Electro Chemistry

1) Galvanic cell
2) Daniel Cell
3) Conductance
4) Electrolytic cell & Electrolysis
5) Fuel Cell & Batteries

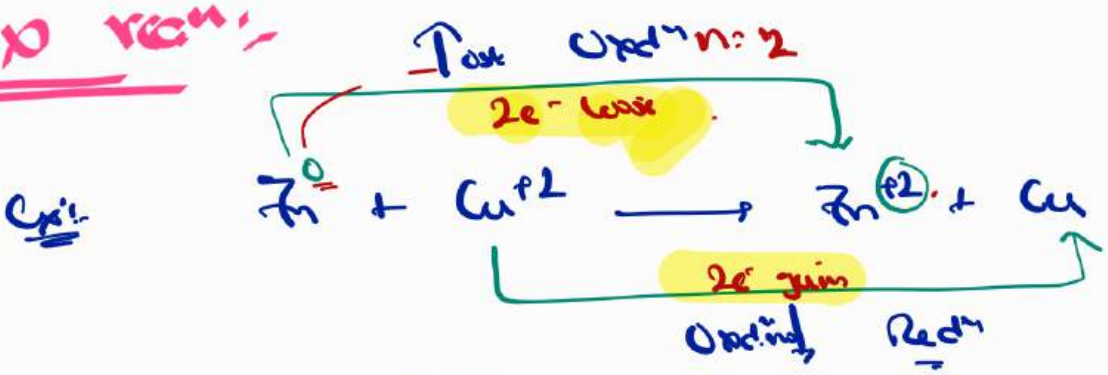
Oxidation (↑ O.St)

- e⁻ :- loose of e⊖
- O :- gain / addition of O
- H :- loss of H

Reduction (↓ O.St)

- e⁻ :- gain of e⊖
- O :- loss of O
- H :- gain of H

Redox reaction :-



n factor — no of e⊖ transfer

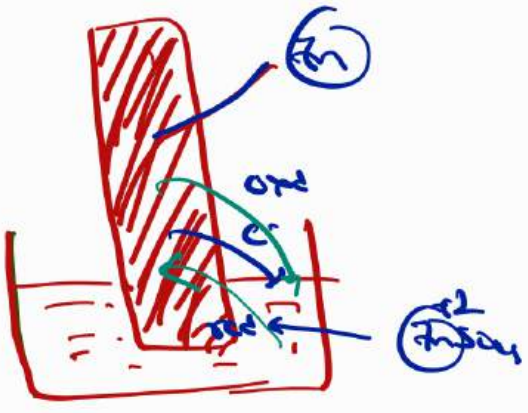
Cells

- Electro Chemical cells ⇓
  - C.E → E.E
- Electrolytic Cells ⇓
  - E.E → C.E
  - Electro plating
  - Gold Solid

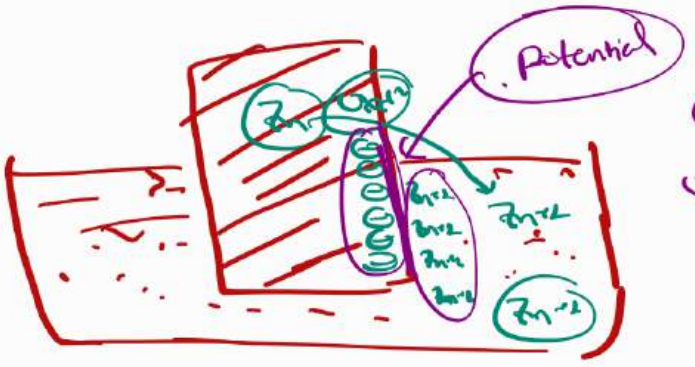
Working Cells :-

1) Electrode (s)
2) Electrolyte (l)

Half Cell



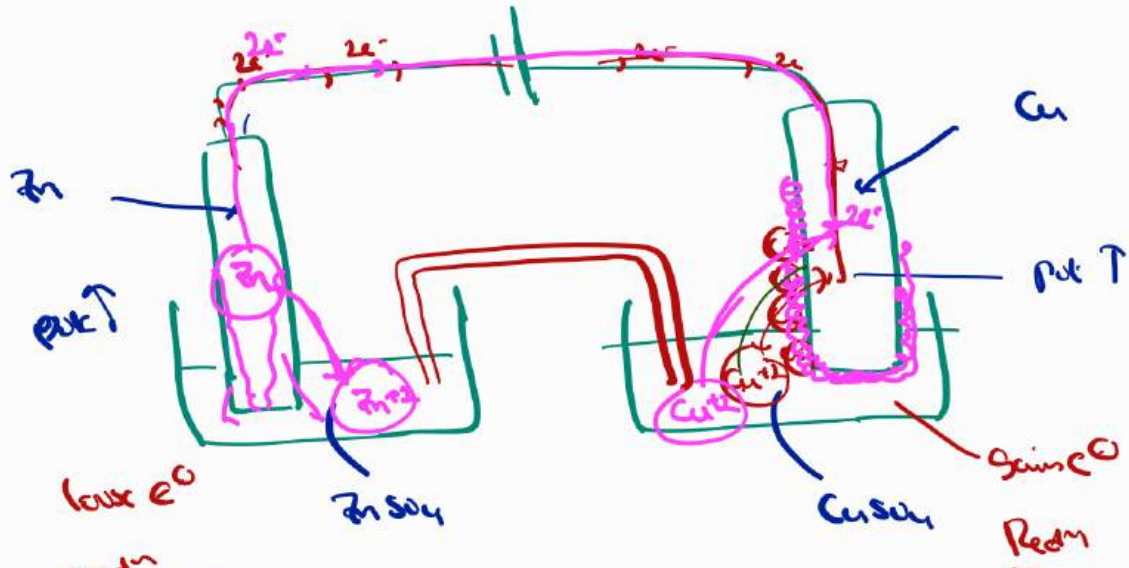
② Oxd
① $Zn \rightarrow Zn^{+2}$
② $Zn^{+2} + e^- \rightarrow Zn$ (Red)



