Free Energy and EMF

Review

The relationship between ΔG and $\Delta G°$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

the change in free energy that occurs if the reactants in their standard states are converted to the products in their standard states

$$\Delta G = \Delta H - T\Delta S$$

the absolute change in free energy change

The relationship between ΔG and ΔG°

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

$$\Delta G = 0$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The relationship between ΔG and ΔG°

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

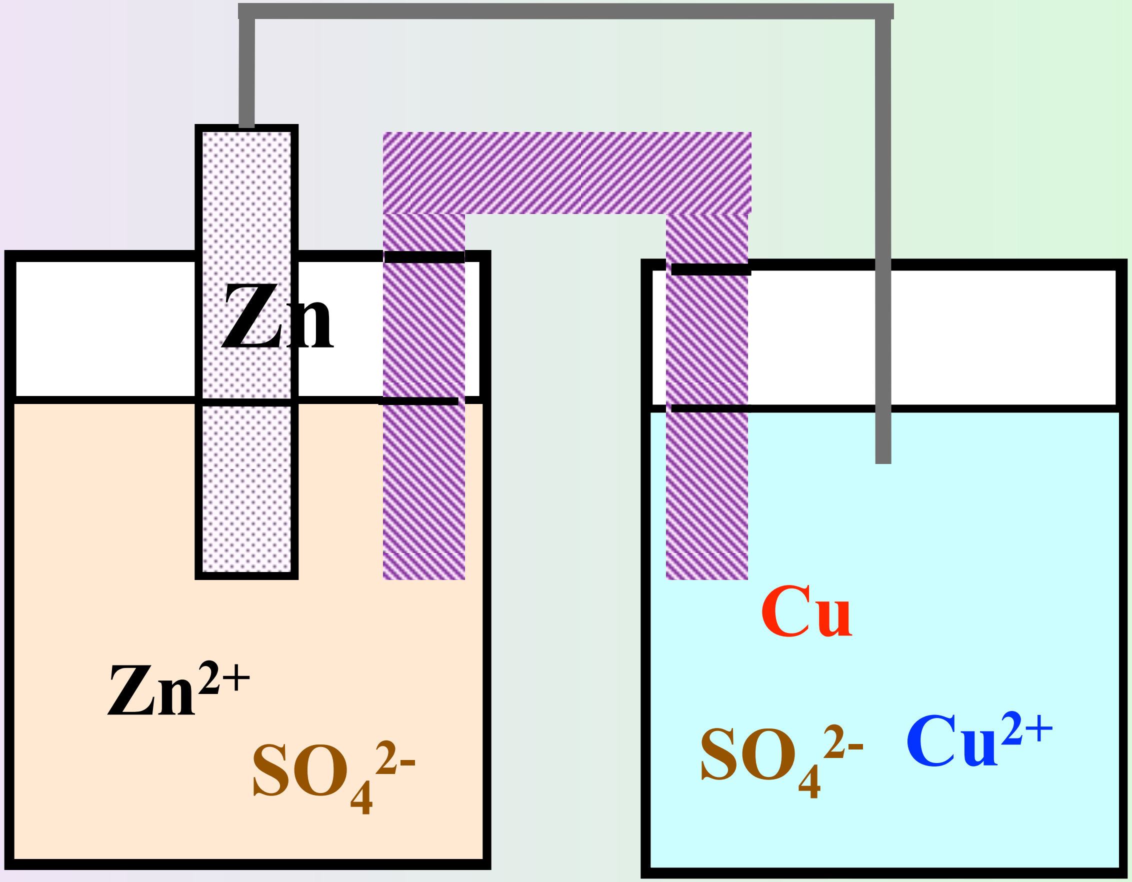
$$\Delta G = 0$$

a large negative value ΔG°

a large relative value for products needed to make (RTlnQ) equivalent to ΔG°

$$0 = \boxed{\Delta G^\circ} + RT \ln \frac{\boxed{[\text{products}]}}{[\text{reactants}]}$$

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C



$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

$$\Delta G^\circ_{rxn} = \Sigma n \Delta G^\circ_f(\text{products}) - \Sigma m\, \Delta G^\circ_f(\text{reactants})$$

