

Chapter 9: Chemical Equilibrium

Review Questions

1. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

Solution

The equilibrium constant expression for pure liquids and solids is as follows:

$$[\text{Pure liquid}] \text{ or } [\text{Pure solid}] = \frac{\text{Number of moles}}{\text{Volume}} = \frac{\text{Mass}}{\text{Molecular mass} \times \text{Volume}} = \frac{\text{Density}}{\text{Molecular mass}}$$

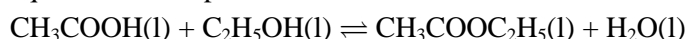
As the density of a pure liquid or pure solid is constant at constant temperature and molecular mass is also constant, therefore, their molar concentrations are constant and included into the equilibrium constant. Hence, the values of pure substances are not mentioned in the equilibrium constant expression.

2. What is the difference between a heterogeneous and homogeneous equilibrium?

Solution

In a homogeneous equilibrium, all of the reactants and products are in the same phase. In heterogeneous equilibrium, at least two different phases are found between the reactants and products.

3. The ester, ethyl acetate, is formed by the reaction of ethanol and acetic acid and the equilibrium is represented as



(a) Write the concentration ratio, Q_c , for this reaction. Note that water is not in excess and is not a solvent in this reaction.

(b) At 293 K, if one starts with 1.000 mol of acetic acid and 1.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(c) Starting with 0.500 mol of ethanol and 1.000 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

(d) We do not use dilute aqueous solutions for this reaction. Why?

(e) Why is some concentrated sulphuric acid usually added to reaction mixture in the laboratory preparation of ethyl acetate?

(f) As the heat of reaction is nearly zero for this reaction, how will the equilibrium constant depend upon the temperature?

Solution

(a) For the given reaction,

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{C}_2\text{H}_5\text{OH}(\text{l})]}$$

(b)

	$\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$			
Initial	1.000 mol	0.180 mol	0	0
At equilibrium	(1 - 0.171) mol	(0.180 - 0.171) mol	0.171 mol	0.171 mol
	0.829 mol	0.009 mol	0.171 mol	0.171 mol

$$\text{So, } K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{0.171 \text{ mol} \times 0.171 \text{ mol}}{0.829 \text{ mol} \times 0.009 \text{ mol}} = 3.92 \text{ mol}$$

(c) Here

	$\text{CH}_3\text{COOH(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$			
Initial	1.500 mol	1.000 mol	0	0
At equilibrium	$(0.500 - 0.214)$	$(1.000 - 0.214)$	0.214	0.214 mol
	0.286 mol	0.786 mol	0.214 mol	0.214 mol

$$\text{So, } Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{0.214 \text{ mol} \times 0.214 \text{ mol}}{0.286 \text{ mol} \times 0.786 \text{ mol}} = 0.20$$

As the value of Q_c ($= 0.20$) is less than the value of K ($= 3.92$), hence the equilibrium is not reached. The reaction is on the left.

So, the reactants are still reaching to form more products.

(d) This reaction is a reversible reaction in which H_2O is one of the products. In dilute solution, the concentration of water is high. High concentration of water (H_2O) will shift the equilibrium toward left (reactant side). As a result, no or very little amount of ester will be formed if dilute aqueous solutions are used in this reaction.

(e) Concentrated sulphuric acid acts as a catalyst in this reaction. Also, concentrated sulphuric acid is a strong dehydrating agent. So, it removes water (H_2O) as soon as it is formed. As a result, the equilibrium shifts to the right, and more amount of ester is formed.

(f) Variation in equilibrium constant for this reaction would be small with a change of temperature.

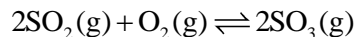
4. Define physical equilibrium with examples.

Solution

The state of a process in which properties such as temperature, pressure, and concentration of the system do not show any change with the passage of time is known as equilibrium. In all processes that attain equilibrium, two opposing processes are involved. Equilibrium is attained when the rates of the two opposing processes become equal. If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium. The most common examples of physical equilibrium are those that involve phase transformation. For example,



5. For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase:



$$K_p = 40.5 \text{ atm}^{-1} \text{ at } 900 \text{ K and } \Delta_r H = -198 \text{ kJ mol}^{-1}$$

(a) Write the expression for the equilibrium constant for the reaction.

(b) At room temperature ($\approx 300 \text{ K}$) will K_p be greater than, less than, or equal to K_p at 900 K .

(c) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?

(d) What is the effect of adding 1 mol of $\text{He}(\text{g})$ to a flask containing SO_2 , O_2 , and SO_3 at equilibrium at constant temperature.

Solution

(a) The equilibrium constant for this reaction is written in terms of the partial pressures of the reactants and products.

$$K_p = \frac{P_{\text{SO}_3(\text{g})}^2}{P_{\text{SO}_2(\text{g})}^2 \times P_{\text{O}_2(\text{g})}}$$

(b) This reaction is exothermic. So, its equilibrium constant should increase with the lowering of temperature. Therefore, the value of K_p at 300 K will be greater than the value at 900 K.

(c) When the volume of the vessel is reduced, the volume of the reaction mixture will decrease. As a result, pressure of the gaseous mixture will increase. According to the Le Chatelier's principle, the system will move in a direction to undo the effect of the pressure increase. The system therefore will move in a direction so as to decrease the number of moles of the gaseous substance in the system. The number of moles decreases in going from reactants to the product side. Therefore, a decrease in the volume of the reacting system will shift the equilibrium to the right. That is, more $\text{SO}_3(\text{g})$ will be formed from the reactants.

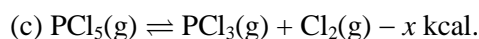
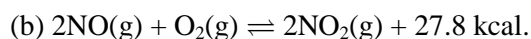
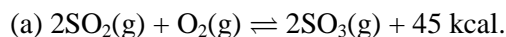
(d) Addition of helium to the reaction mixture at equilibrium under constant volume has no effect on the equilibrium.

6. Why does not a catalyst affect the position of equilibrium in a chemical reaction?

Solution

A catalyst affects the rate of the reaction but does not affect the position of the equilibrium. The catalyst affects both the forward and the reverse reaction to the same extent, so the ratios of the forward and the reverse reactions for the catalyzed and uncatalyzed reactions do not change.

7. Under what conditions will the following reactions go in the forward direction?



Solution

(a) Low T , high p , excess of O_2 and SO_2

(b) Low T , high p , excess of NO and O_2

(c) High T , low p , excess of PCl_5

8. Consider the following equilibrium.



If you were converting between K_p and K_c , what value of Δn_g would you use?

Solution

The value for Δn_g is the difference between the number of moles of reactant gas and the number of moles of product gas:

$$\begin{aligned}\Delta n_g &= (\text{moles of gaseous products}) - (\text{moles of gaseous reactants}) \\ &= 2 \text{ mol} - 0 \text{ mol} = 2 \text{ mol}\end{aligned}$$

9. How will the value of K_p for the following reactions be affected by an increase in temperature?

- (a) $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$; $\Delta H^\circ = -18\text{kJ}$
 (b) $\text{N}_2\text{O(g)} + \text{NO}_2\text{(g)} \rightleftharpoons 3\text{NO(g)}$; $\Delta H^\circ = +155.7\text{kJ}$
 (c) $2\text{NO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{NOCl(g)}$; $\Delta H^\circ = -77.07\text{kJ}$

Solution

(a) This is an exothermic reaction. By increasing the temperature, the equilibrium shifts to the left and more reactants are formed; therefore, the denominator becomes larger and the K_p decreases.

(b) This is an endothermic reaction. By increasing the temperature, the equilibrium is shifted to the right and more products are formed, and the numerator increases and K_p increases.

(c) This is the same as part (a): an exothermic reaction and the increase in temperature shift the reaction to the left and increase the amount of the reactants and K_p decreases.

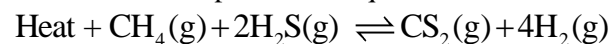
10. Write the equilibrium law for each of the following gaseous reactions in terms of molar concentrations and partial pressures.

- (a) $2\text{PCl}_3\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{POCl}_3\text{(g)}$
 (b) $2\text{SO}_3\text{(g)} \rightleftharpoons 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$
 (c) $2\text{N}_2\text{H}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)} + 2\text{H}_2\text{O(g)}$
 (d) $\text{N}_2\text{H}_4\text{(g)} + 6\text{H}_2\text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)} + 8\text{H}_2\text{O(g)}$
 (e) $\text{SOCl}_2\text{(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{SO}_2\text{(g)} + 2\text{HCl(g)}$

Solution

- (a) $K_c = \frac{[\text{POCl}_3]^2}{[\text{PCl}_3]^2[\text{O}_2]}$, $K_p = \frac{(p_{\text{POCl}_3})^2}{(p_{\text{PCl}_3})^2(p_{\text{O}_2})}$,
 (b) $K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}$, $K_p = \frac{(p_{\text{SO}_2})^2(p_{\text{O}_2})}{(p_{\text{SO}_3})^2}$,
 (c) $K_c = \frac{[\text{NO}]^2[\text{H}_2\text{O}]^2}{[\text{N}_2\text{H}_4][\text{O}_2]^2}$, $K_p = \frac{(p_{\text{NO}})^2(p_{\text{H}_2\text{O}})^2}{(p_{\text{N}_2\text{H}_4})(p_{\text{O}_2})^2}$,
 (d) $K_c = \frac{[\text{NO}_2]^2[\text{H}_2\text{O}]^8}{[\text{N}_2\text{H}_4][\text{H}_2\text{O}_2]^6}$, $K_p = \frac{(p_{\text{NO}_2})^2(p_{\text{H}_2\text{O}})^8}{(p_{\text{N}_2\text{H}_4})(p_{\text{H}_2\text{O}_2})^6}$,
 (e) $K_c = \frac{[\text{SO}_2]^2[\text{HCl}]^2}{[\text{SOCl}_2][\text{H}_2\text{O}]}$, $K_p = \frac{(p_{\text{SO}_2})^2(p_{\text{HCl}})^2}{(p_{\text{SOCl}_2})(p_{\text{H}_2\text{O}})}$

11. How will the position of equilibrium in the following reaction:



be affected by:

- (a) Adding $\text{CH}_4\text{(g)}$? (b) Adding $\text{H}_2\text{(g)}$?

- (c) Removing CS₂(g)?
 (d) Decreasing the volume of the container?
 (e) Increasing the temperature?

Solution

- (a) The system shifts to the right to consume some of the added methane.
 (b) The system shifts to the left to consume some of the added hydrogen.
 (c) The system shifts to the right to make some more carbon disulphide.
 (d) The system shifts to the left to decrease the amount of gaseous moles.
 (e) The system shifts to the right to absorb some of the added heat.

12. Two 1.00 L bulbs are filled with 0.500 atm of F₂(g) and PF₃(g), as illustrated in the Fig. 8.5. At a particular temperature, K_p = 4.0 for the reaction of the gases to form PF₅(g):

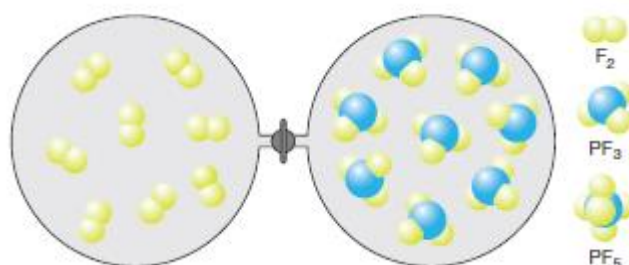
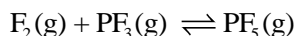
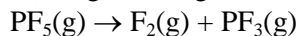
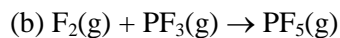
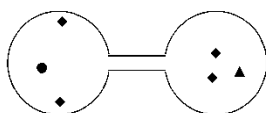


Figure 8.5

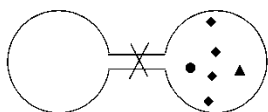
- (a) The stopcock between the bulbs is opened and the pressure falls. Make a sketch of this apparatus showing the gas composition once the pressure is stable.
 (b) List any chemical reactions that continue to occur once the pressure is stable.
 (c) Suppose all the gas in the left bulb is forced into the bulb on the right and then the stopcock is closed. Make a second sketch to show the composition of the gas mixture after equilibrium is reached. Comment on how the composition of the one-bulb system differs from that for the two-bulb system.

Solution

(a)

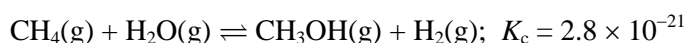
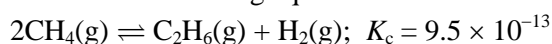


(c)

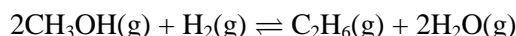


Because the volume is smaller, Le Chatelier's principle states that the equilibrium will favor the products. Consequently, equilibrium will be shifted to the right in a smaller volume. As can be seen here, a higher proportion of the reactants have reacted to form more PF₅ than the case in (a).

13. Use the following equilibria:



to calculate K_c for the reaction

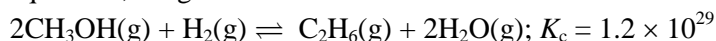


Solution

If we reverse the second reaction and double it, we can then add the first and second reactions together to obtain the desired reaction. When we double the second reaction, we square the rate constant. When we reverse it, we invert the rate constant. Consequently, we get the following:



Adding these equations, we get



where K_c for the final reaction is the product of K_c for the first reaction and K_c for the "modified" second reaction.

14. Define the state of equilibrium. What are the general characteristics of the following equilibria?

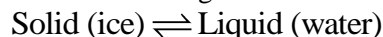
- (a) Solid–liquid (b) Liquid–vapor (c) Solid–vapor

Solution

Equilibrium represents the state of a process in which properties such as temperature, pressure, and concentration of the system do not show any change with the passage of time.