Charge Separation

Oxd / Red

Electrochemical Cell :-

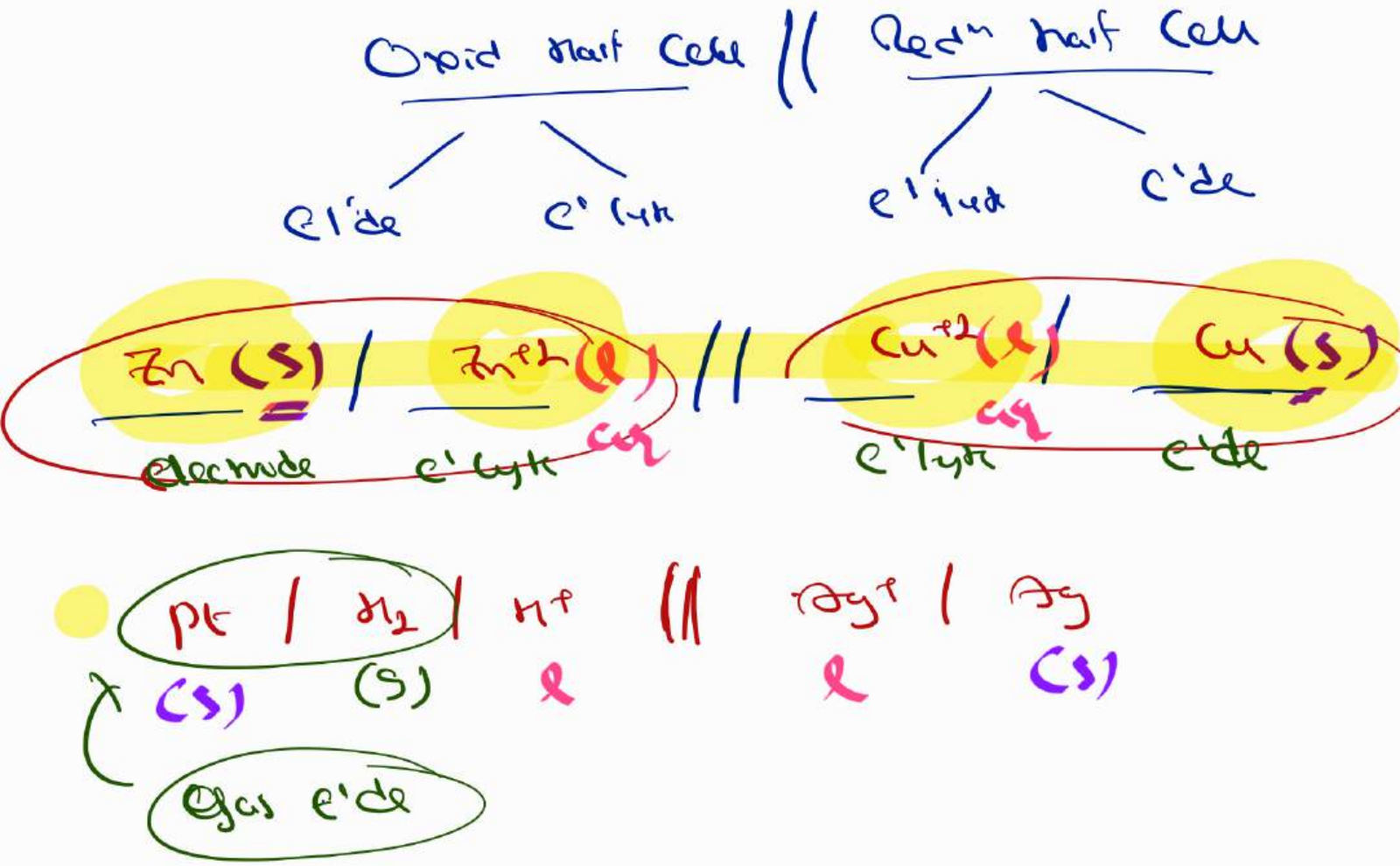


(i) :- $Zn \longrightarrow Zn^{+2} + 2e^-$ (Oxidation)

(ii) :- $Cu^{+2} + 2e^- \longrightarrow Cu$ (Reduction)

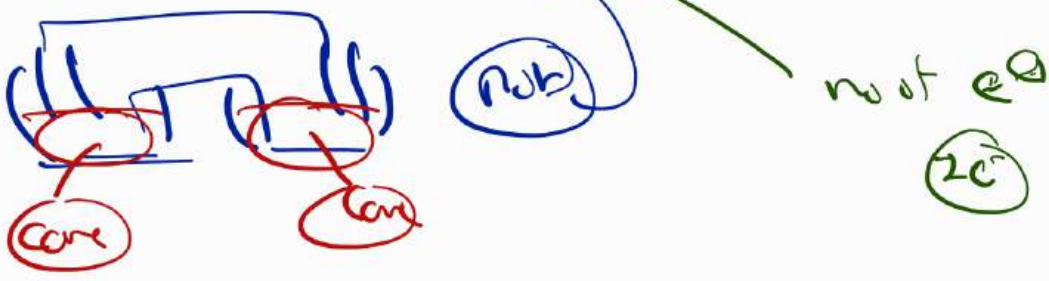
Cell reaction :- $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$

