

ELECTROCHEMISTRY

1. The electrode potential of M^{2+} / M of 3d-series elements shows positive value of :

(1) Zn (2) Fe (3) Co (4) Cu

2. The magnitude of the change in oxidising power of the MnO_4^- / Mn^{2+} couple is $x \times 10^{-4}$ V, if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C. (Assume concentration of MnO_4^- and Mn^{2+} to be same on change in H^+ concentration). The value of x is _____.

(Rounded off to the nearest integer)

$$\left[\text{Given: } \frac{2.303 RT}{F} = 0.059 \right]$$

3. Copper reduces NO_3^- into NO and NO_2 depending upon the concentration of HNO_3 in solution. (Assuming fixed $[Cu^{2+}]$ and $P_{NO} = P_{NO_2}$), the HNO_3 concentration at which the thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same is 10^x M. The value of $2x$ is _____.

(Rounded-off to the nearest integer)

[Given, $E_{Cu^{2+}/Cu}^{\circ} = 0.34$ V, $E_{NO_3^-/NO}^{\circ} = 0.96$ V,

$E_{NO_3^-/NO_2}^{\circ} = 0.79$ V and at 298 K,

$$\frac{RT}{F} (2.303) = 0.059]$$

4. Consider the following reaction



The quantity of electricity required in Faraday to reduce five moles of MnO_4^- is _____.

5. Emf of the following cell at 298 K in V is $x \times 10^{-2}$. $Zn|Zn^{2+} (0.1 \text{ M})||Ag^+ (0.01 \text{ M})|Ag$
The value of x is _____. (Rounded off to the nearest integer)

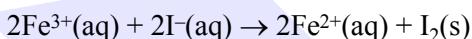
[Given : $E_{Zn^{2+}/Zn}^{\circ} = -0.76$ V; $E_{Ag^+/Ag}^{\circ} = +0.80$ V; $\frac{2.303RT}{F} = 0.059$]

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

(Round off to the Nearest Integer)

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

8. For the reaction



the magnitude of the standard molar free energy change, $\Delta_r G_m^{\circ} = -$ _____ kJ (Round off to the Nearest Integer).

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

9. The molar conductivities at infinite dilution of barium chloride, sulphuric acid and hydrochloric acid are 280, 860 and 426 Scm 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).

10. Potassium chlorate is prepared by electrolysis of KCl in basic solution as shown by following equation.

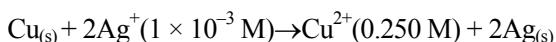


A current of xA has to be passed for 10h to produce 10.0g of potassium chlorate. the value of x is _____. (Nearest integer)

(Molar mass of $KClO_3$ = 122.6 g mol $^{-1}$,

$F = 96500 \text{ C}$)

11. Assume a cell with the following reaction



$$E_{\text{cell}}^{\ominus} = 2.97 \text{ V}$$

E_{cell} for the above reaction is _____ V.

(Nearest integer)

[Given : $\log 2.5 = 0.3979$, $T = 298 \text{ K}$]

12. Consider the cell at 25°C



The fraction of total iron present as Fe^{3+} ion at the cell potential of 1.500 V is $x \times 10^{-2}$. The value of x is _____.

(Nearest integer)

(Given : $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V}$, $E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} = -0.76 \text{ V}$)

13. The conductivity of a weak acid HA of concentration 0.001 mol L^{-1} is $2.0 \times 10^{-5} \text{ S cm}^{-1}$. If $\Lambda_m^{\ominus}(\text{HA}) = 190 \text{ S cm}^2 \text{ mol}^{-1}$, the ionization constant (K_a) of HA is equal to $\text{_____} \times 10^{-6}$.

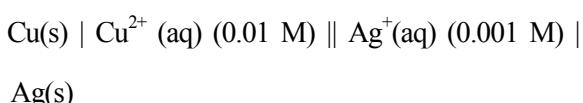
(Round off to the Nearest Integer)

14. For the cell



the cell potential $E_1 = 0.3095 \text{ V}$

For the cell



the cell potential = $\text{_____} \times 10^{-2} \text{ V}$. (Round off the Nearest Integer).

[Use : $\frac{2.303 \text{ RT}}{F} = 0.059$]

15. Given below are two statements :

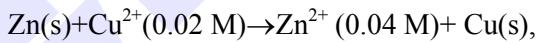
Statement I : The limiting molar conductivity of KCl (strong electrolyte) is higher compared to that of CH_3COOH (weak electrolyte).

