Key

2012

AP Chemistry
Equilibrium Targets
(Chapter 15)

Target #	Target	Section in text
1	I can write the equilibrium expression for a balanced chemical equation.	
2	I can numerically evaluate K_c and Kp from a knowledge of the equilibrium concentrations (or pressures) of reactants or products, or from the initial concentrations and the equilibrium concentration of at least one substance.	
3	I can interconvert K_c and Kp.	
4	I can use the equilibrium constant to calculate equilibrium concentrations.	
5	I can calculate the reaction quotient, Q, and by comparison with the value of K_c or Kp determine whether a reaction is at equilibrium. If it is not at equilibrium, I can predict in which direction it will shift to reach equilibrium.	
6	I can explain how the relative equilibrium quantities of reactants and products are shifted by changes in temperature, pressure or the concentrations of substances in the equilibrium reaction.	
7	I can describe the effect of a catalyst on a system as it approaches equilibrium.	

Target 1: I can write the equilibrium expression for a balanced chemical equation.

Equilibrium: a state in which there are no observable changes as time goes by

Physical Equilibrium: an equilibrium in which only physical properties change

phase change

example: $H_2O(s) \rightleftharpoons H_2O(\ell)$

Chemical Equilibrium: a reversible chemical reaction in which the rate of the forward reaction equals the rate of the reverse reaction

example: $N_2(g) + H_2(g) \rightleftharpoons 2NH_3(g)$

There ***IS*** a relationship between chemical kinetics (ch. 14) and equilibrium (ch. 15).

Consider the following reaction . . .

$$A + 2B \Leftrightarrow AB_2$$

Assume that the above reaction occurs via a mechanism consisting of a single elementary step. The rate at which AB_2 is produced is the same as the rate at which AB_2 is consumed.

$\text{rate}_{\text{forward}} = k_f[A][B]^2$ and $\text{rate}_{\text{reverse}} = k_r[AB_2]$

at equilibrium . . .

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

$k_f[A][B]^2 = k_r[AB_2]$

Now called K_c or K_{eq} (equilibrium constant)

$$K_c = \frac{k_f}{k_r} = \frac{[AB_2]}{[A][B]^2}$$

Note: Because rate constants are temperature dependent, it follows that equilibrium constants are also temperature dependent.

The **Law of Mass Action** is an equation for a chemical equilibrium which shows the relationship between the concentrations of reactants and products. An equilibrium-constant expression (or simply an equilibrium expression) can be written for equilibria as follows: $aA + bB \Leftrightarrow cC + dD$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[ ] = concentration in molarity
K_c = equilibrium constant

Note: The concentrations of pure solids and liquids are never included in equilibrium expressions!

Example: Write the equilibrium constant expression for the following reaction:

$$3\ H_2(g) + N_2(g) \Leftrightarrow 2\ NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[H_2]^3\,[N_2]}$$

The Haber Process is used to produce ammonia which is a chemical used in fertilizers. Examine the chart below regarding 3 different experiments which produce ammonia:

Results of Three Experiments for the Reaction N_2 (g) + $3H_2$ (g) ⇔ $2NH_3$ (g)

Experiment	Initial Concentrations (M)	Equilibrium Concentrations (M)	$K_c = \frac{[NH_3]^2}{[H_2]^3\,[N_2]}$
1	1.000 M N_2 1.000 M H_2 0.000 M NH_3	0.921 M N_2 0.763 M H_2 0.157 M NH_3	$K_c = 6.02 \times 10^{-2}\ L^2\ mol^{-2}$
2	0.000 M N_2 0.000 M H_2 1.000 M NH_3	0.399 M N_2 1.197 M H_2 0.203 M NH_3	$K_c = 6.02 \times 10^{-2}\ L^2\ mol^{-2}$
3	2.00 M N_2 1.00 M H_2 3.00 M NH_3	2.59 M N_2 2.77 M H_2 1.82 M NH_3	$K_c = 6.02 \times 10^{-2}\ L^2\ mol^{-2}$

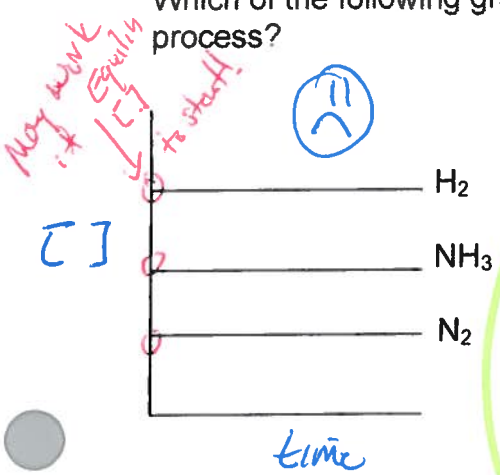
Not need units!