(a) Solid–Liquid equilibrium (melting of ice)

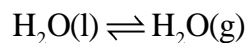
If some ice cubes along with some water at 0°C and normal atmospheric pressure are placed in a thermos flask so that no heat can enter or leave the system, the mass of ice and water is found to remain constant. However, the two opposing processes going on at equilibrium are melting of ice and freezing of water. At equilibrium



$$\text{Rate of melting of ice} = \text{Rate of freezing of water}$$

(b) Liquid–Vapor equilibrium (Evaporation of water in a closed vessel)

Consider a closed vessel connected to a manometer having arrangement for evaluation and addition of liquid into it. Suppose the vessel is first evacuated. The level of mercury in both the limbs of the manometer will be the same. Now suppose water is added into the vessel and the whole apparatus is allowed to stay at room temperature. It is observed that the level of mercury in the left limb of the manometer begins to fall and that in the right limb begins to rise. After some time, the level becomes constant and the equilibrium is attained



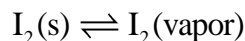
Rate of evaporation = Rate of condensation

(c) Solid–vapor equilibrium

This type of equilibrium is attained for solids that undergo sublimation. For example, if solid iodine is placed in a closed vessel, violet vapors start appearing in the vessel whose intensity increases with time and ultimately it becomes constant. At this stage, equilibrium is attained, that is,

Rate of sublimation of solid iodine to vapor = Rate of condensation of iodine vapor to give solid iodine

The equilibrium may be represented as



15. What are the general characteristics of equilibrium involving physical processes?

Solution

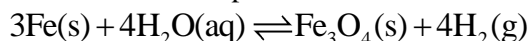
The general characteristics of equilibrium involving physical processes are as follows:

- (a) Equilibria involving gases can be attained only in closed vessels.
- (b) Equilibrium is dynamic in nature.
- (c) Some observable properties of the system become constant at equilibrium.
- (d) The concentration of the different substances becomes constant at constant temperature at equilibrium.
- (e) The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibrium is attained.

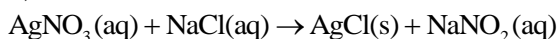
16. What are reversible and irreversible reactions? Give one example of each.

Solution

A reaction in which not only the reactants react to form the products under certain conditions, but the products also react to form reactants under the same conditions is called a reversible reaction. In other words, a reaction that takes place not only in the forward direction but also in the backward direction under the same conditions is known as a reversible reaction. An example of reversible reaction is



If a reaction cannot take place in reverse direction, that is, the products formed do not react to give back the reactants under the same conditions, it is called an irreversible reaction. For example,



17. State the law of mass action.

Solution

According to the law of mass action, the rate at which a substance reacts is proportional to its active mass, and hence, the rate of a chemical reaction is proportional to the product of the active masses of the reactants. The term active mass means the molar concentration, that is, number of moles dissolved per liter of the solution.

18. The equilibrium constant of a reaction is 2×10^{-3} at 25°C and 2×10^{-2} at 50°C . Is the reaction exothermic or endothermic?

Solution

As equilibrium constant has increased with temperature, the reaction is endothermic (proceeds in the forward direction).

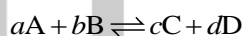
19. Deduce the expression for equilibrium constant using the law of mass action.

Solution

This law states that: "At constant temperature the rate at which a substance reacts is proportional to its active mass, and the rate of a chemical reaction is proportional to the product of active masses of the reactants." The expression for active mass is

$$\text{Active mass (molar concentration)} = \frac{\text{Number of moles}}{\text{Volume in liters}}$$

Active mass of a gas or liquid means its molar concentration; active mass of a solid is always taken as unity. Law of mass action is applicable only to a reversible reaction. In other words, the law states that: "At constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of reacting species, with each concentration term raised to the power equal to the numerical coefficient of that species in the chemical equation." Let us consider a general reversible reaction:



Rate of forward reaction = $k_f [A]^a [B]^b$

Similarly, Rate of backward reaction = $k_b [C]^c [D]^d$

where k_f and k_b are the respective rate constants or velocity constant.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

or

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

therefore,

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

where K_c is equilibrium constant. Conventionally, K_c is always equal to k_f/k_b .

20. What qualitative information can you obtain from the magnitude of equilibrium constant?

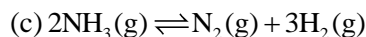
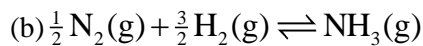
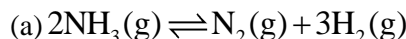
Solution

(a) Large value of equilibrium constant, $K (>10^3)$ shows that forward reaction is favored, that is, concentration of products is much larger than that of the reactants at equilibrium.

(b) Intermediate value of $K (10^{-3}$ to $10^3)$ shows that the concentration of the reactants and product is comparable.

(c) Low value of $K (<10^{-3})$ shows that backward reaction is favored, that is, concentration of reactants is much more than that of the products.

21. For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, at 400 K, $K_p = 41$. Find the value of K_p for each of the following reactions at the same temperature:



Solution

(a) It is the reverse of the given reaction. Hence, $K_p = 1/41$.

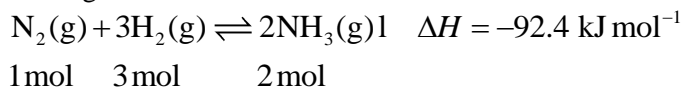
(b) It is obtained by dividing the given equation by 2. Hence, $K_p = (41)^{1/2}$

(c) It is obtained by multiplying the given equation by 2. Hence, $K_p = (41)^2$

22. Why does manufacture of ammonia by Haber's process require higher pressure, low temperature, and use of catalyst?

Solution

The reaction involving formation of ammonia is

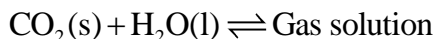


In this equilibrium reaction, the forward reaction is accompanied by a decrease in the total number of moles. If the pressure on the system is increased, then according to Le Chatelier's principle, the equilibrium will shift in the direction in where the pressure decreases. Hence, decrease in the number of moles takes place, which is in favor of formation of ammonia. Thus, higher the pressure, the better would be the yield of ammonia. Now, the forward reaction is exothermic. Therefore, according to Le Chatelier's principle, decrease in temperature will shift the reaction in the forward direction, that is, in favor of formation of ammonia. In this reaction, finely divided iron is used as a catalyst to achieve the equilibrium rapidly. Thus, manufacture of ammonia by Haber's process is favored by high pressure, low temperature, and use of catalyst.

23. Using Le Chatelier's principle, explain the effect of pressure on the solubility of gases in liquids.

Solution

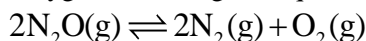
Aerated water is the solution of CO_2 into water.



According to Le Chatelier's principle, high pressure shifts the equilibrium to the right, meaning reduced volume. Low pressure shifts the equilibrium to the left favoring the separation of the gas from the liquid as the volume increases. Therefore, CO_2 remains dissolved in water under pressure.

Numerical Problems

1. Nitrous oxide, N_2O , sometimes called laughing gas, has a strong tendency to decompose into nitrogen and oxygen following the equation:



but the reaction is so slow that the gas appears to be stable at room temperature (25°C). The decomposition reaction has $K_c = 7.3 \times 10^{34}$. What is the value of K_p for this reaction at 25°C ?

Solution

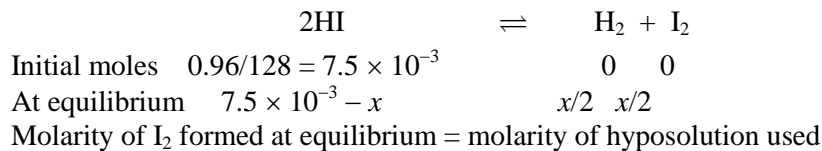
Use the equation $K_p = K_c(RT)^{\Delta n}$. In this reaction, $\Delta n = 3 - 2 = 1$, so

$$K_p = K_c(RT)^{\Delta n} = (7.3 \times 10^{34})(0.0821 \times 298)^1 = 1.8 \times 10^{36}$$

2. 0.96 g of HI was heated to attain equilibrium $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$. The reaction mixture on titration requires 15.7 mL of $N/10$ hyposolution. Calculate the degree of dissociation of HI.

Solution

Consider the reaction



$$\frac{W}{M} \times 1000 = 15.7 \times \frac{1}{10}$$

$$\text{Number of moles of } \text{I}_2 \text{ formed at equilibrium} = \frac{1.57 \times 10^{-3}}{2} = 0.785 \times 10^{-3}$$

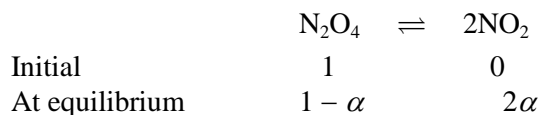
$$\frac{x}{2} = 0.785 \times 10^{-3} \Rightarrow x = 1.57 \times 10^{-3}$$

$$\text{Degree of dissociation} = \frac{x}{7.5} \times 10^{-3} = \frac{1.57 \times 10^{-3}}{7.5 \times 10^{-3}} = 0.209 = 20.9\%$$

3. N_2O_4 dissociates as $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$. At 55°C and 1 atm, the percentage dissociation is 50.3%. At what pressure and same temperature, the equilibrium mixture will have the ratio of $\text{N}_2\text{O}_4 : \text{NO}_2$ as 1:8?

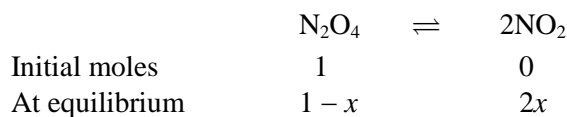
Solution

Consider the reaction



$$K_p = \frac{(2\alpha)^2}{1 - \alpha} \cdot \left(\frac{p}{1 + \alpha} \right)^{\Delta n}$$

$$K_p = \frac{4\alpha^2 p}{1 - \alpha^2} = 4 \times (0.503)^2 \times 1 / 1 - (0.503)^2 = 1.355$$



$$\text{Given that } \text{N}_2\text{O}_4/\text{NO}_2 = \frac{1-x}{2x} = \frac{1}{8} \Rightarrow x = 0.8$$

$$K_p = \frac{4x^2 \times p}{1 - 1.355} = \frac{4 \times (0.8)^2 \times p}{1 - (0.8)^2} = 0.19 \text{ atm}$$

4. One mole of each $\text{Cl}_2(\text{g})$ and $\text{Br}_2(\text{g})$ were taken in a 2 L flask, sealed and heated to some temperature, where the following equilibrium was established, and at equilibrium, the mol% of $\text{ClBr}(\text{g})$ was 40%.



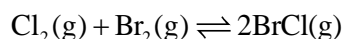
At equilibrium, 2 mol of NO gas was added where the following additional equilibrium was established:



At new equilibrium, mixture was found to contain 0.9 mol of $\text{BrCl}(\text{g})$. Determine K_C for the two equilibria in Eqs. (1) and (2).

Solution

For the reaction



Initial 1 mol 1mol 0 mol

At equil $1-x$ $1-x$ $2x$

Total number of moles at equilibrium = $1-x+1-x+2x=2$

% mol of $\text{ClBr} = 2x/2 = 40\% = 0.4$, therefore, $x = 0.4$

The equilibrium constant can be represented as

$$K_c = \frac{[2x]^2}{(1-x)(1-x)} = \frac{4(0.4)^2}{0.6 \times 0.6} = 1.78$$

5. At a certain temperature, $K_C = 4.50$ for the reaction



If 0.300 mol of N_2O_4 is placed into a 2.00 L container at that temperature, what will be the equilibrium concentrations of both gases?

Solution

The initial concentration of N_2O_4 is $0.300 \text{ mol}/2.00 \text{ L} = 0.150 \text{ M}$. As no NO_2 was placed in the reaction vessel, its initial concentration is 0.000 M . Let us take x to be the number of moles per liter of N_2O_4 that reacts, so the change in the N_2O_4 concentration is $-x$. Because of the stoichiometry of the reaction, the NO_2 concentration must increase by $2x$, so its change in concentration is $+2x$. Hence, the concentration table can be represented as

	$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	
Initial concentration (mol L^{-1})	0.150	0.000
Changes in concentrations	$-x$	$+2x$
Concentration at equilibrium	$0.150 - x$	$2x$

Now we substitute the equilibrium quantities into the expression for equilibrium constant.

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.50 \Rightarrow \frac{(2x)^2}{(0.150 - x)} = 4.50 \Rightarrow \frac{4x^2}{(0.150 - x)} = 4.50$$

Note that where the changes in concentrations are unknown, it is convenient to let the coefficients of x be the same as the coefficients in the balanced equation. This ensures

they are in the correct ratio. Because the equation involves terms in x^2 , x , and a constant, we can use the quadratic formula to obtain the value of x .

$$4x^2 = 4.50(0.150 - x) = 0.675 - 4.50x$$

Arranging terms in the standard order gives

$$4x^2 + 4.50x - 0.675 = 0$$

Therefore, the quantities we will substitute into the quadratic formula are as follows: $a = 4$, $b = 4.50$, and $c = -0.675$. Making these substitutions gives

$$x = \frac{-4.50 \pm \sqrt{(4.50)^2 - 4(4)(-0.675)}}{2(4)} = \frac{-4.50 \pm \sqrt{31.05}}{8} = \frac{-4.50 \pm 5.57}{8} \text{ M}$$

Because of the \pm term, there are two values of x that satisfy the equation, $x = 0.134$ and $x = -1.26$. However, only the first value, $x = 0.134$, makes any sense chemically, as negative concentrations are not possible. Using this value, the equilibrium concentrations are

$$[\text{N}_2\text{O}_4] = 0.150 - 0.134 = 0.016 \text{ M}$$

$$[\text{NO}_2] = 2(0.134) = 0.268 \text{ M}$$

In general, whenever you use the quadratic equation in a chemical calculation, one root will be satisfactory and the other will lead to answers that do not make sense.

6. The standard Gibbs energy change for a reaction is $\Delta G^\circ = -41.8 \text{ kJ mol}^{-1}$ at 700 K and 1 atm. Calculate the equilibrium constant of the reaction at 700 K.

Solution

The standard Gibbs energy and equilibrium constant are related by the equation:

$$\Delta G^\circ = -RT \ln K = -2.303 RT \log K$$

Given that $\Delta G^\circ = -41.8 \text{ kJ} = -41800 \text{ J}$, $T = 700 \text{ K}$, and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. Substituting these values in the equation, we get

$$-41800 = -2.303 \times 8.314 \times 700 \log K$$

$$-41800 = -13403 \log K$$

$$\log K = \frac{41800}{13403} = 3.1187 \Rightarrow K = 1.312 \times 10^4$$

7. The reaction $\text{NO}_2(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$ has $\Delta G_{1273}^\circ = -9.67 \text{ kJ}$. A 1.00 L reaction vessel at 1000°C contains 0.0200 mol NO_2 , 0.040 mol NO , 0.015 mol N_2O , and 0.0350 mol O_2 . Is the reaction at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium?

Solution

$$Q_c = \frac{[\text{N}_2\text{O}][\text{O}_2]}{[\text{NO}_2][\text{NO}]} = \frac{(0.015/1)(0.0350/1)}{(0.200/1)(0.040/1)} = 0.0656$$

$$\Delta G^\circ = -2.303RT \log K$$

$$-9670 = -2.303 \times 8.314 \times 1273 \log K$$

Hence, $\log K = 0.3967 \Rightarrow K = 2.49$

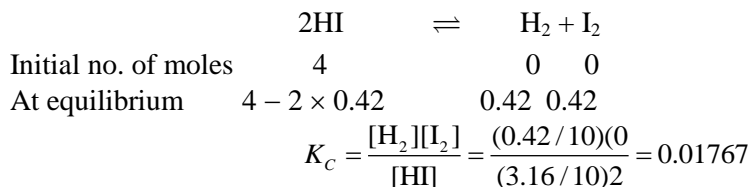
As $K > Q_c$, so the reaction will proceed in forward direction.

