## CHEMICAL EQUILIBRIUM

1. At 1990 K and 1 atm pressure, there are equal number of $\mathrm{Cl}_{2}$ molecules and Cl atoms in the reaction mixture. The value $\mathrm{K}_{\mathrm{P}}$ for the reaction $\mathrm{Cl}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{Cl}_{(\mathrm{g})}$ under the above conditions is $x \times 10^{-1}$. The value of $x$ is $\qquad$ . (Rounded off to the nearest integer)
2. The stepwise formation of $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is given below
$\mathrm{Cu}^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{1}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)\right]^{2+}$
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{2}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{2}\right]^{2+}$
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{2}\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{3}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{3}\right]^{2+}$

$$
\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{3}\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{4}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}
$$

The value of stability constants $\mathrm{K}_{1}, \mathrm{~K}_{2}, \mathrm{~K}_{3}$ and $\mathrm{K}_{4}$ are $10^{4}, 1.58 \times 10^{3}, 5 \times 10^{2}$ and $10^{2}$ respectively. The overall equilibrium constants for dissociation of $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is $\mathrm{x} \times 10^{-12}$. The value of $x$ is $\qquad$ (Rounded off to the nearest integer)
3. A homogeneous ideal gaseous reaction $\mathrm{AB}_{2(\mathrm{~g})} \rightleftharpoons \mathrm{A}_{(\mathrm{g})}+2 \mathrm{~B}_{(\mathrm{g})}$ is carried out in a 25 litre flask at $27^{\circ} \mathrm{C}$. The initial amount of $\mathrm{AB}_{2}$ was 1 mole and the equilibrium pressure was 1.9 atm. The value of $\mathrm{K}_{\mathrm{P}}$ is $x \times 10^{-2}$. The value of $x$ is $\qquad$ .(Integer answer)
4. Consider the reaction $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$. The temperature at which $\mathrm{K}_{\mathrm{C}}=20.4$ and $K_{P}=600.1$, is $\qquad$ K. (Round off to the Nearest Integer).
[Assume all gases are ideal and $\mathrm{R}=0.0831 \mathrm{~L}$ bar K $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$ ]
5. $2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})$

In an equilibrium mixture, the partial pressures are $\mathrm{P}_{\mathrm{SO}_{3}}=43 \mathrm{kPa} \quad ; \quad \mathrm{P}_{\mathrm{O}_{2}}=530 \mathrm{~Pa}$ and $\mathrm{P}_{\mathrm{SO}_{2}}=45 \mathrm{kPa}$. The equilibrium constant $\mathrm{K}_{\mathrm{P}}=$ $\qquad$ $\times 10^{-2}$. (Nearest integer)
$2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})$
6. Value of $K_{P}$ for the equilibrium reaction
$\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})} \rightleftharpoons 2 \mathrm{NO}_{2(\mathrm{~g})}$ at 288 K is 47.9. The $\mathrm{K}_{\mathrm{C}}$ for this reaction at same temperature is $\qquad$ .
(Nearest integer)
( $\mathrm{R}=0.083 \mathrm{~L} \mathrm{bar} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$ )
7. For the reaction

