Electrochemical Engineering
Lecture 02
Equilibrium Electrochemistry

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Equilibrium Electrochemistry

❑Equilibrium Electrochemistry

"…one of the most important subjects of electrochemistry…usually the first and required step in analyzing any electrochemical system" (S. N. Lvov)

Describes thermodynamic properties of reactions in an electrochemical cell and gets an expression for the electric potential of such cell, and the potential can be related to specific cell condition (e.g., T, concentration)

❑Topics

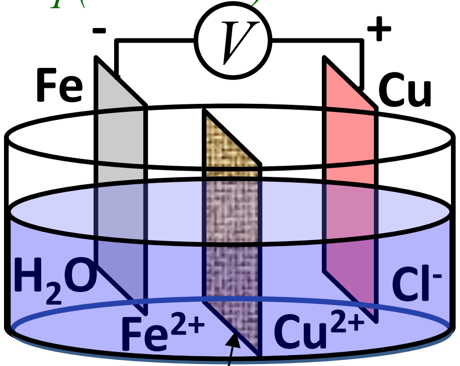
- Equilibrium cell potential
- Standard hydrogen electrode
- Standard electrode potential and standard cell potential
- Common reference electrodes
- Nernst Equation
- Equilibrium constant (K) and cell potential
- Pourbaix diagram
- Gibbs free energy G and Gibbs free energy change (ΔG) and relationship between equilibrium cell potential E_{eq} and ΔG - <u>for graduate student only</u>

Equilibrium Cell Potential E_{eq} Depends on Cell Construction

- ❑ For an electrochemical cell, E_{eq} depends on BOTH the oxidation (anodic) AND the reduction (cathodic) half (cell) reactions involved
- ❑ **Standard condition -** 25°C, 1 atm, concentration 1 mol/kg of water

Cell of Fe^{2+}/Fe vs. Cu^{2+}/Cu

$E^{o}_{eq\ (Fe\ vs.\ Cu)} = -0.780\ \text{V}$



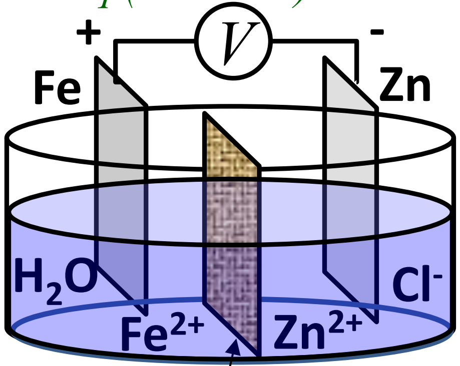
$Fe^{2+} + 2e^- \leftrightarrow Fe$ $Cu^{2+} + 2e^- \leftrightarrow Cu$

Separation membrane

- Fe more negative than Cu
- If connecting the external circuit
  - e^- flow from Fe through ext circuit to Cu
  - Oxidation (anodic) half reaction on Fe
  - Reduction (cathodic) half reaction on Cu
  - Overall: $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

Cell of Fe^{2+}/Fe vs. Zn^{2+}/Zn

$E^{o}_{eq\ (Fe\ vs.\ Zn)} = 0.323\ \text{V}$



$Fe^{2+} + 2e^- \leftrightarrow Fe$ $Zn^{2+} + 2e^- \leftrightarrow Zn$

Separation membrane

- Fe more positive than Zn
- If connecting the external circuit
  - e^- flow from Zn through ext circuit to Fe
  - Oxidation (anodic) half reaction on Zn
  - Reduction (cathodic) half reaction on Fe
  - Overall: $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

Standard Hydrogen Electrode (SHE)

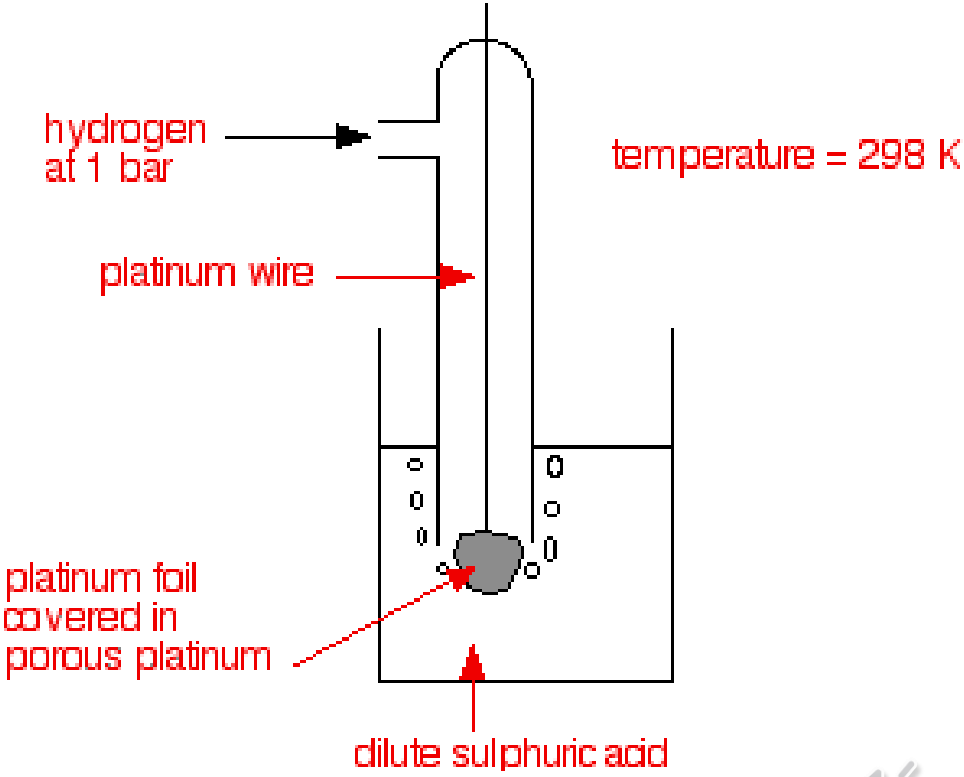
❑ **To establish a common comparison "benchmark" or reference point, a special electrode (reaction) or redox pair of H^+/H_2 with unit H^+ activity and standard H_2 pressure (1 atm.) is chosen and named the Standard Hydrogen Electrode (SHE)**

❑ **Notes:**

- Oxidized species - H^+_{aq}
- Reduced species - H_2
- The redox pair is often called "**H^+/H_2 electrode**"
- The electrode or half-cell reaction is

$$2H^+_{(aq)} + 2e^- = H_{2\ (g)}$$

- Actual electrode (electronic conductor) is Pt - inert and does NOT participate in the redox reaction



http://www.chemguide.co.uk/physical/redoxeqia/introduction.html

Standard Electrode Potential

- **Any other electrode (reaction)/redox pair is compared against the SHE (H^+/H_2 pair), and an equilibrium cell potential is obtained - the electrode potential for that "electrode" (reaction)/redox pair vs. SHE**

  If concentration for redox species in that electrode (reaction) is standard (1 molal or 1 mol/kg of water), the obtained equilibrium cell potential is called the **Standard (Equilibrium) Electrode Potential** E^o for that electrode (reaction)/redox pair

- **Example of a Zn^{2+}/Zn vs. H^+/H_2 cell**

  Under standard condition, $E^o_{eq\ (Zn2+/Zn\ vs.\ H+/H2)} = -0.763$ V

  - **Standard electrode potential** for Zn^{2+}/Zn electrode (reaction) is **<u>-0.763 V</u>**, or 0.763 V more negative than the H^+/H_2 electrode (reaction)
  - When cell is connected through external circuit:

  Zn goes through anodic (oxidation) half cell reaction

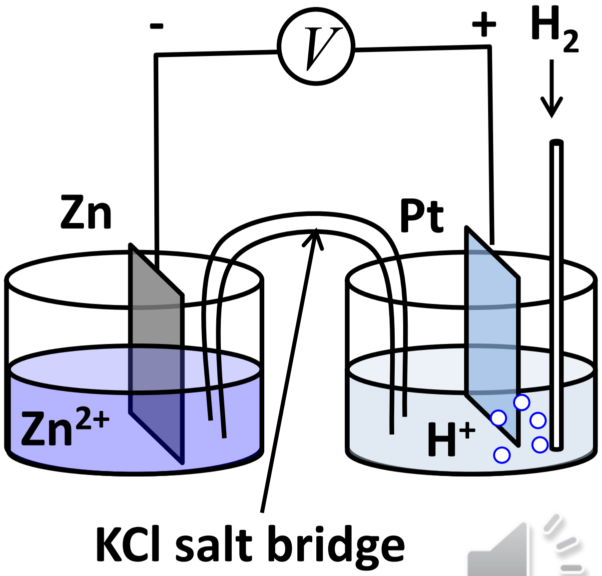
  $$Zn \rightarrow Zn^{2+} + 2e^-$$

  H^+ goes through cathodic (reduction) half cell reaction

  $$2H^+ + 2e^- \rightarrow H_2$$

  Overall or full cell reaction

  $$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$



Standard Electrode Potential Series

- **Researchers constructed various electrochemical cells with different redox pair or electrode (half cell) reactions against SHE and obtained the standard electrode potential series, e.g.,**

