



EMA4303/5305

Electrochemical Engineering

Lecture 02

Equilibrium Electrochemistry

Dr. Junheng Xing, Prof. Zhe Cheng
Mechanical & Materials Engineering
Florida International University



Equilibrium Electrochemistry

□ Equilibrium Electrochemistry

“Equilibrium electrochemistry, which is mainly based on equilibrium thermodynamics, is one of the most important subjects of electrochemistry. Equilibrium electrochemistry is usually the first and required step in analyzing any electrochemical system.” (S. N. Lvov)

It describes thermodynamic properties of reaction in electrochemical cells. Thermodynamic arguments can be used to derive an expression for the electric potential of such cell and the potential can related to their composition.

□ Main contents of this lecture

- Gibbs free energy G and Gibbs free energy change (ΔG)
- Relationship between equilibrium cell potential E_{eq} and ΔG
- Equilibrium constant (K)
- **Nernst Equation**
- Pourbaix diagram



Gibbs Free Energy Change (ΔG)

□ Definition

- If thermodynamic variables are temperature and pressure, the main chemical parameter for determining whether a system or process/reaction is at equilibrium or will proceed spontaneously or not is the Gibbs free energy change (ΔG).
- For electrochemical cells, **ΔG is the thermodynamic function showing the driving force for the electrochemical reaction**

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

Change in free energy = change in enthalpy - (temperature) change in entropy

□ Significance

- $\Delta G < 0$: process/reaction is spontaneous in the direction written
- $\Delta G = 0$: the system is at equilibrium
- $\Delta G > 0$: process/reaction is NOT spontaneous (the process may proceed spontaneously in the reverse direction)

□ Additional notes

- ΔG depends only on the difference in Gibbs free energy of products and reactants (or final state and initial state) and is independent of the path of the transformation and related reaction mechanism.
- ΔG cannot tell us anything about the rate of a reaction.



Standard Gibbs Free Energy of Formation ($\Delta_f G^\circ$)

□ “The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of **1 mole** of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at **1 bar of pressure** and the specified temperature...)” (Wikipedia)

□ **References:**

- M.W. Chase, NIST – JANAF Thermochemical Tables, 4th Edition, Journal of Physical and Chemical Reference Data, Monograph 9, 1998
- Online: JANAF Thermochemical Table
- Others

Water, 1 Bar (H_2O)

$H_2O_1(l,g)$

Enthalpy Reference Temperature = $T_r = 298.15$ K

Standard State Pressure = $p^\circ = 0.1$ MPa

T/K	C_p°	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			$\log K_f$
		S°	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$		
0								
100								
200								
280	75.563	65.215	70.102	-1.368	-286.410	-240.123	44.796	
298.15	75.351	69.950	69.950	0.	-285.830	-237.141	41.546	
300	75.349	70.416	69.952	0.139	-285.771	-236.839	41.237	
320	75.344	75.279	70.134	1.646	-285.137	-233.598	38.131	

<http://kinetics.nist.gov/janaf/>



(Reaction) Gibbs Free Energy Change ($\Delta_r G$)

- ❑ For an reaction, the Gibbs free energy change is the difference in the Gibbs free energy between all products and all reactants.
- ❑ Two ways of calculation of ΔG

$$\Delta_r G = \sum n_i \Delta_f G(\text{react}) - \sum n_j \Delta_f G(\text{prod})$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln k$$

R Ideal gas constant = 8.314 J/mol-K

T Absolute temperature in Kelvin

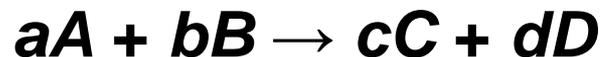
k **Reaction constant**

ΔG° Standard Gibbs free energy change, Gibbs free energy change for standard state, two ways of calculation, also has two ways of calculating:

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

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

Example:

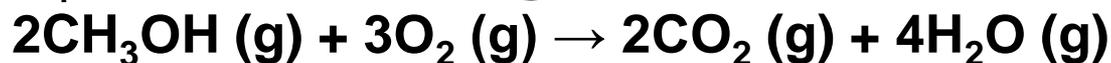


$$\Delta_r G^\circ = [c\Delta_f G^\circ(C) + d\Delta_f G^\circ(D)] - [a\Delta_f G^\circ(A) + b\Delta_f G^\circ(B)]$$



An Example of Calculating $\Delta_r G^\circ$

□ Calculate the $\Delta_r G^\circ$ of the following reaction at 298K:



□ Answer:

From reference

$$\Delta_f G^\circ : \text{CH}_3\text{OH} = -163 \text{ kJ/mol}$$

$$\text{O}_2 = 0 \text{ kJ/mol}$$

$$\text{CO}_2 = -394 \text{ kJ/mol}$$

$$\text{H}_2\text{O} = -229 \text{ kJ/mol}$$

$$\begin{aligned}\Delta_r G^\circ &= [2\Delta_f G^\circ(\text{CO}_2) + 4\Delta_f G^\circ(\text{H}_2\text{O})] - [2\Delta_f G^\circ(\text{CH}_3\text{OH}) + 3\Delta_f G^\circ(\text{O}_2)] \\ &= [2(-394 \text{ kJ/mol}) + 4(-229 \text{ kJ/mol})] - [2(-163 \text{ kJ/mol}) + 3(0 \text{ kJ/mol})] \\ &= -1378 \text{ kJ/mol}\end{aligned}$$

The reaction is spontaneous because of the negative sign of $\Delta_r G$



Electrochemical Cell Potential (E)

□ Cell potential (E)

For a galvanic cell, **the potential difference between the two electrodes is called the cell potential** (or electromotive force, although it is not really a force), which is denoted as E (measured in volts, $1 \text{ V} = 1 \text{ J/C}$). The potential difference is caused by the ability of electrons to flow from one half cell to another. As $W = EQ$, large cell potential means large amount of electrical work can be done by given number of charges (electrons) traveling between the electrodes.

- When the reaction for an electrochemical cell is spontaneous, $E > 0$.
- When the electrochemical cell reaction is at equilibrium, $E = 0$.
- When the reverse reaction is spontaneous, $E < 0$.

□ Standard cell potential (E°)

For standard cell potential, temperature of the reaction is often assumed to **298.15 K** or 25°C , the concentration of the reactants and products is **1 M**, and reactions occurs at **1 atm** pressure. The standard cell potential is denoted as E° and is calculated from the standard electrode potential for the two electrode/half (cell) reaction

$$E^\circ = E^\circ_{cat} - E^\circ_{an}$$



Relationship between E and ΔG

For one mole of electrochemical reaction progression, the maximum amount of work that can be produced by an electrochemical cell (ω_{\max}) is equal to the product of the cell potential (E) and the total charge transferred during the reaction (nF):

$$\omega_{\max} = nFE$$

where n is the number of electrons transferred in the cell reaction, and F is Faraday constant (96485 C/mol). Work is expressed as a positive number because work is being done by a system on its surroundings.

The change in free energy per mole of reaction is ($\Delta G = -\omega_{\max}$), therefore we have:

$$\Delta G = -nFE$$

This equation is the key connection between electrical measurements and thermodynamic properties. A spontaneous cell reaction is therefore characterized by a negative value of ΔG and a positive value of E .

When both reactants and products are in their standard states, the relationship between ΔG° and E° is as follows:

$$\Delta G^\circ = -nFE^\circ$$



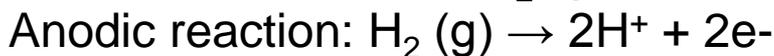
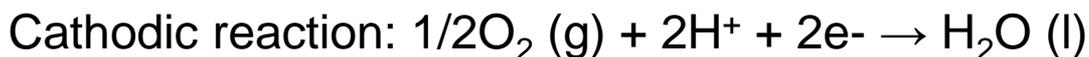
Examples

□ Example (1)

Calculate the standard potential of the hydrogen-oxygen fuel cell at 298 K.



