CALCULATING EQUILIBRIUM CONCENTRATIONS

- We can use equilibrium constant to calculate the equilibrium concentration of all the substances in the mixture. Some of the variations that these problems occur are shown in the examples below:

Example 1:
Nitric oxide, NO, is formed in automobile exhaust by the reaction of N_2 and O_2 (from air):

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

K_c for this reaction equals 0.0025 at 2127 °C. If an equilibrium mixture at 2127 °C contains 0.023 mol N_2 and 0.031 mol O_2 per liter, what is the equilibrium concentration of NO?

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

$$[NO] = \sqrt{K_c\,[N_2][O_2]} = \sqrt{(0.0025)(0.023)(0.031)} = 1.3\text{x}10^{-3}\text{ M}$$

Example 2:
The equilibrium shown below has a K_p value of $1.45\text{x}10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at this temperature, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this mixture?

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

$K_p =$

<u>Example 3:</u>

For the reaction shown below, initially a mixture contains 0.850 mol each of N_2 and O_2 in a 8.00 L vessel. Find the composition of the mixture when equilibrium is reached at 3900 °C. $K_c = 0.0123$ at 3900 °C

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

First: Obtain starting molar concentrations in mol/L

$$[N_2] = [O_2] = \frac{0.850\text{ mol}}{8.00\text{ L}} = 0.10\underline{6}25\text{ M}$$

	N_2 (g) +	O_2 (g) $\rightleftharpoons$	2 NO (g)
Initial	$0.10\underline{6}25$	$0.10\underline{6}25$	0
Δ	–x	–x	+2x
Equilibrium	$0.10\underline{6}25$–x	$0.10\underline{6}25$–x	2x

$$K_c = 0.0123 = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(0.10625 - x)(0.10625 - x)}$$

Taking square roots of both sides: $$0.11\underline{0}9 = \frac{2x}{(0.10625 - x)}$$

Rearranging: $$0.10\underline{6}25 - x = \frac{2x}{0.1109} = 18.\underline{0}3\,x$$

Rearranging further: $$0.10\underline{6}25 = 19.\underline{0}3\,x$$ **$x = 5.5\underline{8}3 \times 10^{-3}$ M**

Equilibrium concentrations are:

$[O_2] = [N_2] = 0.10\underline{6}25 - x = 0.10\underline{6}25 - 0.0055\underline{8}3 = 0.101$ M

$[NO] = 2x = 2 \times 5.5\underline{8}3 \times 10^{-3}$ M $= 0.0112$ M

Example 4:
Ammonium hydrogen sulfide decomposes at room temperature as shown below:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g) \qquad K_p = 0.108 \text{ at } 25°C$$

A sample of ammonium hydrogen sulfide is placed in a flask at 25°C. After equilibrium has been reached, what is the total pressure of the flask? (Note: solids have no pressure)

$K_p = 0.108 =$

Example 5:
At relatively high temperatures, the following reaction can be used to produce methyl alcohol:

$$CO\ (g) + 2\ H_2\ (g) \rightleftharpoons CH_3OH\ (l) \qquad K_c = 13.5$$

If the concentration of CO at equilibrium were found to be 0.010 M, what would be the equilibrium concentration of H_2?

CALCULATIONS INVOLVING QUADRATIC EQUATIONS

- Some of the problems involving equilibrium involve use of the quadratic equation in order to determine the unknown variable. The example below shown one such problem.

Example 6:

PCl_5 decomposes when heated: $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

If the initial concentration of PCl_5 is 1.00 M, what is the equilibrium composition of the gaseous mixture at 160 °C? K_c at 160 °C is 0.0211

	$PCl_5\,(g) \rightleftharpoons$	$PCl_3\,(g)$ +	$Cl_2\,(g)$
Initial	1.00 M	0	0
Δ	–x	+x	+x
Equilibrium	1.00–x	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(1.00-x)} = 0.0211$$

$$(0.0211)(1.00 - x) = x^2 \qquad 0.0211 - 0.0211\,x = x^2$$

$$\mathbf{x^2 + 0.0211\,x - 0.0211 = 0}$$ ← **Quadratic Equation**

$$ax^2 + bx + c = 0 \qquad x_1, x_2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x^2 + 0.0211\,x - 0.0211 = 0$$

