

# Equilibrium In Chemical Reactions

## Section A

Chemical reactions which take place in both directions are called reversible reactions. An equilibrium is a state in which all change has ceased (static) or all change APPEARS to have ceased (dynamic).

An example of static equilibrium is a book resting on a table. Its weight (down) is balanced by the reaction force supplied by the table (up).

We are concerned with **DYNAMIC EQUILIBRIA** in chemical reactions and phase changes, in fact the forward and reverse reaction are still taking place. Since the rates of the forward and reverse reactions are equal, the concentration of each species remains constant.

In dynamic equilibria, the **macroscopic properties** such as pressure and temperature **do not change**.

The “**microscopic**” changes are always occurring in dynamic equilibria. At the **molecular and ionic level, changes are always taking place**.

The reaction has ‘stopped’ short of completion, chemical equilibrium is the state where the concentrations of all reactants remain constant with time.

The following is an example of “**STEADY STATE**”. Standing on the shore of a lake for five days; and it appears as if there is no change in the level of the water, one could assume that it was a static (stopped) equilibrium. Standing by the lake’s outlet river, one would observe the dynamic nature of the lake’s water level. (The inlet river’s flow at the same rate).

## Types of Equilibrium System

### 1. Physical Processes

- pure solid / pure vapour equilibrium
- pure solid / pure liquid
- pure solid in contact with a solution
- pure liquid / pure vapour
- pure solute distributed between two solvents which are immiscible (i.e do not mix, eg oil and water)

### 2. Chemical Processes

- acid / base equilibria
- redox equilibria
- solubility product equilibria
- complex ion formation

## Classification of Different Equilibria

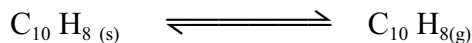
- Homogeneous equilibria: consists of one phase
- Heterogeneous equilibria: consists of more than one phase.

# PHASE CHANGE AND THE SOLUTE-SOLUTION EQUILIBRIA

## Section B

(a) **Sublimation** (Direct change from solid state to gas state)

Naphthalene,  $C_{10}H_8$  is a solid used in solid air fresheners and mothballs, it will “disappear” if left in the open. However, if a moth ball is placed in a closed jar, it will reach an equilibrium between the sublimation and the solid condensation (frosting)



The mass of the solid naphthalene remains the same after equilibrium has been reached.

(b) **Liquid – Vapor Equilibrium**

The vapor pressure of a liquid is the pressure exerted by the vapor molecules of that liquid in a closed container at a given temperature.

Equilibrium vapor pressure of a liquid in an evacuated closed flask is reached and then remains constant for that temperature.

*Note:* the vapor pressure for a given temperature can approach equilibrium from a pressure above or below the equilibrium pressure for that temperature .i.e. the vapor pressure of water at 25 °C is a constant 3.2 kPa

If you start at low temperatures, the pressure will increase as the temperature rises until it reaches 3.2 kPa at 25 °C. conversely, if you start at a high temperature, the pressure will decrease to 3.2 kPa as the temperature drops to 25 °C.

The rate of vaporization is equal to the rate of condensation.

i.e. the rate at which the molecules leave the liquid surface is equal to the rate at which they return to the liquid.



(c) **Solute-Solution Equilibrium**

Unsaturated Solution: This is a solution that can dissolve MORE solute at the particular temperature. (solubility is for a given temp.).

Saturated Solution: This is a solution that has reached the limit of solvation.  
NO MORE solute can be dissolved at the temperature.

When an aqueous solution of iodine,  $I_2$ , is shaken with alcohol,  $I_2$  molecules move into the tetrafluorotetrachloroethane, TTE, layer. As the concentration of iodine increases in the TTE layer, the return to the aqueous layer becomes significant. At the point when the  $I_2$  molecules pass between the two layers at an equal rate, at this point - dynamic equilibrium has been achieved- the concentration of iodine in each layer remains constant, the colour of each layer is constant, (the colour of the bottom TTE layer is greater, since  $I_2$  is more soluble in the non-polar solvent, TTE than in the top polar water layer).

