CHEMICAL EQUILIBRIUM

PROBLEM 335 An equilibrium mixture of:

 $\operatorname{XeF}_{2}(g) + \operatorname{OF}_{2}(g) \rightleftharpoons \operatorname{XeOF}_{2}(g) + \operatorname{F}_{2}(g)$

was found to contain 0.6 mole of $XeF_2(g)$, 0.3 mole of $OF_2(g)$, 0.1 mole of $XeOF_2(g)$ and 0.4 mole of F_2 in a one litre container. How many moles of OF_2 must be added to increase [XeOF₂] to 0.2 M?

PROBLEM 336 A compound HB is formed from H and B according to the following reaction: H + B \rightleftharpoons HB. A solution was prepared by dissolving 0.1 mole of H and 0.1 mole of B in enough water to make the total volume equal to one litre. After equilibrium had been reached, it was found that 20% of H had been reacted. What are the equilibrium concentration of H, B and HB? What is the equilibrium constant, K_c for this reaction?

PROBLEM 337 2.0 g of ammonium chloride was heated in a one litre flask to 300°C. From the measurement of pressure, it was found that 98% of ammonium chloride was dissociated. If to this flask 2.0g of dry ammonia was added, what would be the percentage dissociation?

PROBLEM 338 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If the system is equilibrated at $[H_2] = 0.5$, $[I_2] = 0.5$ and [HI] = 1.23 in a one litre flask and suddenly 0.6 mole of HI is removed, what will be the new equilibrium composition when the equilibrium is re-established?

PROBLEM 339 The equilibrium constant K_p for the gas phase decomposition of *ter*-butyl chloride is 3.45 at 500 K:

$$(CH_3)_3CCl(g) \rightleftharpoons (CH_3)_2C = CH_2(g) + HCl(g)$$

Calculate molar concentration of reactants and products in the equilibrium mixture obtained by heating 1.0 mole of *ter*-butyl chloride in a 5.0 L container at 500 K.

PROBLEM 340 A 79.2 g chunk of dry ice and 30 g of graphite were placed in an empty 5.0 L container, and the mixture was heated to achieve equilibrium. The reaction is:

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

What is the value of K_p at 1000 K if the gas density at this temperature is 16.3 g/L. What is the value of K_p at 1100 K if the gas density at this temperature is 16.9 g/L. Also calculate the enthalpy of the reaction.

PROBLEM 341 The reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is started with an equal number of moles of N_2 and H_2 . Calculate mole fraction of NH₃ at 723 K and a total pressure of 0.5 atm given $K_p = 6 \times 10^{-3}$.

PROBLEM 342 At 1000 K, the equilibrium constant for the dissociation of water, $H_2O \implies H_2 + \frac{1}{2}O_2$

is 8.7×10^{-11} . For a significant production of hydrogen, which may be used as fuel, at least 15% of water should be dissociated. To what temperature should you heat the water? The enthalpy of reaction is 57.8 kcal. For a rough estimate assume that enthalpy is independent of temperature and P = 1.0 atm.

PROBLEM 343 In a study of the equilibrium: $H_2 + I_2 \rightleftharpoons 2HI$, 1.0 mole of H_2 and 3 mole of I_2 gave rise at equilibrium to x mole of HI. Addition of a further 2 mole of H_2 gave an additional x mole of HI. What is x? What is K at the temperature of experiment?

PROBLEM 344 The equilibrium constant for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 20 at 40°C, and vapour pressure of solid iodine is 0.1 bar at that temperature. If 12.7 g of solid iodine are placed in a 10 L vessel at 40°C, what is the minimum amount of hydrogen gas that must be introduced in order to remove all solid iodine?

PROBLEM 345 A standard solution of I_2 in water contains 0.33 g of I_2 in one litre flask. More than this dissolve in a KI solution because of the following equilibrium:

$$I_2 + I^- \rightleftharpoons I_3^-$$

A 0.1 M KI solution actually dissolve 12.5 g of iodine per litre, most of which is converted to I_3^- . Assuming that concentration of I_2 in all saturated solution is same, calculate the equilibrium constant for the above reaction. What is the effect of adding water to a clear saturated solution of I_2 in KI solution? **PROBLEM 346** The following gaseous equilibrium was obtained by heating 0.46 moles of A in a 5.0 L vessel. The equilibrium pressure at 300 K was 3.0 atm. The equilibrium pressure changed to 3.6 atm when temperature was raised to 320 K. Calculate percentage change in degree of dissociation of A at 350 K with respect to that of A at 300 K.

$$A(g) \rightleftharpoons B(g) + Cg)$$

PROBLEM 347 At 400°C, a 1 : 3 mixture of N₂ and H₂ reacts to form an equilibrium mixture of N₂, H₂ and NH₃. The total pressure at equilibrium was found to be 350 bar and mole fraction of NH₃ = 0.5. Calculate K_p for the reaction:

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

PROBLEM 348 Show that the maximum yield of product at equilibrium occurs when stoichiometric amount of reactants are used. Use the reaction:

$$\operatorname{Cl}_2(g) + \operatorname{Br}_2(g) \rightleftharpoons 2\operatorname{Br}\operatorname{Cl}(g)$$

PROBLEM 349 A flask containing 0.06 mole of $F_2(g)$ is allowed to equilibrate with F(g) at 1000 K. If the total pressure of the gases at equilibrium is 2.07 bar, calculate mole fraction of each gases at equilibrium.

Given:
$$F_2(g) \rightleftharpoons 2F(g), K_p(1000 \text{ K}) = 9.5 \times 10^{-3}$$

PROBLEM 350 A mixture of air at 1.0 bar and 2000 K was passed through an electric arc to produce nitric oxide as $N_2(g) + O_2(g) \Longrightarrow 2NO(g)$, $K_{2000} = 4 \times 10^{-4}$. What are the partial pressure of gases once the equilibrium has been established.

PROBLEM 351 At a pressure of one bar, an equilibrium exist at 2000 K between 0.25 mole of $Br_2(g)$, 0.75 mole of $F_2(g)$ gas and 0.497 mole of $BrF_3(g)$. What will be the amounts of each gas after the pressure on the system has been increased to 2.0 bar and equilibrium at 2000 K re-established?

$$\operatorname{Br}_2(g) + 3F_2(g) \rightleftharpoons 2\operatorname{Br}_3(g)$$

PROBLEM 352 Would 1.0% CO₂ in air be sufficient to prevent any loss in weight when Ag₂CO₃ is dried at 120°C

$$Ag_2CO_3(s) \Longrightarrow Ag_2O(s) + CO_2(g), \qquad K_p = 0.0095 \text{ at } 120^{\circ}C$$

PROBLEM 353 In a gas phase reaction $2A + B \rightleftharpoons 3C + 2D$, it was found that when 1.0 mol of A, 2.0 mol of B, and 1.0 mol of D were mixed in one litre flask and came to equilibrium, the resulting mixture contained 0.9 mole of C. Calculate equilibrium constant K_c .

PROBLEM 354 A container whose volume is V constains an equilibrium mixture that consists of 2 mole each of PCl₅, PCl₃ and Cl₂ and the equilibrium pressure is 30.4 kPa at *T*.

A certain amount of $\operatorname{Cl}_2(g)$ is now introduced keeping *P* and *T* constant, until equilibrium volume is 2*V*. Calculate amount of $\operatorname{Cl}_2(g)$ added and K_p .

PROBLEM 355 A 250 ml flask containing NO(g) at 0.46 atm is connected to a 100 mL flask containing oxygen gas at 0.86 atm by means of a stop cock at 350 K. The gases are mixed by opening the stop cock where the following equilibrium established: $2NO + O_2 \longrightarrow 2NO_2 \rightleftharpoons N_2O_4$.

The first reaction is complete while the second is at equilibrium. Calculate K_p if the final total pressure is 0.37 atm.

PROBLEM 356 Equal moles of $F_2(g)$ and $Cl_2(g)$ are introduced into a sealed container and heated to certain temperature where following equilibria established:

$$Cl_2(g) + F_2(g) \rightleftharpoons 2ClF(g), \quad K_p = 3.2$$

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$$

If partial pressure of CIF and CIF₃ at equilibrium are 0.2 and 0.04 atm respectively, calculate K_p for the second equilibrium reaction.

PROBLEM 357 0.2 mole of each $Cl_2(g)$ and $F_2(g)$ are introduced in a sealed flask and heated to 2000 K where following equilibrium established. $Cl_2(g) + F_2(g) \Longrightarrow 2ClF(g)$; and at equilibrium, moles of ClF = 0.267. At this stage, 0.1 mol of Br_2 is added and equilibrium is re-established as:

$$\operatorname{Cl}_2(g) + \operatorname{F}_2(g) \rightleftharpoons 2\operatorname{ClF}(g)$$

 $\operatorname{Cl}_2(g) + \operatorname{Br}_2(g) \rightleftharpoons 2\operatorname{BrCl}(g)$

Now moles of CIF found to be 0.25. Calculate K_c for the second equilibrium reaction.

