

Section 13.2

Equilibrium Constants



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Learning Objectives

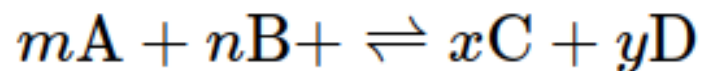


- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Reaction Quotient



- The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient** (Q).
- It can be derived directly from the stoichiometry of the reaction and **either** the concentration or partial pressure of the reactants and products.



$$Q_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n}$$

$$Q_p = \frac{P_{\text{C}}^x P_{\text{D}}^y}{P_{\text{A}}^m P_{\text{B}}^n}$$

Units of Reaction Quotients

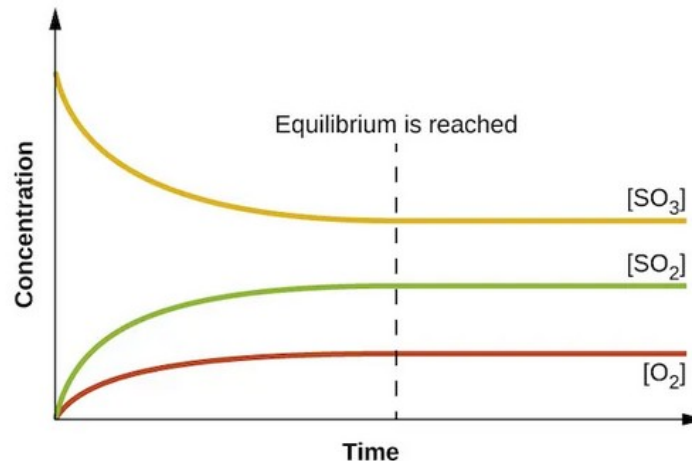
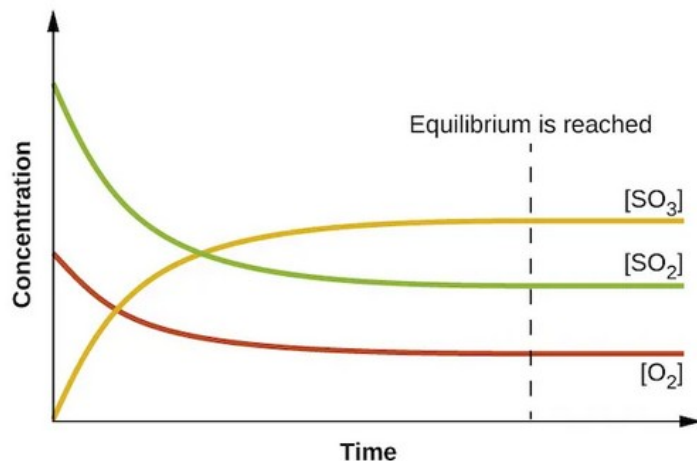
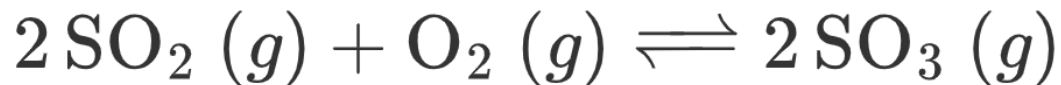


- Reaction quotient equations in our text are a simplification of more rigorous expressions that use *relative values* for concentrations and pressures rather than *absolute values*.
- These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients.
- We will use the simplified equations and disregard units when computing Q .

Directional Equilibrium



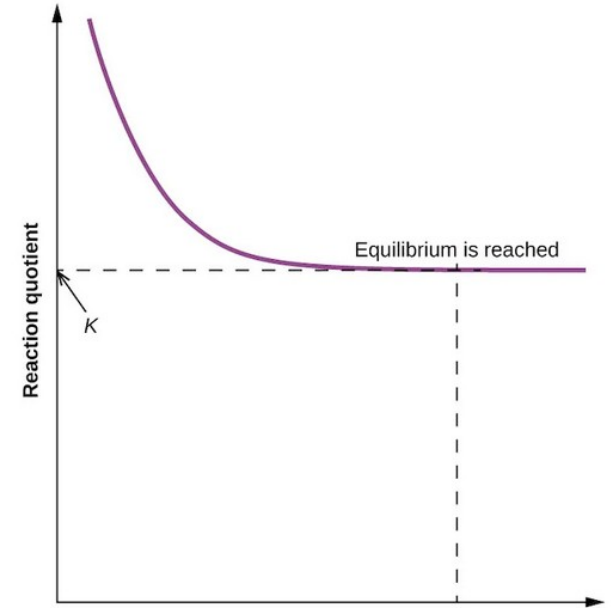
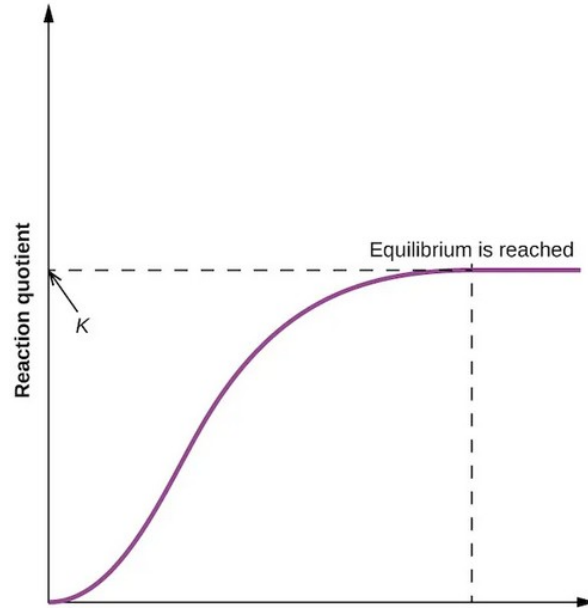
- A reversible reaction can start with an excess of reactants or products and proceed in either direction.
- This means equilibrium can be reached from two directions.



