THE THERMODYNAMICS OF ELECTROCHEMICAL SYSTEMS

CHE2615

The Chemical Potential and the Electric Potential

- The propensity of a substance to contribute to a system's energy is called **Chemical Potential** (μ)
- When the substance is a charged particle we must include the response of the particle to an electrical field in addition to its Chemical Potential. We call this **Electrochemical Potential**.

$$\mu_i = \mu_{i,chem} + zF\varphi$$

$\boldsymbol{z}$ = *charge on the particle*
$\boldsymbol{\mu_{i,chem}} = \boldsymbol{chemical\ part\ of\ the\ chemical\ potential}$
$\boldsymbol{F}$ = *Faraday's constant (96485 C /mol)*
$\boldsymbol{\varphi}$ = *electric potential (field under consideration)*

- These are perhaps the most fundamental measures of thermodynamics.

Chemical Potential

- Chemical potential (or electrochemical potential if it is charged) is the measure of how all the thermodynamic properties vary when we change the amount of the material present in the system.
- The Gibbs "chemical potentials" for component A for example, may be defined in a multiplicity of ways depending on what conditions are held constant as follows:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} \qquad \mu = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$\mu = \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

Here we see that the chemical potential describes how the free energy (Gibbs or Helmholtz) and the enthalpy and internal energy all vary with changes in the amount of the material in the system.

- The first equality is the one generally used in defining the "chemical potential" in that experiments may easily be designed wherein the temperature and pressure are maintained constant.
- It is inconvenient to conduct experiments at constant volume and temperature and It is indeed difficult to conceive of ways to conduct experiments either at constant entropy and volume or at constant entropy and pressure.
- Since the energy, entropy, heat content, Helmholtz energy, and Gibbs energy are defined only by differential equations, we can determine only differences of these quantities between two states of a system containing the same quantity of matter.

Gibbs Free Energy

- The free energy function is the key to assessing the way in which a chemical system will spontaneously evolve.
- Because the chemical potentials depend on composition (pressure and temperature), the Gibbs energy of a mixture may change when these variables change

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

This expression is the **fundamental equation of chemical thermodynamics**

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

constant T

constant P

$$\mathrm{d}G = \sum \mu_i \, \mathrm{d}n_i$$

Partial molar Gibbs energies

- Partial molar Gibbs energy is simply the chemical potential

- The chemical potential μ_J of substance J at some composition:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

n_J is the amount (the number of moles) of **J**

n' the amounts of all other substances

- The total Gibbs energy **G** of the mixture (**A** & **B**)

$$G = n_A \mu_A + n_B \mu_B$$

- where μ_A and μ_B are the chemical potentials at the composition of the mixture.
- That is, the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture.

The Gibbs-Duhem equation

$$\sum_J n_J \, d\mu_J = 0$$

- The change of Gibbs energy G of the mixture (**A** & **B**)

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

- At constant pressure and temperature,

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

- The chemical potentials of a mixture cannot change independently: in a binary mixture, if one increases the other must decrease.

Gibbs Function and Work

- Start with the First Law of Thermodynamics and some standard thermodynamic relations. We find

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}q = T\,\mathrm{d}S$$

$$\mathrm{d}w = -P\,\mathrm{d}V + \mathrm{d}w_{electrical}$$

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \mathrm{d}w_{electrical}$$

$$\mathrm{d}H_P = \mathrm{d}U_P + P\,\mathrm{d}V$$

$$\mathrm{d}G_T = \mathrm{d}H_T - T\,\mathrm{d}S$$

$$= \mathrm{d}U_{T,P} + P\,\mathrm{d}V - T\,\mathrm{d}S$$

$$= T\,\mathrm{d}S - P\,\mathrm{d}V + \mathrm{d}w_{electrical} + P\,\mathrm{d}V - T\,\mathrm{d}S$$

$$\mathrm{d}G_{T,P} = \mathrm{d}w_{electrical}$$

And therefore, the Gibbs function identifies the amount of work we can extract electrically from a system.

THE CELL POTENTIAL

- Cell potential (V) (1 V = 1 J C^{-1} s) is the potential difference between the two electrodes
- When the cell potential is large, a given number of electrons travelling between the electrodes can do a large amount of work;
- When the cell potential is small, the same number of electrons can only do a small amount of work.
- A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

Gibbs and the Cell Potential

- Here we can easily see how this Gibbs function relates to a potential.

$$w_{electrical} = VQ$$

$$\text{since} \quad Q = nF$$

$$= nFE$$

- We identify work which is negative with work which is being done by the system on the surroundings.
- And negative free energy change is identified as defining a spontaneous process.

$$\Delta G_{T,P} = -w_{electrical} = -nFE$$

- Note how a measurement of a cell potential directly calculates the Gibbs free energy change for the process.

