$$dU = dq + dw$$

❶ ❷

$$dU = T\,dS - P\,dV + dw_{electrical}$$

❶ $dq_{rev} = T\,dS$

❷ $dw = -P\,dV + dw_{electrical}$

❸ $dH_P = dU_P + P\,dV$

$$dG_T = dH_T - T\,dS$$

❸

$$= dU_{T,P} + P\,dV - T\,dS$$

$$= \cancel{T\,dS} - \cancel{P\,dV} + dw_{electrical} + \cancel{P\,dV} - \cancel{T\,dS}$$

$$\boxed{dG_{T,P} = dw_{electrical}}$$

Electrical work is just the amount of charge Q and the potential $\mathcal{V}$ through which we move it. Voltage, J coulomb^{-1}, is electric potential energy per unit charge

$$w_{electrical} = \mathcal{V}Q$$

$$Q = n\mathcal{F}$$

$\mathcal{F}$ is the charge carried by 1 mole of electrons = 96485.3365 ± 0.0021 coulombs per mole

A process is spontaneous when the change in its Gibbs function is negative; and the convention of negative sign for work is associated with work the system does on the surroundings.

Must ***choose a convention for the sign of the cell potential*** so that it is consistent with the signs for ΔG and work. If we ***choose to associate a positive potential with a spontaneous process***, then we need a negative sign in the equation relating Δ**G** to EMF or voltage $\mathcal{E}$

$$\Delta \boldsymbol{G}_{T,P} = - \mathcal{w}_{electrical} = - n\mathcal{F}\mathcal{E} \quad \text{joules}$$

$\mu = \mu^{\ominus} + RT \ln \boldsymbol{a}$

$\boldsymbol{G} = \boldsymbol{G}^{\ominus} + RT \ln \boldsymbol{a}$

Standard conditions: $^{\ominus}$, sometimes hypothetical, corresponds to unit activity

For a reaction, aA + bB → cC + dD

$$\Delta_{rxn}\boldsymbol{G}_{T,P} = \Delta_{rxn}\boldsymbol{G}_{T}^{\ominus} + RT \ln \frac{\boldsymbol{a}_C^{\,c}\boldsymbol{a}_D^{\,d}}{\boldsymbol{a}_A^{\,a}\boldsymbol{a}_B^{\,b}}$$

At equilibrium, $\Delta_{rxn}\boldsymbol{G}_{T,P} = 0$

$\Delta_{rxn}\boldsymbol{G}_{T}^{\ominus} = -\ RT \ln K$

K corresponds to activities at chemical equilibrium

$$\mathcal{E}_{cell} = \mathcal{E}^{\ominus}_{cell} - \frac{RT}{n\mathcal{F}} \ln \frac{\boldsymbol{a}_C^{\,c}\boldsymbol{a}_D^{\,d}}{\boldsymbol{a}_A^{\,a}\boldsymbol{a}_B^{\,b}}$$

At equilibrium $\mathcal{E}_{cell} = 0$

$$\mathcal{E}^{\ominus}_{cell} = \frac{RT}{n\mathcal{F}} \ln K$$

Conventions equil. electrochemistry:

- Right hand side of the cell (as written in cell diagram) is *positive*
- A reaction that abstracts electrons from the electrode makes it *positive*
- Tables of half electrode potentials are of *reduction* potentials, e.g.,

$$Cu^{+2} + 2e = Cu^{0}.$$

cell diagram:

$$- \; Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu \; +$$

Half reactions:

RHS $Cu^{2+} + 2\ e \rightarrow Cu$ RED

LHS $Zn \rightarrow Zn^{2+} + 2e$ OXID

$\mathcal{E}_{\text{total}} = \mathcal{E}_{\text{right}} + \mathcal{E}_{\text{left}}$

$\mathcal{E}^{\ominus}_{\text{right}}$ = from table of std *reduction* half cell potentials

$\mathcal{E}^{\ominus}_{\text{left}}$ = *reverse sign* from table of half cells

cell reaction:

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

Knowledge of the standard electrode potentials of the half-cell reactions allows the thermodynamically favored direction of the cell reaction (at standard conditions) to be established. If $\mathcal{E}^{\ominus}_{\text{cell}} > 0$ then $K > 1$, which means that the forward direction of the overall reaction, when written as the summation of the cell reaction at the right-hand electrode (a reduction process) and the cell reaction at the left-hand electrode (an oxidation process) is the spontaneous direction of the cell reaction. If $\mathcal{E}^{\ominus}_{\text{cell}} < 0$ then $K < 1$, so the reverse reaction will be the spontaneous one, or energy will be required to drive the reaction in the forward direction of the cell reaction.