Cell notation :-



Nernst Equation :-

$$E_{cell} = E_0 - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$



$$E_{cell} = E_A + E_C$$

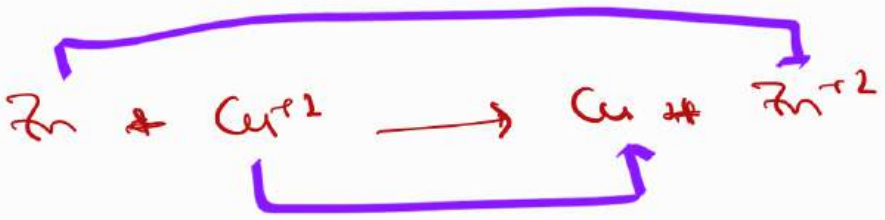
(E_A : Oxd pot^n, E_C : Red pot^n)

$$= E_C - E_A$$

(E_C & E_A red^n pot^n)

$$= E_A - E_C$$

(E_C : E_A Oxd^n pot^n)

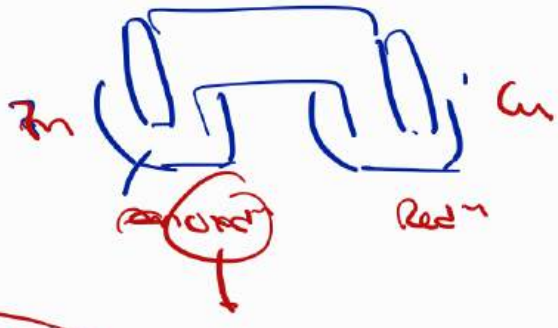


$E_{z_n/z_{n+1}} = x$

$E_{z_{n+2}/z_n} = -x$

$E_{c_n/c_{n+2}} = x$

$E_{z_{n+2}/z_n} = y$



$E_{com} =$

$= -x - y$

$= -(x+y)$

Diff E_{cell} & E°_{cell} :-

25°C / 1 bar (gas)

1 M (soln)

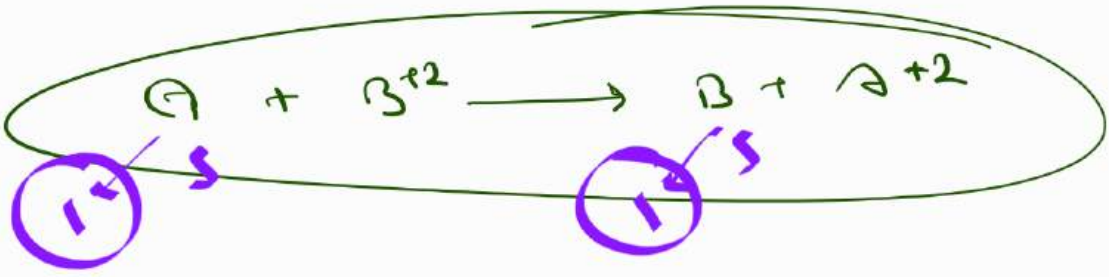
$$E = E^{\circ} - \frac{0.0591}{n} \log(\ )$$

Nernst Cell eqn :-

$A \longrightarrow B$

At Cathode

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \cdot \log \frac{(P)^B}{(R)_A}$$



STP

$$E_{cell} = E^{\circ} - \frac{0.0591}{n} \log \frac{(P)}{(R)}$$

E°
- $E_C - E_A$
- $E_A - E_C$
- $E_A + E_C$

E_{cell} = $E_A + E_C$
- OR
- RCM

$= E_C - E_A$ 90%

Free energy:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$A + B^{+2} \longrightarrow B + A^{+2}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[B][A^{+2}]}{[A][B^{+2}]}$$

Relation ΔG , E.

$$\Delta G = -nFE_{cell}$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$

Equilibrium:

ΔG | E_{cell}

Equilibrium Constant

E

$A + B^{+2} \rightleftharpoons B + A^{+2}$

$E = E^\circ - \frac{0.0591}{n} \log \frac{(B^{+2})}{(B^{+2})}$ → K_{eq}

Or

at eqm $\frac{(B^{+2})}{(B^{+2})} = K_{eq}$

$E = 0$

$E^\circ = \frac{0.0591}{n} \log K_{eq}$

ΔG

$A + B^{+2} \rightleftharpoons B + A^{+2}$

$\Delta G = \Delta G^\circ + RT \ln \frac{(B^{+2})}{(B^{+2})}$ → K_{eq}

$\Delta G = 0$

$\Delta G^\circ = -RT \ln K_{eq}$

$E^\circ = \frac{2.303 \cdot RT}{nF} \log K_{eq}$

$K_{eq} = ?$

$\log K_{eq} = \frac{nFE^\circ_{cell}}{2.303\,RT}$

Electrode potential of Zn^{2+}/Zn is –0.76 V and that of Cu^{2+}/Cu is + 0.34 V. The EMF of the cell constructed between these two electrodes is

(a) 1.10 V (b) 0.42 V

(c) –1.1 V (d) –0.42 V.

[CBSE AIPMT 2001]

red Zn^{+2}/Zn = −0.76 ↓ Anode

red Cu^{+2}/Cu = +0.34 ↑ Cathode

High pot ⇒ Cathode

Low red. pot. ⇒ Anode

$E_c = E_c - E_A$

$= +0.34 - (-0.76)$

$= +1.1$

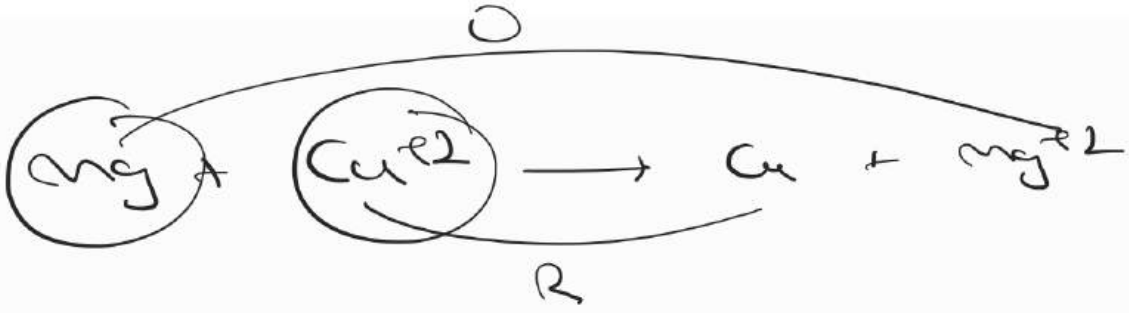
The cell reaction of a cell is

$$Mg(s) + Cu^{2+}(aq) \rightarrow Cu\ (s) + Mg^{2+}(aq)$$

If the standard reduction potentials of Mg and Cu are –2.37 and +0.34 V respectively, the *emf* of the cell is