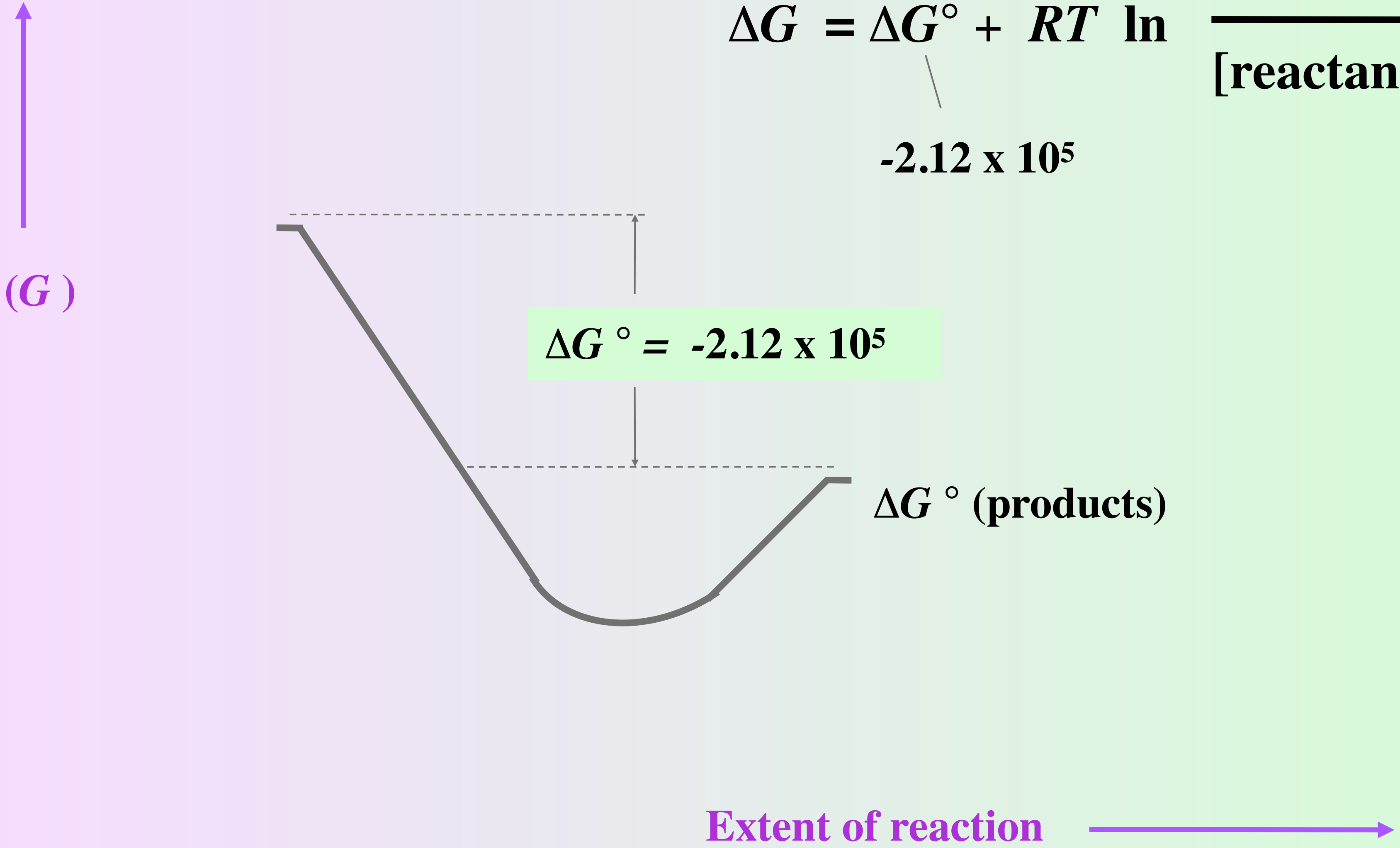
$$= 1\text{mol}(-147.2\ \text{kJ/mol}) - [\ 1\text{mol}(64.98\ \text{kJ/mol})\ ]$$

$$= -212.18\ \text{kJ}$$

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

1M 1M

$$\Delta G = \underbrace{\Delta G^\circ}_{-2.12 \times 10^5} + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