Answer:



$$\Delta_r G^\circ = \Delta_f G^\circ(\text{H}_2\text{O}) - [\Delta_f G^\circ(\text{H}_2) + 1/2\Delta_f G^\circ(\text{O}_2)] = -237190 \text{ J/mol}$$

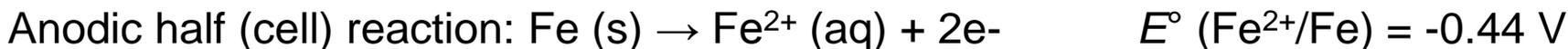
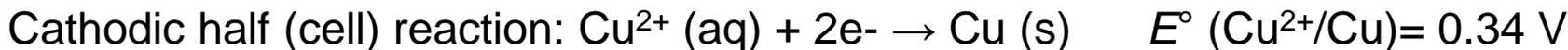
$$E^\circ = -\Delta_r G^\circ/nF = (-237190 \text{ J/mol})/(2)(96485 \text{ C/mol}) = 1.23 \text{ V}$$

□ Example (2)

Using the standard reduction potential series data, calculate ΔG° for the reaction and determine if it is spontaneous.



Answer:



Overall: $E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} = (0.34\text{V}) - (-0.44\text{V}) = 0.78 \text{ V}$

$$\Delta G^\circ = -nFE^\circ = - (2)(96485 \text{ C/mol})(0.78 \text{ J/C})$$

$$= -150516 \text{ J/mol} = -150.52 \text{ kJ/mol}$$

The reaction is spontaneous



Equilibrium Constant (K)

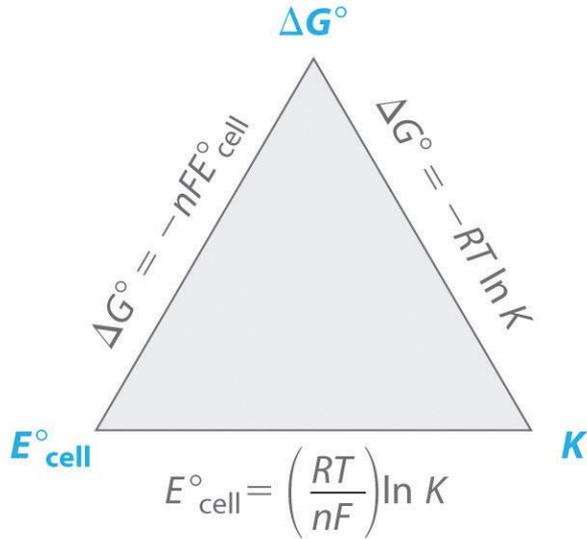
□ Definition

The equilibrium constant of a chemical reaction is the value of the **reaction quotient** when the reaction has reached **equilibrium**. An equilibrium constant value is independent of the analytical concentrations of the reactant and product species in a mixture, but depends on temperature and on ionic strength.

For a general chemical reaction: $aA + bB \leftrightarrow cC + dD$

$$K = Q = \frac{a(\text{products})}{a(\text{reactants})} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

□ Relation between ΔG° , E° , and K



ΔG°	E°_{cell}	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Under **standard** condition



Example

□ Using the standard (reduction) electrode potential series to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give PbSO_4 under standard conditions.

