol} = -(8.314 \text{ J/mol K})(298\text{K})\ln K$$

$$\ln K = 131.9$$

$$K = e^{132} = 1.93 \times 10^{57}$$

What is the K for the reaction of ammonia with hydrochloric acid in aqueous solution?



$$\Delta G^\circ = -53 \text{ kJ}$$

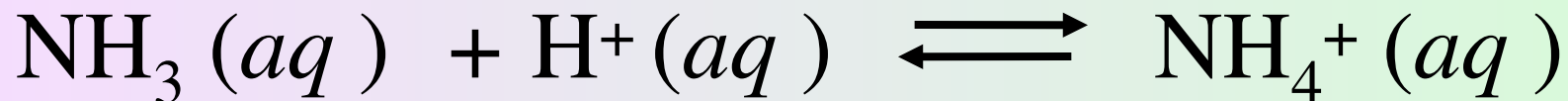
$$\Delta G^\circ = -RT \ln K$$

$$53000 \text{ J/mol} = (2478 \text{ J/mol}) \ln K$$

$$\ln K = 21.4$$

$$K = e^{21.4} = \mathbf{1.9 \times 10^9}$$

What is the K for the reaction of ammonia with hydrochloric acid in aqueous solution?



$$K = e^{21.4} = 1.9 \times 10^9$$

Note: the reverse reaction defines K_a for NH_4^+

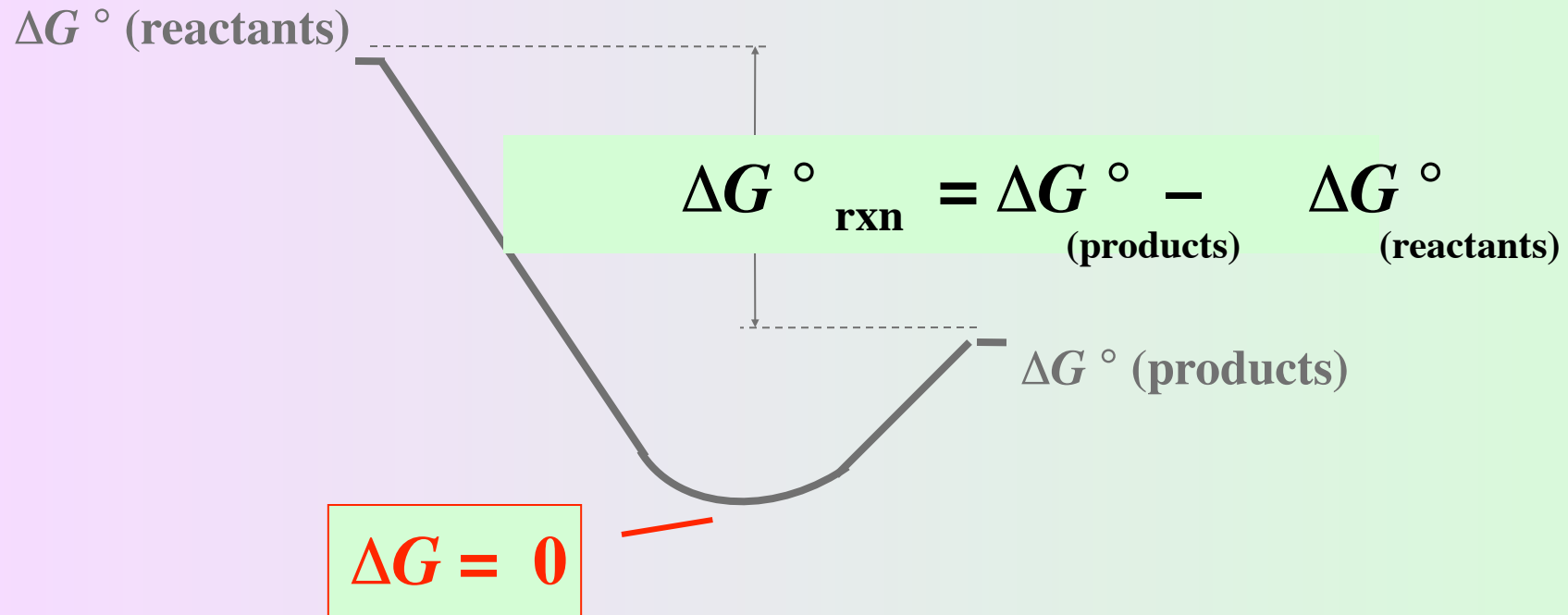
$$K_a = \frac{1}{1.9 \times 10^9} = 5 \times 10^{-10}$$

