

Electrochemistry + Chemical Kinetics

1. Compound *A* is used as a strong oxidizing agent is amphoteric in nature. It is the part of lead storage batteries. Compound *A* is

- ☒ A. Pb_3O_4
- ☒ B. $PbSO_4$
- ☒ C. $PbSO_4$
- ☒ D. PbO_2

PbO_2 is strong oxidizing agent because Pb^{+4} is not stable and can be easily reduced to Pb^{+2} .

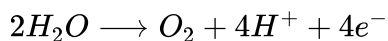
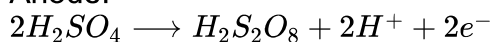
PbO_2 is used in lead storage batteries. It is also amphoteric in nature

So, the answer is (d)

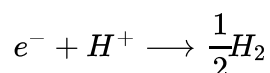
2. The product obtained from the electrolytic oxidation of acidified sulphate solution , is

- ☒ A. HO_3SOOSO_3H
- ☒ B. HO_2SOSO_2H
- ☒ C. HSO_4^-
- ☒ D. HO_3SOSO_3H

Anode:



Cathode :



Main product of electrolysis of conc. H_2SO_4 is HO_3SOOSO_3H or $(H_2S_2O_8)$

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3. Given below are two statements :

Statements I : The limiting molar conductivity of KCl (strong electrolyte) is higher compared to that of CH_3COOH (weak electrolyte) .

Statements II : Molar conductivity decreases with decrease in concentration of electrolyte

In the light of the above statements, choose the most appropriate answer from the options given below :

- ☒ A. Statement I is true but Statement II is false
- ☒ B. Both Statements I and II are false
- ☐ C. Both Statements I and II are true
- ☐ D. Statement I is false but Statement II is true

In aqueous solution, H^+ exist as H_3O^+ which is smaller in size than the hydrate ions of K^+ and Cl^- .

Thus, limiting molar conductivity of H^+ is very large compare to K^+ and Cl^- . Hence, limiting molar conductivity of CH_3COOH is higher than KCl .

Molar conductivity is the conductance property of a solution containing one mole of the electrolyte.

On dilution, the molar conductivity increases.

For strong electrolyte it increases due to decreased ion- ion force of attraction.

For weak electrolyte it increase due to the increase in the degree of dissociation of the electrolyte.

Hence, option (b) is correct.

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4. Match List-I with List - II

List-I (Parameter)	List-II (Unit)
(a) Cell constant	(i) $S\ cm^2\ mol^{-1}$
(b) Molar conductivity	(ii) Dimensionless
(c) Conductivity	(iii) m^{-1}
(d) Degree of dissociation of electrolyte	(iv) $\Omega^{-1}m^{-1}$

Choose the most appropriate answer from the options given below

- ☒ **A.** (a)-(iii) , b-(i) , (c)-(ii), (d)-(iv)
- ☒ **B.** (a)-(i) , b-(iv) , (c)-(iii), (d)-(ii)
- ☒ **C.** (a)-(ii) , b-(i) , (c)-(iii), (d)-(iv)
- ☒ **D.** (a)-(iii) , b-(i) , (c)-(iv), (d)-(ii)

For an electrolytic conductor, cell constant depends on the distance between the electrodes (l) and their area of cross-section (A).

$$\text{Cell constant, } G^* = \frac{l}{A} = m^{-1}$$

$$\text{Conductivity, } \kappa = \frac{1}{R(\text{ohm})} \times G^*(m^{-1}) = \Omega^{-1} m^{-1}$$

$$\text{Molar conductance, } \Lambda_m = \frac{k(S\ cm^{-1}) \times 1000(cm^3\ L^{-1})}{c\ (mol\ L^{-1})} = S\ cm^2\ mol^{-1}$$

Degree of dissociation is dimensionless.

Parameter	Unit
Cell constant	m^{-1}
Molar conductivity	$S\ cm^2\ mol^{-1}$
Conductivity	$\Omega^{-1}m^{-1}$
Degree of dissociation of electrolyte	Dimensionless

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5. The equation that is incorrect is :

- ☒ **A.** $(\Lambda_m^0)_{NaBr} - (\Lambda_m^0)_{NaCl} = (\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{KCl}$
☒ **B.** $(\Lambda_m^0)_{H_2O} = (\Lambda_m^0)_{HCl} + (\Lambda_m^0)_{NaOH} - (\Lambda_m^0)_{NaCl}$
☒ **C.** $(\Lambda_m^0)_{NaBr} - (\Lambda_m^0)_{NaI} = (\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{NaBr}$
☒ **D.** $(\Lambda_m^0)_{KCl} - (\Lambda_m^0)_{NaCl} = (\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{NaBr}$

Kohlrausch law of independent migration of ions:

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

$\lambda_+^0 \rightarrow$ Limiting molar conductivities of cation

$\lambda_-^0 \rightarrow$ Limiting molar conductivities of anion

In general,

$$\Lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

v_+ and v_- are the number of cations and anions after dissociation of an electrolyte.