"Electrode" or Pair of Oxidized/Reduced species (Redox pair)	Electrode/Half cell reaction (Always written as a reduction or cathodic reaction)	Standard Electrode Potential vs. SHE (V)
Li^+/Li	$Li^+ + e^- = Li$	-3.045
Al^{3+}/Al	$Al^{3+} + 3e^- = Al$	-1.706
Fe^{2+}/Fe	$Fe^{2+} + 2e^- = Fe$	-0.440
H^+/H_2	$2H^+ + 2e^- = H_2$	0.000
Cu^{2+}/Cu	$Cu^{2+} + 2e^- = Cu$	+0.340
Ag^+/Ag	$Ag^+ + e^- = Ag$	+0.800
O_2/H_3O^+ (over Pt)	$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.229
Au^+/Au	$Au^+ + e^- = Au$	+1.42
F_2/F^-	$F_2 + 2e^- = 2F^-$	+2.85

From Standard Electrode Potentials to Standard Cell Potential

❑ **When connecting two different half cells (two redox pairs or two “electrodes”) together through an external circuit**

- The electrode (or half cell or redox pair) with **more negative** electrode potential will experience **oxidation (anodic)** half cell reaction, and will be the **anode**
- The electrode (or half cell or redox pair) with **more positive** electrode potential will experience **reduction (cathodic)** half cell reaction, and will be the **cathode**
- Overall, the **standard cell potential** is

$$E^o_{cell} = E^o_{cat} - E^o_{an}$$

E^o_{cat}	**Standard electrode potential for the cathode or the reduction (cathodic) half (cell) reaction**
E^o_{an}	**Standard electrode potential for the anode or the oxidation or anodic) half (cell) reaction**

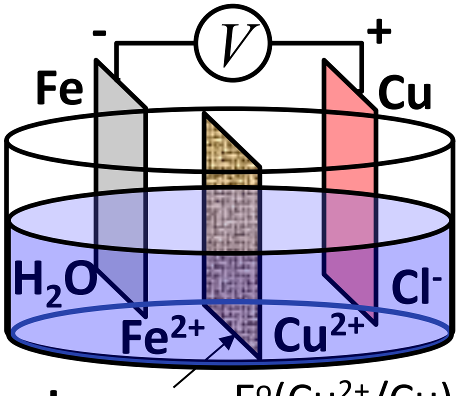
Example of Fe^{2+}/Fe vs. Cu^{2+}/Cu Cell

- **For this electrochemical cell**

$E^o(Fe^{2+}/Fe) = -0.440$ V

$E^o(Cu^{2+}/Cu) = +0.340$ V

$E^o(Fe^{2+}/Fe)$ more negative →



$E^o(Fe^{2+}/Fe) = -0.440$ V

Separation membrane

$E^o(Cu^{2+}/Cu) = +0.340$ V

Oxidation (anodic) half cell reaction for the Fe^{2+}/Fe electrode (redox pair)

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (i)$$

Reduction (cathodic) half cell reaction for Cu^{2+}/Cu electrode (redox pair)

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (ii)$$

Overall/full (cell) reaction = (i) + (ii) (with goal of removing e^-): $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

Standard cell potential:

$$E^o_{cell} = E^o_{cat} - E^o_{an} = E^o(Cu^{2+}/Cu) - E^o(Fe^{2+}/Cu) = +0.340V - (-0.440V) = +0.780\ V$$

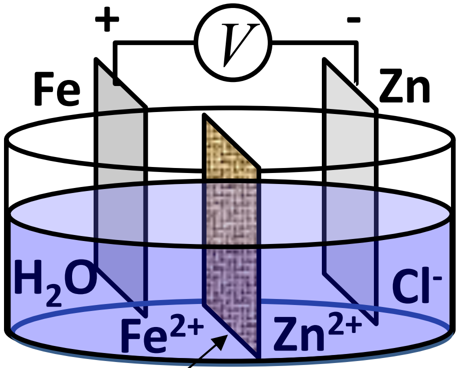
Example of Zn^{2+}/Zn vs. Fe^{2+}/Fe Cell

❑**For this electrochemical cell**

$E^o(Fe^{2+}/Fe) = -0.440$ V

$E^o(Zn^{2+}/Zn) = -0.763$ V

$E^o(Zn^{2+}/Zn)$ is more negative →



$E^o(Fe^{2+}/Fe) = -0.440$ V

$E^o(Zn^{2+}/Zn) = -0.763$ V

Oxidation (anodic) half (cell) reaction for the Zn^{2+}/Zn electrode (redox pair)

$Zn \rightarrow Zn^{2+} + 2e^-$ (i) and $\mathbf{E^o_{an}} = E^o(Zn^{2+}/Zn) = -0.763$ V

Reduction (cathodic) half (cell) reaction for Fe^{2+}/Fe electrode (redox pair)

$Fe^{2+} + 2e^- \rightarrow Fe$ (ii) and $\mathbf{E^o_{cat}} = E^o(Fe^{2+}/Fe) = -0.440$ V

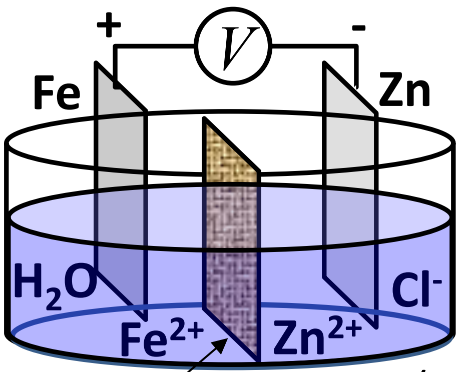
Overall/Full (cell) reaction = (i) + (ii) (with goal of removing e^-): $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

Standard cell potential:

$\mathbf{E^o_{cell} = E^o_{cat} - E^o_{an}} = E^o(Fe^{2+}/Fe) - E^o(Zn^{2+}/Zn) = -0.440V - (-0.763V) = +0.323$ V

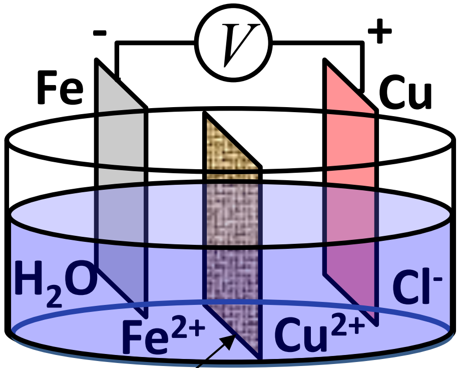
Notes about Standard Electrode Potential (1)

- The **Standard Electrode Potential** for an electrode (essentially, a half cell reaction or redox pair) is the measured equilibrium potential under standard condition vs. the SHE, and it does NOT depend on whether that electrode (or the half cell) reaction is actually cathodic (going through reduction) or anodic (going through oxidation)
- **Example**



$E^o(Fe^{2+}/Fe)$ = -0.440 V
cathodic

$E^o(Zn^{2+}/Zn)$ = -0.763 V



$E^o(Fe^{2+}/Fe)$ = -0.440 V
anodic

$E^o(Cu^{2+}/Cu)$ = +0.340 V

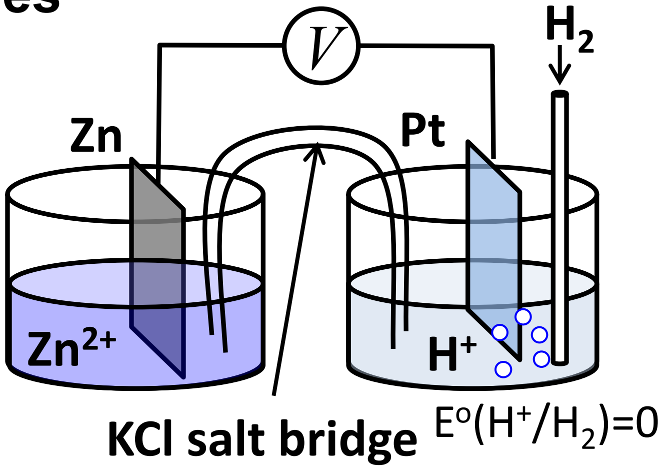
For the Fe^{2+}/Fe electrode or redox pair, $E^o(Fe^{2+}/Fe) = -0.440$ V (vs. SHE)
The standard electrode potential for Fe^{2+}/Fe electrode remains unchanged no matter, in an actual electrochemical full cell, whether Fe^{2+}/Fe electrode goes through