$$
\mathrm{A}+\mathrm{B} \rightleftharpoons 2 \mathrm{C}
$$

the value of equilibrium constant is 100 at 298 K. If the initial concentration of all the three species is 1 M each, then the equilibrium concentration of C is $\mathrm{x} \times 10^{-1} \mathrm{M}$. The value of x is $\qquad$ .
(Nearest integer)
8. Presence of which reagent will affect the reversibility of the following reaction, and change it to a irreversible reaction :
$\mathrm{CH}_{4}+\mathrm{I}_{2} \xrightarrow[\text { Reversible }]{\text { hv }} \mathrm{CH}_{3}-\mathrm{I}+\mathrm{HI}$
(1) HOCl
(2) dilute $\mathrm{HNO}_{2}$
(3) Liquid $\mathrm{NH}_{3}$
(4) Concentrated $\mathrm{HIO}_{3}$
9. $\quad \mathrm{PCl}_{5} \rightleftharpoons \mathrm{PCl}_{3}+\mathrm{Cl}_{3} \quad ; \quad \mathrm{K}_{\mathrm{c}}=1.844$
3.0 moles of $\mathrm{PCl}_{5}$ is introduced in a 1 L closed reaction vessel at 380 K . The number of moles of $\mathrm{PCl}_{5}$ at equilibrium is $\qquad$ $\times 10^{-3}$.
(Round off to the Nearest Integer)
10. The equilibrium constant for the reaction
$\mathrm{A}(\mathrm{s}) \rightleftharpoons \mathrm{M}(\mathrm{s})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g})$
is $\mathrm{K}_{\mathrm{p}}=4$. At equilibrium, the partial pressure of $\mathrm{O}_{2}$ is $\qquad$ atm. (Round off to the nearest integer)
11. The following data was obtained for chemical reaction given below at 975 K .

$$
2 \mathrm{NO}_{(\mathrm{g})}+2 \mathrm{H}_{2(\mathrm{~g})} \rightarrow \mathrm{N}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

[NO] $\left[\mathrm{H}_{2}\right] \quad$ Rate $\mathrm{mol} \mathrm{L}^{-1} \quad \mathrm{~mol} \mathrm{~L}^{-1} \quad \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$
(A) $8 \times 10^{-5}$
$8 \times 10^{-5}$
$7 \times 10^{-9}$
(B) $24 \times 10^{-5}$
$8 \times 10^{-5}$
$2.1 \times 10^{-8}$
(C) $24 \times 10^{-5}$
$32 \times 10^{-5}$
$8.4 \times 10^{-8}$

The order of the reaction with respect to NO is
$\qquad$ . [Integer answer]
12. The equilibrium constant $\mathrm{K}_{\mathrm{c}}$ at 298 K for the reaction $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D}$ is 100 . Starting with an equimolar solution with concentrations of $\mathrm{A}, \mathrm{B}, \mathrm{C}$ and D all equal to 1 M , the equilibrium concentration of D is
$\qquad$ $\times 10^{-2} \mathrm{M}$. (Nearest integer)
13. The reaction rate for the reaction
$\left[\mathrm{PtCl}_{4}\right]^{2-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left[\mathrm{Pt}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{3}\right]^{-}+\mathrm{Cl}^{-}$
was measured as a function of concentrations of different species. It was observed that
$\frac{-\mathrm{d}\left[\left[\mathrm{PtCl}_{4}\right]^{2-}\right]}{\mathrm{dt}}=4.8 \times 10^{-5}\left[\left[\mathrm{PtCl}_{4}\right]^{2-}\right]-2.4 \times$
$10^{-3}\left[\left[\mathrm{Pt}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{3}\right]^{-}\right]\left[\mathrm{Cl}^{-}\right]$.
where square brackets are used to denote molar concentrations. The equilibrium constant $\mathrm{K}_{\mathrm{c}}=$ $\qquad$ (Nearest integer)
14. When 5.1 g of solid $\mathrm{NH}_{4} \mathrm{HS}$ is introduced into a two litre evacuated flask at $27^{\circ} \mathrm{C}, 20 \%$ of the solid decomposes into gaseous ammonia and hydrogen sulphide. The $K_{p}$ for the reaction at $27^{\circ} \mathrm{C}$ is $\mathrm{x} \times 10^{-2}$. The value of x is $\qquad$ . (Integer answer)
[Given $\mathrm{R}=0.082 \mathrm{~L} \mathrm{~atm}^{-1} \mathrm{~mol}^{-1}$ ]