Statement 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 :

- (1) **Statement I** is true but **Statement II** is false.
 (2) **Statement I** is false but **Statement II** is true.
 (3) Both **Statement I** and **Statement II** are true.
 (4) Both **Statement I** and **Statement II** are false.

16. For the galvanic cell,

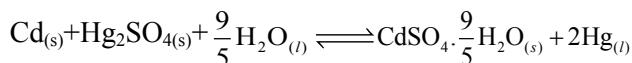


$E_{\text{cell}} = \text{_____} \times 10^{-2} \text{ V}$. (Nearest integer)

[Use : $E_{\text{Cu}/\text{Cu}^{2+}}^{\ominus} = -0.34 \text{ V}$, $E_{\text{Zn}/\text{Zn}^{2+}}^{\ominus} = +0.76 \text{ V}$, $\frac{2.303 \text{ RT}}{F} = 0.059 \text{ V}$]

17. The resistance of a conductivity cell with cell constant 1.14 cm^{-1} , containing 0.001 M KCl at 298 K is 1500Ω . The molar conductivity of 0.001 M KCl solution at 298 K in $\text{S cm}^2 \text{ mol}^{-1}$ is _____ . (Integer answer)

18. Consider the following cell reaction :



The value of $E_{\text{cell}}^{\ominus}$ is 4.315 V at 25°C . If $\Delta H^\circ = -825.2 \text{ kJ mol}^{-1}$, the standard entropy change ΔS° in J K^{-1} is _____ . (Nearest integer)

[Given : Faraday constant = 96487 C mol^{-1}]

19. Match List-I with List-II

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

Choose the **most appropriate** answer from the options given below :

- (1) (a)-(iii), (b)-(i), (c)-(iv), (d)-(ii)
(2) (a)-(iii), (b)-(i), (c)-(ii), (d)-(iv)
(3) (a)-(i), (b)-(iv), (c)-(iii), (d)-(ii)
(4) (a)-(ii), (b)-(i), (c)-(iii), (d)-(iv)

20. If the conductivity of mercury at 0°C is $1.07 \times 10^6 \text{ S m}^{-1}$ and the resistance of a cell containing mercury is 0.243Ω , then the cell constant of the cell is $x \times 10^4 \text{ m}^{-1}$. The value of x is _____.(Nearest integer)

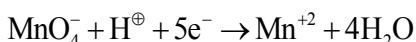
SOLUTION**1. Official Ans. by NTA (4)**

Sol. Only copper shows positive value for electrode potential of M^{2+}/M of 3d-series elements.

$$E^\ominus / V_{(Cu^{2+}/Cu)} : +0.34$$

2. Official Ans. by NTA (3776)

Sol. Eqn is-



Nernst equation:

$$E_{cell} = E_{Cell}^0 - \frac{0.059}{5} \log \left[\frac{[Mn^{+2}]}{[MnO_4^-]} \right] \left[\frac{1}{[H^+]} \right]^8$$

(I) Given $[H^\oplus] = 1M$

$$E_1 = E^0 - \frac{0.059}{5} \log \left[\frac{[Mn^{+2}]}{[MnO_4^-]} \right]$$

(II) Now : $[H^\oplus] = 10^{-4} M$

$$\begin{aligned} E_2 &= E^0 - \frac{0.059}{5} \log \left[\frac{[Mn^{+2}]}{[MnO_4^-]} \right] \times \frac{1}{(10^{-4})^8} \\ &= E^0 - \frac{0.059}{5} \log \left[\frac{Mn^{+2}}{[MnO_4^-]} \right] + \frac{0.059}{5} \log 10^{-32} \end{aligned}$$

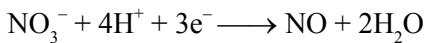
$$\text{therefore : } |E_1 - E_2| = \frac{0.059}{5} \times 32$$

$$= 0.3776 V = 3776 \times 10^{-4}$$

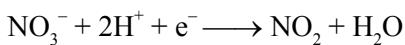
$$x = 3776$$

3. Official Ans. by NTA (4)

Sol. If the partial pressure of NO and NO_2 gas is taken as 1 bar, then Answer is 4, else the question is bonus.



