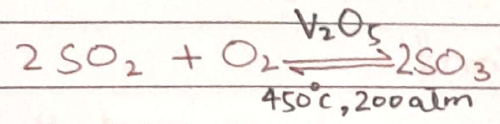


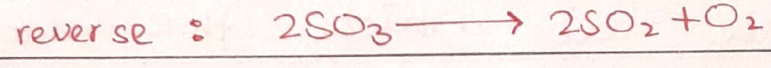
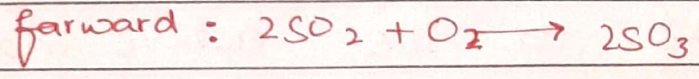
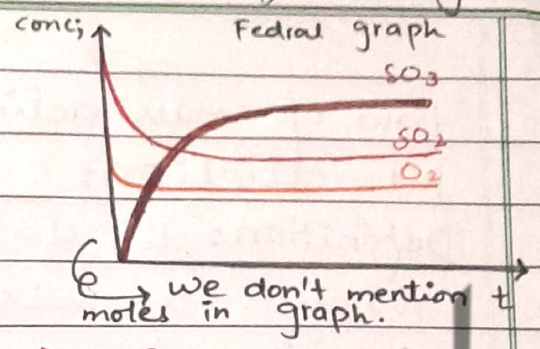
# Chemical Equilibrium

Date 24<sup>th</sup>/Oct/2023.

Day Tuesday.



rate = product / time



Conditions : Temp, Catalyst, Pressure

KPK graph

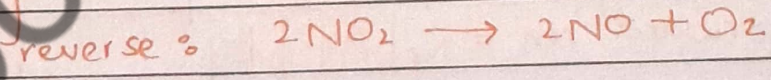
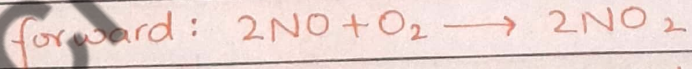
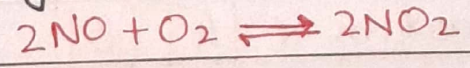
Chemical Equilibrium: "A state of chemical state in which forward and reverse reaction takes place at same rate."



Rate of forward = Rate of Reverse.

Self Assessment

Q write forward and reverse reaction of following expression.



Theoretical Law

"Law of mass action"

Introduction: C.M Guldberg and P.Waage

Definition: "It states that the rate at which a substance react is directly proportional to it's active mass."

The rate at which the reaction proceeds, is directly proportional to the product of active masses of the reactants."

\* Represents the concentration of reactants and products in mol.dm<sup>-3</sup>.

\* -



$$\begin{array}{l} 2 \times 2 = 4 \\ 4 \times 4 = 16 \\ 3 \times 9 = 27 \end{array}$$

Representation: [ ]

Derivation:  $aA + bB \rightleftharpoons cC + dD$

rtn → reaction

Rate of forward rtn  $\propto [A]^a [B]^b$

Rate of forward rtn =  $k_f [A]^a [B]^b$  → (i)

Rate of reverse rtn  $\propto [C]^c [D]^d$

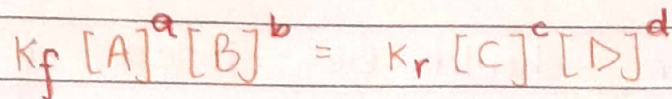
Rate of reverse rtn =  $k_r [C]^c [D]^d$  → (ii)

At equilibrium:

rate of forward rtn = rate of reverse rtn.

Date \_\_\_\_\_

Day \_\_\_\_\_



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

$$\therefore \frac{K_f}{K_r} = K_c$$

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

$$K_c = \frac{[\text{Product}]}{[\text{Reactant}]} \rightarrow \text{Equilibrium constant expression}$$

$K_c \rightarrow K_c$  is the ~~product~~ ratio of product to reactant.