More solid iodine added to the iodine/alcohol/water solution will not change the color of the solution but will rest on the bottom of the beaker. This is a SATURATED SOLUTION and an equilibrium exists between dissolving and crystallization.

i.e Rate of solution equals rate of crystallization.

# CHARACTERISTICS OF A SYSTEM AT EQUILIBRIUM

## Section C

- (1) it is a closed system – nothing is added or removed
- (2) pressure is constant
- (3) temperature is constant
- (4) color is constant

i.e. **macroscopic properties are constant**

- (5) equilibrium may be approached from any direction
  - (6) concentrations at equilibrium are constant, (however, not necessarily 50/50)
- i.e. **microscopic properties are continuous**, *there is frantic activity*

**Equilibrium is not static, but is a highly dynamic situation.**

Any chemical reactions carried out in a closed vessel will attain equilibrium. For some reactions the equilibrium position so much favours the products that the reaction appears to have gone to completion. In this case, we say that the equilibrium position for such reactions lies *far to the right, in the direction of the products*. Some reactions occur only to a small extent, the equilibrium position is said to *lie far to the left, in the direction of the reactants*.

## EQUILIBRIUM IN CHEMICAL SYSTEMS

### Section D

A chemical equilibrium is a two-way reaction, consisting of a FORWARD REACTION and a REVERSE REACTION ...



The production of C and D is the forward reaction, the production of A and B is the reverse reaction.

The RATE of the forward reaction is equal to the RATE of the reverse reaction at equilibrium.

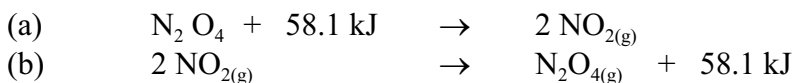
The INITIAL STATE where the rate of the forward reaction is greater than the rate of the reverse reaction is not equilibrium.

This equilibrium can be arrived at from either direction.

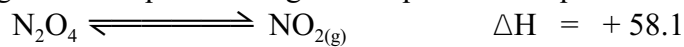
Dinitrogen tetroxide,  $N_2O_4$  is a colorless substance, while nitrogen dioxide,  $NO_2$ , is a red-brown colored substance (gas). They have the same empirical formula.

- if  $N_2O_{4(g)}$ , is heated up from  $0^\circ C$  to  $25^\circ C$ , its color darkens to red-brown.
- $NO_{2(g)}$ , at  $100^\circ C$  is a very dark brown color. As the temperature drops to  $25^\circ C$ , the color lightens.

The darkness of the color indicates the presence of  $NO_2$ .



Combining the two equations we get the equilibrium equation ...



Note: The  $\Delta H$  refers to the forward reaction.

When equilibrium is reached the only thing that has to be equal is that the forward and reverse reaction rates are equal.

The number of moles of product and reactant DO NOT HAVE TO BE EQUAL

## FACTORS THAT ALTER EQUILIBRIUM

(concentration, temperature, and, pressure)

### Section E

#### (i) CONCENTRATION

A change in concentration will move the equilibrium one way or the other, depending on which substance's concentration is changed.

#### (ii) TEMPERATURE

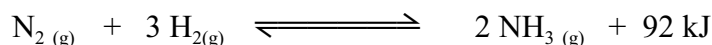
Just as in a one-way reaction, temperature affects the rate of a reaction in the equilibrium system.

All chemical reactions proceed faster at higher temperatures and vice versa.

However, in an equilibrium situation, we are concerned with WHICH of the reactions (forward or reverse) is affected the MOST by a change in temperature.

While both reactions will be speeded up, the ENDOTHERMIC reaction will be affected more at higher temperatures.

Example: The Haber Process (used to produce ammonia)



The forward reaction (production of ammonia) is exothermic. The reverse reaction (decomposition of ammonia) is endothermic.

At equilibrium, the rates of forward and reverse reactions are equal.

At INCREASED TEMPERATURES, both reactions would be speeded up, but the REVERSE reaction would be speeded up to a greater extent since it absorbs heat energy (endothermic)

Therefore, an increase in temperature reduces the amount of ammonia and increases the amount of nitrogen and hydrogen.