EXAMPLE:

Given the following electrochemical cell:

$Fe_{(s)} + Sn^{4+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$

(i) Calculate the standard cell potential.

(ii) Under standard conditions, will this reaction occur spontaneously as written?

(iii) Calculate the equilibrium constant, *K*.

Standard reduction potentials are: $\mathcal{E}^{\ominus}_{Fe2+/Fe} = -0.44$ V;

$\mathcal{E}^{\ominus}_{Sn4+/Sn2+} = +0.15$ V.

Half reduction potentials are:

$Fe^{2+} + 2e \rightarrow Fe_{(s)}$ $E^\circ = -0.44V$
$Sn^{4+} + 2e \rightarrow Sn^{2+}$ $E^\circ = +0.15V$

The half-cell reactions are:

Oxidation: $Fe_{(s)} \rightarrow Fe^{2+} + 2e$
Reduction: $Sn^{4+} + 2e \rightarrow Sn^{2+}$

(i) The standard cell potential

$$\mathcal{E}^{\ominus}_{cell} = \mathcal{E}^{\ominus}_{Sn4+/Sn2+} + -(\mathcal{E}^{\ominus}_{Fe2+/Fe})$$

$$= 0.15 + -(-0.44) = +0.59\ V$$

(ii) Positive $\mathcal{E}^{\ominus}_{cell}$ means reaction will occur spontaneously at std conditions

(iii) Find equilibrium constant

$$\mathcal{E}^{\ominus}_{cell} = \frac{RT}{n\mathcal{F}} \ln K$$

$$\ln K = \frac{2(96485)(0.59)}{8.31451\ (298)} = 45.96$$

$K = 9.13 \times 10^{19}$ **Answer**

EXAMPLE:

Given the following galvanic cell:

$Ag_{(s)}|Ag^{+}(3.0\times10^{-4}\ M)||Fe^{3+}(1.1\times10^{-3}\ M),\ Fe^{2+}(0.040\ M)|Pt_{(s)}$

Predict the cell potential at 25°C.

$Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + e$ Anode

$Fe^{3+}_{(aq)} + e \rightarrow Fe^{2+}_{(aq)}$ Cathode

$Ag_{(s)} + Fe^{3+}_{(aq)} \rightarrow Ag^{+}_{(aq)} + Fe^{2+}_{(aq)}$ Net

$$\mathcal{E}_{cell} = \mathcal{E}^{\ominus}_{cell} - \frac{RT}{n\mathcal{F}} \ln \frac{\boldsymbol{a}_{Ag+}\boldsymbol{a}_{Fe2+}}{\boldsymbol{a}_{Ag}\,\boldsymbol{a}_{Fe3+}}$$

$\boldsymbol{a}_{Ag} = 1$ pure solid substance

$n = 1$

The standard cell potential

$$\mathcal{E}^{\ominus}_{cell} = \mathcal{E}^{\ominus}_{Fe3+/Fe2+} + -(\mathcal{E}^{\ominus}_{Ag+/Ag})$$

$$= +0.77 + -(+0.80) = -0.03\ V$$

Assuming mean ionic activity coefficient =1:

$$\mathcal{E}_{\text{cell}} = -0.03 - \frac{(8.31451)(298)}{(1)\,96485} \ln \frac{(3.0\text{x}10^{-4})(0.040)}{(1)(\,1.1\text{x}10^{-3})}$$

$$\mathcal{E}_{\text{cell}} = +0.086\ \text{V}$$ **Answer**

EXAMPLE:

An electrochemical cell consists of a silver electrode in contact with 346 mL of 0.0100 M $AgNO_3$ solution and a magnesium electrode in contact with 288 mL of 0.100 M $Mg(NO_3)_2$ solution

(i) Predict the cell potential at 25°C.
(ii) A current is drawn from the cell until 1.20 g of silver has been deposited at the silver electrode. Calculate the cell potential at this stage of operation.