PROBLEM 358 A glass bulb initially contains mixture of N₂ and NO at a total pressure of one atm. Some $Br_2(g)$ is added such that the pressure would have been 2.25 atm had not the equilibrium:

 $2NO + Br_2 \rightleftharpoons 2NOBr$

been established, as a result, the actual pressure after adding $Br_2(g)$ was 2.12 atm. A second addition of Br_2 was made such that total pressure would have been 22.75 atm had no reaction at all been occurred, while the actual pressure found to be 22.5 atm. Calculate K_p for the reaction assuming N₂ to be inert.

PROBLEM 359 When 0.1 mole of $Cl_2(g)$ and an excess of solid iodine are placed in 5 L vessel at 300 K, the total pressure is 0.767 atm. The vapour pressure of solid iodine is 0.03 atmosphere at this temperature. After this 1st equilibrium, 0.1 mole of bromine vapour is introduced into the reaction vessel. It is found that the weight of excess solid iodine diminished by an amount corresponding to 0.03 mole when new equilibrium is established. It is also found that partial pressure of bromine in new equilibrium mixture is 0.2 atm. Calculate K_p for the following equilibria at 300 K:

$$Cl_{2}(g) + I_{2}(g) \rightleftharpoons 2ICl(g)$$
$$Cl_{2}(g) + Br_{2}(g) \rightleftharpoons 2BrCl(g)$$
$$I_{2}(g) + Br_{2}(g) \rightleftharpoons 2IBr(g)$$

PROBLEM 360 The equilibrium constant of a reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If a one litre flask containing one mole of $A_2(g)$ is connected to a 2.0 L flask containing two moles of $B_2(g)$, how many moles of AB will be formed at 373 K.

PROBLEM 361 0.96 g of HI was heated till equilibrium $2\text{HI}(g) \rightleftharpoons \text{H}_2 + \text{I}_2(g)$ is reached. The reaction mixture was suddenly cooled and the amount of iodine produced required 15.7 mL N/10 hypo solution. Calculate K_p for the above equilibrium reaction.

PROBLEM 362 Hydrazine was taken in a constant volume container at 27°C and 0.3 atm and equal moles of oxygen gas was injected, sealed and finally heated to 1000 K where the following equilibria established:

$$N_2H_4 + 3O_2 \rightleftharpoons 2NO_2 + 2H_2O$$
 $K_{p_1} = 3$

$$N_2H_4 \Longrightarrow N_2 + 2H_2$$
 $K_{p_2} = ?$

$$N_2H_4 + H_2 \rightleftharpoons 2NH_3$$
 $K_{p_3} = ?$

If the gaseous mixture at equilibrium is passed through moisture absorbent, a decrease of 360 mm in the equilibrium pressure was observed. Now if the dried gaseous mixture is passed through ammonia absorber a further decrease of 20 mm in the equilibrium pressure was observed. Calculate K_{p_2} and K_{p_3} .

PROBLEM 363 Pure nirtosyl chloride (NOCl) gas was heated to 240°C in a 1.0 L container. At equilibrium, the total pressure was found to be 1.00 atmosphere and partial pressure of NOCl was 0.64 atm. Now some $Cl_2(g)$ is added at constant pressure and equilibrium was allowed to re-establish. At new equilibrium, the volume of the container was 1.5 L. Determine the moles of $Cl_2(g)$ added at first equilibrium.

PROBLEM 364 N₂O₄ gas decomposes partially as N₂O₄ \implies 2NO₂. In an experiment, some N₂O₄ is taken in a flask and heated to 300 K, where the above equilibrium is established. At equilibrium pressure of 1.0 atmosphere, density of the equilibrium mixture was found to be 2.33 g/L. Now, the gas is compressed till the density of new equilibrium mixture reaches to 5.08 g/L. Determine the new equilibrium pressure and the density of equilibrium mixture if the equilibrium pressure in this case is 1.5 atm.

PROBLEM 365 H_2S dissociates according to the following reaction: $H_2S \rightleftharpoons H_2 + S(g)$. At 1000 K and total pressure of 1.0 atmosphere, degree of dissociation was found to be 0.3. Determine the degree of dissociation if the gas is compressed isothermally to a new equilibrium pressure of 2.0 atmosphere.

PROBLEM 366 (a) PCl_5 dissociates as: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. When 0.03 mole of PCl_5 was brought to equilibrium at 500 K and 1.0 atmosphere, the equilibrium volume was 2.09 L. Calculate degree of dissociation.

(b) What will be the degree of dissociation when 0.2 mole of PCl₅ is brought to equilibrium in a 3 L flask at 500 K.

PROBLEM 367 0.1 mole of hydrogen gas and 0.2 mole of $CO_2(g)$ are introduced in an evacuated flask at 723 K and the following reaction occurs to give an equilibrium pressure of 50.67 kPa.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Analysis of the mixture shows that it contains 10 mol % of $H_2O(g)$. A mixture of CoO(s) and Co(s) is then introduced such that the additional equilibria:

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)$$
$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$$

are established. Analysis of the new equilibrium mixture thus, obtained is found to contain 30% (mol) of $H_2O(g)$ are present. Determine K_c for the three reactions.

PROBLEM 368 At 25°C, the equilibrium : $2NOBr \rightleftharpoons 2NO + Br_2$ is readily established. When 1.1 g of NOBr is present in 1.0 litre flask at 25°C, total pressure in the flask was found to be 0.335 atmosphere.

Determine the pressure if 5.0 g of NOBr is placed in a two litre evacuated flask at 25°C, sealed and allowed to attain the decomposition equilibrium to establish.

PROBLEM 369 A gaseous mixture containing equimolar amount of HCl and O_2 was taken in a flask, sealed and heated to 500°C where the following equilibrium is established:

$$HCl + O_2(g) \Longrightarrow 2Cl_2 + 2H_2O(g)$$

If the initial gas pressure was 1.0 atmosphere and mole fraction of HCl reacted before the equilibrium was established, was 0.76. Determine K_p .

PROBLEM 370 When N_2O_5 is heated, it dissociates as: $N_2O_5 \rightleftharpoons N_2O_3 + O_2$ $K_c = 4.5$. At the same time, N_2O_3 also decomposes as: $N_2O_3 \rightleftharpoons N_2O + O_2$. If initially 4.0 moles of N_2O_5 are taken in a 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was found to be 4.5 M. Determine equilibrium concentration of other species and K_c for the second equilibrium.

PROBLEM 371 At 25°C, a mixture of NO₂ and N₂O₄ are in equilibrium in a cylinder fitted with a movable piston. The concentration of species present at equilibrium are as follows: $[N_2O_4] = 0.487, [NO_2] = 0.0475$. Now, the piston is pushed to half the volume where the equilibrium was re-establish. Determine concentration of gases present at new equilibrium.

PROBLEM 372 Gaseous nitrosyl chloride (NOCl) and N_2 are taken in a flask, sealed and heated to some temperature where the total pressure would have been 1.0 bar had not the following equilibrium been established:

 $2NOCl \rightleftharpoons 2NO + Cl_2$

The actual pressure was found to be 1.2 bar. Now into the equilibrium mixture, some Cl_2 gas was introduced so that the total pressure would have been 9.0 bar had no further reaction occurred but the actual pressure was found to be 8.9 bar. Determine the equilibrium constant for the decomposition equilibrium under the given experimental condition.

PROBLEM 373 20.85 g of $PCl_5(g)$ is introduced in a vessel washed with a nonvolatile solvent (B.Pt. = 350 K, M.Pt. = 154). The equilibrium is established at 523 K when $PCl_5(g)$ is 52% dissociated and a total pressure was found to be 5.5 bar. If K_p for the decomposition reaction:

$$PCl_5 \Longrightarrow PCl_3 + Cl_2 \text{ is } 1.78.$$

Calculate the weight of solvent left in the vessel during washing.

PROBLEM 374 $Cl_2(g)$ and $O_2(g)$ are taken in the molar ratio of 2 : 7 where the following equilibrium was established:

$$2Cl_2 + 7O_2 \Longrightarrow 2Cl_2O_7$$

At equilibrium, mole fraction of Cl_2O_7 was found to be 0.1 when the total pressure was 100 bar. In an another experiment, two gases were taken in equimolar amount under identifical condition of temperature and mole fraction of Cl_2O_7 at equilibrium was found to be 0.06. Determine the equilibrium pressure in the new flask.

