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## CHEMISTRY

## BOOKS - VIKRAM PUBLICATION ( ANDHRA PUBLICATION)

## ELECTROCHEMISTRY \& CHEMICAL KINETICS

## Textual Examples

1. Represent the cell in which the following reaction takes place
$M g(s)+2 A g^{+}(0.0001 M) \rightarrow M g^{2+}(0.130 M)+2 A g(s)$
Calculates its $E_{\text {cell }}$ if $E_{\text {cell }}^{\Theta}=3.17 \mathrm{~V}$

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2. Calculate the equilibrium constant of the reaction:
$C u_{(s)}+2 A g_{(a q)}^{+} \rightarrow C u_{(a q)}^{2+}+2 A g_{(a)}$
$E_{(\text {cell })}^{\Theta}=0.46 \mathrm{~V}$

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3. The standard emf of Deniell cell is 1.1 V . Calculate the standard Gibbs energy for the cell reactions:

$$
Z n_{(s)}+C u_{(a q)}^{2+} \rightarrow Z n_{(a q)}^{2+}+C u_{(s)}
$$

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4. Resistance of a conductivity cell filled with $0.1 \mathrm{~mol}^{-1} \mathrm{KCl}$ solution is $100 \Omega$. If the resistance of the same cell when filled with $0.02 \mathrm{~mol}^{-1} \mathrm{KCl}$ solution is $520 \Omega$, calculate the conductivity and molar conductivity of $0.02 \mathrm{molL}^{-1} \mathrm{KCl}$ solution. The conductivity of $0.1 \mathrm{molL}^{-1} \mathrm{KCl}$ solutin is $1.29 \mathrm{~s} / \mathrm{m}$.
5. The electrical resistance of a column $0.05 \mathrm{molL}^{-1} \mathrm{NaOH}$ solution of diameter 1 cm and length 50 cm is $5.55 \times 10^{3}$ ohm. Calculate its resistivity, conductivity and molar conductivity.

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6. Calculate $\wedge_{m}^{0}$ for $\mathrm{CaCl}_{2}$ and $\mathrm{MgSO}_{4}$ from the data given in Table 3.4.

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7. $\wedge_{m}^{0}$ for $\mathrm{NaCl}, \mathrm{HCl}$ and NaAc are $126.4,425.0$ and $91.0 \mathrm{Scm}^{2} \mathrm{~mol}^{-1}$ respectively. Calculate $\wedge(0)$ for Hac.

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8. The conductivity of $0.001028 \mathrm{molL}^{-1}$ acetic acid is $4.95 \times 10^{-5} \mathrm{Scm}^{-1}$. Calculate its dissociation constant if $\wedge(m)^{0}$ for acetic acid id $390.5 \mathrm{Scm}^{2} \mathrm{~mol}^{-1}$.

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9. A solution of $\mathrm{CuSO}_{4}$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

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10. From the concentration of $\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Cl}$ (butyl chloride) at different times given below, calculate the average rate of the reaction:

$$
\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Cl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{C}_{4} \mathrm{H}_{9} \mathrm{OH}+\mathrm{HCl}
$$

| $\mathbf{t} / \mathbf{s}$ | 0 | 50 | 100 | 150 | 200 | 300 | 400 | 500 | 700 | 800 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left\|\mathbf{C}_{4} \mathbf{H}_{9} \mathbf{C l}\right\| / \mathrm{mol} \mathrm{L}^{-1}$ | 0.100 | 0.0905 | 0.0820 | 0.0741 | 0.0671 | 0.0549 | 0.0439 | 0.0335 | 0.0210 | 0.017 |

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11. The decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ in $\mathrm{CCl}_{4}$ at 318 K has been studies by monitoring the concentration of $N_{2} O_{5}$ in the solution. Initially the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ is $2.33 \mathrm{molL}^{-1}$ and after 184 minutes, it is reduced to $2.08 \mathrm{~mol}^{-1}$. The reaction takes placed according to the equation
$2 \mathrm{~N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
Calculate the average rate of this reaction in terms of hours, minutres and seconds. What is the rate of proudction of $\mathrm{NO}_{2}$ during this period ?

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12. Calculate the overall order of a reaction which has the rate expression
a) Rate $=k[A]^{1 / 2}[B]^{3 / 2}$
d) Rate $=k[A]^{3 / 2}[B]^{-1}$

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13. Identify the reaction order from each of the following rate constants.
i) $k=2.3 \times 10^{5} \mathrm{Lmol}^{-1} \mathrm{~s}^{-1}$
ii) $\mathrm{K}=3 \mathrm{xx10}^{\wedge}(-4) \mathrm{s}^{\wedge}(-1)^{\wedge}$

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14. The initial concentratin of $\mathrm{N}_{2} \mathrm{O}_{5}$ in the following first order reaction $\mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})+\frac{1}{2 \mathrm{O}_{2}}(\mathrm{~g}) \mathrm{was} 1.24 \times 10^{-2} \mathrm{molL}^{-1}$ at 318 K . The concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ after 60 minutes was $0.20 \times 10^{-2} \mathrm{molL}^{-1}$.