It is spontaneous as ΔG is negative.

8. Four moles of hydrogen iodide are taken in a 10 L flask and kept at 800 K. It undergoes the following decomposition reaction until the equilibrium is attained. The equilibrium mixture is found to contain 0.42 mol of iodine. Calculate the equilibrium constant of the reaction.



Consider the reaction

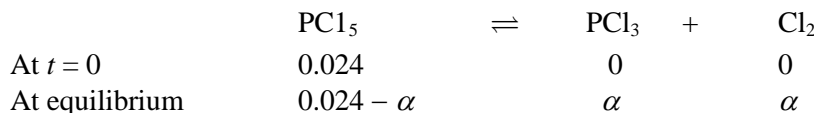


9. Five grams of PCl_5 were completely vaporized at 250°C in a vessel of 1.9 L capacity. The mixture at equilibrium exerted a pressure of 1 atm. Calculate the degree of dissociation K_C and K_p for this reaction.

Solution

$$\text{Number of moles of } \text{PCl}_5 = \frac{\text{Weight}}{\text{Molecular weight}} = \frac{5}{208.5} = 0.024$$

The equilibrium for dissociation of PCl_5 may be represented as



$$\text{Total moles of gas components} = 0.024 - \alpha + 2\alpha = (0.024 + \alpha)$$

We know that $pV = nRT$, so

$$1 \times 1.9 = (0.024 + \alpha) 0.0821 \times 523$$

$$(0.024 + \alpha) = \frac{1.9}{0.0821 \times 523} \Rightarrow \alpha = 0.0202$$

$$\text{Degree of dissociation, } \alpha = \frac{0.0202}{0.024} = 0.843$$

$$[\text{PCl}_5] = \frac{0.024 - \alpha}{1.9} = \frac{0.024 - 0.0202}{1.9} = \frac{0.0038}{1.9}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = \frac{\alpha}{V} = \frac{0.0202}{1.9}$$

$$K_C = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{[0.0202/1.9]^2}{0.0038/1.9} = \frac{4.08 \times 10^{-4}}{1.9 \times 0.0038} = 0.0565 \text{ mol L}^{-1}$$

Now, $K_p = K_C (RT)^{\Delta n}$, where $K_C = 0.0565$ and $\Delta n = 2 - 1 = 1$

Solving, we get $K_p = 0.0565 \times (0.0821 \times 523) = 2.426$

10. The equilibrium constant for the reaction, $\text{I}_2(\text{s}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{IBr}(\text{g})$ is 0.164 at 25°C .

(a) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are 0.164 atm and 25°C , respectively. Find the partial pressure of IBr formed at equilibrium. Assume that the vapor pressure of $\text{I}_2(\text{s})$ is negligible.

(b) Calculate ΔG° for the above reaction.

Solution

$$(a) K_p = \frac{p_{\text{IBr}}^2}{p_{\text{Br}_2}} = 0.164$$

Total equilibrium pressure = 0.164 atm = $p_{\text{IBr}} + p_{\text{Br}_2}$

$$p_{\text{Br}_2} = 0.164 - p_{\text{IBr}}$$

Substituting in the above equation:

$$0.164 = \frac{p_{\text{IBr}}^2}{(0.164 - p_{\text{IBr}})}$$

$$p_{\text{IBr}}^2 + 0.164 p_{\text{IBr}} - 0.0269 = 0$$

Solving, $p_{\text{IBr}} = 0.1014$ atm.

$$(b) \Delta G^\circ = -RT \ln K = -8.314 \times 298 \times 2.303 \log 0.164 = 4.48 \text{ kJ}$$

11. Equilibrium constant, K_C , for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500 K is 0.061. At a particular time, the analysis shows that the composition of the reaction mixture is $3.00 \text{ mol L}^{-1} \text{ N}_2$, $2.00 \text{ mol L}^{-1} \text{ H}_2$, and $0.500 \text{ mol L}^{-1} \text{ NH}_3$. Is the reaction at equilibrium?

If not, in which direction does the reaction tend to proceed to reach equilibrium?

Solution

Given that $[\text{N}_2] = 3.0 \text{ mol L}^{-1}$, $[\text{H}_2] = 2.0 \text{ mol L}^{-1}$, $[\text{NH}_3] = 0.50 \text{ mol L}^{-1}$

The reaction quotient for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3$ is

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.50)^2}{3 \times (2)^3} = 0.0104$$

We have $K_C = 0.061$. Thus, at this stage of the reaction, $Q_c < K_C$. Therefore, the reaction is not at equilibrium. The reaction is on the left of the equilibrium state. That is, the reaction tends to move toward products side to form more products.

12. In the reaction $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{s})$; the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H^\circ = 2750$ cal. What will be the dissociation pressure at 127°C ?

Solution

For given reaction, $K_p = (p_{\text{H}_2\text{O}})^2$

So, $K_p(25^\circ\text{C}) = (7 \times 10^{-3})^2 \text{ atm}^2 = 4.9 \times 10^{-5} \text{ atm}^2$

As $\Delta H^\circ = 2750$ cal, so using Vant Hoff equation

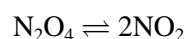
$$\log \frac{[K_p(127^\circ\text{C})]}{[K_p(25^\circ\text{C})]} = \frac{\Delta H^\circ}{2.303 \times R} \left[\frac{400 - 298}{400 \times 298} \right] \Rightarrow \log \frac{[K_p(127^\circ\text{C})]}{[4.9 \times 10^{-5}]} = \frac{2750}{2.303 \times 2} \left[\frac{102}{119200} \right]$$

$$K_p(127^\circ\text{C}) = 3.2426 \times 4.9 \times 10^{-5}$$

$$\text{so } p_{\text{H}_2\text{O}} \text{ at } 127^\circ\text{C} = \sqrt{K_p(127^\circ\text{C})} = 1.26 \times 10^{-2} \text{ atm}$$

13. The vapor density of a mixture of NO_2 and N_2O_4 is 38.3 at 27°C . Calculate the number of moles of NO_2 in 100 g mixture at equilibrium.

Solution



$$1 \quad 0$$

$$1 - \alpha \quad 2\alpha$$

Here x is degree of dissociation of N_2O_4

$$\text{Normal vapor density of } N_2O_4 = \frac{28 + 64}{2} = 46$$

$$\text{so } \alpha = \frac{46 - 38.3}{(2 - 1)38.3} = 0.2$$

Now, moles of $N_2O_4 = (1 - \alpha) = 0.8$ mol

Moles of $NO_2 = 2x = 0.4$ mol

Weight of $N_2O_4 = 92 \times 0.8 = 73.60$ g

Weight of $NO_2 = 0.4 \times 46 = 18.4$ g

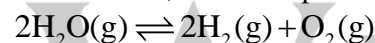
So, weight of mixture = 92 g

In 92 g mixture weight of $NO_2 = 18.4$ g

$$\text{In 100 g mixture weight of } NO_2 = \frac{18.4}{92} \times 100 = 20 \text{ g}$$

$$\text{So, moles of } NO_2 \text{ in 100 g mixture} = \frac{20}{46} = 0.434 \text{ mol.}$$

14. At 500°C , the decomposition of water into hydrogen and oxygen,



has $K_c = 6.0 \times 10^{-28}$. How many moles of H_2 and O_2 are present at equilibrium in a 5.00 L reaction vessel at that temperature if the container originally held 0.015 mol H_2O ?

Solution

$$\text{Given that } K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = 6.0 \times 10^{-28}$$

	$[H_2O]$	$[H_2]$	$[O_2]$
I	0.015 mol/5.00L	–	–
C	$-2x$	$+2x$	$+x$
E	$3.0 \times 10^{-3} - 2x$	$+2x$	$+x$

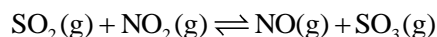
$$K_c = \frac{[2x]^2[x]}{[3.0 \times 10^{-3} - 2x]^2} = 6.0 \times 10^{-28}$$

Assume $2x \ll 3.0 \times 10^{-3}$.

$$\frac{4x^3}{(3.0 \times 10^{-3})^2} = 6.0 \times 10^{-28} \Rightarrow x = 1.1 \times 10^{-11}$$

Hence, $[H_2] = 2.2 \times 10^{-11}$ M, $[O_2] = 1.1 \times 10^{-11}$ M.

15. At 460°C , the reaction



has $K_c = 85.0$. Suppose 0.100 mol of SO_2 , 0.0600 mol of NO_2 , 0.0800 mol of NO , and 0.120 mol of SO_3 are placed in a 10.0 L container at that temperature. What will be the concentrations of all the gases when the system reaches equilibrium?

Solution

All concentrations are a factor of 10 less than the stated value due to the container size. As $Q < K_c$ for this reaction, the reaction proceeds as written, that is, from left to right.

	[SO ₂]	[NO ₂]	[NO]	[SO ₃]
I	0.0100	0.00600	0.00800	0.0120
C	-x	-x	+x	+x
E	0.0100 - x	0.00600 - x	0.00800 + x	0.0120 + x

Substituting the above values for equilibrium concentrations into the mass action expression gives:

$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]} = \frac{(0.00800 + x)(0.0120 + x)}{(0.0100 - x)(0.00600 - x)} = 85.0$$

$$0.00510 - 1.36(x) + 85.0(x)^2 = 9.60 \times 10^{-5} + 0.0200(x) + (x)^2$$

$$84.0(x)^2 - 1.38(x) + 0.00500 = 0$$

The quadratic equation is used with the following values: $a = 84.0$; $b = -1.38$; $c = 0.00500$. Upon solving for x , we find that only the negative root is sensible:

$$x = 0.00542 \text{ M.}$$

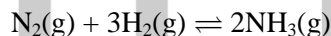
$$[\text{SO}_2] = 0.0100 - 0.00542 = 0.0046 \text{ M}$$

$$[\text{NO}_2] = 0.00600 - 0.00542 = 0.00058 \text{ M}$$

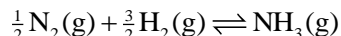
$$[\text{NO}] = 0.00800 + 0.00542 = 0.0134 \text{ M}$$

$$[\text{SO}_3] = 0.0120 + 0.00542 = 0.0174 \text{ M}$$

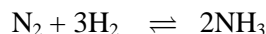
16. One mole of nitrogen is mixed with 3 mol of hydrogen in a 4 L container. If 0.25% of nitrogen is converted to ammonia by the following reaction:



Calculate the equilibrium constant (K_c) in concentration units. What will be the value of K_c for the following equilibrium?

**Solution**

Consider the reaction



$$\text{Initial no. of moles} \quad 1 \quad 3 \quad 0$$

$$\text{At equilibrium} \quad 1 - x \quad 3 - 3x \quad 2x$$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x/V)^2}{(1-x/V)(3-3x/V)^3} = \frac{4 \times 2V^2}{(1-x)(3-3x)^3}$$

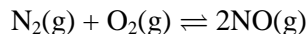
We know that $x = 0.25/100$ and $V = 4 \text{ L}$. Substituting, we get $K_c = 1.49 \times 10^{-5}$.

On multiplying the reaction by (1/2), we get

$$K'_c = (K_c)^{1/2} = (1.49 \times 10^{-5})^{1/2} = 3.86 \times 10^{-3}$$

17. Air containing 79% of nitrogen and 21% of oxygen by volume is heated at 2200 K and 1 atm until equilibrium is established according to the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$. If the K_p of the reaction is 1.1×10^{-3} , calculate the amount of nitric oxide produced in terms of volume percent.

Solution



At equilibrium, we have $[\text{N}_2] = 0.79(1 - \alpha)$;

$[\text{O}_2] = 0.21(1 - \alpha)$, $[\text{NO}] = \alpha$

Total number of moles = $0.79(1 - \alpha) + 0.21(1 - \alpha) + 2\alpha = 1 + \alpha$

$$p_{\text{N}_2} = \frac{0.79(1-\alpha)}{1+\alpha} \times 1; \quad p_{\text{O}_2} = \frac{0.21(1-\alpha)}{1+\alpha} \times 1; \quad p_{\text{NO}} = \frac{2\alpha}{1+\alpha} \cdot 1$$

$$K_p = \frac{p_{\text{NO}}^2}{p_{\text{N}_2} \cdot p_{\text{O}_2}} = \frac{4\alpha^2}{0.79 \times 0.21(1-\alpha)^2} = 1.1 \times 10^{-3}$$

where $\alpha = 0.0067$ and vol. % of NO = 1.33.

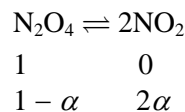
18. N_2O_4 is 25% dissociated at 37°C and 1 atm pressure. Calculate:

(a) K_p for $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

(b) percent dissociation at 37°C and 0.1 atm.

Solution

(a) The reaction can be expressed as



The total number of moles = $1 - \alpha + 2\alpha = 1 + \alpha$.

Therefore, $p_{(\text{N}_2\text{O}_4)} = \left(\frac{1-\alpha}{1+\alpha}\right) \times p$ and $p_{(\text{NO}_2)} = \left(\frac{2\alpha}{1+\alpha}\right) \times p$

Given that $\alpha = 0.25$ and $p = 1$ atm. So,

$$p_{(\text{N}_2\text{O}_4)} = \left(\frac{1-0.25}{1+0.25}\right) = \frac{0.75}{1.25} = 0.6 \text{ atm and } p_{(\text{NO}_2)} = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{(\text{NO}_2)})^2}{p_{(\text{N}_2\text{O}_4)}} = \frac{(0.4)^2}{(0.6)} = \frac{0.16}{0.6} = 0.267 \text{ atm}$$

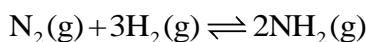
(b) Suppose the degree of dissociation of N_2O_4 at 0.1 atm is x .

$$p_{(\text{N}_2\text{O}_4)} = \left(\frac{1-x}{1+x}\right) \times 0.1 \text{ and } p_{(\text{NO}_2)} = \left(\frac{2x}{1+x}\right) \times p$$

$$\text{Hence, } K_p = \frac{(p_{(\text{NO}_2)})^2}{p_{(\text{N}_2\text{O}_4)}} = \frac{\left(\frac{2x}{1+x}\right)^2 \times 0.1}{\left(\frac{1-x}{1+x}\right) \times 0.1} \Rightarrow 0.267 = \frac{4x^2}{1-x^2}$$

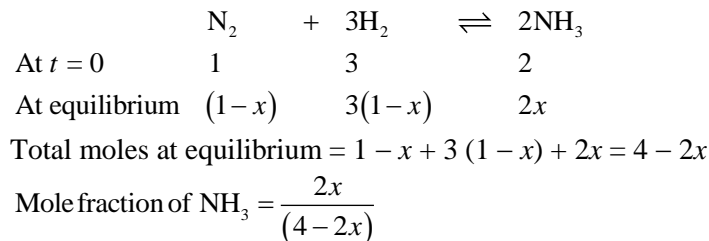
Solving, we get $x = 0.632 \Rightarrow 63.2\%$

19. A mixture of N_2 and H_2 in the ratio 1:3 at 50 atm and 650°C is allowed to react till equilibrium is reached. Ammonia present at equilibrium was at 25 atm pressure. Calculate the equilibrium constant for the reaction.