PROBLEM 375 $PCl_5(g)$ is taken in a flask at 1.0 atmosphere, sealed and allowed to attain the following equilibrium:

$$PCl_5 \Longrightarrow PCl_3 + Cl_2$$

The equilibrium mixture was then allowed to pass through a pin hole and the gases coming out of pin-hole initially, was collected, analyzed and mole fraction of Cl_2 was found to be 0.53. Determine equilibrium constant (K_p) for the decomposition reaction.

PROBLEM 376 A solid substance A decomposes into two gaseous products B and C as:

$$A(s) \rightleftharpoons 2B(g) + C(g)$$

If at equilibrium, some C(g) at 1.0 atmosphere is added in constant volume condition, 10% of B(g) solidified before the equilibrium was re-established. Determine total pressure at final equilibrium.

PROBLEM 377 Toxic level of Pb²⁺ in human blood is reduced by forming a stable Pb²⁺ EDTA complex which is excrete able through kidneys. Formation constant (K_f) for this complex is 10¹⁸. The ligand is administered by infusion of a solution of Na₂[Ca-EDTA] ($K_f = 5 \times 10^{10}$). In the blood stream, exchange of Ca²⁺ for Pb²⁺ occurs. The level of Pb²⁺ in a patient blood was found to be 4µM. To this patient a mixed solution containing Ca(NO₃)₂ and Na₂[Ca-EDTA] was administered so that their initial concentration in their blood were 2.5µM and 1.0µM respectively. Determine the ratio [Pb-EDTA]²⁻/[Pb²⁺] in the patient blood at equilibrium.

PROBLEM 378 NH₄HS(*s*) is an unstable solid, decomposes as:NH₄HS \implies NH₃ + H₂S and the following thermodynamic informations are available: $\Delta H^{\circ}{}_{f}$ (kJ/mol) : NH₄HS = -157, NH₃ = -46 and H₂S = -20.5 ΔS_{f}° (JK⁻¹ mol⁻¹) : NH₄HS = 113.5, NH₃ = 193 and H₂S = 206. Suppose 1.0 mole of solid NH₄HS is introduced into an empty 25 L flask, calculate the equilibrium pressure at 27°C.

PROBLEM 379 N₂O₄ decomposes as N₂O₄ \rightleftharpoons 2NO₂ and at 300 K, ΔG°_{f} of N₂O₄(g) and NO₂(g) are 98 and 52 kJ/mol respectively. Starting with one mole of N₂O₄ at one bar and 300 K, calculate the fraction of N₂O₄ decomposed when equilibrium is established at 1.0 bar and 300 K. Also determine percentage volume change if decomposition is carried out in a cylinder fitted with a mass-less, frictionless piston.

PROBLEM 380 A gaseous substance $AB_2(g)$ convert to AB(g) in presence of solid A(s) as:

$$AB_2(g) + A(s) \Longrightarrow 2AB(g)$$

The initial pressure and equilibrium pressure are 0.7 and 0.95 bar. Now the equilibrium mixture is expanded reversibly and isothermally till the gas pressure falls to 0.4 bar. Determine volume percentage of AB(g) and $AB_2(g)$ at the final equilibrium.

PROBLEM 381 One mole of $N_2(g)$, three moles of $H_2(g)$ and one mole of $H_2S(g)$ were taken in a one litre flask, sealed and heated to 700 K where the following equilibria were established:

$$\begin{split} \mathrm{N}_{2}(g) + 3\mathrm{H}_{2}(g) &\rightleftharpoons 2\mathrm{NH}_{3}(g) \\ \mathrm{H}_{2}\mathrm{S}(g) + \mathrm{NH}_{3}(g) &\rightleftharpoons \mathrm{NH}_{4}\mathrm{HS}(g) \qquad K_{p} = 8 \times 10^{-3} \mathrm{ atm}^{-1} \end{split}$$

At equilibrium, concentration of ammonia gas was found to be 0.9 M. Determine K_p for the first equilibrium and equilibrium concentrations of H₂S.

PROBLEM 382 $N_2O_4(g)$ is taken in a cylinder equipped with movable piston and heated first at constant volume where the following equilibrium is established and the gas was 30% dissociated :

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Now the gaseous mixture was expanded isothermally till volume was doubled. Determine the percentage of N_2O_4 dissociated at this stage.

PROBLEM 383 Consider the following reaction:

$$2NO_2 + O_3 \implies N_2O_5(g) + O_2(g)$$

 $\Delta H_{f}^{\circ}(O_{3}) = 143 \text{ kJ mol}^{-1}, \quad \Delta H_{f}^{\circ}(N_{2}O_{5}) = 11 \text{ kJ mol}^{-1} \text{ and } \Delta H_{f}^{\circ}(NO_{2}) = 33 \text{ kJ mol}^{-1}.$ The

above reaction is spontaneous at lower temperature but turned non-spontaneous as temperature approaches to 1175 K. Assuming ΔH° and ΔS° to be independent of temperature, determine K_p at 500 K.

PROBLEM 384 Consider formation of $N_2O_5(g)$ according to the reaction below :

$$2NO_2 + \frac{1}{2}O_2 \implies N_2O_5 \quad \Delta H^\circ = -55 \text{ kJ}; \Delta S^\circ = -227 \text{ JK}^{-1}$$

Also, ΔH_f° (NO₂) = +33.2 kJ mol⁻¹, S° (NO₂) = 240 JK⁻¹, S° (O₂) = 205 JK⁻¹.

- (a) Determine $\Delta H_f^{\circ} N_2 O_5$, $S^{\circ} (N_2 O_5)$, ΔG° at 25°C.
- (b) State and explain, whether this reaction is spontaneous at 25°C.
- (c) How the relative amounts of reactants and products would be affected at equilibrium?

PROBLEM 385 Cis-2-butene when heated to 500 K, it isomerizes into *trans*-2-butene and 2-methylpropene. If standard state Gibb's free energy of formations of *cis*-2-butene, *trans*-2-butene and 2-methyl-propene are 65.85 kJ mol⁻¹, 62.77 kJ mol⁻¹ and 58.07 kJ mol⁻¹ respectively, determine the equilibrium composition.

PROBLEM 386 A vessel containing 0.015 mol N₂(g) and 0.02 mol PCl₅(g) is heated to 227°C where the pressure was found to be 1.843 atm'. Also at 227°C, K_p for : PCl₅(g) \implies PCl₃(g) + Cl₂(g) = 0.4 atm. Assuming N₂ to be inert gas, determine, volume of the vessel.

PROBLEM 387 The ΔG° for the reaction:

$$SO_2 + \frac{1}{2}O_2 \implies SO_3 \text{ is } -22600 + 21T$$

Determine the temperature at which mixture is 80% (by mole) in SO₃, if initial mixture contain 15% SO₂ and 20% O₂ at one atmosphere total pressure. Assume total pressure is maintained constant at one atmosphere throughout.

PROBLEM 388 A 2.0 L flask, initially containing one mol of each CO and H_2O , was sealed and heated to 700 K, where the following equilibrium was established :

$$CO(g) + H_2O(g) \iff CO_2(g) + H_2(g); \qquad K(700) = 9$$

Now the flask was connected to another flask containing some pure $CO_2(g)$ at same temperature and pressure, by means of a narrow tube of negligible volume. When the equilibrium was restored, moles of CO was found to be double of its mole at first equilibrium. Determine volume of $CO_2(g)$ flask.

PROBLEM 389 Consider the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If we start with 0.5 moles of each $H_2(g)$ and $I_2(g)$ at 700 K in a flask, equilibrium concentration of HI was observed to be 0.15 M. What would have been the concentration of HI at equilibrium had the reaction been started with 0.8 mole of each H_2 and $I_2(g)$ at same temperature and in the same vessel?

PROBLEM 390 For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g), K_p = 63$ atm at 1000 K. What will be the total pressure of the gases above an equilibrium mixture if $P_{CO} = 10 P_{CO_2}$.