□ Answer:

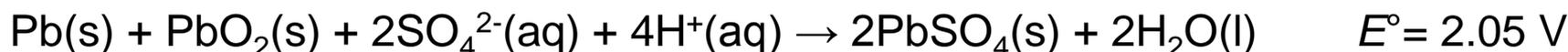
- Cathodic half (cell) reaction:



- Anodeic half (cell) reaction:



- Overall:



- Calculation of equilibrium constant:

$$RT \ln K = nFE^\circ$$

$$\ln K = (2)(96485 \text{ C/mol})(2.05 \text{ J/C}) / (8.314 \text{ J/mol-K})(298.15 \text{ K}) = 159.66$$

$$K = 2.18 \times 10^{69}$$

Thus the equilibrium lies far to the right



Nernst Equation

Substituting $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$ into equation $\Delta G = \Delta G^\circ + RT \ln Q$, we have:

$$-nFE = -nFE^\circ + RT \ln Q$$

Divide both sides of the equation above by $-nF$, we have:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

This is the very important Nernst Equation, which relates the actual cell potential to the standard cell potential and to the activities of the electroactive species.

The Equation can be used for both the electrochemical half-reactions and the total reaction.

Sometimes, the Equation can be rewritten in the form of lg:

$$E = E^\circ - \frac{2.303RT}{nF} \lg Q$$

At room temperature, $T = 298.15$ K, then we have:

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \lg Q$$

- Nernst Equation Calculator: <http://calistry.org/calculate/nernstEquation>



□ Calculation of cell potential using Nernst Equation

A recipe to properly compose a Nernst equation for an electrochemical cell:

1. Write down the electrochemical half-reactions showing chemicals, stoichiometric coefficients, and phases of all chemical components (reactants and products).
2. Define n , ensuring that the amount of electrons in both half-reactions is same.
3. Define all concentrations and activity coefficient for chemical components (Q).
4. Calculate E° from the **Standard Electrode Potentials** or from the **Standard Gibbs Free Energy of Reaction $\Delta_r G^\circ$** (by using equation **$\Delta_r G^\circ = -nFE^\circ$**)
5. Calculate cell potential using Nernst Equation



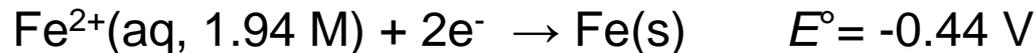
Example

❑ Calculate the following cell potential at nonstandard conditions. Is the process spontaneous? Consider the reaction at room temperature:



❑ Answer:

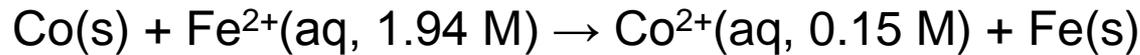
▪ Cathode:



▪ Anode:



▪ Overall:



$$E^\circ = E^\circ_{\text{cat}} - E^\circ_{\text{an}} = (-0.44\text{V}) - (-0.277\text{V}) = -0.163 \text{ V}$$

The process is NOT spontaneous under the standard condition.

The number of electron transferred $n = 2$

Neglect the pure solid phases (Co and Fe)

$$Q = [\text{Co}^{2+}]/[\text{Fe}^{2+}] = 0.15 \text{ M}/1.94 \text{ M} = 0.077$$

$$E = E^\circ - (0.0592 \text{ V}/n)\lg Q$$

$$= -0.163 \text{ V} - (0.0592 \text{ V}/2)\lg 0.077 = -0.163 \text{ V} + 0.033 \text{ V} = -0.13 \text{ V}$$

The process is still NOT spontaneous



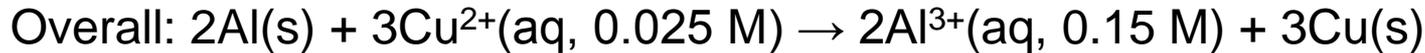
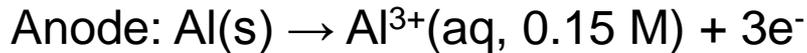
Example

□ What is the cell potential for the following reaction at room temperature?