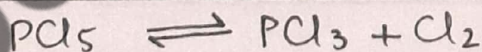


$$K_c = \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$K_c = \frac{[\text{H}_2\text{O}]^2 [\text{Cl}_2]^2}{[\text{HCl}]^4 [\text{O}_2]}$$



$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

# Condition of Equilibrium

Date \_\_\_\_\_

Day \_\_\_\_\_

- i) Container should be closed if any of reactants and products are in gaseous state (Protects for external factors and vaporization).
- ii) Temperature of system should be constant. (Isolated system)
- iii) Pressure of system should be constant.
- iv) Volume of system <sup>should</sup> remain unchanged
- v) Catalyst if used in system remain unchanged
- vi) Conci of reactants and products should remain constant.

## Ways to Recognise Equi

- i) Physical Methods: spectroscopy, Refractometry, polarimetry.
- ii) Chemical Method: titration.

## Equilibrium Constants & unit

$K_c$  may or may not have units. In  $K_c$  expression each reactant and product is shown in square brackets

[ ] which is <sup>no</sup> equal to  $\text{mol}\cdot\text{dm}^{-3}$ .

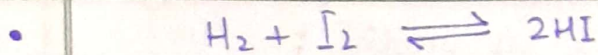
Condition 1: when moles of reactant = mole of product, then  $K_c$  will have no unit.

Mr books & Mr Uniform D.I. Khan

Sign \_\_\_\_\_

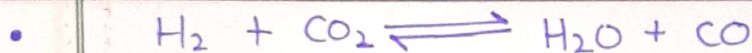
Date \_\_\_\_\_

Day \_\_\_\_\_



$$K_c = \frac{[\text{Product}]}{[\text{Reactant}]}$$

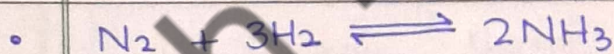
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}]^2}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]} = 1 \text{ No unit.}$$



$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]}$$

$$K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]} = 1 \text{ (No unit)}$$

Condition: 2 when moles of reactant  $\neq$  to moles of product, then  $K_c$  will have unit.



\*  $\rightarrow$  mol. dm<sup>-3</sup>

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$K_c = \frac{[*]^2}{[*][*]^3} = \frac{1}{[*]^2} = \text{mol}^{-2} \cdot \text{dm}^6$$

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Sign \_\_\_\_\_

Date 27/oct/2023.

Importance of  $K_c$ .

Day Friday.

Value of  $K_c$  helps us predict:

## ① Direction of Reaction.

- ratio  $Q_c < K_c$

then  $[R] > [P]$  and it will move in forward directions. When the ratio of product/reactant is less than  $K_c$ . The system is not at Equilibrium and more products are required to reach/acquire equilibrium.

- $Q_c > K_c$   $[R] < [P]$ , reverse.

- $Q_c = K_c$  Equilibrium is attained.

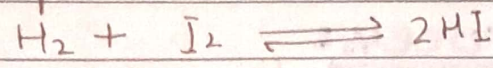
## ② Extent of Chemical Reaction.

- $K_c$  is very small: when value of  $K_c$  is very small/low,  $[R] > [P]$ . Reaction is at initial stage.  $K_c < 1$ . It should proceed more in forward direction.

- $K_c$  is very large: when  $[R] < [P]$ , equilibrium mixture will entirely consist of product and small amount of reactant will be present. This the reaction will now proceed in reverse direction.  $K_c > 1$

- when  $K_c$  is neither large or small: The  $[R] = [P]$ . Equilibrium is maintain  $K_c = 1$

Example 9.3



Given data:

$$[H_2] = 0.04 \text{ mol} \cdot \text{dm}^{-3}$$

$$[I_2] = 0.04 \text{ mol} \cdot \text{dm}^{-3}$$

$$[HI] = 0.08 \text{ mol} \cdot \text{dm}^{-3}$$

Required =  $K_c$

$$\text{Formula: } K_c = \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{Solution: } K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{[0.08]^2}{[0.04][0.04]} = 4$$

Result: So, the value of  $K_c$  is 4.

