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10. Equilibria in Electrochemical Cells

10.1 Definitions

electrochemical cell consists of two electrodes or metallic conductors in contact with an electrolyte, an ionic conductor. It is a device which can produce electrical work in the surroundings.

electrolytic cell electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

galvanic cell electrochemical cell that produces electricity as a result of the spontaneous chemical reaction going on inside it. Electrical work is produced in the surroundings.

oxidation removal of electrons from a species

reduction addition of electrons to a species

anode the electrode at which oxidation occurs

cathode the electrode at which reduction occurs

electrical potential of a point in space $\mathcal{V}$ the work expended in bringing a unit positive charge from infinity, where the electrical potential is zero, to the point in question.

electrical potential difference $\mathcal{E}$ The difference in electrical potential ($\mathcal{V}_2 - \mathcal{V}_1$) between two points is the work expended on taking a unit positive charge from point 1 to point 2.

$$đW_{elec} = \mathcal{E}\,\mathrm{d}Q$$

electrode potential is the electrical potential $\mathcal{V}$ of each electrode

electromotive force of the cell

$\mathcal{E} = \mathcal{V}_{\mathrm{right}} - \mathcal{V}_{\mathrm{left}}$

In a galvanic cell the cathode has higher potential than the anode. In an electrolytic cell it is just the reverse.

The notation for cells: vertical bar | denotes phase boundaries:
Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)

A liquid junction is denoted by ⋮
Zn(s)|$ZnSO_4$(aq) ⋮ $CuSO_4$(aq)|Cu(s)

An interface for which the junction potential has been eliminated is shown as ||
Zn(s)|$ZnSO_4$(aq)||$CuSO_4$(aq)|Cu(s)

The cell reaction is written on the assumption that the right-hand electrode is the cathode, and ∴ the spontaneous reaction is one in which reduction is taking place in the right hand compartment. If it turns out that the reverse of the cell reaction is spontaneous then the cell diagram has to be turned the other way around.

Example, the cell diagram:

$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

has the following cell reaction:

Right: $Cu^{2+}(aq) + 2e- \rightarrow Cu(s)$

Left: $Zn^{2+}(aq) + 2e- \rightarrow Zn(s)$

Right -Left =

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

Agreed-upon Conventions

Right **R**edu**C**tion **C**athode

Oxid**A**tion **A**node

$\mathcal{E}$ positive spontaneous cell reaction

cell diagram:

$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

Right: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Left: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

Right **R**eduction takes place ∴ no need to change the way it is written.

Left has to be changed around

Right -Left = the cell reaction, which is

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

Cathode reaction: Redu**c**tion

Right: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ keep

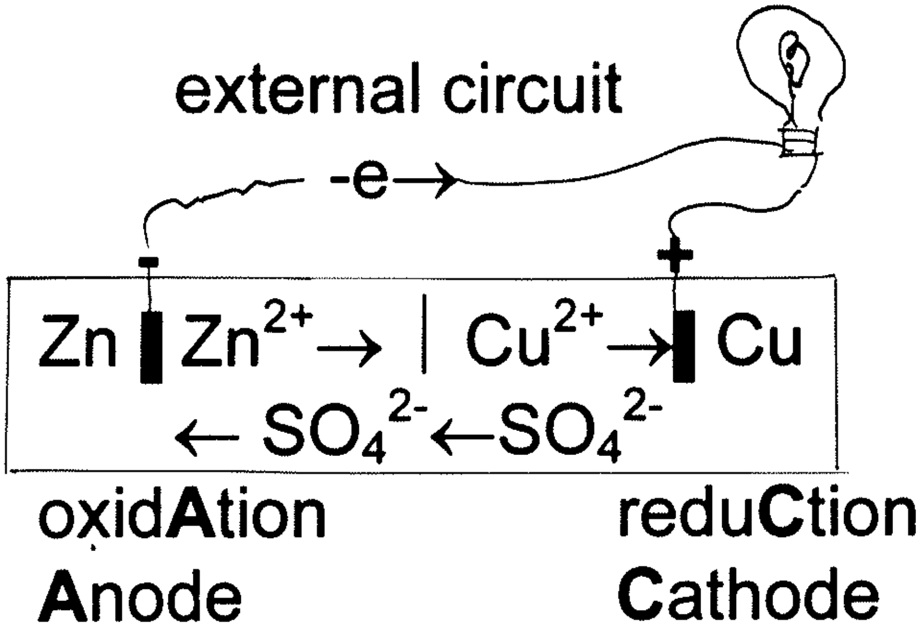
Anode reaction: Oxid**a**tion

reverse to $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$\mathcal{E}$ = +1.1 volt positive ∴ spontaneous cell reaction