## SOLUTION

## 1. Official Ans. by NTA (5)

Sol. $\mathrm{Cl}_{2} \rightleftharpoons 2 \mathrm{Cl}$
Let mol of both of $\mathrm{Cl}_{2}$ and Cl is x
$\mathrm{P}_{\mathrm{Cl}}=\frac{\mathrm{x}}{2 \mathrm{x}} \times 1=\frac{1}{2}$
$\mathrm{P}_{\mathrm{Cl}_{2}}=\frac{\mathrm{x}}{2 \mathrm{x}} \times 1=\frac{1}{2}$
$\mathrm{K}_{\mathrm{p}}=\frac{\left(\frac{1}{2}\right)^{2}}{\frac{1}{2}}=\frac{1}{2}=0.5 \Rightarrow 5 \times 10^{-1}$
2. Official Ans. by NTA (1)

Sol. $\mathrm{Cu}^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{1}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)\right]^{2+}$
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{2}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{2}\right]^{2+}$
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{2}\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{3}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{3}\right]^{2+}$
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{3}\right]^{2+}+\mathrm{NH}_{3} \stackrel{\mathrm{~K}_{4}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
$\mathrm{Cu}^{2+}+4 \mathrm{NH}_{3} \stackrel{\mathrm{~K}}{\rightleftharpoons}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$

So
$\mathrm{K}=\mathrm{K}_{1} \times \mathrm{K}_{2} \times \mathrm{K}_{3} \times \mathrm{K}_{4}$

$$
=10^{4} \times 1.58 \times 10^{3} \times 5 \times 10^{2} \times 10^{2}
$$

$K=7.9 \times 10^{11}$
Where $\mathrm{K} \rightarrow$ Equilibrium constant for formation of $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$

So equilibrium constant ( $\mathrm{K}^{\prime}$ ) for dissociation of
$\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is $\frac{1}{\mathrm{~K}}$
$\mathrm{K}^{\prime}=\frac{1}{\mathrm{~K}}$

$$
\begin{aligned}
\mathrm{K}^{\prime} & =\frac{1}{7.9 \times 10^{11}} \\
& =1.26 \times 10^{-12}=\left(\mathrm{x} \times 10^{-12}\right)
\end{aligned}
$$

So the value of $x=1.26$
OMR Ans $=1$ (After rounded off to the nearest integer)
3. Official Ans. by NTA (73)

Sol. $\mathrm{AB}_{2}=\mathrm{A} \quad+\quad 2 \mathrm{~B}$
1
$1-\alpha \quad \alpha \quad 2 \alpha$
$\begin{array}{lll}=0.535 & 0.465 & 0.93\end{array}$
$1.9 \times 25=\mathrm{n}_{\mathrm{T}} \times 0.08206 \times 300$
$\mathrm{n}_{\mathrm{T}}=1.93=1+2 \alpha$
$\alpha=0.465$

$$
\mathrm{Kp}=\frac{\left(\frac{0.465}{1.93} \times 19\right)\left(\frac{0.93}{1.93} \times 1.9\right)^{2}}{\left(\frac{0.535}{1.93} \times 1.9\right)}
$$

$\simeq 73 \times 10^{-2} \mathrm{~atm}^{2}$

## 4. Official Ans. by NTA (354)

Sol. $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g}) ; \Delta \mathrm{n}_{\mathrm{g}}=2-1=1$
Now, $K_{p}=K_{c} \cdot(R T)^{\Delta n g}$
or, $600.1=20.4 \times(0.0831 \times \mathrm{T})^{1}$
$\therefore \mathrm{T}=353.99 \mathrm{~K}=354 \mathrm{~K}$
5. Official Ans. by NTA (172)