Example 9.4:



$$\text{Given: } [CO] = 0.0600 \text{ mol} \cdot \text{dm}^{-3}$$

$$[H_2O] = 0.120 \text{ mol} \cdot \text{dm}^{-3}$$

$$[CO_2] = 0.150 \text{ mol} \cdot \text{dm}^{-3}$$

$$[H_2] = 0.300 \text{ mol} \cdot \text{dm}^{-3}$$

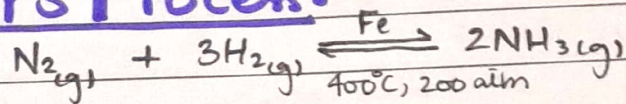
Required:  $K_c$  Formula:  $K_c = \frac{[P]}{[R]}$

$$\text{Solution: } K_c = \frac{[0.150][0.300]}{[0.06][0.12]}$$

$$K_c = 6.25$$

Result: So, the value of  $K_c$  is 6.25.

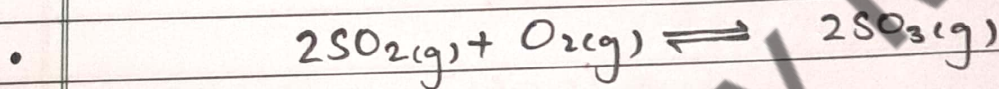
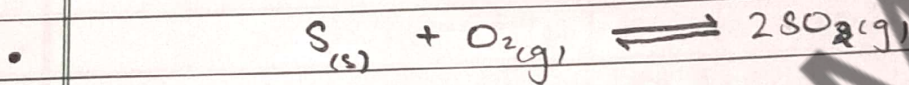
## Haber's Process:



400°C, 200 atm → 33% NH<sub>3</sub>

~~more~~ lower temperature, higher pressure → 98% NH<sub>3</sub>

## Contact Process:

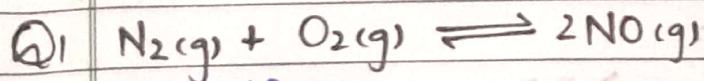


Le-Chatelier's: If you impose a change in concentration, temperature or pressure on a chemical system at equilibrium, the system responds in a way that opposes the change

**Examples:** Haber's process, Contact process.

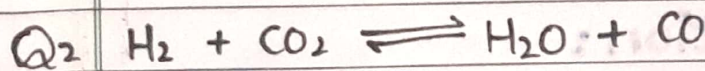


## Self-Assessment Ex : 9.3.



**Solution:**

$$K_c = \frac{[NO]^2}{[N_2][O_2]} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}]^2}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]} \Rightarrow K_c = \text{No unit}$$



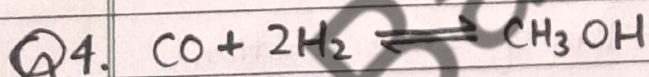
**Solution:**

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]} \Rightarrow K_c = \text{No unit}$$



**Solution:**

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}]} \Rightarrow K_c = \text{mol} \cdot \text{dm}^{-3}$$

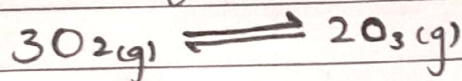


**Solution:**

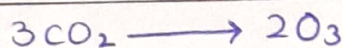
$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]^2} \Rightarrow K_c = \text{dm}^6 \cdot \text{mol}^{-2}$$

## Self Assessment Ex: 9.2

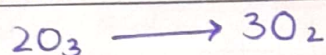
Q1 Derive  $K_c$  of:



**Forward Reaction:**



**Reverse Reaction:**



Rate of Forward Reaction  $\propto [\text{CO}_2]^3$

Rate of Forward Reaction =  $k_f [\text{CO}_2]^3$

Rate of Reverse Reaction  $\propto [\text{O}_3]^2$

Rate of Reverse Reaction =  $k_r [\text{O}_3]^2$

**At Equilibrium:**

Rate of Forward Reaction = Rate of Reverse Reaction

$$k_f [\text{CO}_2]^3 = k_r [\text{O}_3]^2$$

$$\frac{k_f}{k_r} = \frac{[\text{O}_3]^2}{[\text{CO}_2]^3}$$

$$K_c = \frac{[\text{O}_3]^2}{[\text{CO}_2]^3}$$

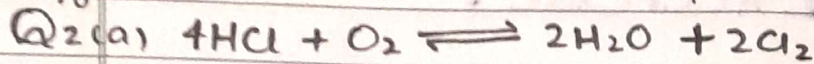
$$\therefore K_c = \frac{k_f}{k_r}$$

Date \_\_\_\_\_

Homework

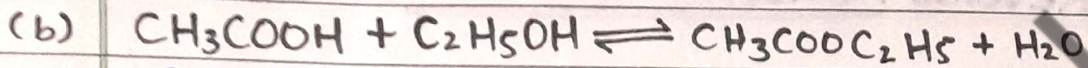
Day \_\_\_\_\_

→ Write  $K_c$ . (Self A. Ex: 9.2)



**Solution:**

$$K_c = \frac{[\text{H}_2\text{O}]^2 [\text{Cl}_2]^2}{[\text{HCl}]^4 [\text{O}_2]}$$



**Solution:**

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}$$



**Solution:**

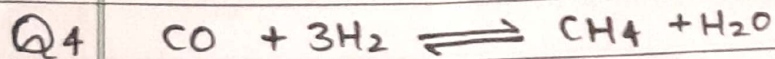
$$K_c = \frac{[\text{H}_2] [\text{F}_2]}{[\text{HF}]^2}$$



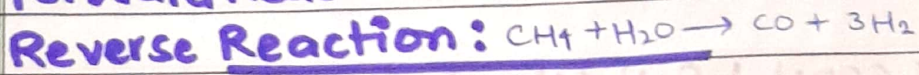
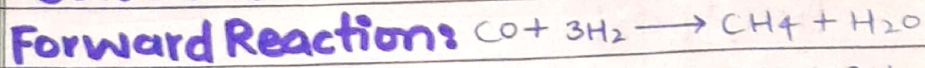
**Solution:**

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

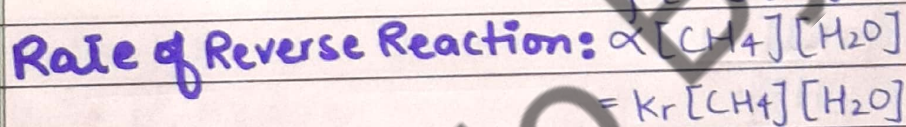
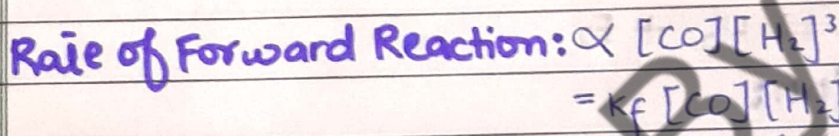
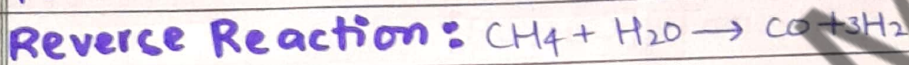
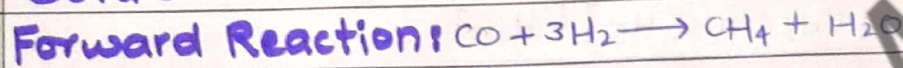
## Review Exercise :



(i) Solution:



(ii) Solution:



### At Equilibrium state:

Rate of Forward Reaction = Rate of Reverse Reaction

$$k_f [\text{CO}][\text{H}_2]^3 = k_r [\text{CH}_4][\text{H}_2\text{O}]$$

$$\frac{k_f}{k_r} = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \quad \therefore K_c = \frac{k_f}{k_r}$$