$\Delta_{rxn}\boldsymbol{G} = -2\mathcal{F}\mathcal{E}$ negative ∴ spontaneous reaction

cell diagram is written as a galvanic cell


external circuit
-e→
−
+
Zn | Zn^{2+}→ | Cu^{2+}→| Cu
← SO_4^{2-} ←SO_4^{2-}
oxid**A**tion
Anode
redu**C**tion
Cathode

10.2 Gibbs Free Energy of Formation of an Ion in Solution

$d\boldsymbol{G} = \text{đ}W_{other,\ rev}$

If we transfer a number of electrons carrying a charge, dQ, from M to M′, the work done on the system is $\text{đ}W_{elec}$. If the transfer is done reversibly, the work produced by the system is equal to the decrease in Gibbs energy of the system

$$\text{đ}W_{elec} = d\boldsymbol{G}.$$

$$\text{đ}W_{elec} = (\mathcal{V}' - \mathcal{V})dQ \qquad d\boldsymbol{G} = \mu'_{e^-}dn - \mu_{e^-}dn$$

$-N_{Avog}e = -\mathcal{F}$ is the charge carried by 1 mole of electrons,
the Faraday $\mathcal{F} = 96490$ coulombs

$dQ = -\mathcal{F}\,dn$

$$\text{đ}W_{elec} = (\mathcal{V}' - \mathcal{V})(-\mathcal{F}\,dn) \qquad d\boldsymbol{G} = (\mu'_{e^-} - \mu_{e^-})dn$$

$$\mu'_{e^-} - \mu_{e^-} = -\mathcal{F}(\mathcal{V}' - \mathcal{V})$$

For the purposes of considering the chemical potential of an electrochemical system we have to consider all the parts and for each part we have to consider the "purely electrical" and the "chemical" part of the chemical potential:

1. the electrons in the metal wire electrodes have (a) a purely electrical part that is - $e\mathcal{V}$, or - $eN_{avog}\mathcal{V}$ for one mole of electrons, (b) a chemical part that is unknown and which we conveniently set to zero for all metals.
2. the positive ions M^{z+} within the metal have (a) a purely electrical part that is $+z_i e\mathcal{V}$ or $+z_i eN_{avog}\mathcal{V}$ for one mole of M^{z+} ions, (b) a chemical part that is zero for every pure metal at 25°C and 1 atm.
3. the positive ions M^{z+} in the aqueous solution have no purely electrical part, only a chemical part that is $\mu_{Mz+\,(aq)}$.

4. the negative ions in the aqueous solution have no purely electrical part, only a chemical part that is $\mu_{X^{z-}\,(aq)}$.

The electrochemical potential μ is a measure of the escaping tendency of the electron or the metal ion from the phase that it is in. For example, for one mole,

- $eN_{avog}V$ for electrons within the metal electrode trying to escape the metal to go to a positive ion in solution

$+z_i eN_{avog}V$ for metal ions M^{z+} within the metal electrode trying to escape the metal to go into aqueous solution as a free metal ion.

Assign arbitrarily the chemical part of the chemical potential to zero in every metal, to write $\mu_{e-} = -\mathcal{F}\mathcal{V}$. For the reaction

$$M \rightarrow M^{+z} + ze^-$$

The equilibrium condition is

$$\mu_M = (\mu_{M+z} + z\mathcal{F}\mathcal{V}) - z\mathcal{F}\mathcal{V}$$

or $\mu_M = \mu_{M+z}$

For ions in aqueous solution,

$$\mu_i(T,p,x) = \mu_i{}^{\ominus}{}_T + RT \ln \, \boldsymbol{a}_i(T,p,x)$$

standard state of zero free energy at 25°C and 1 atm:

$\mu^{\ominus}{}_T$ = 0 for elements in their stable state of aggregation.

For the reaction

$$H^+_{(aq)} + e^-_{(Pt)} \rightarrow \tfrac{1}{2}H_{2(g)}$$

The chemical potentials are

$$\mu_{H+(aq)} \qquad \mu_{e-(Pt)} \qquad \tfrac{1}{2}\mu_{H2(g)}$$

The condition for equilibrium is that

$$\mu_{\mathrm{H+(aq)}} + \mu_{\mathrm{e-(Pt)}} = \tfrac{1}{2}\mu_{\mathrm{H2(g)}}$$

$$\mu_{\mathrm{H+(aq)}} = \mu_{\mathrm{H+(aq)}}{}^{\ominus}{}_{T} + RT \ln \boldsymbol{a}_{\mathrm{H+(aq)}}(T,p,x)$$

$$\mu_{\mathrm{e-(Pt)}} = -\mathcal{F}\mathcal{V}_{\mathrm{(H+,H2)}}$$

$$\mu_{\mathrm{H2(g)}} = \mu_{\mathrm{H2(g)}}{}^{\ominus}{}_{T} + RT \ln (\boldsymbol{f}_{\mathrm{H2(g)}}/1)$$