Calculate the rate constant of the reaction at 138 K .

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15. The following data were obtained during the first order thermal decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g})$ at constant volume :
$2 \mathrm{~N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{4}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$

| S.No. | Time/s | Total Pressure/(atm) |
| :---: | :---: | :---: |
| 1 | 0 | 0.5 |
| 2 | 100 | 0.512 |

Calculate the rate constnat.

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16. A first order reaction is found to have a rate constant, $k=5.5 \times 10^{-14} s^{-1}$. Find the half- life of the reaction.

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17. Show that in a first order reaction, time pequired for fompletion of $99.9 \%$ is 10 times of half-life $\left(t_{1 / 2}\right)$ of the reaction.

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18. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below.

| $\dot{t} / \mathrm{min}$ | 0 | 30 | 60 | 90 |
| :--- | :---: | :---: | :---: | :---: |
| $\mathbf{C} / \mathrm{mol} \mathrm{L}^{-1}$ | 0.8500 | 0.8004 | 0.7538 | 0.7096 |

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant $\left(55 \mathrm{molL}^{-1}\right)$, during the course of the reaction. What is the value of $k$ in this equation?

Rate $=k^{\prime}\left[\mathrm{CH}_{3} \mathrm{COOCH}_{3}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]$

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19. The rate constants of a reaction at 500 K and 700 K are $0.02 s^{-1}$ and $0.04 s^{-1}$ respectively. Calculate the values of $E_{a}$ and A.

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20. The first order rate constant for the decomposition of ethyl iodide by the reaction. $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{I}(\mathrm{g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{HI}(\mathrm{g})$ at $600 \mathrm{Kis} 1.60 \times 10^{-5} \mathrm{~s}^{-1}$. It is energy of activation is $209 \mathrm{~kJ} / \mathrm{mol}$. Calculate the rate constant of the reaction at 700 K.

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## Problems

1. The standard potentials of some electrodes are as follows. Arrange the metals in an increasing order of their reductiong power.
1) $K^{+} / K=-2.93 \mathrm{~V}$
2) $\mathrm{Ag}^{+} / \mathrm{Ag}=0.80 \mathrm{~V}$
3) $\mathrm{Cu}^{2+} / \mathrm{Cu}=0.34 \mathrm{~V}$
4) $M g^{2+} / M g=-2.37 V$
5) $\mathrm{Cr}^{3+} / \mathrm{Cr}=-0.74 \mathrm{C}$
6) $F e^{+} / F e=-$

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2. Calculate the emf of the cell at $25^{\circ} \mathrm{C}$
$C r\left|C r^{3+}(0.1 M)\right|\left|F e^{2+}(0.01 M)\right| F e, \quad$ given that $E_{C r^{3}+C r}^{0}=-0.74 V$ and $E_{F e^{2+} / F e}^{0}=-0.44 V$

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3. Calculate the potential of a $Z n-A n^{2+}$ electrode in which the molarity of $Z n^{2+}$ is $0.001 M$. Given that $E_{Z n^{2+} / Z n}^{0}=-0.76 \mathrm{~V}$ $R=0.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}, F=96500 \mathrm{Cmol}^{-1}$.

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4. Determine $\Delta G^{0}$ for the button cell used in the watches. The cell reactions is

$$
\begin{aligned}
& Z n_{(s)}+\mathrm{Ag}_{2} \mathrm{O}_{(s)} \mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow Z n_{(a q)}^{2+}+2 \mathrm{Ag}_{(s)}+2 \mathrm{OH}_{(a q)}^{-} \\
& E_{A g+/ A g}^{0}=+0.80 \mathrm{~V}, E_{Z n^{2+} / Z n}^{0}=-0.76 \mathrm{~V} .
\end{aligned}
$$

5. Calculate the emf of the cell consisting the following half cells
$A l / A l^{3+}(0.001 M), N i / N i^{2}(0.50 M)$. Given that $E_{N i^{2+} / N i}^{0}=-0.25 V$ $E_{A l l^{++} / A l}=-1.66 V\left(\log 8 \times 10^{-6}=-5.0969\right)$.

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6. Determine the values of $K_{c}$ for the following reacton
$N i_{(s)}+2 A g_{(a q)}^{+} \rightarrow N i_{(a q)}^{2+}+2 A g_{(s)}$
$\mathrm{E}^{\wedge}(0)=1.05 \mathrm{~V}$.

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7. Calculate the potential of the half-cell containing 0.1 M
$\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7(a q)}, 0.2 \mathrm{MCr}_{(a q)}^{3+}$ and $1.0 \times 10^{-4} \mathrm{MH}_{(a q)}^{+}$. The half-reaction
$\mathrm{Cr}_{2} \mathrm{O}_{7(a q)}^{2-}+14 \mathrm{H}_{(a q)}^{+}+6 e^{-} \rightarrow 2 \mathrm{Cr}_{(a q)}^{3+}+7 \mathrm{H}_{2} \mathrm{O}_{(l)}$
$\left(E^{0} o f \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathrm{Cr}^{3+}=1.33 \mathrm{~V}\right)$
8. Calculate $K_{c}$ for the reaction at 298 K
$Z n_{(s)}+C u_{(a q)}^{+2} \Leftrightarrow Z n_{(a q)}^{2+}+C u_{(s)}$
$E_{Z n^{2+} / Z n}^{0}=-0.76 V, E_{C u^{2+} / C u}^{0}=+0.34 V$.