In option (3),

$$(\Lambda_m^0)_{NaBr} - (\Lambda_m^0)_{NaI} = (\Lambda_m^0)_{Br^-} - (\Lambda_m^0)_{I^-}$$

$$(\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{NaBr} = (\Lambda_m^0)_{K^+} - (\Lambda_m^0)_{Na^+}$$

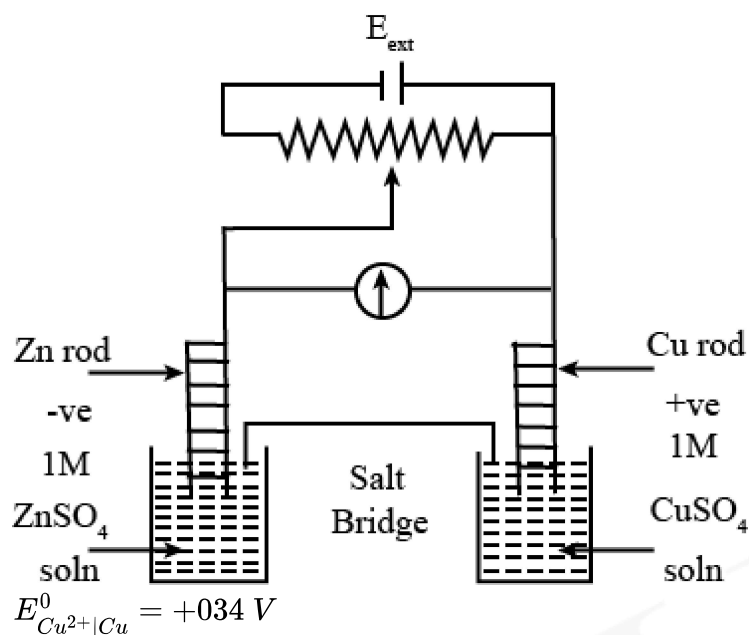
Thus,

$$(\Lambda_m^0)_{NaBr} - (\Lambda_m^0)_{NaI} \neq (\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{NaBr}$$

Hence, option (c) is correct.

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6.



$$E^0_{Zn^{2+}|Zn} = -0.76 V$$

Identify the incorrect statement from the below for the above cell :

- ☒ A. If $E_{ext} = 1.1 V$, no flow of e^- or current occurs
- ☒ B. If $E_{ext} < 1.1 V$, Zn dissolves at anode and Cu deposits at cathode
- ☒ C. If $E_{ext} > 1.1 V$, e^- flow from Cu to Zn
- ☒ D. If $E_{ext} > 1.1 V$, Zn dissolves at Zn electrode and Cu deposits at Cu electrode

$$E^0_{cell} = E^0_{Cu^{2+}|Cu} - E^0_{Zn^{2+}|Zn} = 1.1 V$$

so If $E_{ext} = 1.1 V$, no electron will flow

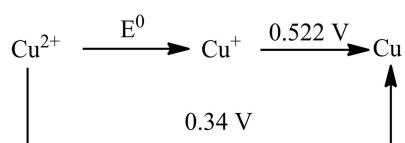
At $E_{ext} > 1.1 V$, cell act as electrolytic cell and electron will flow from Cu to Zn .

At $E_{ext} < 1.1 V$, cell act as electrochemical cell so Zn dissolve and Cu deposit .

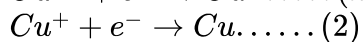
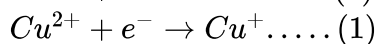
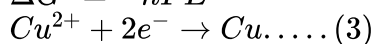
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7. Given that the standard potentials (E^0) of Cu^{2+}/Cu and Cu^+/Cu are 0.34 V and 0.522 V respectively, the E^0 of Cu^{2+}/Cu^+ is-

- ☒ A. $+0.158\text{ V}$
☐ B. 0.182 V
☐ C. -0.158 V
☐ D. -0.182 V



$$\Delta G^0 = -nFE^0$$



Adding equation (1) and (2), we get (3)

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$2 \times 0.34 = E_1^0 + 1 \times 0.522$$

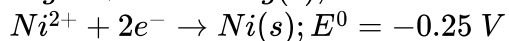
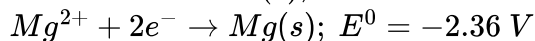
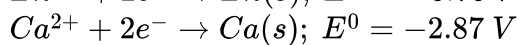
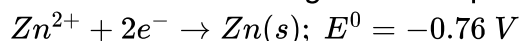
$$E_1^0 = 0.68 - 0.522$$

$$E_1^0 = 0.158\text{ V}$$

Hence, option (a) is correct.