$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e$ Anode

$Ag^{+}_{(aq)} + e \rightarrow Ag_{(s)}$ Cathode

$Mg_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Ag_{(s)}$ Net

$$\mathcal{E}_{cell} = \mathcal{E}^{\ominus}_{cell} - \frac{RT}{n\mathcal{F}} \ln \frac{\boldsymbol{a}_{Ag}\,\boldsymbol{a}_{Mg2+}}{\boldsymbol{a}_{Mg}\,(\boldsymbol{a}_{Ag+})^2}$$

$\boldsymbol{a}_{Ag} = 1$, $\boldsymbol{a}_{Mg} = 1$, pure solid substances

(i) The standard cell potential

$$\mathcal{E}^{\ominus}_{cell} = \mathcal{E}^{\ominus}_{Ag+/Ag} + -(\mathcal{E}^{\ominus}_{Mg2+/Mg})$$

$$= +0.80 + -(-2.37) = +3.17 \text{ V}$$

Assuming mean ionic activity coefficient =1:

$$\mathcal{E}_{cell} = +3.17$$

$$- \frac{(8.31451)(298)}{(2)\ 96485} \ln \frac{(1)(0.0100)}{(1)(0.0100)^2}$$

$\mathcal{E}_{cell} = +3.14$ V **Answer**

(ii) first find the number of moles of Ag deposited in order to find the new concentration of $Ag^{+}_{(aq)}$

Originally in solution,

$0.100 \text{ mol L}^{-1}\ Ag^{+}_{(aq)} \bullet 0.346 \text{ L} =$

$0.0346 \text{ mol } Ag^{+}_{(aq)}$

$$\text{Ag deposited} = 1.20 \text{ g} \bullet \frac{1 \text{ mol}}{107.9 \text{ g}}$$

$$= 0.0111 \text{ mol}$$

Ag remaining in solution,

0.0346 - 0.0111 = 0.0235 mol

$[Ag^{+}_{(aq)}] = 0.0235 \text{ mol} / 0.346 \text{ L}$

$= 0.0679 \text{ M}$

Originally in solution,

$0.100\ \text{mol L}^{-1}\ \text{Mg}^{2+}{}_{(aq)} \bullet 0.288\ \text{L} =$

$0.0288\ \text{mol Mg}^{2+}{}_{(aq)}$

Reaction which deposited $\text{Ag}_{(s)}$ also produced more $\text{Mg}^{2+}{}_{(aq)}$:

$$\text{Mg}_{(s)} + 2\text{Ag}^{+}{}_{(aq)} \rightarrow \text{Mg}^{2+}{}_{(aq)} + \text{Ag}_{(s)}$$

New moles $\text{Mg}^{2+}{}_{(aq)}$ in solution,

$$\frac{0.0288 + \tfrac{1}{2}(0.0111)}{0.288\ \text{L}}\ \text{mol}$$

$$[\text{Mg}^{2+}{}_{(aq)}] = 0.199\ \text{M}$$

Assuming mean ionic activity coefficient =1:

$$\mathcal{E}_{cell} = +3.17$$

$$- \frac{(8.31451)(298)}{(2)\ 96485} \ln \frac{(1)(0.199)}{(1)(0.0679)^2}$$

$$\mathcal{E}_{cell} = +3.13\ \text{V}$$

Answer

EXAMPLE:

Electroplating of a copper crown is carried out in an aqueous solution of KCN with a current density of 100 A/m^2, using an electrochemical reaction:

$Au(CN)_2^- + e \rightarrow Au + 2CN^-$

The surface area of the crown is 0.73 m^2. The density of gold is 19.32 g/cm^3 and the atomic mass of gold is 196.967 g/mol. Determine the time required for plating 0.20 mm thickness of gold on the crown surface.