- cathodic (reduction) reaction (i.e., $Fe^{2+} + 2e^- \rightarrow Fe$, as in Fe^{2+}/Fe vs. Zn^{2+}/Zn cell)
- anodic (oxidation) reaction (i.e., $Fe \rightarrow Fe^{2+} + 2e^-$, as in Cu^{2+}/Cu vs. Fe^{2+}/Fe cell)

Notes about Standard <u>Electrode</u> Potential (2)

- ❑ **The polarity (positive or negative) of the Standard Electrode Potential is a measure of how easily the oxidized (or reduced) species for that electrode (redox pair) can be reduced (or oxidized) <u>vs. the SHE</u>**
- ❑ **Examples**

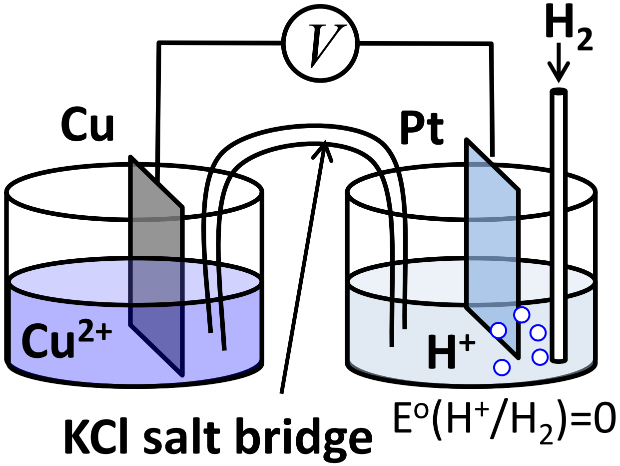
$E^o(Zn^{2+}/Zn)$ = -0.763 V



$E^o(Zn^{2+}/Zn)$ more negative than $E^o(H^+/H_2)$ → Zn is more easily oxidized than H_2 (or H^+ is more easily reduced than Zn^{2+}) → For a Zn^{2+}/Zn vs. H^+/H_2 cell, e^- will flow out from the Zn^{2+}/Zn electrode to the H^+/H_2 electrode (redox pair)→

Overall: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

$E^o(Cu^{2+}/Cu)$ = +0.340 V

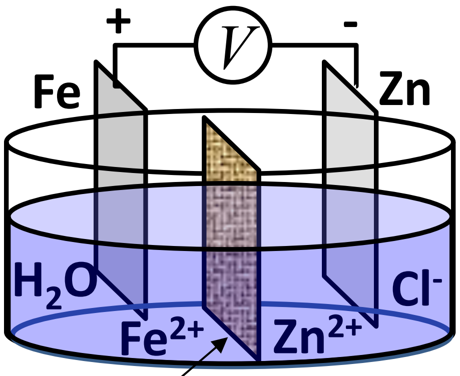


$E^o(Cu^{2+}/Cu)$ more positive than $E^o(H^+/H_2)$ → Cu^{2+} is more easily reduced than H^+ (or H_2 is more easily oxidized than Cu) → For a Cu^{2+}/Cu vs. H^+/H_2 cell, e^- flow out from the H^+/H_2 electrode (redox pair) to the Cu^{2+}/Cu electrode→

Overall: $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$

Note about Standard Cell Potential (1)

- **If the standard cell potential for a given overall (full cell) reaction is <u>positive</u>, the reaction, at standard condition, will proceed <u>spontaneously</u>; if it is *negative*, the *reverse* reaction will proceed**
- **Example of Fe^{2+}/Fe vs. Zn^{2+}/Zn cell**



$E^o(Fe^{2+}/Fe) = -0.440\ V$

$E^o(Zn^{2+}/Zn) = -0.763\ V$

Assuming:

the reduction (cathodic) reaction is

$Zn^{2+} + 2e^- \rightarrow Zn$

the oxidation (anodic) reaction is

$Fe \rightarrow Fe^{2+} + 2e^-$

The overall reaction would be

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

The standard cell potential for such a **hypothetical** reaction would be:

$\mathbf{E^o_{cell} = E^o_{cat} - E^o_{an}} = E^o(Zn^{2+}/Zn) - E^o(Fe^{2+}/Fe) = (-0.763\ V) - (-0.440\ V) = -0.323\ V$

The negative sign for $\mathbf{E^o_{cell}}$ means the reaction as written ($Fe + Zn^{2+} \rightarrow Fe^{2+} + Zn$) is **NOT spontaneous at standard condition,**

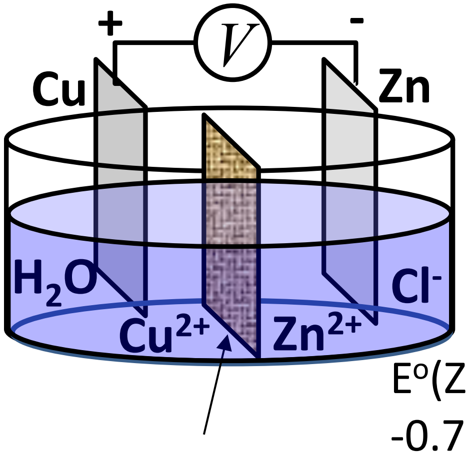
while **<u>the reverse reaction</u>** of $\mathbf{Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe}$ would having a standard cell potential of $\mathbf{E^o_{cell} = E^o_{cat} - E^o_{an} =} E^o(Fe^{2+}/Fe) - E^o(Zn^{2+}/Zn) = +0.323\ V \rightarrow$

it would happen spontaneously, if the external circuit has finite resistance

Class Example (1)

For an electrochemical cell connecting Cu/Cu^{2+} (1 M) electrode with Zn/Zn^{2+} (1 M) electrode through a membrane

Q1: ***On which electrode does oxidation reaction (metal dissolution) and reduction (metal deposition) reaction happen, respectively? Write half cell as well as overall reactions. Knowing $E^o(Zn/Zn^{2+}) = -0.763V$ and $E^o(Cu/Cu^{2+}) = +0.340V$***



$E^o(Cu^{2+}/Cu) = +0.340$ V

$E^o(Zn^{2+}/Zn) = -0.763$ V

Separation membrane

Solution:

$E^o(Zn/Zn^{2+})$ is more negative than $E^o(Cu/Cu^{2+})$

Zn/Zn^{2+} electrode:

anodic/oxidation half (cell) reaction: $Zn \rightarrow Zn^{2+} + 2e^-$

Cu/Cu^{2+} electrode:

cathodic/reduction half (cell) reaction: $Cu^{2+} + 2e^- = Cu$

Overall reaction is written as: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Q2 Determine the standard cell potential for such a cell?

$E^o_{cell} = E^o_{cat} - E^o_{an} = E^o(Cu/Cu^{2+}) - E^o(Zn/Zn^{2+}) = 0.340V - (-0.763V) = 1.103V$

Class Example (2)

Between copper and aluminum, when each of them is immersed in an acidic aqueous solution WITHOUT dissolved oxygen (two separate experiments), which metal will corrode and which one will not? Please also write down the half cell reactions and the overall corrosion reaction and standard cell potential.
Knowing $E^o(Cu/Cu^{2+}) = 0.340V$ and $E^o(Al/Al^{3+}) = -1.662V$, $E^o(H_2/H^+) = 0.0V$, $E^o(O_2/H_2O) = 1.229$ V

Solution:

For Al, $E^o(Al/Al^{3+}) = -1.662V$ more negative than $E^o(H_2/H^+) = 0$ V

Note: the system does not contain significant oxygen, electrode reaction of O_2/H_2O (at = 1.229 V) is neglected

Therefore, Al will oxidize with respect to H_2/H^+, while Cu will NOT

For Al:

anodic (oxidation) half cell reaction: $Al \rightarrow Al^{3+} + 3e^-$

cathodic (reduction) half cell reaction: $2H^+ + 2e^- \rightarrow H_2$

Overall reaction: $2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2$

Standard cell potential:

$E^o_{cell} = E^o_{cat} - E^o_{an} = E^o(H_2/H^+) - E^o(Al/Al^{3+}) = 0 - (-1.662) = 1.662$ V

For Cu, it does not really corrode as $E^o(Cu/Cu^{2+}) = 0.340V$ is more positive than $E^o(H_2/H^+) = 0$ V, while the system does not contain much oxygen.