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9. Calculate the emf of the cell at 298 K
$S n_{(s)}\left|S n^{2+}(0.05 M)\right|\left|H_{(a q)}^{+}(0.02 M)\right| H_{2} 1$ atm. Pt
Given that $E_{s n^{2+} / S n}^{0}=-0.144 V$

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10. Calculate the concentration of silver ions in the cell constructed by using 0.1 M concentration of $\mathrm{Cu}^{2+}$ and $\mathrm{Ag}^{+}$ions. Cu and Ag metals are used as electrodes. The cell potential is 0.422 V .

$$
\left[E_{A g^{2+} / A g}=0.80 \mathrm{~V}, E_{C u^{2+} / \mathrm{Cu}}=+0.34 \mathrm{~V}\right]
$$

11. Calculate the emf of the cell with the cell reaction

$$
\begin{aligned}
& N i_{(s)}+2 A g^{+}(0.002 M) \rightarrow N i^{2+}(0.160 M)+2 A g_{(s)} \\
& E_{\text {cell }}^{0}=1.05 \mathrm{~V} .
\end{aligned}
$$

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12. $C u^{2+}+2 e^{-} \Leftrightarrow C u, E^{0}=+0.34 V$
$A g^{+}+e^{-} \Leftrightarrow A g, E^{0}=+0.80 \mathrm{~V}$
For what concentration of $\mathrm{Ag}^{+}$ions will the emf of the cell be zero at $25^{\circ} \mathrm{C}$. The concentration of $\mathrm{Cu}^{2+}$ is 0.1 M . $(\log 3.919=0.539)$.

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13. The conductivity of 0.20 M solution of KCl at 298 K is $0.0248 \mathrm{Scm}^{-1}$.

Calculate molar conductance.

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14. Calculate the degree of dissociation $(\alpha) o f \mathrm{CH}_{3} \mathrm{COOHat} 298 \mathrm{~K}$. Itbr Given that $\wedge_{C H_{3} \mathrm{COOH}}^{\infty}=11.75 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\wedge_{C M_{3} \mathrm{COO}^{-}}^{\infty}=40.65 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\wedge_{H^{+}}^{0}=349.15 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$

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15. A reaction is $50 \%$ completed in 2 hours and $75 \%$ conmpleted in 4 hours. What is the order of the reaction.

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16. A reaction has a half-life of 10 minutes. Calculate the rate constant for the first order reaction.

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17. In a first order ractin, the concentration of the reaction is reduced from $0.6 \mathrm{~mol} / \mathrm{L}$ to $0.2 \mathrm{~mol} / \mathrm{L}$ in 5 min . Calculate the rate fconstnat (k).

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18. The rate constant for a zero order reaction in A is $0.0030 \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$. How long it will take for the initial concentration of A to fall from 0.10 M to $0.075 M$.

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19. A first order decomposition reaction takes 40min. For $30 \%$ decomposition. Calculate it's $t_{1 / 2}$ value.

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20. Calculate the half-life of first order reaction whose rate constant is $200 s^{-1}$.

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21. The thermal decomposition of HCOOH is a first order reaction. The rate constant is $2.4 \times 10^{-3} s^{-1}$ at a certain temperature. Calculate how long will it take for $3 / 4$ of initial quantity of HCOOH to decompose

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22. The decomposition of a compound is found to follow first order rate law. If it takes 15 minutes for $20 \%$ of original meterial to react, calculate the rate constant.

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23. In a pesudo first order hydrolysis of ester in water, the following results are obtained

| t (sec) | 0 | 30 | 60 | 90 |
| :--- | :---: | :---: | :---: | :---: |
| [ester] M | 0.55 | 0.31 | 0.17 | 0.085 |

Calculate the averagte rate of reaction between the time inverval 30 to 60
S.

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24. The half-life for a first order reaction is $5 \times 10^{6} \mathrm{~s}$. What percentage of the initial reactant will react in 2 hours ?

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25. $\mathrm{H}_{2} \mathrm{O}_{2(a q)}$ decomposes to $\mathrm{H}_{2} \mathrm{O}_{(l)}$ and $\mathrm{O}_{2(g)}$ in a first reaction w.r.t.
$\mathrm{H}_{2} \mathrm{O}_{2}$. The rate constant is $k=1.06 \times 10^{-3} \mathrm{~min}^{-1}$. How long it will take $15 \%$ of the sample of defcompose?
26. Show that in the case of first order reaction, the time required for $99.9 \%$ completion of the reaction is 10 times that required for $50 \%$ completion $(\log 2=0.3010)$

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27. The rate constant of a reaction is doubled when the temperature is raised from 298 K to 308 K . Calculate the activation energy.

