

$$P_{N_2O_4} = X_{N_2O_4} \times P_T$$

$$= \frac{2(1-f)}{(1+f)} \times P_T$$

We know,

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$$

So,

$$K_p = P_T \times \frac{4f^2}{(1-f^2)}$$

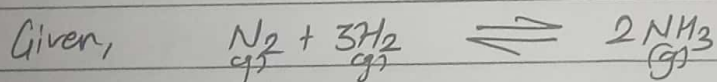
Here, P_T = total pressure of reactant and product.
 f = fraction of reactant dissociated.

Numericals and Question

Q-17: For reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$K = 6.0 \times 10^{-2}$ at $500^\circ C$. Predict the direction in which system shifts to reach equilibrium if
 $[NH_3] = 1.0 \times 10^{-5} M$, $[N_2] = 1.0 \times 10^{-5} M$, $[H_2] = 2.0 \times 10^{-3} M$.

Sol:



$$K = 6.0 \times 10^{-2}$$

$$[NH_3] = 1.0 \times 10^{-5} M \quad [N_2] = 1.0 \times 10^{-5} M, \quad [H_2] = 2.0 \times 10^{-3} M$$

So, equilibrium expression for the reaction.

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

So,

$$Q = \frac{[1.0 \times 10^{-5}]^2}{[1.0 \times 10^{-5}] \times [2.0 \times 10^{-3}]^3}$$

$$\therefore Q = 1.25 \times 10^3$$

Here, $Q > K$.

So, the equilibrium shifts towards left i.e., towards reactants.

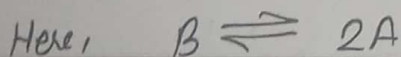
Q.27: For the reaction, $\text{B} \rightleftharpoons 2\text{A}$. $K_c = 2$.

Suppose 3.0 moles of A and B are introduced into 2.00 L flask.

(a): In which direction will proceed to attain equilibrium.

(b): What will happen to the concentration of B as reaction shifts towards equilibrium.

Soln:



$$K_c = 2$$

$$n_A = 3$$

$$n_B = 3$$

$$V = 2.00 \text{ L}$$

$$\therefore [A] = \frac{3}{2} = 1.5$$

$$[B] = \frac{3}{2} = 1.5$$

Writing equilibrium expression for the reaction,

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

So,

$$Q = \frac{[1.5]^2}{[1.5]} \quad \therefore Q = 1.5$$

Here, $Q < K_c$.

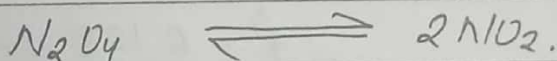
(a) So, the equilibrium shifts towards right i.e., towards products.

(b) Here, as the system attains equilibrium, the concentration of B decreases.

Q.37 (a) A mixture of N_2O_4 and NO_2 has at eq^m a total pressure of 1.5 atm. What fraction of N_2O_4 has dissociated to NO_2 at 25°C? [$K_p = 0.14$].

So/12:

Given,



Here,

$$K_p = 0.14$$

$$P_T = 1.5$$

We know,

$$K_p = \frac{4f^2}{1-f^2} \times P_T$$

$$\text{or, } 0.14 = \frac{4f^2}{1-f^2} \times 1.5$$

$$\text{or } \left(\frac{0.14}{1.5} \right) - \left(\frac{0.14}{1.5} \right) f^2 = 4f^2$$

$$\text{or } \left(\frac{0.14}{1.5} \right) = \left(4 + \frac{0.14}{1.5} \right) f^2$$

$$\therefore f = 0.15$$

Q.367: If the pressure falls to 1 atm. what is original fraction of N_2O_4 dissociated?
Soln.

Here,

$$K_p = 0.14$$

$$P_T = 1$$

We know,

$$K_p = \frac{4f^2}{1-f^2} \times P_T$$

$$\text{or, } 0.14 - 0.14f^2 = 4f^2$$

$$\Rightarrow \sqrt{\frac{0.14}{4+0.14}} = f$$

$$\therefore f = 0.183$$

Q.47: Suppose a reaction $\text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$.

(i) $K_p = P_{\text{NH}_3} P_{\text{H}_2\text{S}} = 0.11$. Find the partial pressure of each NH_3 and H_2S at equilibrium.

(ii) if NH_4HS is placed in flask containing 0.50 atm of NH_3 . What are pressures of NH_3 and H_2S when equilibrium is achieved?