Solutions

CHEMICAL EQUILIBRIUM

335. $K = \frac{2}{9} = \frac{0.5 \times 0.2}{0.5(0.2 + x)} \implies x = 0.7 \text{ mol}$ **336.** H + B → HB 0.1 0.1 0 0.08 0.08 0.02 Initial At equilibrium $\Rightarrow K_c = 3.125$. **337.** NH₄Cl(s) \rightleftharpoons NH₃(g) + HCl(g) 3.66 × 10⁻² 3.66 × 10⁻² (0.154 - x) (3.66 × 10⁻² - x) moles at equilibrium $K_c = 1.34 \times 10^{-3}$ after adding 2.0 g NH₃. $\Rightarrow K_c = 1.34 \times 10^{-3} = (0.154 - x)(3.66 \times 10^{-2} - x).$ Solving, x = 0.163 and 0.026 x cannot be greater than 3.66×10^{-2} , hence it is 0.026. Therefore, on adding 0.2 g NH₃, 0.026 moles of both HCl and NH₃ will combine forming equal amount of $NH_4Cl(s)$ before equilibrium was re-established. Thus, amount of $NH_4Cl(s)$ at new equilibrium = 1.431g; % dissociation = 28.45. **338.** $K = 6.05 = \left(\frac{0.63 + 2x}{0.5 - x}\right)^2 \implies x = 0.134 \implies [H_2] = [I_2] = 0.366, [HI] = 0.898.$ **339.** $(CH_3)_3CC1 \iff (CH_3)_2C = CH_2 + HC1$ $0.2 - x \qquad x \qquad x$ Molarity $K_C = \frac{K_P}{RT} = 0.084 = \frac{x^2}{0.2 - x} \implies x = 0.094$ **340.** $\operatorname{CO}_2(g) + \operatorname{C}(s) \rightleftharpoons 2\operatorname{CO}_{\frac{56}{44}x}$ At 1000 K $\frac{56}{44}x - x = 2.3 \implies x = 8.433 \text{ g}$ $P_{CO(g)} = 6.286 \text{ atm}, P_{CO_2(g)} = 26.38 \text{ atm} \implies K_P (1000 \text{ K}) = 1.49 \text{ atm}$ At 1100 K : $\frac{56}{44}x - x = 5.3 \implies x = 19.43 \text{ g}.$ $P_{\text{CO}(g)} = 15.93 \text{ atm}, P_{\text{CO}_2(g)} = 24.5 \text{ atm}; \implies K_P (1100 \text{ K}) = 10.35 \text{ atm}$ $\ln \frac{K_P(2)}{K_P(1)} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \implies \Delta H = 177.25 \text{ kJ}$ Also **341.** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ Total 1-x 1-3x 2x 2(1-x)2(1-x) $K_P = \frac{16x^2(1-x)}{(1-3x)^2n^2} \approx \frac{16x^2}{P^2} = 64x^2$ \Rightarrow $x = 9.68 \times 10^{-3}, \quad x_{\rm NH_2} = 9.78 \times 10^{-3}.$ \Rightarrow **342.** $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$ Total moles 0.85 0.15 0.075 1.075 $K_{P}(T) = 4.66 \times 10^{-2}$ \Rightarrow

Solutions

345.

$$\Rightarrow \ln\left[\frac{4.66 \times 10^{-2}}{8.7 \times 10^{-11}}\right] = \frac{57.8 \times 10^3}{2} \left(\frac{T - 1000}{1000 T}\right) \Rightarrow T = 3284 \text{ K}$$
343.

$$\begin{array}{rcl} H_2 &+ I_2 &\rightleftharpoons & 2HI \\ 1 - \frac{x}{2} & 3 - \frac{x}{2} & x \\ 3 - x & 3 - x & 2x \\ \end{array}$$

$$\Rightarrow \frac{x^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} = \frac{4x^2}{(3 - x)^2} \Rightarrow x = 1.5, \quad K = 4.$$

344. Iodine in the gaseous state = 0.0386 mole; Iodine in solid state = 0.0114. Minimum H₂(g) would be required when solid I₂(s) has just been exhausted and the following equilibrium is maintained :

$$H_{2}(g) + I_{2}(g) \rightleftharpoons 2HI(g)$$
moles at equilibrium x 0.0386 0.0228

$$\Rightarrow \qquad 20 = \frac{(0.0228)^{2}}{x(0.0386)} \Rightarrow x = 0.67 \times 10^{-3}$$

$$\Rightarrow \qquad \text{moles of } H_{2} \text{ required} = 0.012$$

$$I_{2} + I^{-} \rightleftharpoons I_{3}^{-} K = \frac{0.0492}{1.299 \times 10^{-3} \times 0.0508} = 745.57 \text{ L mol}^{-1}$$

346.

$$A(g) \rightleftharpoons B(g) + C(g) \atop_{x}$$

$$\Rightarrow \qquad 3 = \frac{(0.46 + x)(0.082) \times 300}{5} \Rightarrow x = 0.15$$

$$\Rightarrow \qquad K_{P}(300 \text{ K}) = \frac{\left(\frac{0.15}{0.61}\right)^{2}}{\left(\frac{0.31}{0.61}\right)^{2}} \times 3 = 0.357$$
Similarly,

$$K_{P}(320 \text{ K}) = \mathbf{1.145}$$
Now,
$$\ln \frac{1.145}{0.357} = \frac{\Delta H}{R} \left(\frac{20}{300 \times 320}\right) \text{ and } \ln \frac{K_{P}(350)}{1.145} = \frac{\Delta H}{R} \left(\frac{30}{350 \times 320}\right)$$
Solving,

$$K_{P}(350) = 5.12, \quad P_{0}(350) = 2.64$$

$$\Rightarrow \qquad 5.12 = \frac{P^{2}}{2.64 - P} \Rightarrow P = 1.92 \Rightarrow \qquad \alpha(350 \text{ K}) = \frac{1.92}{2.64} = 0.7272$$
Also,

$$\alpha(300 \text{ K}) = \frac{0.15}{0.46} = 0.326$$

$$\% \text{ increase} = \frac{0.4012}{0.326} \times 100 = \mathbf{123.06\%}$$

347. $P_{(NH_3)} = 175 \text{ bar} \implies P_{N_2} = \frac{175}{4} = 43.75 \text{ bar}$ and $P_{H_2} = 3 \times 43.75 = 131.25 \text{ bar}$ $\implies \qquad K_P = \frac{(175)^2}{(43.75)(131.25)^3} = 3.096 \times 10^{-4} \text{ bar}^{-2}$

348. Let *r* be the ratio of $P(Cl_2)$ to $P(Br_2)$. Thus, $P(Cl_2) = rP(Br_2)$

$$\Rightarrow P_t = P(Cl_2) + P(Br_2) + P(BrCl) = rP(Br_2) + P(Br_2) + P(BrCl) = (1+r)P(Br_2) + P(BrCl)$$

$$\Rightarrow P_{Br_2} = \frac{P_t - P(BrCl)}{r+1}, \quad P(Cl_2) = r\left(\frac{P_t - P(BrCl)}{r+1}\right)$$

$$\Rightarrow$$

 $K_{P} = \frac{P(\text{BrCl})^{2}}{\left[r\left(\frac{P_{t} - P_{\text{BrCl}}}{r+1}\right)\right]\left(\frac{P_{t} - P(\text{BrCl})}{r+1}\right)} = \frac{P(\text{BrCl})^{2}}{r\left\{\frac{[P_{t} - P(\text{BrCl})]}{(r+1)}\right\}^{2}}$

Taking logarithm of each side and differentiating w.r.t. r:

$$\ln K_p = 2 \ln [P(\text{BrCl})] - \ln r - 2 \ln [P_t - P(\text{BrCl})] + 2 \ln (r+1)$$

$$0 = 2 \frac{1}{P(\text{BrCl})} \left(\frac{\partial P(\text{BrCl})}{\partial r}\right) - \frac{1}{r} - 2 \left(\frac{1}{P_t - P(\text{BrCl})}\right) \left(\frac{-\partial P(\text{BrCl})}{\partial r}\right) + 2 \frac{1}{r+1}$$

Assigning $\frac{\partial P(\text{BrCl})}{\partial r} = 0$ and solving for 'r' gives $r = 1$

Hence, stoichiometric amounts of Cl₂ and Br₂ generate maximum yield of BrCl. **349.** $F_2 \rightleftharpoons 2F_{0.06-x} 2F_{2x}$

$$K_P = \left(\frac{2x}{0.06 + x}\right)^2 \cdot \left(\frac{0.06 + x}{0.06 - x}\right) P = \frac{4x^2}{36 \times 10^{-4} - x^2} \times 2.07 = 9.5 \times 10^{-3}$$

$$\Rightarrow x = 2.03 \times 10^{-3} \Rightarrow \text{ mole fraction of } F = 0.065, \text{ mole fraction of } F_2 = 0.935$$

350.

$$K = \frac{\frac{N_2(g) + O_2(g)}{0.8 - x} \implies 2NO(g)}{(0.8 - x)(0.2 - x)} = 4 \times 10^{-4} \implies x = 3.95 \times 10^{-3}$$

⇒ mole fraction of NO(g) = 0.08, N₂(g) = 0.796, O₂(g) = 0.196

351. $Br_{2} + 3F_{2} \iff 2BrF_{3}$ $\frac{0.25}{1.497} \quad \frac{0.75}{1.497} \quad \frac{0.497}{1.497}$ $K = \frac{(0.497 \times 1.497)^{2}}{0.25(0.75)^{3}} = 5.248$

After increasing equilibrium pressure = 2 bar, reaction will shift in forward direction and let x mole of Br_2 reacted further.