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28. The first order rate constant for the decomposition of ethyl iodide by the reaction.
$\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{I}(\mathrm{g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{HI}(\mathrm{g})$ at 600 Kis $1.60 \times 10^{-5} \mathrm{~s}^{-1}$. It's energy of activation is $209 \mathrm{~kJ} / \mathrm{mol}$. Calculate the rate constant of the reaction at 700 K.
29. The activation energy for the reactio $2 H I_{(g)} \rightarrow H_{2(g)}+I_{2(g)}$ at581 K is $209.5 \mathrm{~kJ} / \mathrm{mol}$. Calculte the fraction of molecules having energy equal to or grater than activation energy. $\left[R=8.31 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}\right]$

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30. For a reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of the reaction using the units of seconds.

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31. In a reaction $2 A \rightarrow$ Products, the concentration of A decreases from $0.5 \mathrm{molI}^{-1}$ to $0.4 \mathrm{molL}^{-1}$ in 10 minutes. Calculate the rate during this interval.
32. For a reaction, $A+B \rightarrow$ Product : the rate law is given by $r=k[A]^{1 / 2}[B]^{2}$ What is the order of the reaction ?
A. 3
B. 2
C. 5/2
D. 5/4

## Answer: C

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33. The convertion of molecules $X$ to $Y$ follows second order kinetics. If concentration of $X$ is increased by three times, how will it affect the rate of formation of Y .
34. A first order reaction has a rate constatn $1.15 \times 10^{-3} s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g ?

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35. Time required to decompose $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

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36. From the rate expression for the following reactions, determine their order of reaction and the admensions of the rate constants.
i) $3 \mathrm{NO}(\mathrm{g}) \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{g}) \quad$ Rate $=k[N O]^{2}$
ii)
$\mathrm{H}_{2} \mathrm{O}_{2}(a q)+3 \mathrm{I}^{-}(a q)+2 \mathrm{H}^{+} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)+I_{3} \quad$ Rate $=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right][I$
iii) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}(\mathrm{g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{CO}(\mathrm{g}) \quad$ Rate $=k\left[\mathrm{CH}_{3} \mathrm{CHO}\right]^{3 / 2}$

$$
\left.\mathrm{C}_{2} \mathrm{H} 5\right) \mathrm{Cl}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{2} \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g}) \quad \text { Rate }=k\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}\right]
$$

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37. For the reaction $2 A+B \rightarrow A, B$, the rate $=K[A][B]^{2}$ with $k=2.0 x 10^{-6} \mathrm{vmol}^{-2} L^{2} s^{-1}$. Calculate the initial rate of the reaction when $[A]=0.1 \mathrm{molL}^{-1},[B]=0.2 \mathrm{molL}^{-1}$, Calculate the rate of reaction after [A] is reduced to $0.06 \mathrm{molL}^{-1}$.

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38. The decomposition of $\mathrm{NH}_{3}$ on platjinum surface is zero order reaction. Want are the rates of production of $N_{2}$ and $H_{2}$ if $k=2.5 \times 10^{-4} \mathrm{~mol}^{-1} \mathrm{Ls}^{-1}$.
39. The rate expression for the decomposition of dimethyl ether in terms of partial pressures is given as Rate $=k\left(p \mathrm{CH}_{3} \mathrm{OCH}_{3}\right)^{3 / 2}$. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant ?

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40. A reaction is second order with respect to a reactant. How is the rate of reaction is affected if the concentration of the reactant is i) doubled ii) reduced to half

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41. $A$ reaction is first order in $A$ and second order in $B$.
i) Write the differential rate equation
ii) How is the rate affected on increasing the concentrations of $B$ there times ?
iii) How is the rate effected when the concentrations of both $A$ and $B$ are doubled ?

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42. In a reactio between A and B , the initial rate of reaction $\left(r_{0}\right)$ was measured for different initial concentrations of $A$ and $B$ as given below :

| $A / \mathrm{mol} \mathrm{L}^{-1}$ | 0.20 | 0.20 | 0.40 |
| :--- | :--- | :--- | :--- |
| $\mathbf{B} / \mathrm{mol} \mathrm{L}^{-1}$ | 0.30 | 0.10 | 0.05 |
| $\mathrm{r}_{\boldsymbol{0}} / \mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}$ | $5.07 \times 10^{-5}$ | $5.07 \times 10^{-5}$ | $1.43 \times 10^{-5}$ |

What is the order of the reaction with respect to A and B ?

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43. The following results have been obtained during the kinetic studies of the reaction :
$2 A+B \rightarrow C+D$

| Experiment | $[\mathrm{A}] \mathrm{mol} \mathrm{L}^{-1}$ | $[\mathrm{~B}] \mathrm{mol} \mathrm{L}^{-1}$ | Initial rate of formation <br> of $\mathrm{D} / \mathrm{mol} \mathrm{L}^{-1} \mathrm{~min}^{-1}$ |
| :---: | :---: | :---: | :---: |
| 1. | 0.1 | 0.1 | $6.0 \times 10^{-3}$ |
| 2. | 0.3 | 0.2 | $7.2 \times 10^{-2}$ |
| 3. | 0.3 | 0.4 | $2.88 \times 10^{-1}$ |
| 4. | 0.4 | 0.1 | $2.40 \times 10^{-2}$ |

Determine the rate law and rate constant for the reaction.