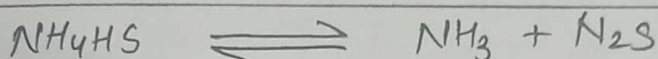
Soln:

Here,

$$K_p = 0.11 = [P_{NH_3}][P_{H_2S}]$$

Let P^0 be the pressure of NH_4HS before dissociation.

Reaction:



Initially, P^0 0 0

At eq^m, $(P^0 - P)$ P P

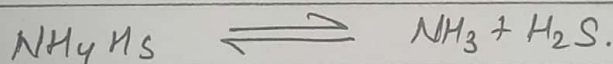
We know,

$$K_p = [P_{NH_3}] \times [P_{H_2S}]$$

$$\text{or } 0.11 = P \times P$$

$$\therefore P = 0.332 \text{ atm} \quad \text{--- (i)}$$

Again,



Initially, P^0 0 0

At eq^m: $(P^0 - P)$ $(P + 0.5)$ (P)

We know,

$$K_p = [P + 0.5][P]$$

$$\text{or, } 0.11 = P^2 + 0.5P$$

$$\therefore P = 0.165 = P_{H_2S}.$$

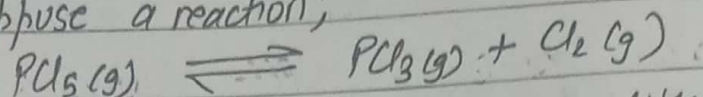
$$\therefore P_{NH_3} = P_{H_2S} + 0.165$$

$$= 0.5 + 0.165$$

$$\therefore P_{NH_3} = 0.665$$

So, if partial pressure of one component increases, then partial pressure of another component decreases.

Q.57a) Suppose a reaction;



$K_p = 11.5$ at 300°C . If pressure of dissociation of PCl_5 before was 1.5 i.e., $P^0 = 1.5$, find eq^m pressure of PCl_5 , PCl_3 , Cl_2 and mole fraction of PCl_5 dissociated.

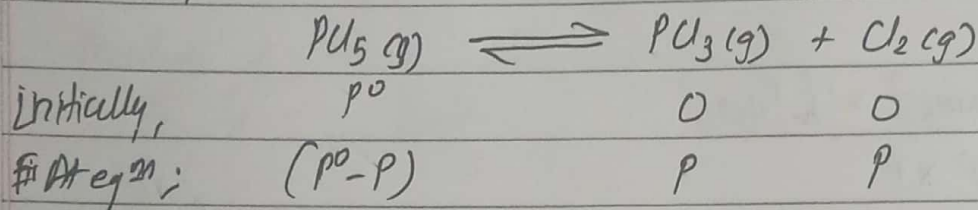
Solⁿ:

Given,

$$K_p = 11.5$$

$$P^0 = 1.5$$

Here,



We know,

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

$$\text{or } 11.5 = \frac{P \times P}{P^0 - P}$$

$$\text{or } 11.5 = \frac{P^2}{1.5 - P}$$

$$\text{or } P^2 + 1.5P - 17.25 = 0$$

$$\therefore P = 1.343$$

$$\text{So, eq^m pressure for } \text{PCl}_5 = 1.5 - 1.343 = 0.157$$

$$\text{eq^m pressure for } \text{PCl}_3 = 1.343$$

$$\text{eq^m pressure for } \text{Cl}_2 = 1.343$$

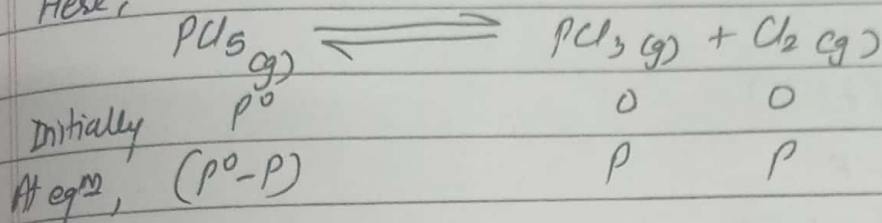
$$\text{Mole fraction of } \text{PCl}_5 \text{ dissociated (} f_{\text{P}_{\text{d}}}) = \frac{P}{P^0} = \frac{1.343}{1.5} = 0.895$$

Q.56: If P^0 is 3 atm, find eqm pressure of PCl_5 , PCl_3 , Cl_2 and mole fraction of PCl_5 dissociated.
Soln.

