$\Delta_r G$ at and far from equilibrium

@ equilibrium: Q → K ⇒ $K = \left(\dfrac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b} \right)_{equilibrium}$

equilibrium constant

$$\Rightarrow \; \Delta_r G = 0 = \Delta_r G^{\ominus} + RT \ln K$$

$$\Rightarrow \; \Delta_r G^{\ominus} = -RT \ln K$$

Table 7.1 *Thermodynamic criteria of spontaneity*

$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$

1 If the reaction is exothermic ($\Delta_r H^{\ominus} < 0$) and $\Delta_r S^{\ominus} > 0$

$\Delta_r G^{\ominus} < 0$ and $K > 1$ at all temperatures

2 If the reaction is exothermic ($\Delta_r H^{\ominus} < 0$) and $\Delta_r S^{\ominus} < 0$

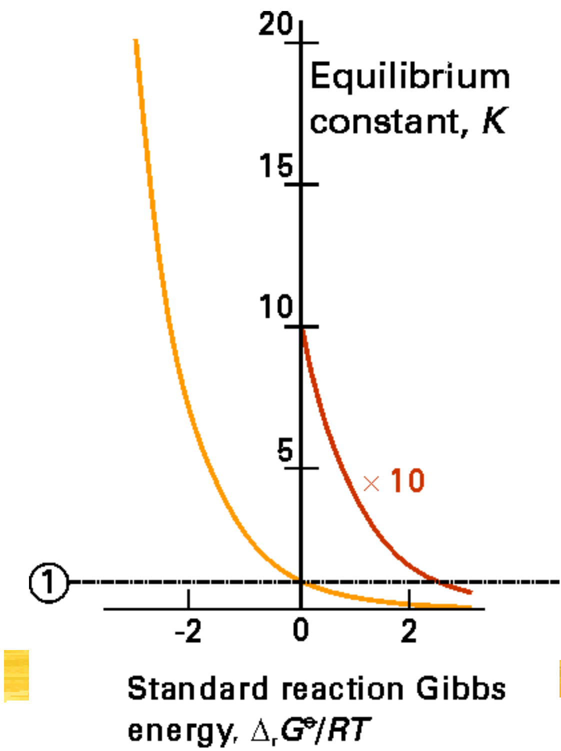
$\Delta_r G^{\ominus} < 0$ and $K > 1$ provided that $T < \Delta_r H^{\ominus}/\Delta_r S^{\ominus}$

3 If the reaction is endothermic ($\Delta_r H^{\ominus} > 0$) and $\Delta_r S^{\ominus} > 0$

$\Delta_r G^{\ominus} < 0$ and $K > 1$ provided that $T > \Delta_r H^{\ominus}/\Delta_r S^{\ominus}$