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44. The rate constant for a first order reaction is $60 s^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its $1 / 6^{\text {th }}$ value?

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45. For a first order reaction,k show that the time required for $99 \%$ completion is twice the time required for completion of $99 \%$ reaction.
46. For the decomposition of azosiopropane to hexane and nitrogen at 543 k , the following data obtained.

| $\mathbf{t}(\mathrm{sec})$ | $\mathbf{P}(\mathrm{mm}$ of $\mathbf{H g})$ |
| :--- | :--- |
| 0 | 35.0 |
| 360 | 54.0 |
| 720 | 63.0 |

Calculate the rate constant.

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47. The following data were obtained during the first order thermal decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ at a constant volume.
$\mathrm{SO}_{2} \mathrm{Cl}_{2}(g) \rightarrow \mathrm{SO}_{2}(g)+\mathrm{Cl}_{2}(g)$

| Experiment | Time $/ \mathrm{s}^{-1}$ | Total pressure $/ \mathrm{atm}$ |
| :---: | :---: | :---: |
| 1 | 0 | 0.5 |
| 2 | 100 | 0.6 |

Calculate the rate of reaction when total pressure is 0.65 atm .
48. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} \mathrm{~s}^{-1}$ at 546 K . If the energy of activatin is $179.9 \mathrm{~kJ} / \mathrm{mol}$. What will be the value of per-exponential factor ?

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49. Consider a certain reaction $A \rightarrow$ Products with $k=2.0 \times 10^{-2} s^{-1}$.

Calculate the concentration of A remaining after 100 s if the initial concentration of $A$ is $1.0 \mathrm{molL}^{-1}$.

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50. Sucrose decompose in acid solution into glucose and fructose according to the first order rate law, with $t_{\frac{1}{2}}=3.00$ hours. What fraction of sample of sucrose remains after 8 hours ?
51. The decomposition of hydrocarbon follows the equation
$K=\left(4.5 \times 10^{11} s^{-1}\right) e^{-18000 K / T}$. Calculate $E_{a}$.

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52. The rate constant for the first order decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ is given by the following equation : $\log k=14.34-1.25 K / T$. Calculate $E_{a}$ for this reactin and at what temperature will its half-life period be 256 minutes?

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53. The decomposition of $A$ into product has value of $k$ as $4.5 \times 10^{3} \mathrm{~s}^{-1}$ at $10^{\circ} \mathrm{C}$ and energy of activation $60 \mathrm{kJmol}^{-1}$. At what temperature would k be $1.5 \times 10^{4} \mathrm{~s}^{-1}$ ?

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54. The time required for $10 \%$ completion of a first order reaction at 298 K is equal to that required for its $25 \%$ completiion at $308 K$. If the value of A is $4 \times 10^{10} s^{-1}$. calculate k at 318 K and $E_{a}$,

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55. The rate of a reaction quadruples when temperature charges from 293 K to 312 K , Calculate the energy of activation of the reaction assuming that it does not charge with temperature.

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## Very Short Answer Questions

1. What is a galvanic cell or a valtaic cell ? Give one example.

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2. Write the chemical reaction used in the construction of the Daniell cll together with the half-cell reactions.

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3. Name the two half-cell reactions that are taking place in the Daniell cell.

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4. Hos is a galvanic cell rpresented on paper as per IUPAC convention ? Give one example.

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5. Write the cell reaction taking plce in the cell
$C U_{(s)}\left|C u_{(a q)}^{+2}\right|\left|A g_{(a q)}^{+}\right| A g_{(s)}$
6. What is standard hydrogen electrode ?

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7. Give a neat sketch of standard hydrogen electrode.

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8. What is Nernst equation ? Write the equation for an electrode with electrode reaction $M^{n+}(a q)+\not \neq-^{-} \Leftrightarrow M(s)$.

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9. A negative $E^{0}$ indicates that the rodox couple is $\qquad$ reducing couple than $H^{+} / H_{2}$, couple. (powerful or weak)
10. A positive $E^{0}$ indicates that the redox couple is a weaker $\qquad$ couple than $H^{+} / H_{2}$ couple. (oxidising or reducing)

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11. Write the Nernst equation for the EMF of the cell
$N i_{(s)}|N i+\underset{(a q)}{2+}|\left|A g_{(a q)}^{+}\right| A g$

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12. Write the cell reaction for which $E_{\text {cell }}=E_{\text {cell }}^{0}-\frac{R T}{2 F} \ln \frac{\left[\mathrm{Mg}^{2+}\right]}{\left[\mathrm{Ag}^{+}\right]^{2}}$

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13. How is $E^{0}$ cell related mathematically to the equilibrium constant $K_{c}$ of the cell reaction?
14. How is Gibbs energy ( G ) related to the cell emf (E) mathematically ?

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15. Diffine conductivity of a material. Give its SI units.

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16. What is cell constant of a conductivity cell ?

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17. Define molar conducticity $\wedge_{m}$ and how is it related to conductivity (K)
18. Give the mathematical equation which gives the variation of molar conductivity with $\wedge_{m}$ the molarity (c) of the solution ?