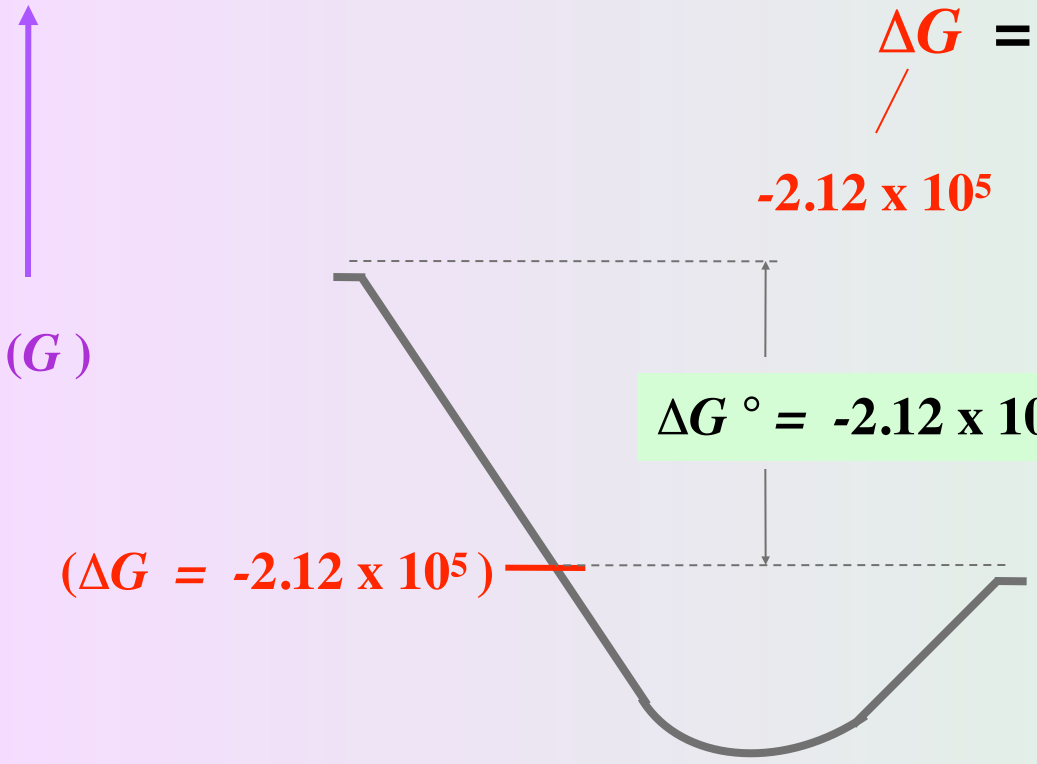


$$Cu^{2+}\,(aq) + Zn(s) \rightleftharpoons Zn^{2+}\,(aq) + Cu\,(s)$$

25°C

1M **1M**

$$\underset{-2.12 \text{ x } 10^{5}}{\Delta G} = \underset{-2.12 \text{ x } 10^{5}}{\Delta G^\circ} + \underset{0}{RT \ln} \frac{[1]}{[1]}$$