Solution

Equilibrium of formation of NH_3 may be given as,

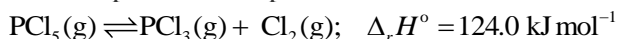


$$\text{Partial pressure NH}_3 = \frac{2x}{(4-2x)} \times p = \frac{2x}{(4-2x)} \times 50$$

$$25 = \frac{2x \times 50}{(4-2x)} = 0.666$$

$$K_p = \frac{16x^2(2-x)^2}{27p^2(1-x)^4} = \frac{16 \times (0.666)^2 (2-0.666)^2}{27 \times (50)^2 \times (0.334)^2} = 1.677 \times 10^{-3}$$

20. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride PCl_5 is 8.3×10^{-3} . If decomposition is depicted as



- (a) What is the value of K_c for the reverse reaction at the same temperature?
 (b) What would be the effect on K_c if (i) more PCl_5 is added, (ii) pressure is increased, or (iii) temperature is increased?

Solution

(a) Expression of K_c for the reaction is

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

Value of K_c for the reverse reaction at the same temperature is

$$K'_c = \frac{1}{K_c} = \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 = 120.48$$

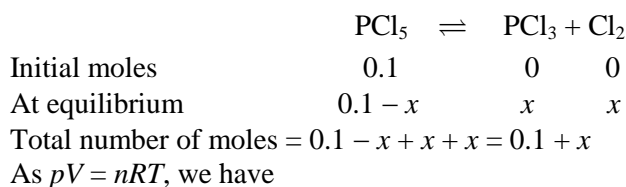
- (b) (i) K_c would remain the same because in this case, the temperature remains the same.
 (ii) K_c is constant at constant temperature. Thus, in this case, K_c would not change.
 (iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. As the given reaction is an endothermic reaction, the value of K_c will increase if the temperature is increased.

21. At 540 K, 0.10 mol of PCl_5 is heated in an 8 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for reaction.

[IIT-JEE 1998]

Solution

Consider the reaction



$$n = \frac{pV}{RT} = \frac{1 \times 8}{0.0821 \times 540} = 0.18$$

So, $0.1 + x = 0.18 \Rightarrow x = 0.08$

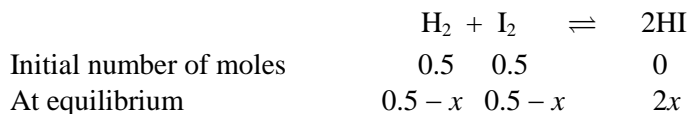
$$K_c = \frac{(0.08/8)(0.08/8)}{(0.02/8)} = 0.04$$

$$K_p = (K_c RT)^{\Delta n} = 0.04 \times (0.0821 \times 540)^1 = 1.77$$

22. The K value for the reaction: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm, respectively, determine the partial pressure of each gas at equilibrium. **[IIT-JEE 1999]**

Solution

Consider the reaction



$$K = \frac{(2x)^2}{(0.5-x)^2} = 49 \Rightarrow 7 = \frac{2x}{0.5-x} \Rightarrow x = 0.39$$

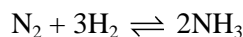
Pressure of H_2 and I_2 at equilibrium = $0.5 - 0.39 = 0.11$ atm

Pressure of HI at equilibrium = $2 \times 0.39 = 0.78$ atm

23. Calculate the value of $\log K$ for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 25°C . The standard enthalpy of formation of $\text{NH}_3(\text{g})$ is -46 kJ and standard entropies of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$ are 191, 130, 192 $\text{J K}^{-1} \text{mol}^{-1}$, respectively. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) **[IIT-JEE 1999]**

Solution

Consider the reaction



From the given values, we have

$$\Delta S^\circ = \Delta S^\circ(\text{products}) - \Delta S^\circ(\text{reactants})$$

$$= 2\Delta S^\circ(\text{NH}_3) - [\Delta S^\circ(\text{N}_2) + 3\Delta S^\circ(\text{H}_2)]$$

$$= 2 \times 192 - [191 + 3 \times 130] = -197 \text{ J K}^{-1} \text{ mol}^{-1} = -0.197 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 2x(-46) - (298 \times -0.197) = -92 + 58.706 = -33294 \text{ J}$$

Now, $\Delta G^\circ = -2.303 RT \log K$. So,

$$\log K = \frac{\Delta G^\circ}{2.303RT} = \frac{33294}{2.303 \times 8.314 \times 298} = 5.845$$

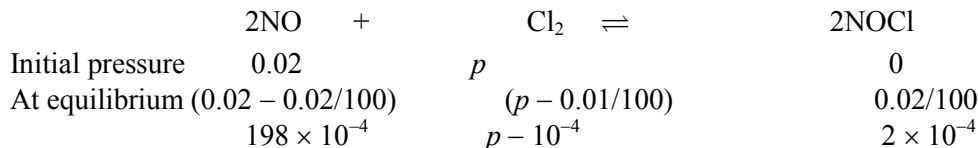
$$\log K = \Delta G^\circ / 2.303RT = 33294 / 2.303 \times 8.314 \times 298 = 5.845$$

24. The value of K_p is $1 \times 10^{-3} \text{ atm}^{-1}$ at 25°C for the reaction: $2\text{NO} + \text{Cl}_2 \rightleftharpoons 2\text{NOCl}$. A flask contains NO at 0.02 atm and at 25°C . Calculate the moles of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the

flask is such that 0.2 mol of gas produces 1 atm pressure at 25°C. (Ignore probable association of NO to N₂O₂.) [IIT-JEE 2001]

Solution

Consider the reaction:



$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \times P_{\text{Cl}_2}} \Rightarrow 10^{-3} = \frac{(2 \times 10^{-4})^2}{(198 \times 10^{-4})^2 \times (p - 10^{-4})^2} \Rightarrow p = 0.1021 \text{ atm}$$

We know that $pV = nRT$, so

$$V = \frac{nRT}{p} = \frac{0.2 \times 0.0821 \times 273}{1} = 4.88 \text{ L}$$

$$n = \frac{pV}{RT} = \frac{0.1021 \times 4.887}{0.0821 \times 298} = 0.0204 \text{ mol}$$

25. The equilibrium constant K_c for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in chloroform at 291 K is 1.14. Calculate the free energy change of the reaction when the concentration of the two gases is 0.5 mol dm⁻³ each at the same temperature. ($R = 0.082 \text{ L atm K}^{-1}\text{mol}^{-1}$)

Solution

From the given data, we have $T = 291 \text{ K}$; $R = 0.082 \text{ L atm K}^{-1}\text{mol}^{-1}$, $K_c = 1.14$; $C = 0.5 \text{ mol dm}^{-3}$.

As $Q_p = Q_c (RT)^{\Delta n}$ and $\Delta n = 2 - 1 = 1$ in this case, the reaction quotient Q_c for the reaction is

$$Q_c = \frac{0.5}{(0.082 \times 291)} = 11.93$$

The equilibrium constant is

$$K_p = K_c (RT)^{\Delta n} = 1.14 \times (0.082 \times 291) = 27.1$$

Substituting these values in the equation

$$\Delta G = \Delta G^\circ + RT \ln Q_p = -RT \ln K_p + RT \ln Q_p = -2.303 RT (\log K_p - \log Q_p)$$

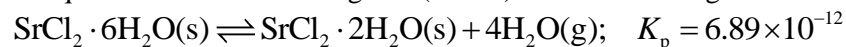
we get

$$\Delta G = -(0.082 \times 291 \times 2.303) [\log 27.2 - \log 11.93] \\ = -54.95(1.4346 - 1.0766) = -19.67 \text{ L atm}$$

Additional Objective Questions

Single Correct Choice Type

1. Equilibrium constants are given (in atm) for the following reactions at 0°C



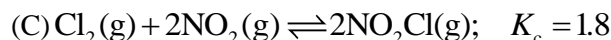
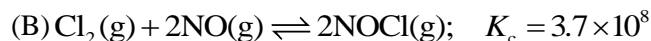
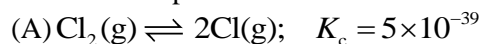
The vapor pressure of water at 0°C is 4.58 torr. Calculate the pressure of water vapor in equilibrium at 0°C

- | | |
|---------------------------------------|---------------------------------------|
| (A) $2.6 \times 10^{-3} \text{ atm}$ | (B) $1.62 \times 10^{-3} \text{ atm}$ |
| (C) $1.20 \times 10^{-4} \text{ atm}$ | (D) $4.28 \times 10^{-3} \text{ atm}$ |

Solution

(B) $K_p = p_{\text{H}_2\text{O}}^4 = 6.89 \times 10^{-12}$ therefore $p_{\text{H}_2\text{O}} = 1.62 \times 10^{-3}$ atm

2. Predict which of the following reaction will have appreciable concentration of reactants and products:



(D) All of these

Solution

(C) As K_c is neither too high nor very low, reactants and products will be present in comparable amounts.

3. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ When 46 g I_2 and 1 g of H_2 are heated, an equilibrium is reached at 450°C . The equilibrium mixture contained 1.9 g of I_2 . How many moles of I_2 and HI are present at equilibrium?

(A) 0.0075 and 0.147 mol (B) 0.0050 and 0.147 mol

(C) 0.0075 and 0.347 mol (D) 0.0052 and 0.347 mol

Solution

(C) Moles of I_2 taken = $\frac{46}{254} = 0.181$

Moles of H_2 taken = $\frac{1}{2} = 0.5$

Moles of I_2 remaining = $\frac{1.9}{254} = 0.0075$

Moles of I_2 used = $0.181 - 0.0075 = 0.1735$

Moles of H_2 used = 0.1735

Moles of H_2 remaining = $0.5 - 0.1735 = 0.3265$

Moles of HI formed = $0.1735 \times 2 = 0.347$

4. The partial pressures of CH_3OH , CO , and H_2 in the equilibrium mixture for the reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ at 427°C are 2.0, 1.0, and 0.1 atm, respectively. The

value of K_p for the decomposition of CH_3OH into CO and H_2 is

(A) 1×10^2 atm (B) 2×10^2 atm⁻¹

(C) 50 atm² (D) 5×10^{-3} atm²

Solution

(B) $K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2} = \frac{2.0}{1.0 \times (0.1)^2} = 200 \text{ atm}^{-1}$

5. Consider the following equilibrium in a closed container $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K) and degree of dissociation (α): (IIT-JEE 2002)

(A) Neither K_p nor α changes (B) Both K and α change

(C) K_p changes but α does not (D) K does not change but α changes

Solution

(D)

6. For the reaction $2\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_5(\text{g})$

If the equilibrium constant is K_p , then the equilibrium constant for the reaction $2\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 4\text{NO}_2 + \text{O}_2(\text{g})$ would be

(A) K_p^2 (B) $\frac{2}{K_p}$ (C) $\frac{1}{K_p^2}$ (D) $\frac{1}{\sqrt{K_p}}$

Solution

(C) By writing the equation for the reverse reaction

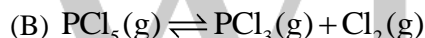


as $\frac{1}{K_p}$ and relating it to the desired reaction, the result can be obtained.

7. A container whose volume is V contains an equilibrium mixture that consists of 2 mol each of PCl_5 , PCl_3 , and Cl_2 (all gases). The pressure is 30.3975 kPa and temperature is T . A certain amount of $\text{Cl}_2(\text{g})$ is now introduced keeping the pressure and temperature constant until the equilibrium volume changes to $2V$. Calculate the amount of Cl_2 that was added

(A) 10/3 mol (B) 20/3 mol (C) 1/3 mol (D) 1/4 mol

Solution



At equilibrium, 2 mol 2 mol 2 mol

Total pressure = 30.3975 kPa = 3 atm = p (say)

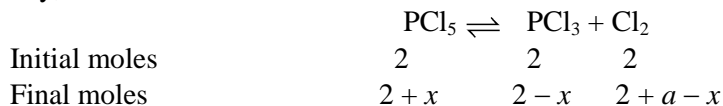
$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{p/3 \times p/3}{p/3} = p/3 \quad (1)$$

When chlorine is added to the system, the system will try to nullify the effect, and hence, formation of PCl_5 will be preferred.

As p and T are constant, and given that $V_2 = 2V_1$; $n_1 = 6$ mol, so

$$\frac{V_1}{V_2} = \frac{n_1}{n_2} \Rightarrow n_2 = 12 \text{ mol}$$

Say, “ a ” moles of Cl_2 were added



Total number of moles = 12 = $6 + a - x \Rightarrow a - x = 6$

$$K_p = \frac{\frac{2+a-x}{12} \times \frac{2-x}{12}}{\frac{2+x}{12}} \times p = \frac{(2+a-x)(2-x)}{12 \times (2+x)} p = \frac{(2+6)(2-x)}{12 \times (2+x)} p = \frac{2}{3} \times \frac{(2-x)}{(2+x)} p$$

(2)

Equating Eqs. (1) and (2), we get $x = 2/3$ and hence $a = 20/3$ mol.

Hence, $20/3$ mol of Cl_2 was added.

8. For a certain equilibrium, over the temperature range 500–700 K, the equilibrium

constant, K_p confirms to the equation $\log K_p = 30.1 - \frac{6.36 \times 10^3}{T} - 5.7 \log T$

Calculate ΔG° at 600 K.

