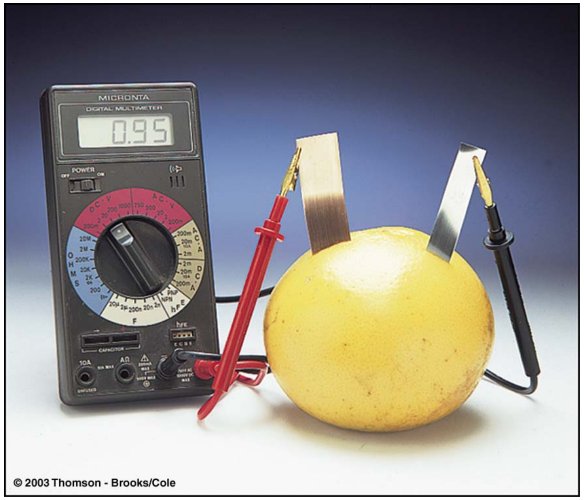

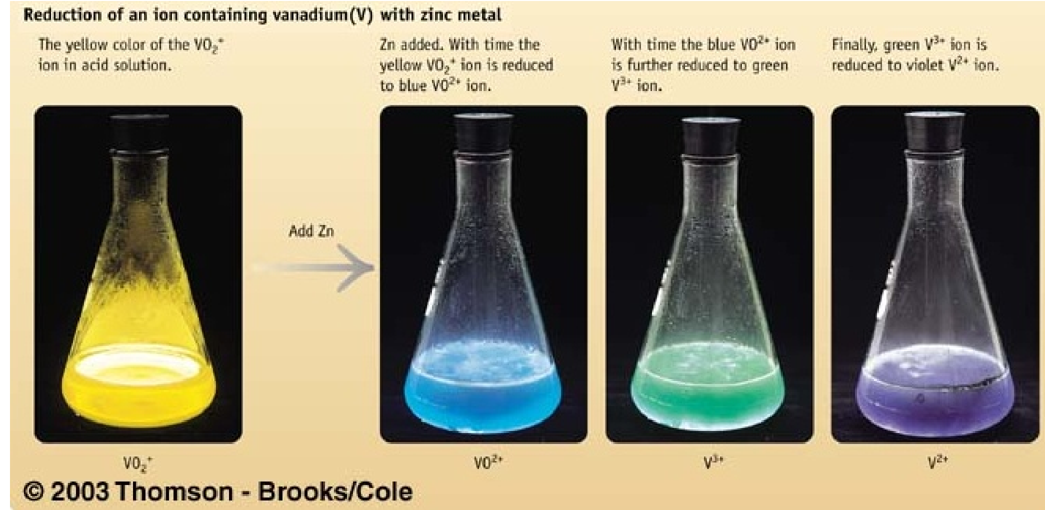

CHEMISTRY 2000

Topic #2: Thermochemistry and Electrochemistry –

What Makes Reactions Go?

Fall 2020

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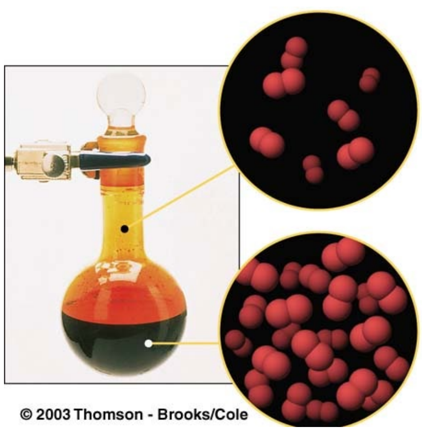
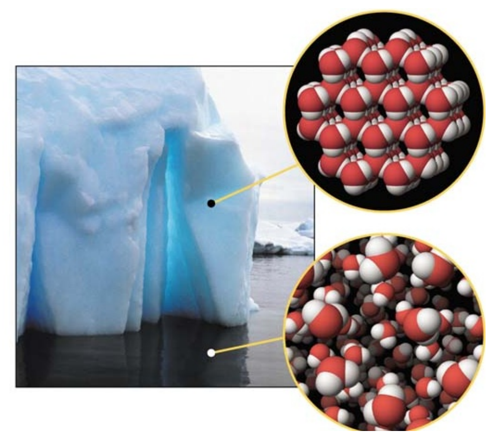
See Exercises 7.1 to 7.5





Q vs. K

$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$ and $$K = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

So, what's the difference?

- Consider a very generic equilibrium reaction:

  $$\textbf{reactants} \rightleftharpoons \textbf{products}$$

  - When does Q = K?
  - When is Q < K?
  - When is Q > K?

Free Energy Change and Equilibrium

- We saw that the free energy change for a reaction under any conditions ($\Delta_r G$) can be calculated from the free energy change of the same reaction under standard conditions ($\Delta_r G°$):

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

where Q is the reaction quotient:

$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

- We also know that:
  - The forward reaction is spontaneous if ____________
  - The <u>reverse</u> reaction is spontaneous if ____________.

- What if $\Delta_r G = 0$?

Free Energy Change and Equilibrium

- When $\Delta_r G = 0$, we can say that:

  Which rearranges to give:

- But what is Q at equilibrium?