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(-0.0211)}}{2} = \frac{-0.0211 \pm 0.2913}{2}$$

- In theory: There are two mathematical solutions
- In practice: Only one solution makes physical sense

$$x_1 = \frac{-0.0211 + 0.2913}{2} = 0.1351$$

correct

$$x_2 = \frac{-0.0211 - 0.2913}{2} = -0.1562$$

reject
(concentration cannot be negative)

Equilibrium Concentrations are:

$[PCl_5] = 1.00\text{ M} - x = 1.00\text{ M} - 0.1351\text{ M} = 0.86\text{ M}$

$[PCl_3] = [Cl_2] = x = 0.135\text{ M}$

Example 7:
Calculate the composition of the gaseous mixture obtained when 1.25 mol of carbon dioxide is exposed to hot carbon at 800 °C in a 1.25-L vessel. The equilibrium constant K_c at 800 °C is 14.0 for the reaction:

	$CO_2\ (g)$ +	$C\ (s)$ $\rightleftharpoons$	$2\ Cl\ (g)$
Initial			
Δ			
Equilibrium			

$[CO_2] =$

$K_c = 14.0 =$

LE CHATELIER'S PRINCIPLE

- The **effect of changes on the equilibrium** can be predicted using the **Le Chatelier's principle**.

- Le Chatelier's principle states that:
  "If a stress is applied to a system at equilibrium, the system will respond in such a way as to relieve the stress and restore a new equilibrium under a new set of conditions".

- Note sequence of events:
  1. Stress applied
  2. Equilibrium system response (equilibrium shift)
  3. New equilibrium

- Stress is a change in any of the following:
  A) Concentration of Reactants or Products
  B) Pressure
  C) Temperature

A) <u>Effect of Concentration Change on Equilibrium</u>
(Adding or Removing Reactants or Products)

Consider:

$$A + B \rightleftharpoons C + D$$

Stress: B increased to B*

Response:

- Forward reaction speeds up
- Equilibrium shifts to the right
- Products are favored

New Equil.:

$$A' + B' \rightleftharpoons C' + D'$$

A'	B'	C'	D'
decreased	increased	increased	increased
A' < A	B<B'<B*	C'>C	D'>D

EFFECT OF CONCENTRATION CHANGE ON EQUILIBRIUM

In General:

- **Adding Reagent**
  - Equilibrium always shifts in the direction that tends to **reduce** the concentration of the added reacting species.
  - When concentration of **reactant is increased** equilibrium **shifts forward** ($\longrightarrow$)
  - When concentration of **product is increased** equilibrium **shifts reverse** ($\longleftarrow$)
- **Removing Reagent**
  - Equilibrium always shifts in the direction that tends to **increase** the concentration of the removed reacting species.
  - When concentration of **reactant is decreased** equilibrium **shifts reverse** ($\longleftarrow$)
  - When concentration of **product is decreased** equilibrium **shifts forward** ($\longrightarrow$)

Example 1:

	H_2 (g)	+	I_2 (g)	$\rightleftharpoons$	2 HI (g)	(700K)
Starting conc's	1.00 M		1.00 M		0	
Change:	–0.79 M		–0.79 M		+ 1.58 M	
Equil Conc's:	0.21 M		0.21 M		1.58 M	
Stress:			**+ 0.20 M**			

Response: - Equilibrium shifts forward to use up added reactant

	H_2 (g)	+	I_2 (g)	$\rightleftharpoons$	2 HI (g)	(700K)
New Equil. Conc's:	**0.15 M**		**0.35 M**		**1. 70 M**	

0.21M<0.35 M<0.41 M

Example 2:

$Cl_2\,(g)$ + $2\,H_2O\,(l)$ $\rightleftharpoons$ $HOCl\,(aq)$ + $H_3O^+\,(aq)$ + $Cl^-\,(aq)$

Reagent Species	Change in concentration	Equilibrium Shift
Cl_2	increase	
Cl_2	decrease	
H_2O	increase	
H_2O	decrease	
HOCl	increase	
HOCl	decrease	
Cl^-	increase	
Cl^-	decrease	

Example 3:

	CO (g) +	$3\,H_2\,(g)$ $\rightleftharpoons$	$CH_4\,(g)$ +	$H_2O\,(g)$
Molar Equil. Composition:	0.613 mol	1.839 mol	0.387 mol	0.387 mol

What changes in the amount of reagents would produce more CH_4?