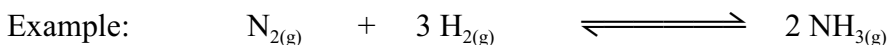
So, to increase the amount of ammonia, cool everything down, right? WRONG!! At low temperatures, NO ammonia is formed!! WHY???

(iii) **PRESSURE** (volume changes, usually)

The effect of pressure is important in the GAS PHASE and it can be *more important than temperature effects where the effects are contrary to each other* (note for tests etc.)

An increase in pressure will affect the equilibrium concentrations. The system will tend to re-adjust if possible, to re-establish the equilibrium.

On the other hand, a decrease in pressure will also upset the equilibrium, and the system will re-establish equilibrium by causing an increase in pressure, if the system allows it.



The way this reaction goes depends on the number of molecules present.

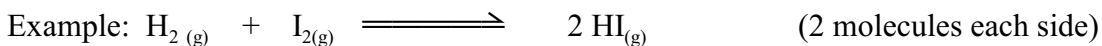
NOTE: SINCE MOLECULES CAUSE PRESSURE, THE MORE MOLECULES, THE HIGHER WILL BE THE PRESSURE AND VICE-VERSA.

If the pressure on the above system is increased, there is an observed increase in the concentration of  $\text{NH}_3$ .

On the other hand, a decrease in pressure leads to an increase in the concentration of  $\text{H}_2$  and  $\text{N}_2$ .

NOTE: the reason pressure is a factor in the above equilibrium system is that there are different numbers of molecules of reactants and products. Since more molecules mean more pressure, the reaction can move left or right depending on condition.

\*\*\*However, when the forward and reverse reactions BOTH result in the same number of molecules, the equilibrium cannot be affected by changes in pressure.\*\*\*



Generally, an **increase in pressure will result in a favoring of the reaction that produces fewer molecules** (lower pressure). Conversely, a decrease in pressure will favor the side with more molecules (high pressure)

#### (iv) THE EFFECT OF A CATALYST

**The addition of a positive (or negative) catalyst will have NO CHANGE in the equilibrium.**

Reason: the addition of a catalyst will reduce the activation energies EQUALLY for the forward and reverse reactions. Thus both forward and reverse reactions will be speeded up by an equal amount, which is really no change.

#### (v) THE EFFECT OF VOLUME CHANGES

When the volume of an equilibrium mixture of gases is reduced, a net reaction occurs in the direction producing fewer moles of gases. Conversely, when the volume is increased, a net reaction occurs in the direction producing more moles of gases.

#### (vi) The effect of adding an inert gas

An inert gas has no effect on an equilibrium condition if the gas is added to a system maintained at constant volume.

# LE CHATERLIER'S PRINCIPLE - Altering Equilibrium Conditions

## Section F

To explain how to predict the changes that occur when a system at equilibrium is disturbed. The principle proposed by Henri Louis Le Chatelier helps us understand **qualitatively** what happens when an equilibrium system is disturbed by various means.

(“if you kick a sleeping dog, he will either (a) move or (b) bite your leg”)

**“if a system is at equilibrium, and that EQUILIBIUM is disturbed (affected by concentration, temperature, or pressure changes) then the system will ADJUST until equilibrium is re-established.”**

(This principle applies to all equilibria, whether chemical, physical, social or political.)

OR **“if an equilibrium is subjected to a change, processes occur that tend to counteract partially the imposed change”**

i.e. in an equilibrium system, if you push one reaction too much, the counter reaction will be favored to some extent.

Equilibrium is a compromise of forward and reverse reactions, of temperature and pressure, of randomness and order. At equilibrium,  $\Delta G = 0$

### Another Aspect of Le Chatelier:

If you remove some product from an equilibrium system, the system will try to produce more of the product. The reverse also applies.

TAKE THE GENERAL EQUILIBRIUM :  $A + B \rightleftharpoons C + D$

The forward reaction can be favored by (a) an increase in the concentration of A and/or B or by (b) a decrease in the concentration of C and/or D.