- So, we can say that:

Free Energy Change and Equilibrium

- So, if we know the equilibrium constant for a reaction, we can calculate its standard free energy change:

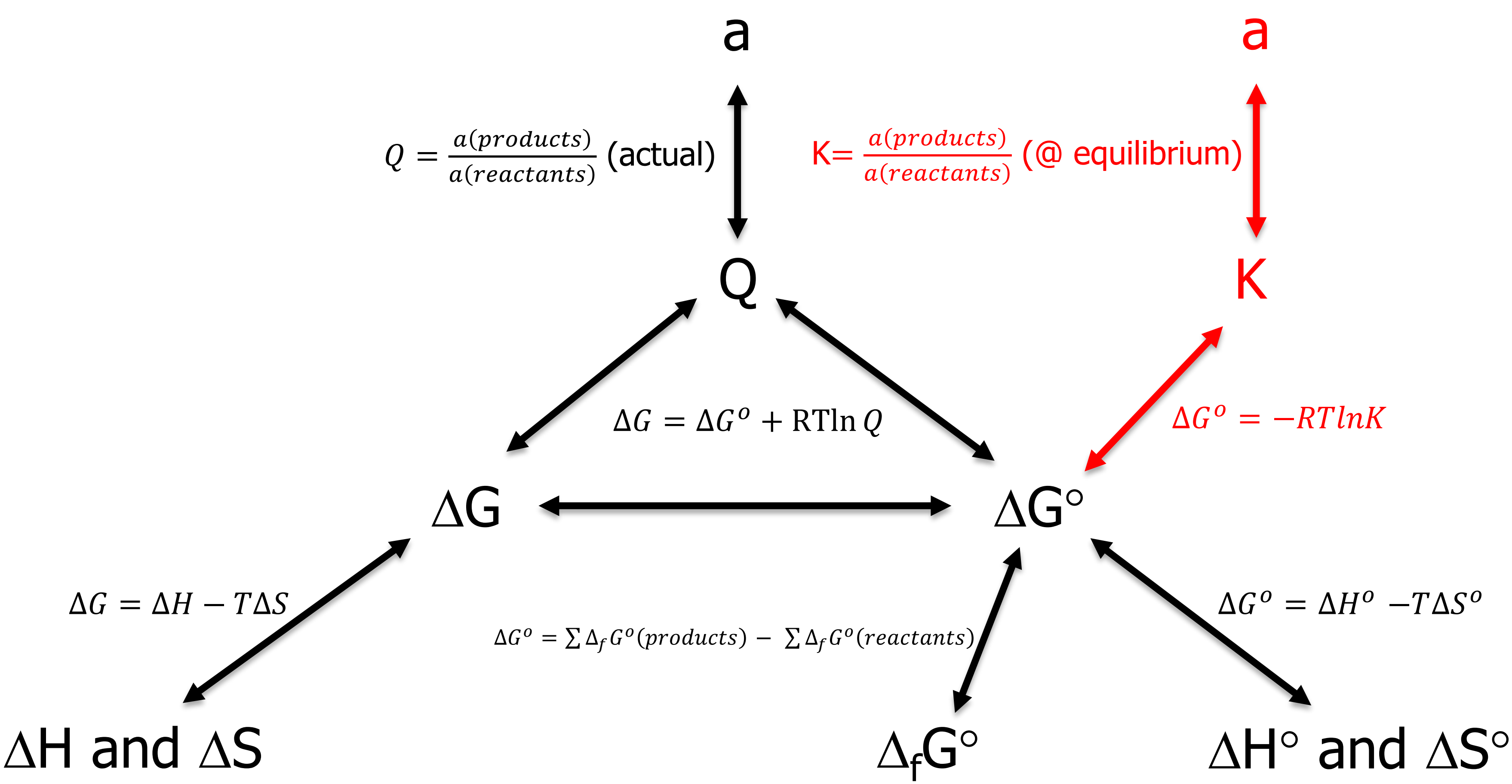
$$\Delta_r G° = -RT \ln K$$

- And if we know the standard free energy change for a reaction, we can also calculate its equilibrium constant:

Note that these equations refer to $\Delta_r G°$ (for standard conditions) NOT to $\Delta_r G$ (which is ZERO at equilibrium!)

Free Energy Change and Equilibrium

- We can add these relationships to our equation map:



Free Energy Change and Equilibrium

- Now, consider a real reaction, the dimerization of NO_2:

  $$2\ NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

  Calculate the equilibrium constant for this reaction at 25 ºC.

$$\Delta_f G^\circ(NO_{2(g)}) = 51.31 \frac{kJ}{mol}$$

$$\Delta_f G^\circ(N_2O_{4(g)}) = 97.89 \frac{kJ}{mol}$$

Free Energy Change and Equilibrium

- Is the dimerization of NO_2 spontaneous at 25 ºC if the partial pressure of NO_2 is 0.4 bar and the partial pressure of N_2O_4 is 1.8 bar?

Free Energy Change and Equilibrium: Acids

- The acid ionization constant, K_a, is the equilibrium constant for the reaction in which an acid ionizes. As an equilibrium constant (and therefore based on activities), K_a has no units.

  e.g. $HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$ $\quad K_a = 6.6 \times 10^{-4}$

- In CHEM 1000, we used pK_a as a measure of strength of an acid. An acid with a low pK_a was ____________________ than an acid with a high pK_a. The pK_a value for an acid comes from its acid ionization constant:

$$pK_a = -\log K_a$$

- So, we can also say that an acid will be ______________________ than another acid whose K_a value is smaller. (Even a "big" K_a value is pretty small. K_a values range from about 10^{-50} to 10^{10}.)

Free Energy Change and Equilibrium: Acids

- Calculate the standard molar free energy of formation for $HF_{(aq)}$.

$$HF_{(aq)} \rightleftharpoons H^{+}_{(aq)} + F^{-}_{(aq)} \qquad K_a = 6.6 \times 10^{-4}$$

$$\Delta_f G^\circ(H^{+}_{(aq)}) = 0 \frac{kJ}{mol}$$

$$\Delta_f G^\circ(F^{-}_{(aq)}) = -278.8 \frac{kJ}{mol}$$