$$\mathcal{F}\mathcal{V}_{\mathrm{(H+,H2)}} = \mu_{\mathrm{H+(aq)}}{}^{\ominus}{}_{T} - \tfrac{1}{2}\mu_{\mathrm{H2(g)}}{}^{\ominus}{}_{T} - RT \ln \boldsymbol{f}^{1/2}/\boldsymbol{a}_{\mathrm{H+}}$$

$$\mathcal{V}_{\mathrm{(H+,H2)}} = \{\mu_{\mathrm{H+(aq)}}{}^{\ominus}{}_{T} - \tfrac{1}{2}\mu_{\mathrm{H2(g)}}{}^{\ominus}{}_{T}\}/\mathcal{F} - (RT/\mathcal{F}) \ln \boldsymbol{f}^{1/2}/\boldsymbol{a}_{\mathrm{H+}}$$

$$\{\mu_{\mathrm{H+(aq)}}{}^{\ominus}{}_{T} - \tfrac{1}{2}\mu_{\mathrm{H2(g)}}{}^{\ominus}{}_{T}\}/\mathcal{F} = \mathcal{V}_{\mathrm{(H+,H2)}}{}^{\ominus}{}_{T}$$

If we assign

$\mathcal{V}_{\mathrm{(H+,H2)}}{}^{\ominus}{}_{T}$ (SHE)= 0, then, $\mu_{\mathrm{H+(aq)}}{}^{\ominus}{}_{T} = 0$ &

and we find that

$$\mathcal{V}_{\mathrm{(H+,H2)}} = -(RT/\mathcal{F}) \ln \boldsymbol{f}^{1/2}/\boldsymbol{a}_{\mathrm{H+(aq)}}$$

This is the **Nernst eqn**. for the hydrogen electrode. In words, the electrode potential of a hydrogen electrode relative to the standard hydrogen electrode (SHE) is related to the activity of H^+ ions in the solution and the fugacity of the H_2 gas over it.

The free energy of the electrons in any metal is measured relative to the value in the SHE.

&The standard free energy $\mu_{M+n(aq)}{}^{\ominus}{}_{T}$ of other ions in aqueous solution is measured relative to that of the H^+ ion in the SHE.

10.3 Thermodynamic Functions from Cell Measurements, $\Delta G^{\ominus}$

Recall $\mathrm{d}\boldsymbol{G} = \text{đ}W_{other,\,rev}$

If we transfer a number of electrons carrying a charge, dQ, from M to M′, the work done on the system is $\text{đ}W_{elec}$. If the transfer is done reversibly, the work produced by the system is equal to the decrease in Gibbs energy of the system

$$\text{đ}W_{elec} = \mathrm{d}\boldsymbol{G}$$

$$\text{đ}W_{elec} = (\mathcal{V}' - \mathcal{V})\mathrm{d}Q \qquad \mathrm{d}\boldsymbol{G} = \mu'_{e\text{-}}\mathrm{d}n - \mu_{e\text{-}}\mathrm{d}n$$

the charge carried by 1 mole of electrons,
$-\mathrm{N_{Avog}}e = -\mathcal{F} = -96490$ coulombs

$$\mathrm{d}Q = -\mathcal{F}\,\mathrm{dn}$$

$$\text{đ}W_{elec} = (\mathcal{V}' - \mathcal{V})(-\mathcal{F}\,\mathrm{dn}) \qquad \mathrm{d}\boldsymbol{G} = (\mu'_{e\text{-}} - \mu_{e\text{-}})\mathrm{d}n$$

$$\mu'_{e\text{-}} - \mu_{e\text{-}} = -\mathcal{F}(\mathcal{V}' - \mathcal{V})$$

The maximum electrical work that a system (the cell) can do is given by the value of $\Delta_{rxn}\boldsymbol{G}$ for the cell reaction

$$\boxed{\Delta_{rxn}\boldsymbol{G} = \nu(-e)\mathrm{N_{Avog}}\,(\mathcal{V}_{\mathrm{right}} - \mathcal{V}_{\mathrm{left}}) = -\,\nu\,\mathcal{F}\,\mathcal{E}}$$

$$\boxed{\Delta_{rxn}\boldsymbol{G} = -\,\nu\,\mathcal{F}\,\mathcal{E}}$$

We therefore find the important relation that the reversible emf is a measure of the free energy of the cell reaction. The reaction can proceed spontaneously only if $\Delta_{rxn}\boldsymbol{G} < 0$. Thus only if $\mathcal{E} > 0$ can a cell reaction proceed spontaneously, and the cell serve as a source of electrical energy. When $\mathcal{E} > 0$ the cell reaction can proceed as written.

