I.8 Electrochemistry

Civil Services 2016–2026: **35** parts, **365** marks · IFoS 2016–2025: **27** parts, **271** marks

Syllabus. Debye-Huckel theory of strong electrolytes and Debye-Huckel limiting law for various equilibrium and transport properties. Galvanic cells, concentration cells; electrochemical series, measurement of e.m.f. of cells and its applications; fuel cells and batteries. Processes at electrodes; double layer at the interface; rate of charge transfer, current density; overpotential; electroanalytical techniques: amperometry, ion selective electrodes and their uses.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	20	40	25	50	40	40	30	25	25	40	30
IFoS	25	35	15	28	18	38	23	28	28	33	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q1(f) Concentration cell of two silver electrodes [5 marks]

One silver rod is immersed in a silver nitrate solution of the concentration $C_1(AgNO_3) = 5 \times 10^{-4}$ kmol m^{-3} and a second silver rod in the concentration $C_2(AgNO_3) = 1 \times 10^{-2}$ kmol m^{-3}. The electrolyte solutions are connected by salt bridge. Calculate the difference ΔE of the redox potential for the electrochemical cell at 25 °C (under equilibrium conditions).

CSE 2026 · Q1(g) Why the cell potential is measured at zero current [5 marks]

Why is it necessary to measure the cell potential using potentiometer under zero-current conditions?

CSE 2026 · Q3(b) Stokes radius and diffusion coefficient of Zn^{2+} [10 marks]

In a homogeneous electric field E = 5 V cm^{-1}, the speed v of Zn^{2+} ions in aqueous solution at 25 °C is 2.74×10^{-5} m s^{-1}.

(i) Estimate the radius r of the hydrated Zn^{2+} ion. The coefficient of viscosity η of water at the given temperature is 0.890 mPa s.

(ii) Calculate the diffusion coefficient D of the ion.

CSE 2026 · Q4(a) The polarographic wave at a dropping mercury electrode [10 marks]

Draw and discuss the polarographic wave obtained in the case of a dropping mercury electrode in polarography.

2025

CSE 2025 · Q1(i) Time to plate a gold layer [5 marks]

The surface area of an object to be gold plated is 49.8 cm^2, and the density of gold is 19.3 g/cm^3. A current of 3.25 A is applied to a solution that contains gold in the +3 oxidation state. Calculate the time required to deposit an even layer of gold, 1×10^{-3} cm thick, on the object.

(Given: Molecular mass of gold = 196.97 g/mol)

CSE 2025 · Q2(b) Standard potential of O_2 reduction in base [15 marks]

The standard reduction potential of oxygen under acidic conditions at 298 K is +1.23 V. What is the standard reduction potential for the four-electron reduction of O_2(g) under basic conditions?

CSE 2025 · Q4(b) Diffusion-limited current at an electrode [10 marks]

Calculate the diffusion limiting current for the oxidation of an organic compound at an electrode in a quiescent solution.
Assume six electrons are involved in the reaction and the thickness of diffusion layer is taken as 0.05 cm in an unstirred solution.
Given:
(i) Concentration of organic compound, $C_{organic} = 10^{-2}$ mole litre^{-1}
(ii) Diffusion coefficient of organic compound, $D_{organic} = 2 \times 10^{-5}$ cm^2 sec^{-1}

CSE 2025 · Q4(c) Molar conductivity and transport numbers of $Ca(NO_3)_2$ [10 marks]

The level of conductivity in a decimolar aqueous solution of calcium nitrate, which is a strong electrolyte, is measured as $\sigma = 26.2$ mS cm^{-1} at 25 °C. Calculate the molar conductivity of the electrolyte, that of calcium ions and the transport numbers of the two types of ions present in the solution, with the data given below.
Molar conductivity at infinite dilution in an aqueous solution at 25 °C:

(i)	λ_+° (mS m^2 mol^{-1})
Ca^{2+}	11.9
(ii)	λ_-° (mS m^2 mol^{-1})
NO_3^-	7.14

IFoS 2025 · Q1(e) Fast and slow electrode systems [8 marks]

