Chem 116
Approach to Eq and Le'Chatelier's Principle

Reaction Quotient (Q_c)

The value of Q_C is used to predict the equilibrium position and the approach to equilibrium.
Remember…..all reactions proceed spontaneously toward equilibrium!!

1.

2.

$$\text{Reaction Quotient} = Q_c = \frac{[\text{Products}]_i}{[\text{Reactants}]_i}$$

Example: At 927°C $K_c = 3.91$ for the reaction: $CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
Initially $[CO] = [H_2] = 0.0200$ M and $[CH_4] = [H_2O] = 0.00100$ M. Under these initial conditions, is this reaction at equilibrium? If not, which direction will the reaction proceed to attain equilibrium?

In General

* If $Q_c > K_c$, then…
* If $Q_c < K_c$, then…
* If $Q_c = K_c$, then…

Sample Questions

1. At 1000 °C, $K_c = 1.17$ for the reaction: $CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$
A 10.0 L vessel contains 1.5×10^{-3} mol of CO_2 and 5.5×10^{-3} mol of CO. Some solid carbon is added and the temperature increased to 1000 °C. Will more CO(g) form?

2. Consider the reaction: $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$ $K_C = 3.07 \times 10^{-4}$ at 24°C. For each of the following sets of initial conditions, describe in which direction the reaction will proceed to reach equilibirum.

A. $[NOBr]_I = 0.0610$ M, $[NO]_I = 0.0151$ M, $[Br_2]_I = 0.0108$ M

B. $[NOBr]_I = 0.115$ M, $[NO]_I = 0.0169$ M, $[Br_2]_I = 0.0142$ M

C. $[NOBr]_I = 0.500$ M, $[NO]_I = 0.0170$ M, $[Br_2]_I = 0.0140$ M

3. A mixture of 1.57 mol of N_2, 1.92 mol of H_2, and 8.13 mol of NH_3 is introduced into a 20.0 L reaction vessel at 500 K. At this temperature, the equilibrium constant for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction? (Because $Q_c > K_c$, the reaction is not at equilibrium. The reaction will proceed to the left to reach equilibrium)

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Relationship between Initial concentrations and Equilibrium concentrations

"The Concentration or ICE Table"

Initial Conc.
\+ Change in Conc.
Equilibrium Conc.

* The initial concentrations of the chemicals are going to **CHANGE** as the reaction occurs before equilibrium is reached.

* The changes in the different chemicals are **RELATED** via the coefficients in a **BALANCED** chemical equation!!

Example: Consider the equilibrium and initial conditions shown below. Is this reaction at equilibrium? If not, which way will the reaction proceed to attain equilibrium?

	$2\ ICl(g) \rightleftharpoons$	$I_2(g)$ +	$Cl_2(g)$	$K_C = ?$
Initial:	0 M	0.22 M	0.22 M	
Change:				
Eq:				

After reaching equilibrium, the concentration of the Cl_2 is 0.09 M. What is the numerical value of K_C?

Sample Questions

Calculate the missing concentrations, and the numerical value of K_C for the equilibria below:

1.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$	$K_C = ?$
Initial:	0 M	0 M	5.000 M	
Change:			-0.730 M	
Equilibrium:				

2.

	$3\ A(aq)$ +	$2\ B(aq) \rightleftharpoons$	$C(aq)$ +	$2\ D(aq)$	$K_C = ?$
Initial:	6.00 M	2.00 M	1.00 M	0 M	
Change:				+0.50 M	
Equilibrium:					

3.

	$2N_2O(g)$ +	$3O_2(g) \rightleftharpoons$	$4NO_2(g)$	$K_C = ?$
Initial:	0.020 M	0.056 M	0 M	
Change:				
Equilibrium:	0.010 M			

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Calculation of Equilibrium Concentrations from Initial Concentration and K_c

Example: If 0.50 mol PCl_5 is injected into a 2.0 L vessel, what will be the equilibrium concentrations of all species? The equilibrium equation is given below.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K_C = 1.8 \text{ at } 250°C$$

HINT: For the general Quadratic Equation: $ax^2 + bx + c = 0$

the solution is …. $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Sample Questions

1. The air pollutant NO is produced in automobile engines from the high-temperature reaction

   $$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \quad K_c = 1.7 \times 10^{-3} \text{ at } 2300 \text{ K}$$

   If the initial concentrations of N_2 and O_2 at 2300 K are both 1.40 M, what are the concentrations of NO, N_2, and O_2 when the reaction mixture reaches equilibrium?