Reference Electrodes other than SHE

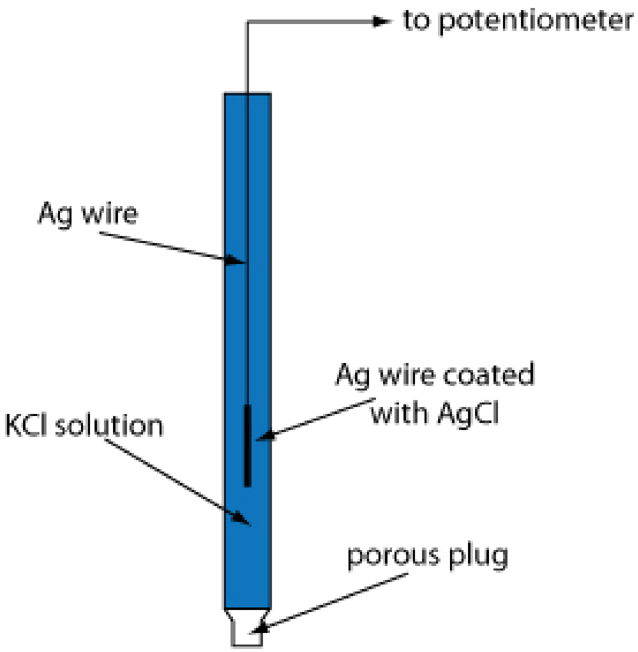
- **SHE is a reference electrode to compare with other "electrodes" or half cell reactions (or redox pairs) - but NOT convenient to use!**
  - Relative complex design including the need for H_2 gas and unit **activity** for H^+
  - Needs expensive Pt and the Pt surface also needs to be kept clean
- **Alternative reference electrodes**

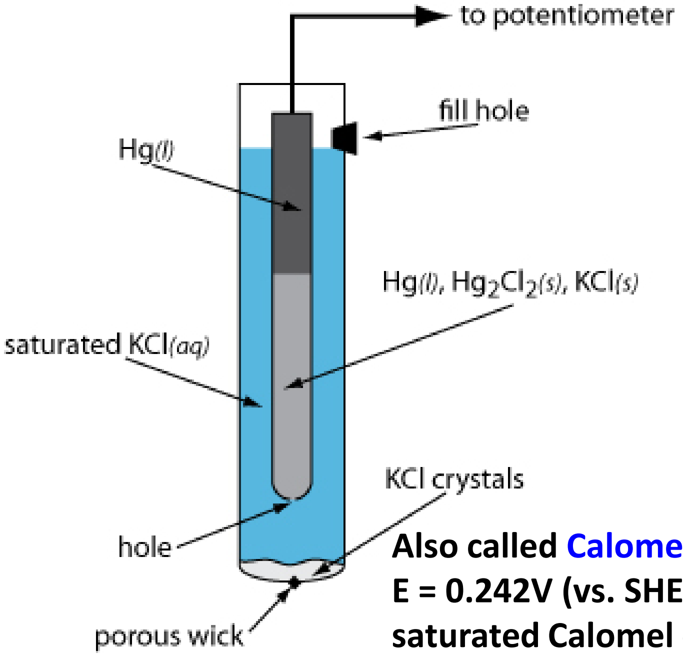
Ag/AgCl: $AgCl_{(s)} + e^- = Ag_{(s)} + Cl^-_{(aq)}$

$E^o(Ag/AgCl) = 0.222V$ (vs. SHE) at 25°C

Hg/Hg_2Cl_2: $Hg_2Cl_{2(s)} + 2e^- = 2Hg_{(l)} + 2Cl^-_{(aq)}$

$E^o(Hg/Hg_2Cl_2) = 0.268V$ (vs. SHE) at 25°C





Also called Calomel electrode
E = 0.242V (vs. SHE) for saturated Calomel electrode

http://community.asdlib.org/imageandvideoexchangeforum/2013/07/31/reference-electrodes/

Nernst Equation

- ❑ **For electrochemical (full cell) reaction under non-standard condition, cell potential (sometimes called electromotive force or emf) satisfy:**

$$E_{Cell} = E^{\circ} - \frac{RT}{nF} lnQ$$

$E°$	Standard cell potential for the electrochemical reaction
R	Gas constant, 8.314 J/(mol · K)
T	Absolute temperature, K
n	Number of element charge transferred in the redox reaction
F	Faraday constant, 96485 C/mol
Q	Reaction quotient is the ratio of the product of each product's activity raised to the power of stoichiometric coefficient (v) to the product of each reactant, or

$$Q = \frac{\prod_j^{product} (a_j)^{v_j}}{\prod_i^{reactant} (a_i)^{v_i}}$$

For a simple chemical reaction: $\alpha A + \beta B \leftrightarrow \gamma C + \delta D$

$$Q = \frac{(a_C)^{\gamma} \cdot (a_D)^{\delta}}{(a_A)^{\alpha} \cdot (a_B)^{\beta}}$$

https://en.wikipedia.org/wiki/Reaction_quotient

Notes about Activity

https://en.wikipedia.org/wiki/Thermodynamic_activity

❑Thermodynamic or chemical activity a

- Unitless
- 1 (unity) for pure solid or liquid
- 1 (unity) for solvents in most solutions
- For ideal gas (mixture), activity for gas j

$$a_j^{gas} = \frac{p_j}{p^0}$$

- For an ideal liquid solution (usually very dilute), activity for solute j

$$a_j^{ideal} = \frac{c_j}{c^0} = \frac{b_j}{b^0}$$

- For practical dilute, non-ionic solutions, activity of a solute can be defined in different way, such as:

$$a_{c,j} = \gamma_{c,j}\frac{c_j}{c^0} \qquad \boxed{a_{b,j} = \gamma_{b,j}\frac{b_j}{b_0}} \qquad a_{X,j} = \gamma_{X,j}X_j$$

- For the same species, “activity is the same regardless of the ways to express composition and the standard state chosen”, i.e.,

$$a_j = \gamma_{c,j}\frac{c_j}{c^0} = \gamma_{b,j}\frac{b_j}{b_0} = \gamma_{X,j}X_j$$

Nernst Equation for Half-cell Reaction

- **For a simple electrochemical half cell reaction**

$$Ox + ne^- = Red$$

Nernst equation takes the form:

$$E = E° - \frac{RT}{nF} ln \frac{a_{Red}}{a_{Ox}}$$

E	Electrode potential vs SHE for the electrode (reaction) or redox pair
$E°$	Standard electrode potential (vs SHE) for the electrode (reaction) or redox pair
a_{Red}	Activity for the reduced species, unitless
a_{Ox}	Activity for the oxidized species, unitless

Additional Notes for Nernst Equation

❑**Calculation of potential (or emf) 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 number of electrons in both half-reactions is same.
3. Define activity for all chemical components (***Q***).
4. Calculate ***E*°** from **Standard Electrode Potentials**
    - (or from Standard Gibbs Free Energy of Reaction **Δr*G*°** using **Δr*G*° = -*nFE*°**)
5. Calculate cell potential using Nernst Equation

❑**Also written as:**

$$E = E^{\circ} - \frac{RT}{nF} \cdot lnQ = E^{\circ} - \frac{RT}{nF} \cdot ln10 \cdot lgQ = E^{\circ} - \frac{2.303RT}{nF} lgQ$$

At **25°C** or **298.15 K**,

$$E = E^{\circ} - \frac{0.0592\ V}{n} lgQ$$

Nernst Potential Example (1)

Calculate the cell potential (emf) at 25°C. Is the process spontaneous? Assume activity coefficients are 1 or $a_\mathrm{i} = c_i/c^0$.

$\mathrm{Co(s)} + \mathrm{Fe^{2+}}\mathrm{(aq,\ 1.94\ M)} \rightarrow \mathrm{Co^{2+}}\mathrm{(aq,\ 0.15\ M)} + \mathrm{Fe(s)}$

Anodic/oxidation half cell reaction:

$\mathrm{Co(s)} \rightarrow \mathrm{Co^{2+}} + 2e^-$ $E° = -0.277$ V from standard electrode potential table

Cathodic/reduction half cell reaction:

$\mathrm{Fe^{2+}} + 2e^- \rightarrow \mathrm{Fe(s)}$ $E° = -0.440$ V from standard electrode potential table

Standard cell potential:

$E° = E^o_{cat} - E^o_{an} = (-0.440\ \mathrm{V}) - (-0.277\ \mathrm{V}) = -0.163\ \mathrm{V}$

The process is NOT spontaneous at **standard** condition (25°C, 1 atm, 1 mol/kg H_2O)

The number of electron transferred $n = 2$

Activity for pure solid phases (Co and Fe) are taken as unity or 1

Reaction quotient $Q = ([\mathrm{Co^{2+}}]/c^0)/([\mathrm{Fe^{2+}}]/c^0) = 0.15\ \mathrm{M}/1.94\ \mathrm{M} = 0.077$

$E = E° – (0.0592\ \mathrm{V}/n)\lg Q$

$= -0.163\ \mathrm{V} – (0.0592\ \mathrm{V}/2)\lg 0.077 = –0.163\ \mathrm{V} – (–0.033\ \mathrm{V}) = –0.130\ \mathrm{V}$

The process - Co oxidation and $\mathrm{Fe^{2+}}$ reduction is NOT spontaneous under the specified condition.

However, the reverse reaction - Fe oxidation and $\mathrm{Co^{2+}}$ reduction IS spontaneous.