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8. Consider the following reduction processes :



The reducing power of the metals increases in the order :



A. $\text{Ca} < \text{Zn} < \text{Mg} < \text{Ni}$



B. $\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}$



C. $\text{Zn} < \text{Mg} < \text{Ni} < \text{Ca}$



D. $\text{Ca} < \text{Mg} < \text{Zn} < \text{Ni}$

More the value of reduction potential higher will be the oxidising power of metal and lower will be the reducing power of metal.

Here, Ca^{2+}/Ca couple has the least value of reduction potential so it readily go oxidation and its reducing power is high.

Thus, order of reducing power of metal is



Electrochemistry + Chemical Kinetics

9. For a reaction of order (n), the unit of the rate constant is :

- ☒ A. $\text{mol}^{1-n} \text{L}^{2n} \text{s}^{-1}$
- ☒ B. $\text{mol}^{1-n} \text{L}^{1-n} \text{s}^{-1}$
- ☒ C. $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$
- ☒ D. $\text{mol}^{1-n} \text{L}^{1-n} \text{s}$

Generalized formula for the unit of rate constant (k) for a n^{th} order reaction.

Let ,

$A \rightarrow \text{Products}$

is a n^{th} order reaction.

Rate (R) = $k[A]^n$

$$\text{Units of } k = \frac{\text{Units of rate}}{\text{Units of } [A]^n}$$

Since, rate is change of concentration w.r.t time

So, units of rate are $\frac{\text{mol}}{\text{L} \cdot \text{s}}$

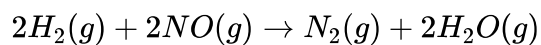
$$\text{Units of } k = \frac{\frac{\text{mol}}{\text{L} \cdot \text{s}}}{\left(\frac{\text{mol}}{\text{L}}\right)^n}$$

$$\text{Units of } k = \left(\frac{\text{mol}}{\text{L}}\right)^{(1-n)} \times \text{s}^{-1} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$

Option (c) is correct

Electrochemistry + Chemical Kinetics

10. For the reaction



the observed rate expression is,

rate = $k_f[NO]^2[H_2]$. The rate expression for the reverse reaction is :

☐ A. $k_b \frac{[N_2][H_2O]^2}{[NO]^2}$

☐ B. $k_b[N_2][H_2O]$

☐ C. $k_b[N_2][H_2O]^2$

☒ D. $k_b \frac{[N_2][H_2O]^2}{[H_2]}$

$$k_{eq} = \frac{k_f}{k_b} = \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2}$$

Rearranging

$$k_f[NO]^2[H_2] = \frac{k_b[N_2][H_2O]^2}{[H_2]}$$

on comparing R_f and R_b at equilibrium,

$$R_b = k_b \frac{[N_2][H_2O]^2}{[H_2]}$$

Electrochemistry + Chemical Kinetics

11. The rate of a certain biochemical reaction at physiological temperature (T) occurs 10^6 times faster with enzyme than without. The change in the activation energy upon adding enzyme is

- ☒ A. $-6RT$
☐ B. $+6RT$
☐ C. $+6(2.303)RT$
☒ D. $-6(2.303)RT$

The rate constant of a reaction is given by

$$k = Ae^{-\frac{E_a}{RT}}$$

where,

k : Rate constant

E_a : Activation energy (in J/mol)

R : Gas constant

T : Temperature of reaction (in Kelvin(K))

A : Arrhenius factor or frequency factor or pre-exponential factor. It is constant, specific to a particular reaction

The rate constant in presence of catalyst is given by

$$k' = Ae^{-E'_a/RT}$$

$$\frac{k'}{k} = e^{-(E'_a/RT)}$$

$$10^6 = e^{-(E'_a - E_a)/RT}$$

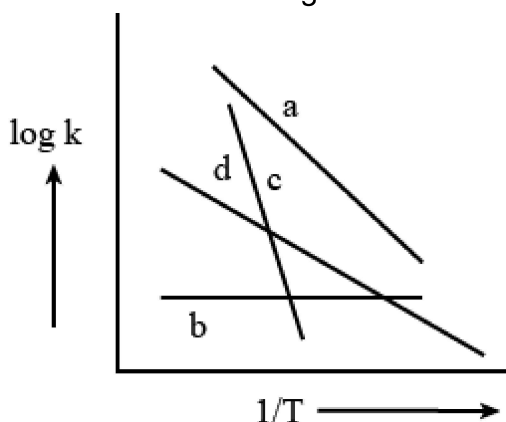
$$\ln 10^6 = -\frac{(E'_a - E_a)}{RT}$$

$$E'_a - E_a = -6(2.303)RT$$

Option (d) is correct

Electrochemistry + Chemical Kinetics

12. Consider the following plots of rate constant versus $\frac{1}{T}$ for four different reactions. Which of the following orders is correct for the activation energies of these reactions?



