



Question 21. Bromine monochloride (BrCl) decomposes into bromine and chlorine and reaches the equilibrium:



The value of K_c is 32 at 500 K. If initially pure BrCl is present at a concentration of $3.3 \times 10^{-3} \text{ mol L}^{-1}$ what is its molar concentration in the mixture at equilibrium?

Answer: Let x moles of BrCl decompose in order to attain the equilibrium. The initial molar concentration and the molar concentration at equilibrium point of different species may be represented as follows:

	$2\text{BrCl}(g)$	\rightleftharpoons	$\text{Br}_2(g)$	$+$	$\text{Cl}_2(g)$
Initial moles/litre	0.0033		0		0
Moles/litre at eqm. point	$0.0033 - x$		$x/2$		$x/2$

$$\text{Applying Law of chemical equilibrium, } K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} \text{ or } 32 = \frac{(x/2) \times (x/2)}{(0.0033 - x)^2}$$

$$\text{On taking the square root, } 5.656 = \frac{x/2}{(0.0033 - x)}$$

$$\frac{x}{(0.0033 - x)} = 11.31 \text{ or } 12.31x = 0.037 ; x = \frac{0.037}{12.31} = 0.003$$

$$\therefore \text{Molar concentration of BrCl at equilibrium point} = 0.0033 - 0.003 = 0.0003 \text{ mol L}^{-1} = 3 \times 10^{-4} \text{ mol L}^{-1}$$

Question 22. At 1127 K and 1 atmosphere pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass.



Calculate K_c for the reaction at the above temperature.

Answer:

Step I: Calculation of K_p for the reaction

Let the total mass of the gaseous mixture = 100 g

Mass of CO in the mixture = 90.55 g

Mass of CO_2 in the mixture = $(100 - 90.55) = 9.45$ g

$$\text{No. of moles of CO} = \frac{90.55 \text{ g}}{(28 \text{ g mol}^{-1})} = 3.234 \text{ mol}$$

$$\text{No. of moles of CO}_2 = \frac{9.45}{(44 \text{ g mol}^{-1})} = 0.215 \text{ mol}$$

$$p_{\text{CO}} \text{ in the mixture} = \frac{(3.234 \text{ mol})}{(3.234 + 0.215)} \times 1 \text{ atm} = \frac{(3.234 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.938 \text{ atm}$$

$$p_{\text{CO}_2} \text{ in the mixture} = \frac{(0.215 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.062 \text{ atm}$$

$$\begin{array}{ccc} \text{Eqm. pressure} & \text{C}(s) + \text{CO}_2(g) & \rightleftharpoons & 2\text{CO}(g) \\ & 0.062 \text{ atm} & & 0.938 \text{ atm} \end{array}$$

$$K_p = \frac{p^2_{\text{CO}}}{p_{\text{CO}_2}} = \frac{(0.938 \text{ atm})^2}{(0.062 \text{ atm})} = 14.19 \text{ atm}$$

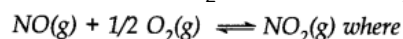
Step II. Calculation of K_c for the reaction.

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}}$$

$$K_p = 14.19 \text{ atm, } R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}, T = 1127 \text{ K; } \Delta n_g = 2 - 1 = 1$$

$$K_c = \frac{(14.19 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (1127 \text{ K})^1} = 6.46$$

Question 23. Calculate (a) ΔG^\ominus and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K



$$\Delta_f G^\ominus (\text{NO}_2) = 52.0 \text{ kJ/mol}, \Delta_f G^\ominus (\text{NO}) = 87.0 \text{ kJ/mol}, \Delta_f G^\ominus (\text{O}_2) = 0 \text{ kJ/mol},$$

Answer:

Step I. Calculation of ΔG^\ominus

$$\begin{aligned} \Delta G^\ominus &= \Delta_f G^\ominus (\text{NO}_2) - [\Delta_f G^\ominus (1/2 \text{O}_2)] \\ &= 52.0 - (87 + 0) = -35 \text{ kJ mol}^{-1} \end{aligned}$$