Note about Cell Potential

❑ $E_{cell} > 0$	**Spontaneous reaction in the forward direction**
❑ $E_{cell} < 0$	**Spontaneous reaction in the reverse direction**
❑ $E_{cell} = 0$	**Reaction is at equilibrium - the forward reaction rate is the same as backward or reverse reaction rate** ▪ NO net current or electron flow even with finite external resistance ▪ No charge transfer & net oxidation/reduction reactions ▪ No change in concentration of redox species due to reactions

Reaction Equilibrium Constant Example (1)

Use the standard (reduction) electrode potential series to calculate the <u>equilibrium constant</u> for the reaction of metallic Pb with PbO_2 in the presence of H_2SO_4 acid to form $PbSO_4$ under <u>standard</u> condition

Anodic/oxidation half cell reaction:

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ $\qquad E° = -0.36$ V

Cathodic/reduction half cell reaction:

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ $\qquad E° = 1.69$ V

Overall or full cell reaction:

$$\mathbf{Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)}$$

$$E° = E^o_{cat} - E^o_{an} = 1.69\text{ V} - (-0.36\text{ V}) = \mathbf{2.05\text{ V}}$$

When reaching equilibrium, cell potential should be zero:

$$E = E^{\circ} - \frac{RT}{nF} \cdot lnQ = E^0 - \frac{RT}{nF} lnK_{eq} = 0$$

Equilibrium constant satisfy $\qquad lnK_{eq} = \dfrac{nF}{RT} E^0$

$$K_{eq} = exp\left(\frac{2 \times 96485C/mol}{8.314 \dfrac{J}{mol \cdot K} \times 298.15K} \times 2.05V \right) = 2.03 \times 10^{69}$$

Therefore, equilibrium lies far to the right - greatly favoring $PbSO_4$ formation

Reaction Equilibrium Constant Example (2)

Use data from the standard electrode potential series table to determine the solubility product constant K_{sp} for AgCl at 25°C, essentially the equilibrium constant for the dissolution reaction AgCl → $Ag^+ + Cl^-$

Overall reaction can be viewed as $AgCl_{(s)} + Ag \rightarrow Ag^+ + Ag + Cl^-$

Anodic/oxidation half cell reaction:

$Ag_{(s)} \rightarrow Ag^+ + e^-$ $E°(Ag^+/Ag) = 0.799\ V$

Cathodic/reduction half cell reaction:

$AgCl_{(s)} + e^- \rightarrow Ag + Cl^-$ $E°(AgCl/Ag) = 0.222V$

For overall or full cell reaction: $E° = E^o_{cat} - E^o_{an} = 0.222\ V - 0.799\ V = \mathbf{-0.577\ V}$

At equilibrium, cell potential should be zero:

$$E = E^{\circ} - \frac{RT}{nF} \cdot lnQ = E^0 - \frac{RT}{nF} lnK_{eq} = 0$$

Therefore $RT lnK_{eq} = nFE^0$

Equilibrium constant $K_{eq} = exp\left[\frac{1 \times 96485C/mol}{8.314\frac{J}{mol \cdot K} \times 298.15K} \times (-0.577V)\right] = 1.76 \times 10^{-10}$

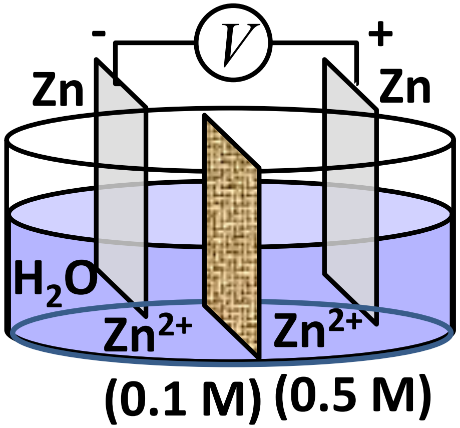
Equilibrium lies far to the left - greatly favoring AgCl precipitation instead of dissolution

Concentration Cell

❑Concept

- Two electrodes (or redox pairs/half cells) of the electrochemical cell are of the same materials/redox reactions, differing only in concentration
- Cell potential determined by Nernst equation

❑Example



Potential of concentration cell at 25°C:

$Zn(s)|Zn^{2+}$ (aq, 0.10 M)||Zn^{2+}(aq, 0.5 M)|Zn(s)

Overall: $Zn^{2+}_{(aq,\ 0.5\ M)} \rightarrow Zn^{2+}_{(aq,\ 0.1\ M)}$

View it as: $Zn^{2+}_{(aq,\ 0.5\ M)} + Zn \rightarrow Zn + Zn^{2+}_{(aq,\ 0.1\ M)}$

Anodic: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq,\ 0.1\ M)} + 2e^-$ $E^o(Zn^{2+}/Zn) = -0.763V$

Cathodic: $Zn^{2+}_{(aq,\ 0.5\ M)} + 2e^- \rightarrow Zn_{(s)}$ $E^o(Zn^{2+}/Zn) = -0.763V$

$n = 2$ (**not** zero due to redox between Zn^{2+} & Zn!) $Q = 0.1\ M/0.5\ M = 0.2$

$E = E^\circ - (0.0592V/n)\lg Q = [-0.763V - (-0.763\ V)] - (0.0592V/2)\lg 0.2 =$ **0.021 V or 21 mV**

Zn^{2+} reduced on concentrated side & Zn dissolved on dilute side w/ emf of 0.021 V

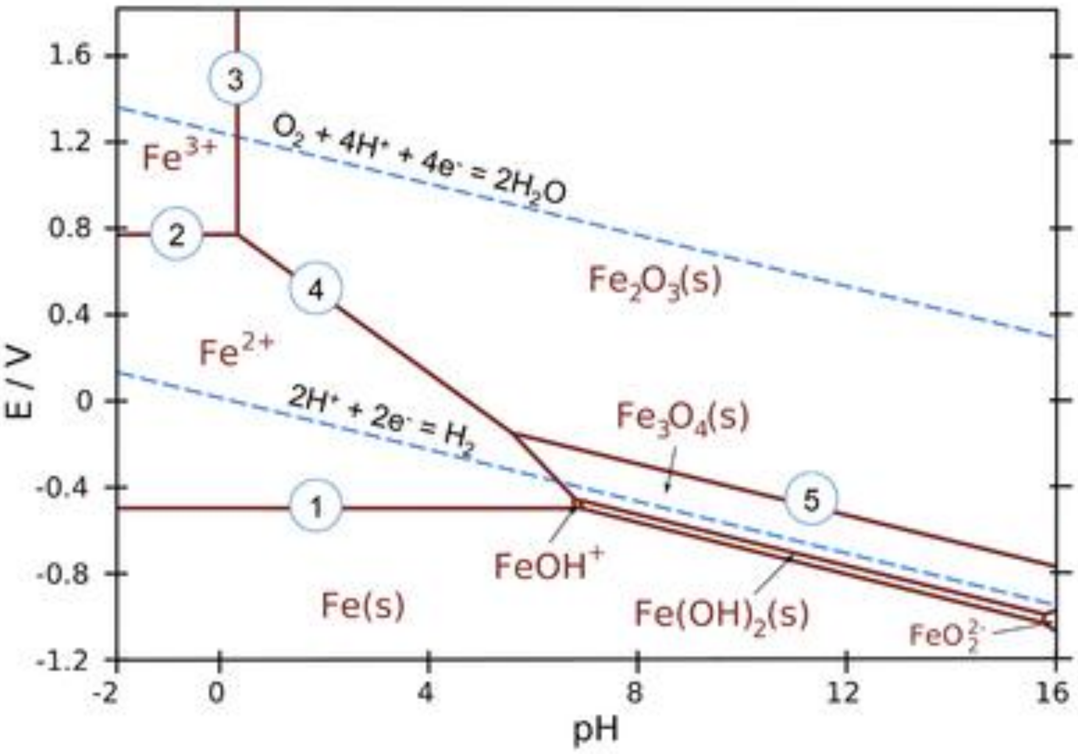
❑Notes

- Standard cell potential E° for concentration cells always zero
- To get a positive cell potential (spontaneous process), reaction quotient $Q < 1$

Potential-pH (Pourbaix) Diagram

- **Diagrams that maps the conditions/regions, i.e., potential (vs. SHE) and pH as typical in aqueous solutions, where redox species are stable**
- **Features**
  - **Areas** - regions where a (single) species is stable
  - **Dashed lines** - the two half-cell reactions associated with water splitting
  - **Solid lines** - conditions where two species exist in equilibrium
    - **Horizontal lines -** redox reactions that do not involve H^+/OH^- species
    - **Vertical lines** - acid-base reactions w/o charge transfer
    - **Inclined lines** - reactions involving both redox & acid or base

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (1)