364

Then new partial pressure : Br₂ = $\frac{0.25 - x}{1.497 - 2x} \times 2$; F₂ = $\frac{0.75 - 3x}{1.497 - 2x} \times 2$ BrF₃ = $\frac{0.497 + 2x}{1.497 - 2x} \times 2$

Substituting these partial pressure in equilibrium constant expression and solving gives x = 0.061. Therefore, new compositions would be:

$$Br_2 = 0.189$$
, $F_2 = 0.567$, $BrF_3 = 0.619$ moles.

352. $Ag_2CO_3(g) \iff Ag_2O(s) + CO_2(g)$ $K_P = 0.0095$ bar at 120°C. $P(CO_2)$ at 120°C = $K_P = 0.0095$ which is less than 0.01 bar, the partial pressure of CO₂ in air. Therefore, $Ag_2CO_3(s)$ will not effervess at 120°C.

353. At equilibrium : $2A + B \iff 3C + 2D$

Let x mole of Cl_2 is added out of which y mole reacted with PCl_3 , giving y mol PCl_5 . Also, at new equilibrium n = 12.

$$\Rightarrow \qquad 6+x-y=12 \qquad \Rightarrow \qquad x-y=6$$

and
$$\frac{P}{3} = \frac{2P(2-y)}{3(2+y)} \qquad \Rightarrow \qquad y = \frac{2}{3} \qquad \text{and} \qquad x = \frac{20}{3}$$

355. In the combined system partial pressure of the gases before any reaction occurred are :

NO =
$$0.46 \times \frac{250}{350} = 0.3285$$
; O₂ = $0.86 \times \frac{100}{350} = 0.2457$

Here, NO is limiting reagent : Partial pressure after 1st step :

$$NO = 0$$
, $O_2 = 0.0814$, $NO_2 = 0.3285$

Now, let p-be the decrease in partial pressure of NO₂ due to equilibrium.

$$\Rightarrow 0.0814 + 0.3285 - p + \frac{p}{2} = 0.37 \Rightarrow p = 0.0798 \Rightarrow K_p = 0.645 \text{ atm}^{-1}$$

356. Let us consider P_0 be the initial partial pressure of each $Cl_2(g)$ and $F_2(g)$. Then at equilibrium partial pressure of each gas would be :

$$\Rightarrow \qquad P_{\text{Cl}_2} = P_0 - 0.12, \quad P_{\text{F}_2} = P_0 - 0.16$$

$$\Rightarrow \qquad 3.2 = \frac{P(\text{ClF})^2}{P(\text{Cl}_2)P(\text{F}_2)} = \frac{(0.2)^2}{(P_0 - 0.12)(P_0 - 0.16)}$$

Solving, gives $P_0 = 0.253$ and 0.026, where the second value is not acceptable.

$$\Rightarrow K_p \text{ for second equilibrium} = \frac{(0.04)^2}{(0.133)(0.093)^3} = 14.95$$

357. $Cl_2 + F_2 \implies 2ClF \qquad K = 16.12$ 0.0665 0.0665 0.267

When Br₂ is added : Cl₂ + F₂
$$\implies 2ClF$$

 $0.075 - x = 0.075 = 0.25$
 $16.12 = \frac{(0.25)^2}{0.075(0.075 - x)} \implies x = 0.023$
 $Cl_2 + Br_2 \implies 2BrCl$
 $0.07 - x = 0.1 - x \implies 2BrCl$
 $K_c = \frac{(0.046)^2}{0.052 \times 0.077} = 0.528$

358. $2NO + Br_2 \rightleftharpoons 2NOBr$. Let initial partial pressure of $NO = p_0$ and decrease in partial pressure before the 1st equilibrium be p_1 . Then :

$$p_0 - p_1 + 1.25 - \frac{p_1}{2} + p_1 + 1 - p_0 = 2.12$$

$$\Rightarrow \qquad p_1 = 0.26 \quad \text{and} \quad K_p = \frac{(0.26)^2}{(P_0 - 0.26)^2 (1.12)}$$

Similarly, if p_2 be the total decrease in partial pressure of NO before the second equilibrium was established then

$$p_0 - p_2 + 21.75 - \frac{p_2}{2} + p_2 + 1 - p_0 = 22.5$$

$$\Rightarrow \qquad p_2 = 0.5 \quad \text{and} \quad K_P = \frac{(0.5)^2}{(p_0 - 0.5)^2 (21.5)}$$

Equating the two K_P ; $P_0 = 0.69$ and $K_P = 0.326$.

359. Before addition of $\operatorname{Br}_2(v)$: $\operatorname{Cl}_2(g) + \operatorname{I}_2(g) \rightleftharpoons K_1$ 0.492 bar - x = 0.03 $\xrightarrow{K_1} 2\operatorname{ICl}_2 x$

$$\Rightarrow \qquad 0.522 + x = 0.767 \Rightarrow x = 0.245 \text{ and } K_1 = 32.4$$

After adding $Br_2(v)$

$$\begin{array}{c} \text{Cl}_{2}(g) &+ \text{I}_{2}(g) \rightleftharpoons K_{1} \\ 0.247 + q - p & 0.03 & 0.49 - 2q \\ \hline \\ 1_{2}(g) &+ & \text{Br}_{2}(g) \\ 0.03 & 0.492 - 0.1476 - p & \rightleftharpoons & 2IBr(g) \\ 0.2952 & 0.2952 \\ \hline \\ \text{Also,} & P(\text{Br}_{2}) = 0.2 \implies p = 0.1444 \\ \implies & K_{2} = \frac{(0.2952)^{2}}{0.03 \times 02} = 14.52 \end{array}$$

Also,

$$Cl_{2}(g) + Br_{2}(g) \rightleftharpoons 2ClBr(g)$$

$$K_{1} = 32.4 = \frac{(0.49 - 2q)^{2}}{(0.03)(0.1026 + q)}$$

$$\Rightarrow \qquad q = 0.05 \quad \Rightarrow \quad K_3 = \frac{(0.2888)^2}{(0.1526)(0.2)} = 2.73$$

360. $K = \frac{4x^2}{(1-x)(2-x)} = 50 \implies 2x \text{ (moles of } AB\text{)} = 1.87$

361. m mol of I_2 reacted with hypo = 0.785

⇒ At equilibrium : *m* mol of H₂ = I₂ = 0.785, *m* mol of HI = 5.93
$$K = \left(\frac{0.785}{5.93}\right)^2 = 17.52 \times 10^{-3}$$

362. Let the equilibrium partial pressure of NO₂ =
$$H_2O(v) = 2p_1$$

Equilibrium pressure of N₂ = p_2 and equilibrium pressure of NH₃ = $2p_3$

 \Rightarrow Equilibrium pressure of H₂ = 2p₂ - p₃. Then,

$$N_{2}H_{4} + 3O_{2} \rightleftharpoons 2NO_{2} + 2H_{2}O \qquad K_{1} = 3$$

$$I - p_{1} - p_{2} - p_{3} + 1 - 3p_{1} \swarrow 2p_{1} + 2H_{2}O \qquad K_{1} = 3$$

$$N_{2}H_{4} \implies N_{2} + 2H_{2} \\ 1 - p_{1} - p_{2} - p_{3} \implies p_{2} + 2p_{2} - p_{3} \\ K_{p}(2) = ?$$

$$\begin{array}{c} N_{2}H_{4} \\ 1 - p_{1} - p_{2} - p_{3} \end{array} \xrightarrow{} \begin{array}{c} N_{2} \\ 2 p_{2} - p_{3} \end{array} + \begin{array}{c} 2NH_{3} \\ 2 p_{3} \end{array} \end{array}$$

$$\begin{array}{c} K_{P}(3) = ? \\ K_{P}(3) = ? \end{array}$$

$$\begin{array}{c} 2 p_{1} = \frac{9}{19} \text{ bar and } 2 p_{3} = \frac{1}{38} \text{ bar} \end{array}$$

Given,

$$\Rightarrow \qquad P_{N_2H_4} = \frac{3}{4} - p_2 \qquad \text{and} \qquad P_{O_2} = \frac{11}{38} \text{ bar}$$
$$\Rightarrow \qquad K_1 = 3 = \frac{\left(\frac{9}{19}\right)^4}{\left(11\right)^3} \qquad \text{Solving } p_2 = 0.233$$

=

 \Rightarrow

$$\begin{pmatrix} \frac{11}{38} \\ \end{pmatrix} (0.75 - p_2)$$

Using values of p_1 , p_2 and p_3 gives $p(N_2H_4) = 0.517$, $p(N_2) = 0.233$
 $p(H_2) = 0.4528$ and $p(NH_3) = 0.0263$ bar.
 $\Rightarrow \qquad K_p(2) = 9.24 \times 10^{-2} \text{ bar}^2 \text{ and } K_p(3) = 2.95 \times 10^{-3}.$

363.

$$P: \\ mole: P: \\ mole: Cl_{0.64} \rightleftharpoons 2NO + Cl_{2} \\ 0.24 & 0.12 \\ 15.2 \times 10^{-3} & 5.7 \times 10^{-3} & 2.85 \times 10^{-3} \\ K_{P} = 16.875 \times 10^{-3} \text{ bar.}$$
 Total = 23.75 × 10⁻³

Let at this stage x mole of Cl₂ is added, out of which y mole react back. Also volume is increased to 1.5 litre but at same temperature and pressure, therefore new total mole $=23.75 \times 1.5 \times 10^{-3} = 35.625 \times 10^{-3}$.