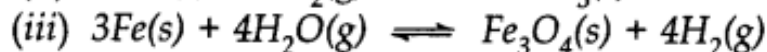
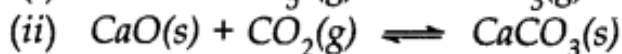
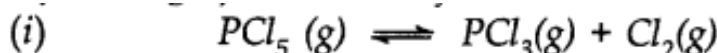
Step II. Calculation of K_c

$$\Delta G^\ominus = -2.303 RT \log K_c$$

$$\log K_c = -\frac{\Delta G^\ominus}{2.303 RT} = -\frac{(-35 \times 10^3 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ kJ mol}^{-1}) \times (298 \text{ K})} = 6.134$$

$$K_c = \text{Antilog } 6.134 = 1.36 \times 10^6.$$

Question 24. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



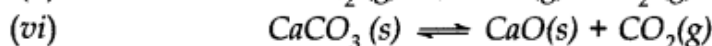
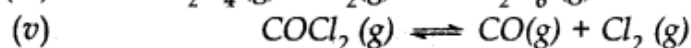
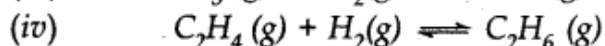
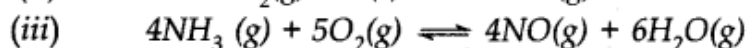
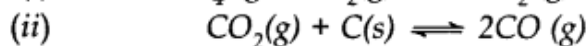
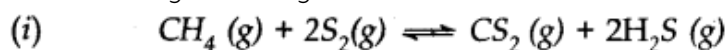
Answer:

(i) Pressure will increase in the forward reaction and number of moles of products will increase.

(ii) Pressure will increase in backward reaction and number of moles of products will decrease.

(iii) The change in pressure will have no effect on the equilibrium constant and there will be no change in the number of moles.

Question 25. Which of the following reactions will get affected by increase in pressure? Also mention whether the change will cause the reaction to go to the right or left direction.



Answer: Only those reactions will be affected by increasing the pressure in which the number of moles of the gaseous reactants and products are different ($n_p \neq n_r$) (gaseous). With the exception of the reaction (1); all the remaining five reactions will get affected by increasing the pressure. In general,

- The reaction will go to the left if $n_p > n_r$.
- The reaction will go to the right if $n_r > n_p$.

Keeping this in mind,

(i) Increase in pressure will not affect equilibrium because $n_p = n_r = 3$.

(ii) Increase in pressure will favour backward reaction because $n_p (2) > n_r (1)$

(iii) Increase in pressure will favour backward reaction because $n_p (10) > n_r (9)$

(iv) Increase in pressure will favour forward reaction because $n_p (1) < n_r (2)$

(v) Increase in pressure will favour backward reaction because $n_p (2) > n_r (1)$

(vi) Increase in pressure will favour backward reaction because

$$\eta_p(1) > \eta_r(0).$$

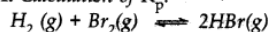
Question 26. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.



Ans.

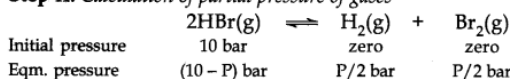
Step I. Calculation of K_p .



$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^0 \quad (\because \Delta n = 2 - 2 = \text{zero})$$

$$K_p = K_c = 1.6 \times 10^5.$$

Step II. Calculation of partial pressure of gases



$$K_p' = \frac{p_{H_2} \times p_{Br_2}}{p_{HBr}^2} \text{ or } \frac{1}{1.6 \times 10^5} = \frac{P/2 \times P/2}{(10 - P)^2} = \frac{P^2}{4(10 - P)^2}$$

$$\text{On taking square root; } \frac{P^2}{4(10 - P)^2} = \left(\frac{1}{1.6 \times 10^5} \right)^{1/2} \text{ or } \frac{2(10 - P)}{P} = (1.6 \times 10^5)^{1/2}$$

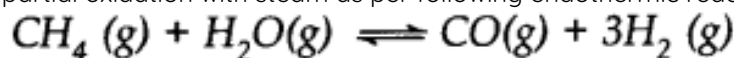
$$= 4 \times 10^2$$

$$20 - 2P = 4 \times 10^2 P \text{ or } P(4 \times 10^2 + 2) = 20$$

$$\text{or } P = \frac{20}{(400 + 2)} = \frac{20}{402} = 0.050 \text{ bar}$$

$$p_{H_2} = 0.025 \text{ bar; } p_{Br_2} = 0.025 \text{ bar; } p_{HBr} = 10 - 0.05 = 9.95 \text{ bar} \approx 10.0 \text{ bar.}$$

Question 27. Hydrogen gas is obtained from the natural gas by partial oxidation with steam as per following endothermic reaction:



Write the expression for K_p for the above reaction

How will the value of K_p and composition of equilibrium mixture be affected by:

- (i) increasing the pressure,
- (ii) increasing the temperature,
- (iii) using a catalyst?