We need to find the moles of Au plated, which will provide us with the required number of moles of electrons that passed as current.

moles of gold =

$$0.020 \text{ cm} \bullet 0.73 \times 10^4 \text{ cm}^2 \bullet 19.32 \text{ g/cm}^3 \bullet \frac{1 \text{ mol}}{196.967 \text{ g}}$$

$$= 14.3208 \text{ mol}$$

$1 \text{ Amp} = 1 \text{ C s}^{-1}$

$$14.3208 \text{ mol of electrons} \bullet 96485 \text{ C mol}^{-1}$$

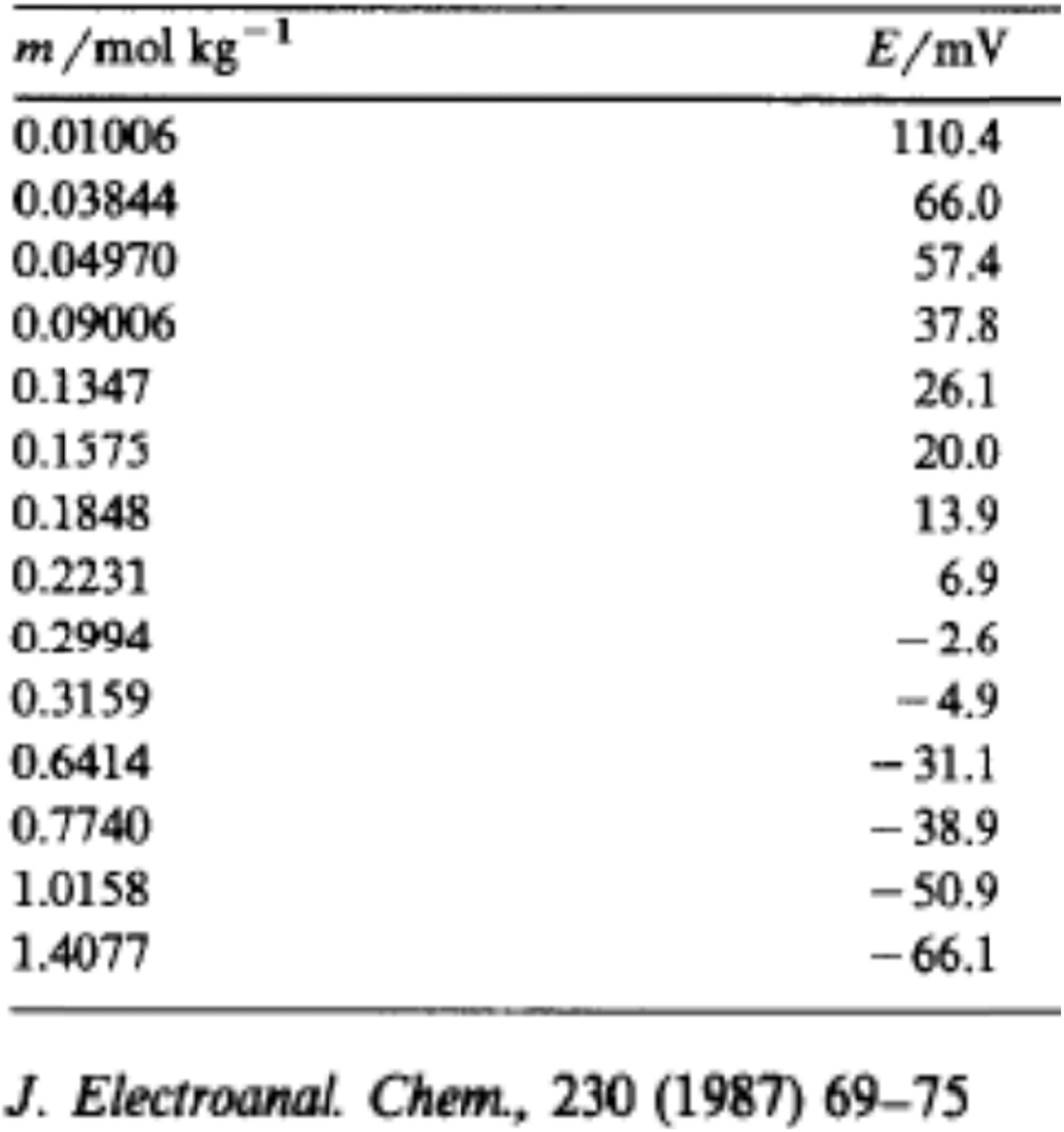
$$= 0.73 \text{ C s}^{-1} \bullet (\text{time}) \text{ s}$$