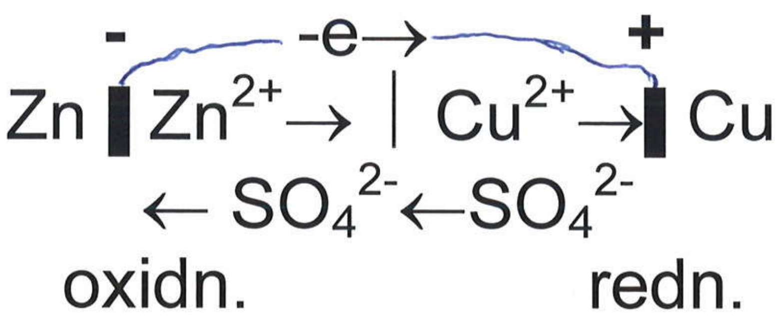
This cell has $\mathcal{E} = 1.100$v at 25°C:

$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

Acting as a galvanic cell, the cell reaction is

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

external circuit



- -e→ +

$Zn \,|\, Zn^{2+}\rightarrow \;|\; Cu^{2+}\rightarrow \,|\, Cu$

$\leftarrow SO_4^{2-} \leftarrow SO_4^{2-}$

oxidn. redn.

The standard cell potential is $\mathcal{E}^{\ominus}$

$\mathcal{E}^{\ominus} = (\mathcal{V}_{\text{right}}^{\ominus} - \mathcal{V}_{\text{left}}^{\ominus})$ where $\mathcal{V}^{\ominus}$ corresponds to the electrode potential for the half reactions, with the chemical substances in their respective standard states. for example, the standard hydrogen electrode (SHE) has

$\mathcal{V}^{\ominus}_{\text{SHE}} = 0$ by convention and the $\mathcal{V}^{\ominus}$ of other half reactions are obtained by coupling the half cell (containing the substances at their standard states) with the SHE and measuring $\mathcal{E}$ of the cell.

$\text{Pt}|\text{H}_2(\text{g})|\text{HCl}(\text{aq})|\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$

has $\mathcal{E}^{\ominus} = +0.80$ volts

$\therefore \ \mathcal{V}^{\ominus} = +0.80$ volts for $(\text{Ag}+/\text{Ag}_{(\text{s})})$

$$\boxed{\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus} = -\nu\,\mathcal{F}\,\mathcal{E}^{\ominus}}$$

Equilibrium Constants

For the reaction

$$aA \quad + bB \quad \rightarrow \quad cC \quad + \quad eE$$

$\mu_i(T,p,x) = \mu_i{}^{\ominus}{}_T + RT \ln \, \boldsymbol{a}_i\,(T,p,x)$

leads to

$\Delta_{rxn}\boldsymbol{G} = \Delta_{rxn}\boldsymbol{G}^{\ominus} + RT \ln Q_{rxn}$

where $Q_{rxn} = \{(\boldsymbol{a}_C)^c(\boldsymbol{a}_E)^e / (\boldsymbol{a}_A)^a(\boldsymbol{a}_B)^b\}$

Since we had found $\Delta_{rxn}\boldsymbol{G} = -\nu\mathcal{F}\mathcal{E}$

$-\nu\mathcal{F}\mathcal{E} = -\nu\mathcal{F}\mathcal{E}^{\ominus} + RT \ln Q_{rxn}$ **Nernst eq.**

At equilibrium, $\Delta_{rxn}\boldsymbol{G} = 0$, and

$K = \{(\boldsymbol{a}_C)^c(\boldsymbol{a}_E)^e / (\boldsymbol{a}_A)^a(\boldsymbol{a}_B)^b\}_{equil}$

$0 = \Delta_{rxn}\boldsymbol{G}^{\ominus} + RT \ln K$

$$\boxed{\therefore \quad \nu\mathcal{F}\mathcal{E}^{\ominus} = RT \ln K}$$

That is, we can obtain equilibrium constants for ionic reactions from standard electrode potentials.

How to measure standard potentials

For the cell:

$Zn(s)|ZnCl_2\ (aq)|AgCl(s)|Ag(s)$

The cell reaction is:

Right: $AgCl_{(s)} + e- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$

Left: $Zn^{2+}_{(aq)} + 2e- \rightarrow Zn_{(s)}$

Right - Left =

$2AgCl_{(s)}+Zn_{(s)} \rightarrow 2Ag_{(s)}+Zn^{2+}_{(aq)}+2Cl^-_{(aq)}$

$Q_{rxn} = a_{Zn2+(aq)}\, a_{Cl-(aq)}^{\ 2}, \quad \nu = 2$

$$a_{Zn2+(aq)}\, a_{Cl-(aq)}^{\ 2} = \gamma_\pm^{\ 3}\, m_{Zn2+(aq)}\, m_{Cl-(aq)}^{\ 2}$$

$$=\gamma_\pm^{\ 3} m(2m)^2 = 4\gamma_\pm^{\ 3} m^3$$

$$-\nu\mathcal{F}\mathcal{E} = -\nu\mathcal{F}\mathcal{E}^{\ominus} + RT\ \ln Q_{rxn}$$

$$\mathcal{E} = \mathcal{E}^{\ominus} - (RT/\nu\mathcal{F})\ \ln Q_{rxn}$$

$$\mathcal{E} = \mathcal{E}^{\ominus} - (RT/2\mathcal{F})\ \ln (4\gamma_\pm^{\ 3}m^3)$$