A new equilibrium : mole $Cl_2 = 2.85 \times 10^{-3} + x - y$

NO =
$$5.7 \times 10^{-3} - 2y$$
 and NOCl = $15.2 \times 10^{-3} + 2y$

Adding moles and equating to total moles gives $x - y = 11.875 \times 10^{-3}$

Therefore, at new equilibrium, mole-fractions are:

$$Cl_{2} = (2.85 + 11.875) \times 10^{-3} / 35.625 \times 10^{-3} = 0.4133$$
$$NO = \frac{5.7 \times 10^{-3} - 2y}{35.625 \times 10^{-3}} \text{ and } NOCl = \frac{15.2 \times 10^{-3} + 2y}{35.625 \times 10^{-3}}$$

Substituting in expression of K_p gives $y = 1.108 \times 10^{-3}$

 $\Rightarrow x = 12.983 \times 10^{-3} \text{ mol}$

364.

$$N_2O_4 \implies 2NO_2 \quad K_p = \frac{4\alpha^2 p}{1-\alpha^2}$$

At $P = 1, \rho = 2.33$: Applying, $\frac{M}{1 + \alpha} = \frac{\rho RT}{P}$ where $M = \text{molar mass of N}_2O_4$.

 $\Rightarrow \alpha = 0.6$ and $K_p = 2.25$.

Let β -be the degree of dissociation at new equilibrium. Then,

$$\frac{M}{1.6} = \frac{2.33RT}{1} \text{ and } \frac{M}{1+\beta} = \frac{5.08RT}{P} \implies 1+\beta = 0.734 P$$

$$\Rightarrow 2.25 = \frac{4\beta^2 P}{(1-\beta)(1+\beta)} = \frac{4\beta^2}{0.734(1-\beta)} \implies \beta = 0.468 \text{ and } P = 2 \text{ bar.}$$

At $P = 1.5$, using K_p ; $\alpha = 5.22$ and $\rho = \frac{92 \times 1.5}{1.522RT} = 3.685 \text{ g/L}$
365. $H_2S(g) \implies H_2(g) + S(g) \qquad K_p = 0.099 = \frac{P^2}{2(1-P)}$
where, P is partial pressure of $H_2(g)$ at new equilibrium.

$$\Rightarrow \qquad P = 0.356 \text{ and } \alpha = \frac{0.356}{1.644} = 0.21$$

366. (a) $n = \frac{PV}{RT} = 0.05$, *i.e.*, out of 0.03 mole of PCl₅, 0.02 mol has decomposed into PCl₃ and Cl₂ giving 0.05 mole of gaseous mixture.

$$\Rightarrow \qquad \qquad \alpha = \frac{2}{3} = 0.67$$

	(b) From the information in part ' <i>a</i> '; $K_p = \frac{\alpha^2 P}{1 - \alpha^2} = 0.8$	
	<i>P</i> :	$\begin{array}{ccc} \operatorname{PCl}_{5} & \rightleftharpoons & \operatorname{PCl}_{3} + \operatorname{Cl}_{2} \\ 2.73 - p & p & p \end{array}$
	\Rightarrow	$0.8 = \frac{p^2}{2.73 - p} \implies p = 1.13$ atm.
	\Rightarrow	$\alpha = \frac{1.13}{2.73} = 0.42$
367.	Ι:	$\begin{array}{ccc} H_2(g) + CO_2(g) \iff & H_2O(g) + CO(g) \\ 0.07 & 0.17 & 0.03 & 0.03 \end{array}$
	\Rightarrow	$K_1 = 7.563 \times 10^{-2}$.
	II :	$\begin{array}{c} H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \\ 0.07 - x 0.17 + y & 0.03 + x 0.03 - y \end{array}$
		$\operatorname{CoO}(s) + \operatorname{H}_{2}(g) \underset{-x}{\overset{K_{2}}{\longleftrightarrow}} \operatorname{Co}(s) + \operatorname{H}_{2}\operatorname{O}(g) \underset{+x}{\overset{K_{2}}{\longleftrightarrow}}$
		$\operatorname{CoO}(s) + \operatorname{CO}(g) \rightleftharpoons_{-y}^{K_3} \operatorname{Co}(s) + \operatorname{CO}_2(g) + y$
	Also	$0.03 + x = 0.09 \implies x = 0.06$
	Hence,	$n(\mathrm{H}_2) = 0.01 \qquad \Rightarrow \qquad K_2 = \frac{0.09}{0.01} = 9;$
	Also,	$K_1 = 7.563 \times 10^{-2} = \frac{0.09(0.03 - y)}{0.01(0.17 + y)}$
	Solving,	$y = 2.83 \times 10^{-2}$
368.	\Rightarrow	$K_3 = \frac{0.17 + 2.83 \times 10^{-2}}{0.03 - 2.83 \times 10^{-2}} = 116.64$
		$2\text{NOBr} \rightleftharpoons 2\text{NO} + \text{Br}_2$ $0.01 - x \qquad x \qquad x/2$
		$n = 0.01 + \frac{x}{2} = \frac{PV}{RT}$
	Solving,	$x = 0.0074 \qquad \Rightarrow \alpha = \frac{x}{0.01} = 0.74$
	If 5 g of NOBr is take	n, initial mole = $\frac{5}{110} = 0.045$
	Moles at equilibrium	$=0.045\left(1+\frac{\alpha}{2}\right)=0.045\times1.37=0.06165$

370.

 \Rightarrow

$$K_{p} = \frac{(0.19)^{4} (0.905)}{(0.12)^{4} (0.405)} \cdot \frac{1}{P} \quad \text{Also} \quad P = P_{0}(0.905) = 0.905 \text{ atm.}$$

$$= \left(\frac{0.19}{0.12}\right)^{4} \left(\frac{1}{0.405}\right) = \mathbf{15.5 \ atm^{-1}}.$$

$$N_{2}O_{5} \rightleftharpoons N_{2}O_{3} + O_{2}$$

$$x - y \qquad \stackrel{K_{c}}{\longrightarrow} \qquad N_{2}O_{7} + O_{2}$$

$$y + y$$

$$K = 4.5 = \frac{(x + y)(x - y)}{4 - x} \quad \text{and} \quad x + y = 4.5$$

$$y = \frac{5}{3} \quad \text{and} \quad x = \frac{17}{6}$$

$$K_{c} = \frac{4.5 \times 5 \times 6}{3 \times 7} = \mathbf{6.428}.$$

 $P = \frac{nRT}{V} = 0.753$ atmosphere.

 $4HCl + O_2 \iff 2Cl_2 + 2H_2O$

 $\frac{0.405}{0.905}$

 $\frac{0.12}{0.905}$

 $\frac{0.19}{0.905} \quad \frac{0.19}{0.905}$

mole fraction

371. Let initial volume = 1 L.

Equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2 \\ 0.487 \circlearrowright 0.0475 \\ K_c = 4.633 \times 10^{-3}$$

After compression moles : $N_2O_4 = 0.487 + x$; $NO_2 = 0.0475 - 2x$ $\Rightarrow \qquad K_c = \frac{(0.0475 - 2x)^2 \times 2}{(0.487 + x)} = 4.633 \times 10^{-3}$

Solving, *x* = **0.041** and **0.0068**

The 1st value of x is rejectable, therefore $[NO_2] = 0.0678$, $[N_2O_4] = 0.9876$ 372. Let the initial partial pressure of NOCl be p_0 .

$$2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$$

$$p_0 - p_1 \qquad p_1 \qquad \frac{p_1}{2}$$

$$\text{Total } P = 1 + \frac{p_1}{2} = 1.2 \implies p_1 = 0.4$$

At equilibrium, additional pressure of $Cl_2 = 7.8$

Therefore, at new equilibrium :

$$2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$$

$$p_0 - 0.4 + p_2 \qquad 0.4 - p_2 \qquad 8 - \frac{p_2}{2}$$

$$\text{Total } P = 9 - \frac{p_2}{2} = 8.9 \implies p_2 = 0.2$$

Now, equating equilibrium constant for the above two stages :

$$\frac{0.2(0.4)^2}{(p_0 - 0.4)^2} = \frac{7.9(0.2)^2}{(p_0 - 0.2)^2} \implies \left(\frac{p_0 - 0.2}{p_0 - 0.4}\right)^2 = \frac{7.9 \times 0.04}{0.2 \times 0.16} \implies p_0 = 0.493$$

 $K_P = 3.7$ bar.