$$\text{time} = 14.3208(96485)/0.73$$

$$= 18928 \text{ s or } 5.26 \text{ hours}$$

Answer

EXAMPLE:



m /mol kg^{-1}	E/mV
0.01006	110.4
0.03844	66.0
0.04970	57.4
0.09006	37.8
0.1347	26.1
0.1575	20.0
0.1848	13.9
0.2231	6.9
0.2994	−2.6
0.3159	−4.9
0.6414	−31.1
0.7740	−38.9
1.0158	−50.9
1.4077	−66.1

J. Electroanal. Chem., 230 (1987) 69–75

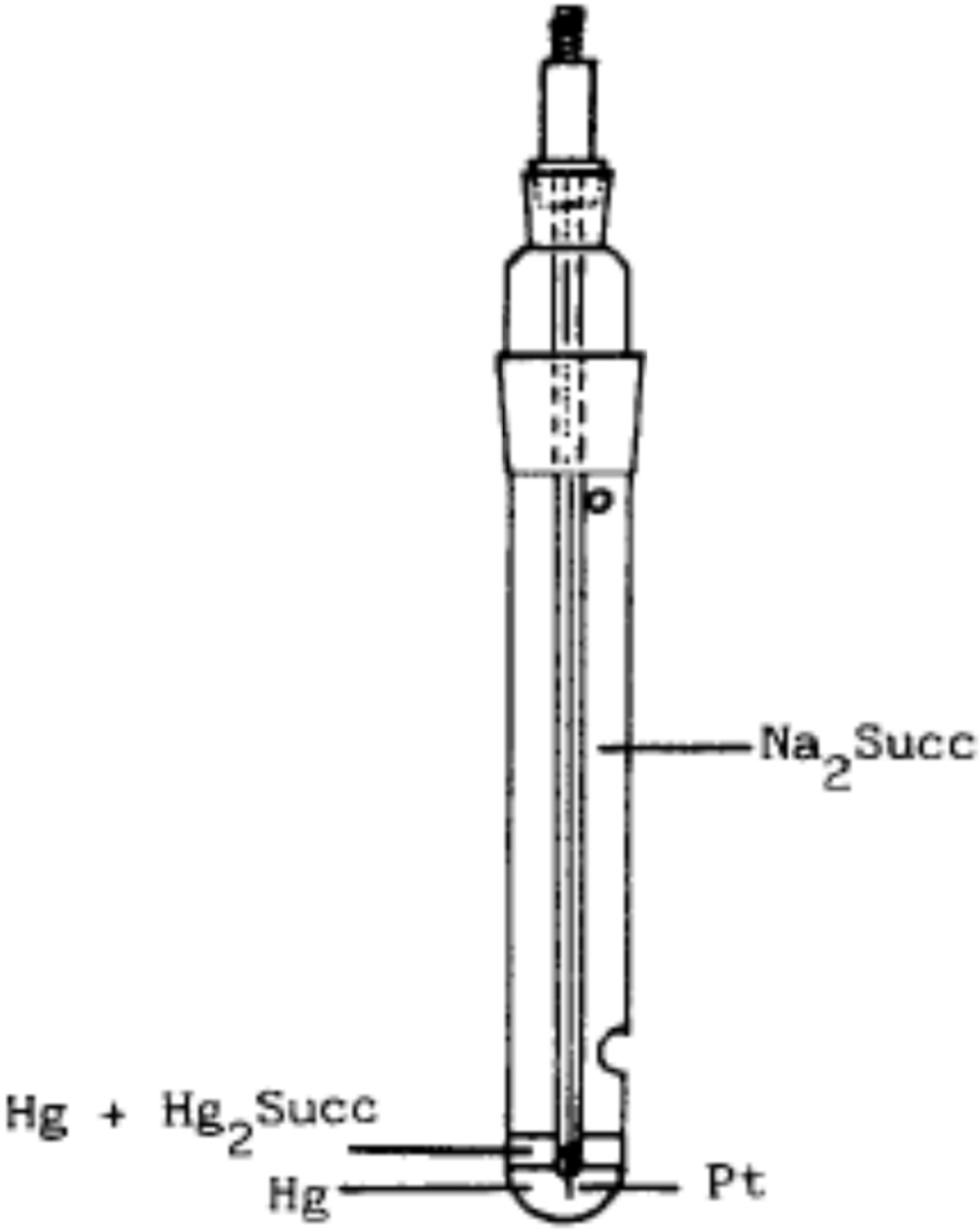
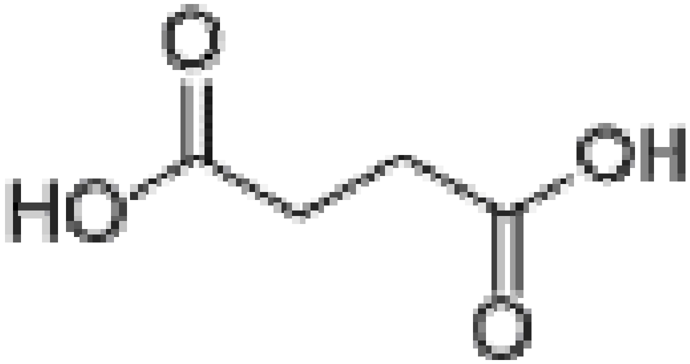