(a) 2.03 V (b) –2.03 V

(c) +2.71 V (d) –2.71 V [CBSE AIPMT 2002]



$$E_{cell} = E_c - E_a$$

E_c → +0.34

E_a (Mg) → −2.37

$$= +0.34 - (-2.37)$$

$$= +0.34 + 2.37$$

$$= +2.71$$

15. The equilibrium constant for the reaction :

$Cu + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag$; $E^\circ = 0.46$ V at 298 K is :

(a) 2.0×10^{10} (b) 3.9×10^{15}

(c) 4.0×10^{10} (d) 2.4×10^{10}

[CBSE AIPMT 2007]

$E = E^\circ - \frac{0.0591}{n} \log K_{eq}$

$0 = E^\circ - \frac{0.0591}{n} \log K_{eq}$

$E^\circ = + \frac{0.0591}{n} \log K_{eq}$

$\frac{2}{0.0591} E^\circ = \log K_{eq}$ $E^\circ = 0.46$

$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag^0$

$n = 2$

$\frac{2 \times 0.46}{0.0591} = \log K_{eq}$

$\log K_{eq} = 15.56$

$K_{eq} = 10^{15.56}$ / antilog (15.56)

$K_{eq} = 10^{15.56}$

$= 10^{15} \times 10^{0.56}$

$= 10^{15} \times 3.9$

$K_c = 3.9 \times 10^{15}$

$\log 3 = 0.4771$

$\log 4 = 0.6020$

$\log 3.9 \approx 0.56$

$3.9 = 10^{0.56}$

24. The correct value of e.m.f. of cell is given by :

(*i*) $E_{cell} = E_{OP}$ anode $- E_{RP}$ cathode

(*ii*) $E_{cell} = E_{OP}$ anode $+ E_{RP}$ cathode

(*iii*) $E_{cell} = E_{RP}$ anode $+ E_{RP}$ cathode

(*iv*) $E_{cell} = E_{OP}$ anode $- E_{OP}$ cathode

(a) (*iii*) and (*i*)

(b) (*i*) and (*ii*)

(c) (*iii*) and (*iv*)

(d) (*ii*) and (*iv*)

[CBSE AIPMT 2010]

The electrode potentials for

$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $\quad +2 \longrightarrow +1$ ✓

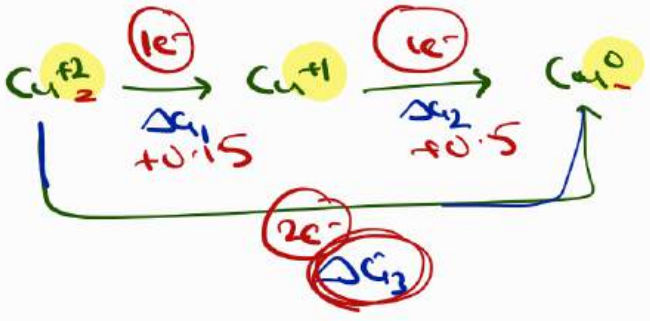
and $Cu^+(aq) + e^- \rightarrow Cu(s)$ $\quad +1 \longrightarrow 0$ ✓

are +0.15 V and +0.50 V respectively. The value of $E^\circ_{Cu^{2+}/Cu}$ will be :

$+2 \rightarrow 0$

(a) 0.150 V (b) 0.325 V

(c) 0.500 V (d) 0.650 V **[CBSE AIPMT 2011]**



12th

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

$-nFE_{cell} = -nFE_1 + nFE_2$

$nE_3 = nE_1 + nE_2$

$2 \quad 1 \quad +0.15 \quad 1 \quad +0.5$

$E_3 = \dfrac{1 \times 0.15 + 1 \times 0.5}{2}$

$= \dfrac{0.65}{2}$

$= 0.325$

Standard reduction potentials of the half reactions are given below :

$F_2^{(g)} + 2e^- \rightarrow 2F^-(aq)$; $E^\circ = +2.85$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$; $E^\circ = +1.36$ V

$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$; $E^\circ = +1.06$ V

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$; $E^\circ = +0.53$ V

The strongest oxidising and reducing agents respectively are :