$$E_{NO_3^-/NO}^0 = 0.96V$$



$$E_{NO_3^-/NO_2}^0 = 0.79$$

$$\text{Let } [HNO_3] = y \Rightarrow [H^+] = y \text{ and } [NO_3^-] = y$$

for same thermodynamic tendency

$$E_{NO_3^-/NO} = E_{NO_3^-/NO_2}$$

$$\text{or, } E_{NO_3^-/NO}^0 - \frac{0.059}{3} \log \frac{P_{NO}}{y \times y^4}$$

$$= E_{NO_3^-/NO_2}^0 - \frac{0.059}{1} \log \frac{P_{NO_2}}{y \times y^2}$$

$$\text{or, } 0.96 - \frac{0.059}{3} \log \frac{P_{NO}}{y^5} = 0.79 - \frac{0.059}{1} \log \frac{P_{NO_2}}{y^3}$$

$$\text{or, } 0.17 = -\frac{0.059}{1} \log \frac{P_{NO_2}}{y^3} + \frac{0.059}{3} \log \frac{P_{NO}}{y^5}$$

$$0.17 = -\frac{0.0591}{1} \log \frac{P_{NO_2}}{y^3} + \frac{0.0591}{3} \log \frac{P_{NO}}{y^5}$$

$$\begin{aligned} 0.17 &= \frac{0.0591}{3} \left[\log \frac{P_{NO}}{y^5} - \log \frac{P_{NO_2}}{y^9} \right] \\ 0.17 &= \frac{0.0591}{3} \left[\log \frac{P_{NO}}{y^5} \times \frac{y^9}{P_{NO_2}^3} \right] \end{aligned}$$

Assume $P_{NO} \approx P_{NO_2} = 1 \text{ bar}$

$$\frac{0.17 \times 3}{0.059} = \log y^4 = 8.644$$

$$\log y = \frac{8.644}{4}$$

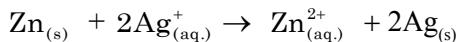
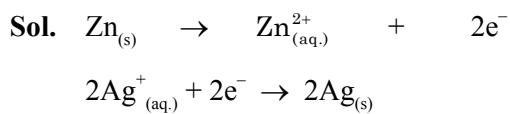
$$\log y = 2.161$$

$$y = 10^{2.161}$$

$$\therefore 2x = 2 \times 2.161 = 4.322$$

Answer (4)

4. Official Ans. by NTA (25)

5 Official Ans by NTA (147)

$$E_{cell}^0 = E_{Ag^+/Ag}^0 - E_{Zn^{2+}/Zn}^0$$

$$= 0.80 - (-0.76)$$

$$= 1.56 \text{ V}$$

$$\begin{aligned} E_{cell} &= 1.56 - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Ag^+]^2} \\ &= 1.56 - \frac{0.059}{2} \log \frac{0.1}{(0.01)^2} \\ &= 1.56 - \frac{0.059}{2} \times 3 \\ &= 1.56 - 0.0885 \\ &= 1.4715 \\ &= 147.15 \times 10^{-2} \end{aligned}$$

6. Official Ans. by NTA (14)

Sol. Given concⁿ of KCl = $\frac{m \cdot mol}{L}$

: Conductance (G) = 0.55 mS

: Cell constant $\left(\frac{\ell}{A}\right) = 1.3 \text{ cm}^{-1}$

To Calculate : Molar conductivity (λ_m) of sol.

$$\rightarrow \text{Since } \lambda_m = \frac{1}{1000} \times \frac{k}{m} \quad \dots \dots (1)$$

$$\rightarrow \text{Molarity} = 5 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$\rightarrow \text{Conductivity} = G \times \left(\frac{\ell}{A}\right) = 0.55 \text{ mS} \times \frac{1.3}{100} \text{ m}^{-1}$$

$$= 55 \times 1.3 \text{ mSm}^{-1}$$

$$\text{eq}^n (1) \lambda_m = \frac{1}{1000} \times \frac{55 \times 1.3}{\left(\frac{5}{1000}\right)} \frac{\text{mSm}^2}{\text{mol}}$$

$$\Rightarrow \lambda_m = 14.3 \frac{\text{mSm}^2}{\text{mol}}$$

7. Official Ans. by NTA (57)

Sol. $\kappa = \frac{1}{R} \cdot G^*$

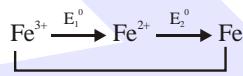
For same conductivity cell, G* is constant and hence $\kappa \cdot R = \text{constant}$.

$$\therefore 0.14 \times 4.19 = \kappa \times 1.03$$

$$\text{or, } \kappa \text{ of HCl solution} = \frac{0.14 \times 4.19}{1.03}$$

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

$$= 56.95 \times 10^{-2} \text{ Sm}^{-1} \approx 57 \times 10^{-2} \text{ Sm}^{-1}$$

8. Official Ans. by NTA (46)**Official Ans. by ALLEN (45)**

Sol.