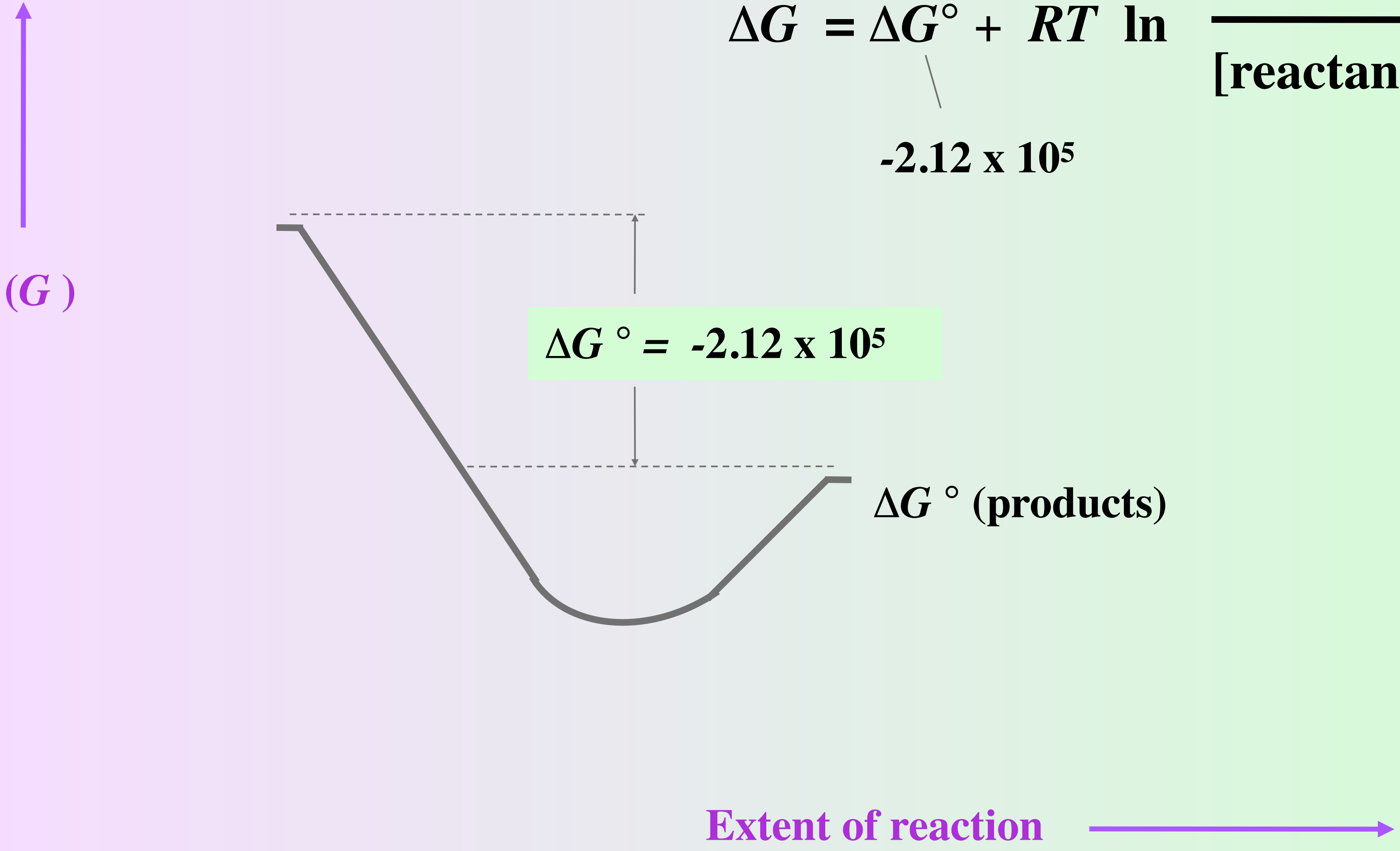
Extent of reaction →

$$Cu^{2+}\,(aq) + Zn(s) \rightleftharpoons Zn^{2+}\,(aq) + Cu\,(s)$$

25°C

0.1M (under Cu^{2+}) 1M (under Zn^{2+})

$$\Delta G = \underbrace{\Delta G^\circ}_{-2.12 \times 10^5} + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

