Lecture 10

Free Energy and Equilibrium

$$\Delta G = \Delta G^o + RT \ln Q$$

Lecture Question – p. 32

Given:

1. $Ba(NO_3)_2(s) \rightarrow Ba^{2+}(aq) + 2\ NO_3^-(aq)$

$\Delta G^o = 18\ kJ$

2. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ $\Delta G^o = -34\ kJ$

Predict whether each reaction is endothermic or exothermic.

a. Rxn 1 is endothermic; rxn 2 is endothermic.

b. Rxn 1 is endothermic; rxn 2 is exothermic.

c. Rxn 1 is exothermic; rxn 2 is endothermic.

d. Rxn 1 is exothermic; rxn 2 is exothermic.

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Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependance of Spontaneity on Temperature

Table 17.5 ▶ **Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature**

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at any temperature (reverse process is spontaneous at all temperatures)

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

Calculating ΔG at Nonstandard Concentrations – p. 32

For the reaction $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$, $\Delta G^o = -34$ kJ. Is this reaction spontaneous when 0.10 atm of N_2, 0.10 atm of H_2, and 2.0 atm of NH_3 are reacted together?

$\Delta G = \Delta G^o + RT \ln Q$

Calculating ΔG at Nonstandard Concentrations

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$$\Delta G = \Delta G^o + RT \ln \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3}, \quad R = 8.3145\ J/K\ mol$$

Calculating ΔG at Nonstandard Concentrations – p. 33

$$\Delta G = \Delta G^{o} + RT \ln \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3}, \quad R = 8.3145 \text{ J/K mol}$$

$$\Delta G = -34,000 \text{ J} + 8.3145 \text{ J/K}(298 \text{ K}) \ln \frac{(2.0)^2}{(0.10)(0.10)^3}$$

Calculating ΔG at Nonstandard Concentrations – p. 33

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Calculating ΔG at Nonstandard Concentrations – p. 33

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$$\Delta G = -34,000 \text{ J} + 26,200 \text{ J} = -7800 \text{ J}$$

The forward reaction is still spontaneous at these conditions.

ΔG° and Equilibrium – p. 33

ΔG = ΔG° + RT ln Q

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At equilibrium, $\Delta G = 0$ and $Q = K$.

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$$\ln K = \frac{-\Delta G^{o}}{RT} \quad \text{and} \quad K = e^{-\Delta G^{\circ}/RT}$$

ΔG° and Equilibrium – p. 33

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$\Delta G° = -RT \ln K$, and

$$\ln K = \frac{-\Delta G°}{RT} \quad \text{and} \quad K = e^{-\Delta G°/RT}$$

$\Delta G°$ allows one to calculate the equilibrium constant while ΔG allows one to predict spontaneity.

Calculating Equilibrium Constants

Calculate the equilibrium constants for the dissolution of $Ba(NO_3)_2$ reaction and for the production of NH_3 reaction.