Use the Debye-Hückel limiting law:

$$\ln \gamma_\pm = (2\pi N_{Avog})^{1/2}\,(e^2/10\varepsilon k_B T)^{3/2}\ z_+z_-\,I^{1/2}$$

$$I \equiv (1/2) \sum\nolimits_{i=\text{all ions}} C_i\, z_i \ = 2m$$

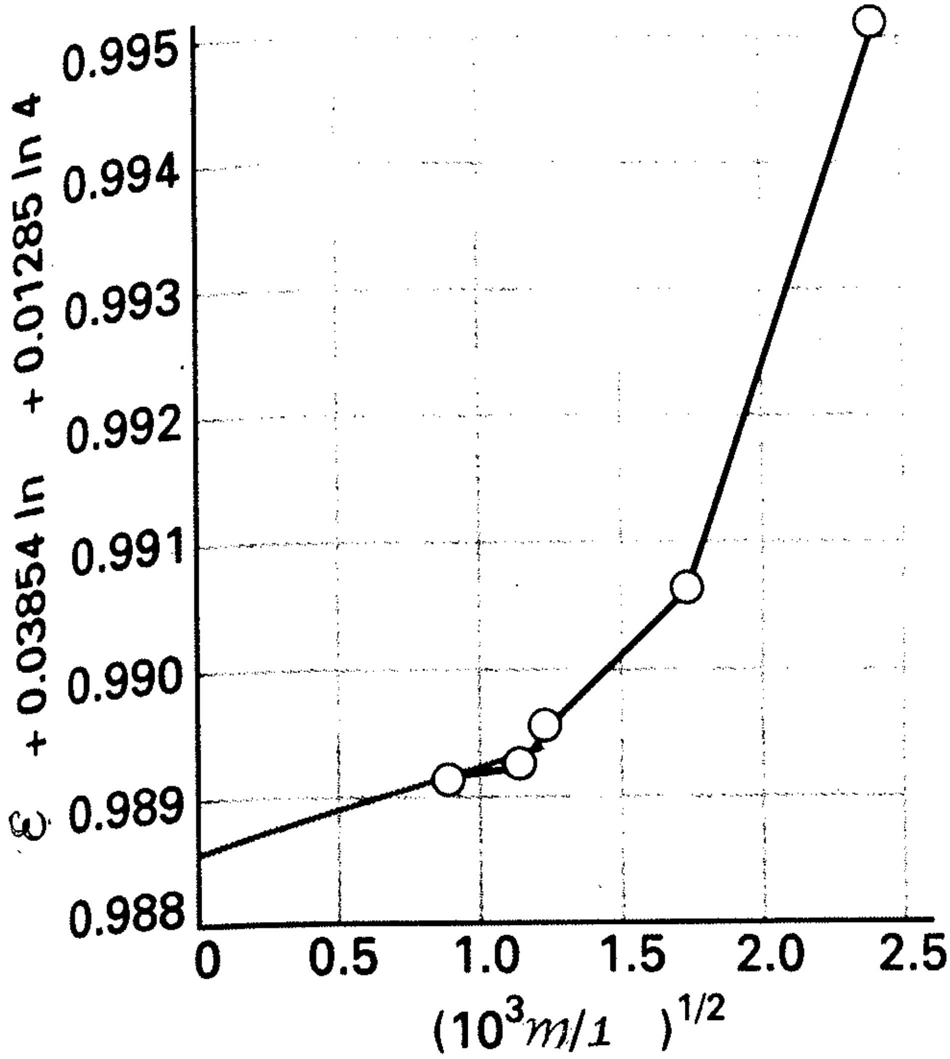
Collect constants in front of $m^{1/2}$ into A

$$\mathcal{E} + (RT/2\mathcal{F}) \ln 4 + (3RT/2\mathcal{F}) \ln (m/1)$$
$$= \mathcal{E}^{\ominus} + Am^{1/2}$$

Plot the left hand side against $m^{1/2}$

In the limit of $m^{1/2} \rightarrow 0$, the intercept is $\mathcal{E}^{\ominus}$

The reaction is spontaneous as written if $\mathcal{E}^{\ominus} > 0$.