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19. State Kohlrausch's law of independent magration of ions.

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20. State Faraday's first law of electrolysis.

## - Watch Video Solution

21. State Faraday's seconed law of electroystis.

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22. What are the products obtainded at the platinum anode and the platinum cathode respectively in the electrolystis of fused or molten NaCl

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23. Give the products obtained at the platinum electrodes (cathode and anode) when aqueous solution of $\mathrm{K}_{2} \mathrm{SO}_{4}$ is electrolysed.

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24. Give the chemical equation that represents the reduction of liquid water $\mathrm{H}_{2} \mathrm{O}_{(l)}$ at the platinum cathode.

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25. Give the chemical equation that represents the reduction of liquid water $\mathrm{H}_{2} \mathrm{O}_{(l)}$ at the platinum cathode.
26. What is a primary battery ? Give one example.

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27. Give one example for a secondary battery. Give the cell reaction.

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28. Give the cell reaction of nickel-cadimuim secondary battery.

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29. What are the fuel cells ? How are they different from galvanic cells ?

Give the construction of $\mathrm{H}_{2}, \mathrm{O}_{2}$ fuel cell ?
30. Give the electrode reactions occuring at the anode and at the cathode in $H_{2}, O_{2}$, fuel cell.

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31. What is metallie corrosion ? Give one example.

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32. Give the electro-chemical reaction that represents the corrosion or rusting of iron.

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33. Define the speed or rate of a raction.
34. Assuming that the volume of the system is constant, derive the average rate of the system $R \rightarrow p$ in terms of R and P . [time $=\mathrm{t} \mathrm{t}$ 'sec] [ R $=$ reactant, $\mathrm{P}=$ product $]$.

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35. What are the units of rate of reaction ?

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36. Drawn the graphs that relate the concentrations (C ) of the reactants and the reaction times $(\mathrm{t})$ and the concentrations of the products $(\mathrm{C})$ and the reaction times ( t ) in chemical reactions.

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37. Write the equation for rthe rate of the reaction
$5 \mathrm{Br}_{(a q)}^{-}+\mathrm{BrO}_{3(a q)}^{-}+6 H_{(a q)}^{+} \rightarrow 3 \mathrm{Br}_{(a q)}+3 \mathrm{H}_{2} \mathrm{O}_{(l)}$

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38. What is rate law ? Illustrate with an example.

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39. Mention a reaction for which the exponnts of concentration terms are not the same as their stoichiometric coefficients in the rate equation.

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40. Define order of a reaction. Illustrate your answer with an example.

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41. What are elementary reactions ?

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42. What are compelex reactions? Name one complex reaction.

## - Watch Video Solution

43. Give the units of rate constants for Zero, first order and second order reactions.

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44. Define molecularity of a reaction, Illustrate with an example.
45. What is rate determining step in a complex reaction ?

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46. Give the mechanism for the decomposition reacton of $\mathrm{H}_{2} \mathrm{O}_{2}$ in alkaline medium catalysed by $I^{-}$ions.

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47. Write the equation relating $[R],[R]_{0}$ and reaction time ' t ' for a zero order reaction. $[R]=$ concentration of reactant at time 't' and $[R]_{0}=$ initial concentration of reactiant.

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48. Drawn the graph that the concentration ' R ', of the reactant and ' t ' the reaction time for a zero Order reaction.
49. Give two examples for zero order reaction.

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50. Write the intergrated equation for a fiest order reaction in terms of $[R],[R]_{0}$ and 't'.

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51. Give two examples for gaseous first order reactions.

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52. For the reaction $A(g) \rightarrow B(g)+C(g)$, write the intergrated rate equation in terms of total pressure ' P ' and the partial pressures

## $P_{A} P_{B} P_{C}$.

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53. What is half-life of a reaction? Illustrate your answer with an example.

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54. Write the equation relating the half-life $\left(t_{1 / 2}\right)$ of a reaction and the rate constant ' k ' for first order reaction.

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55. Write the equation useful to calculate half-life $\left(t_{1 / 2}\right)$ values for zero and first order reactions.

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56. What are pseudo first order reactions ? Give one example.

## - Watch Video Solution

57. Write the Arrhenius equation for the rate constant (k) of a reaction.

## - Watch Video Solution

58. By how many times the rate constant inhcreases for a rise of reaction temperature by $10^{\circ} \mathrm{C}$ ?

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59. Explain the term 'activation energy' of a reaction with a suitable diagram.

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60. Write the equation which ralates th rate constants $k_{1}$ and $k_{2}$ at temperatures $T_{1}$ and $T_{2}$ of a reaction.

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61. What is collision frequency $(Z)$ of a reaction ? How is rate related to it for the reaction $A+B \rightarrow$ Products.

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62. Draw the graphs between potential energy - reaction coordinates for catalysed and uncatalysed reactions.

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63. What is the effect of temperature on the rate constant ?

## Short Answer Questions

1. What are galvanic cells ? Explain the woriking of a galvanic cell with a neat sketch taking Denicell cell as example.

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2. Give the construction and working of a standard hydrogen electode with a neat diagram.