(iii) Unit of  $K_c$

$$K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}][\text{mol} \cdot \text{dm}^{-3}]^3}$$

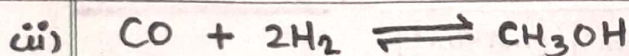
$$K_c = \text{dm}^6 \cdot \text{mol}^{-2}$$

write Equilibrium constant



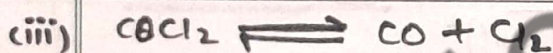
**Solution:**

$$K_c = \frac{[\text{H}_2][\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]}$$



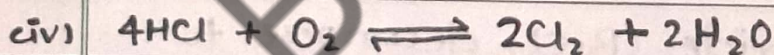
**Solution:**

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$



**Solution:**

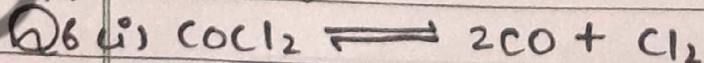
$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$



**Solution:**

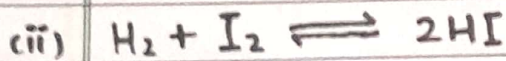
$$K_c = \frac{[\text{Cl}_2]^2[\text{H}_2\text{O}]^2}{[\text{HCl}]^4[\text{O}_2]}$$

units of  $K_c$



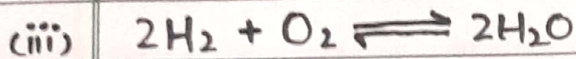
**Solution:**

$$K_c = \frac{[\text{CO}]^2[\text{Cl}_2]}{[\text{COCl}_2]} \Rightarrow K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}]^2 [\text{mol} \cdot \text{dm}^{-3}]}{[\text{mol} \cdot \text{dm}^{-3}]} \Rightarrow K_c = \text{dm}^6 \cdot \text{mol}^{-2}$$



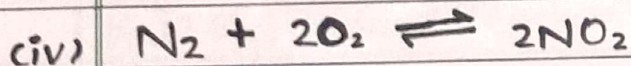
**Solution:**

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \Rightarrow K_c = \frac{[\text{mol}\cdot\text{dm}^{-3}]^2}{[\text{mol}\cdot\text{dm}^{-3}][\text{mol}\cdot\text{dm}^{-3}]} \Rightarrow K_c = \text{No unit.}$$



**Solution:**

$$K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]} \Rightarrow K_c = \frac{[\text{mol}\cdot\text{dm}^{-3}]^2}{[\text{mol}\cdot\text{dm}^{-3}]^2[\text{mol}\cdot\text{dm}^{-3}]} \Rightarrow K_c = \text{dm}^3\cdot\text{mol}^{-1}$$

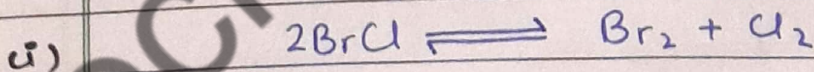


**Solution:**

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} \Rightarrow K_c = \frac{[\text{mol}\cdot\text{dm}^{-3}]^2}{[\text{mol}\cdot\text{dm}^{-3}][\text{mol}\cdot\text{dm}^{-3}]^2} \Rightarrow K_c = \text{dm}^6\cdot\text{mol}^{-2}$$

**“THINK TANK”**

Q1 Bromine chloride (BrCl) decomposes to form chlorine and bromine.



(ii) **Solution:**

$$K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2}$$

(iii)  $K_c = \text{No unit.}$

Q2)

Reactant:  $[N_2O_4]$

Product:  $[NO_2]^2$

Unit:  $K_c = \frac{[\text{mol} \cdot \text{dm}^{-3}]^2}{[\text{mol} \cdot \text{dm}^{-3}]}$

$K_c = \text{mol} \cdot \text{dm}^{-3}$

Q3 The first reaction is an irreversible reaction while the second one is the reversible reaction. Since only reversible reaction goes to completion, that's why in the second reaction, both reactants and products will be found.