- ☒ A. $E_b > E_a > E_d > E_c$
- ☒ B. $E_c > E_a > E_d > E_b$
- ☒ C. $E_a > E_c > E_d > E_b$
- ☒ D. $E_b > E_d > E_c > E_a$

Denoting activation energy by E_x

$$K = Ae^{\frac{-E_x}{RT}}$$

$$\log K = \log A - \frac{E_x}{2.303RT} \quad \dots (1)$$

Here, the graph given in the question is of a straight line and we know that the equation of straight line is

$$y = mx + c \quad \dots (2)$$

Comparing equation 1 with 2 we get,

$$\text{Slope} = \frac{-E_x}{2.303R}$$

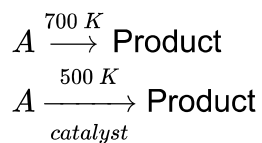
So, from the graph we can conclude that the line with the most negative slope will have the maximum activation energy value.

The correct order will be

$$E_c > E_a > E_d > E_b$$

Electrochemistry + Chemical Kinetics

13. For following reactions



it was found that the E_a is decreased by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same)

- ☒ A. 75 kJ/mol
- ☐ B. 198 kJ/mol
- ☐ C. 105 kJ/mol
- ☐ D. 135 kJ/mol

Rate of reaction at 700 K in the absence of catalyst is equal to rate of reaction at 500 K in the presence of catalyst

$$(E_a) - (E_a)_c = 30\text{ kJ/mol}$$

\therefore Rate is same

\therefore Rate constant will also be same

(Assuming same value of pre exponential factor)

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow \frac{-E_a}{R \times 700} = \frac{-(E_a)_c}{R \times 500}$$

$$\Rightarrow -5E_a = -7(E_a)_c$$

$$-5E_a = -7(E_a - 30)$$

$$2E_a = 210 \Rightarrow E_a = 105\text{ kJ/mol}$$

$$\therefore \text{Activation energy in the presence of catalyst} = 105 - 30 = 75\text{ kJ/mol}$$

Electrochemistry + Chemical Kinetics

14. It is true that

- ☐ A. A zero order reaction is a single step reaction
- ☒ B. A zero order reaction is a multistep reaction
- ☐ C. A first order reaction is always a single step reaction
- ☐ D. A second order reaction is always a multistep reaction

Zero order reaction has complex mechanism. Zero order reaction is a multistep reaction

For elementary or single step reactions the order and molecularity of the reaction are same.

Now assume that zero order reactions are elementary or single step reaction, then its molecularity=0.

But since zero order reactions exist therefore its molecularity can never be zero. A zero molecularity implies that no effective collisions between reactant molecules take place i.e. reaction does not occur at all. This implies that molecularity for the overall zero order reaction is not defined or doesn't exist. Thus a zero order reaction must be a multi step/complex reaction such that the individual steps have their own molecularity but molecularity for the overall reaction is not defined as seen in multi step/complex reaction..

Electrochemistry + Chemical Kinetics

15. If a reaction follows the Arrhenius equation, the plot $\ln k$ vs $\frac{1}{(RT)}$ gives straight line with a gradient $(-y)$ unit. The energy required to activate the reactant is :

☐ A. yR unit

☐ B. $\frac{1}{R}$ unit

☐ C. $-y$ unit

☒ D. y unit

Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

Taking ln on both side,

$$\ln k = \ln A - \frac{E_a}{RT}$$

It is a form of $y = mx + c$, straight line equation.

For $\ln k$ vs $\frac{1}{RT}$,

Slope $= -y$

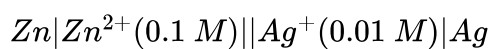
$$\therefore -y = -E_a$$

$$\Rightarrow E_a = y$$

Hence, option (d) is correct.

Electrochemistry + Chemical Kinetics

16. Emf of the following cell at 298 K in V in $x \times 10^{-2}$.



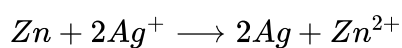
The value of x is _____. (Rounded off to the nearest integer)

$$[(\text{Given}) : E_{\text{Zn}^{2+}/\text{Zn}}^{\theta} = -0.76\text{V}; E_{\text{Ag}^+/\text{Ag}}^{\theta} = +0.80\text{V}; \frac{2.303RT}{F} = 0.059]$$

Accepted Answers

147 147.0 147.00

Solution:



$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{(0.1)}{(10^{-2})^2} = 10^3$$

$$\text{emf} = 0.80 + 0.76 - \frac{0.059}{2} \log 10^3$$

$$\text{emf} = 1.47\text{ V}$$

$$\text{emf} = 147 \times 10^{-2} \text{ volt}$$

$$x = 147$$

Electrochemistry + Chemical Kinetics

17. A 5.0 mol dm^{-3} aqueous solution of KCl has a conductance of 0.55 mS when measured in a cell of cell constant 1.3 cm^{-1} . The molar conductivity of this solution in $\text{mS m}^2 \text{ mol}^{-1}$ is

(Round off to the Nearest Integer)

Accepted Answers

14 14.0 14.00

Solution:

$$\text{Conductance} = \frac{\text{Conductivity}}{\text{Cell Constant}}$$

$$\therefore \text{Conductivity} = 0.55 \times 10^{-3} \times 1.3 \text{ S cm}^{-1}$$

$$\text{Molar conductivity} = \frac{\text{Conductivity}(\text{S cm}^{-1}) \times 1000}{\text{Molarity}(\text{mol/L})}$$

$$\text{Molar conductivity} = \frac{0.55 \times 10^{-3} \times 1.3 \times 100}{5 \times 10^{-3}}$$

$$\text{Molar conductivity} = 143 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Molar conductivity} = 14.3 \text{ mS m}^2 \text{ mol}^{-1}$$

$$\text{Molar conductivity} \approx 14 \text{ mS m}^2 \text{ mol}^{-1}$$

Electrochemistry + Chemical Kinetics

18. A KCl solution of conductivity 0.14 Sm^{-1} shows a resistance of 4.19Ω in a conductivity cell. If the same cell is filled with an HCl solution, the resistance drops of 1.03Ω . The conductivity of the HCl solution is $\text{_____} \times 10^{-2} \text{ Sm}^{-1}$. (Round off to the Nearest Integer).

Accepted Answers

57 57.0 57.00

Solution:

For KCl

$$k_1 = 0.14 \text{ Sm}^{-1}$$

$$R_1 = 4.19 \Omega$$

For HCl

$$k_2 = x \text{ Sm}^{-1} \text{ (Let)}$$

$$R_2 = 1.03 \Omega$$

$$R = \rho \left(\frac{l}{a} \right) \Rightarrow kR = \underbrace{\left(\frac{l}{a} \right)}_{\text{Cell constant}}$$

$$k_1 R_1 = k_2 R_2$$

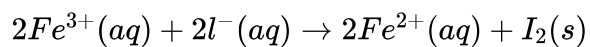
$$0.14 \times 4.19 = 1.03 \times k_2$$

$$k_2 = 0.5695 \text{ Sm}^{-1}$$

$$k_2 = 57 \times 10^{-2} \text{ Sm}^{-1}$$

Electrochemistry + Chemical Kinetics

19. For the reaction



The magnitude of the standard molar free energy

Change, $\Delta_r G_m^0 = - \text{ ______ } \text{ kJ}$

(Round off to the Nearest Integer).

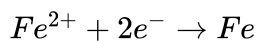
$$\left[\begin{array}{ll} E_{Fe^{2+}/Fe(s)}^0 = 0.440 \text{ V}; E_{Fe^{3+}/Fe(s)}^0 = -0.036 \text{ V} \\ E_{I_2/2I^{-}}^0 = 0.539 \text{ V}; F = 96500 \text{ C} \end{array} \right]$$

Accepted Answers

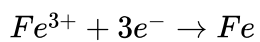
45 45.0 45.00

Solution:

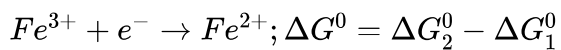
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$$\Delta G_1^0 = -2FE_{Fe^{2+}/Fe}^0$$



$$\Delta G_2^0 = -3FE_{Fe^{3+}/Fe}^0$$

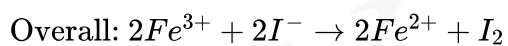
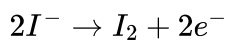
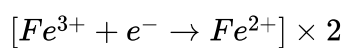


$$\Rightarrow FE_{Fe^{3+}/Fe^{2+}}^0 = -3FE_{Fe^{3+}/Fe}^0 + 2FE_{Fe^{2+}/Fe}^0$$

$$\Rightarrow E_{Fe^{3+}/Fe^{2+}}^0 = 3E_{Fe^{3+}/Fe}^0 - 2E_{Fe^{2+}/Fe}^0$$

$$E_{Fe^{3+}/Fe^{2+}}^0 = -3 \times 0.036 + 2 \times 0.440$$

$$E_{Fe^{3+}/Fe^{2+}}^0 = 0.772 \text{ V}$$



$$\Delta_r G_m^0 = -2F \times 0.772 - 2F(-0.539)$$

$$\Delta_r G_m^0 = -2F(0.772 - 0.539)$$

$$\Delta_r G_m^0 = 44969 \text{ J}$$

$$\Delta_r G_m^0 = 44.969 \text{ kJ}$$

$$\Delta_r G_m^0 \approx 45 \text{ kJ}$$

Electrochemistry + Chemical Kinetics

20. The molar conductivities at infinite dilution of barium chloride, sulphuric acid and hydrochloric acid are 280, 860 and 426 $S\ cm^{(2)}\ mol^{-1}$ respectively. The molar conductivity at infinite dilution of barium sulphate is ____ $S\ cm^2\ mol^{-1}$. (Round off to the Nearest Integer)