The effects of temperature are as previously mentioned.

### USE OF THE LE CHATELIER'S PRINCIPLE IN PREDICTING REACTIONS

The following are examples of changes made to establish equilibrium.



**Change:** add  $\text{SCN}^{-1}_{(aq)}$

**Reaction Behavior:** the forward reaction dominates for a while, causing an increase in the concentration of  $\text{FeSCN}^{+2}_{(aq)}$ , and using up some of the  $\text{Fe}^{+3}_{(aq)}$  and  $\text{SCN}^{-1}_{(aq)}$ , ( $\therefore$  observed ... )

**Final Result** (at new equilibrium):

The concentration of  $\text{SCN}^{-1}_{(aq)}$  is lower than the sum or the original concentration plus the added concentration.

The  $\text{Fe}^{+3}_{(aq)}$  is lower than before and the  $\text{FeSCN}^{+2}_{(aq)}$  is higher than before.

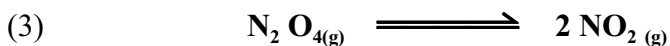


**CHANGE:** add heat energy (raise the temperature)

REACTION BEHAVIOR: the color of the gas darkens. ( $\text{NO}_2$  is brown) some of  $\text{N}_2\text{O}_4$  decomposes to produce  $\text{NO}_2$  absorbing energy.

FINAL RESULT (at new equilibrium)

The temperature is lower than expected from such an addition of energy. (note: heating a non-reactive gas causes an increase in temperature- faster molecules, but heating a reactive gas undergoing an ENDOTHERMIC REACTION does not cause as much of an increase in temperature since energy is absorbed by the reaction).

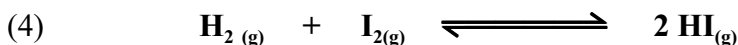


**CHANGE:** INCREASE IN PRESSURE, by reducing volume

REACTION BEHAVIOR: color darkens(a shift to the right). This is caused by the increase in concentration of the dark  $\text{NO}_2$ . Increased pressure also results in an increase in temperature which favors the forward reaction (example (2) above)

FINAL RESULT: (at new Equilibrium)

Pressure is lower than expected from the volume change and the color is lighter than it was at the beginning of the change. Reason: the back reaction occurred to some extent to reduce the pressure.



**CHANGE:** increase pressure, by decreasing the volume

REACTION BEHAVIOR: both rates increase equally because of the increased concentration. The total number of molecules is constant.

FINAL RESULT (at a new equilibrium)

The pressure is what you would expect from such a volume change

(5) **Any reaction at equilibrium**

**CHANGE:** Add a catalyst

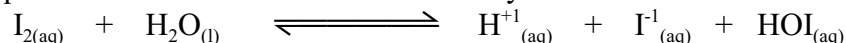
REACTION BEHAVIOR: equilibrium state remains the same, but it is reached more rapidly.

FINAL RESULT: (at New Equilibrium)

A catalyst does NOT affect equilibrium concentration, since it speeds up the forward and reverse reactions by the same amount.

### Assignment

A dilute aqueous solution of iodine is continuously stirred ...



The solution has a light brown colour due to the reactants, as the products are essentially colourless. Deduce the colour change that would occur upon the addition of a few drops of concentrated solutions of the following to separate samples of the aqueous solutions of iodine. Justify your response in each case.

i)  $\text{HCl}$     ii)  $\text{NaOH}$     iii)  $\text{KI}_{(aq)}$     iv)  $\text{NaOI}_{(aq)}$

## QUANTITATIVE ASPECTS OF EQUILIBRIUM: The Equilibrium Law

### Section G

Law of Mass Action states that a rate of reaction is proportional to the concentration of the reactants.