$$E_1^0 + 2E_2^0 = 3E_3^0$$

$$E_1^0 = 3E_3^0 - 2E_2^0$$

$$= 3(-0.036) - 2(-0.44)$$

$$= + 0.772 \text{ V}$$

$$E_{cell}^0 = E_{Fe^{3+}/Fe^{2+}}^0 + E_{I^-/I_2}^0 = 0.233$$

$$\Delta_r G^0 = -2 \times 96.5 \times 0.233 = -45 \text{ kJ}$$

9. Official Ans. by NTA (288)

Sol. From Kohlrausch's law

$$\Lambda_m^\infty (BaSO_4) = \lambda_m^\infty (Ba^{2+}) + \lambda_m^\infty (SO_4^{2-})$$

$$\Lambda_m^\infty (BaSO_4) = \Lambda_m^\infty (BaCl_2) + \Lambda_m^\infty (H_2SO_4)$$

$$-2 \Lambda_m^\infty (HCl)$$

$$= 280 + 860 - 2(426)$$

$$= 288 \text{ Scm}^2 \text{ mol}^{-1}$$

10. Official Ans. by NTA (1)

Sol. Given balanced equation is



$$\rightarrow 10 \text{ g KClO}_3 \Rightarrow \frac{10}{122.6} \text{ mol KClO}_3 \text{ in obtained}$$

→ from the above reaction, it is concluded that by 6F charge 1 mol KClO₃ is obtained.

→ By the passage of 6F charge = 1 mol KClO₃

$$\therefore \text{By the passage of } \frac{x \times 10 \times 60 \times 60}{96500} \text{ F charge}$$

$$= \frac{1}{6} \times \frac{x \times 10 \times 60 \times 60}{96500}$$

$$\text{Now } \frac{x \times 10 \times 60 \times 60}{6 \times 96500} = \frac{10}{122.6}$$

$$\Rightarrow x = \frac{10 \times 965}{60 \times 122.6} = \frac{965}{735.6} = 1.311 \approx 1$$

OR

$$W = \frac{E}{F} \times I \times t$$

$$10 = \frac{122.6}{96500 \times 6} \times x \times 10 \times 3600$$

$$X = 1.311$$

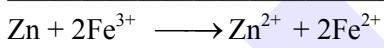
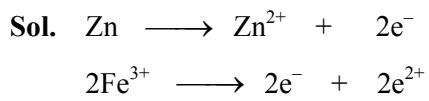
Ans.(1)

11. Official Ans. by NTA (3)

$$\text{Sol. } E = E^\circ - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 2.97 - \frac{0.059}{2} \log \frac{0.25}{(10^{-3})^2} = 2.81 \text{ V}$$

12. Official Ans. by NTA (24)



$$E_{\text{cell}}^0 = 0.77 - (0.76) \\ = 1.53 \text{ V}$$

$$1.50 = 1.53 - \frac{0.06}{2} \log \left(\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right)^2$$

$$\log \left(\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right) = \frac{0.03}{0.06} = \frac{1}{2}$$

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 10^{1/2} = \sqrt{10}$$

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{1}{\sqrt{10}}$$

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}] + [\text{Fe}^{3+}]} = \frac{1}{1 + \sqrt{10}} = \frac{1}{4.16}$$

$$= 0.2402$$

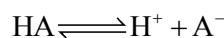
$$= 24 \times 10^{-2}$$

13. Official Ans. by NTA (12)

$$\text{Sol. } \Lambda_m = 1000 \times \frac{\kappa}{M}$$

$$= 1000 \times \frac{2 \times 10^{-5}}{0.001} = 20 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Rightarrow \alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{20}{190} = \left(\frac{2}{19} \right)$$

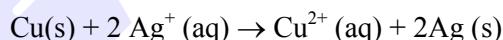


$$0.001 (1 - \alpha) 0.001 \alpha 0.001 \alpha$$

$$\Rightarrow k_a = 0.001 \left(\frac{\alpha^2}{1 - \alpha} \right) = \frac{0.001 \times \left(\frac{2}{19} \right)^2}{1 - \left(\frac{2}{19} \right)} \\ = 12.3 \times 10^{-6}$$