Accepted Answers

288 288.0 288.00

Solution:

$$\Lambda^{\infty}(BaCl_2) = 280\ S\ cm^2\ mol^{-1}$$

$$\Lambda^{\infty}(H_2SO_4) = 860\ S\ cm^2\ mol^{-1}$$

$$\Lambda^{\infty}(HCl) = 426\ S\ cm^2\ mol^{-1}$$

$$\Lambda^{\infty}(BaSO_4) = \Lambda^{\infty}(BaCl_2) + \Lambda^{\infty}(H_2SO_4) - 2\Lambda^{\infty}(HCl)$$

$$\Lambda^{\infty}(BaSO_4) = 280 + 860 - 2 \times 426$$

$$\Lambda^{\infty}(BaSO_4) = 288\ S\ cm^2\ mol^{-1}$$

Electrochemistry + Chemical Kinetics

21. For an electrochemical cell $\text{Sn}(s)|\text{Sn}^{2+}(aq, 1M)||\text{Pb}^{2+}(aq, 1M)|\text{Pb}(s)$, the ratio $\frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$ when this cell attains equilibrium is ____.

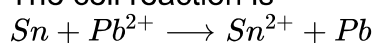
(Given : $E_{\text{Sn}^{2+}|\text{Sn}}^0 = -0.14 \text{ V}$, $E_{\text{Pb}^{2+}|\text{Pb}}^0 = -0.13 \text{ V}$, $\frac{2.303RT}{F} = 0.06$)

Accepted Answers

2.15 2.154

Solution:

The cell reaction is



In the given reaction, Pb^{2+} get reduced and Sn get oxidised.

Hence,

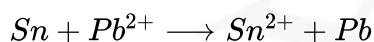
$$E_{\text{cell}}^0 = E_{\text{cathode (red)}}^0 - E_{\text{anode (red)}}^0$$

$$E_{\text{cell}}^0 = -0.13 - (-0.14)$$

$$E_{\text{cell}}^0 = +0.01$$

At equilibrium,

$$E_{\text{cell}} = 0$$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.06}{2} \log Q$$

$$0 = 0.01 - \frac{0.06}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$0.01 = \frac{0.06}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$\frac{1}{3} = \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$\frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 10^{1/3} = 2.154$$

Electrochemistry + Chemical Kinetics

22. 108 g of silver (molar mass 108 g mol^{-1}) is deposited at cathode from $\text{AgNO}_3(\text{aq})$ solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is _____ (up to two decimal)

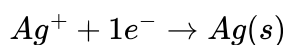
Accepted Answers

5.67 5.670

Solution:

Number of moles of $\text{Ag}(s)$ gets deposited,

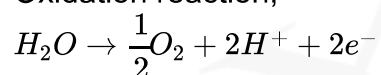
$$n_{\text{Ag}} = \frac{108}{108} = 1 \text{ mol}$$



1 F charge is required for 1 mol of Ag

Electrolysis of water:

Oxidation reaction,



$\frac{1}{2}$ mole of O_2 liberated from 2 F charge.

Thus,

$\frac{1}{4}$ mole of O_2 liberated from 1 F charge.

By gas law,

$$PV = n R T$$

$$V = \frac{1}{4} \times \frac{0.083 \times 273}{1}$$

$$V = 5.675 \text{ L}$$

Electrochemistry + Chemical Kinetics

23. An exothermic reaction $X \rightarrow Y$ has an activation energy 30 kJ mol^{-1} . If energy change ΔE during the reaction is -20 kJ , then the activation energy for the reverse reaction in kJ is _____. (Integer answer)

Accepted Answers

50 50.0 50.00

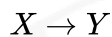
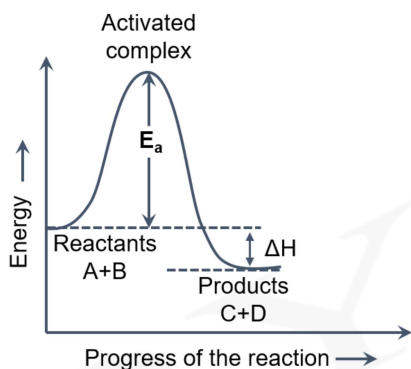
Solution:

For exothermic reaction, the enthalpy change is negative.

$$\Delta H = -ve$$

Thus, for exothermic reaction, the energy of products will be lesser than reactants.