Directional Reaction Quotient



- Reaction Quotients will change as the reaction proceeds to equilibrium.
- But it always converges to the same value once equilibrium is reached.



Equilibrium Constant



- The value that Q takes on at equilibrium is called the **equilibrium constant**, K .

$$K \equiv Q \text{ at equilibrium}$$

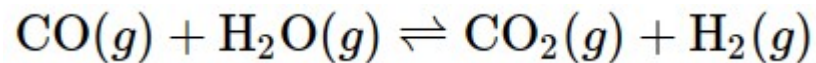
- **Law of Mass Action:** At a given temperature, the reaction quotient for a system at equilibrium is constant.
- When K is known for a reaction and temperature, Q can be used to predict the direction of the reaction.
- K has nothing to do with the speed of the reaction.

Predicting Direction



- When $Q < K$, there is an excess of reactants and the reaction will proceed in the forward direction towards the products.
- When $Q > K$, there is an excess of products and the reaction will proceed in the reverse direction towards the reactants.
- When $Q = K$, equilibrium has been reached.
 - The forward rate is equal to the reverse rate.
 - The concentration of products and reactants remains constant.

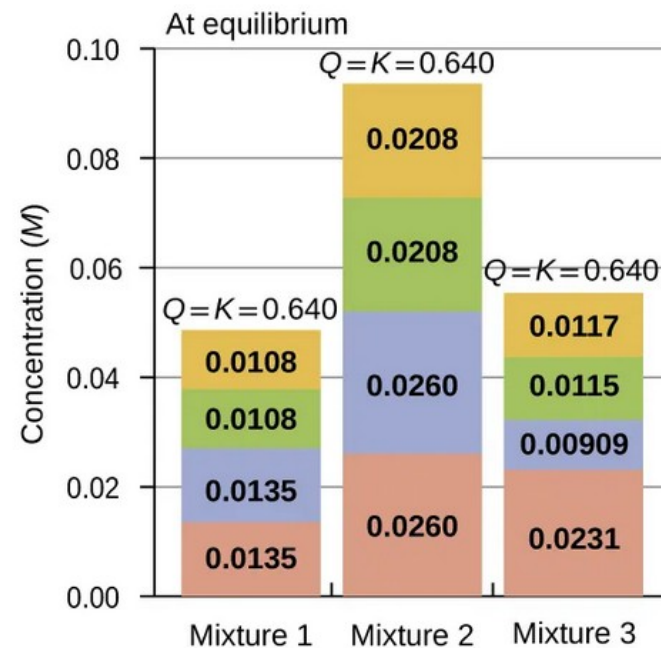
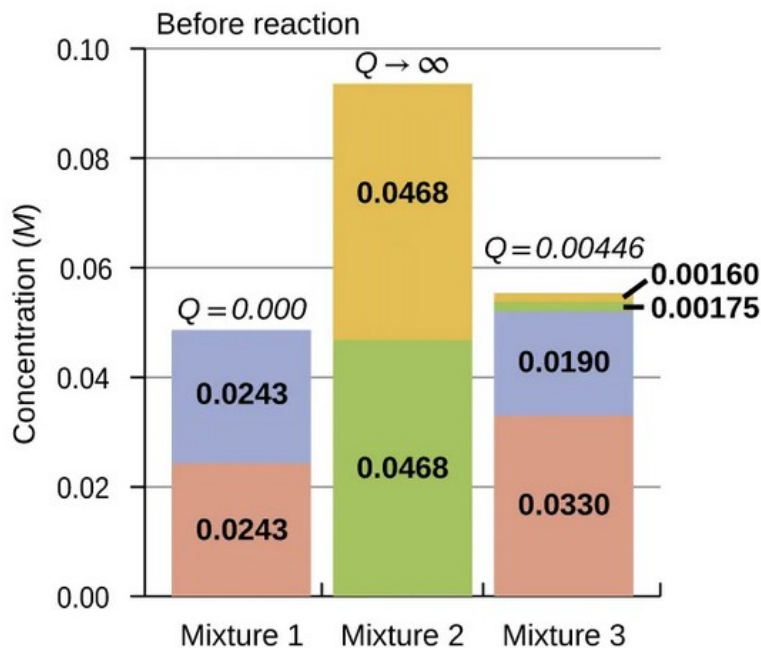
Reaction Quotient Example