(a) F_2 and I^- (b) Br_2 and Cl^-

(c) Cl_2 and Br^- (d) Cl_2 and I_2

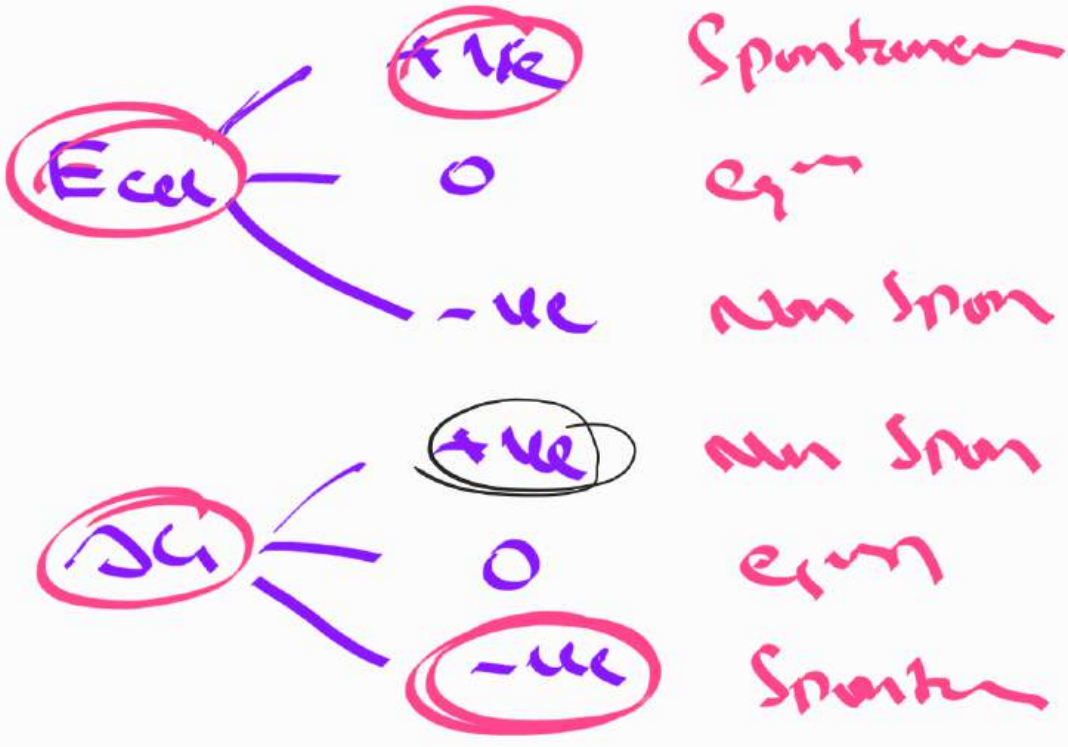
[CBSE AIPMT 2012]

If the E°_{cell} for a given reaction has a negative value, which of the following gives correct relationships for the values of ΔG° and K_{eq} ?

(a) $\Delta G^{\circ} > 0$; $K_{eq} < 1$ (b) $\Delta G^{\circ} > 0$; $K_{eq} > 1$

(c) $\Delta G^{\circ} < 0$; $K_{eq} > 1$ (d) $\Delta G^{\circ} < 0$; $K_{eq} < 1$

[NEET 2011, 2016]



Keq > 1 fwd

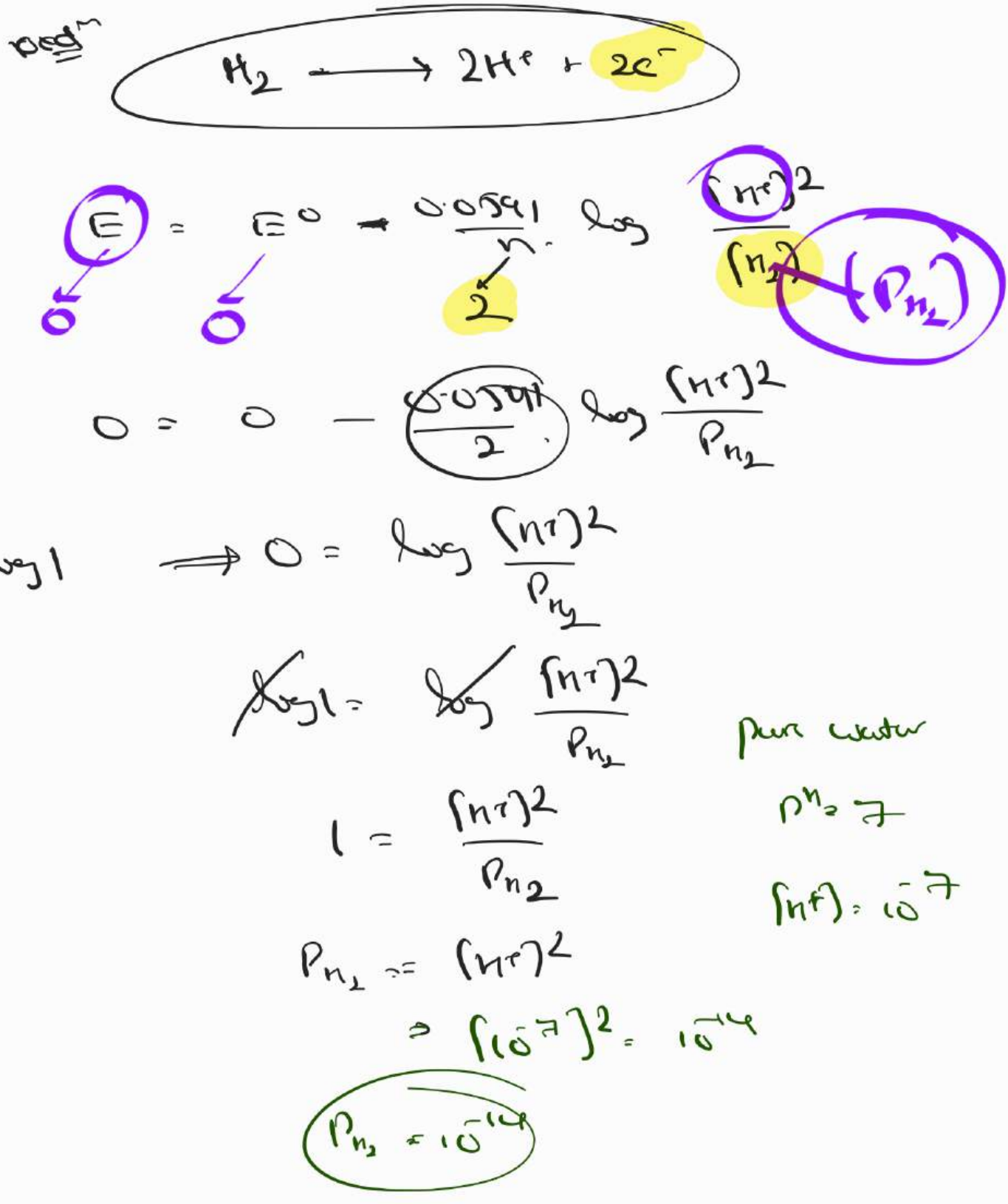
Keq < 1 bwd

The pressure of H_2 required to make the potential of H_2-electrode zero in pure water at 298 K is

(a) 10^{-12} atm (b) 10^{-10} atm

(c) 10^{-4} atm (d) 10^{-14} atm

[NEET 2016, Phase II]



In the electrochemical cell

$Zn \| ZnSO_4$ (0.01 M) $\| CuSO_4$ (1.0 M) Cu,

the emf of this Daniel cell is E_1. When the concentration $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to E_2. From the following, which one is the relationship between E_1 and E_2 ?