What conclusions can you make based upon the chart above?

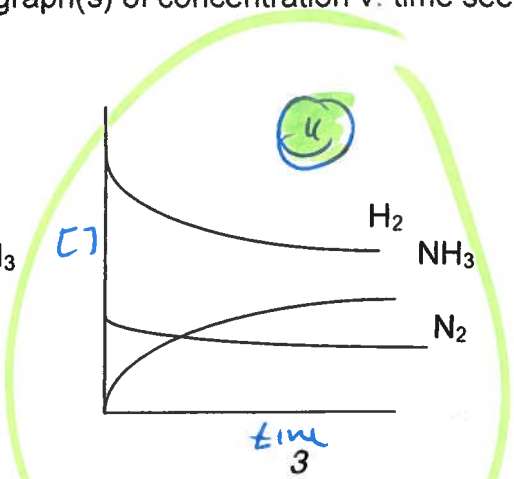
K_c is the same!

Equilibrium Achieved if you begin with Reactant, Products, or both.

Which of the following graph(s) of concentration v. time seem unlikely for the Haber process?

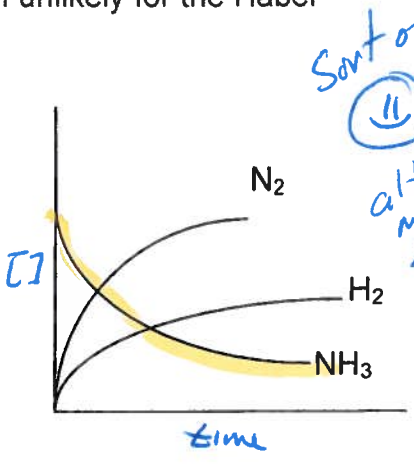


No, because H_2 & N_2 would go ↓ & NH_3 ↑



3

This is also possible!!



This is possible to start w/ NH_3 & form H_2 & N_2 (Exp 2 Above)

Sort of although more H_2 vs N_2 should be formed!

Target 2: I can numerically evaluate K_c and K_p from a knowledge of the equilibrium concentrations (or pressures) of reactants or products, or from the initial concentrations and the equilibrium concentration of at least one substance.

Target 3: I can interconvert K_c and K_p.

Solving for K_p instead of K_c! When the reactants and products of a chemical equilibrium are all gases, we can write equilibrium expressions in terms of partial pressures instead of molar concentrations. When the partial pressures are given in atmospheres, we write the equilibrium constant as K_p instead of K_c. The numerical values of K_p and K_c are usually different. There is a way to convert from one constant to another by using the following relationship:

$PV = nRT$

$P = \frac{n}{V}RT$

$K_p = K_c (RT)^{\Delta n}$ ← (moles gas product − moles gas reactant) in the balanced Equation!

R = .0821 $\frac{L\,atm}{mole\,K}$; T in K

Practice problem: Methanol, CH_3OH, is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen:

$CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(g)$ at 25°C

An equilibrium mixture in a 2.00 liter vessel is found to contain 0.046 mol CH_3OH, 0.170 mol CO, and 0.302 mol H_2. Calculate the value of K_c and K_p at this temperature.

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(.046\ mol/2.00\ L)}{(.170\ mol/2.00\ L)(.302\ mol/2.00\ L)^2} = 12.1\ (2\ S.F.)$$

$$K_p = (118.17)\left[(.0821\ \tfrac{L\,atm}{mol\,K})(298\ K)\right]^{-3} = .0220$$

Target 4: I can use the equilibrium constant to calculate equilibrium concentrations.

What does an equilibrium constant tell us? The value of the equilibrium constant depends upon the nature of the reaction and upon temperature. At constant temperature, we find that the magnitude of K varies greatly from one reaction to another. The value of K tells us the relative quantities of reactants and products formed at equilibrium.

If $K >> 1$, then the equilibrium lies to the right; products are favored.
If $K << 1$, then the equilibrium lies to the left; reactants are favored.

Consider the following three examples with varying magnitudes of K_c:

Example 1: $2\ O_3(g) \rightleftharpoons 3\ O_2(g)$ at 2300°C ; $K_c = 2.54 \times 10^{12}$

Since K_c is so large, there is much more oxygen than ozone! (In the atmosphere!)