- (A) $-16.04 \text{ kcal mol}^{-1}$ (B) $-14.60 \text{ kcal mol}^{-1}$
(C) $-10.064 \text{ kcal mol}^{-1}$ (D) $-14.00 \text{ kcal mol}^{-1}$

Solution

$$(C) \log K_p = 30.0 - \frac{6.36 \times 10^3}{T} - 5.7 \log T$$

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_p = -2.303RT \log K_p \\ &= -2.303 \times 1.987 \times 600 \left[30.1 - \frac{6.36 \times 10^3}{600} - 5.7 \log 600 \right] \\ &= -2.303 \times 1.987 \times 600 [30.1 - 10.6 - 5.7 \times 2.778] \\ &= -[2.303 \times 1.987 \times 600 \times 3.6654] \text{ cal mol}^{-1} \\ &= -10063.9 \text{ cal mol}^{-1} = -10.064 \text{ kcal mol}^{-1} \end{aligned}$$

9. PCl_5 is 80% dissociated at 523 K. Calculate the vapor density of the equilibrium mixture at 523 K.

- (A) 75.9 (B) 57.9 (C) 97.5 (D) 95.7

Solution

$$(B) \text{ Vapor density} = \frac{\text{Molecular weight of } \text{PCl}_5}{2} = \frac{208.5}{2} = 104.25$$

Applying the formula,

$$0.8 = \frac{104.25 - d}{(2 - 1)d} \Rightarrow 0.8d = 104.25 - d \Rightarrow 1.8d = 104.25 \Rightarrow d = \frac{104.25}{1.8} = 57.9$$

10. In the melting of ice, which one of the conditions will be more favorable?

- (A) High temperature and high pressure.
(B) Low temperature and low pressure.
(C) Low temperature and high pressure.
(D) High temperature and low pressure.

Solution

(A) Melting of ice is the endothermic process, and on melting, volume decreases. Hence, high temperature and high pressure is favorable.

11. Example of physical equilibrium is

- (A) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ (B) $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$
(C) $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ (D) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

Solution

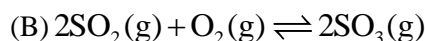
(C) Physical equilibrium, do not include any chemical change.

12. For the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3$

If the partial pressure of SO_2 , O_2 , and SO_3 are 0.559, 0.101, and 0.331 atm, respectively. What would be the partial pressure of O_2 gas to get equal moles of SO_2 and SO_3 .

- (A) 0.188 atm (B) 0.288 atm (C) 0.388 atm (D) 0.488 atm

Solution



$$K_p = \frac{[p_{\text{SO}_3}]^2}{[p_{\text{SO}_2}]^2 [p_{\text{O}_2}]} = \frac{(0.331)^2}{(0.559)^2 (0.101)} = 3.47$$

SO_2 and SO_3 have same number of moles; their partial pressure will be equal

$$p_{\text{SO}_3} = p_{\text{SO}_2}, \text{ therefore } p_{\text{SO}_2} \frac{1}{3.47} = 0.288 \text{ atm}$$

13. When ethanol and acetic acid were mixed together in equimolecular proportion, 66.6% is converted into ethyl acetate. Calculate K_c . Also calculate quantity of ester produced if 1 mol of acetic acid is treated with 0.5 and 4 mol of alcohol, respectively.

- (A) 4, 0.93, 0.43 (B) 0.93, 4, 0.43
(C) 0.43, 0.93, 4 (D) 4, 0.43, 0.93

Solution



$$\begin{array}{cccc} 1 & 1 & 0 & 0 \\ 1 - 0.666 & 1 - 0.666 & 0.666 & 0.666 \end{array}$$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{[0.666][0.666]}{[0.333][0.333]}$$

(A) Let x mol of ester is formed from 1 mol of acid and 0.5 mol of alcohol, then

$$K_c = \frac{x^2}{(1-x)(0.5-x)} = 4 \Rightarrow x = 0.43$$

$$(B) K_c = \frac{x^2}{(1-x)(4-x)} \text{ or } 4 = \frac{x^2}{(1-x)(4-x)} \Rightarrow x = 0.93$$

14. Calculate the temperature at which the product gases at equilibrium at 1 atm will contain 400 ppm (parts per million) of carbon monoxide.

- (A) 399 K (B) 400 K (C) 275 K (D) 200 K

Solution

(A) For the given reaction $p_{\text{CO}} \gg p_{\text{CO}_2}$, hence $K_p = \frac{1}{p_{\text{CO}}} = \frac{1}{400 \times 10^6} = 2500$

$$\Delta G^\circ = -RT \ln K_p; \ln K_p = \frac{\Delta G^\circ}{RT} = \frac{20700 + 11.97T}{RT}$$

The equation when solved for T using $R = 8.314 \text{ K}^{-1} \text{ mol}^{-1}$ gives $T = 399 \text{ K}$.

15. For the reversible reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500°C , the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c , with concentration in mol L^{-1} , is (IIT-JEE 2000)

- (A) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (B) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$

$$(C) \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$$

$$(D) \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

Solution

(B) $K_p = K_c (RT)^{\Delta n}$ where $K_p = 1.44 \times 10^{-5}$, $\Delta n = 2 - 4 = -2$. Hence,

$$K_c = \frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$$

16. Le Chatelier's principle is applicable to

(A) only homogeneous chemical reversible reaction.

(B) only heterogeneous chemical reversible reaction.

(C) only physical equilibria.

(D) all systems chemical or physical, in equilibrium.

Solution

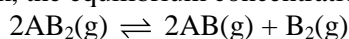
(D)

17. At temperature T , a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with degree of dissociation α , which is small compared with unity. The expression for K_p in terms of α and the total pressure p_T is

(A) $\frac{p_T \alpha^3}{2}$ (B) $\frac{p_T \alpha^2}{3}$ (C) $\frac{p_T \alpha^2}{2}$ (D) None of these

Solution

(A) For the given equilibrium, the equilibrium concentration is



Equilibrium concentration $c(1 - \alpha)$, $c\alpha$, $\frac{c\alpha}{2}$

Therefore,
$$K_p = \frac{(p_{B_2})(p_{AB})^2}{(p_{AB_2})^2} = \frac{(c\alpha/2) \times (c\alpha)^2}{[c(1-\alpha)]^2} \times \frac{p_T}{[c(1+\alpha/2)]} = \frac{\alpha^3 \times p_T}{2(1-\alpha)^2 \left(1 + \frac{\alpha}{2}\right)}$$

As α is small compared with unity, so $1 - \alpha \approx 1$ and $1 + \frac{\alpha}{2} \approx 1$ therefore $K_p = \frac{\alpha^3 \times p_T}{2}$

18. Starting with 3:1 mixture of H_2 and N_2 at $450^\circ C$, the equilibrium mixture is found to be 9.6% NH_3 , 22.6% N_2 , and 67.8% H_2 by volume. The total pressure is 50 atm. What will be the value of K_p . The reaction is $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(A) $3.25 \times 10^{-5} \text{ atm}^{-2}$

(B) $5.23 \times 10^{-5} \text{ atm}^{-2}$

(C) $6.23 \times 10^{-2} \text{ atm}^{-2}$

(D) $8 \times 10^{-5} \text{ atm}^{-2}$

Solution

(B) The ratio of number of moles will be the same as the ratio of volume.

According to Dalton's law, the partial pressure of a gas in a mixture is given by the product of its volume fraction and the total pressure.

Therefore, the equilibrium pressure of each gas is,

$$p_{NH_3} = \frac{9.6}{100} \times 50 \text{ atm} = 4.8 \text{ atm}$$

$$p_{\text{N}_2} = \frac{22.6}{100} \times 50 \text{ atm} = 11.3 \text{ atm}$$

$$p_{\text{H}_2} = 67.6/100 \times 50 \text{ atm} = 33.9 \text{ atm}$$

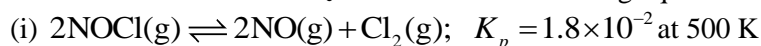
Total pressure = 50 atm

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

Substituting the values of partial pressures,

$$K_p = \frac{(4.80 \text{ atm})^2}{(11.3 \text{ atm})(33.9 \text{ atm})^3} = 5.23 \times 10^{-5} \text{ atm}^{-2}$$

19. Find out the value of K_c for each of the following equilibrium from the value of K_p :



the value of K_c are, respectively

(A) 4.4×10^{-4} and 1.90

(B) 8.8×10^{-4} and 3.8

(C) 4.4×10^{-4} and 1.90

(D) 8.8×10^{-4} and 3.8

Solution

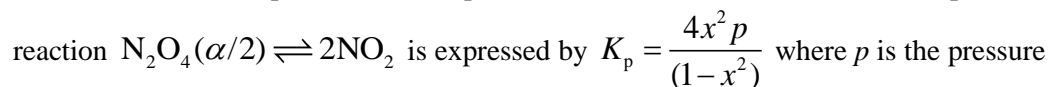
(A) (i) $K_p = K_c(RT)^{\Delta n}$

(ii) Therefore, $\Delta n = 1$ and

$$K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1073} = 1.90$$

Since $\Delta n = 1$, therefore $K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.082 \times 500} = 4.4 \times 10^{-4}$

20. At constant temperature, the equilibrium constant (K) for the decomposition



and x is the extent of decomposition. Which one of the following statements is true?

(IIT-JEE 2000)

(A) K increases with increase of p

(B) K increases with increase of x

(C) K increases with decrease of x

(D) K remains constant with change in p and x

Solution

(D)

21. The vapor density of N_2O_4 at a certain temperature is 30. The percentage dissociation of N_2O_4 at this temperature is

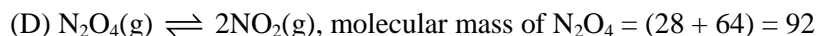
(A) 55.5%

(B) 60%

(C) 70%

(D) 53.3%

Solution



Vapor density, $D = \frac{92}{6} = 46$

Let the degree of dissociation be x . Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

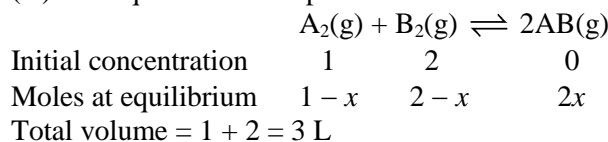
Degree of dissociation = 53.3%.

22. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If 1 L flask containing 1 mol of A_2 is connected to a 2 L flask containing 2 mol of B_2 , the number of moles of AB formed at 373 K will be

- (A) 1.886 (B) 2.317 (C) 0.943 (D) 18.86

Solution

(A) The equilibrium is represented as:



$$[A_2] = \frac{1-x}{3}, [B_2] = \frac{2-x}{3}, [AB] = \frac{2x}{3}$$

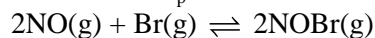
$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{(2x/3)^2}{(1-x)/3(2-x)/3} = 50$$

On solving, we get $23x^2 - 75x + 50 = 0 \Rightarrow x = 2.31$ or 0.943 .

As x cannot be more than 1, so $x = 0.943$

Number of moles of AB formed = $2 \times 0.943 = 1.886$ mol.

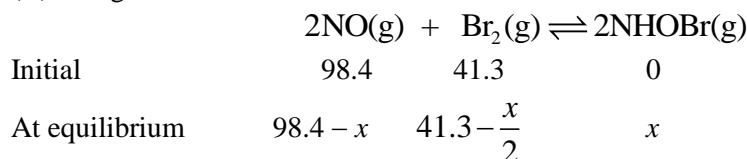
23. NO and Br_2 at initial partial pressure of 98.4 and 41.3 torr, respectively, were allowed to react at 300 K. At equilibrium, the total pressure was 110.5 torr. Calculate the value of K_p for the following reaction at 300 K.



- (A) 124 (B) 134 (C) 154 (D) 174

Solution

(B) The given reaction is,



Total pressure at equilibrium = 110.5 torr.

$$(98.4-x) + \left(41.3-\frac{x}{2}\right) + x = 110.5$$

Solving, we get $x = 58.4$ torr (760 torr = 1 atm)

$$p_{NOBr} = 58.4 \text{ torr} = 7.68 \times 10^{-2} \text{ atm.}$$

$$p_{NO} = 98.4 - 58.4 = 40 \text{ torr} = 5.26 \times 10^{-2} \text{ atm.}$$

$$K_p = \frac{p_{NOBr}^2}{p_{NO}^2 \times p_{Br_2}} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})^2 (1.59 \times 10^{-2})} = 134$$

24. In the equilibrium $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ at 2000 K and 10 atm pressure, percent Cl_2 = percent SO_2 = 40 by volume. Then

- (A) $K_p = 2$ atm (B) $\frac{n(\text{SO}_2\text{Cl}_2)}{n(\text{SO}_2)} = \frac{1}{4}$ at equilibrium
 (C) $K_p = 8$ atm (D) $n(\text{SOCl}_2) = n(\text{SO}_2) = n(\text{Cl}_2)$

Solution

(C) At 40% SO_2 and 40% Cl_2 by volume $p_{\text{SO}_2} = \left(\frac{40}{100}\right)p$ and $p_{\text{Cl}_2} = \left(\frac{40}{100}\right)p$

So, $p_{\text{SO}_2\text{Cl}_2} = \left(\frac{20}{100}\right)p$ and given that $p = 10$ atm. Therefore,

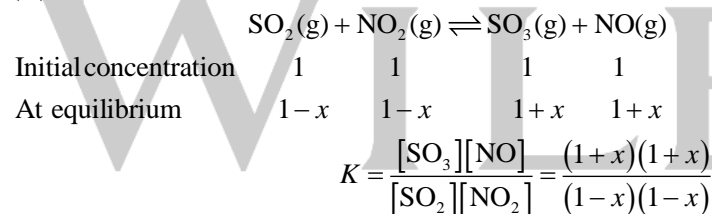
$$\text{Therefore, } K_p = \frac{(p_{\text{SO}_2})(p_{\text{Cl}_2})}{(p_{\text{SO}_2\text{Cl}_2})} = \frac{(40/100)p \times (40/100)p}{(20/100)p} = \frac{16 \times 10}{2 \times 10} = 8 \text{ atm}$$

25. At a certain temperature, the equilibrium constant K_c is 16 for the reaction, $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$. If 1.0 mol each of all the four gases is taken in a 1 L container, the concentration of NO_2 at equilibrium would be

- (A) 1.6 mol L^{-1} (B) 0.8 mol L^{-1} (C) 0.4 mol L^{-1} (D) 0.6 mol L^{-1}

Solution

(C) The reaction is



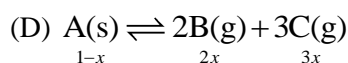
$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \quad \text{or } x = 0.6$$

$$[\text{NO}_2] = 1 - x = 1 - 0.6 = 0.4 \text{ mol L}^{-1}$$

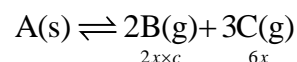
26. In a system $\text{A}(\text{s}) \rightleftharpoons 2\text{B}(\text{g}) + 3\text{C}(\text{g})$. If the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to

- (A) two times of its original value. (B) one half of its original value.
 (C) $2\sqrt{2}$ times of its original value. (D) $1/2\sqrt{2}$ times of its original value.

Solution



$$K_c = 4x^2 \times 27x^3 = 108x^5$$



$$108x^5 = 4x^2 \times c^2 \times 216x^3 \Rightarrow 108 = c^2 \times 216 \times 4$$

$$c^2 = \frac{108}{4 \times 216} \Rightarrow c = \frac{1}{2\sqrt{2}}$$

27. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by

- (A) temperature and pressure. (B) temperature only.
(C) pressure only. (D) temperature, pressure, and catalyst.