(Given, $\frac{RT}{F} = 0.059$)

(a) $E_1 = E_2$

(b) $E_1 < E_2$

(c) $E_1 > E_2$

(d) $E_2 = 0 \neq E_1$

[NEET 2017]

$$E_{cell} = E^0 - \frac{0.0591}{n} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

E_1 ↓ E_{cell} = E^0 + $\frac{0.0591}{n} \log \frac{[Cu^{+2}]}{[Zn^{+2}]}$ ↑

Cu^{+2} ↑ E ↑

Zn^{+2} ↓ E_{cell} ↑

Zn^{+2} ↑ 0.01 ↓ 1.0

Cu^{+2} ↓ 1.0 ↓ 0.01

E_{cell} ↓

At 298 K, the standard electrode potentials of Cu^{2+}/Cu, Zn^{2+}/Zn, Fe^{2+}/Fe and Ag^{+}/Ag are 0·34 V, –0·76 V, –0·44 V and 0·80 V, respectively.

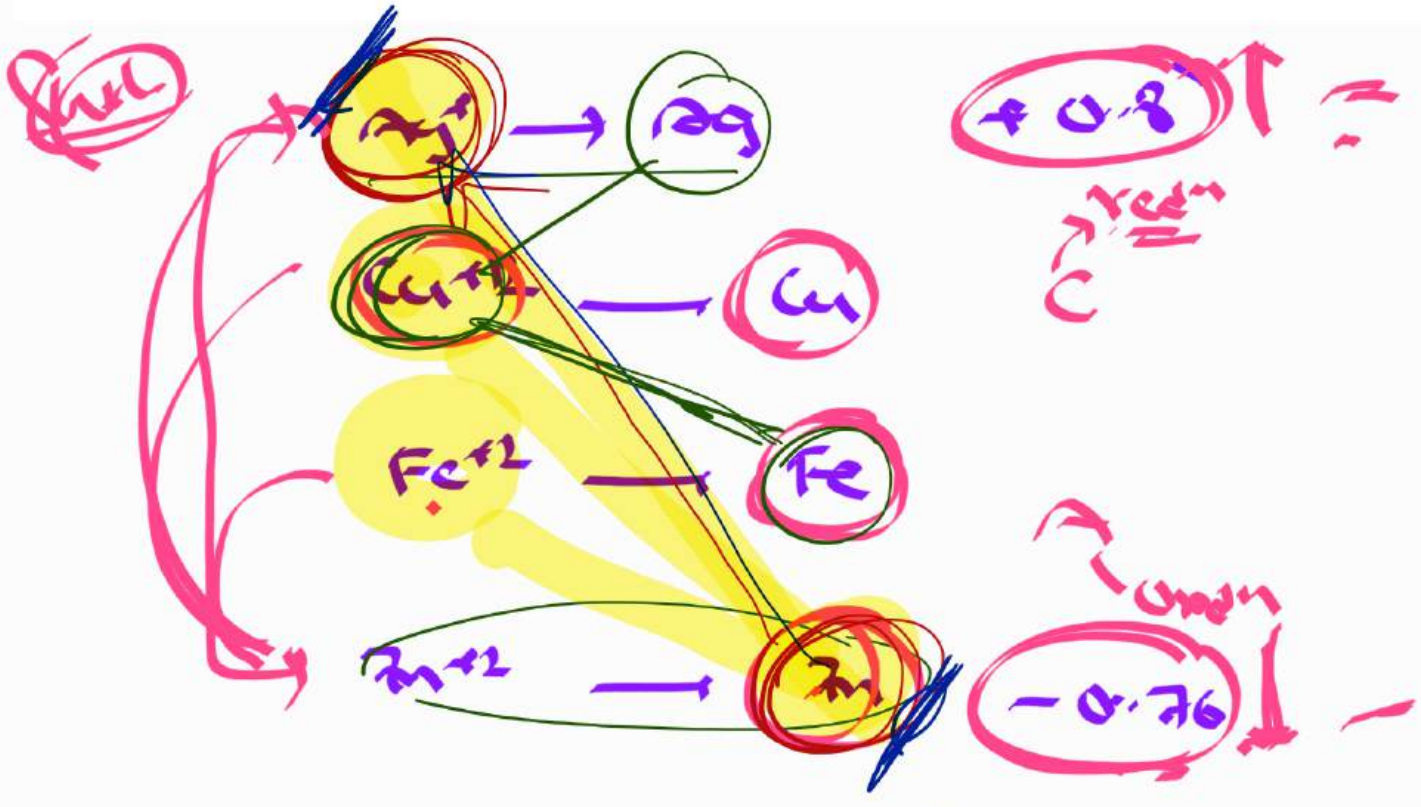
On the basis of standard electrode potential, predict which of the following reaction cannot occur ?