For:  $w A + x B \rightleftharpoons y C + z D$   
the rate of the forward reaction, Rate(f), is written as:

$$\text{Rate(f)} = k_f [A]^w [B]^x$$

Similarly, the rate expression for the reverse reaction, Rate(r) can be written as:

$$\text{Rate(r)} = k_r [C]^y [D]^z$$

At equilibrium, the rate of the forward and reverse reactions are equal . . .

$$\text{Rate(f)} = \text{Rate(r)}$$

Equating the two rates we get:

$$k_f [A]^w [B]^x = k_r [C]^y [D]^z$$

$$\frac{k_f}{k_r} = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

$$\frac{k_f}{k_r} = K_c = \frac{[C]^y [D]^z}{[A]^w [B]^x} = \text{Equilibrium Constant Expression} \\ = \text{Equilibrium Constant, } K_c \\ = \text{Equilibrium Law}$$

**The Equilibrium Constant ( $K_c$ )**, or the Equilibrium Law, expressed in terms of concentrations (as molarities), sometimes written as  $K$  or  $K_{eq}$ , can be stated as follows:

"If a reversible reaction is allowed to reach equilibrium, then the product of the concentrations of the products, (raised to the appropriate powers), divided by the product of the concentrations of the reactants, (raised to the appropriate powers), has a constant value at a particular temperature."

(The 'appropriate power' is the coefficient of that substance in the stoichiometric equation for the reaction.)

Summary:

1. It is a constant for an equilibrium system at a given temperature, refers only to one particular temperature.
2. The form of the equilibrium law expression (and therefore the value of  $K_c$ ) depends on the way the equation is written.
3. The units of  $K_c$  vary from one equilibrium to another.



## INTERPRETATIONS OF THE K<sub>c</sub> VALUES

- (1) large K value means that products (forwards reaction) predominate
- (2) small K value means that reactants (reverse reaction) predominates (or the forwards reaction may not take place readily)
- (3) Generally, intermediate values (from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{+2}$ ) indicate a readily reversible reaction

**Solids and liquids** are not included in the equilibrium expression and in calculation of the equilibrium constant, K<sub>c</sub>. Only (g) and (aq).

**REASON:** solids and liquids do not vary in concentration. (e.g. a precipitate has zero concentration in mol dm<sup>-3</sup>, it is not dissolved)

**Equilibrium Constant values vary with temperature only**, they do not vary with changes in concentrations of the reactants or products, and they do not vary with changes in pressure.

If  $\Delta H^0_{\text{rxn}}$  is positive, i.e. an endothermic reaction, then K<sub>c</sub> will increase as temperature of the system increases (because ... ?)

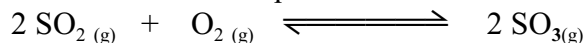
If  $\Delta H^0_{\text{rxn}}$  is negative, i.e. an exothermic reaction, then K<sub>c</sub> will decrease as temperature of the system increases (because ... ?)

## Writing Equilibrium Constant Expressions

I. Write K<sub>c</sub> expressions for the following reactions:

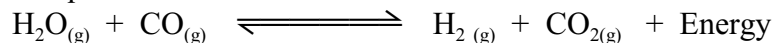
1.  $\text{N}_{2(\text{g})} + 3 \text{H}_{2(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$
2.  $\text{AgCl}_{(\text{s})} \rightleftharpoons \text{Ag}^{+1}_{(\text{aq})} + \text{Cl}^{-1}_{(\text{aq})}$
3.  $\text{CaCO}_{3(\text{s})} \rightleftharpoons \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$
4.  $\text{Cu}(\text{NH}_3)_4^{+2}_{(\text{aq})} \rightleftharpoons \text{Cu}^{+2}_{(\text{aq})} + 4 \text{NH}_{3(\text{aq})}$
5.  $\text{Pb}^{+2}_{(\text{aq})} + 2 \text{Cl}^{-1}_{(\text{aq})} \rightleftharpoons \text{PbCl}_{2(\text{s})}$
6.  $\text{C}_{(\text{s})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightleftharpoons \text{CO}_{(\text{g})}$
7.  $\text{Mn}^{+2}_{(\text{aq})} + \text{H}_2\text{S}_{(\text{aq})} \rightleftharpoons \text{MnS}_{(\text{s})} + 2 \text{H}^{+1}_{(\text{aq})}$
8.  $2 \text{Cr}^{+3}_{(\text{aq})} + \text{Fe}_{(\text{s})} \rightleftharpoons 2 \text{Cr}^{+2}_{(\text{aq})} + \text{Fe}^{+2}_{(\text{aq})}$

II. The Contact process involves the equilibrium:



- a) Write an expression for K<sub>c</sub>
- b) Explain why industrial plants operate at pressures of around 2 atm (> 200 kPa).