Q4 Yes, we can use cobalt chloride ( $\text{CoCl}_2$ ) as an experiment to test for water. In anhydrous state, it is blue but when water is added, it turns pink.

### KPK Board: Practise Problem 9.4:

**Given:**

$$[\text{N}_2] = 6.4 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$$

$$[\text{O}_2] = 1.7 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$$

$$[\text{NO}] = 1.1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$$

**Reaction:**  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$

**Required:**  $K_c = ?$

**Calculation:** 
$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$K_c = \frac{[1.1 \times 10^{-5}]^2}{[6.4 \times 10^{-3}][1.7 \times 10^{-3}]}$$

$$K_c = 1.1121 \times 10^{-5}$$



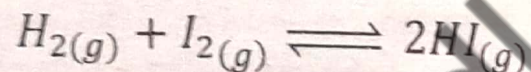


## Review Questions

HW

### 1. Encircle the correct answer.

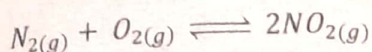
- (i) Which is true about the equilibrium state?
- (a) The forward reaction stops.
  - (b) The reverse reaction stops.
  - (c) Both forward and reverse reactions stop.
  - (d) Both forward and reverse reactions continue at the same rate.
- (ii) When a mixture of  $H_2$  and  $I_2$  is sealed in a flask and temperature is kept at  $25^\circ\text{C}$ , following equilibrium is established.



Which substance or substances will be present in the equilibrium mixture?

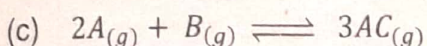
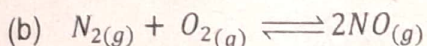
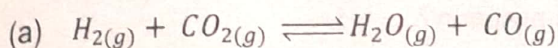
- (a)  $H_2$  and  $I_2$
- (b) HI only
- (c)  $H_2$  only
- (d)  $H_2$ ,  $I_2$  and HI

(iii) What are the units for



- (a)  $\text{mol}\cdot\text{dm}^{-3}$
- (b)  $\text{mol}^2\cdot\text{dm}^{-6}$
- (c)  $\text{dm}^3\cdot\text{mol}^{-1}$
- (d) No units

(iv) Which of the following reaction will not have any units for  $K_c$ ?



(d) All of these

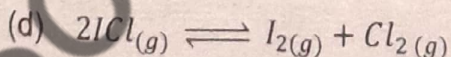
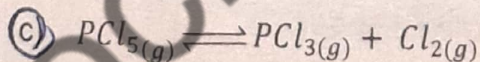
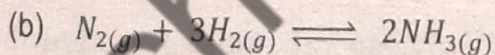
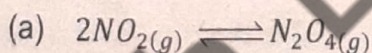
(v) Concentration of reactants and products at equilibrium remains unchanged if

- (a) concentration of any reactant or product is not changed.
- (b) temperature of the reaction is not changed.
- (c) pressure or volume of the system is not changed.
- (d) all of the above are observed

(vi) Which of the following does not happen, when a system is at equilibrium state?

- (a) forward and reverse reactions stop.
- (b) forward and reverse rates become equal.
- (c) concentration of reactants and products stop changing.
- (d) reaction continues to occur in both the directions.

(vii) For which reaction,  $K_c$  has units of  $\text{mol}\cdot\text{dm}^{-3}$ .



(viii) In an irreversible reaction equilibrium is

- (a) established quickly
- (b) established slowly
- (c) never established
- (d) established when reaction stops.



(ix) Active mass means

- (a) total mass of reactants
- (b) total mass of products
- (c) total mass of reactants and products
- (d) mass of substance in moles per  $\text{dm}^3$  in a dilute solution

(x) For a reversible reaction

$$K_c = \frac{[C]^2}{[A][B]}$$

Which substance is product of the reaction?

- (a) A
- (b) B
- (c) Both A and B
- (d) C