The maximum amount work:

- The maximum non-expansion work, in which the current context is electrical work, that a system (the cell) can do is given by

$$w_{e,max} = \Delta G \text{ (at constant T and P)}$$

- It follows that, to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly, for only then is it producing maximum work.
- Since the reaction Gibbs energy is a property relating to a specified composition of the reaction mixture, to make use of $\Delta_r G$ we must ensure that the cell is operating reversibly at a specific, constant composition.

- Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows: in effect, the cell reaction is poised for change, but not actually changing.
- The resulting potential difference is called the zero-current cell potential E (electromotive force or emf of the cell)
- Relation between E and $\Delta_r G$:

$$-\nu F E = \Delta_r G$$

Faraday's constant $F = 96485\ \mathrm{C\ mol^{-1}}$

Chemical Potential and Activity

- How does chemical potential change with activity?

$$\mu = \mu^{\circ} + RT \ln a$$

- Integration of the expressions for the dependence of amount of material on the Gibbs function, leads to the following relationship:

Reaction Quotient

$$\text{w}A + \text{x}B \rightarrow \text{y}C + \text{z}D$$

- In order to analyze a chemical process mathematically, we form this reaction quotient.

$$Q = \frac{a_C^y \, a_D^z}{a_A^w \, a_B^x}$$

- It always has products in the numerator and reactants in the denominator
- It explicitly requires the activity of each reaction participant.
- each term is raised to the power of its stoichiometric coefficient.

Simplifying Approximations

- Leave out terms involving solids, pure liquids, and solvents
- Solutes appear as the concentration (in M).
- Gases appear as the partial pressure (in atm).

REACTION QUOTIENT IS UNITLESS.

- But its value does depend upon the chosen reference state.

Concentration Dependence

- How does Gibbs free energy change with activity (concentration)?
- Same dependence as with the chemical potential. We have

$$G = G^{\circ} + RT \ln a$$

- When we apply this to a reaction, the reaction quotient comes into to play, giving us

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

Equilibrium

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

- When all participants have unit activity (a=1), then Q=1 and ln Q = 0.

$$\Delta G = \Delta G^{\circ}$$

- Reaction proceeds, Q changes, until finally ΔG = 0. The reaction stops. This is equilibrium.

$$0 = \Delta G^{\circ} + RT \ln Q^{*}$$

$$\therefore \quad \Delta G^{\circ} = -RT \ln Q^{*} \qquad\qquad Q^{*} \equiv K_{eq}$$

- This special Q* (the only one for which we achieve this balance) is renamed K_{eq}, the equilibrium constant.

- The chemical potential of a single charged species cannot be measured, since charged particles cannot easily be added to a system without adding ions of the opposite charge at the same time.

ELECTROCHEMICAL CELLS

- Redox reactions involving reduction half cell reaction and oxidation half cell reaction
- Consider the overall reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = \Delta G^{o} + RT ln \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$$

$$\Delta G < 0$$

$$\Delta G^{o} < 0$$

Nernst equation

$$\Delta G = -\nu_e F E_{cell} \quad \text{and} \quad \Delta G = -\nu_e F E^o_{cell}$$

$$-\nu_e F E_{cell} = -\nu_e F E^o_{cell} + RT ln \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$$

$$E_{cell} = E^o_{cell} - \frac{RT}{\nu_e F} ln \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$$

$$E_{cell} = E^o_{cell} - 2.3026 \frac{RT}{\nu_e F} log \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$$

At T 298.15 K: F = 96485 C/mol

$$E_{cell} = E^o_{cell} - \frac{0.05916}{\nu_e} log \frac{(a_c)^c (a_d)^d}{(a_a)^a (a_b)^b}$$

