

Nernst Equation:

13-14

~~What~~. What is the difference between E and E° for a redox reaction? Which one runs down to 0 when the complete cell comes to equilibrium?

E° is the potential measured when all activities of reactants and products are unity.

E is the potential measured for arbitrary activities that happen to exist when E is measured.

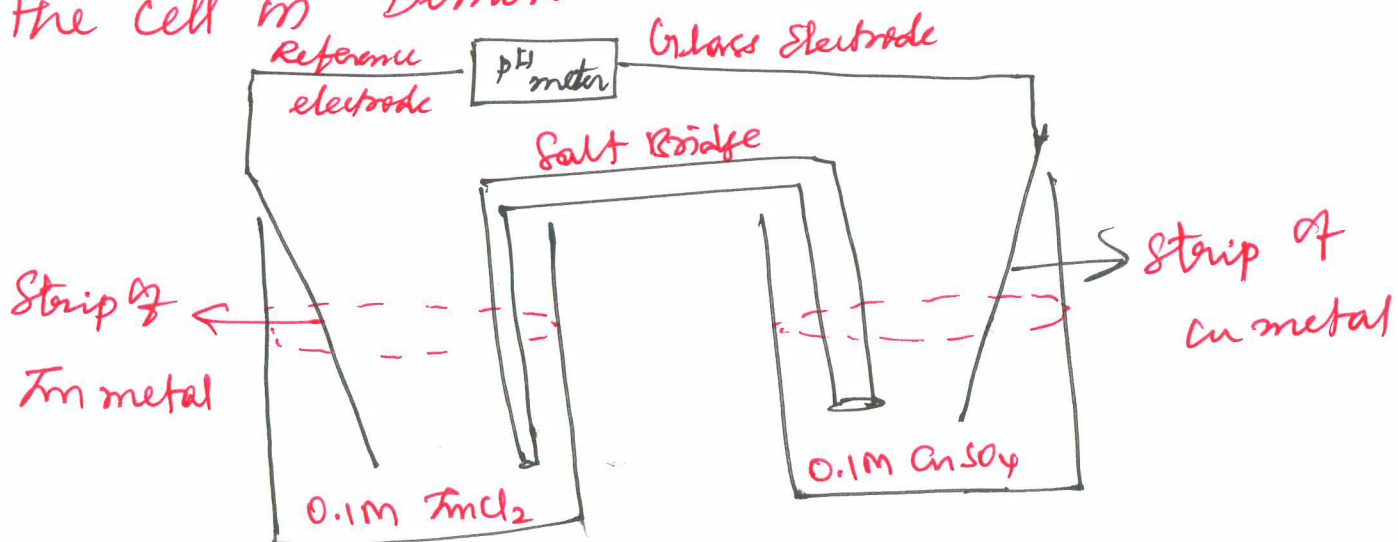
At equilibrium, E goes down to zero. E° is a

constant that does not change.

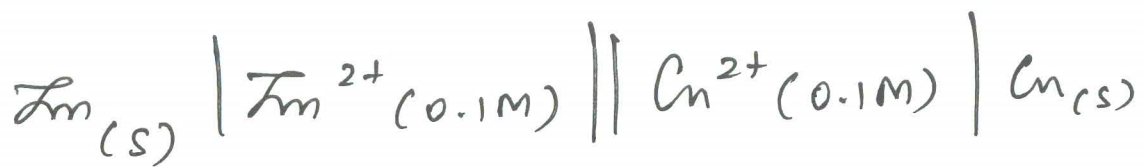
13-15.

~~What~~. (a) Use the Nernst equation to write the spontaneous chemical reaction that occurs in

the cell in Demonstration 14-1.



(2)



Right half-cell: $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}_{(s)}$

$$E^{\circ}_{+} = 0.339 \text{ V}$$

Left half-cell: $\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}_{(s)}$

$$E^{\circ}_{-} = -0.762 \text{ V}$$

$$\therefore E = \left\{ 0.339 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\} - \left\{ -0.762 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\}$$

$E = 1.101 \text{ V}$

Since the voltage is +ve, electrons are transferred from Zn to Cu. The net reaction is



(b) If you use your fingers as a salt bridge in demonstration 14-1, will your body take in Cu^{2+} or Zn^{2+} ?

Ans:

Since Cu^{2+} ions are consumed in the right half-cell, Zn^{2+} ions must migrate from the left half-cell into the salt bridge to help balance charge.