Sol. $2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}=2 \mathrm{SO}_{3(\mathrm{~g})}$
$\mathrm{K}_{\mathrm{p}}=\frac{\left(\mathrm{pSO}_{3(\mathrm{~g})}\right)^{2}}{\mathrm{pSO} 2(\mathrm{~g})} \times \mathrm{pO}_{2(\mathrm{~g})}$
$=\frac{43 \times 43}{45 \times 45} \times 530 \mathrm{~Pa}^{-1}$
$=172.28 \times 10^{-5} \mathrm{~Pa}^{-1}$
$=172.28 \mathrm{~atm}$
$=17228 \times 10^{-2} \mathrm{~atm}$
Ans is 17228
6. Official Ans. by NTA (2)

$$
\mathrm{K}_{\mathrm{C}}=\frac{\mathrm{K}_{\mathrm{P}}}{\mathrm{RT}}=\frac{47.9}{0.083 \times 288}=2
$$

7. Official Ans. by NTA (25)

Sol.

| A | $+\mathrm{B} \rightleftharpoons$ | 2 C |
| :--- | :---: | :---: |
| 1 | 1 | 1 |
| -x | -x | 2 x |
|  |  |  |
| $1-\mathrm{x}$ | $1-\mathrm{x}$ | $1+2 \mathrm{x}$ |

$\mathrm{K}=\frac{[\mathrm{C}]_{\mathrm{eq}}^{2}}{[\mathrm{~A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}}=\frac{(1+2 \mathrm{x})^{2}}{(1-\mathrm{x})(1-\mathrm{x})}$
$100=\left(\frac{1+2 \mathrm{x}}{1-\mathrm{x}}\right)^{2}$
$\left(\frac{1+2 \mathrm{x}}{1-\mathrm{x}}\right)=10$
$\mathrm{x}=\frac{3}{4}$
$[\mathrm{C}] \mathrm{e}_{\mathrm{q} .}=1+2 \mathrm{x}$
$=1+2\left(\frac{3}{4}\right)$
$=2.5 \mathrm{M}$
$25 \times 10^{-1} \mathrm{M}$
8. Official Ans. by NTA (4)

Sol. lodination of alkane is reversible reaction.
It can be irreversible in the presence of strong oxidising agent like conc. $\mathrm{HNO}_{3}$ or conc. $\mathrm{HIO}_{3}$
9. Official Ans. by NTA (1396)

Sol. $\quad \mathrm{PCl}_{5(\mathrm{~g})} \rightleftharpoons \mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})} \mathrm{K}_{2}=1.844$

$$
\mathrm{t}=03 \text { moles }
$$

$t=\infty \quad x \quad x$
$\Rightarrow \frac{\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{PCl}_{5}\right]}=\frac{\mathrm{x}^{2}}{3-\mathrm{x}}=1.844$
$\Rightarrow x^{2}+1.844-5.532=0$
$\Rightarrow \mathrm{x}=\frac{-1.844+\sqrt{(1.844)^{2}+4 \times 5.532}}{2}$
$\cong 1.604$
$\Rightarrow$ Moles of $\mathrm{PCl}_{5}=3-1.604 \cong 1.396$
10. Official Ans. by NTA (16)

Sol. $\mathrm{k}_{\mathrm{p}}=\mathrm{Po}_{2}^{1 / 2}=4$
$\therefore \mathrm{Po}_{2}=16 \mathrm{bar}=16 \mathrm{~atm}$
11. Official Ans. by NTA (1)

Sol. $7 \times 10^{-9}=\mathrm{K} \times\left(8 \times 10^{-5}\right)^{\mathrm{x}}\left(8 \times 10^{-5}\right)^{\mathrm{y}}$
$2.1 \times 10^{-8}=K \times\left(24 \times 10^{-5}\right)^{\mathrm{x}}\left(8 \times 10^{-5}\right)^{\mathrm{y}}$
$\frac{1}{3}=\left(\frac{1}{3}\right)^{\mathrm{x}} \Rightarrow \mathrm{x}=1$
12. Official Ans. by NTA (182)