Draw and explain the shapes of steady-state current potential curves of the following systems with the same open-circuit potential and same diffusion limiting currents:
(i) A fast system
(ii) A slow system

IFoS 2025 · Q4(b)(ii) Testing the stated activity-coefficient result [10 marks]

(ii) An electrochemical cell is represented by

$$\mathrm{Ag\,(s),\ AgBr\,(s)\ |\ KBr\,(aq)\ \|\ Cd(NO_3)_2(aq.,\ 0.01\ \mathit{M})\ |\ Cd\,(s)}$$

The standard potentials on the hydrogen scale of the pairs $Cd^{2+}|Cd$ and $AgBr|Ag$ are −0.40 V and +0.07 V respectively. At 25 °C, the potential of the cell is −0.62 V. Show that

$$\gamma_{C\pm,\,KBr} = \frac{0.035}{C_{KBr}} \qquad (\gamma_{C\pm} = \text{mean activity coefficient})$$

when the Debye-Hückel ion cloud model holds good. 10

IFoS 2025 · Q4(c) Hydrogen and propane fuel cells; Competition between zinc deposition and hydrogen [15 marks]

(i) Describe the functioning of (1) hydrogen-oxygen and (2) propane-oxygen fuel cells. What type of fuel cells is used in manned space flights? 10
(ii) The standard potential of $Zn^{2+}|Zn$ electrode is −0.76 V at 25 °C. The exchange current density for H^+ discharge at platinum is 0.79 mA cm^{-2}. Can Zn be plated on platinum at that temperature? [Take unit activities and assume transfer coefficient, $\alpha = 0.50$] 5

2024

CSE 2024 · Q1(d)(ii) Overvoltage and its applications [5 marks]

(ii) Define overvoltage. Mention the applications of overvoltage. *5*

CSE 2024 · Q4(b) Polarography and concentration polarisation; Concentration cells; fuel cells as energy converters [20 marks]

(i) What is polarography? Explain the concentration polarization at the electrode. Give the labelled diagram of polarographic cell assembly. *15*

(ii) Define concentration cell and mention its types. Justify the statement "Fuel cells are energy conversion devices and not energy storage devices." *5*

IFoS 2024 · Q1(e) Aluminium–magnesium galvanic cell [8 marks]

In a galvanic cell, if $E^\circ_{Al^{3+}/Al}$ and $E^\circ_{Mg^{2+}/Mg}$ are −1.66 and −2.37 V respectively, calculate the standard free energy change for the cell reaction and also calculate the equilibrium constant for the cell reaction.

IFoS 2024 · Q2(d) Ordering metal reduction potentials [5 marks]

A metal M_1 can displace hydrogen but another metal M_2 can not. Metal M_2 can displace another metal M_3 from its salt solution. Arrange the metals M_1, M_2, M_3 in decreasing order of the E° values. Justify.

IFoS 2024 · Q4(b) Mean ionic activity coefficients [15 marks]

Calculate the mean ionic activity coefficient $\gamma_\pm$ of (i) NaCl at a molality of 0.01, and (ii) Na_2SO_4 at a molality of 0.001 in aqueous solution at 25 °C.

2023

CSE 2023 · Q1(e)(i) E° of Cr^{3+}/Cr from two couples [5 marks]

(i) Calculate the E° value for the half-reaction $Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr$

Given that at 25 °C $Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$ $E^\circ = -0.424$ V

$Cr^{2+}(aq) + 2\,e^- \longrightarrow Cr$ $E^\circ = -0.90$ V

CSE 2023 · Q3(c) Thermodynamics of the H_2–O_2 fuel cell [20 marks]

Consider the reaction $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, which occurs in a H_2–O_2 fuel cell.

(i) Identify the elements that undergo oxidation and reduction.

(ii) Calculate the standard reaction Gibbs free energy ($\Delta_r G^\circ$) at 25 °C.