I hope you like our Zn^{2+} , because that is what your body will take up.

13-16

~~13-16~~ Consider the half-reaction



Arising

(a) write the Nernst equation for the half-reaction.

Ans:

$$E = -0.238 - \frac{0.05916}{3} \log \frac{P_{\text{AsH}_3}}{[\text{H}^+]^3}$$

(b) Find E (not E°) when $p^{\text{H}} = 3.00$ and

$$P_{\text{AsH}_3} = 1.0 \text{ atm.}$$

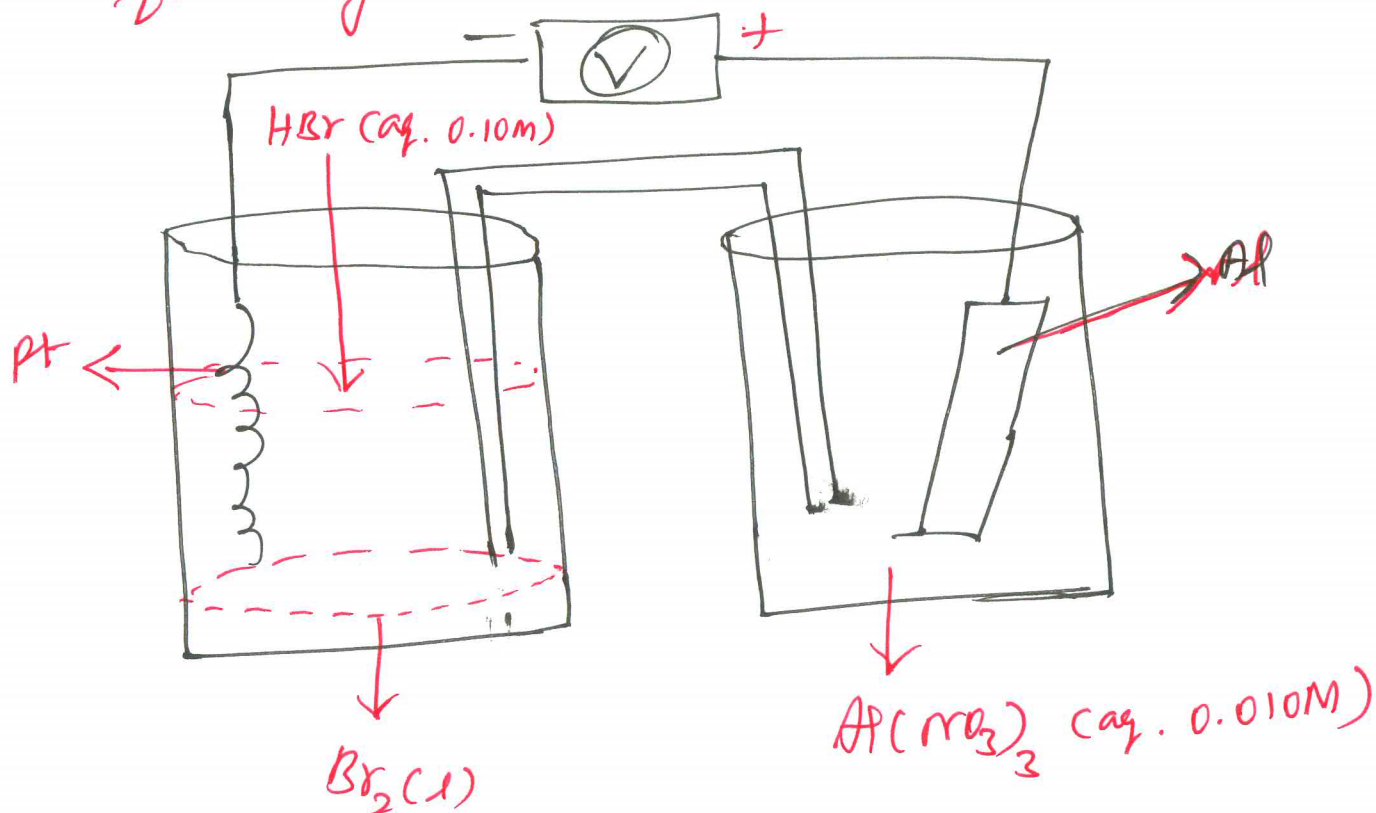
Ans:

$$E = -0.238 - \frac{0.05916}{3} \log \frac{1.0 \times 10^{-3}}{(10^{-3.00})^3}$$