$$K_c = 0.640$$

$$T = 800\text{ }^{\circ}\text{C}$$

■ [CO]
 ■ [H₂O]
 ■ [CO₂]
 ■ [H₂]



Homogeneous Equilibria

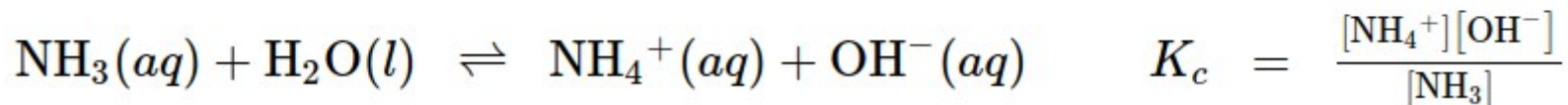
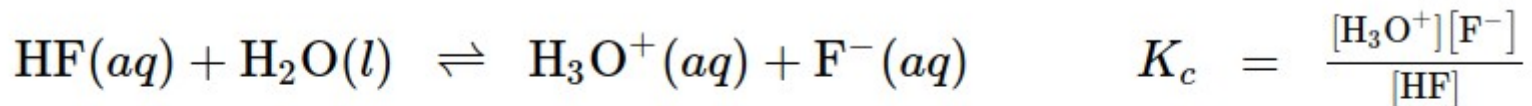
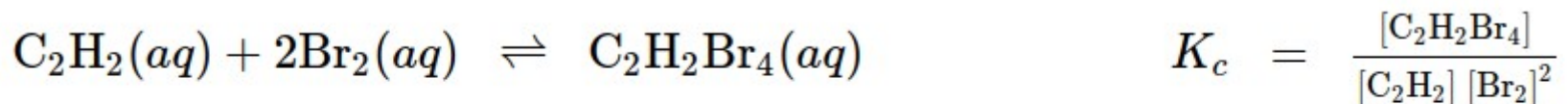


- A **homogeneous equilibrium** is one in which all reactants, products, and any catalysts are present in the same phase.
- Homogeneous equilibria take place in *solutions*
- These solutions are most commonly either liquid or gaseous phases

Omitting Solids and Liquids



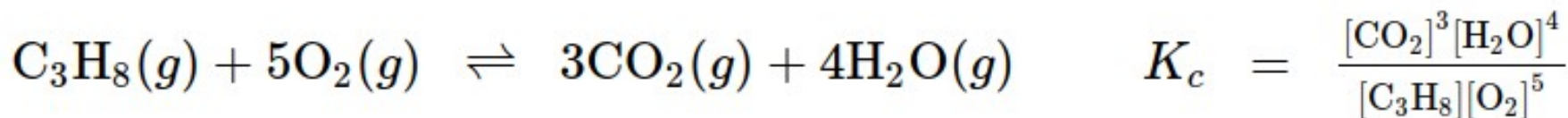
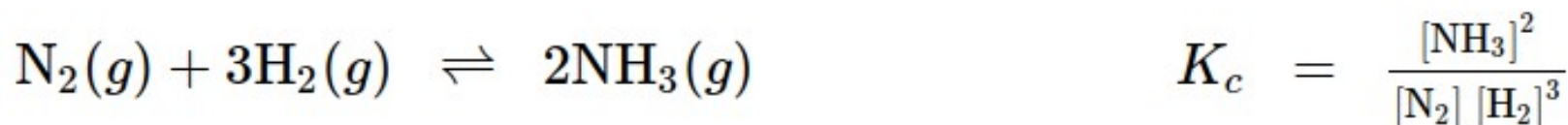
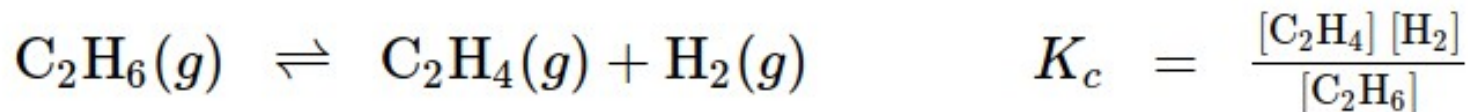
- When pure solids and liquids are present in a chemical equation, they are omitted from Q and K .
- The reason for this omission is related to the more rigorous form of the Q (or K) expression.