(iii) Write down the two reduction half-reactions for the cell.

(iv) Calculate the E_{cell}.

Given that $\Delta_f H^\circ(H_2O, l) = -285.83$ kJ mol^{-1}; $S^\circ_m(H_2O, l) = 69.91$ J K^{-1} mol^{-1};

$S^\circ_m(H_2, g) = 130.68$ J K^{-1} mol^{-1}; $S^\circ_m(O_2, g) = 205.14$ J K^{-1} mol^{-1}

IFoS 2023 · Q1(e) Ionic atmosphere and electrode currents [8 marks]

(i) What is meant by ionic atmosphere? How can we eliminate it?

(ii) Differentiate between Faraday current and Diffusion current.

IFoS 2023 · Q4(c) Cell voltage under load and electrolysis [10 marks]

(i) The following cell has a resistance of 5.00 Ω. Calculate its potential when it is producing a current of 0.100 A:

$$Cd \,|\, Cd^{2+}\ (0.0100\ M) \,\|\, Cu^{2+}\ (0.0100\ M) \,|\, Cu$$

Given: $E_{Cu} = 0.278$ V, $E_{Cd} = -0.462$ V

(ii) Calculate the potential required to generate a current 0.100 A in the reverse direction of the cell.

Given: $E_{Cd} = -0.462$ V, $E_{Cu} = 0.278$ V, $I = 0.100$ A, $R = 5.00$ Ω

IFoS 2023 · Q4(d) Selective electrodes and ionic activity [10 marks]

(i) Write the working principle of ion-selective electrode with an example.
(ii) Using the Debye-Hückel limiting law, calculate the activity coefficients of sodium and sulfate ions, and the mean ionic activity coefficient of a 0.01 molal solution of sodium sulfate in water at room temperature.

2022

CSE 2022 · Q1(e) ΔG° and K for the zinc–copper cell reaction [10 marks]

For a cell reaction $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$
the standard electrode potential for Zn/Zn^{2+} = 0.339 V and for Cu^{2+}/Cu = 0.762 V at 25 °C. Calculate standard change in free energy ΔG° and equilibrium constant K for the reaction. [R = 8.314 J mol^{-1} k^{-1}]

CSE 2022 · Q3(e) Forces on an ion moving through a strong-electrolyte solution [10 marks]

Provide briefly a qualitative account of different forces which influence the speed of an ion in solution of strong electrolyte moving under an externally applied electric field.

CSE 2022 · Q4(d) Principle of polarography; reading a polarogram [10 marks]

Write down the basic principle of polarography. With the help of a neat typical polarogram discuss the significance of halfwave potential, diffusion current and limiting current.

IFoS 2022 · Q1(e) Activity coefficient of potassium ferricyanide [8 marks]

Calculate the mean ionic activity coefficient of 0.002 M aqueous solution of potassium ferricyanide at 25 °C. (Given A = 0.509)

IFoS 2022 · Q4(c) Ionic atmosphere and mobility; pH from a quinhydrone cell [15 marks]

(i) What is ionic atmosphere? How do relaxation and electrophoretic effects retard the velocity of central ion in the ionic atmosphere? Explain with illustration. 10
(ii) The EMF of a cell set-up by using hydrochloric acid solution, standard calomel electrode and quinhydrone electrode was found to be 0.1595 V at 25 °C. Calculate the pH of hydrochloric acid solution.
(Given the electrode potential of calomel electrode = 0.244 V, and that of quinhydrone electrode = 0.699 V) 5

2021

CSE 2021 · Q1(e) Electrochemical series and its significance [10 marks]

Define electrochemical series. Give its significance.

CSE 2021 · Q3(b) Ion-selective electrodes; pH with the glass electrode [20 marks]

What are ion-selective electrodes? How is glass electrode used in the determination of pH of a given solution?