Fig. 1. Scheme of the $Hg_2Succ|Hg$ electrode used.

The emf of the $Hg_2Succ|Hg$ electrode cell at 25°C shown in the figure has been measured against a standardized glass electrode as a function of the molality ***m*** of the Na_2Succ solution. (The values are shown in the table.) This is the salt of succinic acid or butanedioic acid:



$C_4H_6O_4$ 118.09

$Succ^{2-} = [C_4H_4O_4]^{2-}$

Determine the $\mathcal{E}^{\ominus}{}_{\mathrm{Hg2Succ|Hg}}$ by making the appropriate plot of the experimental data and knowing the standard potential of the standardized glass electrode is $(486.4 \pm 0.3)\times10^{-3}$ V.

$$\mathcal{E}^{\ominus}{}_{\mathrm{cell}} = \mathcal{E}^{\ominus}{}_{\mathrm{Hg2Succ|Hg}} - (-0.134)$$

$$\mathcal{E}_{\mathrm{cell}} = \mathcal{E}^{\ominus}{}_{\mathrm{cell}} - \frac{RT}{2\mathcal{F}} \ln (\boldsymbol{a}_{\mathrm{Na+}})^2 \boldsymbol{a}_{\mathrm{Succ2-}}$$

$$\mathcal{E}_{\mathrm{cell}} = \mathcal{E}^{\ominus}{}_{\mathrm{cell}} - \frac{RT}{2\mathcal{F}} \ln (\boldsymbol{m})^3 \gamma_{\pm}{}^3$$

$$\mathcal{E}_{\mathrm{cell}} + \frac{3RT}{2\mathcal{F}} \ln \boldsymbol{m} = \mathcal{E}^{\ominus}{}_{\mathrm{cell}} - \frac{3RT}{2\mathcal{F}} \ln \gamma_{\pm}$$

$(3RT/2\mathcal{F}) = 0.03852$ V

$\gamma_{\pm}$ is the mean ionic activity coefficient which is a function of $\boldsymbol{m}$