III. Study the equilibrium:

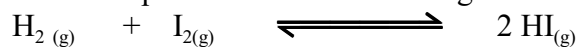


- a) Write an expression for K<sub>c</sub>
- b) Would you expect an increase in total pressure to affect the yield of hydrogen? Explain your answer.
- c) would you expect the numerical value of K<sub>c</sub> to decrease, increase, or remain unchanged if the temperature of the system was increased. Explain your answer.

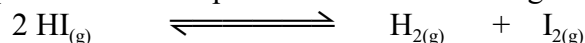
# Manipulating Equilibrium Constant Expressions

## Section H

Write the equilibrium law expression for the following reaction ...



Now, write the equilibrium law expression for the following reaction ...



What can you deduce???

Really Cool Eh!!!

As can be seen from the above, **the equilibrium constant for a reaction and its reverse reaction are always the reciprocal of one another.**

$$K_{\text{new}} = \frac{1}{K_{\text{old}}} \quad (\text{Or: } K_2 = K_1^{-1})$$

Also, in general when the stoichiometric coefficients of a balanced equation are **multiplied by some factor 'n'**, then the equilibrium constant for the new equation,  $k$  (new) is the  $k$  (old) raised to the power of the multiplication factor, 'n' ...

$$K_{\text{new}} = (K_{\text{old}})^n$$

When **adding equations** two or more equations, then ...

$$K_{\text{new}} = K_1 \cdot K_2 \cdot K_3 \dots$$

When **subtracting** two equations, then ...

$$K_{\text{new}} = \frac{K_1}{K_2}$$

When **dividing** an equation by a factor 'n', then ...

$$K_{\text{new}} = \frac{1}{\sqrt[n]{K_{\text{old}}}}$$

For **gases**:

$$K_p = K_c (RT)^{\Delta n_{(\text{gas})}} \quad (\text{What is } K_p?)$$

where:  $R =$   $T =$

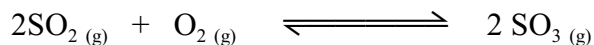
$\Delta n_{(\text{gas})} =$  difference in the stoichiometric coefficients of gaseous products and reactants

$\Delta n_{(\text{gas})} = 0$ , then  $K_p = K_c (RT)^0$ , since any number raised to the zero power equals 1, thus  $K_p = K_c$

# Sample Calculations involving the Equilibrium Constant, $K_c$

## Section I

### Type 1: where the equilibrium concentrations are given



The equilibrium concentrations are as follows:

$$[\text{SO}_2] = 1.2 \text{ mol dm}^{-3}, \quad [\text{O}_2] = 1.0 \text{ mol dm}^{-3}, \quad [\text{SO}_3] = 0.8 \text{ mol dm}^{-3}$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

### Type 2: where the equilibrium concentrations have to be calculated before obtaining the K value

*See the attached sheet (page 13), on how to prepare an ICE CHART*

**NOTE:** concentrations are expressed in  $\text{mol dm}^{-3}$ . Always, divide the number of moles by the total volume unless the volume of the container is one decimeter, (litre).

For gaseous reactions and reactions in solutions: if the equation shows equal numbers of molecules on both sides, then the equilibrium law expression is independent of the volume, and  $K_c$  is unitless.

**Example:**  $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2(\text{g})$   
6.00 moles of HCl and 2 moles of  $\text{O}_2$  are placed in a 1.00 litre container and allowed to react for 2.00 hours. (A closed container). When equilibrium is established, 2.40 moles of  $\text{H}_2\text{O}(\text{g})$  were present.