CSE 2021 · Q4(a) E.m.f. of a hydrogen–copper cell at 25 °C [10 marks]

Calculate the e.m.f. of the following electrochemical cell at 25 °C:

$$Pt/H_{2\,(1\,atm)} \mid H^{+}_{(C=0.01\,M)} \parallel Cu^{2+}_{(C=0.1\,M)} \mid Cu\,(s)$$

IFoS 2021 · Q1(e) Equilibrium constant of a Zn–Ag cell [8 marks]

Calculate the equilibrium constant of the cell reaction $2\,Ag^{+} + Zn \longrightarrow 2\,Ag + Zn^{2+}$ occurring in the zinc-silver cell at 25 °C when $[Zn^{2+}]$ = 0.10 M and $[Ag^{+}]$ = 10 M. The e.m.f. of the cell is found to be 1.62 V.

IFoS 2021 · Q3(c) Ion-selective and glass electrodes [15 marks]

What are ion-selective electrodes? How can glass electrode be used to determine the pH of a given solution?

IFoS 2021 · Q4(a) Conductance and dilution of strong electrolytes [15 marks]

How does Debye-Huckel theory of strong electrolytes explain the increase of molar conductance with dilution?

2020

CSE 2020 · Q1(e) E°(Ag $^{+}$ /Ag) from the equilibrium constant [10 marks]

The equilibrium constant for the reaction :

$Fe^{3+}(aq) + Ag(s) \rightleftharpoons Fe^{2+}(aq) + Ag^{+}(aq)$; is 0.531 at 298 K. Calculate $E^{\circ}_{Ag^{+}(aq)/Ag(s)}$ when $E^{\circ}_{Fe^{3+}(aq)/Fe^{2+}(aq)}$ = 0.770 V at 298 K.

CSE 2020 · Q3(e) Debye–Hückel limiting law for an ion i [10 marks]

Write down Debye-Huckel limiting equation for i^{th} type of ionic species in a salt solution with symbolic significances and units.

CSE 2020 · Q4(c) Does a KCl salt bridge eliminate the liquid junction? [10 marks]

To eliminate liquid-junction potential, KCl-salt bridge is used, generally. Does it eliminate liquid-junction? If not, how salt-bridge eliminates liquid junction potential?

CSE 2020 · Q8(a) Electrode reactions and Nernst equation of a Zn | calomel cell [10 marks]

Write down the respective electrode reactions, cell reaction and Nernst equation for cell EMF of the following galvanic cell :

$Zn(s) \mid ZnCl_2(aq) \mid Hg_2Cl_2(s) \mid Hg(l)(Pt)$

IFoS 2020 · Q1(d) Liquid junction potential and how to minimise it [8 marks]

State the factors contributing to liquid junction potential. Suggest ways to minimize it.

IFoS 2020 · Q4(a) Electrorefining of copper: impurities from mass changes [10 marks]

Assume that impure copper contains only iron, silver and gold as impurities. After passage of 140 A of current for 482·5 seconds, the mass of the anode decreases by 22·260 g and the cathode increased in mass by 22·011 g. Estimate the iron and copper originally present in percentage.

2019

CSE 2019 · Q3(d) Electrolysis of aqueous $CuSO_4$ between Pt electrodes [20 marks]

800 milliampere of current is passed through an aqueous solution of $CuSO_4$ using two Pt electrodes for a period of 20 minutes. Predict the products at anode and cathode. Estimate the quantity of products. (At. weight of Cu is 63.6)

CSE 2019 · Q5(c) Equivalent conductance of NaCl from ionic mobilities [10 marks]

The ionic mobilities of Na^+ and Cl^- are 5.19×10^{-8} and 7.91×10^{-8} $m^2\ v^{-1}\ s^{-1}$ respectively. Calculate the equivalent conductance of 0.1 M NaCl.

CSE 2019 · Q7(d) A cell for AgBr(s) → $Ag^+ + Br^-$ [10 marks]

Devise an electrochemical cell in which the following reaction takes place :

$AgBr(s) \longrightarrow Ag^+ + Br^-$

CSE 2019 · Q8(d) Electrode reactions of the fuel cell and the lead–acid cell [10 marks]

Write electrode reactions for the following :

(i) H_2–O_2 fuel cell under acidic condition.