Standard potentials

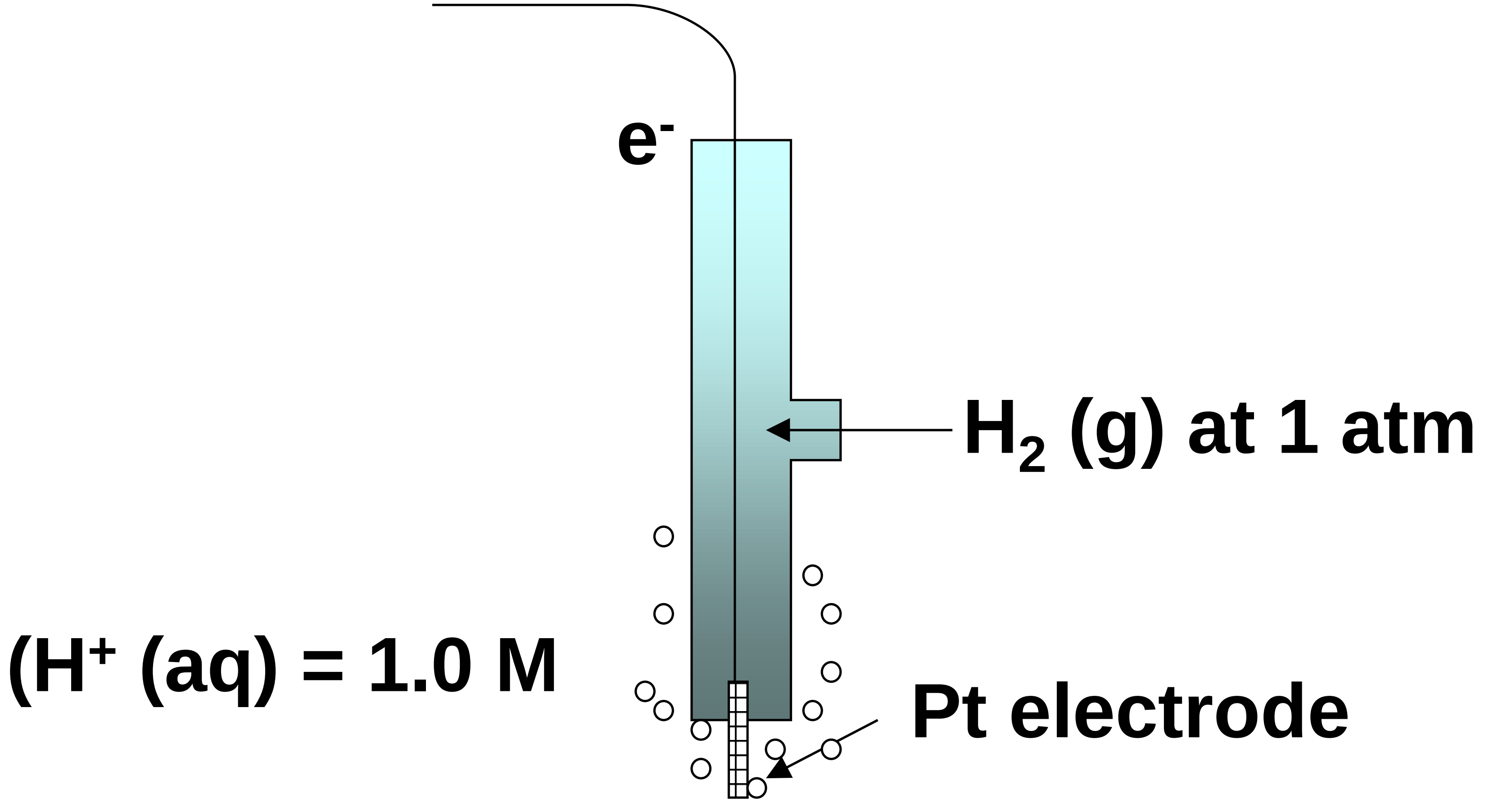
- It is not possible to measure the contribution of a single electrode, we may define the potential of one of the electrodes as having a zero potential and then assign values of others

*Standard hydrogen electrode (SHE):

$Pt \mid H_2(g) \mid H^+(aq)$ at all temperatures

The Standard Hydrogen Electrode

E^o (H^+/H_2) half-cell = 0.000 V



*Standard potential E^0 of another couple may be assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is left-hand electrode

- e.g.