373. The equilibrium reaction is :

$$PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}$$

$$K_{p} = \frac{\alpha^{2}}{1 - \alpha^{2}} P = 1.78 \implies P = 4.8 \text{ (Pressure due to PCl_{5}, PCl_{3} and Cl_{2})}$$

$$\Rightarrow \qquad P_{\text{Solvent}} = 0.7$$
Now,
$$\frac{P(\text{PCl}_{5} + \text{PCl}_{3} + \text{Cl}_{2})}{P(\text{solvent})} = \frac{0.1(1 + \alpha)}{n_{\text{Solvent}}} \implies n_{\text{Solvent}} = 0.022, \text{ mass} = 3.388 \text{ g.}$$

374. At equilibrium $P(Cl_2O_7) = 10$, $P(O_2) = 70$, $P(Cl_2) = 20 \implies K_P = \frac{100}{(20)^2 (70)^7} = 3.035 \times 10^{-14}$

A when gases are taken in equimolar ratio, mole-fractions are :

Cl₂O₇ = 0.06, Cl₂ = 0.545, O₂ = 0.395
⇒
$$K_P = \frac{(0.06)^2}{(0.545)^2 (0.395)^7} \cdot \frac{1}{P^7} = 3.035 \times 10^{-14} \implies P = 115 \text{ bar.}$$

375. Molar ratio of the gases coming out of flask initially will be equal to their rate of effusion.

$$\begin{array}{ccc} \operatorname{PCl}_5 &\rightleftharpoons & \operatorname{PCl}_3 + \operatorname{Cl}_2 \\ 1 - \alpha & \alpha & \alpha \end{array}$$

Here, α = degree of dissociation.

$$\Rightarrow \qquad \qquad \frac{r(\text{Cl}_2)}{r(\text{PCl}_3)} = \sqrt{\frac{137.5}{71}} = \frac{0.53}{x}$$

where x = mole fraction of PCl₃ in the gaseous mixture coming out initially $\Rightarrow x = 0.38$ Hence, mole fraction of PCl₅ outside of flask = 0.09

Now,

$$\frac{r(\text{PCl}_5)}{r(\text{Cl}_2)} = \frac{1-\alpha}{\alpha} \sqrt{\frac{71}{208.5}} = \frac{0.09}{0.53} \implies \alpha = 0.77$$

$$K_p = \frac{(0.77)^2}{0.23} = 2.577 \text{ bar.}$$

376. Case I Case II $A(s) \rightleftharpoons 2B(g) + C(g) \qquad K_p = 4p^3$ $\frac{2p}{p} \qquad p \qquad p$ $2p - 0.2p \qquad p + 1 - 0.1p$ $K = (1, 0, y)^2 (0, 0, y+1) = (1, y)^3$

$$K_P = (1.8p)^2 (0.9p+1) = 4p^3$$

 $P = 2.988$ bar

 \Rightarrow

P(case II) = 2.7 p + 1 = 9.06 bar

377. The exchange equilibrium is :

$$[Ca - EDTA]^{2^{-}} + Pb^{2^{+}} \rightleftharpoons [Pb - EDTA]^{2^{-}} + Ca^{2^{+}}]$$
$$K = \frac{\{[Pb - EDTA]^{2^{-}}\}[Ca^{2^{+}}]}{\{[Ca - EDTA]^{2^{-}}\}[Pb^{2^{+}}]} = \frac{10^{18}}{5 \times 10^{10}} = \mathbf{2} \times \mathbf{10}^{7}$$

The very high *K* value for the exchange reaction indicate that all Pb^{2+} will be converted into $[Pb - EDTA]^{2-}$, but since concentration of both Ca^{2+} and $[Cd - EDTA]^{2-}$ are very high, will remain unchanged. Therefore :

Ratio
$$\frac{[Pb - EDTA]^{2-}}{[Pb^{2+}]} = \frac{K[Ca - EDTA]^{2-}}{[Ca^{2+}]} = 2 \times 10^7 \frac{1}{2.5} = 8 \times 10^6$$

378. From the thermodynamic informations : $\Delta H^{\circ} = 90.5$ kJ and $\Delta S^{\circ} = 285.5$ JK⁻¹

$$\Rightarrow \qquad \Delta G^{\circ} = 4.85 \text{ kJ} = -RT \ln K \Rightarrow K = 0.143 = p$$

 $(p = partial pressure of NH_3)$

...(ii)

 $\Rightarrow p = 0.378 \text{ bar} \text{ and } P(\text{eqm}) = 2P = 0.756 \text{ bar}.$ **379.** $\Delta G^{\circ}(\text{reaction}) = 2 \times 52 - 98 = 6 \text{ kJ} = -RT \ln K \Rightarrow K = 0.09$

Also, for

$$N_2O_4 \rightleftharpoons 2NO_2$$

 $K = \frac{4\alpha^2}{1 - \alpha^2} P = 0.09 \Rightarrow \alpha = 0.1483$

Also, since reaction is occurring at constant pressure and temperature :

 $v \propto n \implies \%$ volume increase would be **14.83**.

380. $AB_2(g) + A(s) \implies 2AB(g)$ $K = \frac{5}{9}$

Let at new equilibrium partial pressure of AB(g) = x and of $AB_2(g) = y$ bar.

$$\frac{5}{9} = \frac{x^2}{y} \qquad \dots (i)$$

Also

 \Rightarrow

x + y = 0.4

Solving, Eqs. (i) and (ii) gives x = 0.27; y = 0.13

Volume % of
$$AB_2(g) = \left(\frac{0.13}{0.4}\right) \times 100 = 32.5$$

Volume % of
$$AB(g) = 67.5$$
.

381. Since, volume of container is 1.0 litre, concentrations of each species will be equal to their moles. Now, setting the equilibrium table

$$N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$$

$$1-x \quad 3-3x \qquad 2x-y$$

$$NH_{3}(g) + H_{2}S(g) \rightleftharpoons NH_{4}HS(g), \qquad K_{p} = 8 \times 10^{-3} = K_{c}(RT)^{-1}$$

$$2x-y \qquad 1-y \qquad y \qquad \Rightarrow \quad K_{c} = 0.4592$$

$$K_{c} = 0.4592 = \frac{y}{(1-y)(2x-y)} \text{ also } 2x-y=0.9$$

$$\frac{1-y}{y} = 2.42 \qquad \Rightarrow \qquad y=0.3 \quad \text{and} \quad x=0.6$$

$$\Rightarrow \qquad K_{c} \text{ (for the 1st reaction)} = \frac{(2x-y)^{2}}{27(1-x)^{4}} = \frac{(0.9)^{2}}{27(0.4)^{4}} = 1.17$$

$$\Rightarrow \qquad K_{p} \text{ (for 1st reaction)} = K_{c}(RT)^{-2} = 3.55 \times 10^{-4}$$

$$[H_{2}S] = 1-y=0.7 \text{ M}$$

382. Let P_0 be the initial pressure of $N_2O_4(g)$, then:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

 $P_0 - 0.3 P_0 \qquad 0.6 P_0 \qquad K_p = \frac{18}{35} P_0 \qquad \dots(i)$

On doubling volume, the initial pressure will be halved.

$$\Rightarrow \qquad K_{p} = \frac{4P^{2}}{\frac{P_{0}}{2} - P} = \left(\frac{2P}{P_{0}}\right)^{2} P_{0}^{2} \left[\frac{1}{\left(1 - \frac{2P}{P_{0}}\right)\frac{P_{0}}{2}}\right] = \frac{\alpha^{2}}{1 - \alpha} \cdot 2P_{0} = \frac{18}{35} P_{0} \qquad \text{(from Eq. (i))}$$

 $\Rightarrow \qquad 35\,\alpha^2 + 9\,\alpha - 9 = 0$

$$\Rightarrow \qquad \qquad \alpha = \frac{-9 + \sqrt{81 + 36 \times 35}}{70} = 0.3945$$

 \Rightarrow 39.45% N₂O₄ dissociated.