$$K_p = 11.5$$

$$P^0 = 3$$

Here,



We know,

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$\text{or } 11.5 = \frac{P^2}{3 - P} \quad \text{or, } P^2 + 11.5P - 34.5 = 0$$

$$\therefore P = 2.47$$

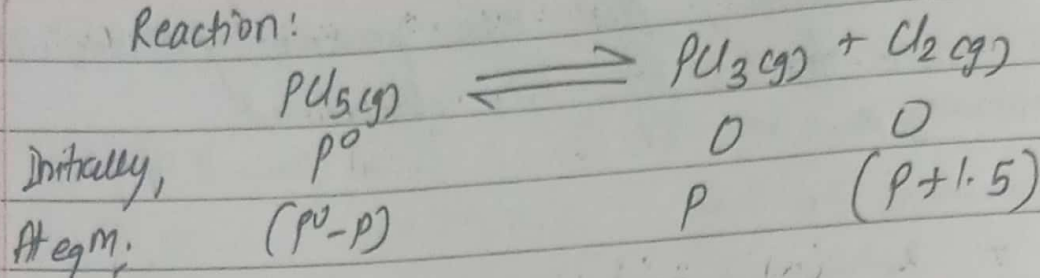
$$P_{PCl_3} = P_{Cl_2} = 2.47$$

$$P_{PCl_5} = 3 - 2.47 = 0.53$$

$$\begin{aligned}
 \text{Mole fraction of } PCl_5 \text{ dissociated} &= \frac{P}{P^0} = \frac{2.47}{3} \\
 &= 0.82
 \end{aligned}$$

Q.56: If 1.5 atm Cl_2 is added, what happens to the reaction mixture? Q.56.
Soln.

Reaction:



We know,

$$K_p = \frac{(p)(p+1.5)}{p^0 - p}$$

$$\text{or, } 11.5 = \frac{p^2 + 1.5p}{3 - p} \quad \text{or,}$$

Here,

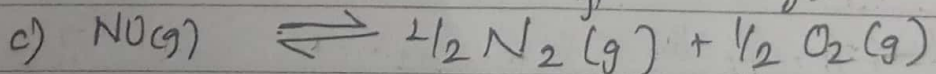
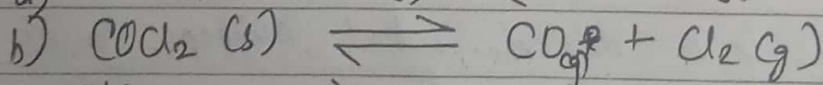
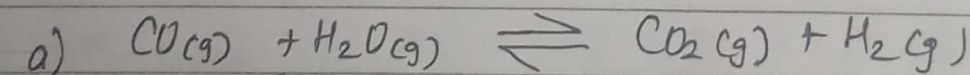
$$p = p_{\text{Cl}_3} = 2.26 \text{ atm}$$

$$\therefore p_{\text{Cl}_2} = 1.5 + 2.26 = 3.76 \text{ atm}$$

$$\text{Mole fraction of PCl}_2 \text{ dissociated} = \frac{2.26}{3} = 0.75$$

Here, addition of Cl_2 decreases dissociated amount of PCl_5 .

Q.67: For which reaction is equilibrium constant dependent on concentration?



Ans:

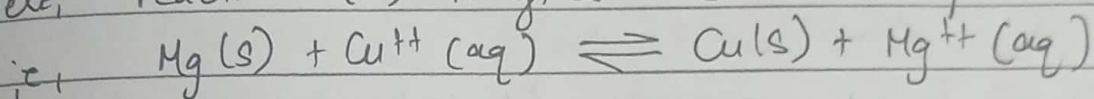
$\text{COCl}_2(\text{s}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ has equilibrium constant dependent on concentration.

Q.7: Of the metals, Zn, Mg and Fe, which removes cupric ion from the solution most completely?

- (a) $\text{Zn(s)} + \text{Cu}^{++}(\text{aq}) \rightleftharpoons \text{Cu(s)} + \text{Zn}^{++}(\text{aq})$ $\{K = 2 \times 10^{37}\}$
 (b) $\text{Mg(s)} + \text{Cu}^{++}(\text{aq}) \rightleftharpoons \text{Cu(s)} + \text{Mg}^{++}(\text{aq})$ $\{K = 6 \times 10^{90}\}$
 (c) $\text{Fe(s)} + \text{Cu}^{++}(\text{aq}) \rightleftharpoons \text{Cu(s)} + \text{Fe}^{++}(\text{aq})$ $\{K = 3 \times 10^{26}\}$

Ans:

Here, reaction (b) gives the most cupric ion.