Calculate the equilibrium constant,  $K_c$ , for this reaction at this temperature (temperature is kept constant).

Since the volume is 1 litre, the concentrations are as given.

Initial concentration	6.0	2.0	0.0	0.0
	- 4x	- x	+ 2x	+ 2x
Increase or Decrease	-4.8	-1.2	+ 2.4	+2.4
Equilibrium Concentration ( $\text{mol dm}^{-3}$ )	1.2	0.8	2.4	2.4

$$K_c = \frac{[\text{H}_2\text{O}]^2 [\text{Cl}_2]^2}{[\text{HCl}]^4 [\text{O}_2]} = \frac{[2.4]^2 [2.4]^2}{[1.2]^4 [0.8]} = 20.0 \quad (\text{Units } \dots???)$$

- What information may be deduced from the numerical value of the equilibrium constant,  $K_c$ , obtained above?
- If the above reaction is determined to be exothermic, will the numerical value of  $K_c$ , increase, decrease, or remain constant if the temperature of the system is increased?
- What is the numerical value of the equilibrium constant for the reverse reaction?

**Type 3: where both products and reactants are present initially, and the volume of the container is not one litre.**

**Example (a):**  $2\text{NO}_{(g)} + \text{Br}_2 \rightleftharpoons 2\text{NOBr}_{(g)}$   
 6.00 moles of NO, 5.00 moles of Br<sub>2</sub> and 1.00 moles of NOBr are placed in a 10 litre container and sealed. They are allowed to react at a certain temperature. After a while, equilibrium is attained and it is found that there are 5.00 moles of NOBr are present. What is the numerical value of the equilibrium constant, K<sub>c</sub>?

First: divide all the mole quantities by 10 to obtain the concentration in mol dm<sup>-3</sup>

	$2\text{NO}_{(g)}$	+	$\text{Br}_2$	$\rightleftharpoons$	$2\text{NOBr}_{(g)}$	
Initial Conc.	0.6		0.5		0.1	mol dm <sup>-3</sup>
Change(Δ)	-2x -0.4		-x -0.2		+2x +0.4	mol dm <sup>-3</sup>
Equil. Conc.	0.2		0.3		0.5	mol dm <sup>-3</sup>

$$K_c = \frac{[\text{NOBr}]^2}{[\text{NO}]^2 [\text{Br}_2]} = \frac{[0.5]^2}{[0.2]^2 [0.3]} = 20.8 \quad (\text{Units ???})$$

**Example (b):**  $2\text{A} + 3\text{B} \rightleftharpoons 4\text{C} + 5\text{F}$   
 If there are 10.0 mol of A, 20.0 mol of B in a 5.00 L container at 500 K, and at equilibrium [F] = 0.800 mol dm<sup>-3</sup>. Calculate K<sub>c</sub> at 500 K.  
 (Answer: 3.45 x 10<sup>-4</sup> M<sup>4</sup>)

**Example (c):**  $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$   
 When 2.00 mol each of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH are all allowed to react at 100 °C in a sealed container. At equilibrium 2/3 mol of each reactant remains. Calculate K<sub>c</sub>.  
 (Answer: 4)

**Example (d):**  $\text{S}_2\text{Cl}_{4(g)} \rightleftharpoons 2\text{SCl}_{2(g)}$   
 4.21 mol of S<sub>2</sub>Cl<sub>4(g)</sub> are introduced into a 2 dm<sup>3</sup> vessel, and the reaction is allowed to attain equilibrium, 1.25 mol of S<sub>2</sub>Cl<sub>4(g)</sub> are found to remain in the container. Calculate K<sub>c</sub>.  
 (Answer: 14.0 mol dm<sup>-3</sup>)

**Example (e):**  $\text{SO}_2\text{Cl}_{2(g)} \rightleftharpoons \text{SO}_{2(g)} + \text{Cl}_{2(g)}$   
 6.75 g of SO<sub>2</sub>Cl<sub>2(g)</sub> was put into a 2.00 dm<sup>3</sup> vessel, the vessel was sealed and its temperature raised to 375 °C. At equilibrium, the vessel contained 0.0345 mol of Cl<sub>2</sub>. Calculate the equilibrium constant for the reaction at 375 °C.  
 (Answer: 0.0386 mol dm<sup>-3</sup>).