What are the values of n and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer:



therefore, $n = 6$; $Q = [\text{Al}^{3+}]^2/[\text{Cu}^{2+}]^3 = 0.15^2/0.025^3 = 1440$

$$\begin{aligned} \Delta_r G^\circ &= [2\Delta_f G^\circ(\text{Al}^{3+}\text{aq}) + 3\Delta_f G^\circ(\text{Cu})] - [2\Delta_f G^\circ(\text{Al}) + 3\Delta_f G^\circ(\text{Cu}^{2+}\text{aq})] \\ &= [2(-481.2 \text{ kJ}) + 3(0 \text{ kJ})] - [2(0 \text{ kJ}) + 3(64.98 \text{ kJ})] \\ &= -1157.34 \text{ kJ} \end{aligned}$$

$$E^\circ = -\Delta_r G^\circ/nF = -(-1157.34 \text{ kJ})/(6 \text{ mol}) (96485 \text{ C/mol}) = 1.999 \text{ V}$$

$$\begin{aligned} E &= E^\circ - (0.0592\text{V}/n)\lg Q \\ &= 1.999 \text{ V} - (0.0592\text{V}/6)\lg 1440 \\ &= 1.999 \text{ V} - 0.031 \text{ V} \\ &= 1.968 \text{ V} \end{aligned}$$

The process is spontaneous



Concentration Cell

□ Concentration cell

In a concentration cell, the electrodes are the same material and the two half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials, there will be a potential difference, which can be determined with the aid of the Nernst equation.

□ Example

What is the cell potential of the concentration cell at room temperature described by $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq}, 0.10 \text{ M})||\text{Zn}^{2+}(\text{aq}, 0.5 \text{ M})|\text{Zn(s)}$

Answer:

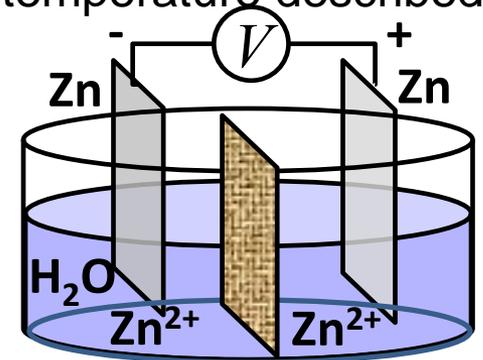


therefore, $n = 2$; $Q = 0.1/0.5 = 0.2$

$$E = E^{\circ} - (0.0592\text{V}/n)\lg Q = 0 \text{ V} - (0.0592\text{V}/2)\lg 0.2 = \mathbf{0.021 \text{ V}} \quad (0.1 \text{ M}) \quad (0.5 \text{ M})$$

The Zn^{2+} ions try to move from the concentrated half cell to the dilute half cell, and the driving force is equivalent to 0.021 V.

- In a concentration cell, the standard cell potential will always be zero because the anode and cathode involve the same reaction. To get a positive cell potential (spontaneous process) the reaction quotient Q must lower than 1.





Potential-pH (Pourbaix) Diagram

□ Essentially phase diagrams that map the conditions (in terms of potential and pH as typical in aqueous solutions) where redox species are stable.

□ Notes:

Areas: regions where a single species is stable

Dashed lines: the two half-reactions associated with the water splitting reaction