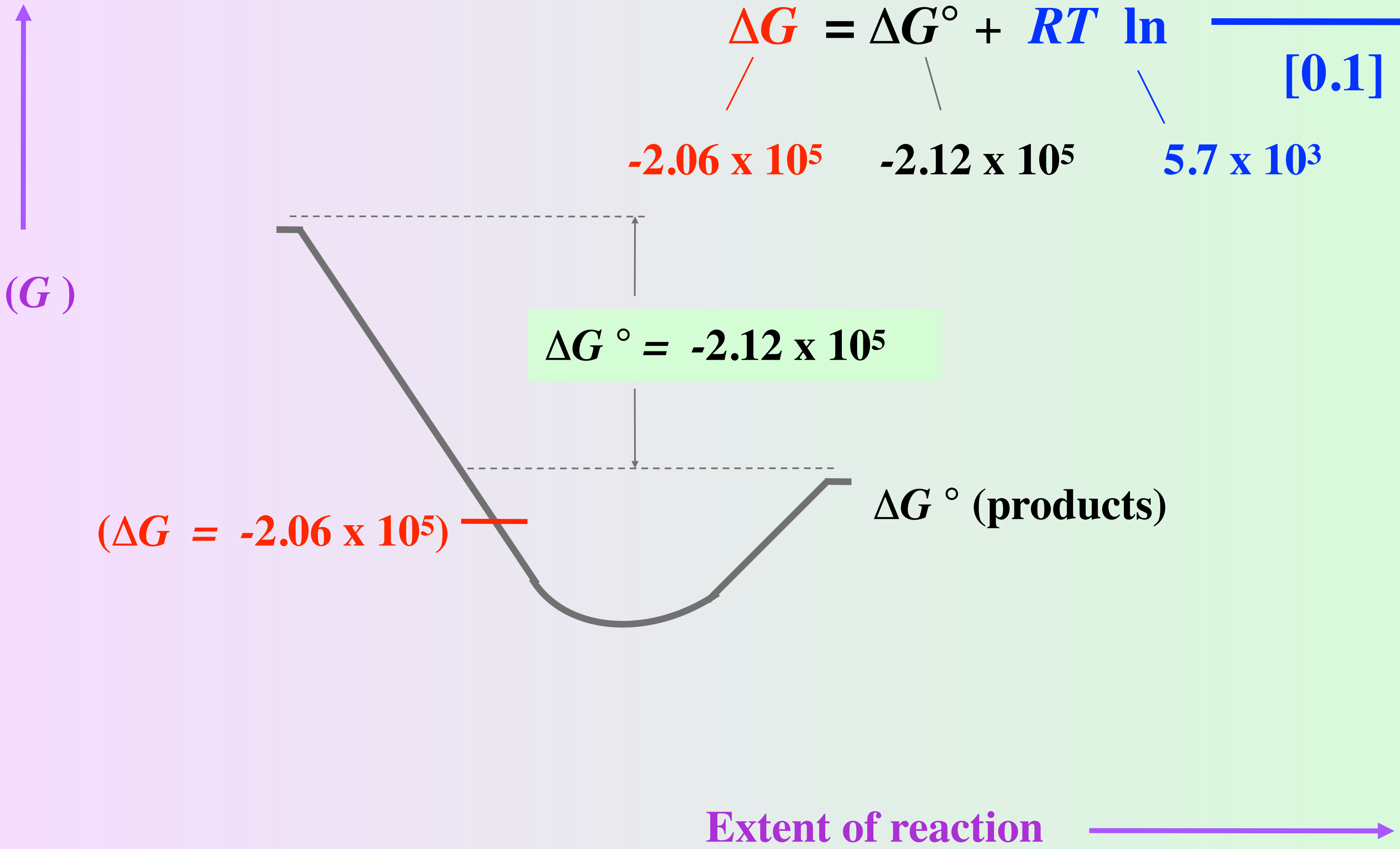


$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

0.1M 1M

$$\Delta G = \Delta G^\circ + RT \ln \frac{[1]}{[0.1]}$$

-2.06×10^5 -2.12×10^5 5.7×10^3



(G)

$\Delta G^\circ = -2.12 \times 10^5$

($\Delta G = -2.06 \times 10^5$)

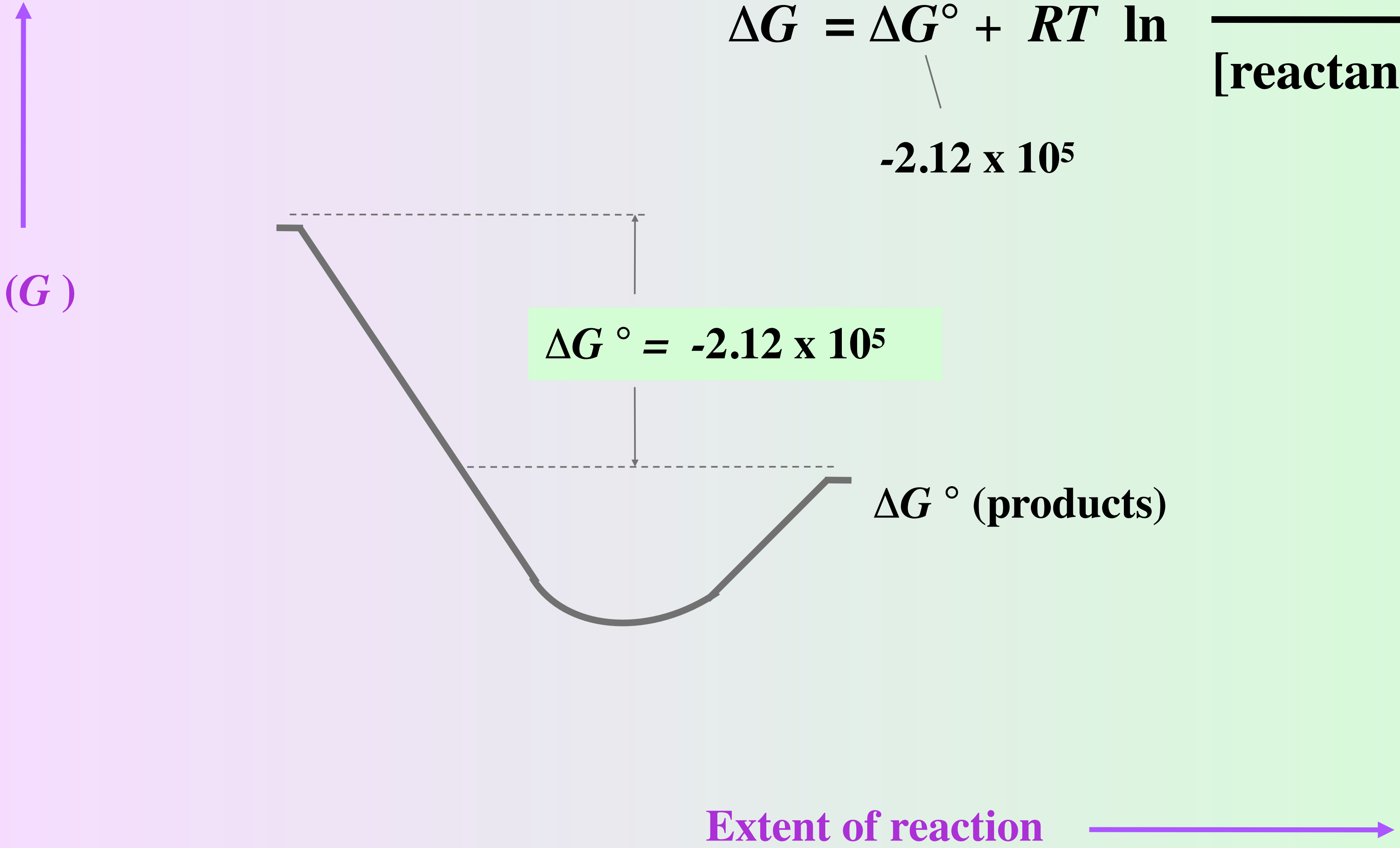
ΔG° (products)