The equilibrium mixture will contain very little O_3.

Example 2: $Cl_2(g) \Leftrightarrow 2Cl(g)$ at 25°C; $K_c = 1.4 \times 10^{-38}$
At equilibrium, the mixture of gases will contain mostly $Cl_2(g)$.

Example 3: $CO(g) + H_2O(g) \Leftrightarrow H_2(g) + CO_2(g)$ at 830°C; $K_c = 5.10$
The quantities of reactants and products will be comparable.

Other notes concerning equilibrium constants:

- When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

Ex: The K_c for the reaction $2NO(g) + O_2(g) \Leftrightarrow 2NO_2(g)$ is 5.0×10^{12}. Find the K_c for the reaction $2NO_2(g) \Leftrightarrow 2NO(g) + O_2(g)$.

So $K'_c = \frac{1}{5.0 \times 10^{12}} =$ 2.0×10^{-13}

- The value of K also depends upon how the equilibrium is balanced. Therefore, when quoting an equilibrium constant, you not only need to state the temperature, but you must also write the chemical equilibrium!

Ex: The reaction for the production of ammonia can be written in a number of ways:

a) $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$
b) $1/2\ N_2(g) + 3/2\ H_2(g) \Leftrightarrow NH_3(g)$
c) $1/3\ N_2(g) + H_2(g) \Leftrightarrow 2/3\ NH_3(g)$

Write the equilibrium constant expression (K_c) for each of the above. How are the equilibrium constants related to one another?

(a.) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(b.) $K_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

(c.) $K_c = \frac{[NH_3]^{2/3}}{[N_2]^{1/3}[H_2]}$

ex: $A\,(g) + 2B\,(g) \Leftrightarrow C\,(g)$; $K_c = 4$

$3A\,(g) + 6B\,(g) \Leftrightarrow 3C\,(g)$; $K'_c = ?$ $4^3 = 64$

cubed since 3 x the first Equation

- If a reaction can be expressed as the sum of 2 or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

$A + B \Leftrightarrow C + D$ $\quad K_c = 10^4$

$C + D \Leftrightarrow E + F$ $\quad K'_c = 10^3$

$A + B \rightleftharpoons E + F$ $\quad K''_c = 10^4 \times 10^3 = 10^7$

Section 15.3: Heterogeneous Equilibria

HETEROGENEOUS EQUILIBRIA are those equilibria which contain reactants and/or products which are in different phases. *Homogeneous equilibria* would be equilibria in which all reactants and products are in the same phase.

Heterogeneous equilibrium: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Homogeneous equilibrium: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

If a pure solid or liquid is involved in an equilibrium, its concentration is not included in the equilibrium constant expression! Even though they do not appear in the equilibrium expression, the pure solids and liquids participating in the reaction must be present for an equilibrium to be established.

ex: Write the equilibrium constant expressions for K_c and Kp for the following reaction . .

$SnO_2(s) + 2\,CO(g) \Leftrightarrow Sn(l) + 2\,CO_2(g)$

$K_c = \dfrac{[CO_2]^2}{[CO]^2}$ $\qquad K_p = \dfrac{(P_{CO_2})^2}{(P_{CO})^2}$

P stands for Pressure!

Solving Equilibrium Problems . . . Let the fun begin!

When solving equilibrium problems, you are usually asked to solve for the equilibrium constant or the concentration (or partial pressure for K_p problems) of a reactant or product. In some problems you will be asked to solve for the equilibrium concentration(s), and in other problems you will be asked to solve for initial

concentration(s). Let's work through some examples. **NOTE**: We will not have time to work very many problems in class. Therefore, it is imperative that you take time outside of class to do your problem sets and any additional assigned problems.

1. Solving for *K* when given equilibrium conditions:

Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas:

$PCl_3(g) + Cl_2(g) \Leftrightarrow PCl_5(g)$

A gas vessel is charged with a mixture of PCl3(g) and Cl2(g), which is allowed to equilibriate at 450 K. At equilibrium the partial pressures are P_{PCl3} = 0.124 atm, P_{Cl2} = 0.157 atm, and P_{PCl5} = 1.30 atm. What is the value of K_p at this temperature? Does the equilibrium favor the reactants or products?

typo

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

$$K_p = \frac{P_{PCl_5}}{(P_{PCl_3})(P_{Cl_2})} = \frac{1.30\,atm}{(.124\,atm)(.157\,atm)} = 66.8$$

Since the $K_p > 1$ the product (PCl_5) is "favored" or the equilibrium lies slightly to the Right on the Product side! (1)

2. Solving for *K* when only one of the equilibrium concentrations is known:

Strategy:

1) Tabulate the known initial and equilibrium concentrations of all species.
2) For any (and all) species that you know both its initial and equilibrium concentrations, calculate its change in concentration.
3) Use the balanced equation to find the changes in concentrations for all other species in the equilibrium.
4) Find the equilibrium concentrations of all species through their changes in concentrations . . . now plug in and solve for *K*!