Answer: The expression for K_p for the reaction is:

$$K_p = \frac{(p_{CO}) \times (p_{H_2})^3}{(p_{CH_4}) \times (p_{H_2O})}$$

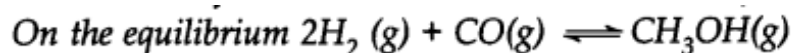
(i) By increasing the pressure, the number of moles per unit volume will increase. In order to decrease the same, the equilibrium gets shifted to the left or in the backward direction. As a result, more of reactants will be formed and the value of K_p will decrease.

(ii) If the temperature is increased, according to Le Chatelier's principle, the forward reaction will be favoured as it is endothermic. Therefore, the equilibrium gets shifted to the right and the value of K_p will increase.

(iii) The addition of catalyst will not change the equilibrium since it influences both the forward and the backward reactions to the same extent. But it will be attained more quickly.

Question 28. What is the effect of:

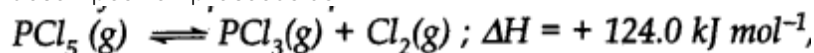
- (i) addition of H_2
- (ii) addition of CH_3OH
- (iii) removal of CO
- (iv) removal of CH_3OH



Answer:

- (i) Equilibrium will be shifted in the forward direction.
- (ii) Equilibrium will be shifted in the backward direction.
- (iii) Equilibrium will be shifted in the backward direction.
- (iv) Equilibrium will be shifted in the forward direction.

Question 29. At 473 K, the equilibrium constant K_c for the decomposition of phosphorus pentachloride (PCl_5) is 8.3×10^{-3} . if decomposition proceeds as:



- (a) Write an expression for K_c for the reaction
- (b) What is the value of K_c for the reverse reaction at the same temperature.
- (c) What would be the effect on K_c if
 - (i) More of PCl_5 is added
 - (ii) Temperature is increased.

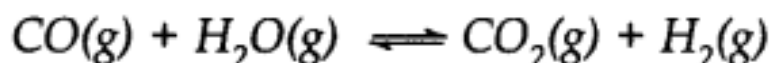
Answer:

(a) The expression for $K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

(b) For reverse reaction (K_c') = $\frac{PCl_5(g)}{[PCl_3(g)][Cl_2(g)]} = \frac{1}{8.3 \times 10^{-3}} = 120.48$

- (c) (i) By adding more of PCl_5 , value of K_c will remain constant because there is no change in temperature.
- (ii) By increasing the temperature, the forward reaction will be favoured since it is endothermic in nature. Therefore, the value of equilibrium constant will increase.

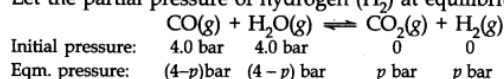
Question 30. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2 . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam so that $P_{CO} = P_{H_2O} = 4.0 \text{ bar}$, what will be the partial pressure of H_2 at equilibrium? $K_p = 0.1$ at 400°C .

Answer:

Let the partial pressure of hydrogen (H_2) at equilibrium point = $p \text{ bar}$



$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \text{ or } 0.1 = \frac{(p \text{ bar}) \times (p \text{ bar})}{(4-p) \text{ bar} \times (4-p) \text{ bar}}$

$\frac{p^2}{(4-p)^2} = 0.1 \text{ or } \frac{p}{(4-p)} = (0.1)^{1/2} = 0.316$

$p = 0.316 (4-p) \text{ or } p = 1.264 - 0.316 p$

$1.316 p = 1.264 \text{ or } p = \frac{1.264}{1.316} = 0.96 \text{ bar}$

***** END *****