Q.7: N_2 and H_2 combine to form NH_3 by reaction,
 $\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightleftharpoons \text{NH}_3$ $\Delta H = -2.42 \text{ kcal.}$

If a mixture of three gas in equilibrium, what would be the effect on the amount of NH_3 if.

- (a) the mixture were compressed
 (b) temperature were raised
 (c) additional H_2 were introduced?

Ans:

For (a):

If the mixture were compressed, the volume of the mixture decreased as pressure increases, the amount of NH_3 increases.

For (b):

If the temperature is increased, the equilibrium shifts towards the reactants i.e., the amount of NH_3 decreases.

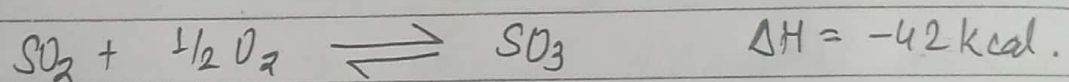
For exothermic, increase in temp shifts towards right side.

(c): If additional H_2 is added, the pressure increases and hence, the amount of NH_3 increases.

Q.8: Would you expect the equilibrium constant for the reaction, $I_2(g) \rightleftharpoons 2I(g)$ to increase or decrease as temperature increases?

Ans: For $I_2(g) \rightleftharpoons 2I(g)$ if temperature increases the equilibrium constant also increases as heat cleaves I_2 molecule producing more I atoms.

Q.9: Suggest four ways in which the equilibrium concentration of SO_3 can be increased in a closed vessel if the only reaction is:



Ans:

Four ways in which the equilibrium concentration of SO_3 can be increased in a closed vessel are:

(i): By decreasing temperature of this exothermic reaction, the concentration of SO_3 can be increased.

(ii) If we increase the pressure, the equilibrium shifts towards SO_3 as SO_3 has less number of moles than reactants.

(iii): If the ~~increase~~ concentration of both reactants or products or either one of this can increase ~~that~~ equilibrium concentration of SO_2 .

Q.10: $\text{NH}_4\text{CO}_2\text{NH}_2$ (Solid ammonium carbamate), dissociates completely into ammonia and carbon dioxide

$$\text{NH}_4\text{CO}_2\text{NH}_2 \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$$

At 25°C , the total pressure of the gases in eqm with solid is 0.116 atm . What is equilibrium constant of reaction? If 0.1 atm of CO_2 is introduced after eqm is reached, will the final pressure of CO_2 be greater or less than 0.1 atm ? Will the pressure of NH_3 increase or decrease?

Soln:

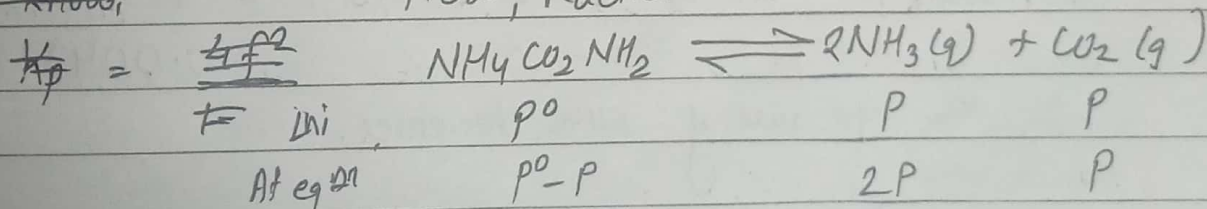
Given,

$$P_T = 0.116 \text{ atm}$$

$$K_p = ?$$

We know,

Here, reaction:



So, the eqm constant;

$$K_p = [2P]^2 [P]$$

$$\therefore K_p = 4P^3$$

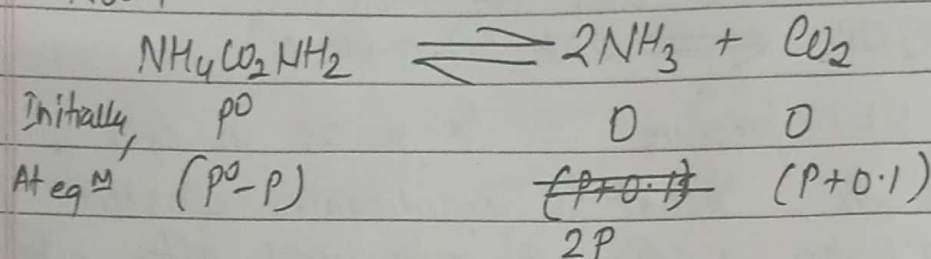
Here, total pressure (P_T) = $2P + P = 3P$