A mixture of 1.374 g of H_2 and 70.31 g of Br_2 is heated in a 2.00 liter vessel at 700 K. These substances react as follows:

$$H_2(g) + Br_2(g) \Leftrightarrow 2HBr(g)$$

At equilibrium the vessel is found to contain 0.566 g of H_2. Calculate the equilibrium concentrations of the H_2, Br_2, and the HBr. Calculate K_c.

	$H_2(g)$ +	$Br_2(g)$ →	$2HBr(g)$
[Initial]	.344 M	.220 M	0
[change]	−.202	−.202	+.404
[Equilibrium]	.142 M	.018	.404

Form twice as much HBr as H_2 disappears

$$[H_2]_I = \frac{1.374\text{ g } H_2}{2.00\text{ L}} \left| \frac{\text{mol } H_2}{2\text{ g } H_2} \right| = .344\text{ M} \quad (.3435)$$

$$[Br_2]_I = \frac{70.31\text{ g}}{2.00\text{ L}} \left| \frac{\text{mole}}{159.89} \right| = .220\text{ M} \quad (.21999)$$

$$[H_2]_{Eq} = \frac{.562\text{ g } H_2}{2.00\text{ L}} \left| \frac{\text{mol } H_2}{2\text{ g } H_2} \right| = .142\text{ M} \quad (.1415)$$

$$[H_2]_{Chg} = .344 - .142 = .202$$

$$K_c = \frac{[HBr]^2}{[H_2][Br_2]}$$

$$= \frac{(.404)^2}{(.142)(.018)}$$

$$= 64$$

3. Solving for *K* when only the initial concentrations are given:

Target 5: I can calculate the reaction quotient, Q, and by comparison with the value of K_c or K_p determine whether a reaction is at equilibrium. If it is not at equilibrium, I can predict in which direction it will shift to reach equilibrium.

When given initial concentrations of reactants and products, a reaction will usually shift to the right (forward reaction favored) or shift to the left (reverse reaction favored) until the system reaches equilibrium. If you are only given the initial concentrations (or the initial partial pressures of gases), then you must . . .

1- calculate the Q (reaction quotient) for the given conditions in a very similar way that you calculated *K* . . .

$$aA + bB \Leftrightarrow cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Whenever you solve for Q, you are solving for conditions which are NOT at equilibrium!

2- Next determine if the system is at equilibrium. If it is not at equilibrium, determine which direction that the equilibrium will shift in order to reach equilibrium.

K=Q If Q = K, then the system is at equilibrium!
K<Q If Q > K, (←) then the equilibrium will shift left (forming more reactants)
K>Q If Q < K, (→) then the equilibrium will shift right (forming more products)

3- Finally complete an equilibrium table as described in the previous problem.

example: Consider the following reaction:

$$Ag^+(aq) + Fe^{2+}(aq) \Leftrightarrow Fe^{3+}(aq) + Ag(s) \; ; \; K_c = 2.98$$

The initial concentrations are $[Ag^+] = 0.200$ M, $[Fe^{2+}] = 0.100$ M, and $[Fe^{3+}] = 0.300$ M. What are the ion concentrations when equilibrium is established?

$$Q = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{.300\,M}{(.200\,M)(.100\,M)} = 15$$

Since K < Q or Q > K

2.98 < 15

I have too ~~much~~ great of a $[Fe^{3+}]$ so Reaction will shift to the Left and use up the excess Fe^{3+}

WARM-UPS! (non-calculator)

1. Assume 10.0 mol of HBr (g) is placed in a 20.0 liter flask at 300 K. ~~Estimate~~ if 40.0% of the HBr decomposes when equilibrium is reached.

Determine K_c

$.500M \times \frac{40}{100} = .200M$ → amount that decomposes or "x".