$Pt \mid H_2(g) \mid H^+(aq) \| Ag^+(aq) \mid Ag(s)$

$$E^o(Ag^+ / Ag) = 0.80\ V \quad \text{at } 25^oC$$

Similarly, $E^o(AgCl / Ag, Cl^-) = 0.22\ V$

The standard potential of a cell in terms of reduction potentials

*Standard potential of a cell formed from any two electrodes can be calculated by taking the difference of their standard potentials. e.g.

$$Ag(s) \mid Ag^+(aq) \mid\mid Cl^-(aq) \mid AgCl(s) \mid Ag(s)$$

is equivalent to two cells joined back-to-back:

$$Ag(s) \mid Ag^+(aq) \mid\mid H^+(aq) \mid H_2(g) \mid Pt$$

$$Pt \mid H_2(g) \mid H^+(aq) \mid\mid Cl^-(aq) \mid AgCl(s) \mid Ag(s)$$

The overall potential of the composite cell:

$$E^o_{cell} = E^o(AgCl/Ag, Cl^-) - E^o(Ag^+ / Ag) = -0.58 \text{ V}$$

Example

Consider the following cell reaction at 25oc and 1 bar

Pt(s)|H_2(g)1bar|H^+(aq)||HBr(0.01)|AgBr(s)|Ag(s)

Given that:

$$\mathrm{AgBr\ (s)} + e^- \rightarrow Ag(s) + Br^-\ (aq) \qquad E^o = 0.073\ V$$

$$\frac{1}{2} H_2\ \mathrm{(g)}\ +\ e^- \rightarrow H^+\ (aq) \qquad E^o = 0.0\ V$$

a) Calculate the mean ion coefficient of HBr using the DHLL
b) Determine the emf of the cell and compare this with the measured emf of 0.3127V

a) $\mathrm{HBr\ (aq)} \rightarrow H^{+}(aq) + Br^{-}(aq)$

This is a 1:1 electrolyte, thus;

$$I = c$$

$$\log \gamma_{\pm} = -0.509|z_{+}z_{-}|\sqrt{I}$$

$$\log \gamma_{\pm} = -0.509|1\mathrm{x} - 1|\sqrt{(0.01)}$$

$$\log \gamma_{\pm} = -0.0509$$

$$\gamma_{\pm} = 10^{-0.0509} = 0.8894$$

b) Cell reaction

Red. Rxn:

$$\mathrm{AgBr}\ (\mathrm{s}) + e^- \rightarrow Ag(s) + Br^-\ (aq) \qquad E^o = 0.073\ V$$

Oxd. Rxn:

$$\frac{1}{2} H_2\ (\mathrm{g}) \rightarrow H^+\ (aq) + e^- \qquad E^o = 0.0\ V$$

Overall cell rxn:

$$\frac{1}{2} H_2\ (\mathrm{g}) + \mathrm{AgBr}\ (\mathrm{s}) \rightarrow H^+\ (aq) + Br^-\ (aq) + 2Ag(s)$$

$$E^o_{cell} = E^o_{red} - E^o_{ox}$$

$$E^o_{cell} = 0.073 - 0 = 0.073V$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{\nu_e} log \frac{(v_{H^+} a_{H^+})^{v_{H^+}} (v_{Br^-} a_{Br^-})^{v_{Br^-}}}{(a_{H_2})^{\frac{1}{2}}}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{1} log \frac{(c\,\gamma_{H^+})^1 (c\,\gamma_{Br^-})^1}{\left(\frac{P}{P^o}\right)^{\frac{1}{2}}}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{1} \log c^2 \gamma_{\pm}^2$$

$$E_{cell} = 0.073\ V - \frac{0.05916}{1} \log(0.01)^2 (0.8894)^2$$

$$E_{cell} = 0.073\ V\ - (-0.24266)$$

$$E_{cell} = 0.3138\ \ V$$

a) $ZnCl_2\ (aq) \rightarrow Zn^{2+}(aq) + 2Cl^-\ (aq)$

This is a 1:2 electrolyte, thus;

$$I = 3c$$

$$\log \gamma_{\pm} = -0.509|z_+z_-|\sqrt{I}$$

$$\log \gamma_{\pm} = -0.509|2\mathrm{x} - 1|\sqrt{3(0.000772)}$$

$$\log \gamma_{\pm} = -0.048991$$

$$\gamma_{\pm} = 10^{-0.048991} = 0.89332$$

b) Cell reaction

Red. Rxn:

$$2AgCl(s) + 2e^- \rightarrow 2Ag(s) + 2Cl^-(aq) \quad E^o = 0.2223V$$

Oxd. Rxn:

$$Zn(g) \rightarrow Zn^{2+}(aq) + 2e^- \qquad -E^o = -(-0.7626)\,V$$

Overall cell rxn:

$$Zn(g) + 2AgCl(s) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq) + 2Ag(s)$$

$$E^o_{cell} = E^o_{red} - E^o_{ox}$$

$$E^o_{cell} = 0.2223 - (-0.7626) = 0.9849V$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{\nu_e} \log(v_{Zn^{2+}} a_{Zn^{2+}})^{v_{Zn^{2+}}} (v_{Cl^-} a_{Cl^-})^{v_{Cl^-}}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{2} \log(c\,\gamma_{Zn^{2+}})^{1}\ (2c\gamma_{Cl^-})^{2}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{2} \log 4c^{3}\gamma_{\pm}^{3}$$

$$E_{cell} = 0.9849\,V - \frac{0.05916}{2} \log(0.000772)^{3}(0.89332)^{3}$$

$$E_{cell} = 0.9849\,V\ - (-0.26273)$$

$$E_{cell} = 1.2476\,V$$

c) Measured emf is 1.2475 V

Example 3

Consider the cell reaction below:

$Pt(s)|H_2(g)1bar|H^+(aq)||HBr(0.01)|AgBr(s)|Ag(s)$

If the emf of of the cell is 0.3127 V and E^o_R =0.073 V, determine the mean activity coefficient of HBr

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{\nu_e} \log m^2\gamma_{\pm}^2$$

$$\log m^2\gamma_{\pm}^2 = \frac{(E_{cell} - E^{o}_{cell})\nu_e}{-0.05916}$$

$$2\mathrm{lo}\gamma_{\pm} = \frac{(E_{cell} - E^{o}_{cell})\nu_e}{-0.05916} - 2\log m$$

$$2\mathrm{lo}\gamma_{\pm} = \frac{(0.3127 - 0.0711)V x 1}{-0.05916V} - 2\log 0.01$$

$$= -4.08384 + 4000$$

$$\mathrm{lo}\gamma_{\mp} = \frac{-0.08384}{2} = -0.04192$$

$$\gamma_{\pm} = 10^{-0.04192} = 0.90799$$

Example 4

Consider a cell in Example 2 with a measured emf 1.2475V.

Determine mean activity coefficient of 0.000772M $ZnCl_2$.

$$E_{cell} = E^o_{cell} - \frac{0.05916}{\nu_e} \log 4m^3\gamma^3_{\pm}$$

$$\log m^3\gamma^3_{\pm} = \frac{(E_{cell} - E^o_{cell})\nu_e}{-0.05916}$$

$$3lo\gamma_{\pm} = \frac{(E_{cell} - E^o_{cell})\nu_e}{-0.05916} - \log 4 - 3\log m$$

$$3lo\gamma_{\pm} = \frac{(1.2475 - 0.9849)V\,x2}{-0.05916V} - \log 4 - 3\log 0.000772$$

$$= --8.8776 + -0.60206 + 9.3371$$

$$lo\gamma_{\mp} = \frac{-0.14253}{3} = -0.04751$$

$$\gamma_{\pm} = 10^{-0.04751} = 0.89637$$

Thermodynamic properties from emf measurements

Fundamental thermodynamic equations

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

$$\frac{\partial(\Delta G)}{\partial T} = -\Delta S$$

$$\Delta G = -\nu_e F E_{cell}$$

$$\Delta G^o = -\nu_e F E^o_{cell}$$

$$\nu_e F \frac{\partial E_{cell}}{\partial T} = \Delta S$$

$$\nu_e F \frac{\partial E^o_{cell}}{\partial T} = \Delta S^o$$

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

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

$$\Delta H = -\nu_e F E_{cell} + T\nu_e F \frac{\partial E_{cell}}{\partial T}$$

$$\nu_e F \frac{\partial E_{cell}}{\partial T} \text{ in V } K^{-1} \, and \, V = \frac{J}{C}$$

Similar expression

$$\Delta H^o$$

$$\Delta S^o$$

Temperature coefficients

- The measurement of emf values at various temperatures provides a very convenient method of obtaining thermodynamic values for chemical reactions

$$E_{cell} = a + b\left(\frac{T}{K}\right) + c\left(\frac{T}{K}\right)^2 + d\left(\frac{T}{K}\right)^3 + \ldots$$

$$\frac{\partial E_{cell}}{\partial T} = b + 2c\left(\frac{T}{K}\right) + 3d\left(\frac{T}{K}\right)^2 + \cdots$$