(ii) Lead acid battery during discharge.

IFoS 2019 · Q1(b) Oxidant and fuel in a fuel cell; the Bacon cell [8 marks]

What oxidant and fuel are generally used in a fuel cell? Explain the working of Bacon fuel cell.

IFoS 2019 · Q2(a) Polarography, cyclic voltammetry and an amperometric EDTA titration of Zn^{2+} [20 marks]

Discuss the principle of the following : 4+4+12=20

(i) Polarography

(ii) Cyclic Voltammetry

(iii) Given a 50·00 mL of an unknown concentration of Zinc solution (taken in a polarographic cell). To this unstirred solution, the following measures of 0·10 M EDTA solution was added. After each increment of EDTA (titrant), the resultant limiting current was measured at −1·20 V versus SCE.

EDTA (mL) (Titrant)	i_L (mA) (Limiting current)
0·00	0·3
2·0	0·231
4·0	0·167
6·0	0·107
8·0	0·052
10·0	0·0
12·0	0·0
14·0	0·0
16·0	0·0

Z, Zn = 30

Atomic weight 65

2018

CSE 2018 · Q1(e) Spontaneity of four redox reactions from E° [10 marks]

Observe the following half cell reactions:
(i) $I_2 + 2\,e^- \longrightarrow 2\,I^-$; $E^\circ = +0.54$ V
(ii) $2\,Br^- \longrightarrow Br_2 + 2\,e^-$; $E^\circ = -1.09$ V
(iii) $Fe \longrightarrow Fe^{2+} + 2\,e^-$; $E^\circ = +0.44$ V
Using the above Standard Electrode Potential Values, explain the spontaneity or non-spontaneity for the following reactions:
(A) $Br_2 + 2\,I^- \longrightarrow 2\,Br^- + I_2$ (B) $Fe + Br_2 \longrightarrow Fe^{2+} + 2\,Br^-$
(C) $Fe + I_2 \longrightarrow Fe^{2+} + 2\,I^-$ (D) $I_2 + 2\,Br^- \longrightarrow 2\,I^- + Br_2$

CSE 2018 · Q3(c)(i) Galvanic cell and concentration cell [5 marks]

Distinguish between Galvanic cells and concentration cells with an example each.

CSE 2018 · Q3(c)(ii) Transport number of Ag^+ by the Hittorf method [10 marks]

A silver nitrate solution containing 0.00739 gm of $AgNO_3$ per gm of water is electrolysed between silver electrodes. During the experiment 0.078 gm of Ag was deposited on the cathode. At the end of the experiment anode solution contained 23.14 gm of H_2O and 0.236 gm of $AgNO_3$. What is the transport number of Ag^+? After electrolysis, the anode solution has (a) 23.14 gm water and (b) 0.236 gm $AgNO_3$.

IFoS 2018 · Q4(c) Hydrogen–silver cell: reactions and equilibrium constant [15 marks]

What are the respective electrode reactions and cell reaction of the following galvanic cell?

$$Pt(s) \mid H_2(g) \mid H^+(aq) \,||\, Ag^+(aq) \mid Ag(s).$$

Calculate the equilibrium constant value of the cell reaction at 25 °C. Given : E°_{cell} = + 0·7996 V at 25 °C.

2017

CSE 2017 · Q1(e) Debye–Hückel limiting law; $\gamma_\pm$ of 0.1 M NaCl [10 marks]

Write down the Debye-Hückel limiting equation with symbolic significances and their units. Calculate mean ionic activity co-efficient of 0.1 M NaCl (aq) solution at 25 °C. The value of Debye-Hückel constant (A) is 0.51 $mol^{-1/2}\,L^{1/2}$.