[IIT-JEE 2009]

Solution

(A)

28. In reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the concentration of H_2 , I_2 , and HI at equilibrium are 8.0, 3.0, and 28 mol L^{-1} , respectively. What will be the equilibrium constant?

- (A) 30.61 (B) 32.66 (C) 29.40 (D) 20.90

Solution

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

Applying law of mass action,

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

Given that $[H_2] = 8.0 \text{ mol } L^{-1}$, $[I_2] = 3.0 \text{ mol } L^{-1}$ $[HI] = 28.0 \text{ mol } L^{-1}$

$$K_c = \frac{(28.0)^2}{(8.0) \times (3.0)} = 32.66$$

29. When two reactants A and B are mixed to give products C and D, the reaction quotient at the initial stages of the reaction (IIT-JEE 2000)

- (A) is zero. (B) decreases with time.
(C) is independent of time. (D) increases with time.

Solution

(D) The equilibrium constant K for the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm at 400°C .

30. What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is -105185.8 J .

- (A) 0.144×10^{-4} atm (B) 0.144×10^{-3} atm
(C) 0.144×10^{-2} atm (D) 0.144×10^{-1} atm

Solution

(A) Given that $K_p = 1.64 \times 10^{-4}$ atm, $K_{p2} = ?$; $T_1 = 400 + 273 = 673 \text{ K}$, $T_2 = 500 + 273 = 773 \text{ K}$; $\Delta H = -105185.8 \text{ J}$, $R = 8.314 \text{ J } K^{-1} \text{ mol}^{-1}$

Applying the equation

$$\log K_{p2} - \log K_{p1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log K_{p_2} = \log 1.64 \times 10^{-4} - \frac{105185.8}{2.303 \times 8.314} \left(\frac{773 - 673}{773 \times 673} \right)$$

$$\text{or } K_{p_2} = 0.144 \times 10^{-4} \text{ atm.}$$

31. The following reactions are known to occur in the body, $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$. If CO_2 escapes from the system, then

- (A) pH will decrease.
 (B) hydrogen ion concentration will diminish.
 (C) H_2CO_3 concentration will remain unchanged.
 (D) the forward reaction will be favored.

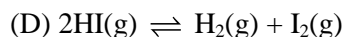
Solution

(B) This is according to Le Chatelier's principle.

32. For the reaction: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, the degree of dissociation (α) of $\text{HI}(\text{g})$ is related to equilibrium constant K_p by the expression

- (A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$ (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{2K_p}}{1+2\sqrt{K_p}}$

Solution



$$1-\alpha \qquad \frac{\alpha}{2} \qquad \frac{\alpha}{2}$$

$$K_p = \frac{\left(\frac{\alpha}{2} p_T\right)^2}{(1-\alpha)^2 p_T^2} \text{ or } \frac{\alpha}{1-\alpha} = 2\sqrt{K_p} \text{ or } \alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

33. For which of the following reactions the degree of dissociation cannot be calculated from the vapor density data

- (I) $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ (II) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
 (III) $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$ (IV) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (A) I and III (B) II and IV (C) I and II (D) III and IV

Solution

(A) The degree of dissociation cannot be calculated from the vapor density data because here, the number of moles remains unchanged before and after reaching equilibrium.

34. An example of reversible reaction is

- (A) $\text{Pb}(\text{NO}_3)_2 + 2\text{NaI} = \text{PbI}_2 + 2\text{NaNO}_3$ (B) $\text{AgNO}_3 + \text{HCl} = \text{AgCl} + \text{HNO}_3$
 (C) $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$ (D) $\text{KNO}_3 + \text{NaCl} = \text{KCl} + \text{NaNO}_3$

Solution

(D)

35. For the reaction $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$, at a given temperature, the equilibrium amount of $\text{CO}_2(\text{g})$ can be increased by (IIT-JEE 1998)

- (A) adding a suitable catalyst.

- (B) adding an inert gas.
 (C) decreasing the volume of the container.
 (D) increasing the amount of CO(g).

Solution

(D)

36. A reaction mixture containing H₂, N₂, and NH₃ has partial pressures 2, 1, and 3 atm, respectively, at 725 K. N₂(g) + 3H₂(g) ⇌ 2NH₃(g) is 4.28 × 10⁻⁵ atm⁻² at 725 K. In which direction the net reaction will go?

- (A) Forward. (B) Backward.
 (C) No net reaction. (D) Cannot be predicted.

Solution

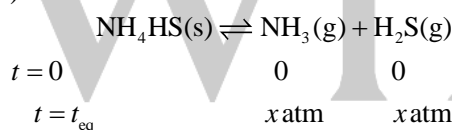
$$(B) Q_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{(3)^2}{(1)(2)^3} = \frac{9}{8} \text{ atm}^{-1} = 1.125 \text{ atm}^{-2}$$

37. Ammonium hydrogen sulphide dissociates according to the equation NH₄HS(s) ⇌ NH₃(g) + H₂S(g). If the observed pressure of the mixture is 1.12 atm at 106°C, what is the equilibrium constant K_p of the reaction?

- (A) 0.3136 atm² (B) 2 atm²
 (C) 1 atm² (D) 0.4842 atm²

Solution

(A) The reaction is



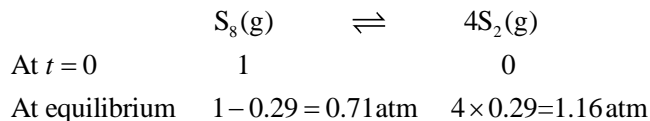
Now, p_T = 2x = 1.12 ⇒ x = 0.56; K_p = x² = 0.3136 atm²

38. When sulphur in the form of S₈ is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S₈ to S₂. Find the value of equilibrium constant for this reaction

- (A) 1.16 atm³ (B) 0.71 atm³ (C) 2.55 atm³ (D) 5.1 atm³

Solution

(C) The reaction is



$$K_p = \frac{[p_{\text{S}_2}]^4}{[p_{\text{S}_8}]} = \frac{(1.16)^4}{(0.71)} = 2.55 \text{ atm}^3$$

39. BiCl₃(g) + H₂O(g) ⇌ BiOCl(s) + 2HCl(g) in the above system at equilibrium, the pressure of water vapor is doubled. The new equilibrium partial pressure of HCl increases

- (A) 1.73 times (B) 1.414 times (C) 2.0 times (D) 1.0 times

Solution

(B) When the denominator is increased by 2, $p_{\text{HCl}}^2 = 2$

Therefore $p_{\text{HCl}} = \sqrt{2} = 1.414$

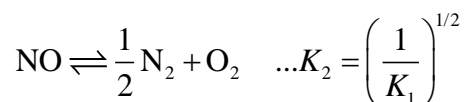
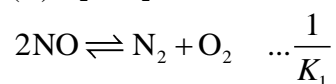
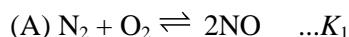
40. K_1 and K_2 are equilibrium constant for reactions



Then, from (I) and (II)

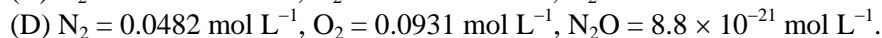
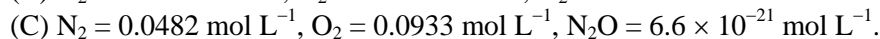
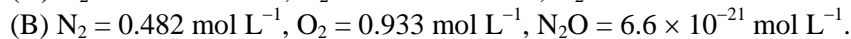
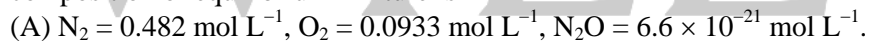
(A) $K_1 = \left(\frac{1}{K_{\text{II}}}\right)^2$ (B) $K_1 = K_{\text{II}}^2$ (C) $K_1 = \frac{1}{K_{\text{II}}}$ (D) $K_1 = (K_{\text{II}})^0$

Solution



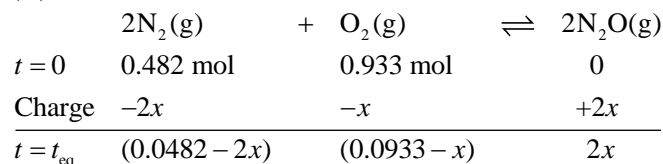
$K_2 = \left(\frac{1}{K_1}\right)^{1/2} \Rightarrow K_2^2 = \left(\frac{1}{K_1}\right) \Rightarrow K_1 = \left(\frac{1}{K_2^2}\right)$ or

41. If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, then the composition of equilibrium mixture is



Solution

(C) The reaction involved is



$$K_c = 2 \times 10^{-37} = \frac{(2x)^2}{(0.0482 - 2x)^2 \times (0.0933 - x)}$$

As K_c has small value, x should be low

$0.0482 - 2x \approx 0.0482$

$0.0933 - x - x = 0.0933$

$$2 \times 10^{-37} = \frac{4x^2}{0.0482 \times 0.0933}$$

On solving, $x = 3.3 \times 10^{-21}$

$$[\text{N}_2\text{O}] = 2x = 6.6 \times 10^{-21}$$

$$[\text{N}_2] \approx 0.0482 \text{ M}; [\text{O}_2] = 0.0993 \text{ M}$$

42. One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and carbon dioxide, that is,
 $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Fe}(\text{s}) + \text{CO}_2(\text{g}); K_p = 0.265 \text{ atm}$

at 1050 K. What are the equilibrium partial pressures of CO and CO_2 , respectively, at 1050 K if the initial partial pressures are: $p_{\text{CO}} = 1.4 \text{ atm}$ and $p_{\text{CO}_2} = 0.80 \text{ atm}$?

(A) $p_{\text{CO}} = 1.739 \text{ atm}$ and $p_{\text{CO}_2} = 0.461 \text{ atm}$

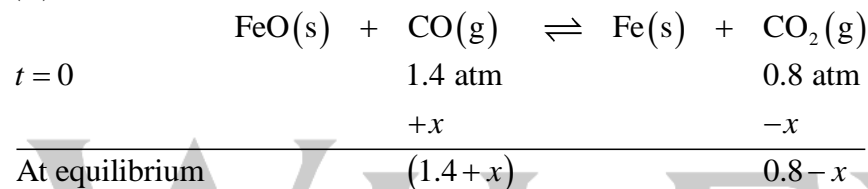
(B) $p_{\text{CO}} = 17.39 \text{ atm}$ and $p_{\text{CO}_2} = 0.461 \text{ atm}$

(C) $p_{\text{CO}} = 1.79 \text{ atm}$ and $p_{\text{CO}_2} = 0.46 \text{ atm}$

(D) $p_{\text{CO}} = 2.739 \text{ atm}$ and $p_{\text{CO}_2} = 1.461 \text{ atm}$

Solution

(A)



$$Q = \frac{0.8}{1.4} = \frac{4}{7} = 0.55$$

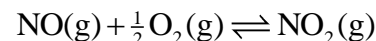
Since $Q > K$, system is not at equilibrium, and to attain equilibrium, it will shift in backward direction

$$K_p = 0.265 = \frac{0.8 - x}{1.4 + x}$$

On solving, we get $x = 0.339$

Therefore $[p_{\text{CO}}] = 1.739 \text{ atm}$ and $p_{\text{CO}_2} = 0.461 \text{ atm}$

43. What are the values of ΔG° and the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K?



where

$$\Delta G_f^\circ(\text{NO}_2) = 52.0 \text{ kJ mol}^{-1}, \Delta G_f^\circ(\text{NO}) = 87.0 \text{ kJ mol}^{-1}, \Delta G_f^\circ(\text{O}_2) = 0 \text{ kJ mol}^{-1}.$$

(A) 35 kJ mol^{-1} and 1.365×10^6 (B) -35 kJ mol^{-1} and 1.365×10^{-6}

(C) -350 kJ mol^{-1} and 1.3×10^6 (D) -35 kJ mol^{-1} and 1.365×10^6

Solution

(D) $\Delta G^\circ = \Delta G_{\text{NO}_2}^\circ - \Delta G_{\text{NO}}^\circ = (52 - 87) \text{ kJ mol}^{-1} = -35 \text{ kJ mol}^{-1}$

Since $\Delta G^\circ = -2.303 RT \log K$

$$\log K = \frac{-35 \text{ kJ mol}^{-1}}{-8.301 \text{ kJ mol}^{-1} \times 298 \text{ K}}$$

on solving $K = 1.365 \times 10^6$

44. A reversible chemical reaction is having two reactants in equilibrium. If the concentration of the reactants is doubled, then the equilibrium constant will

- (A) also be doubled. (B) be halved.
(C) become one-fourth. (D) remain the same.

Solution

(D) K_c is a characteristic constant for the given reaction.

Multiple Correct Choice Type

1. Solid ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$, dissociates into ammonia and carbon dioxide when it evaporates as shown by $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. At 25°C , the total pressure of the gases in equilibrium with the solid is 0.116 atm. If 0.1 atm of CO_2 is introduced after equilibrium is reached, then

- (A) final pressure of CO_2 will be less than 0.1 atm.
(B) final pressure of CO_2 will be more than 0.1 atm.
(C) pressure of NH_3 will decrease due to addition of CO_2 .
(D) pressure of NH_3 will increase due to addition of CO_2 .

Solution

(B, C) The pressure of NH_3 will decrease due to addition of CO_2 , (backward, shifting Le Chatelier's principle). The pressure of CO_2 will be more than 0.1 atm.

2. The equilibrium of which of the following reaction will not be disturbed by the addition of an inert gas at constant volume?

- (A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ (B) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
(C) $\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ (D) $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$

Solution

(A, B, C, D)

3. Consider the reactions given below. In which cases, will the reaction proceed toward the right by increasing the pressure?

- (A) $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
(B) $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$
(C) $\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
(D) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

Solution

(A, C) With the increase in pressure, forward reaction is favored, because for forward reaction, lesser number of molecules are involved. This is in accordance with Le Chatelier's principle.

4. For the reaction $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g})$; $\Delta H = +13.6 \text{ kJ}$, which of the following will increase the extent of the reaction at equilibrium

- (A) increasing the temperature. (B) increasing the pressure.
(C) addition of catalyst. (D) removing C.

Solution

(B, C, D)

5. The following reaction attains equilibrium at high temperature



The yield of NO is affected by

- (A) increasing the nitrogen concentration.
- (B) decreasing the hydrogen concentration.
- (C) compressing the reaction mixture.
- (D) None of these.

Solution

(A, B, C). As the concentration of reaction (gaseous) is increased at equilibrium, reaction will go in the forward direction. Also, the above reaction is endothermic. Therefore, an increase in temperature will favor it.