## - Watch Video Solution

3. State and explain Nernst equation with the help of a metallic electrode and a non-metallic electrode.

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4. Explain with a suitable example the relation between the gibbs energy of chemical reaction $(\mathrm{G})$ and the functioning of the electrochemical cell.

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5. On what factors the electrical conductance of an aqueous solution of electrolyte depends?

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6. How is molar conductivity of an aqueous electrolyte solution measured experimentally

## - Watch Video Solution

7. Explain the varition of molar conductivity with the charge in the concentration of the electrolyte. Give resons.
8. State and explain Kohlrausch's law of indendent migration of ions.

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9. What is electrolysis ? Give Faraday's first law of electrolysis.

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10. What are the products obtained at the cathode and anode during the electrolysis of the following when platinum electrodes are used in the electrolysis
a) Molten b) Aq . $\mathrm{CuSO} \mathrm{O}_{4}$ solution c) $\mathrm{Aq} . \mathrm{K}_{2} \mathrm{SO}_{4}$ solution

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11. What are primary and secondary batteries? Give one example for each.
12. What are the fuel cells ? How are they different from galvanic cells ? Give the construction of $\mathrm{H}_{2}, \mathrm{O}_{2}$ fuel cell ?

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13. What is metallic corrosion ? Explain it with respect to iron corrosion.

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14. Define average rate of a reaction. How is the rate of reaction expressed in term of charge in the concentration of reactansts and products for the following reactions.
1) $2 \mathrm{HI}_{(g)} \rightarrow \mathrm{H}_{2(g)}+I_{2(g)}$
2) $\mathrm{Hg}_{(l)}+\mathrm{CL}_{2(g)} \rightarrow \mathrm{HgCl}_{2(g)}$
3) $5 \mathrm{Br}_{(a q)}+\mathrm{BrO}_{(a q)}^{-}+6 \mathrm{H}_{(a q)}^{+} \rightarrow 3 \mathrm{Br}_{2(a q)}+3 \mathrm{H}_{2} \mathrm{O}_{(l)}$
15. What is rate equation ? How is it obtained ? Write the rate equations for
1) $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$
2) $\mathrm{CHCl}_{3}+\mathrm{Cl}_{2} \rightarrow \mathrm{CCl}_{4}+\mathrm{HCl}$
3) $\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(l)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{CH}_{3} \mathrm{H}_{5} \mathrm{OH}(a q)$

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16. Define and explain the order of a reaction. How is it obtained exprimentally?

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17. What is "molecularity" of a reaction ? How is it different from the 'order' of a reaction? Name one bimolecular and one trimolecular gaseous reactions.
18. Derive the intergrate rate equation for a zero order rection.

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19. Derive an integrated rate equatin for a first order reaction.

## - Watch Video Solution

20. Derive an integrated rate equation in terms of total pressure $(P)$ and the partial pressures $P_{A}, P_{B}, P_{C}$ for the gaseous reaction $A(g) \rightarrow B(g)+C(g)$.

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21. What is half-life $\left(t_{1 / 2}\right)$ of a reaction ? Derive the equations for the 'half-life' value of zero and first order reactions.
22. What is Arrhenius equation ? Derive an equation which describes the effect of rise of temperature ( T ) on the rate constant $(k)$ of a reaction.

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23. Discuss the effect of catalyst on the kinetics of a chemical reaction with a suitable diagram.

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24. Give a detailed account of the Collision theory of reaction rates of biomolecular reaction.

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25. Explain the terms
a) Activation energy $\left(E_{a}\right)$
b) Collision frequency ( $Z$ )
c) Probability factor ( $P$ ) with respect to Arrhenius equation.

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## Long Answer Questions

1. What are electro chemical cells ? How are they constructed ? Explain the working of the different types of galvanic cells?

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2. What is electrical conductance of a solution ? How is it measured experimentally?
3. Give the applications of Kohlracsch's law of independent migration of ions.

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4. Given the different types of batteries and explain the construction and working of each type of battery.

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5. Explain the terms with suitable exapmples.

Average rate of a reaction

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6. Explain the terms with suitable exapmples.

Slow and fast reactions
7. Explain the terms with suitable exapmples.

Order of a reaction

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8. Explain the terms with suitable exapmples.

Molecularity of a reaction

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9. Explain the terms with suitable exapmples.

Activation energy of reaction.
10. Give two examples for each of zero order and first order reactions.

Write the equations for the rate of reaction in terms of concentration changes of reactants and products for the following ractions.

1) $A(g)+B(g) \rightarrow C(g)+D(g)$
2) $A(g) \rightarrow B(g)+C(g)$
3) $A(g)+B(g) \rightarrow C(g)$

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11. Discuss the effect of temperature on the rate of a reaction. Derive necessary equations in this contaxt.

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12. Give a detailed account of the collision theory of reaction rates of biomolecular geseous reactions.
13. How would you determine the standard electrode potential of the system $M g^{2+} / M g$ ?

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2. Can you store copper sulphate soolutions in a zinc pot ?

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3. Consult the table on standard electrode potentials and suggest three substance that can oxidise ferrous ions under suitable conditions.