❑**Lower dash line - hydrogen evolution reaction**

$2H^+_{(aq)} + 2e^- = H_{2\,(g)}$

Electrode potential (vs. SHE) by Nernst equation at 25°C

$$E = E^0 - \frac{0.0592\,V}{n} \lg \frac{a_{H_2}}{(a_{H^+})^2}$$

$E^0(H^+/H_2) = 0\ V$

$n = 2$

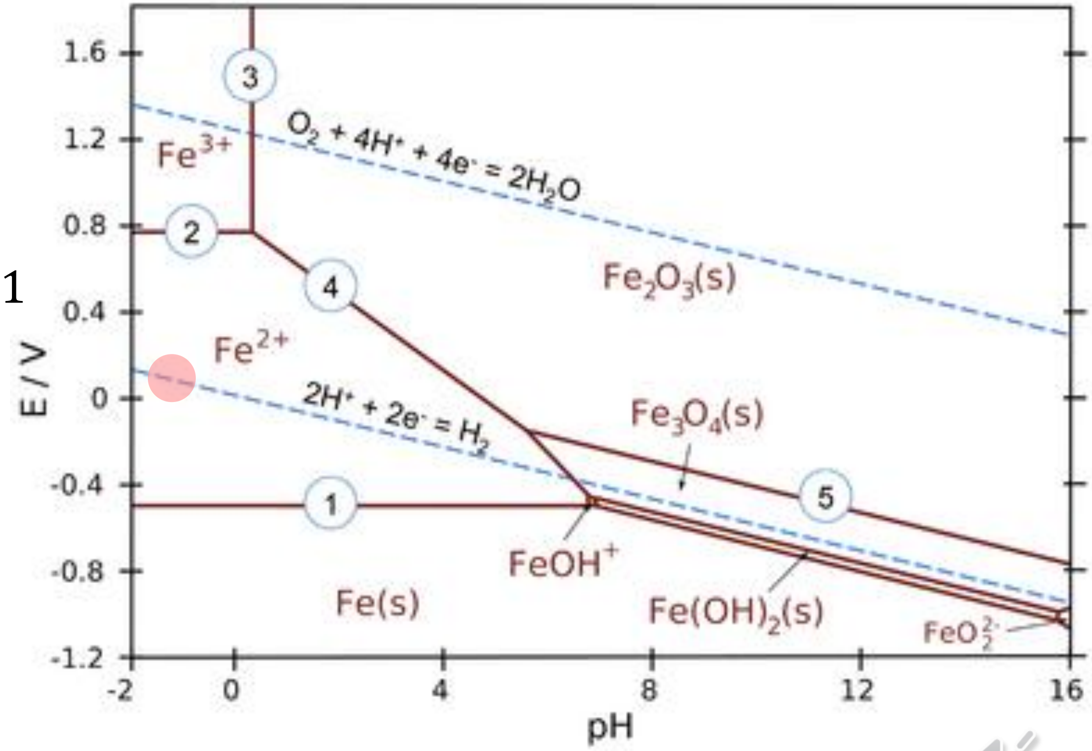
Assume 1 atm H_2 ideal gas, $a_{H_2} = 1$

$$\lg \frac{1}{a_{H^+}} = pH$$

$$E = 0V - \frac{0.0592\,V}{2} \cdot 2 \lg \frac{1}{a_{H^+}}$$

$$\boldsymbol{E = -0.0592\,V \cdot pH\ (\text{vs. SHE})}$$

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (2)

- **Upper dash line – oxygen evolution reaction**

$O_{2(g)} + 4H^+_{(aq)} + 4e^- = 2H_2O_{(l)}$

Electrode potential by Nernst eq:

$$E = E^\circ - \frac{0.0592\ V}{n} \lg \frac{\left(a_{H_2O}\right)^2}{a_{O_2} \cdot (a_{H^+})^4}$$

$E^\circ(O_2/H_2O) = 1.229$ V (vs. SHE)

$n = 4$

Assume 1 atm O_2 ideal gas, $a_{O_2} = 1$

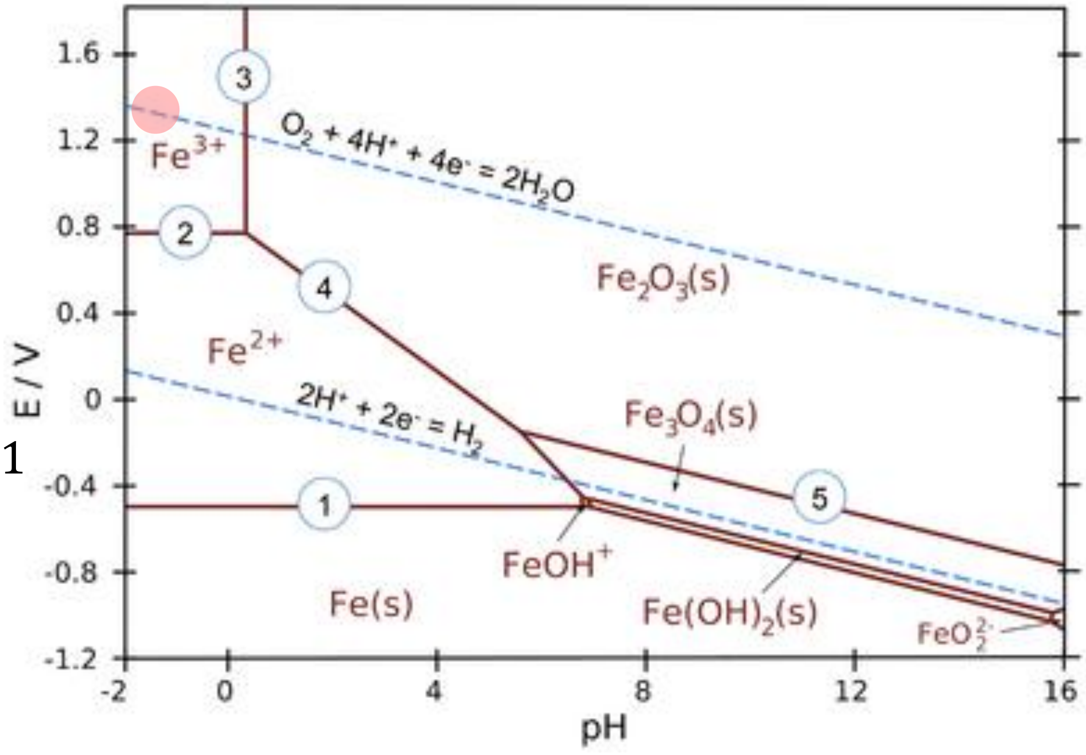
H_2O solvent, $a_{H_2O} = 1$

$$E = 1.229\ V - \frac{0.0592\ V}{4} \lg \frac{1}{(a_{H^+})^4}$$

$$E = 1.229\ V - 0.0592\ V \cdot \lg\left(\frac{1}{a_{H^+}}\right)$$

$$\boldsymbol{E = 1.229V - 0.0592\ V \cdot pH\ (\text{vs. SHE})}$$

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (3)

- **Line (1) - pure redox reaction (does NOT involve H^+ or OH^-)**

$Fe^{2+}_{(aq)} + 2e^- = Fe_{(s)}$

$$E = E^\circ - \frac{0.0592\ V}{n} \lg \frac{a_{Fe}}{a_{Fe^{2+}}}$$

$E^\circ(Fe^{2+}/Fe) = -0.440$ V (vs. SHE)