6. If K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 and $T_2 > T_1$ then

- (A) when $\Delta H = 0$; $K_2 = K_1$
- (B) when $\Delta H > 0$; $K_2 > K_1$
- (C) when $\Delta H < 0$; $K_2 < K_1$
- (D) when $\Delta H > 0$; $K_2 < K_1$

Solution

(A, B, C) The relation is expressed as

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

If $T_2 > T_1$ and $\Delta H = 0$, we have $\log(K_2/K_1) = 0 \Rightarrow K_2/K_1 = 1 \Rightarrow K_2 = K_1$

If $T_2 > T_1$ and $\Delta H > 0$, we have $\log(K_2/K_1) > 0 \Rightarrow K_2/K_1 > 1 \Rightarrow K_2 > K_1$

If $T_2 > T_1$ and $\Delta H < 0$, we have $\log(K_2/K_1) < 0 \Rightarrow K_2/K_1 < 1 \Rightarrow K_2 < K_1$

7. $2\text{CaSO}_4(\text{s}) \rightleftharpoons 2\text{CaO}(\text{s}) + \text{O}_2(\text{g})$, $\Delta H > 0$. Above equilibrium is established by taking sufficient amount of $\text{CaSO}_4(\text{s})$ in a closed container at 1600 K. Then which of the following may be a correct option (Assume that solid CaSO_4 is present in the container in each case)?

- (A) Moles of $\text{CaO}(\text{s})$ will increase with the increase in temperature.
- (B) If the volume of the container is doubled at equilibrium, then partial pressure of $\text{SO}_2(\text{g})$ will change at new equilibrium.
- (C) If the volume of the container is halved, partial pressure of $\text{O}_2(\text{g})$ at new equilibrium will remain same.
- (D) If 2 mol of the He gas are added at constant pressure, then the moles of $\text{CaO}(\text{s})$ will increase.

Solution

(A, C, D)

(A) As the reaction is endothermic, therefore it will go in the forward direction. Hence, moles of CaO will increase.

(C) With the increase or decrease of volume, partial pressure of the gases will remain same.

(D) Due to the addition of inert gas at constant pressure, reaction will proceed in the direction in which more number of gaseous moles are formed.

8. In presence of a catalyst, what happens to the chemical equilibrium?

- (A) Energy of activation of the forward and backwards reactions is lowered by same amount.
 (B) Equilibrium amount is not disturbed.
 (C) Rates of forward and reverse reaction increase by the same factor.
 (D) More product is formed.

Solution

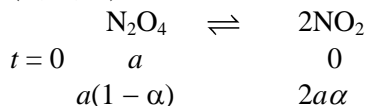
(A, B, C) Catalyst only speeds up the reaction.

9. 138 g of $\text{N}_2\text{O}_4(\text{g})$ is placed in 8.2 L container at 300 K. The equilibrium vapor density of mixture was found to be 30.67. Then ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$).

- (A) $\alpha =$ degree of dissociation of $\text{N}_2\text{O}_4 = 0.25$.
 (B) K_p of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2(\text{g})$ will be 9 atm.
 (C) Total pressure at equilibrium mixture will be 6.75 atm.
 (D) The density of equilibrium mixture will be 16.83 g L^{-1} .

Solution

(B, C, D) The reaction is



$$\text{Vapor density} = \frac{46}{1 - \alpha} = 30.67 \Rightarrow \alpha = 0.5 = 50\%$$

$$\text{Total pressure} = \frac{1.5 \times 1.5 \times 0.082 \times 300}{8.2} = 6.67 \text{ atm}$$

$$\text{So, } K_p = \frac{4\alpha^2}{1 - \alpha^2} p = 9 \text{ atm}$$

$$\text{and density of mixture} = \frac{138}{8.2} \text{ g L}^{-1} = 16.83 \text{ g L}^{-1}$$

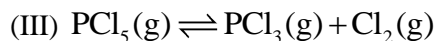
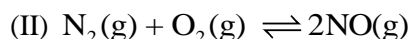
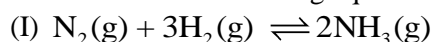
10. $\text{N}_2\text{F}_4 \rightleftharpoons 2\text{NF}_2(\text{g}); \Delta H^\circ = 38.5 \text{ kJ}$. Which of the following conditions will favor the formation of NF_2 ?

- (A) Adding He to the equilibrium mixture at constant temperature and volume.
 (B) Increasing the temperature.
 (C) NF_2 gas is removed from the reaction mixture.
 (D) Decreasing the pressure at constant temperature.

Solution

(B, C, D) In accordance with Le Chatelier's principle

11. Consider the following equilibria:



Choose the correct statement(s):

- (A) Addition of an inert gas at constant volume has no effect on all the three equilibria.
 (B) Addition of an inert gas at constant pressure favors the forward reaction in (III), backward reaction in (I), and has no effect on (II).

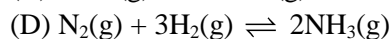
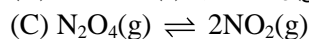
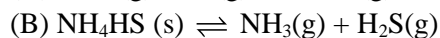
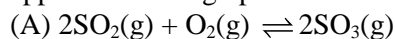
(C) Addition of an inert gas at constant pressure has no effect on equilibrium (II), but favors the forward reaction in (I) and backward reaction in (III).

(D) Addition of an inert gas has no effect on all the three equilibria at constant temperature and also at constant pressure.

Solution

(A, B)

12. The reactions in which the yield of the products cannot be increased by the application of high pressure are



Solution

(B, C)

13. For which of the following statements about the reaction quotient, Q , are correct?

(A) The reaction quotient, Q , and the equilibrium constant always have the same numerical value.

(B) Q may be $>$ or $<$ or $= K_c$

(C) Q (numerical value) varies as reaction proceeds.

(D) $Q = 1$ at equilibrium

Solution

(B, C)

14. Consider the exothermic reaction



[Consider initially only CoCl_4^{2-} is added to water]

(a) If HCl is added to the above equilibrium, then concentration of $\text{CoCl}_4^{2-}(\text{aq})$ will increase.

(b) On dilution with water, the concentration of $\text{CoCl}_4^{2-}(\text{aq})$ will decrease.

(c) On doubling the volume of solution by addition of water, the final concentration of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ will be more than its initial concentration.

(d) On increasing temperature, the concentration of CoCl_4^{2-} will decrease.

Solution

(A, B, D) On adding Cl^- ion, the equilibrium will shift in the backward direction. So, $[\text{CoCl}_4]^{2-}$ will increase on dilution and hence the volume will increase.

Now,

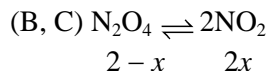
$$K_c = \frac{n_{[\text{Co}(\text{H}_2\text{O})_6]^{2+}} \cdot n_{\text{Cl}^-}^4}{n_{\text{CoCl}_4^{2-}}} \cdot \frac{1}{V^4}$$

So, Q will get decreased and equilibrium will shift in the forward direction. Although the amount of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ will get increased, but its concentration cannot get doubled as volume has increased. As the reaction is exothermic in nature, so increasing temperature will shift the equilibrium in backward direction.

15. For the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, the value of equilibrium constant is 2×10^{-4} at a particular temperature if equilibrium is established by taking 2 mol of N_2O_4 in 1 L container then

- (A) concentration of NO_2 at equilibrium is 0.02 M approximately.
 (B) concentration of NO_2 at equilibrium is 0.01 M approximately.
 (C) concentration of N_2O_4 at equilibrium is 2 M approximately.
 (D) concentration of N_2O_4 at equilibrium is 1 M approximately.

Solution



$$K_p = \frac{4x^2}{2} = 2 \times 10^{-4} \Rightarrow x = 0.01$$

$$[\text{NO}] = 2x = 0.02 \text{ M}, [\text{N}_2\text{O}_4] = 2/1 = 2 \text{ M}$$

16. Which of the following relationship(s) describe the quantitative effect of temperature on the equilibrium constant?

- (A) $\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$ (B) $\frac{d \ln K_p}{dT} = \frac{\Delta E}{RT^2}$
 (C) $\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2}$ (D) $\frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2}$

Solution

(A, C)

Assertion–Reasoning Type

Choose the correct option from the following:

- (A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
 (B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1
 (C) Statement 1 is True, Statement 2 is False.
 (D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** Addition of an inert gas at constant pressure to dissociation equilibrium of $\text{PCl}_5 \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ favors forward reaction.

Statement 2: $K_c = \frac{\alpha^2 V}{1 - \alpha}$ for dissociation equilibrium of PCl_5 , where α is degree of dissociation of PCl_5 .

Solution

(C) $K_p = \frac{n_{\text{PCl}_3} \times n_{\text{Cl}_2}}{n_{\text{PCl}_5}} \times \left(\frac{p}{n_T} \right)^1$ with addition of more and more inert gas n_T will increase that

leads to decrease in the value of p/n_T , and hence to keep K_p constant, moles of the product would increase, that is, α increases.

2. **Statement 1:** In the Haber process, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$; $\Delta H < 0$. Then concentration of NH_3 increases by decreasing the temperature and increasing the pressure.

Statement 2: For an exothermic reaction, equilibrium constant increases by increasing the temperature.

Solution

(C) In the exothermic reaction, equilibrium constant increases by decreasing the temperature.

3. Statement 1: The equilibrium amount of NO will be less with an increase in temperature.

Statement 2: Heat is absorbed by increasing the temperature and the equilibrium shifts toward left.

Solution

(A)

4. Statement 1: $\Delta G = \Delta G^\circ + 2.303RT \log_{10}Q$, where Q is reaction quotient.

Statement 2: Q may be greater or lesser than K or equal to K if $\Delta G = 0$.

Solution

(B) $Q < K_c$ forward reaction; $Q = K_c$ equilibrium; $Q > K_c$ backward direction.

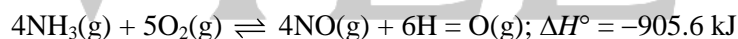
5. Statement 1: Pure liquids and solids can be ignored while writing the equilibrium constant expression.

Statement 2: The concentration of pure liquids and solids does not remain constant.

Solution

(C) The concentration of pure liquids and solids remain constant, and these terms are amalgamated (or merged) in the equilibrium constant. That is why pure liquids and solids are ignored while writing the equilibrium constant expressions.

In the first step of Ostwald's process for synthesis of nitric acid, ammonium is oxidized to NO by the reaction



6. Statement 1: The equilibrium constant for a reaction having positive ΔH° increases with an increase of temperature.

Statement 2: The temperature dependence of the equilibrium constant is related to ΔH° and not ΔS° for the reaction.

Solution

$$(B) \log_{10} \frac{k_2}{k_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

7. Statement 1: The equilibrium attained in a closed vessel remains unaltered by the addition of $\text{CaCO}_3(\text{s})$, which is as follows: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2 \uparrow$

Statement 2: Heterogeneous reaction is unaffected by solid and liquid.

Solution

(A)

8. Statement 1: $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{heat}$. Forward reaction is favored at high temperature and low pressure.

Statement 2: Reaction is exothermic.

Solution

(D) Reaction is exothermic, and low temperature favors forward reaction. High pressure favors forward reaction; it is accompanied by a decrease in the number of moles.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The difference in free energy of the reaction when all the reactants and products are in STP (1 atm and 298 K) is ΔG° , and K_c and K_p are the thermodynamic equilibrium constants of the reaction. The relationship between them is as follows:

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

and

$$\Delta G^\circ = -2.303RT \log K_p \text{ (in case of ideal gas)}$$

This equation relates the equilibrium constant of a reaction to a thermodynamic property. It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant. The standard free energy change can be calculated as

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° is the standard enthalpy change and ΔS° is the standard entropy change.

1. Which of the following statement is correct for a reversible process in state of equilibrium?

(A) $\Delta G = -2.303RT \log K$

(B) $\Delta G = 2.303RT \log K$

(C) $\Delta G^\circ = -2.303RT \log K$

(D) $\Delta G^\circ = 2.303RT \log K$

Solution

(C)

2. Calculate the equilibrium concentration ratio of C to A if 2.0 mol each of A and B were allowed to come to equilibrium at 300 K



(A) 1.0

(B) 0.5

(C) 0.8

(D) 0.679

Solution

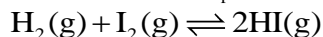
(D) $\Delta G^\circ = -2.303RT \log k$

$$\log k = \bar{1}.665 \Rightarrow k = \text{Antilog of } \bar{1}.665 = 0.4625$$

	A	+	B	\rightleftharpoons	C	+	D
Initial concentration	2		2		0		0
At equilibrium	2 - x		2 - x		x		x

$$K_c = \frac{x^2}{(2-x)^2} = 0.4625 \Rightarrow \frac{[C]}{[A]} = \frac{x}{2-x} = 0.68$$

3. At 490°C, the value of equilibrium constant K_p is 45.9 in the reaction



Calculate the value of ΔG° for the reaction at that temperature

(A) -3.5 kcal

(B) 3.5 kcal

(C) 5.79 kcal

(D) -5.79 kcal

Solution

(D) $\Delta G^\circ = -2.303RT \log K_p = -5.79 \text{ kcal}$

Paragraph II

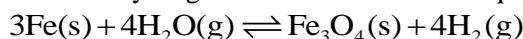
Chemical equilibrium is a dynamic state in which the composition of a system does not change, and net reaction is zero. In reversible reactions, a stage is reached when the rate of transformation of reactants into products equals the rate of transformation of products into reactants. At this stage, the composition of reactants and products does not change with time. The reaction has not stopped, but the rates of forward and reverse reactions are equal. For a general reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, we have

$$K_c = \frac{[C][D]}{[A][B]} \quad \text{and} \quad K_p = \frac{P_C \times P_D}{P_A \times P_B}$$

where K_c is the equilibrium constant for the ratio of the concentrations of the product to reactants and K_p is the equilibrium constant for the ratio of partial pressure and of products to reactants. The relation between K_p and K_c is as follows.