- increase amount of CO or H_2
- remove CH_4 or H_2O

- Most practical and least expensive solution is to remove H_2O (cool reaction mixture to condense water vapor)

	CO (g) +	$3\,H_2\,(g)$ $\rightleftharpoons$	$CH_4\,(g)$ +	$H_2O\,(g)$
Molar Equil. Composition:	0.613 mol	1.839 mol	0.387 mol	0.387 mol
Stress:				**– 0.387 mol**
Response:	Equilibrium shifts $\longrightarrow$			
New Equilibrium Composition:	0.491 mol decreased	1.473 mol decreased	0.509 mol increased	0.122 mol decreased

- Equilibrium shift can also be predicted from an evaluation of Q_c (Reaction Quotient)

EFFECT OF PRESSURE CHANGE ON EQUILIBRIUM

- A change in pressure has an effect on equilibrium only when the following two conditions exist:

  1. At least one of the reacting species (reactant or product) is a gas.
  2. Total number of moles of gaseous reactants $\neq$ Total number of moles of gaseous products

- The Pressure of a gas may be:
  - increased by decreasing the volume, at constant temperature (achieved by decreasing the size of the reaction vessel)
  - decreased by increasing the volume, at constant temperature (achieved by increasing the size of the reaction vessel)

- To predict the equilibrium shift caused by a change in pressure, consider the following:

The effect of **increasing the pressure** (decreasing the volume) of the equilibrium system	=	**Increasing the concentration** of gaseous reacting species (reactants and products)

Example 1:
(One reacting species is a gas)

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Stress	**Pressure Change**	**Direction of Equilibrium shift**	**Amounts of Reacting Species**		
			$CaCO_3$	**CaO**	**CO_2**
Decrease in volume	increased	Reverse ($\longleftarrow$) (removes gas)	increased	decreased	decreased
Increase in volume	decreased	Forward ($\longrightarrow$) (adds gas)	decreased	increased	increased

<u>Example 2</u>:
(All reacting species are gases)

- Number of moles of reactants $\neq$ Number of moles of products

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

4 moles **2 moles**

Stress: Pressure is increased (Volume is decreased)

Response: Equilibrium shifts to the side that has the fewer number of moles ($\longrightarrow$)
Reason: Fewer moles of gas will exert less pressure
(provided temperature is constant)

New Equil: $N_2\,(g) \quad + \quad 3\,H_2\,(g) \quad \rightleftarrows \quad 2\,NH_3\,(g)$

decreased decreased increased

Stress	Pressure Change	Direction of Equilibrium shift	Amounts of Reacting Species		
			N_2	H_2	NH_3
Decrease in volume	increased	Forward ($\longrightarrow$) (fewer mol of gas)	decreased	decreased	increased
Increase in volume	decreased	Reverse ($\longleftarrow$) (more mol of gas)	increased	increased	decreased

<u>Example 3</u>: (Some (not all) reacting species are gases)

$$C\,(s) \quad + \quad 1\,CO_2\,(g) \quad \rightleftarrows \quad 2\,CO\,(g)$$

Stress	Pressure Change	Direction of Equilibrium shift	Amounts of Reacting Species		
			C	CO_2	CO
Decrease in volume					
Increase in volume					

Example 4: (Evaluating Q_c to predict Equilibrium Shift)

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

4 moles **2 moles**

Stress: Equilibrium mixture is compressed to half its volume, at constant temperature

Pressure Change: Pressure is doubled

Result: Partial pressure of all gaseous reactants (concentrations) are doubled

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \qquad Q_c = \frac{(2[CH_4])(2[H_2O])}{(2[CO])(2[H_2])^3}$$

$$Q_c = \frac{4[CH_4][H_2O]}{16[CO][H_2]^3} \qquad Q_c = \frac{K_c}{4}$$

$Q_c < K_c$

- Reaction proceeds in the forward direction
- Equilibrium shifts $\longrightarrow$
- Products are favored

CONCLUSIONS:

At constant temperature:

1. If the pressure is increased (Volume is decreased), the reaction shifts in the direction of fewer moles of gas
2. If the pressure is decreased (Volume is increased), the reaction shifts in the direction of more moles of gas.