Activities and Activity Coefficients

In the previous example, using the cell

$Zn(s)|ZnCl_2\ (aq)|AgCl(s)|Ag(s)$

in which the molality of of the $ZnCl_2$ solution is m, we had found

$\mathcal{E} = \mathcal{E}^{\ominus} - (RT/2\mathcal{F}) \ln (4\gamma_{\pm}^3 m^3)$

Once $\mathcal{E}^{\ominus}$ is known from the extrapolation procedure, this equation can be turned around to determine the activity coefficient $\gamma_{\pm}$ at any molality m by simply measuring $\mathcal{E}$. That is, if we rearrange

$\mathcal{E} = \mathcal{E}^{\ominus} - (RT/2\mathcal{F}) \ln (4\gamma_{\pm}^3 m^3)$ we get,

$\mathcal{E} = \mathcal{E}^{\ominus} - (RT/2\mathcal{F}) \ln (\gamma_{\pm}^3) -(RT/2\mathcal{F}) \ln(4m^3)$

$(RT/2\mathcal{F}) \ln (\gamma_{\pm}^3) = \mathcal{E}^{\ominus}-\mathcal{E} - (RT/2\mathcal{F}) \ln(4m^3)$

More generally,

$(\mathrm{s}RT/\nu \mathcal{F})\ln(\gamma_{\pm}) = \mathcal{E}^{\ominus}-\mathcal{E} -(RT/\nu \mathcal{F}) \ln \mathrm{p}^{\mathrm{p}}\mathrm{q}^{\mathrm{q}}m^{\mathrm{s}}$

From this example we see that it was possible to determine the mean ionic activity coeffient of any aqueous solution of the electrolyte $ZnCl_2$ by the following procedure:

(a) set up cells

$Zn(s)|ZnCl_2\ (m,aq)|AgCl(s)|Ag(s)$

of various molalities in $ZnCl_2$.

(b) measure $\mathcal{E}$ for these cells

(c) Plot the quantities

$\mathcal{E} + (RT/2\mathcal{F})\ \ln 4 + (3RT/2\mathcal{F})\ \ln (m/1)$

against $m^{1/2}$, extrapolate to $m^{1/2} \rightarrow 0$, the intercept is $\mathcal{E}^{\ominus}$

(d) Calculate the mean ionic activity coefficient at any molality from

$$(RT/2\mathcal{F})\ \ln (\gamma_{\pm}^{3}) = \mathcal{E}^{\ominus} - \mathcal{E} - (RT/2\mathcal{F})\ \ln(4m^{3})$$

(e) The activities are then given by

$\boldsymbol{a}_{\pm} = \gamma_{\pm} m_{\pm}$ where $(m_{\pm})^{s} = (p^{p}q^{q})m^{s}$

$\therefore\ \boldsymbol{a}_{\pm} = \gamma_{\pm}\ (p^{p}q^{q})^{(1/s)} m$

Where the ionic activities

$a_+ = \gamma_+ m_+ \qquad a_- = \gamma_- m_-$

themselves appear in a Nernst equation, the collection of γ_+ and γ_- and the terms in $m_+ = \mathrm{p}m$ and $m_- = \mathrm{q}m$ may be grouped together, and this makes possible the replacement of $(\gamma_+)^{\mathrm{p}}(\gamma_-)^{\mathrm{q}}$ by $(\gamma_\pm)^{\mathrm{s}}$.

Determination of $\Delta \boldsymbol{S}^{\ominus}$ and $\Delta \boldsymbol{H}^{\ominus}$ for a reaction

$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -\nu\mathcal{F}\mathcal{E}^{\ominus}$

Take the derivative with respect to T

since $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$, we obtain

$(\partial\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}/\partial T)_p = -\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus} = -\nu\mathcal{F}(\partial\mathcal{E}^{\ominus}/\partial T)_p$

and since

$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} - T\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus}$

then

$$\boxed{\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} = -\nu\mathcal{F}\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}}$$

The reversible emf that is measured for a cell gives the reversible work associated with the cell reaction. Since this is reversible work at constant temperature and pressure, it is therefore the free energy change. The maximum electrical work that a system (the cell) can do is given by the value of $\Delta_{rxn}\boldsymbol{G}$ for the cell reaction,

$$\boxed{\Delta_{rxn}\boldsymbol{G} = -\nu\mathcal{F}\mathcal{E} \qquad (1)}$$

Starting from this equation, and its standard state version, $\Delta_{rxn}\boldsymbol{G}^{\ominus} = -\nu\mathcal{F}\mathcal{E}^{\ominus}$

we may write the counterparts of the following relationships (a)- (h)

(that we had derived previously, starting from $\boldsymbol{G} = \boldsymbol{H} - T\boldsymbol{S}$ and $\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$) in terms of $\mathcal{E}$.