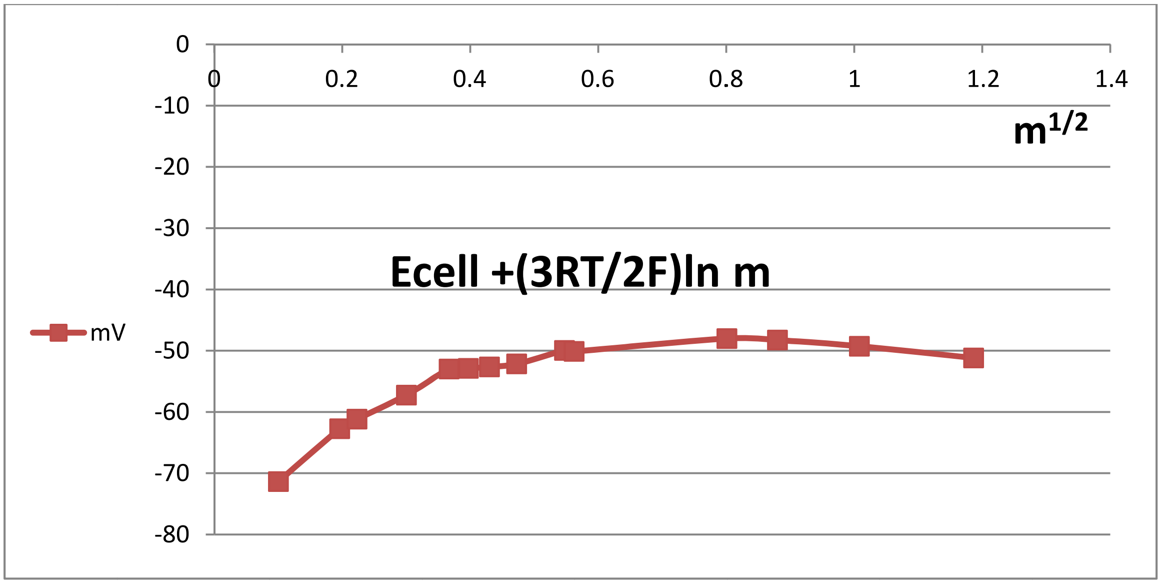
$\mathcal{E}_{\text{cell}}+0.03852\ \ln \boldsymbol{m} = \mathcal{E}^{\ominus}_{\text{cell}} - 0.03852\ \ln\gamma_{\pm}$

As suggested by the Debye-Huckel limiting behavior, $\gamma_{\pm}$ goes as $\mathrm{I}^{½}$

$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ $\mathrm{I} = (½)\{2\boldsymbol{m}(+1)^2 + \boldsymbol{m}(-2)^2\}=(5/2)\boldsymbol{m}$

Since $\gamma_{\pm}$ goes to 1 at infinitely dilute limit, we use a plot of

$\mathcal{E}_{\text{cell}} + 0.03852\ \ln \boldsymbol{m}$ vs. $\boldsymbol{m}^{½}$



At the intercept, $m^{½} \to 0$, $\gamma_{\pm} \to 1$ and $\{\mathcal{E}_{\text{cell}} + 0.03852\ \ln \boldsymbol{m}\} \to \mathcal{E}^{\ominus}_{\text{cell}}$

from which we get $\mathcal{E}^{\ominus}_{\text{Hg2Succ|Hg}}$ by

$\mathcal{E}^{\ominus}_{\text{cell}} = \mathcal{E}^{\ominus}_{\text{Hg2Succ|Hg}} - (486.4\ \text{mV})$

Intercept is ≈ -80 mV

-80 mV= $\mathcal{E}^{\ominus}_{\mathrm{Hg2Succ|Hg}}$ -(486.4 mV)

$\mathcal{E}^{\ominus}_{\mathrm{Hg2Succ|Hg}} \approx$ 406 mV **Answer**

Incidentally, a more accurate representation of the behavior of $\gamma_{\pm}$ than the Debye-Huckel limit yields 425 mV.