14. Official Ans. by NTA (28)

Sol. Cell reaction is :



$$\text{Now, } E_{\text{cell}} = E_{\text{Cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \dots (1)$$

$$\therefore E_1 = 0.3095 = E_{\text{Cell}}^\circ - \frac{0.059}{2} \cdot \log \frac{0.01}{(0.001)^2} \dots (2)$$

$$\text{From (1) and (2), } E_2 = 0.28 \text{ V} = 28 \times 10^{-2} \text{ V}$$

15. Official Ans. by NTA (4)

Ion	H ⁺	K ⁺	Cl ⁻	CH ₃ COO ⁻
$\Lambda_m^\infty \text{ Scm}^2/\text{mole}$	349.8	73.5	76.3	40.9

$$\text{So } \Lambda_m^\infty \text{ CH}_3\text{COOH} = \Lambda_m^\infty \text{ (H}^+) + \Lambda_m^\infty \text{ CH}_3\text{COO}^-$$

$$= 349.8 + 40.9$$

$$= 390.7 \text{ Scm}^2/\text{mole}$$

$$\Lambda_m^\infty \text{ KCl} = \Lambda_m^\infty \text{ (K}^+) + \Lambda_m^\infty \text{ (Cl}^-)$$

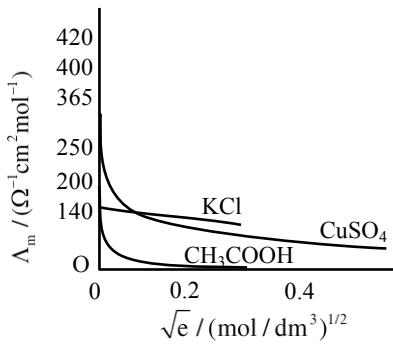
$$= 73.5 + 76.3$$

$$= 149.3 \text{ Scm}^2/\text{mole}$$

So statement-I is wrong or False.

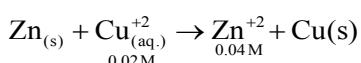
As the concentration decreases, the dilution increases which increases the degree of dissociation, thus increasing the no. of ions, which increases the molar conductance.

So statement-II is false.



16. Official Ans. by NTA (109)

Sol. Galvanic cell:



$$\begin{aligned} \text{Nernst equation} &= F_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[2\text{n}^{+2}]}{[\text{Cu}^{+2}]} \\ &\Rightarrow E_{\text{cell}} \left[E_{\text{cell}}^{\circ} - E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} \right] - \frac{0.059}{2} \log \frac{0.04}{0.02} \\ &\Rightarrow E_{\text{cell}} [0.34 - (-0.76)] - \frac{0.059}{2} \log^2 \\ &\Rightarrow E_{\text{cell}} [1 - 1 - \frac{0.059}{2} \times 0.3010] \\ &= 1.0911 = 109.11 \times 10^{-2} \\ &= 109 \end{aligned}$$

17. Official Ans. by NTA (760)

$$\begin{aligned} \text{Sol. } K &= \frac{1}{R} \times \frac{1}{A} = \left(\left(\frac{1}{1500} \right) \times 1.14 \right) \text{S cm}^{-1} \\ &\Rightarrow \Lambda_m = 1000 \times \frac{\left(\frac{1.14}{1500} \right)}{0.001} \text{ S cm}^2 \text{ mol}^{-1} \\ &= 760 \text{ S cm}^2 \text{ mol}^{-1} \\ &\Rightarrow 760 \end{aligned}$$

18. Official Ans. by NTA (25)

$$\begin{aligned} \text{Sol. } \Delta G^{\circ} &= -nFE^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \\ &= \frac{\Delta H^{\circ} + nFE^{\circ}}{T} \\ &= \frac{(-825.2 \times 10^3) + (2 \times 96487 \times 4.315)}{298} \\ &= \frac{-825.2 \times 10^3 + 832.682 \times 10^3}{298} \\ &= \frac{7.483 \times 10^3}{298} = 25.11 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

∴ Nearest integer answer is 25

19. Official Ans. by NTA (1)

$$\text{Sol. Cell constant} = \left(\frac{\ell}{A} \right) \Rightarrow \text{Units} = \text{m}^{-1}$$

Molar conductivity (Λ_m) \Rightarrow Units = $\text{Sm}^2 \text{ mole}^{-1}$

Conductivity (K) \Rightarrow Units = S m^{-1}

Degree of dissociation (α) \rightarrow Dimensionless

∴ (a) – (iii)

(b) – (i)

(c) – (iv)

(d) – (ii)

20. Official Ans. by NTA (26)

$$\text{Sol. } k = 1.07 \times 10^6 \text{ Sm}^{-1}, \quad R = 0.243 \Omega$$

$$G = \frac{1}{R} = \frac{1}{0.243} \Omega^{-1}$$

$$k = G \times G^*$$

$$G^* = \frac{k}{G} = \frac{1.07 \times 10^6}{\frac{1}{0.243}} \simeq 26 \times 10^4 \text{ m}^{-1}$$