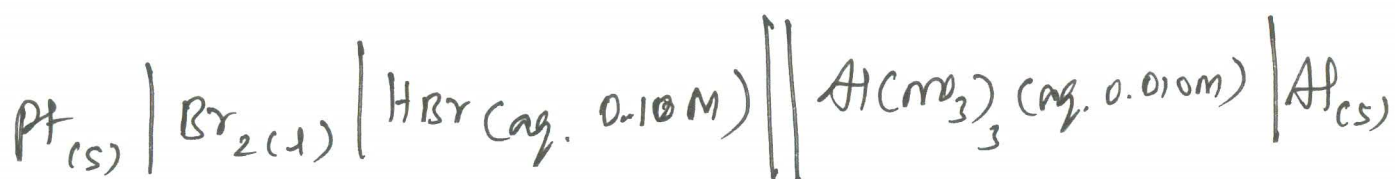
$E = -0.356\text{V}$

$$\begin{aligned} &\therefore \\ &p^{\text{H}} = 3.00 \\ &\therefore [\text{H}^+] = 10^{-3.0} \end{aligned}$$

13-17
~~13-17~~. (a) write the line notation for the following cell.



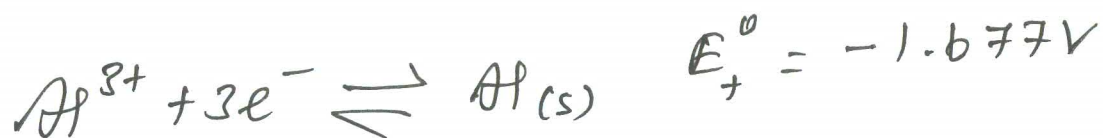
Ans:



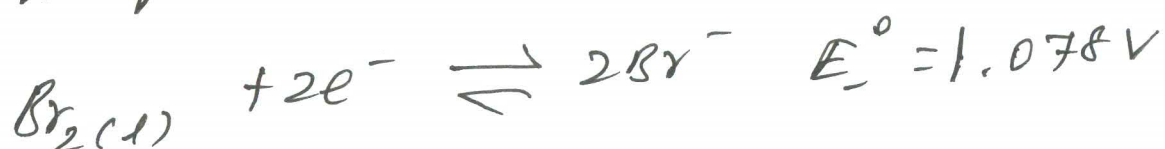
(b) Calculate the cell voltage (E , not E°), and state the direction in which electrons will flow through the potentiometer. write the spontaneous net cell reaction.

Ans:

Right half cell:



Left half cell:



Nernst equation for right half cell:

$$E_{+} = \left\{ -1.677 - \frac{0.05916}{3} \log \frac{1}{(0.0100)} \right\}$$

$$E_{+} = -1.7164 \text{ V}$$

Nernst equation for Left half cell:

$$E_{-} = \left\{ 1.078 - \frac{0.05916}{2} \log [0.10]^2 \right\}$$

$$= 1.1372 \text{ V.}$$

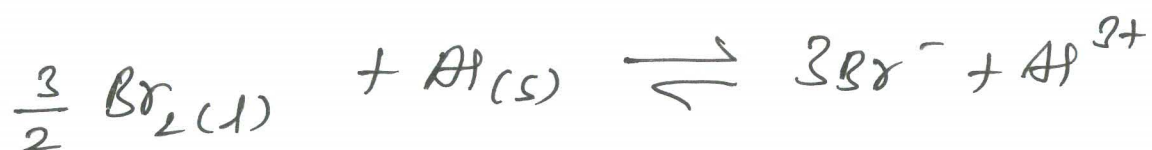
$$\therefore E = E_{+} - E_{-}$$

$$= -1.7164 - 1.1372 = -2.854 \text{ V.}$$

(26)

Since the voltage is -ve electrons flow from the right-hand electrode to the left hand electrode.

Reduction occurs at the left hand electrode. The spontaneous reaction is



(c) The left half-cell was loaded with 14.3 mL of $\text{Br}_2(l)$ (density = 3.12 g/mL). The aluminium electrode contains 12.0 g of Al. Which element, Br_2 or Al, is the limiting reagent in this cell? (That is, which reagent will be used up first?).

Ans: 14.3 mL of Br_2 = 0.721 g of Br_2 = 0.279 mol of Br_2 .

12.0 g of Al = 0.445 mol of Al.

The reaction requires $\frac{3}{2}$ mol of Br_2 for every mol of Al. The Br_2 will be used up first.