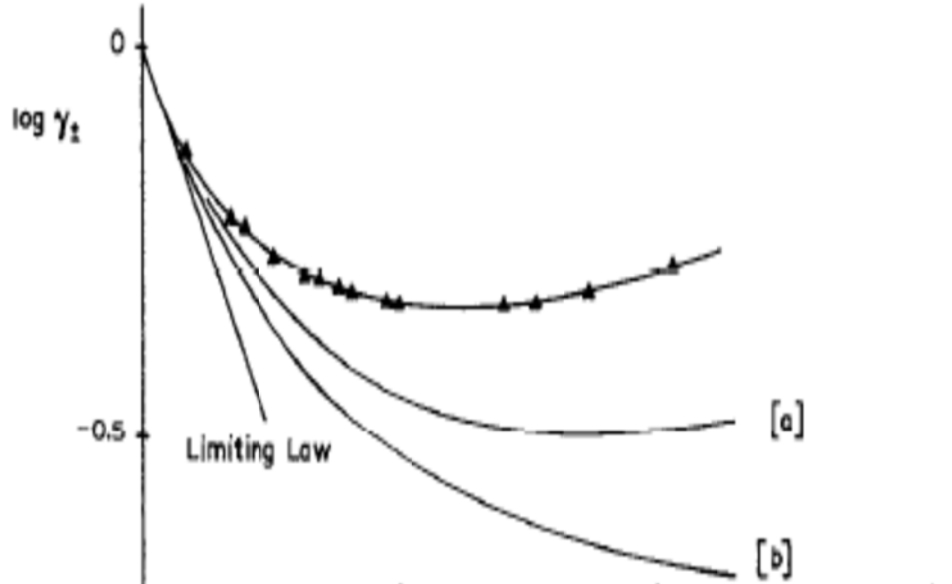
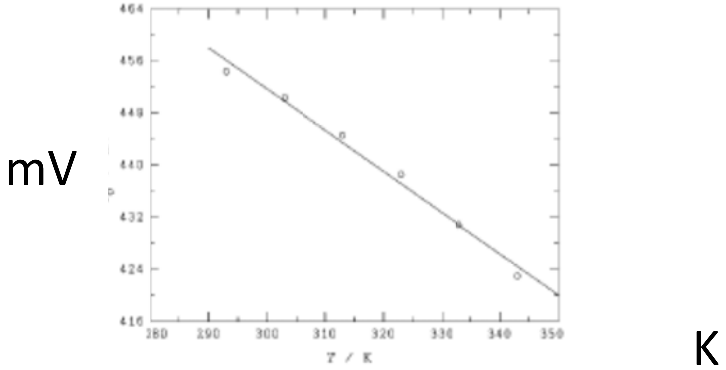


Fig. 2. Plot of log $\gamma_{\pm}$ against $I^{1/2}$. (▲) This work; (a) sodium fumarate and (b) sodium maleate

EXAMPLE:

The temperature dependence of the voltage of a copper-silver cell has been measured and is shown below:



Temperature dependence of the cell voltage of a copper-silver-cell

Find the reaction entropy from the data.

d$\mathbf{G}$ = Vdp - $\mathbf{S}$dT

$(\partial \mathbf{G} / \partial T)_p = - \mathbf{S}$

When applied to products and reactants of a chemical reaction

$(\partial \Delta_{rxn}\mathbf{G} / \partial T)_p = - \Delta_{rxn} \mathbf{S}$

Using $\Delta_{rxn}\mathbf{G}_{T,P} = - n\mathcal{F}\mathcal{E}$ joules,

$n\mathcal{F}(\partial \mathcal{E} / \partial T)_p = \Delta_{rxn} \mathbf{S}$

Cathode (reduction) : $Cu^{2+} + 2e \rightarrow Cu$
Anode (oxidation): $Zn \rightarrow Zn^{2+} + 2e$
Cell reaction: $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

The reaction entropy for this reaction is therefore the value of $n\mathcal{F}(\partial \mathcal{E}/\partial T)_p$.

The temperature coefficient of the cell voltage (slope of the plot) is $(\partial \mathcal{E}/\partial T)_p = -0.63$ mV K^{-1}

$\Delta_{rxn}\mathbf{S}$ for $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
$= 2(96485\ C\ mol^{-1})(-0.63\times10^{-3}\ V\ K^{-1})$
$= 121.6\ J\ K^{-1}\ mol^{-1}$ **Answer**