$2HBr(g) \Leftrightarrow H_2(g) + Br_2(g)$

	HBr	H_2	Br_2
I	.500M		
C	−.200M	.100M	.100M
E	.300M	.100M	.100M

$K_c = \frac{(.100)(.100)}{(.300M)^2} = .111$

(Note since HBr : H_2 : Br_2 is 2:1 then If .200M disappears of HBr .100M reappears)

2. $N_2(g) + O_2(g) \Leftrightarrow 2\,NO(g)$; $K_c = 4.00$ @ 500°C

If 6.00 mol of N_2 and 6.00 mol of O_2 are placed in a 2.00-L flask and allowed to reach equilibrium, what is the equilibrium concentration of NO?

$[N_2] = [O_2] = .300M$

	N_2	O_2	2NO
I	3.00M	3.00M	
C	−x	−x	2x
E	3.00−x	3.00−x	2x

$K_c = \frac{[NO]^2}{[N_2][O_2]}$

$4.00 = \frac{(2x)^2}{(.300-x)^2}$

$4x^2 = (.300)^2 4.00$

Ignore −x or use your Solver!

$x^2 = (.300)^2$

$x = .300M$ (quadratic)

Be $[NO]_{EQ} = .600M$

3. $2\,A(aq) + 3\,B(aq) \Leftrightarrow D(aq)$; $K_c = 5000$ at 100 K.

A 3.00-L flask is initially filled with 0.200 M A, 0.100 M B, and 0.200 M D. Calculate the equilibrium concentrations of A, B, & D.

OMIT unrealistic calcs! B

	2A	3B	D
I	.200M	.100M	.200M
C	−2x	−3x	x
E	(.200−2x)	(.100−3x)	.200+2x

$5000 = \frac{(.200+2x)}{(.200-2x)^2 (.100-3x)^3}$

4. Consider the following:

$HF(aq) \Leftrightarrow H^+(aq) + F^-(aq)$ $K_c = 6.8 \times 10^{-4}$

$H_2C_2O_4(aq) \Leftrightarrow 2\,H^+(aq) + C_2O_4^{2-}(aq)$ $K_c = 3.8 \times 10^{-6}$

Determine K for the following reaction:

$2\,HF(aq) + C_2O_4^{2-}(aq) \Leftrightarrow 2\,F^-(aq) + H_2C_2O_4(aq)$

$2(HF \rightleftharpoons H^+ + F^-) \quad (6.8\times10^{-4})^2$

$2H^+ + C_2O_4^{2-} \rightleftharpoons H_2C_2O_4 \quad \frac{1}{K_c} = \frac{1}{3.8\times10^{-6}}$

$2HF + C_2O_4^{2-} \rightleftharpoons 2F^- + H_2C_2O_4 \quad K = (6.8\times10^{-4})^2 \left(\frac{1}{3.8\times10^{-6}}\right) = .12$

Choices:
a) 4.1×10^{-3}
b) 0.12
c) 6.3×10^{2}
d) 2.8×10^{7}

Section 15.6 - Le Chatlier's Principle

Target 6: I can explain how the relative equilibrium quantities of reactants and products are shifted by changes in temperature, pressure or the concentrations of substances in the equilibrium reaction.

$$\text{Heat} + N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Target 7: I can describe the effect of a catalyst on a system as it approaches equilibrium.

Le Chatlier's Principle: if a chemical system is at equilibrium and is disturbed by a change in temperature, pressure, or concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

Changes in reactant or product concentration

As ya increas $[N_2]$ & $[H_2]$ in the reaction above the reaction will shift (move) to the Rt due to more reactant collisions!

Changes in Pressure or Volume

Increase P shifts to side w/ the fewest gas moles. (or Decrase V) More collisions on side w/ more gas moles.

Changes in Temperature

Treat Heat as a Reactant (Endo) or Product (Exo). Heat an Endo shift to the Rt.

Heat an Exo shift left

Effects of Adding a Catalyst

Benefits both the forward & reverse Rxn

Practice: For the following reaction, $\Delta H = 2816$ kJ

$$2816\text{KJ} + 6CO_2(g) + 6H_2O(l) \Leftrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

$$K_c = \frac{[O_2]^6}{[CO_2]^6}$$

How is the equilibrium yield of $C_6H_{12}O_6$ affected by:

→ a) increasing the partial pressure of CO_2? shift → temporarily due to more reactant collisions

→ b) increasing the temperature? Since Endo shift Rt

← c) removing CO_2? shift left to obtain CO_2 back

None d) decreasing the total pressure? No effect since moles of gas are equal on both reactant & product side

Non e) removing part of the $C_6H_{12}O_6$? No effect since not part of the K_c

f) adding a catalyst?

benefits both forward & reverse.