For exothermic reaction, $\Delta H = -ve$



$$(E_a)_f = 30 \text{ kJ mol}^{-1}$$

$$\Delta E = (E_a)_f - (E_a)_b$$

$$-20 = 30 = -(E_a)_b$$

$$\Rightarrow (E_a)_b = 50 \text{ kJ}$$

Electrochemistry + Chemical Kinetics

24. If the activation energy of a reaction is 80.9 kJ mol^{-1} , the fraction of molecules at 700 K , having enough energy to react to form products is e^{-x} . The value of x is _____ (Rounded off to the nearest integer)

[Use $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$]

Accepted Answers

14 14.0 14.00

Solution:

Energy of activation, $E_a = 80.9 \text{ kJ mol}^{-1}$

Temperature of reaction, $T = 700 \text{ K}$

Fraction of molecules having enough energy to react $= e^{-E_a/RT} = e^{-x}$

$$\therefore x = \frac{E_a}{RT} = \frac{80900}{8.31 \times 700} = 13.9 \approx 14$$

25. The decomposition of formic acid on gold surface follows first order kinetics. If the rate constant at 300 K is $1.0 \times 10^{-3} \text{ s}^{-1}$ and the activation energy $E_a = 11.488 \text{ kJ mol}^{-1}$, the rate constant at 200 K is _____ $\times 10^{-5} \text{ s}^{-1}$ (Round off to the Nearest Integer)

Accepted Answers

10 10.0 10.00

Solution:

Expression for rate constant at two different temperature is given by

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

k_1 (at 200 K) = ?

k_2 (at 300 K) $= 1 \times 10^{-3} \text{ s}^{-1}$

$$\log \frac{1 \times 10^{-3}}{k_1} = \frac{11.488 \times 10^3}{2.303 \times 8.314} \left[\frac{1}{600} - \frac{1}{200} \right] = 1$$

$$\frac{1 \times 10^{-3}}{k_1} = 10$$

$$k_1 = 10 \times 10^{-5} \text{ s}^{-1}$$

Electrochemistry + Chemical Kinetics

26. *A and B* decompose via first order kinetics with half-lives 54.0 min and 18.0 min respectively. Starting from an equimolar non reactive mixture of *A and B*, the time taken for the concentration of *A* to become 16 times that of *B* is _____ min. (Round off to the Nearest Integer) Take $\ln 2 = 0.693$.

Accepted Answers

108 108.0 108.00

Solution:

Initially : $[A_o] = [B_o] = a$

After time 't' min, $[A] = 16 [B]$

$$[A] = [A_o] e^{-k_A t}$$

$$[B] = [B_o] e^{-k_B t}$$

$$\Rightarrow a \cdot e^{-k_A t} = 16 a e^{-k_B t}$$

$$\Rightarrow e^{-(k_A - k_B)t} = 16$$

$$\Rightarrow (k_B - k_A)t = \ln 16$$

$$\Rightarrow (k_B - k_A)t = \ln 2^4$$

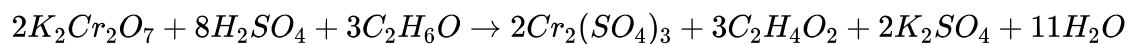
$$\Rightarrow \ln 2 \left(\frac{1}{18} - \frac{1}{54} \right) t = 4 \ln 2 \quad (\ln 2 = 0.693)$$

$$\Rightarrow \left(\frac{1}{18} - \frac{1}{54} \right) t = 4$$

$$\Rightarrow t = \frac{54 \times 18 \times 4}{36} = 108 \text{ min}$$

Electrochemistry + Chemical Kinetics

27. The reaction that occurs in a breath analyser, a device used to determine the alcohol level in a person's blood stream is



If the rate of appearance of $Cr_2(SO_4)_3$ is $2.67 \text{ mol min}^{-1}$ at a particular time, the rate of disappearance of C_2H_6O at the same time is in mol min^{-1} .