Extent of reaction

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

1M 0.1M

$$\Delta G = \underset{-2.12 \times 10^{5}}{\Delta G^\circ} + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$



(*G*)

$\Delta G^\circ = -2.12 \times 10^5$

ΔG° (products)

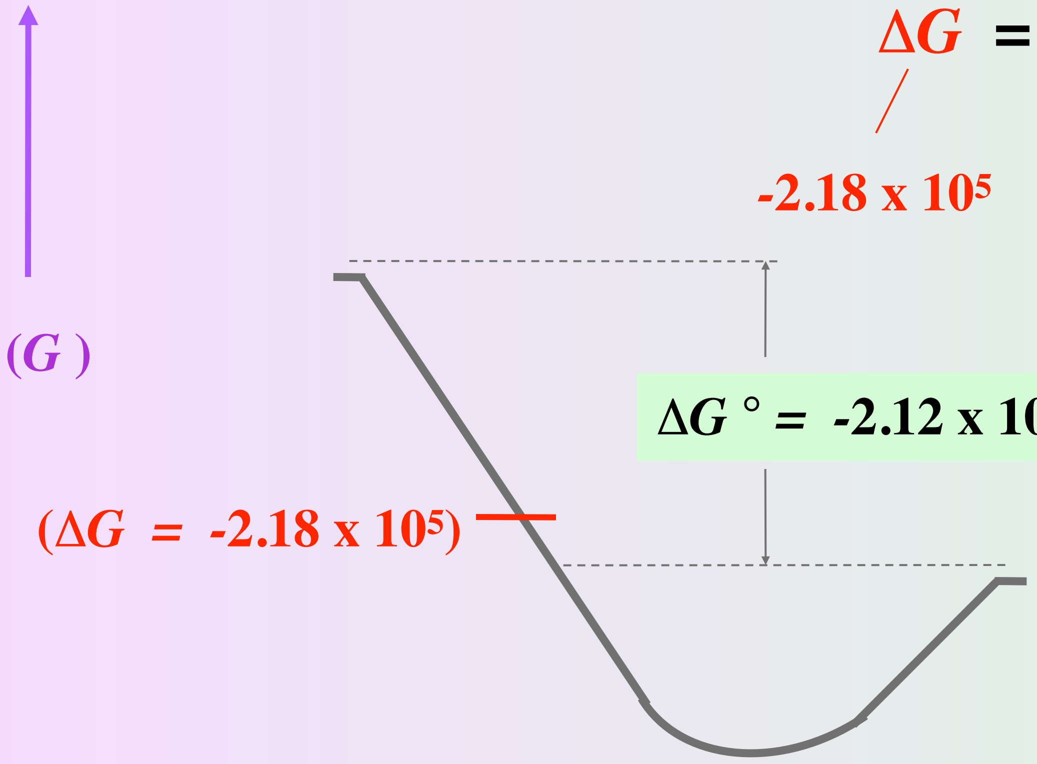
Extent of reaction

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

1M 0.1M

$$\Delta G = \Delta G^\circ + RT \ln \frac{[0.1]}{[1]}$$

-2.18×10^5 -2.12×10^5 -5.7×10^3



(*G*)

$\Delta G^\circ = -2.12 \times 10^5$

$(\Delta G = -2.18 \times 10^5)$

ΔG° (products)