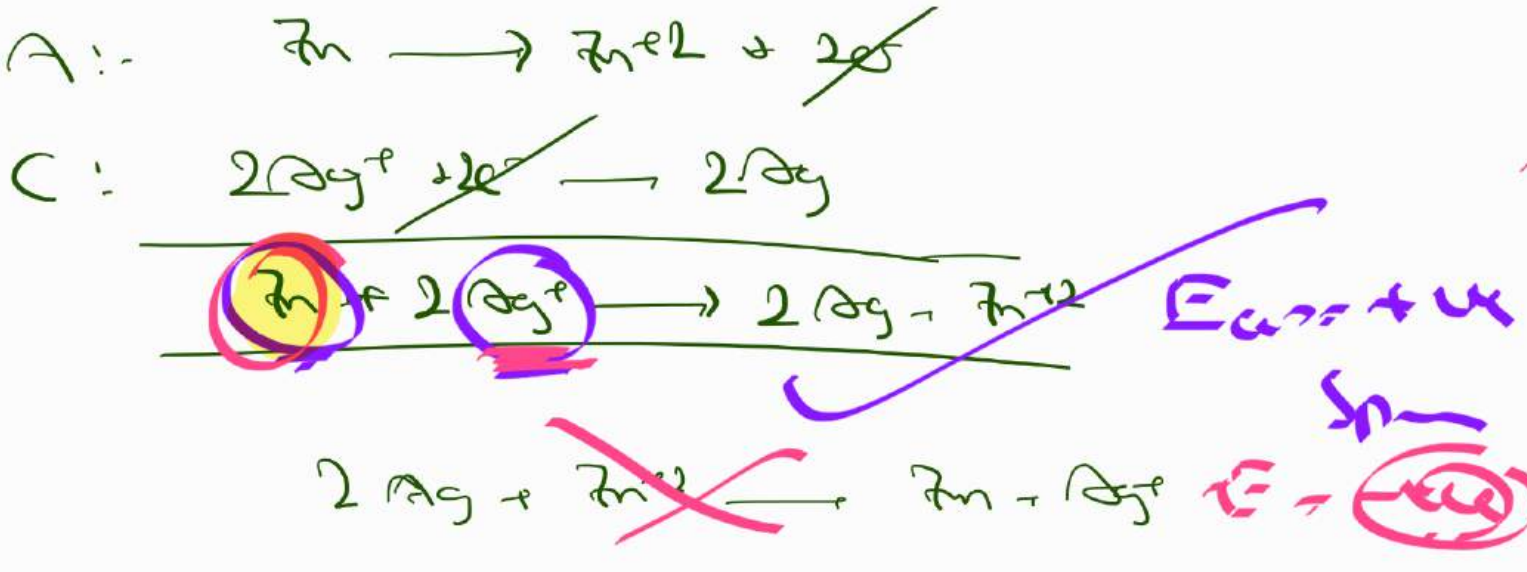
(a) $CuSO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + Cu(s)$

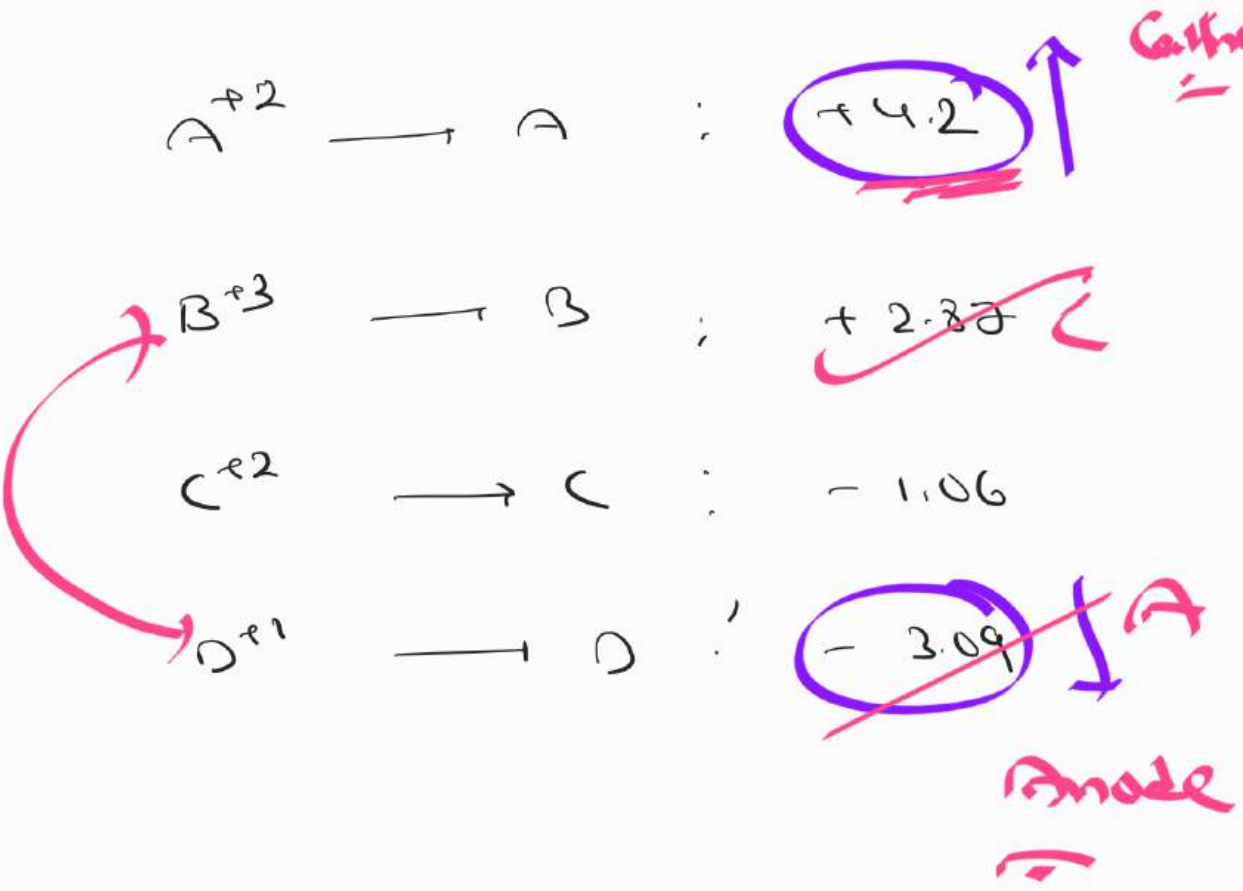
(b) $FeSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Fe(s)$