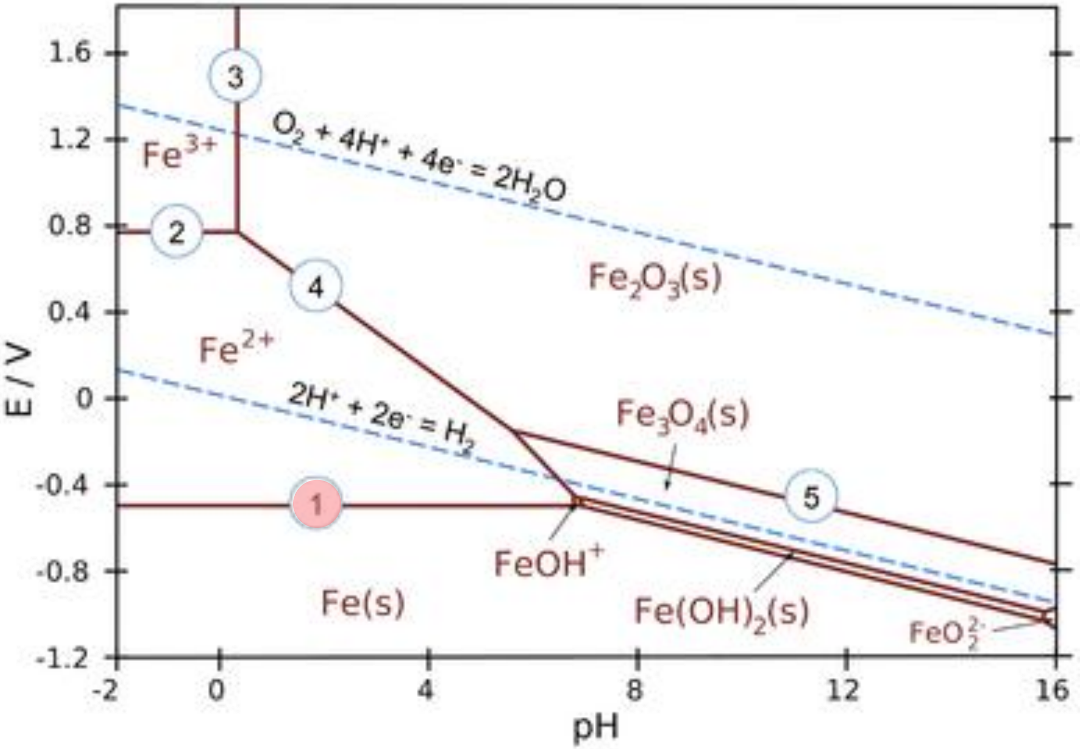
Fe solid, $a_{Fe} = 1$

$n = 2$

$$E = -0.440V - \frac{0.0592\ V}{2} \lg \frac{1}{a_{Fe^{2+}}}$$

$$E = -0.440V + \frac{0.0592\ V}{2} \lg a_{Fe^{2+}}$$

Pourbaix diagram for Fe at 1.0 mM



$$E = -0.440V + 0.0296\ V \cdot \lg a_{Fe^{2+}} (\text{vs SHE})$$

For 0.001 M Fe^{2+}, $a_{Fe^{2+}} \approx \frac{c_{Fe^{2+}}}{c^0} = \frac{0.001M}{1M} = 0.001$ $\quad \boldsymbol{E = -0.528\ V}$ **(vs. SHE)**

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Pourbaix Diagram for Fe in Water (4)

- **Line (2) - pure redox reaction (does NOT involve H^+ or OH^-)**

$Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}$

$$E = E^{\circ} - \frac{0.0592\ V}{n} \lg \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

$E^{\circ}(Fe^{3+}/Fe^{2+}) = 0.770$ V (vs. SHE)

$n = 1$

$$E = 0.770V - 0.0592\ V \cdot \lg \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

(vs. SHE)

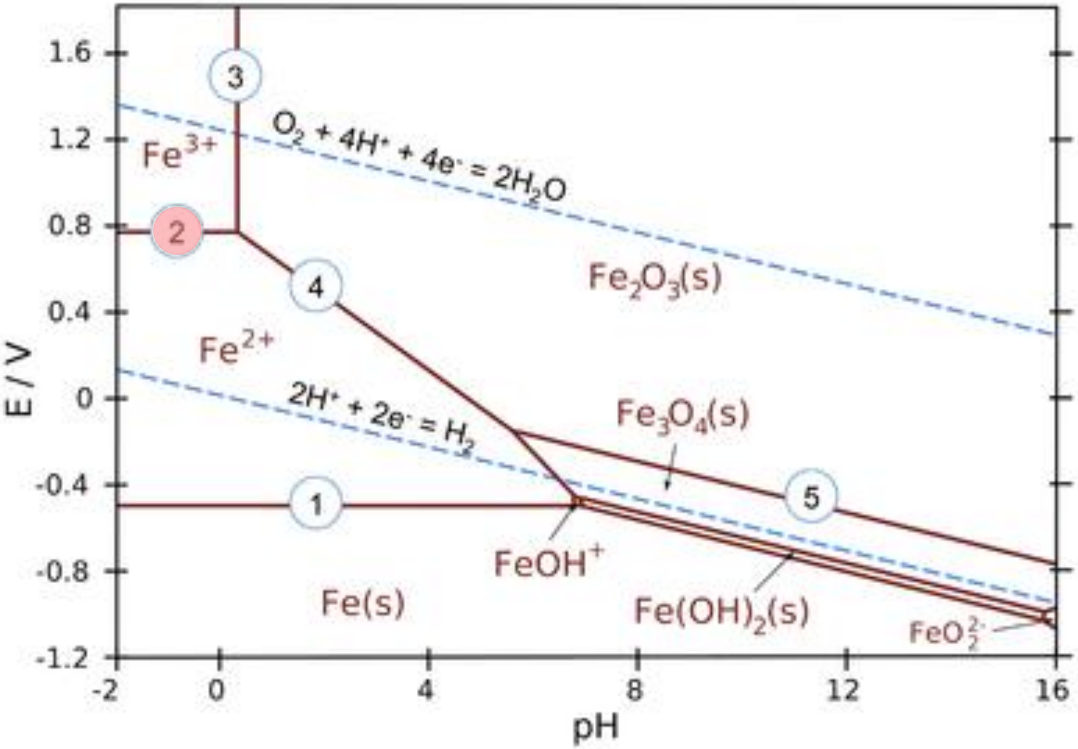
For 0.001 M Fe^{2+} and Fe^{3+}

$$a_{Fe^{2+}} \approx \frac{c_{Fe^{2+}}}{c^0} = 0.001$$

$$a_{Fe^{3+}} \approx \frac{c_{Fe^{3+}}}{c^0} = 0.001$$

$$E = 0.770V - 0.0592\ V \cdot \lg \frac{0.001}{0.001} \quad \boldsymbol{E = 0.770\ V\ \text{(vs. SHE)}}$$

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (5.1)

- **Line (3) - pure acid-base reaction w/o redox or charge transfer**

$2Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} = Fe_2O_{3(s)} + 6H^+{}_{(aq)}$

$2Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} + 2Fe^{2+} = Fe_2O_{3(s)} + 6H^+{}_{(aq)} + 2Fe^{2+}$

Anodic:

$2Fe^{2+} + 3H_2O = Fe_2O_{3(s)} + 6H^+ + 2e^-$

$E^\circ(Fe_2O_3/Fe^{2+}) = 0.728\ V$ (vs. SHE)

Cathodic

$Fe^{3+} + e^- = Fe^{2+}$

$E^\circ(Fe^{3+}/Fe^{2+}) = 0.770\ V$ (vs. SHE)

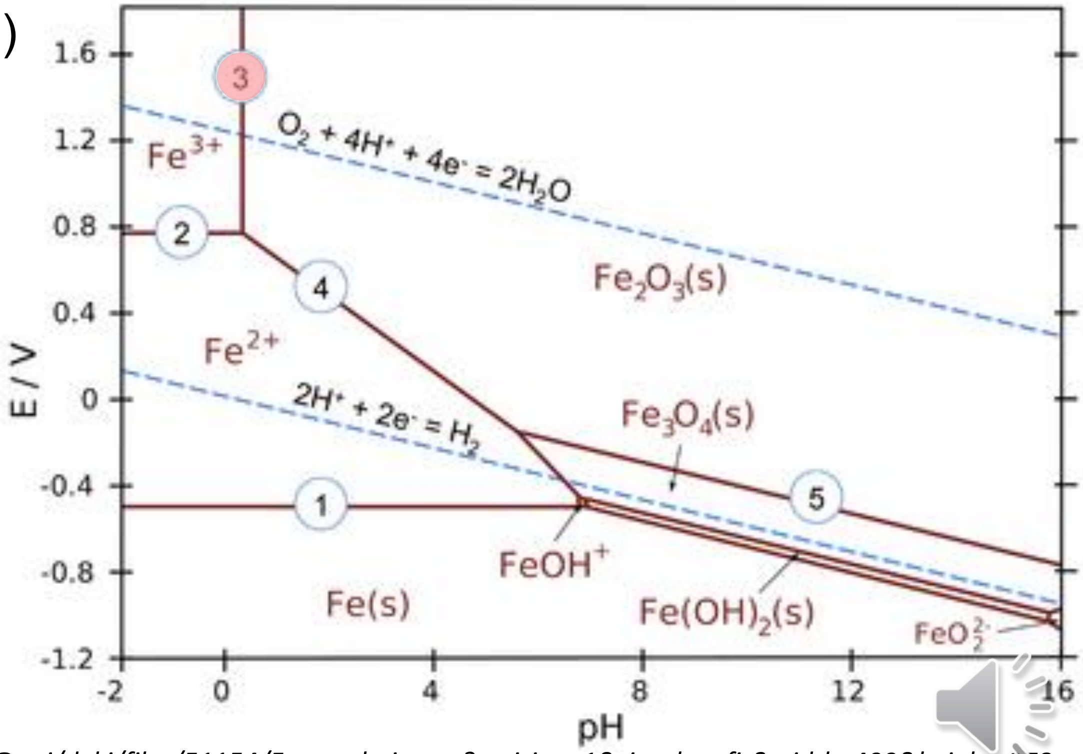
Overall:

$E^\circ = E^o{}_{cat} - E^o{}_{an}$

$= 0.770\ V - 0.728\ V$

$= 0.042\ V$

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (5.2)

- **Line (3) - pure acid-base reaction**

An: $2Fe^{2+} + 3H_2O = Fe_2O_{3(s)} + 6H^+ + 2e^-$

$$2Fe^{3+}_{(aq)} + 3H_2O_{(l)} + 2Fe^{2+} = Fe_2O_{3(s)} + 6H^+_{(aq)} + 2Fe^{2+}$$