Sol. $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D}: \mathrm{K}_{\mathrm{eq}}=100$
1M 1M 1M 1M
First check direction of reversible reaction.
Since $\mathrm{Q}_{\mathrm{C}}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}=1<\mathrm{K}_{\text {eq. }} \Rightarrow$ reaction will move in forward direction to attain equilibrium state.
$\Rightarrow \mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D}: \mathrm{K}_{\mathrm{eq}}=100$
$\begin{array}{lllll}\text { to } & 1 & 1 & 1 & 1\end{array}$
$\mathrm{t}_{\text {eq. }} 1-\mathrm{x} \quad 1-\mathrm{x} \quad 1+\mathrm{x} \quad 1+\mathrm{x}$
Now : $\mathrm{K}_{\mathrm{eq}}=100=\frac{(1+\mathrm{x})(1+\mathrm{x})}{(1-\mathrm{x})(1-\mathrm{x})}$

$$
\Rightarrow 100=\left(\frac{1+x}{1-x}\right)^{2}
$$

(i) $10=\left(\frac{1+x}{1-x}\right)$
$\Rightarrow 10-10 \mathrm{x}=1+\mathrm{x} \quad \Rightarrow 11 \mathrm{x}=9$
$\Rightarrow \mathrm{x}=\frac{9}{11}$
(ii) $-10=\frac{1+\mathrm{x}}{1-\mathrm{x}}$
$\Rightarrow-10+10 \mathrm{x}=1+\mathrm{x} \quad \Rightarrow-9 \mathrm{x}=-11$
$\Rightarrow \mathrm{x}=\frac{11}{9}$
$\rightarrow$ 'x' cannot be more than one, therefore not valid.
therefore equation concretion of $(D)=1+x$

$$
\begin{aligned}
& =1+\frac{9}{11}=\frac{20}{11} \\
& =1.8181=181.81 \times 10^{-2} \\
& \simeq 182 \times 10^{-2}
\end{aligned}
$$

13. Official Ans. by NTA (50)

Sol. $\left[\mathrm{PtCl}_{4}\right]^{-2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left[\mathrm{Pt}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{3}\right]^{-}+\mathrm{Cl}^{-}$

$$
\frac{-\mathrm{d}\left[\mathrm{Pt} \mathrm{Cl}_{4}\right]^{-2}}{\mathrm{dt}}=4.8 \times 10^{-5}\left[\mathrm{PtCl}_{4}^{-2}\right]-2.4 \times 10^{3}
$$

$\left[\mathrm{Pt}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{3}\right][\stackrel{0}{\mathrm{u}}]$
$\Rightarrow \mathrm{K}_{\mathrm{eq}}=\frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{k}_{\mathrm{b}}}=\frac{4.8 \times 10^{-5}}{2.4 \times 10^{-3}}=0.02$
14. Official Ans. by NTA (6)

Sol. $\quad$ moles of $\mathrm{NH}_{4} \mathrm{HS}$ initially taken $=\frac{5.1 \mathrm{~g}}{51 \mathrm{~g} / \mathrm{mol}}$

$$
=0.1 \mathrm{~mol}
$$

volume of vessel $=2 \ell$
$\mathrm{NH}_{4} \mathrm{HS}_{(\mathrm{s})} \rightleftharpoons \mathrm{NH}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})}$
$\mathrm{t}=0 \quad 0.1 \mathrm{~mol}$
$t=\infty \quad 0.1(1-0.2) \quad 0.1 \times 0.2 \quad 0.1 \times 0.2$
$\Rightarrow$ partial pressure of each component
$\mathrm{P}=\frac{\mathrm{nRT}}{\mathrm{V}}=\frac{0.1 \times 0.2 \times 0.082 \times 300}{2}$
$=0.246 \mathrm{~atm}$

$$
\begin{gathered}
\Rightarrow \mathrm{k}_{\mathrm{P}}=\mathrm{P}_{\mathrm{NH}_{3}} \times \mathrm{P}_{\mathrm{H}_{2} \mathrm{~S}}=(0.246)^{2}=0.060516 \\
=6.05 \times 10^{-2} \quad \Rightarrow 6
\end{gathered}
$$