(c) $2CuSO_4(aq) + 2Ag(s) \rightarrow 2Cu(s) + Ag_2SO_4(aq)$

(d) $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$ [NEET 2022]






$A^{+2} \longrightarrow A$: +4.2
Cathode
$B^{+3} \longrightarrow B$: + 2.37
$C^{+2} \longrightarrow C$: - 1.06
$D^{+1} \longrightarrow D$: - 3.09
Anode

$\log_{10} K_{eq} = 7.30$

$K_{eq} = ?$

$\log_b a = x$

$a = b^x$

$K_{eq} = 10^{7.3}$

$= 10^{7} \times 10^{0.3}$

$= 2$

$= 2 \times 10^{7}$

$\log_{10} 2 = 0.3010$

$2 = 10^{0.3}$

$\log K_{eq} = -7.7$

$K_{eq} = 10^{-7.7}$

$= 10^{-7} \times 10^{-0.7}$

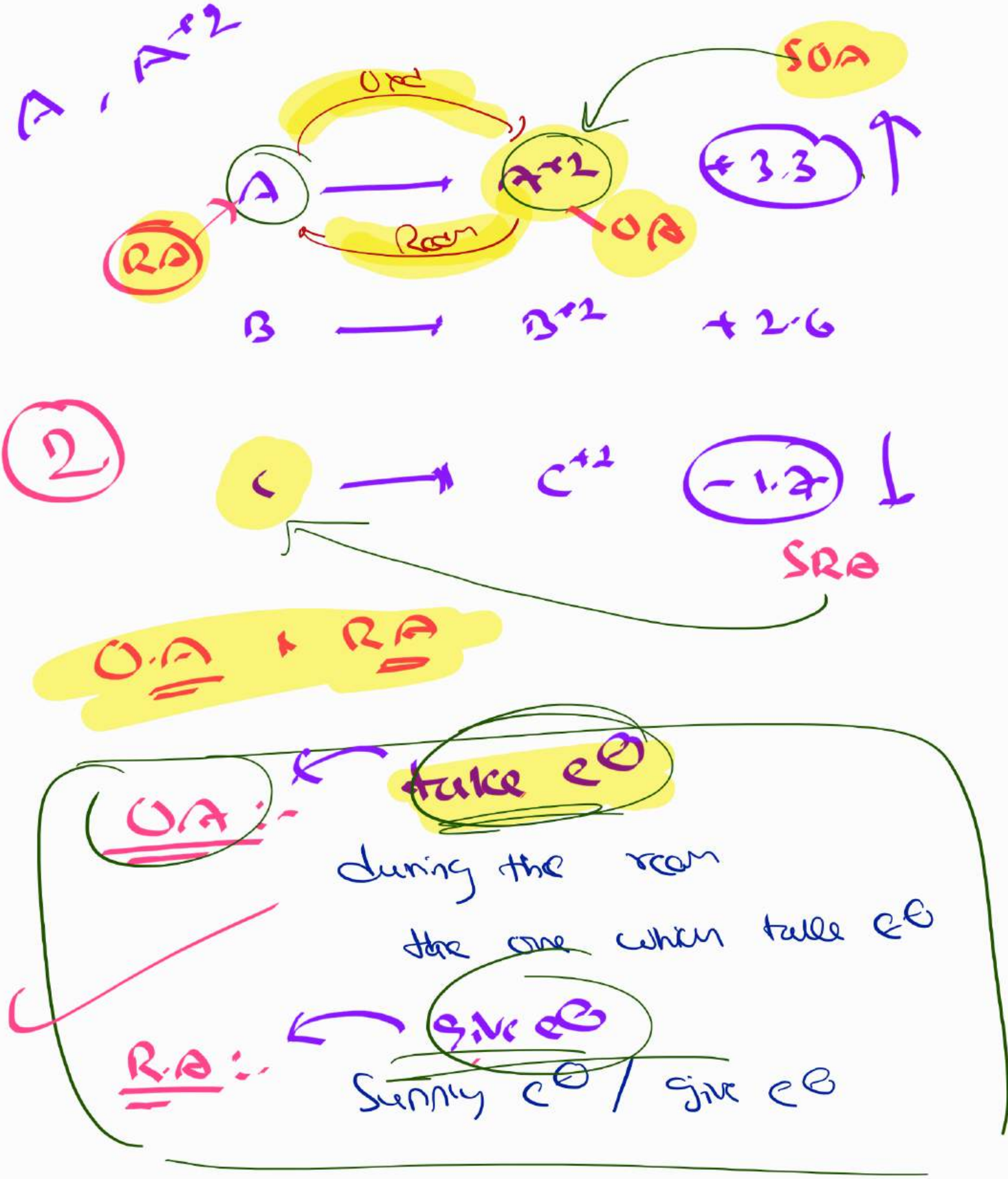
$= 10^{-8} \times 10^{+0.3}$

$= 10^{-8} \times 2$

$= 2 \times 10^{-8}$

$\log 2 = +0.3$

$2 = 10^{0.3}$


A , A+2
OA
SOA
A
A+2
+3.3
RA
RA
OA
B
B+2
+2.6
2
C
C+1
-1.7
SRA
OA + RA
take e⊖
OA :-
during the ram
the one which take e⊖
give e⊖
RA :-
Supply e⊖ / give e⊖