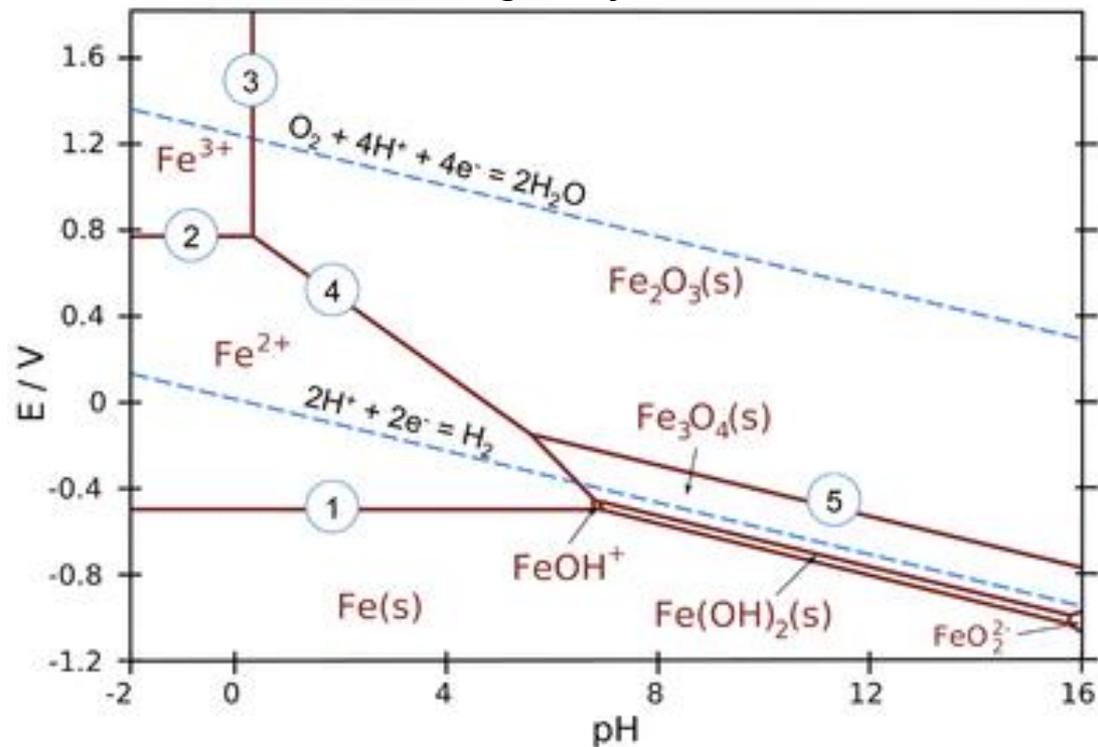
Solid lines: conditions where two species exist in equilibrium

horizontal lines - Redox reactions that do not involve H⁺/OH⁻ species

Vertical lines - Pure acid-base (w/o charge transfer) reactions

Inclined lines - Reactions that involve **both** redox & acid-base

Pourbaix diagram for Fe at 1.0 mM





Pourbaix Diagram for Fe in Water

□ How to construct Pourbaix diagram

- The **upper dash line** corresponds to oxygen evolution reaction:
 $O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l)$, with the following Nernst equation:

$$E = E^\circ - \frac{0.0592 V}{n} \lg Q$$
$$E = 1.229 V - \frac{0.0592 V}{4} \lg \left(\frac{a_{H_2O}}{(a_{H^+})^4} \right) = 1.229 V - \frac{0.0592 V}{4} 4 \lg \left(\frac{1}{a_{H^+}} \right)$$

$$E = 1.229 - 0.0592 \text{ pH (V)}$$

- The **lower dash line** corresponds to hydrogen evolution reaction:
 $2H^+(aq) + 2e^- = H_2(g)$, with the following Nernst equation:

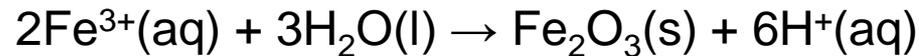
$$E = 0 V - 0.0592 V \lg \left(\frac{1}{a_{H^+}} \right)$$

$$E = -0.0592 \text{ pH (V)}$$

- The **line (1)** represents the pure redox reaction (does not involve H^+ or OH^-):
 $Fe^{2+}(aq) + 2e^- = Fe(s)$, thus, $E^\circ = -0.44 V$ can be used for the line for standard activity of Fe^{2+} .
- The **line (2)** represents the pure redox reaction (does not involve H^+ or OH^-):
 $Fe^{3+}(aq) + e^- = Fe^{2+}(aq)$, thus, $E^\circ = 0.77 V$ can be used for the line for standard activity of both Fe^{2+} and Fe^{3+} .