CSE 2017 · Q2(c) Equilibrium constant for disproportionation of Cu^+ [15 marks]

Calculate the equilibrium constant for the disproportion reaction :
$2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq)$ at 298 *K*. Given : $E^\circ_{Cu^+/Cu}$ = +0.52 V and $E^\circ_{Cu^{2+}/Cu^+}$ = +0.16 V at 298 *K*.

CSE 2017 · Q6(c) Molar conductivity, drift velocity and transport numbers from mobilities [15 marks]

In aqueous solution, at 298 K, the mobility of NH_4^+ ion is 7.62×10^{-8} $m^2\,s^{-1}\,V^{-1}$. Calculate its (i) molar conductivity; (ii) velocity if 15.0 V is applied across the electrodes of 25.0 cm apart. Calculate the transport numbers of the ions in CH_3COONH_4 (aq) solution if the mobility of CH_3COO^- ion is 4.24×10^{-8} $m^2\,s^{-1}\,V^{-1}$ under same condition.

IFoS 2017 · Q3(a) Mean activity coefficients of LiCl and $BaCl_2$ (Debye–Hückel) [10 marks]

Calculate the mean activity coefficient at 25 °C of (i) 0·01 molal solution of LiCl, and (ii) 0·001 molal solution of $BaCl_2$. Given : A = 0·509 for water at 25 °C.

IFoS 2017 · Q4(c) Equilibrium constant of the Daniell cell reaction [10 marks]

Calculate the equilibrium constant for the following reaction at 25 °C :

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Given at 25 °C :
$E^0(Zn^{2+}/Zn)$ = −0·76 V and
$E^0(Cu^{2+}/Cu)$ = 0·34 V

IFoS 2017 · Q7(b) Overpotential in electrodeposition and corrosion [15 marks]

Explain the term 'over potential'. Discuss the application of over potential in (i) electro-deposition of metals from solutions, and (ii) corrosion of metals.

2016

CSE 2016 · Q1(e) Specific conductance of saturated $BaSO_4$ [10 marks]

The solubility product of $BaSO_4$ is 1×10^{-10} md^2 dm^{-6}. If the ionic conductance at infinite dilution at 25 °C of Ba^{+2} = 127.28×10^{-4} m^2 mho mol^{-1} and SO_4^{-2} = 160.0×10^{-4} m^2 mho mol^{-1}, calculate the specific conductance of $BaSO_4$.

CSE 2016 · Q4(a)(ii) Principle of polarography; the half-wave potential [10 marks]

Discuss the principle of polarographic analysis. Explain the meaning and significance of half wave potential.

IFoS 2016 · Q1(b)(ii) Ionic strength of 0.01 m H_2SO_4 + 0.02 m NaCl [5 marks]

Calculate the ionic strength of a solution that contains 0.01 mol kg^{-1} H_2SO_4 and 0.02 mol kg^{-1} sodium chloride.

IFoS 2016 · Q3(a)(i) Polarography: principle, half-wave potential, resolving close waves [10 marks]

Discuss the principle of polarographic analysis. Explain the meaning and significance of half-wave potential ($E_{1/2}$). If $E_{1/2}$ values of two electroactive species are too close, how can these be separated?

IFoS 2016 · Q4(b) Standard and actual potential of the Cu / Fe^{3+}, Fe^{2+} cell [10 marks]

Consider a galvanic cell that uses the reaction

$$Cu\,(s) + 2\,Fe^{3+}(aq) \longrightarrow 2\,Fe^{2+}(aq) + Cu^{2+}(aq)$$

Given, $E^\circ(Fe^{3+}/Fe^{2+})$ = +0.77 V and $E^\circ(Cu^{2+}/Cu)$ = +0.34 V.
(i) Calculate the standard cell potential.
(ii) Obtain the cell potential at 25 °C that has the following concentration values:
$[Fe^{3+}] = 1.0 \times 10^{-4}$ M; $[Cu^{2+}]$ = 0.25 M; $[Fe^{2+}]$ = 0.2 M
(Given, F = 96500 C, R = 8.314 J K^{-1} mol^{-1})