or $0.116 = 3P$

$\therefore P = 0.038$

So, $K_p = 4 \times (0.038)^3 = 2.19 \times 10^{-4}$

Now,



Now,

$K_p = 2P \times (P + 0.1)^{0.2}$

or, $2.19 \times 10^{-4} = 2P^2 + 2P$

$\therefore P = 2.166 \times 10^{-3}$

So, $P_{\text{CO}_2} = 2.166 \times 10^{-3} + 0.1 = 0.1021 \text{ atm.}$

So, the pressure of CO_2 increases.

So, $P_{\text{NH}_3} = 2P = 2 \times 2.166 \times 10^{-3} = 4.332 \times 10^{-3}$
 $= 0.004332 \text{ atm.}$

So, the pressure of NH_3 decreases.

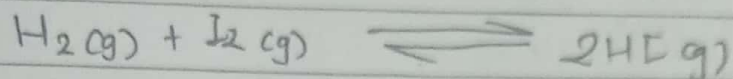
Q.11. For the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}$

$K = 55.3$ at 699 K. $K_p = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

In a mixture that consists of 0.70 atm of HI and 0.02 atm each of H_2 and I_2 at 699 K , will there be any net reaction? If so, will HI be consumed or formed?

Solⁿ:

Given reaction,



$$K = 55.3$$

$$K_p = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$P_{\text{HI}} = 0.70 \text{ atm}$$

$$P_{\text{H}_2} = P_{\text{I}_2} = 0.02 \text{ atm.}$$

Solⁿ:

$$K_p = \frac{[P_{\text{HI}}]^2}{[P_{\text{H}_2}][P_{\text{I}_2}]}$$

$$= \frac{[0.70]^2}{[0.02][0.02]} \quad \therefore K_p = 1225 = Q.$$

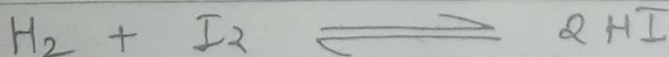
Since, $Q > K$, the reaction goes in backward direction i.e. towards left.

This means HI is consumed.

Q.102: Hydrogen and iodine react at 699 K according to $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. If 1.00 mole of H_2 and 1.00 mole of I_2 are placed in 1.00 litre vessel and allowed to react, what weight of HI is present at equilibrium? At 699 K, $K = 55.3$.

Solⁿ:

At initial Given reaction,



$$\text{At initial,} \quad 1 \quad 1 \quad 0$$

$$\text{At eqm,} \quad 1-x \quad 1-x \quad 2x$$

Writing eq^m expression,

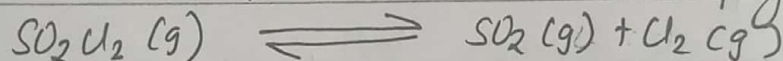
$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$\alpha, 55.3 = \frac{[2\alpha]^2}{(1-\alpha)^2}$$

$$\therefore \alpha = 0.787$$

$$\begin{aligned} \text{Weight of HI} &= 2 \times \alpha \times \text{Mol wt of HI} \\ &= 2 \times 0.787 \times 128 \\ \therefore \text{weight of HI} &= 201.472 \text{ gm.} \end{aligned}$$

[Q.13]: At 375 K, equilibrium constant K_p of reaction.



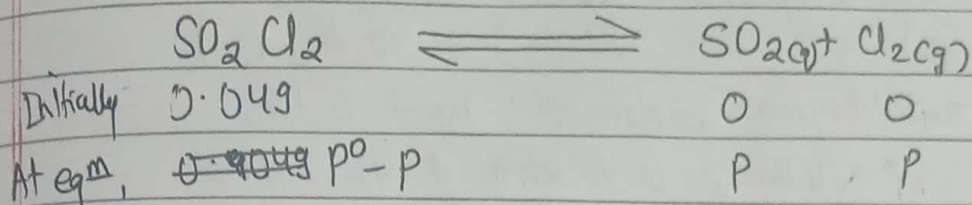
is 2.4 when pressure are expressed in atm. Assume that 6.7 gm of SO_2Cl_2 (mol wt = 135) are placed into 1 litre bulb and temp raised to 375 K. What would be pressure of SO_2Cl_2 be if none of it dissociated. What are pressure of SO_2 , Cl_2 and SO_2Cl_2 at eq^m? Solⁿ.