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

4. The mass ratio of steam and hydrogen is found to be 1:2 at equilibrium.



The value of equilibrium constant (K_c) for the above reaction is

- (A) 3.05×10^3 (B) 1.05×10^5 (C) 0.75×10^2 (D) 2.42×10^7

Solution

(B) As $\Delta n = 0$, so $K_c = K_p = K_x$

$$K_x = \frac{x_{\text{H}_2}^4}{x_{\text{H}_2\text{O}}^4} = \frac{(2/2)^4}{(1/18)^4} = 18^4 = 1.05 \times 10^5$$

5. For the reaction $\text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$, the equilibrium constant $K_p = 2.9 \times 10^{-5} \text{ atm}^3$. The total pressure of gases at equilibrium when 1 mol of reactant was heated will be

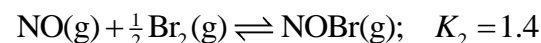
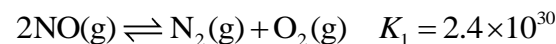
- (A) 0.0194 atm (B) 0.0388 atm (C) 0.0580 atm (D) 0.0667 atm

Solution

(C) $K_p = (p_{\text{NH}_3})^2 \times p_{\text{CO}_2} = (2p)^2 \times p = 4p^3$

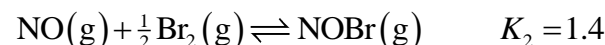
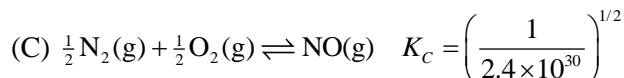
$$p = \left(\frac{K_p}{4} \right)^{1/3} = 0.0667 \text{ atm}$$

6. K_c for the reaction $\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) + \frac{1}{2}\text{Br}_2(g) \rightleftharpoons \text{NOBr}(g)$ from the following information at 298 K



- (A) 3.15×10^{-9} (B) 6.35×10^{-18}
 (C) 9.03×10^{-16} (D) 17×10^{-17}

Solution



7. The equilibrium constant for the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ at 1000 K is 3.5. What would the partial pressure of oxygen gas to give equal moles of SO_2 and SO_3 ?
 (A) 0.29 atm (B) 3.5 atm (C) 0.53 atm (D) 1.87 atm

Solution

$$(A) K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \cdot P_{\text{O}_2}}$$

$$\text{Therefore } p_{\text{O}_2} = \frac{1}{K_p} = \frac{1}{3.5} \text{ atm} = 0.29 \text{ atm}$$

Paragraph III

In dissociation reactions involving gaseous molecules, the total mass remains same and the number of moles increases as a result of the reaction. Hence, the average molecular weight and vapor density decrease. So, the volume increases at constant temperature and pressure, and hence the vapor density decreases. The relationship between initial vapor density and that at equilibrium can be found as follows:

At constant temperature and constant pressure for a fixed mass of gaseous mixtures,

$$\text{Vapor density} \propto \rho \propto \frac{1}{V}$$

Now, for ideal gas, $pV = nRT$ or volume \propto number of moles. So,

$$\text{Vapor density} \propto \frac{1}{\text{Number of moles}} \Rightarrow \frac{D}{D_0} = \frac{n}{n_0}$$

where D_0 and D are the vapor densities in the beginning and at equilibrium, respectively, and n_0 and n are the number of moles in the beginning and at equilibrium, respectively. The vapor densities of PCl_5 at 200°C and 252°C are 70.2 and 57.2, respectively, at 1 atm.

8. From the given data, it can be interpreted that
 (A) if degree of dissociation is more, then vapor density is more for PCl_5 .
 (B) more is the degree of dissociation, less is the vapor density of PCl_5 .
 (C) degree of dissociation and vapor density cannot be correlated.
 (D) α is independent of temperature.

Solution

- (B) More is the degree of dissociation, less is the vapor density of PCl_5

9. X, Y, and Z react in the 1:1:1 stoichiometric ratio. The concentration of X, Y, and Z was found to vary with time as shown in Fig. 8.6.

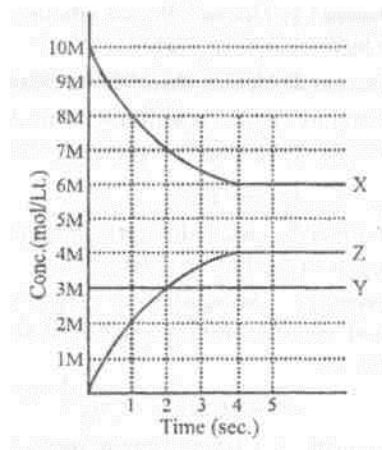


Figure 8.6

Which of the following equilibrium reaction represents the correct variation of concentration with time?

- (A) $X(g) + Y(g) \rightleftharpoons Z(g)$ (B) $X(g) + Y(s) \rightleftharpoons Z(g)$
 (C) $Z(g) + Y(s) \rightleftharpoons X(g)$ (D) $Z(g) + X(g) \rightleftharpoons Y(g)$

Solution

(B) Clearly, concentration of Y is not changing with the time. Hence, it will be pure solid or liquid. Concentration of X is decreasing. Hence, it will be in reactant and Z will be in product.

10. Value of the equilibrium constant (K_c) for the equilibrium represented in above sketch will be

- (A) $\frac{9}{2}$ (B) $\frac{21}{4}$ (C) $\frac{2}{3}$ (D) $\frac{12}{7}$

Solution

$$(C) K_c = \frac{[Z(g)]_{eq}}{[X(g)]_{eq}} = \frac{4}{6} = \frac{2}{3}$$

11. If above equilibrium is established in a 2 L container by taking reactants in sufficient amount, then how many moles of component Y must have reacted for establishment of the equilibrium.

- (A) 0 (B) 6 (C) 12 (D) 8

Solution

(D) From the graph, we can see that 4 mol L^{-1} of Z is formed. Therefore, $4 \times 2 \text{ mol}$ of solid will be required.

Integer Answer Type

The answer is a **non-negative integer**.

1. For the reaction: $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$, K is 0.63 at 700°C and 1.66 at 1000°C . The average ΔH° for the temperature range considered is ____.

Solution

(8) Given that $T_1 = 700 + 273 = 973 \text{ K}$, $T_2 = 1000 + 273 = 1273 \text{ K}$,
 $K_1 = 0.63$, $K_2 = 1.66$

Using the van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{1.66}{0.63} \right) = \frac{\Delta H^\circ}{2.303 \times 1.99} \left(\frac{1273 - 973}{1273 \times 973} \right) \Rightarrow \Delta H^\circ = 8.0 \times 10^3 \text{ cal} = 8.0 \text{ kcal}$$

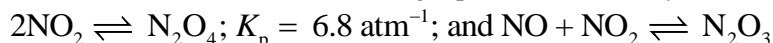
Note: The units of R and ΔH must be same.

2. Equilibrium constant for the reaction $A_3(g) + 3B_2(g) \rightleftharpoons 3AB_2(g)$ is 64.0. Then the equilibrium constant for the reaction $\frac{1}{3}A_3(g) + B_2(g) \rightleftharpoons AB_2(g)$ will be ____.

Solution

$$(4) K_C' = (64)^{1/3} = 4$$

3. When NO and NO₂ are mixed, the following equilibria are readily obtained:



In an experiment when NO and NO₂ are mixed in the ratio of 1:2, then the total pressure was 5.05 atm and the partial pressure of N₂O₄ was 1.7 atm. Calculate the equilibrium partial pressure of NO in atmospheres.

Solution

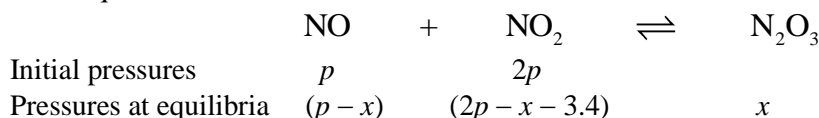
(2) For 1 equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$$K_p = \frac{p'_{N_2O_4}}{(p_{NO_2})^2} = 6.8 \quad (1)$$

$p'_{N_2O_4} = 1.7 \text{ atm}$ therefore by Eq. (1) $p'_{NO_2} = 0.5 \text{ atm}$.

The equilibria are maintained using NO and NO₂ in the ratio of 1:2

For 2 equilibria



3.4 atm of NO₂ are used for 1 equilibrium to have $p'_{N_2O_4} = 1.7 \text{ atm}$

At equilibrium $(p - x)$ 0.5 x

(Since p'_{NO_2} is same for both the equilibria, as both reactions are at equilibrium at a time)

Total pressure at equilibrium = $p'_{NO} + p'_{NO_2} + p'_{N_2O_3} + p'_{N_2O_4} = p - x + 0.5 + x + 1.7$

$$5.05 = p + 2.20 \Rightarrow p = 2.85 \text{ atm}$$

$$2p - x - 3.4 = 0.5 \Rightarrow 2 \times 2.85 - x - 3.4 = 0.5 \Rightarrow x = 1.80 \text{ atm} \approx 2 \text{ atm}$$

4. Ammonium carbamate when heated to 200°C gives a mixture of vapors ($\text{NH}_2\text{COONH}_4 \rightleftharpoons 2\text{NH}_3 + \text{CO}_2$) with a density 13.0. The degree of dissociation of ammonium carbamate is ____.

Solution

(1) Density of ammonium carbamate before dissociation

$$D = \frac{\text{Molecular weight}}{2} = \frac{78}{2} = 39$$

Density after dissociation (d) = 13.0 (given). Hence,

$$\alpha = \frac{D - d}{(n-1)d} = \frac{39 - 13}{(3-1) \times 13} = \frac{26}{26} = 1$$

So, ammonium carbamate will be 100% dissociated.

5. For the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$,

$$(\Delta G_{\text{N}_2\text{O}_4}^\circ)_{298\text{K}} = 100 \text{ kJ mol}^{-1} \text{ and } (\Delta G_{\text{NO}_2}^\circ)_{298\text{K}} = 50 \text{ kJ mol}^{-1}$$

When 5 mol L⁻¹ of each in taken, calculate the value of ΔG for the reaction at 298 K.

Solution

(4) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$; $\Delta G_{\text{N}_2\text{O}_4}^\circ = 100 \text{ kJ mol}^{-1}$

Concentration at $t = 0$ 5 5 $\Delta G_{\text{NO}_2}^\circ = 50 \text{ kJ mol}^{-1}$

$$\Delta G^\circ \text{ for reaction} = 2 \times \Delta G_{\text{NO}_2}^\circ - \Delta G_{\text{N}_2\text{O}_4}^\circ = 2 \times 50 - 100 = 0$$

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$$\text{Now, } \Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \frac{5^5}{5} = +3.99 \text{ kJ} \approx 4 \text{ kJ}$$

6. If concentrations of SO_2 and O_2 in the equilibrium reaction, $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ are quadrupled, the concentration of SO_3 now will be ____ times.

Solution

(8) For the reaction

$$K_C = \frac{[\text{SO}_3]_{\text{initial}}^2}{[\text{SO}_2]^2[\text{O}_2]} \quad (1)$$

When concentrations of SO_2 and O_2 are quadrupled, the expression becomes

$$K_C = \frac{[\text{SO}_3]_{\text{final}}^2}{[4\text{SO}_2]^2[4\text{O}_2]} \quad (2)$$

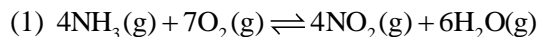
Dividing Eq. (2) by Eq. (1), we get

$$\frac{[\text{SO}_3]_{\text{final}}^2}{[4\text{SO}_2]^2[4\text{O}_2]} = \frac{[\text{SO}_3]_{\text{initial}}^2}{[\text{SO}_2]^2[\text{O}_2]} \Rightarrow \frac{[\text{SO}_3]_{\text{final}}^2}{[\text{SO}_3]_{\text{initial}}^2} = \frac{[4\text{SO}_2]^2[4\text{O}_2]}{[\text{SO}_2]^2[\text{O}_2]} = 16 \times 4 = 64$$

Hence,
$$\frac{[\text{SO}_3]_{\text{final}}}{[\text{SO}_3]_{\text{initial}}} = 8$$

7. For the reaction involving oxidation of ammonia by oxygen to form nitric oxide and water vapor, the equilibrium constant has the units (bar)ⁿ. Then *n* is ____.

Solution



Water and oxygen will not contribute to partial pressure.

$$K_p = \frac{(p_{\text{NO}_2})^4}{(p_{\text{NH}_3})^4} = 1$$

Answer should be -1.

Matrix–Match Type

1. Match the reactions of the column I with the relations in Column II

Column I	Column II
(A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	(p) $K_p = K_c (RT)$
(B) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	(q) $K_p = K_c (RT)^2$
(C) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(r) $K_p = K_c (RT)^{-2}$
(D) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$	(s) $K_p = K_c$
	(t) $K_p = K_c (RT)^{-1}$

Solution

(A) → (s); (B) → (r); (C) → (p); (D) → (q)

Using the relation $K_p = K_c(RT)^{\Delta n}$

2.

Match the relation with the prediction of equilibrium.

Column I	Column II
(A) $Q = K$	(p) Reaction is nearer to completion
(B) $Q < K$	(q) Reaction is not at equilibrium
(C) $Q > K$	(r) Reaction is fast in forward direction;
(D) $K \gg 1$	(s) Reaction at equilibrium
	(t) Rate of forward reaction = rate of backward reaction

Solution

(A) → (s, t); (B) → (q, r); (C) → (q); (D) → (p)

3. Match the chemical reaction in equilibrium with the pressure dependent on degree of dissociation of the reaction:

Column I	Column II
(A) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	(p) $\alpha \propto \sqrt{p}$
(B) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	(q) $\alpha \propto \sqrt{1/p}$
(C) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(r) $\alpha \propto p$
(D) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$	(s) $\alpha \propto p^0$
	(t) $K_p = K_c$

Solution

(A) → (r); (B) → (p); (C) → (q); (D) → (s, t)

4. Match the effect of change administered to its effect on equilibrium.

Column I	Column II
(A) For the equilibrium $\text{NH}_4\text{I(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HI(g)}$, if pressure is increased at equilibrium	(p) Forward shift
(B) For the equilibrium $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ At equilibrium volume is increases at equilibrium	(q) No change
(C) For the equilibrium $\text{H}_2\text{O(g)} + \text{CO(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{CO}_2\text{(g)}$ inert gas is added at constant pressure at equilibrium	(r) Backward shift
(D) For the equilibrium $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, Cl_2 is removed at equilibrium	(s) Final pressure is more than initial pressure

Solution

(A) → (r),(s); (B) →(r); (C) → (q); (D) → (p),(s)

(A) As $\Delta n > 0$ therefore if $p \uparrow$, reaction will go in the backward direction.

(B) As $\Delta n < 0$ therefore if $V \uparrow$, $p \downarrow$ reaction will go in the direction in which more number of gaseous moles are formed that is backward direction.

(C) As $\Delta n = 0$, hence no effect.

(D) If concentration of the product is decreased, reaction will go in the forward direction.

5. Match the quantity with the effect/relation.

Column I	Column II
(A) $K_C < 1$	(p) Affected by temperature
(B) Degree of dissociation	(q) Affected by pressure
(C) Equilibrium constant	(r) $K_f < K_b$
(D) Melting of ice	(s) $K_f > K_b$

Solution

(A) → (r); (B) → (p, q); (C) → (p); (D) → (p, q)

(A) Backward reaction is favored.

(B) α is affected by both temperature and pressure.

(C) K_C is affected by temperature only.

(D) On increasing temperature and pressure, ice melts.