**Type 4: the equilibrium concentrations have to be determined given  $K_c$**

At 400 °C,  $K_c = 64$  for the equilibrium: 
$$\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2 \text{HI}_{(g)}$$
If 2.00 mol of  $\text{H}_2$  and 2.00 mol of  $\text{I}_2$  are introduced into an empty 4.00 L flask, find the equilibrium concentration at 400 °C of all the species at equilibrium.

**Type 5: The reaction Quotient, Q: predicting the direction of a net reaction.**

See page:

To calculate the reaction quotient, Q, the initial concentrations and not the equilibrium concentrations of reactants and products are used, and if ...

**Q <  $K_c$  the reaction will proceed in the direction of the products**

**Q >  $K_c$  the reaction will proceed in the direction of the reactants**

**Q =  $K_c$  the reaction is at equilibrium, ∴ no change.**

**Example (a):** 
$$2 \text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2 \text{SO}_{3(g)}$$

At 700 K, the above reaction has an equilibrium constant,  $K_c = 4.30 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ , and the following concentrations are present:

$[\text{SO}_2] = 0.010 \text{ mol dm}^{-3}$      $[\text{O}_2] = 0.010 \text{ mol dm}^{-3}$      $[\text{SO}_3] = 10.0 \text{ mol dm}^{-3}$

Is the mixture at equilibrium?

If not, in which direction, left to right, or right to left will reaction occur to reach equilibrium?

(Answer: No, right  $\longrightarrow$  left)

**Example (b):** For the reaction: 
$$\text{PCl}_{3(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{PCl}_{5(g)} \quad K_c = 24.3$$

A system is prepared with:

$[\text{PCl}_3] = 0.10 \text{ mol dm}^{-3}$ ,     $[\text{Cl}_2] = 0.15 \text{ mol dm}^{-3}$ ,     $[\text{PCl}_5] = 0.60 \text{ mol dm}^{-3}$

Is the reaction at equilibrium?

If not, then in which direction will it proceed in order to attain equilibrium?

**Type 6: When the numerical value of  $K_c$  is extremely small**

At 100 °C, the following reaction has an equilibrium constant,  $K_c = 2.20 \times 10^{-10}$  ...

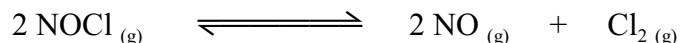


If 1.00 mol of phosgene,  $\text{COCl}_{2(g)}$ , is placed in a 10.0 L flask, calculate the concentration of carbon monoxide at equilibrium.

## CALCULATING $K_c$ FROM EXPERIMENTAL INFORMATION:

### Sample: How to Prepare an ICE Chart:

Calculate the equilibrium constant,  $K_c$ , at 25 °C for the reaction ...



In one experiment, 2.00 moles of NOCl were placed in a 1.00 L flask, and the concentration of NO after equilibrium was attained was 0.66 mol dm<sup>-3</sup>.

Write the expression for  $K_c$  from the balanced chemical equation ...

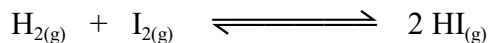
Determine the concentration of each reagent at equilibrium.

Determine  $K_c$  (Answer:  $8.1 \times 10^{-2} \text{ mol dm}^{-3}$ )

Organize the data in a small table

	[NOCl]	[NO]	[Cl <sub>2</sub> ]
<b>Initial concentration</b>			
<b>Change in concentration</b>			
<b>Equilibrium concentration</b>			

### Example 2



When 1.00 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a 1.00 dm<sup>3</sup> flask at 450 °C and  $1.01 \times 10^5 \text{ Nm}^{-2}$ , the amount of hydrogen iodide at equilibrium is 1.56 mol. Calculate  $K_p$  at 450 °C.