(d) If the cell is somehow operated under conditions in which it produces a constant voltage of 1.50 V, how much electrical work will have been done when 0.231 mL of $\text{Br}_2(l)$ has been consumed? (27)

Ans:

$$0.231 \text{ mL of } \text{Br}_2 = 0.721 \text{ g of } \text{Br}_2$$

$$= 4.51 \times 10^{-3} \text{ mol } \text{Br}_2$$

$$= 9.02 \times 10^{-3} \text{ mol } e^-$$

$$= 870 \text{ C}$$

$$\text{Work} = E \cdot q$$

$$= (1.50) (870)$$

$$= 1.31 \text{ kJ.}$$

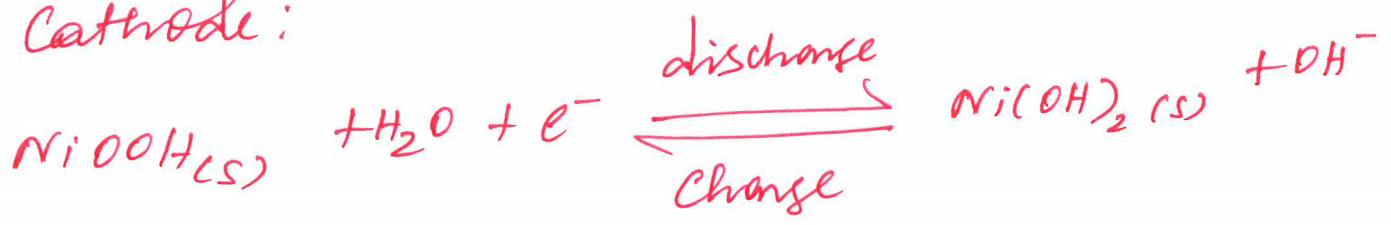
∴
(i) Convert mol e^- to no. of e^- by multiplying with 6.023×10^{23}

(ii) Convert no. of e^- to Coulomb by multiplying no. of e^- with charge of electron $1.6 \times 10^{-19} \text{ C}$

13-18

~~13-18~~. The nickel-metal hydride rechargeable battery for lap-top Computers is based on the following chemistry.

Cathode:



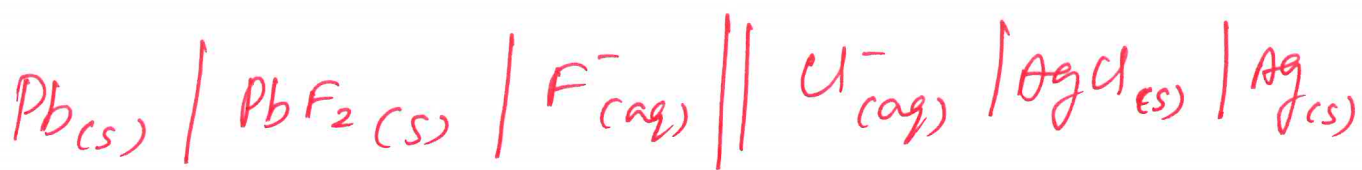
Anode:



The anode material, MH, is a metal hydride in which the metal is one of several transition metal or rare earth alloys. Explain why the voltage of this cell remains nearly constant during its entire discharge cycle.

Ans: The activities of the solid reagents do not change until they are used up. The only aqueous species, OH^- , is created at the cathode and consumed in equal amounts at the anode, so its concentration remains constant in the cell. Therefore none of the activities in the Nernst equation change during the life cycle of the cell (until something is used up).

13-19 (29)
~~13-20~~. Suppose that the concentrations of NaF and KCl are each 0.10 M in the cell.



(a) Using the half-reactions $2\text{AgCl}_{(s)} + 2e^{-} \rightleftharpoons 2\text{Ag}_{(s)} + 2\text{Cl}^{-}$

and $\text{PbF}_{2(s)} + 2e^{-} \rightleftharpoons \text{Pb}_{(s)} + 2\text{F}^{-}$

Calculate the cell voltage.

Ans:

Right half-cell:

$$E_{+} = \left\{ 0.222 - \frac{0.05916}{2} \log [\text{Cl}^{-}]^2 \right\}$$

$$= 0.2812 \text{ V.}$$

Left half-cell:

$$E_{-} = \left\{ -0.350 - \frac{0.05916}{2} \log [\text{F}^{-}]^2 \right\}$$

$$= -0.2908 \text{ V.}$$

$$\therefore E = E_{+} - E_{-} = 0.2812 - (-0.2908) = 0.572 \text{ V.}$$

(b) now calculate the cell voltage by using the reactions



and



For this part, you will need the solubility products for PbF_2 and AgCl .