$$\ln K = \frac{-\Delta G^o}{RT} \quad \text{and} \quad K = e^{-\Delta G^o/RT}$$
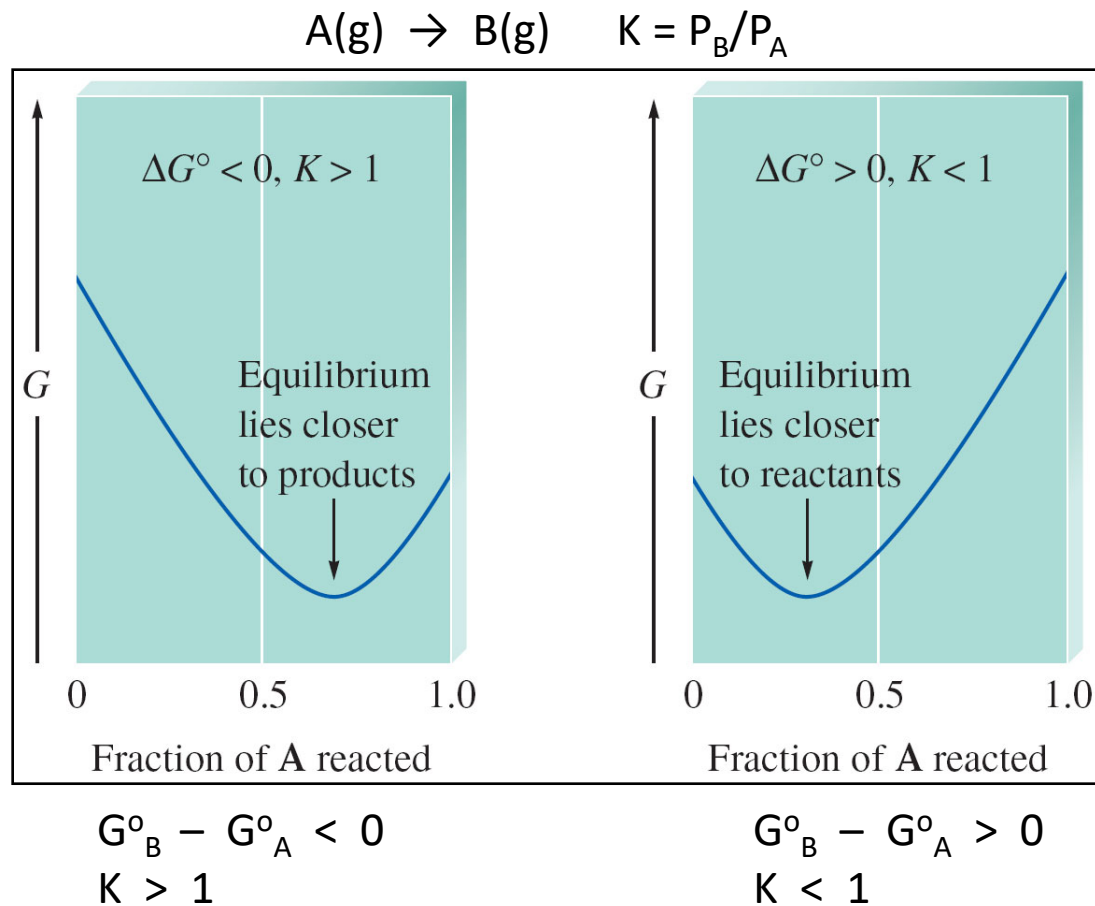
Qualitative Relationship Bewteen the
Change in Standard Free Energy and the Equlibrium Constant
for a Given Reaction

Table 17.6 ▶ **Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction**

$\Delta G°$	K
$\Delta G° = 0$	$K = 1$
$\Delta G° < 0$	$K > 1$
$\Delta G° > 0$	$K < 1$

$\Delta G° = -RT \ln K$

Figure 17.10: The Relationship of ΔG^o for a Reaction to Its Eventual Equilibrium Position

$A(g) \rightarrow B(g)$ $K = P_B/P_A$

$\Delta G° < 0, K > 1$

G

Equilibrium lies closer to products

$\Delta G° > 0, K < 1$

G

Equilibrium lies closer to reactants

0   0.5   1.0
Fraction of **A** reacted

0   0.5   1.0
Fraction of **A** reacted

$G^o_B - G^o_A < 0$
$K > 1$

$G^o_B - G^o_A > 0$
$K < 1$

Lecture Question – p. 34

Consider the reaction $2 NO_2(g) \rightarrow N_2O_4(g)$ where $P_{NO2} = 0.29$ atm and $P_{N2O4} = 1.6$ atm. At these conditions ($T = 25^\circ C$), $\Delta G = 1000$ J and $\Delta G^o = -6000$ J. Which of the following statements (a-c) is false?

a. K is greater than 1 for this reaction.

b. The forward reaction is spontaneous.

c. At equilibrium, $P_{N2O4} < 1.6$ atm.

d. None of these statements are false.

Lecture Question

Consider the reaction $2\ NO_2(g) \rightarrow N_2O_4(g)$ where P_{NO2} = 0.29 atm and P_{N2O4} = 1.6 atm. At these conditions (T = 25°C), ΔG = 1000 J and ΔG^o = -6000 J. Which of the following statements (a-c) is false?

a. K is greater than 1 for this reaction. True since $\Delta G^o < 0$.

b. The forward reaction is spontaneous. False; since $\Delta G > 0$, the reverse reaction is spontaneous.

c. At equilibrium, P_{N2O4} < 1.6 atm. True; since reverse reaction is spontaneous, the amount of products will decrease while the amount of reactants will increase.

d. None of these statements are false.

Equilibrium/Thermodynamic Problem p. 34

Consider the reaction 2 HBr(g) → H_2(g) + Br_2(g) where ΔH^o = 104 kJ. In a particular experiment, 2.00 atm of HBr were placed a 1.00 L flask at 25°C and allowed to react to reach equilibrium. At equilibrium, P_{H2} = 5.0 x 10^{-10} atm. Calculate K, ΔG^o, and ΔS^o for this reaction.