Extent of reaction →

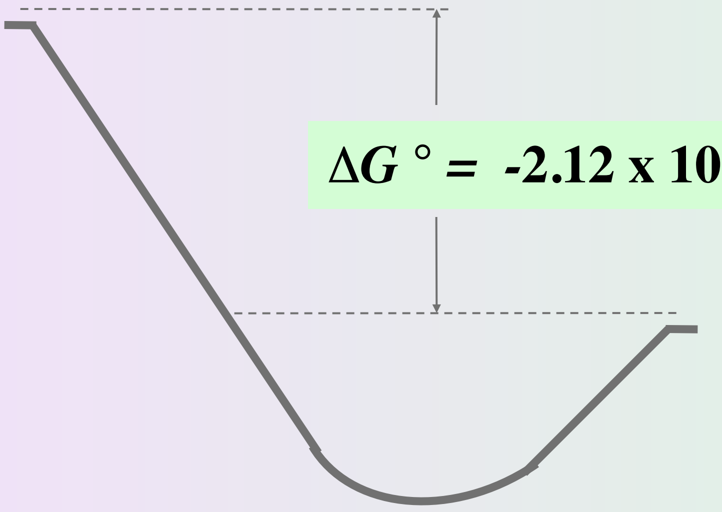
$Cu^{2+}\,(aq) \;+\; Zn(s) \rightleftharpoons Zn^{2+}\,(aq) \;+\; Cu\,(s)$ 25°C

6.90×10^{-38} M 1M

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

-2.12×10^{5}

(*G*)



$\Delta G^\circ = -2.12 \times 10^{5}$

ΔG° (products)