Ans:

$$[\text{Pb}^{2+}] = \frac{k_{sp}(\text{for } \text{PbF}_2)}{[\text{F}^-]^2} = \frac{(3.6 \times 10^{-8})}{(0.10)^2} = 3.6 \times 10^{-6} \text{ M}$$

$$[\text{Ag}^+] = \frac{k_{sp}(\text{for } \text{AgCl})}{[\text{Cl}^-]} = \frac{(1.8 \times 10^{-10})}{(0.10)} = 1.8 \times 10^{-9} \text{ M}$$

\therefore Right half cell:

$$E_+ = \left\{ 0.759 - \frac{0.05916}{2} \log \frac{1}{[\text{Ag}^+]^2} \right\} = 0.2812 \text{ V}$$

Left half-cell:

$$E_- = \left\{ -0.126 - \frac{0.05916}{2} \log \frac{1}{[Pb^{2+}]} \right\}$$

$$= -0.2870 \text{ V.}$$

$$\therefore E = E_+ - E_-$$

$$= 0.2812 - (-0.2870)$$

$$\boxed{E = 0.568 \text{ V.}}$$

The agreement between the two calculations is reasonable.

13-22

(32)

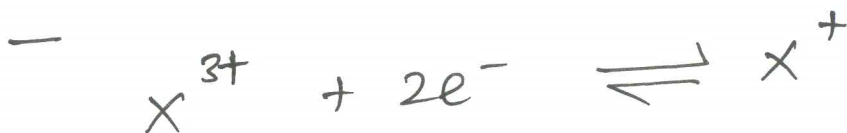
~~Q1032~~ What must be the relationship between E_1^0 and E_2^0 if the species X^+ is to disproportionate spontaneously under standard conditions to X^{3+} and $X_{(s)}$? Write a balanced equation for the disproportionation.



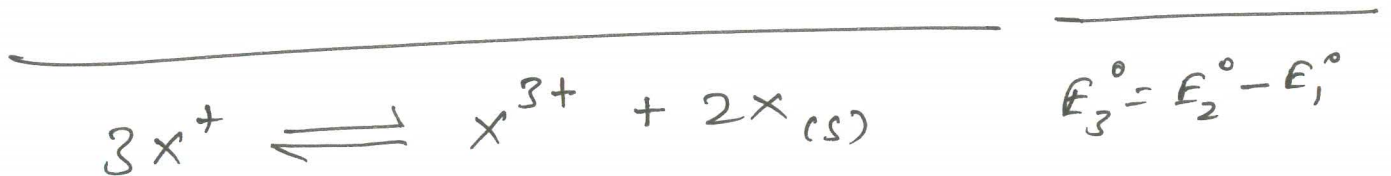
Ans:



$$E_+^0 = E_2^0$$



$$E_-^0 = E_1^0$$

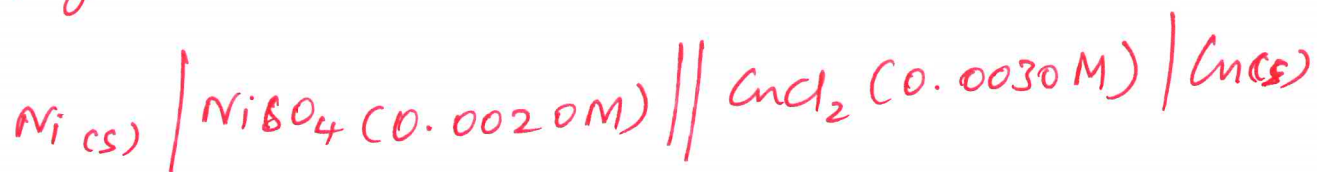


$$E_3^0 = E_2^0 - E_1^0$$

Whenever $E_2^0 > E_1^0$, then E_3^0 will be greater than 0 and disproportionation will be spontaneous.

13-23

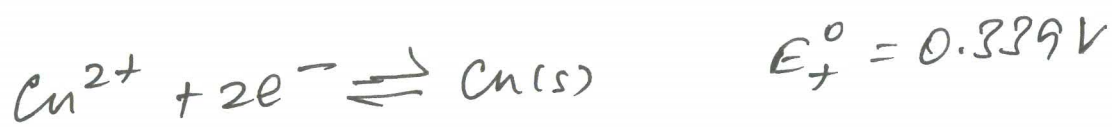
~~13-23~~. Without neglecting activities, calculate the voltage of the cell.