383.
$$\Delta H^{\circ}$$
 (Reaction) = ΔH_{f}° (N₂O₅) - ΔH_{f}° (O₃) - $2\Delta H_{f}^{\circ}$ (NO₂) = 11 - 143 - 2 × 33 = -198 kJ

: Reaction turned spontaneous to non-spontaneous at 1175 K implies that at this temperature $\Delta G^{\circ} = 0$.

i.e., $-198 \times 10^3 - 1175 \Delta S^\circ = 0 \implies \Delta S^\circ = -168.5 \text{ JK}^{-1}$ Now at 500 K, $\Delta G^\circ = -198 \times 10^3 - 500 (-168.5) = -113.75 \times 10^3$

Also,
$$\Delta G^{\circ} = -RT \ln K = -113.75 \times 10^3$$

$$\ln K = 27.36$$
 and $K_n = 7.65 \times 10^{11}$

384. (a) ΔH° (Reaction) = ΔH_{f}° (Products) – ΔH_{f}° (Reactants)

$$\Rightarrow \qquad -55 = \Delta H_f^{\circ} (N_2 O_5) - 2 \times 33.2 \qquad \Rightarrow \qquad \Delta H_f^{\circ} (N_2 O_5) = +11.4 \text{ kJ}$$

 ΔS° (Reaction) = S° (Products) – S° (Reactants) Also. $-227 = S^{\circ} (N_2O_5) - 2 \times 240 - \frac{1}{2} \times 205 \qquad \Rightarrow \qquad S^{\circ} (N_2O_5) = 355.5$ $\Delta G^{\circ} = -55 \times 10^3 + 298 \times 227 = 12.646 \times 10^3 \text{ J}$

- (b) :: $\Delta G^{\circ} > 0$, reaction is non-spontaneous at 298 K.
- (c) $\therefore \Delta G^{\circ} > 0$, increasing temperature will drive the reaction in backward direction.





$$\Delta G_{1} = 62.97 - 65.85 = -2.88 \text{ kJ} = -RT \ln K_{P_{1}}$$

$$\Rightarrow \qquad \ln K_{P_{1}} = \frac{2880}{8.314 \times 500} = 0.693 \implies K_{P_{1}} = 2$$

$$\Delta G_{2}^{\circ} = 58.07 - 65.85 = -7.78 \text{ kJ} = -RT \ln K_{P_{2}}$$

$$\Rightarrow \qquad \ln K_{P_{2}} = \frac{7780}{8.314 \times 500} \implies K_{P_{2}} = 6.5$$

Now let us consider initially there was 1.0 mol of *cis*-2-butene only and at equilibrium, there are x-mol trans-2-butene and y mol 2-methyl propene.

$$\Rightarrow K_{P_1} = \frac{x}{1 - x - y} = 2, K_{P_2} = \frac{y}{1 - x - y} = 6.5$$

Solving, $x = 0.21$ and $y = 0.6842$

Solving,

 \Rightarrow At equilibrium, mixture contain 21% trans-2-butene, 68.42% 2-methyl propene and rest 10.58% cis-2-butene.

386. Let *x* mol $PCl_5(g)$ decomposes into $PCl_3(g)$ and $Cl_2(g)$ as:

. ~ 0

$$PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g)$$

$$0.02 - x \qquad x \qquad x$$
At equilibrium.: Total moles of gaseous species = $0.02 + x + 0.015 = 0.035 + x$

$$\Rightarrow \qquad Partial pressure : PCl_{5}(g) = \frac{0.02 - x}{0.035 + x} \times 1.843$$

 \Rightarrow

$$Cl_{2}(g) = PCl_{3}(g) = \frac{x}{0.035 + x} \times 1.843$$

$$\Rightarrow \qquad K_{P} = 0.4 = \frac{x^{2} \times 1.843}{(0.035 + x)(0.02 - x)}$$

Solving, $x = 0.01 \implies$ Total moles at equilibrium = 0.035 + 0.01 = 0.045 $\Rightarrow \qquad V = \frac{0.045 \times 0.082 \times 500}{1.843} = 1.0$ L.

387. Let initially, there are 100 moles of gaseous mixture. Then

$$SO_2 + \frac{1}{2}O_2 \implies SO_3$$

15 20 65

After changing temperature to *T*, let *x* mole of SO₂ is consumed. Now at new equilibrium : SO₂ = 15 - x

$$O_2 = 20 - x/2$$

SO₃ = 65 + x
From the given condition : 65 + x = 0.8 $\left(100 - \frac{x}{2}\right) \implies x = 10.7$

Therefore, partial pressures at new equilibrium are :

$$SO_3 = \frac{75.7}{94.65} atm, SO_2 = \frac{4.3}{94.65}, O_2 = \frac{14.65}{94.65}$$

 $K_P(T) = \frac{75.7}{94.65} \times \frac{94.65}{4.3} \times \sqrt{\frac{94.65}{14.65}} = 44.75$

 \Rightarrow

Also, $\Delta G^{\circ} = -RT \ln K_P = -22600 + 21T \implies \ln K_P = \frac{22600}{RT} - \frac{21}{R} = 3.8$

Solving, *T* = 429.7 K.

388. Initially:
$$\operatorname{CO}(g) + \operatorname{H}_2\operatorname{O}(g) \rightleftharpoons \operatorname{CO}_2(g) + \operatorname{H}_2(g)$$

 $1 - x \quad 1 - x \qquad x \quad x$
 $K = 9 = \left(\frac{x}{1 - x}\right)^2 \implies x = \frac{3}{4}$

At this equilibrium, moles of $CO = H_2O = \frac{1}{4}$ and moles of $CO_2 = H_2 = \frac{3}{4}$. Now, let us assume that $CO_2(g)$ flask contained x mole of $CO_2(g)$. Then

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\left(\frac{1}{4} + y\right) \quad \left(\frac{1}{4} + y\right) \quad \left(\frac{3}{4} + x - y\right) \quad \left(\frac{3}{4} - y\right) \quad \text{Also } y = \frac{1}{4}$$

$$\Rightarrow \qquad K = 9 = \frac{0.5 (0.5 - x)}{(0.5) (0.5)} \quad \Rightarrow \quad x = 4$$

Hence, volume of $CO_2(g)$ flask = 4.00 litre.

389.

$$H_{2} + I_{2} \rightleftharpoons 2HI$$

$$0.5 - x \quad 0.5 - x \quad 2x \quad \Rightarrow \quad \frac{2x}{V} = 0.15 \qquad \dots(i)$$

$$0.8 - y \quad 0.8 - y \quad 2y \quad \Rightarrow \quad \frac{2y}{V} = ?$$

$$K = \left(\frac{2x}{0.5 - x}\right)^{2} = \left(\frac{2y}{0.8 - y}\right)^{2} \Rightarrow \quad y = 1.6 x$$

$$\Rightarrow \qquad \qquad \frac{2y}{V} = \frac{3.2x}{2x} \times 0.15 = 0.24 \text{ M}$$
390. For
$$C(s) + CO_{2}(g) \rightleftharpoons 2CO(g)$$

$$K_{P} = \frac{P_{CO}^{2}}{P_{CO_{2}}} = 100 P_{CO_{2}} = 63$$

$$\Rightarrow \qquad \qquad P_{CO_{2}} = 0.63 \quad \text{and} P_{CO_{2}} = 63$$

$$\Rightarrow \qquad P_{CO_{2}} = 0.63 \quad \text{and} P_{CO_{2}} = 63$$

$$\Rightarrow \qquad P_{CO_{2}} = 0.63 \quad \text{and} P_{CO_{2}} = 63$$

IONIC EQUILIBRIUM

391. For weak acid H*A*, the ionization equilibrium is :

$$HA \underset{C(1-\alpha)}{\Longrightarrow} H^{+} + A^{-}$$
Also,
$$[H^{+}] = 10^{-2} = C\alpha = 0.1 \alpha \implies \alpha = 0.1$$

$$\Rightarrow K_{a} = \frac{C\alpha^{2}}{1-\alpha} = 1.1 \times 10^{-3}$$

Now, let us assume that 100 mL 0.1 M HCl is added to V mL of the above weak acid.

$$\begin{array}{l} \mbox{m mol of HCl added} = 100 \times 0.1 = 10 \\ \mbox{m mol of } A^{-} \mbox{ in the solution} = x \\ \mbox{m mol of } HA = 0.1 \ V \end{array} \\ \mbox{If, in presence of HCl, } x \mbox{ m mol of } HA \mbox{ is ionized,} \\ \mbox{m mol of } H^{+} \mbox{ in the solution} = x + 10 \\ \mbox{m mol of } A^{-} \mbox{ in the solution} = x \\ \mbox{m mol of unionized } HA = 0.1 V - x \\ \m$$