Similarly

$$\frac{\partial E^{o}_{cell}}{\partial T} = b + 2c\left(\frac{T}{K}\right) + 3d\left(\frac{T}{K}\right)^2 + \cdots$$

Example

The $E_{Ag/AgCl(s)/Cl^-}$ at various T are shown below

a) Calculate E^o at 25oC

b) Determine the temperature coefficient of the cell at 25oC

T(K)	E^o V
283.15	0.2314
288.15	0.2286
298.15	0.2224
303.15	0.2191
308.15	0.2115

$$a)\ E^{o}_{cell,\ Ag/AgCl/Cl^-} = a + b\left(\frac{T}{K}\right) + c\left(\frac{T}{K}\right)^2$$

Use quadratic regression (QUAD)

a) = -1.35359

b) = 0.011432

c) = -2.0611 x 10^{-5}

(b)

(a)

$$E_{Ag|AgCl|Cl^-}(V) = -1.3535 + 0.01143\left(\frac{T}{K}\right) - 2.061x10^{-5}\left(\frac{T}{K}\right)^2$$

At 298.15K

$$E_{Ag|AgCl|Cl^-}(V) = -1.3535 + 0.01143\left(\frac{298.15K}{K}\right) - 2.061x10^{-5}\left(\frac{298.15}{K}\right)^2$$

$$= 0.2227V$$

(b)

$$E_{Ag|AgCl|Cl^-}(V) = -1.3535 + 0.01143\left(\frac{T}{K}\right) - 2.061\left(\frac{T}{K}\right)^2$$

At 298.15 K

$$E_{Ag|AgCl|Cl^-}(V) = -1.3535 + 0.01143\left(\frac{T}{K}\right) - 2.061\left(\frac{T}{K}\right)^2$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 0.01143 + 2\,(-2.061 x 10^{-5})\left(\frac{T}{K}\right)$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 0.01143 + 2\,(-2.061 x 10^{-5})\left(\frac{298.15\,K}{K}\right)$$

$$= -8.597 x 10^{-4}\,V\,K$$

At 25^{o} C the emf and $\partial E / \partial T$ of the cell

$Pb(s)|PbCl_2(s), KCl, AgCl(s)|Ag$

are 0.4902V and -1.86×10^{-4} V K^{-1} respectively.

The silver electrode is the cathode.

(a) Write the cell reaction

(b) Calculate ΔG and ΔH of the reaction:

$$Pb(s) + 2AgCl(s) \Leftarrow PbCl_2 + 2Ag(s)$$

(c) Compare with the data provided

(a)

$$\text{Red rxn}: 2AgCl(s) + 2e \rightarrow 2Ag(s) + 2Cl^{-}(aq)$$

$$\text{Oxd. rxn}: Pb(s) \rightarrow Pb^{2+}(aq) + 2e^{-}$$

$$\text{Cell rxn}: 2AgCl(s) + Pb(s) \Leftrightarrow 2Ag(s) + PbCl_2(s)$$

(b)

$$\Delta G = -\nu_e F E_{cell}$$

$$= -2 \text{ x } 96485 \text{ C mol}^{-1} \text{ x } 0.4902 \text{ J C}^{-1}$$

$$= -9.4594 \text{x} 10^4 \text{ J mol}^{-}$$

(c)

$$2AgCl(s) + Pb(s) \Leftrightarrow 2Ag(s) + PbCl_2(s)$$

$$\Delta G_{rxn} = \sum_{Products} \nu \Delta G_f^o - \sum_{reac\ tan\ ts} \nu \Delta G_f^o$$

$$\Delta H_{rxn} = \sum_{Products} \nu \Delta H_f^o - \sum_{reac\ tan\ ts} \nu \Delta H_f^o$$

$$\Delta G_{rxn} = 1x\nu\Delta G^o_{f,PbCl_2(s)} - 2\nu\Delta G^o_{f,AgCl}$$

$$= [1x - 314.0 - \_\ 2(-109.79)]10^3 \, J\,mol^{-1} = -9.442x10^4 \, J\,mol^{-1}$$

$$\Delta H_{rxn} = 1x\nu\Delta H^o_{f,PbCl_2(s)} - 2\nu\Delta H^o_{f,AgCl}$$

$$\Delta H_{rxn} = [1x - 359.2 \quad - 2(-127.07)]10^3 \, J\,mol^{-1} = 1.0506x10^5 \, J\,mol^{-1}$$