- The **line (3)** corresponds to a pure acid-based equation:



$$\Delta rG^\circ = -RT \ln K$$

$$\Delta rG^\circ = -2.303RT \lg \left[\frac{(a_{\text{Fe}_2\text{O}_3})(a_{\text{H}^+})^6}{(a_{\text{Fe}^{3+}})^2(a_{\text{H}_2\text{O}})^3} \right]$$

$$\Delta rG^\circ = -2.303RT \lg \frac{(a_{\text{H}^+})^6}{(10^{-3})^2} = -2.303RT [6 + 6 \lg(a_{\text{H}^+})]$$

$$\frac{1}{6} \left(\frac{\Delta rG^\circ}{2.303RT} + 6 \right) = -\lg(a_{\text{H}^+}) = \text{pH}$$

$$\text{pH} = \frac{1}{6} \left(\frac{-8242.5 \frac{\text{J}}{\text{mol}}}{2.303 \times 8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K}} + 6 \right) = 0.755$$

- The **line (4)** corresponds to the reaction that is both acid-base and redox:



$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \lg Q$$

$$E = -\frac{\Delta rG^\circ}{nF} - \frac{0.0592 \text{ V}}{n} \lg \left[\frac{(a_{\text{Fe}^{2+}})^2(a_{\text{H}_2\text{O}})^3}{(a_{\text{Fe}_2\text{O}_3})(a_{\text{H}^+})^6} \right] = -\frac{\Delta rG^\circ}{nF} - \frac{0.0592 \text{ V}}{n} \left[-6 + 6 \lg \left(\frac{1}{a_{\text{H}^+}} \right) \right]$$



$$E = -\frac{-140.4 \frac{\text{kJ}}{\text{mol}}}{2 \times 96485 \frac{\text{C}}{\text{mol}}} - \frac{0.0592 \text{ V}}{2} [-6 + 6\text{pH}]$$

$$E = 0.909 - 0.1788\text{pH (V)}$$

- The **line (5)** corresponds to the reaction that is both acid-base and redox:



$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \lg Q$$

$$E = -\frac{\Delta rG^\circ}{nF} - \frac{0.0592 \text{ V}}{n} \lg \left[\frac{(a_{\text{Fe}_3\text{O}_4})^2 a_{\text{H}_2\text{O}}}{(a_{\text{Fe}_2\text{O}_3})^3 (a_{\text{H}^+})^2} \right] = -\frac{\Delta rG^\circ}{nF} - \frac{0.0592 \text{ V}}{n} 2 \lg \left(\frac{1}{a_{\text{H}^+}} \right)$$

$$E = -\frac{-45.12 \frac{\text{kJ}}{\text{mol}}}{2 \times 96485 \frac{\text{C}}{\text{mol}}} - 0.0592 \text{ V} \times \text{pH}$$

$$E = 0.234 - 0.0592\text{pH (V)}$$



Example of E Dependence on Temperature

Calculate the standard potential of the hydrogen-oxygen fuel cell at different temperature. $\text{H}_2 (\text{g}) + 1/2\text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g})$

Answer:

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{H}_2\text{O}) - [\Delta_f G^\circ(\text{H}_2) + 1/2\Delta_f G^\circ(\text{O}_2)] = \Delta_f G^\circ(\text{H}_2\text{O})$$

$$E = E^\circ - RT/nF(\ln Q) = -\Delta_r G^\circ/nF = \Delta_f G^\circ(\text{H}_2\text{O}) / (2)(96485 \text{ C/mol})$$

T / K	298.15	300	400	500	600	700	800	900	1000	1100	1200	1300
$-\Delta_f G^\circ(\text{H}_2\text{O}) / \text{kJ/mol}$	237.141	236.839	223.937	219.069	214.008	208.814	203.501	198.091	192.603	187.052	181.450	175.807
E° / V	1.23	1.23	1.16	1.14	1.11	1.08	1.05	1.03	1.00	0.97	0.94	0.91