- when $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$ is applied to each reactant and product of a chemical equation,

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

by direct substitution of (1)

$$(\partial \nu \mathcal{F} \mathcal{E}/\partial T)_p = \Delta_{\mathrm{rxn}} \boldsymbol{S}$$

$$\boxed{\begin{gathered}(\partial \Delta_{\mathrm{rxn}} \boldsymbol{G}/\partial T)_p = -\Delta_{\mathrm{rxn}} \boldsymbol{S} \\ \nu \mathcal{F} (\partial \mathcal{E}/\partial T)_p = \Delta_{\mathrm{rxn}} \boldsymbol{S}\end{gathered}}$$

- when applied to each reactant and product of a chemical equation, in their standard states,

(b) $(\partial \Delta_{\mathrm{rxn}} \boldsymbol{G}^{\ominus}/\partial T)_p = -\Delta_{\mathrm{rxn}} \boldsymbol{S}^{\ominus}$

as in above

$$\boxed{\begin{gathered}(\partial \Delta_{\mathrm{rxn}} \boldsymbol{G}^{\ominus}/\partial T)_p = -\Delta_{\mathrm{rxn}} \boldsymbol{S}^{\ominus} \\ \nu \mathcal{F} (\partial \mathcal{E}^{\ominus}/\partial T)_p = \Delta_{\mathrm{rxn}} \boldsymbol{S}^{\ominus}\end{gathered}}$$

- when $\boldsymbol{G} = \boldsymbol{H} - T\boldsymbol{S}$ is applied to each reactant and product of a chemical equation at constant temperature,

(c) $\Delta_{\mathrm{rxn}}\boldsymbol{H} = \Delta_{\mathrm{rxn}}\boldsymbol{G}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S}$

from (1) and (a),

$$\Delta_{\mathrm{rxn}}\boldsymbol{H} = -\nu\mathcal{F}\mathcal{E} + T\nu\mathcal{F}\,(\partial\mathcal{E}/\partial T)_p$$

$$\Delta_{\mathrm{rxn}}\boldsymbol{H} = -\nu\mathcal{F}\cdot\{\mathcal{E} + T(\partial\mathcal{E}/\partial T)_p\}$$

$$\boxed{\begin{aligned} \Delta_{\mathrm{rxn}}\boldsymbol{H} &= \Delta_{\mathrm{rxn}}\boldsymbol{G}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S} \\ \Delta_{\mathrm{rxn}}\boldsymbol{H} &= -\nu\mathcal{F}\cdot\{\mathcal{E} - T(\partial\mathcal{E}/\partial T)_p\} \end{aligned}}$$

- when applied to each reactant and product of a chemical equation, in their standard states,

(d) $\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} = \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus}$

as in above

$$\boxed{\begin{aligned} \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} &= \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus} \\ \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} &= -\nu\mathcal{F}\cdot\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\} \end{aligned}}$$

- when the Gibbs-Helmholtz relation $(\partial(\boldsymbol{G}/T)/\partial T)_p = -\boldsymbol{H}/T^2$ is applied to each reactant and product of a chemical equation, in their standard states,

(e) $(\partial(\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}/T)/\partial T)_p = -\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2$

Using $\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus} = -\nu\mathcal{F}\mathcal{E}^{\ominus}$

$\nu\mathcal{F}(\partial(\mathcal{E}^{\ominus}/T)/\partial T)_p = \Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2$

doing the differentiation on the left,

$(\partial(\mathcal{E}^{\ominus}/T)/\partial T)_p = \mathcal{E}^{\ominus}(-T^{-2}) + (1/T)(\partial\mathcal{E}^{\ominus}/\partial T)_p$

we see this leads to same result as (d):

$$\boxed{\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus} = -\nu\mathcal{F}\cdot\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}}$$

- when applied to the equilibrium state of the chemically reacting system

(f) $d(\ln K_p)/dT = -\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2$

from (d) or (e),

$d(\ln K_p)/dT = \nu\mathcal{F}\cdot\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}/T^2$

$$\boxed{\begin{array}{l} d(\ln K_p)/dT = -\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2 \\ d(\ln K_p)/dT = \nu\mathcal{F}\cdot\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}/T^2 \end{array}}$$

•when $\mu(T) = \mu^{\ominus}(T) + RT \ln \boldsymbol{a}$ is applied to each reactant and product of a chemical equation,

(g) $\Delta_{\mathrm{rxn}}\boldsymbol{G}_T = \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + RT \ln \boldsymbol{Q}$

where $\boldsymbol{Q}$ is in the same form as the true equilibrium constant $\boldsymbol{K}$ for the reaction

$\mathrm{bB} + \mathrm{cC} \rightarrow \mathrm{pP} + \mathrm{rR}$, $\quad \boldsymbol{Q} = \boldsymbol{a}_{\mathrm{P}}{}^{\mathrm{p}}\, \boldsymbol{a}_{\mathrm{R}}{}^{\mathrm{r}} / \boldsymbol{a}_{\mathrm{B}}{}^{\mathrm{b}}\, \boldsymbol{a}_{\mathrm{C}}{}^{\mathrm{c}}$