Free Energy and Equilibrium Summary

The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} < 0$$

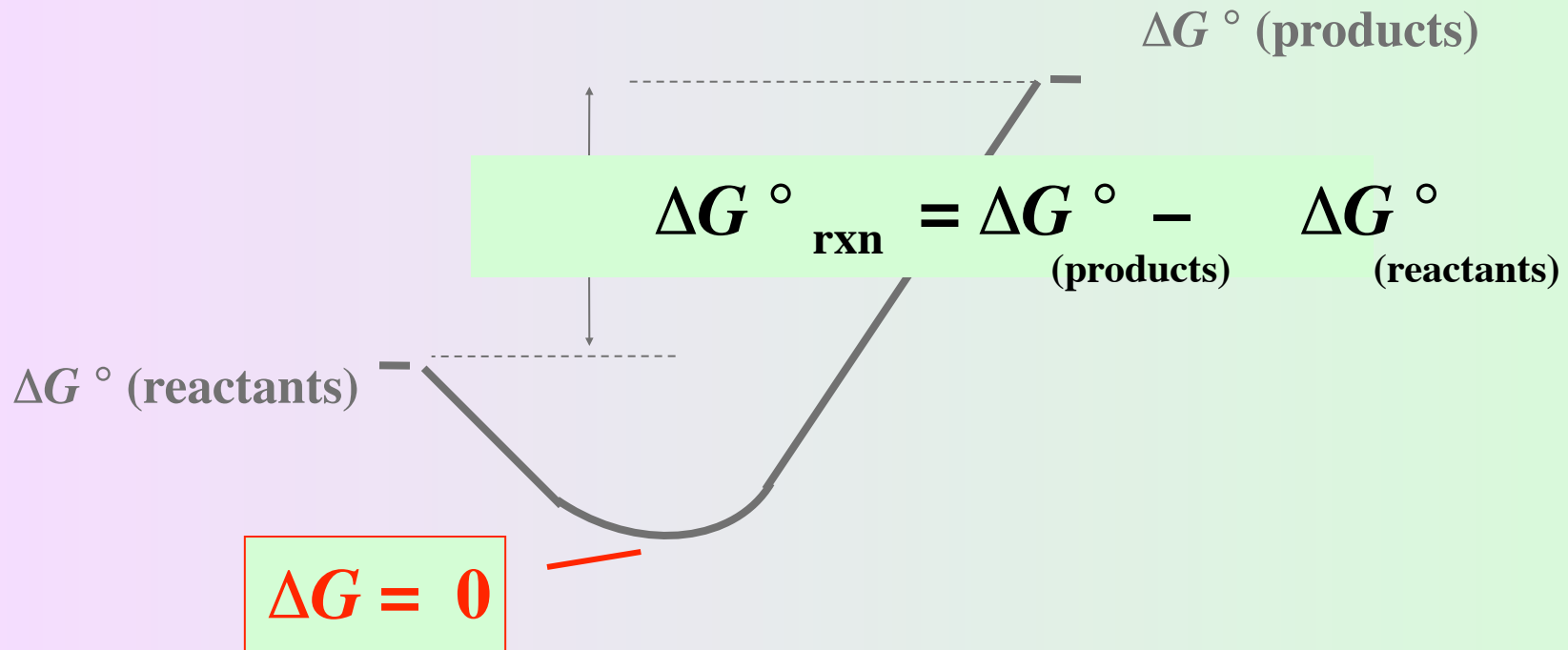
spontaneous



The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} > 0$$

nonspontaneous



The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} = 0$$

at equilibrium

$$\Delta G^\circ (\text{reactants}) - \text{-----} - \Delta G^\circ (\text{products})$$

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{(products)}} - \Delta G^\circ_{\text{(reactants)}}$$

The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} < 0 \quad \textit{spontaneous}$$

$$\Delta G^\circ_{\text{rxn}} > 0 \quad \textit{nonspontaneous}$$

$$\Delta G^\circ_{\text{rxn}} = 0$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

at equilibrium

$$Q = K$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} < 0 \quad \textit{spontaneous}$$

$$\Delta G^\circ_{\text{rxn}} > 0 \quad \textit{nonspontaneous}$$

$$\Delta G^\circ_{\text{rxn}} = 0$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

when

$$K = 1$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} < 0 \quad \textit{spontaneous}$$

$$\Delta G^\circ_{\text{rxn}} > 0 \quad \textit{nonspontaneous}$$

$$\Delta G^\circ_{\text{rxn}} = 0$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

when

$$K = 1$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[1 M]}{[1 M]}$$

$$\Delta G = 0$$

The relationship between ΔG and ΔG°

$$\Delta G^\circ_{\text{rxn}} < 0 \quad \textit{spontaneous}$$

$$\Delta G^\circ_{\text{rxn}} > 0 \quad \textit{nonspontaneous}$$

$$\Delta G^\circ_{\text{rxn}} = 0$$

if

$$\Delta G = 0$$

when

$$\Delta G^\circ = -RT \ln K$$

$$K = 1$$

$$\Delta G^\circ = 0$$

The relationship between ΔG and ΔG° and equilibrium

$$\Delta G^\circ_{\text{rxn}} < 0 \quad \textit{spontaneous} \quad K > 1$$

$$\Delta G^\circ_{\text{rxn}} > 0 \quad \textit{nonspontaneous} \quad K < 1$$

$$\Delta G^\circ_{\text{rxn}} = 0 \quad K = 1$$