Gas Phase Components



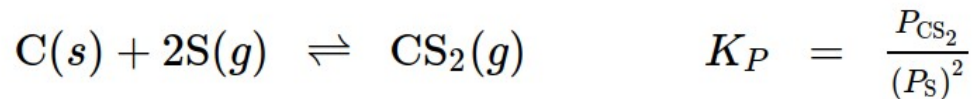
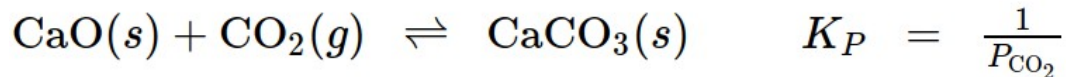
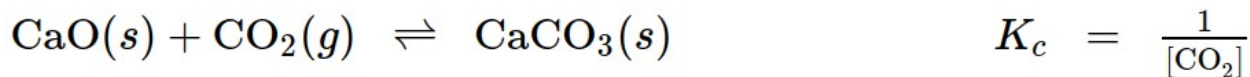
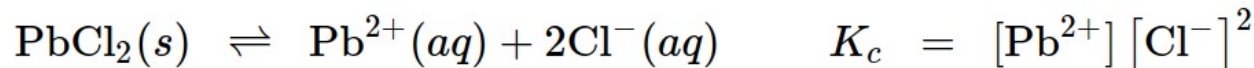
- Be careful, gas phase species are always included in Q and K , even when they are often seen as liquids or solids.



Heterogeneous Equilibria



- A **heterogeneous equilibrium** involves reactants and products in two or more different phases
 - The same rules about solids and liquids apply



Relationship Between K_p and K_c



- To derive a relationship between K_c and K_p , we will begin by considering the Ideal Gas Law.

$$PV = nRT$$

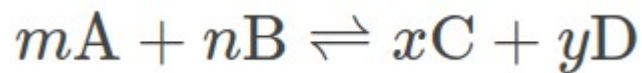
$$P = \left(\frac{n}{V} \right) RT$$

$$= MRT$$

Relationship Between K_p and K_c



- We can now substitute this result into a generic K_p expression.



$$K_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n}$$

$$\begin{aligned} K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\ &= \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_c (RT)^{(x+y)-(m+n)} \end{aligned}$$

Relationship Between K_p and K_c



- We now have a relationship between K_p and K_c .

$$K_P = K_c(RT)^{\Delta n} \quad K_c = \frac{K_P}{(RT)^{\Delta n}} = K_P(RT)^{-\Delta n}$$

$$\Delta n = (x+y) - (m+n)$$

Coupled Equilibria



- Many systems involve two or more **coupled equilibrium reactions**, which have one or more reactant or product species in common.
- The K value for a system involving coupled equilibria can be related to the K values of the individual reactions.
- There are three basic manipulations we can do.

Rule One



- 1) Changing the direction of a chemical equation essentially swaps the identities of “reactants” and “products,” and so the equilibrium constant for the reversed equation is simply the reciprocal of that for the forward equation.



$$K_{c'} = \frac{1}{K_c}$$

Rule Two



- 2) Changing the stoichiometric coefficients in an equation by some factor x results in an exponential change in the equilibrium constant by that same factor:

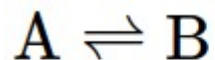


$$K_{c'} = K_c^x$$

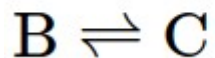
Rule Three



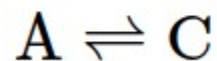
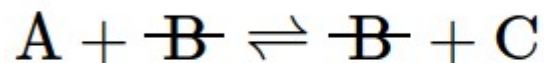
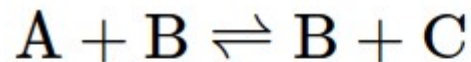
- 3) Adding two or more equilibrium equations together yields an overall equation whose equilibrium constant is the mathematical product of the individual reaction's K values:



$$K_{c1} = \frac{[B]}{[A]}$$



$$K_{c2} = \frac{[C]}{[B]}$$



$$K_{c'} = \frac{[C]}{[A]}$$

Proof of Rule Three



- Comparing the equilibrium constant for the net reaction to those for the two coupled equilibrium reactions we can prove that the product of K_{c1} and K_{c2} is K_c

$$K_{c1} K_{c2} = \frac{[B]}{[A]} \times \frac{[C]}{[B]} = \frac{\cancel{[B]}[C]}{[A]\cancel{[B]}} = \frac{[C]}{[A]} = K_c$$

$$K_{c'} = K_{c1} K_{c2}$$