4 If the reaction is endothermic ($\Delta_r H^{\ominus} > 0$) and $\Delta_r S^{\ominus} < 0$

$\Delta_r G^{\ominus} < 0$ and $K > 1$ at no temperature



$\Delta_r G$ can be calculated

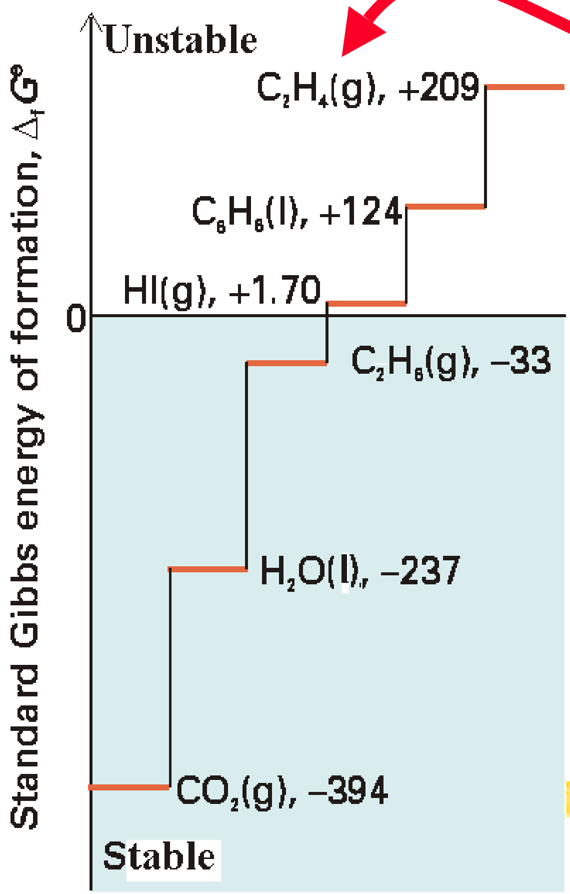
1 M; 1 bar; 25 °C

$$\Delta_r G^{\ominus} = \Sigma \nu\, G_m^{\ominus}(\text{products}) - \Sigma \nu\, G_m^{\ominus}(\text{reactants})$$

$$= \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

tabulated

$$= \Sigma \nu\, \Delta_f G^{\ominus}(\text{products}) - \Sigma \nu\, \Delta_f G^{\ominus}(\text{reactants})$$



} endergonic

Elements: $\Delta_f G^{\ominus} = 0$ kJ mol^{-1}

} exergonic

Coupled reactions can overcome an unfavorable $\Delta_r G$

@ equilibrium: $\boxed{\Delta_r G^{\ominus} = -RT \ln K}$ $\quad K = \dfrac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b}$

exergonic:

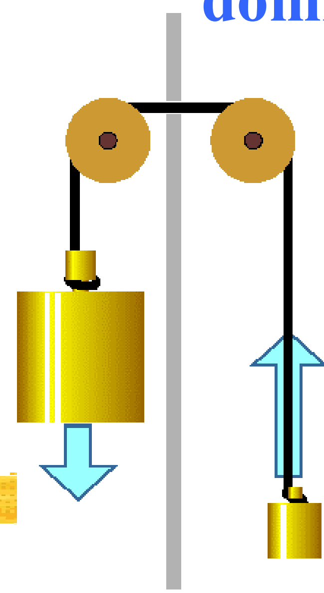
$\Delta_r G^{\ominus} < 0 \Rightarrow K > 1 \Rightarrow a_C{}^c \times a_D{}^d > a_A{}^a \times a_B{}^b$ **⇒ products will dominate in equilibrium**

endergonic:

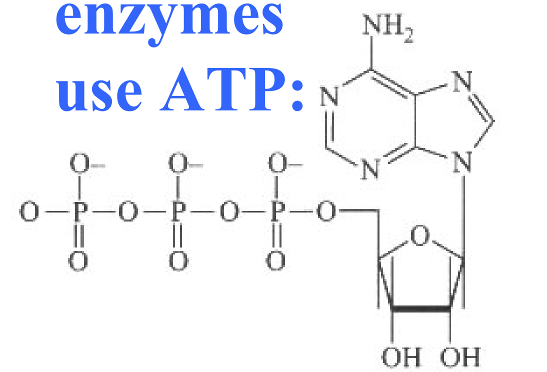
$\Delta_r G^{\ominus} > 0 \Rightarrow K < 1 \Rightarrow a_C{}^c \times a_D{}^d < a_A{}^a \times a_B{}^b$ **⇒ reactants will dominate in equilibrium**

BUT: If an endergonic reaction ($\Delta_r G^{\ominus} > 0$) is coupled with a strongly exergonic one ($\Delta_r G^{\ominus}{}' < 0$):

$\Delta_r G^{\ominus} + \Delta_r G^{\ominus}{}' < 0$



enzymes use ATP:



Sample problem 1:

Estimate the composition of a solution in which G6P and F6P are in equilibrium at 25°C, and draw a graph to show how the spontaneity of the reaction varies with composition;

$$\Delta_r G^{\ominus} = +1.7 \text{ kJ mol}^{-1}$$

Sample problem 2:

In an industrial process N_2 at 1 bar is mixed with H_2 at 3 bar and the two gases are allowed to reach equilibrium with the product ammonia in a reactor of constant volume. At the temperature of the reaction, K = 977. What are the equilibrium partial pressures of the three gases?