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4. Calculate the potential of hydrogten electrode placed in a solution of pH 10.

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5. Calculate the emf of the cell with the cell reaction

$$
\begin{aligned}
& N i_{(s)}+2 A g^{+}(0.002 M) \rightarrow N i^{2+}(0.160 M)+2 A g_{(s)} \\
& E_{\text {cell }}^{0}=1.05 V
\end{aligned}
$$

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6. The cell in which the following cell reaction occurs,
$2 \mathrm{Fe}_{(a q)}^{3+}+2 I_{(a q)}^{-} \rightarrow 2 \mathrm{Fe}_{(a q)}^{2+}+I_{2(s)}$
has $E_{\text {cell }}^{0}=0.236 \mathrm{~V}$ at 298 K . Calculate the standard Gibbs energy and the equilibrium costant of the cell reaction.

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7. Why does the conductivity of a solution decrease with dilution ?
8. Suggest a way to determine the $\Lambda_{m}^{0}$ value of water .

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9. The molar conductivity of $0.025 \mathrm{molL}^{-1}$ methanoic acid is $46.1 \mathrm{Sm}^{2} \mathrm{~mol}^{-1}$. Calculate its degree of dissociation and dissociation constant.

Given, $\lambda^{0}\left(H^{+}\right)=349.6 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ and $\lambda^{0}\left(\mathrm{HCOO}^{-}\right)=54.6 \mathrm{Scm}^{2} \mathrm{~mol}^{-1}$

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10. If a current of 0.5 ampere flows through a metallic wire for 2 h , then how many electrons would flow through the wire ?

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11. Suggest a list to metals that are extracted electrolytically.

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12. Consider the reaction,
$\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 e^{-} \rightarrow 2 \mathrm{Ce}^{3+}+7 \mathrm{H}_{2} \mathrm{O}$
What is the quantity of electricity in coulombs needed to reduce 1 mole $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ ?

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13. Write the chemistry of recharging the lead stronge battery, highlighting all the materials that are involved during recharging.

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14. Suggest two materials other than hydrogen that can be used as fuels in fule cells.

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15. Explain how rusting of iron is envisaged as electrochemical cell.

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16. For the reaction, $R \rightarrow P$, the concentration of a reactant changes fro 0.03 M to 0.02 in 25 min . Calculate the average rate of reaction using units of time both in minutes an second.

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17. In a reaction $2 A \rightarrow$ Products, the concentration of A decreases from $0.5 \mathrm{molI}^{-1}$ to $0.4 \mathrm{molL}^{-1}$ in 10 minutes. Calculate the rate during this

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18. For a reaction, $A+B \rightarrow$ Product : the rate law is given by $r=k[A]^{1 / 2}[B]^{2}$ What is the order of the reaction ?

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19. The convertion of molecules $X$ to $Y$ follows second order kinetics. If concentration of $X$ is increased by three times, how will it affect the rate of formation of Y .

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20. A first order reaction has a rate constatn $1.15 \times 10^{-3} s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g ?
21. Time required to decompose $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

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22. What is the effect of temperature on the rate constant ?

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23. The rate constant of the chemical reaction doubled for an increase of

10 K in absolute temperature from 298 K . Calculate $E_{a}$.

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24. The activation energy for the reactio $2 H I_{(g)} \rightarrow H_{2(g)}+I_{2(g)}$ at581 K is $209.5 \mathrm{~kJ} / \mathrm{mol}$. Calculte the fraction of molecules having energy equal to or grater than activation energy. $\left[R=8.31 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}\right]$

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## Dam Sure

1. Diffine conductivity of a material. Give its SI units.

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2. State Faraday's seconed law of electroystis.

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3. State Kohlrausch's law of independent magration of ions.
4. Define electrochemical equivalent (e.c.e).

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5. State and explain Kohlrausch's law of indendent migration of ions.

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6. Define emf. Calculat the emf of the following galvanic cell :

$$
\begin{aligned}
& Z n_{(s)}+C u_{(a q)}^{+2} \rightarrow Z n_{(a q)}^{+2}+C u_{(s)} \\
& E_{z n^{+2 / Z n}}^{0}=0.76 V(\text { anode }), E_{c u+3 / C_{u}}^{0}=+0.34 \text { (Cathode) }
\end{aligned}
$$

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7. Write Nernst equation for a metal and non metal eletrode.
8. What is Rate of a reaction

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9. What is Rate equation (or) Rate expression (or) Rate Law ?

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10. Write the difference between Order and Molecularity of a reaction.

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11. A first order reaction is found to have a rate constant, $k=5.5 \times 10^{-14} s^{-1}$. Find the half- life of the reaction.
12. What is Zero Order reaction ?

## - Watch Video Solution

13. What is First Order reaction ? Give example.

## - Watch Video Solution

14. What are pseudo first order reactions ? Give one example.

## - Watch Video Solution

15. What is Half life of a reaction?

## - Watch Video Solution

16. Give two example for gaseous first order reactions.

## - Watch Video Solution

17. What is a second order reaction ? Give one example.

## - Watch Video Solution

18. Explain the factors influencing rate of reaction.

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