Here,

$$K_p = 2.4.$$

$$\text{no. of moles of } SO_2Cl_2 = \frac{6.7}{135} = 0.049$$

The reaction,



$$K_p = \frac{[P]^2}{[P^0 - P]} \quad \text{or,} \quad 2.4 = \frac{p^2}{p^0 - p} \quad \text{--- (i).}$$

So,

We have, $PV = nRT$

or $P_0 = 0.049 \times 0.0821 \times 375 / 1$

$\therefore P_0 = 1.528$

Putting in eqn (i),

$$2.4 = \frac{p^2}{1.528 - p}$$

$$1.528 - p$$

or $p^2 = 2.4(1.528 - p)$

$\therefore p = 1.06 \text{ atm.}$

So, at eqm,

$$P_{\text{SO}_2\text{Cl}_2} = 1.528 - 1.06 = 0.468$$

$$P_{\text{Cl}_2} = P_{\text{SO}_2} = ~~0.468~~ 1.06 \text{ atm}$$

Date _____ No. _____

Q.14) The gaseous compound NOBr decomposes

$$\text{NOBr (g)} \rightleftharpoons \text{NO (g)} + \frac{1}{2} \text{Br}_2 \text{ (g)}$$

At 350 K, equilibrium constant $K_p = 0.15$.

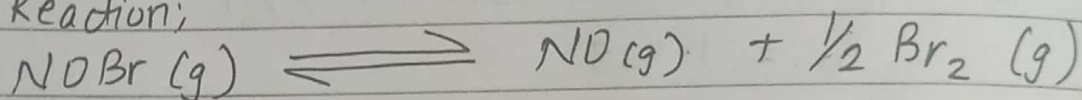
If 0.50 atm of NOBr, 0.40 atm of NO and 0.20 atm of Br_2 are mixed at this temperature, will any net reaction occur? If so, will Br_2 be consumed or formed?

Soln.

Given,

$$K_p = 0.15$$

Reaction;



~~Initially,~~ ~~At eqm,~~ ~~for~~ writing eqm constant expression. \emptyset

$$K_p = \frac{[\text{P}_{\text{NO}}][\text{P}_{\text{Br}_2}]^{1/2}}{[\text{P}_{\text{NOBr}}]}$$

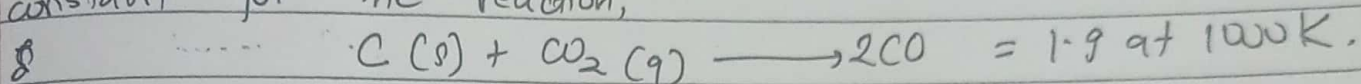
$$\text{So, } Q_p = \frac{[0.40][0.20]^{1/2}}{0.50} = 0.357$$

Here,

$Q_p > K_p$ so reaction moves towards reactants.

Hence, Br_2 is consumed.

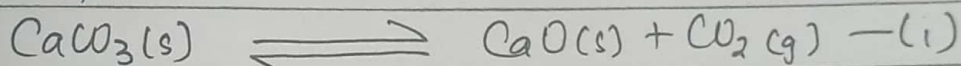
Q.15: At 1000 K, the pressure of CO_2 in equilibrium with CaCO_3 and CO_2 is equal to 3.9×10^{-2} atm. The equilibrium constant for the reaction,



Solid C , CaO and CaCO_3 are mixed and allowed to come at eqm at 1000 K in closed vessel. what is pressure of CO at eqm.

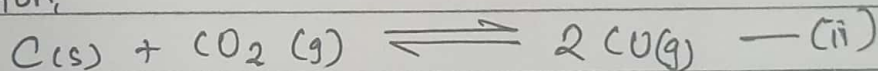
Soln.

For reaction,



$$K_1 = [\text{CO}_2] = 3.9 \times 10^{-2}$$

For reaction,



$$K_2 = \frac{[\text{CO}]^2}{[\text{CO}_2]} = 1.9$$

$$\text{or, } \sqrt{1.9 \times 3.9 \times 10^{-2}} = [\text{CO}]$$

$$\therefore [\text{CO}] = 0.272 = 2.7 \times 10^{-1} \text{ atm.}$$