EFFECT OF TEMPERATURE CHANGE ON EQUILIBRIUM

1. <u>Effect on Rates of Reactions</u>

An increase in temperature:

- increases the rate of both forward and reverse reactions
- causes the system to reach equilibrium faster

2. <u>Effect on Equilibrium</u>

- Depends on the type of reaction (exothermic or endothermic)

$$N_2(g) + 3\,H_2 \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -91.8\text{ kJ}$$

Meaning:

$$N_2(g) + 3\,H_2 \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 2\,NH_3(g) + 91.8\text{ kJ}$$

- An **increase in temperature** favors the **endothermic** reaction ($\longleftarrow$)
  Reason:
  - the endothermic reaction absorbs heat and thus lowers the temperature
  - decreases K_c of the equilibrium system

- A **decrease in temperature** favors the **exothermic** reaction ($\longrightarrow$)
  Reason:
  - the exothermic reaction gives off heat and thus increases the temperature
  - increases K_c of the equilibrium system

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -91.8\text{ kJ}$$

Stress	Equilibrium Shift	Amounts of Reacting Species			K_c
		N_2	H_2	NH_3	
Increase in temp. (Heat added)	$\longleftarrow$	increased	increased	decreased	decreased
Decrease in temp. (Heat removed)	$\longrightarrow$	decreased	decreased	increased	increased

<u>CONCLUSIONS:</u>

1. <u>Equilibrium Shift with Temperature Change</u>
   In order to increase the amount of products obtained:
   (a) the temperature must be increased if the reaction is endothermic ($\Delta H^0 > 0$)
   (b) the temperature must be decreased if the reaction is exothermic ($\Delta H^0 < 0$)

2. <u>Effect of Temperature on Kc</u>
   If the amount of products is to be increased, K_c should also increase:
   (a) For an endothermic reaction, K_c is larger at higher temperatures
   (b) For an exothermic reaction, K_c is larger at lower temperatures.

EFFECT OF CATALYS ON EQUILIBRIUM

- A catalyst is a substance that increases the rate of a reaction but is not consumed by it.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \qquad K_c = 1.7 \times 10^{26}$$

- K_c is very large, therefore the reaction should go almost to completion.
- However, both forward and reverse reactions are very slow (if un-catalyzed) and it takes a very long time to reach equilibrium with very little SO_3 obtained in a reasonable amount of time.
- The use of a Pt catalyst speeds up both forward and reverse reactions and as a result equilibrium is reached fast.
- The equilibrium mixture contains mostly SO_3 due to the large K_c.

<u>A CATALYST</u>:

1. Has no effect on the equilibrium composition
2. Speeds up the attainment of equilibrium
3. Is very useful for reactions:
   - that are slow, if un-catalyzed
   - that have a large K_c,
4. Is not useful for reactions with a small K_c
5. May have an effect on the amount of product obtained if it affects the rate of one reaction out of several possible reactions:

   - **GOAL**: production of NO (used to obtain HNO_3) by the oxidation of NH_3

(a) $4\ NH_3(g) + \cancel{5}\ O_2(g) \rightleftharpoons \cancel{4\ NO} + 6\ H_2O(g)$ Large K_c (slow)

(b) $\cancel{4NO} \rightleftharpoons 2\ N_2(g) + \cancel{2\ O_2(g)}$ Large K_c (slow)

Overall: $4\ NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6\ H_2O(g)$

NOTE: No NO is produced

SOLUTION:

- Use of a Pt catalyst speeds up reaction (a) but not reaction (b).
- Therefore use of Pt catalyst at moderate temperatures produces NO selectively, since decomposition of NO is too slow at these temperatures to be significant.

RESULT:

Equilibrium mixture will contain mostly NO