(Nearest integer)

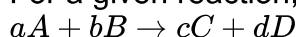
Accepted Answers

4 4.0 4.00

Solution:

Electrochemistry + Chemical Kinetics

For a given reaction, if:



Overall rate r can be expressed as:

$$r = \frac{-1}{a} \times \frac{d[A]}{dt} = \frac{-1}{b} \times \frac{d[B]}{dt} = \frac{+1}{c} \times \frac{d[C]}{dt} = \frac{+1}{d} \times \frac{d[D]}{dt}$$

where:

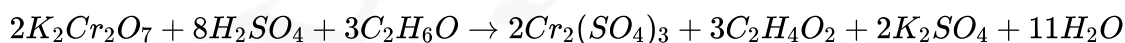
$$-\frac{d[A]}{dt} = \text{Rate of disappearance of A}$$

$$-\frac{d[B]}{dt} = \text{Rate of disappearance of B}$$

$$+\frac{d[C]}{dt} = \text{Rate of formation of C}$$

$$+\frac{d[D]}{dt} = \text{Rate of formation of D}$$

Given:



$$\text{Rate} = -\frac{1}{3} \frac{d[C_2H_6O]}{dt} = \frac{1}{2} \frac{d[Cr_2(SO_4)_3]}{dt}$$

$$\frac{d[Cr_2(SO_4)_3]}{dt} = 2.67 \text{ mol min}^{-1}$$

$$-\frac{d[C_2H_6O]}{dt} = \frac{3}{2} \times \frac{d[Cr_2(SO_4)_3]}{dt}$$

$$-\frac{d[C_2H_6O]}{dt} = 1.5 \times 2.67 \approx 4 \text{ mol min}^{-1}$$

Electrochemistry + Chemical Kinetics

28. The first order rate constant for the decomposition of $CaCO_3$ at 700 K is $6.36 \times 10^{-3}\text{ s}^{-1}$ and activation energy is 209 kJ mol^{-1} . Its rate constant (in s^{-1}) at 600 K is $x \times 10^{-6}$. The value of x is (Nearest integer)

[Given $R = 8.31\text{ J K}^{-1}\text{ mol}^{-1}$; $\log 6.36 \times 10^{-3} = -2.19$, $10^{-4.79} = 1.62 \times 10^{-5}$]

Accepted Answers

16 16.0 16.00

Solution:

$$k_1 = 6.36 \times 10^{-3}\text{ s}^{-1}$$

$$T_1 = 700\text{ K}$$

$$E_a = 209\text{ kJ mol}^{-1}$$

$$k_2 = x \times 10^{-6}\text{ s}^{-1}$$

$$T_2 = 600\text{ K}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \left(\frac{x \times 10^{-6}}{6.36 \times 10^{-3}} \right) = \frac{209 \times 10^3}{8.31 \times 2.303} \left(\frac{1}{700} - \frac{1}{600} \right)$$

$$\log (x \times 10^{-6}) = -4.79$$

$$x \times 10^{-6} = 10^{-4.79}$$

$$x \times 10^{-6} = 1.62 \times 10^{-5}$$

$$x = 16.2 = 16 \text{ (Nearest integer)}$$

Electrochemistry + Chemical Kinetics

29. For the reaction $A \rightarrow B$, the rate constant $k(\text{s}^{-1})$ is given by

$$\log_{10} k = 20.35 - \frac{(2.47 \times 10^3)}{T}$$

The energy of activation in kJ mol^{-1} is
 (Nearest integer)

[Given : $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$]

Accepted Answers

47 47.0 47.00

Solution:

$$\log_{10} k = 20.35 - \frac{(2.47 \times 10^3)}{T} \dots (1)$$

$$\log k = \log A - \frac{E_a}{2.303 RT} \dots (ii)$$

Comparing (i) and (ii),

$$\frac{E_a}{2.303 RT} = \frac{2.47 \times 10^3}{T}$$

$$E_a = 2.47 \times 10^3 \times 2.303 \times 8.314$$

$$E_a = 47293.44 \text{ J mol}^{-1}$$

$$E_a = 47.2934 \text{ kJ mol}^{-1}$$

Nearest integer is 47

Electrochemistry + Chemical Kinetics

30. During the nuclear explosion, one of the products is ^{90}Sr with half life of 6.93 years. If $1\ \mu\text{g}$ of ^{90}Sr was absorbed in the bones of a newly born baby in place of Ca, how much time, in years (nearest integer), is required to reduced it by 90% if it is not lost metabolically

Accepted Answers

23 23.00 23.0

Solution:

Since half life is in the unit of time, so it is a first order reaction.

Decay constant or rate constant is denoted by λ

For a first order reaction:

$$\text{Decay constant}(\lambda) = \frac{\ln 2}{(t_{1/2})} = \frac{0.693}{6.93}$$

$$\lambda = 0.1\ \text{yr}^{-1}$$

$$\lambda t = \ln\left(\frac{C_0}{C}\right)$$

C_0 and C being the initial concentration and final concentration at time t respectively

$$\text{Now } \lambda (t_{90\%}) = \ln\left(\frac{100}{10}\right)$$

$$t_{90\%} = 10 \ln 10$$

$$t_{90\%} = 10 \times 2.303$$

$$t_{90\%} = 23.03\ \text{yr} \approx 23 (\text{Nearest integer})$$