2. The equilibrium constant, Kc, for the reaction:

   $$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

   is 4.2 at 1650 ºC. Initially 0.80 mol H_2 and 0.80 mol CO_2 are injected into a 5.0 L flask. Calculate the concentration of each species at equilibrium. ($[H_2] = [CO_2] = 0.05$ M; $[H_2O] = [CO] = 0.11$ M)

3. Consider the reaction at equilibrium below:

   $$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

   Eq: 0.25 atm 0.25 atm

   Calculate the equilibrium partial pressures of NO_2 and N_2O_4 when the total pressure is increased to 20. atm.

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Le` Chatelier's Principle

If a stress is applied to a chemical system at equilibrium (Qc=Kc) that removes the system from equilibrium ($Q_C \neq K_C$), then that system will act to alleviate the stress and regain equilibrium.

Stresses that may remove system from Eq:

1.
2.
3.

Stresses that do NOT remove system from Eq:

1.
2.

NOTE: Reactions always proceed spontaneously toward equilibrium!!!

Effect of Addition or Removal of Reactant/Product

1. Consider the equilibrium: $2\ ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)\ \ K_C = 0.12$

   A. If [ICl] = 0.26 M and $[I_2] = [Cl_2]$ = 0.09 M, is this reaction at equilibrium?
   B. Which way will the reaction proceed if the concentration of ICl is increased by 0.74 M?
   C. Which way will the reaction proceed if the concentration of I_2 is increased by 0.74 M?
   D. Which way will the reaction proceed if all of the Cl_2 is removed?

2. Consider that the reaction shown below is at equilibrium.

   $$BaSO_4(s) \rightleftharpoons BaO(s) + SO_3(g)$$

   A. Which way will the reaction proceed if the amount of $BaSO_4$ is doubled?
   B. Which way will the reaction proceed if half of the BaO is removed?
   C. Which way will the reaction proceed if half of the SO_3 is removed?

3. The reaction of iron(III) oxide with carbon monoxide occurs in a blast furnace when iron ore is reduced to iron metal: $Fe_2O_3(s) + 3\ CO(g) \rightleftharpoons 2\ Fe(l) + 3\ CO_2(g)$

   Use Le' Chatelier's principle to predict the direction of the net reaction when an equilibrium mixture is disturbed by:

   A. Adding Fe_2O_3 B. Removing CO_2 C. Adding Fe
   D. Removing CO

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Effect of Change in Pressure Due to Change in Volume

Especially important for gas phase reactions.

* As pressure **increases** due to a *decrease in volume*, the net reaction will occur in the direction that….. _____ the number of moles of gas!

* As pressure **decreases** due to an *increase in volume*, the net reaction will occur in the direction that….. _____ the number of moles of gas!

Consider the following reactions which have already attained equilibrium. Which way will the reaction proceed to regain equilibrium if the pressure is increased by decreasing the volume?

A. $N_2O(g) + NO_2(g) \rightleftharpoons 3\ NO(g)$ $K_C = 1.4 \times 10^{-10}$ at 200°C
B. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
C. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

Consider the following reactions which have already attained equilibrium. Which way will the reaction proceed to regain equilibrium if the pressure is decreased by increasing the volume?

A. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
B. $2\ CO(g) \rightleftharpoons C(s) + CO_2(g)$
C. $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

Effect of Change in Temperature

When temperature changes, the numerical value of K_c changes!

* We will treat temperature as heat
* Treat heat as either a product of reaction (exothermic) or reactant (endothermic)

Endothermic reaction ($\Delta H = +$):

Heat + Reactants $\rightleftharpoons$ Products

* As temperature is increased, are products or reactants more favored?
* As temperature is increased, what happens to the numerical value of K_C?

Exothermic reaction ($\Delta H = -$):

Reactants $\rightleftharpoons$ Products + Heat

* As temperature is increased, are products or reactants more favored?
* As temperature is increased, what happens to the numerical value of K_C?

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Sample Questions

1. In the first step of the Ostwald process for the synthesis of nitric acid, ammonia is oxidized to nitric oxide by the reaction:

   $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g) \qquad \Delta H^o = -905.6\ kJ$

   How does the equilibrium amount of NO vary with an increase in temperature?

2. Consider the reaction below which has already attained equilibrium

   $N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad \Delta H^o = +57.2\ kJ$

   colorless brown

   In which direction will the reaction proceed if the temperature is increased?

3. Consider that the reaction: $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ $\Delta H = +181$ kJ, is already at equilibrium. If the temperature is decreased, which way will this reaction proceed to regain equilibrium?

4. Consider the equilibrium: $N_2H_4(g) + H_2(g) \rightleftharpoons 2\ NH_3(g)$ $\Delta H = -188$ kJ. In what two ways could the production of ammonia be maximized?