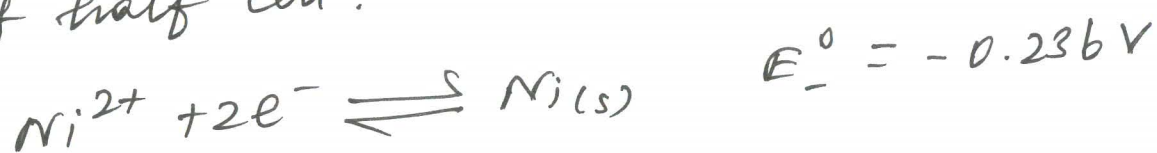
For simplicity, assume that the salts are completely dissociated. (This is an approximation because ion pair formation cannot be neglected entirely).

Ans:

Right half cell:



Left half cell:



The ionic strength of the right half-cell is 0.0090 M and the ionic strength of the left half-cell is 0.0080 M .

$$\text{At } \mu = 0.0090 \text{ M}, \gamma_{\text{Cu}^{2+}} = 0.690$$

$$\text{At } \mu = 0.0080 \text{ M}, \gamma_{\text{Ni}^{2+}} = 0.705$$

$$E_+ = E_+^0 - \frac{0.05916}{2} \log \frac{1}{[Cu^{2+}] \gamma_{Cu^{2+}}}$$

$$= 0.339 - \frac{0.05916}{2} \log \frac{1}{[0.0030](0.690)}$$

$$E_+ = 0.2596 \text{ V.}$$

$$E_- = E_-^0 - \frac{0.05916}{2} \log \frac{1}{[Ni^{2+}] \gamma_{Ni^{2+}}}$$

$$= -0.236 - \frac{0.05916}{2} \log \frac{1}{(0.0020)(0.705)}$$

$$E_- = -0.3203 \text{ V.}$$

$$\therefore E = E_+ - E_-$$

$$E = 0.580 \text{ V.}$$

How to Calculate Ionic strength:

$$I = \frac{1}{2} \sum m_i Z_i^2$$

where m_i - is the concentration

Z_i - is the valency.

$$I_{\text{NiSO}_4} = \frac{1}{2} \left(\text{Ni}^{2+} \times Z_{\text{Ni}}^2 + \text{SO}_4^{2-} \times Z_{\text{SO}_4}^2 \right)$$

$$= \frac{1}{2} (0.002 \times 2^2 + 0.002 \times 2^2)$$

$$= \frac{1}{2} (0.002 \times 4 + 0.002 \times 4)$$

$$= \frac{1}{2} (0.008 + 0.008)$$

$$= 0.008$$

Debye-Huckle
Relation

$$\log \gamma_i = -A Z_i^2 \sqrt{I}$$

$$\therefore \log \gamma_{\text{Ni}^{2+}} = -0.509 \times 2^2 \times (0.008)^{1/2}$$

$$= -0.509 \times 4 \times 0.0894$$

$$= -0.1821$$

$$\therefore \gamma_{\text{Ni}^{2+}} = 10^{-0.1821} = 0.6575$$

$A = 0.509$ $Z_i = \text{valency}$ $I = \text{Ionic strength}$
--

$$I = \frac{1}{2} m_i Z_i^2$$

$$\begin{aligned} I_{\text{CuCl}_2} &= \frac{1}{2} \left(m_{\text{Cu}^{2+}} \cdot Z_{\text{Cu}^{2+}}^2 + m_{\text{Cl}^-} \cdot Z_{\text{Cl}^-}^2 \right) \\ &= \frac{1}{2} (0.003 \times 4 + 2 \times 0.003 \times 1^2) \\ &= \frac{1}{2} [0.012 + 0.006] \end{aligned}$$

$$\text{ionic strength} = 0.009.$$

$$\therefore \log \gamma_i = -A Z_i^2 \sqrt{I}$$

$$\begin{aligned} \log \gamma_{\text{Cu}^{2+}} &= -0.509 \times 2^2 \times (0.009)^{1/2} \\ &= -0.509 \times 4 \times 0.095 \\ &= -0.1934 \end{aligned}$$

$$\therefore \gamma_{\text{Cu}^{2+}} = 10^{-0.1934} = 0.6406.$$