Using $\Delta_{\mathrm{rxn}}\boldsymbol{G} = -\nu\mathcal{F}\mathcal{E}$ and $\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -\nu\mathcal{F}\mathcal{E}^{\ominus}$

$-\nu\mathcal{F}\mathcal{E} = -\nu\mathcal{F}\mathcal{E}^{\ominus} + RT \ln \boldsymbol{Q}$

or $\mathcal{E} = \mathcal{E}^{\ominus} - (RT\nu\mathcal{F}) \ln \boldsymbol{Q}$ Nernst eq.

$$\boxed{\begin{array}{l} \Delta_{\mathrm{rxn}}\boldsymbol{G}_T = \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + RT \ln \boldsymbol{Q} \\ \qquad \mathcal{E} = \mathcal{E}^{\ominus} - (RT\nu\mathcal{F}) \ln \boldsymbol{Q} \quad \text{Nernst eq.} \end{array}}$$

•when applied to the equilibrium state of the chemically reacting system,

(h) $\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -RT \ln \boldsymbol{K}$

using $\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -\nu\mathcal{F}\mathcal{E}^{\ominus}$, $\mathcal{E}^{\ominus} = (RT\nu\mathcal{F}) \ln K$

$$\boxed{\begin{array}{l} \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -RT \ln \boldsymbol{K} \\ \qquad \mathcal{E}^{\ominus} = (RT\nu\mathcal{F}) \ln \boldsymbol{K} \end{array}}$$

$\Delta_{\mathrm{rxn}}\boldsymbol{G}$	$-\ \nu\mathcal{F}\mathcal{E}$
$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}$	$-\ \nu\mathcal{F}\mathcal{E}^{\ominus}$
$(\partial\Delta_{\mathrm{rxn}}\boldsymbol{G}/\partial T)_p = -\Delta_{\mathrm{rxn}}\boldsymbol{S}$	$\nu\mathcal{F}\,(\partial\mathcal{E}\,/\partial T)_p = \Delta_{\mathrm{rxn}}\boldsymbol{S}$
$(\partial\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}/\partial T)_p$ $= -\Delta_{\mathrm{rxn}}\ \boldsymbol{S}^{\ominus}$	$\nu\mathcal{F}(\partial\mathcal{E}^{\ominus}/\partial T)_p = \Delta_{\mathrm{rxn}}\ \boldsymbol{S}^{\ominus}$
$\Delta_{\mathrm{rxn}}\boldsymbol{H} =$ $\Delta_{\mathrm{rxn}}\boldsymbol{G}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S}$	$\Delta_{\mathrm{rxn}}\boldsymbol{H} =$ $-\nu\mathcal{F}\cdot\{\,\mathcal{E} - T(\partial\mathcal{E}\,/\partial T)_p\,\}$
$\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} =$ $\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + T\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus}$	$\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus} =$ $-\nu\mathcal{F}\cdot\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\,\}$
$\mu(T) = \mu^{\ominus}(T) + RT\ln \boldsymbol{a}$	$\mu(T) = \mu^{\ominus}(T) + RT\ln \boldsymbol{a}$
$\mathrm{d}(\ln\boldsymbol{K})/\mathrm{d}T =$ $-\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}/T^2$	$\mathrm{d}(\ln\boldsymbol{K})/\mathrm{d}T =$ $\nu\mathcal{F}\,\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}/T^2$
$\Delta_{\mathrm{rxn}}\boldsymbol{G}_T$ $= \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + RT\ln\boldsymbol{Q}$	$\mathcal{E} = \mathcal{E}^{\ominus} - (RT\nu\mathcal{F})\ln\boldsymbol{Q}$
$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -\ RT\ln\boldsymbol{K}$	$\mathcal{E}^{\ominus} = (RT\nu\mathcal{F})\ln\boldsymbol{K}$

Therefore we can determine thermodynamic functions from emf measurements:

To obtain this	measure this
$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}$	$-\nu\mathcal{F}\mathcal{E}^{\ominus}$
$\Delta_{\mathrm{rxn}}\boldsymbol{S}^{\ominus}$	$\nu\mathcal{F}(\partial\mathcal{E}^{\ominus}/\partial T)_p$
$\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}$	$-\nu\mathcal{F}\{\mathcal{E}^{\ominus} - T(\partial\mathcal{E}^{\ominus}/\partial T)_p\}$
$RT \ln \boldsymbol{K}$	$\nu\mathcal{F}\mathcal{E}^{\ominus}$
for any m $(sRT/\nu\mathcal{F}) \ln(\gamma_{\pm})$	for example, $\mathcal{E}^{\ominus}-\mathcal{E} - (RT/\nu\mathcal{F}) \ln p^{p} q^{q} m^{s}$