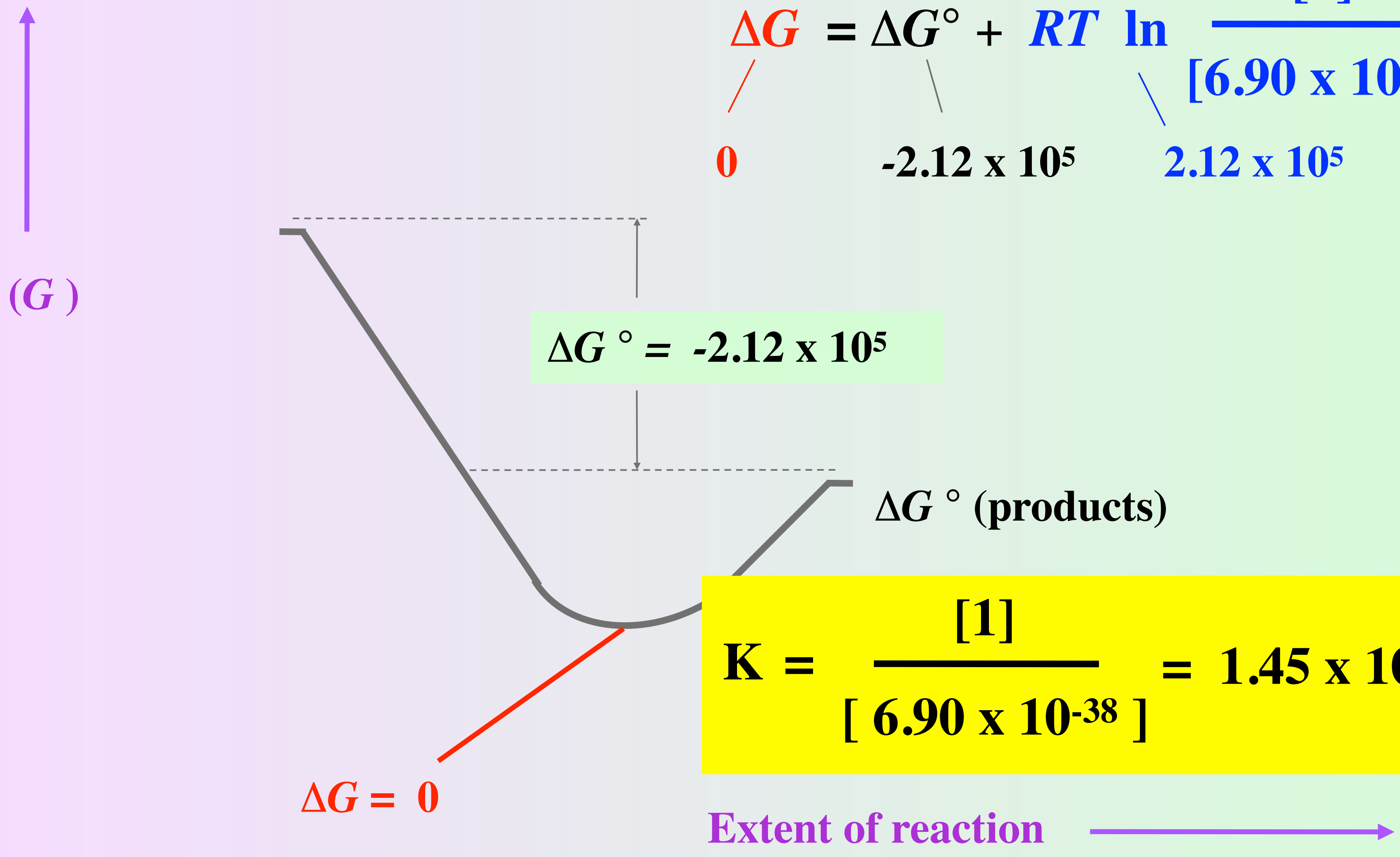
Extent of reaction

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

6.90×10^{-38} M 1M

$$\Delta G = \Delta G^\circ + RT \ln \frac{[1]}{[6.90 \times 10^{-38}]}$$

0 -2.12×10^{5} 2.12×10^{5}



$$K = \frac{[1]}{[6.90 \times 10^{-38}]} = 1.45 \times 10^{37}$$

Cell potential and concentration

the dependence of the cell potential on concentration results directly from the dependence of free energy on concentration

$$\Delta G = \Delta G^{o} + RTln\,(Q)$$

$$-n\,f\,\varepsilon = -n\,f\,\varepsilon^{o} + RTln\,(Q)$$

$$\varepsilon = \varepsilon^{o} - \frac{RT}{n\,f}\,ln\,(Q)$$

$$\varepsilon = \varepsilon^{o} - \frac{0.0592\text{ v}}{n}\,log\,\frac{[\text{products}]}{[\text{reactants}]}$$

$$\underset{\text{1M}}{Cu^{2+}}\,(aq) + Zn(s) \rightleftharpoons \underset{\text{1M}}{Zn^{2+}}\,(aq) + Cu\,(s) \qquad 25^{o}C$$

$$\varepsilon = \underset{\text{1.10 V}}{\varepsilon^{o}} - \frac{0.0592v}{n}\, log\, \frac{[\text{products}]}{[\text{reactants}]}$$

$Cu^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ 25°C

1M 1M

$$\varepsilon = \varepsilon^{o} - \frac{0.0592v}{2} \log \frac{[1]}{[1]}$$

1.10 V 1.10 V 0

$Cu^{2+}\,(aq) + Zn(s) \rightleftharpoons Zn^{2+}\,(aq) + Cu\,(s)$ 25°C

0.1M 1M

$$\varepsilon = \varepsilon^{o} - \frac{0.0592\text{v}}{n}\,\log\frac{[\text{products}]}{[\text{reactants}]}$$

1.10 V

$Cu^{2+}\ (aq) + Zn(s) \leftrightarrows Zn^{2+}\ (aq) + Cu\ (s)$ 25°C

0.1M 1M

$$\varepsilon = \varepsilon^{o} - \frac{0.0592v}{2} \log \frac{[1]}{[0.1]}$$

1.07 V 1.10 V 0.0296

$Cu^{2+}\ (aq) + Zn(s) \rightleftharpoons Zn^{2+}\ (aq) + Cu\ (s)$ 25°C

1M 0.1M

$$\varepsilon = \varepsilon^{o} - \frac{0.0592v}{n}\ log\ \frac{[\text{products}]}{[\text{reactants}]}$$

1.10 V

$Cu^{2+}\,(aq) + Zn(s) \rightleftharpoons Zn^{2+}\,(aq) + Cu\,(s)$ 25°C

1M 0.1M

$$\varepsilon = \varepsilon^{\circ} - \frac{0.0592\text{v}}{2}\, log\, \frac{[0.1]}{[1]}$$

1.13 V 1.10 V -0.0296

$Cu^{2+}\,(aq) + Zn(s) \rightleftharpoons Zn^{2+}\,(aq) + Cu\,(s)$ 25°C

6.90×10^{-38} M 1M

$$\varepsilon = \varepsilon^{o} - \frac{0.0592\text{v}}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

1.10 V

$Cu^{2+}\,(aq)\ +\ Zn(s) \rightleftharpoons Zn^{2+}\,(aq)\ +\ Cu\,(s)$ 25°C

6.90×10^{-38} M 1M

$$\underset{0}{\varepsilon} = \underset{1.10\text{ V}}{\varepsilon^{o}} - \frac{0.0592\text{v}}{2}\ \underset{1.1}{\log \frac{[1]}{[6.90 \times 10^{-38}]}}$$

$$K = \frac{[1]}{[\ 6.90 \times 10^{-38}\ ]} = 1.45 \times 10^{37}$$