Cath: $Fe^{3+} + e^- = Fe^{2+}$

At equilibrium,

$E° = 0.042$ V $\quad E = E^0 - \dfrac{0.0592\ V}{n} \lg K_{eq} = 0 \quad nE^0 = 0.0592\ V \cdot \lg K_{eq}$ $\quad$ ***n* = 2**

$$\lg K_{eq} = \frac{nE^0}{0.0592\ V} = \frac{2 \times 0.042\ V}{0.0592\ V} = 1.42$$

$$\lg \frac{a_{Fe_2O_3} \cdot (a_{H^+})^6}{(a_{Fe^{3+}})^2 \cdot \left(a_{H_2O}\right)^3} = 1.42$$

$$a_{Fe_2O_3} = 1 \quad a_{H_2O} = 1$$

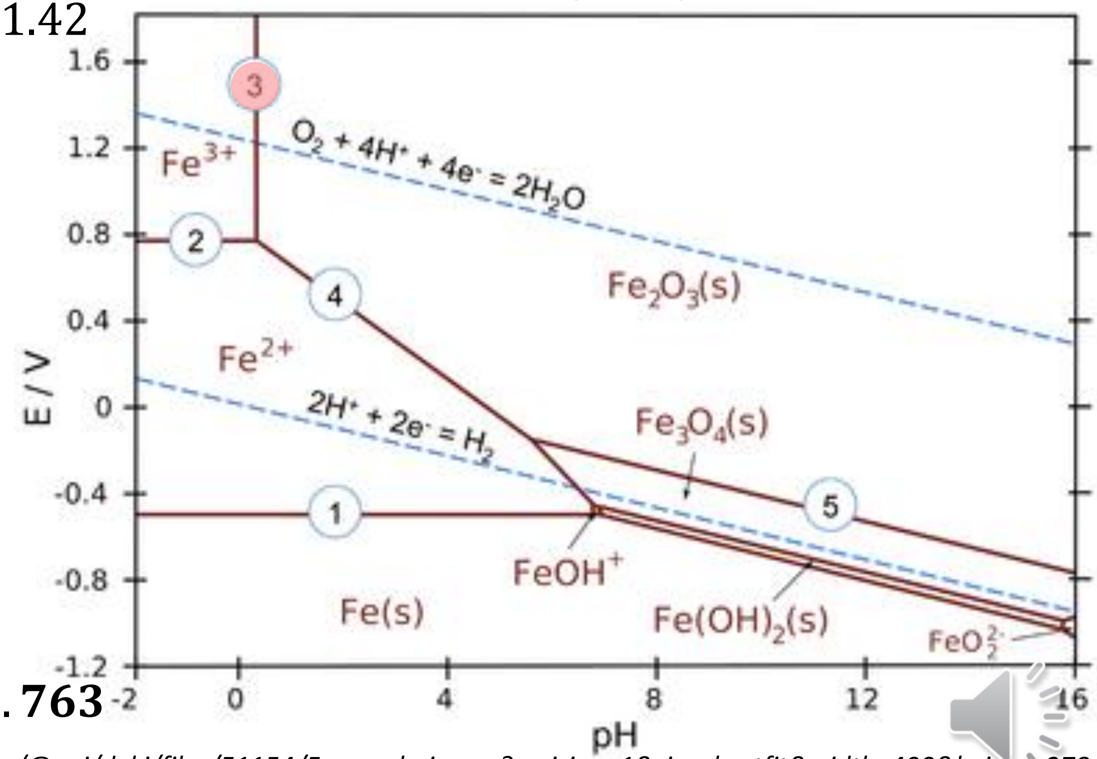
For 0.001 M Fe^{3+}

$$a_{Fe^{3+}} \approx \frac{c_{Fe^{3+}}}{c^0} = 0.001$$

$$6 \lg a_{H^+} + 2 \lg \frac{1}{0.001} = 1.42$$

$$\boldsymbol{pH = -lg a_{H^+} = \frac{2 \times 3 - 1.42}{6} = 0.763}$$

Pourbaix diagram for Fe at 1.0 mM



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Pourbaix Diagram for Fe in Water (6)

- **Line (4) - acid-base reaction involving charge transfer (redox)**

$Fe_2O_{3\,(s)} + 6H^+_{(aq)} + 2e^- \rightarrow 2Fe^{2+}_{(aq)} + 3H_2O_{(l)}$

$E^\circ(Fe_2O_3/Fe^{2+}) = 0.728$ V (vs. SHE)

Nernst equation

$$E = E^\circ - \frac{0.0592\,V}{n}\lg\frac{(a_{Fe^{2+}})^2\cdot(a_{H_2O})^3}{a_{Fe_2O_3}\cdot(a_{H^+})^6}$$

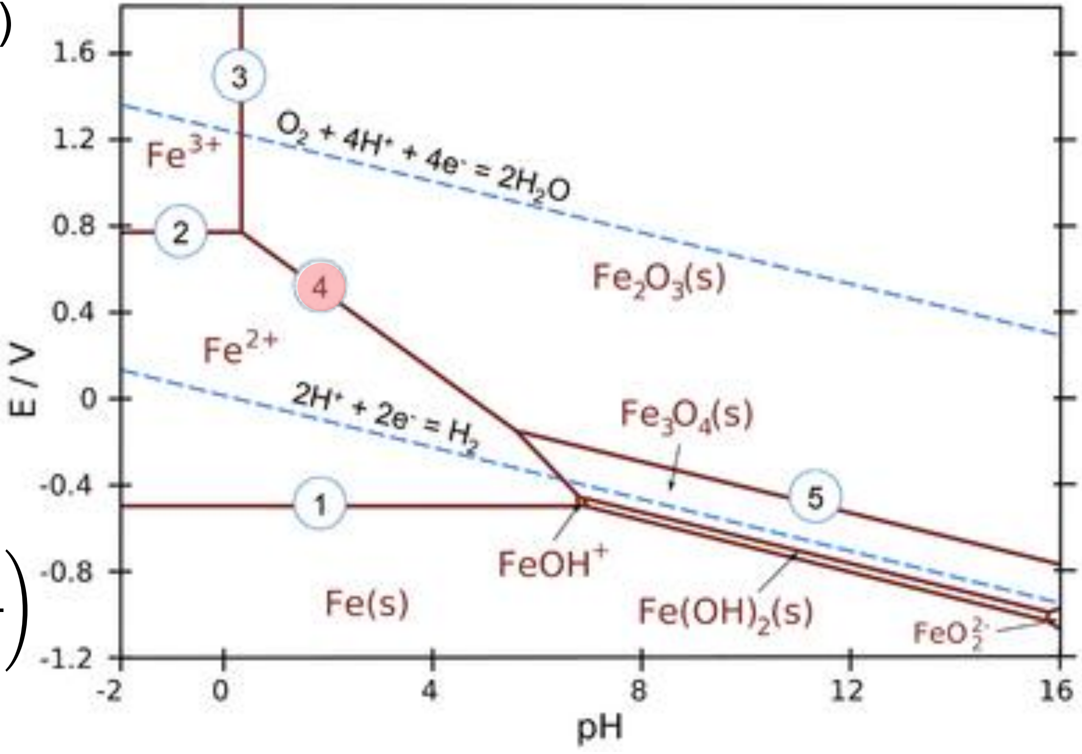
$$a_{H_2O} = 1 \qquad a_{Fe_2O_3} = 1$$

$$E = E^\circ - \frac{0.0592\,V}{n}\lg\frac{(a_{Fe^{2+}})^2}{(a_{H^+})^6}$$

$$= E^\circ - \frac{0.0592\,V}{n}\cdot\left(2\lg a_{Fe^{2+}} + 6\lg\frac{1}{a_{H^+}}\right)$$

$$n = 2 \qquad a_{Fe^{2+}} \approx \frac{c_{Fe^{2+}}}{c^0} = 0.001$$

Pourbaix diagram for Fe at 1.0 mM



$$E = 0.728V - \frac{0.0592\,V}{2}\cdot(2\lg 0.001 + 6pH)$$

$$\boldsymbol{E = 0.9056V - 0.1776V\cdot pH}\ \textbf{(vs. SHE)}$$

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Pourbaix Diagram for Fe in Water (7)

❑Line (5) - acid-base reaction involving charge transfer (redox)

$3Fe_2O_{3(s)} + 2H^+_{(aq)} + 2e^- \rightarrow 2Fe_3O_4(s) + H_2O_{(l)}$

$E^\circ(Fe_2O_3/Fe_3O_4) = 0.220$ V (vs. SHE)

Nernst equation

$$E = E^\circ - \frac{0.0592\ V}{n} \lg \frac{\left(a_{Fe_3O_4}\right)^2 \cdot a_{H_2O}}{\left(a_{Fe_2O_3}\right)^3 \cdot (a_{H^+})^2}$$

$$a_{H_2O} = 1 \quad a_{Fe_3O_4} = 1 \quad a_{Fe_2O_3} = 1$$

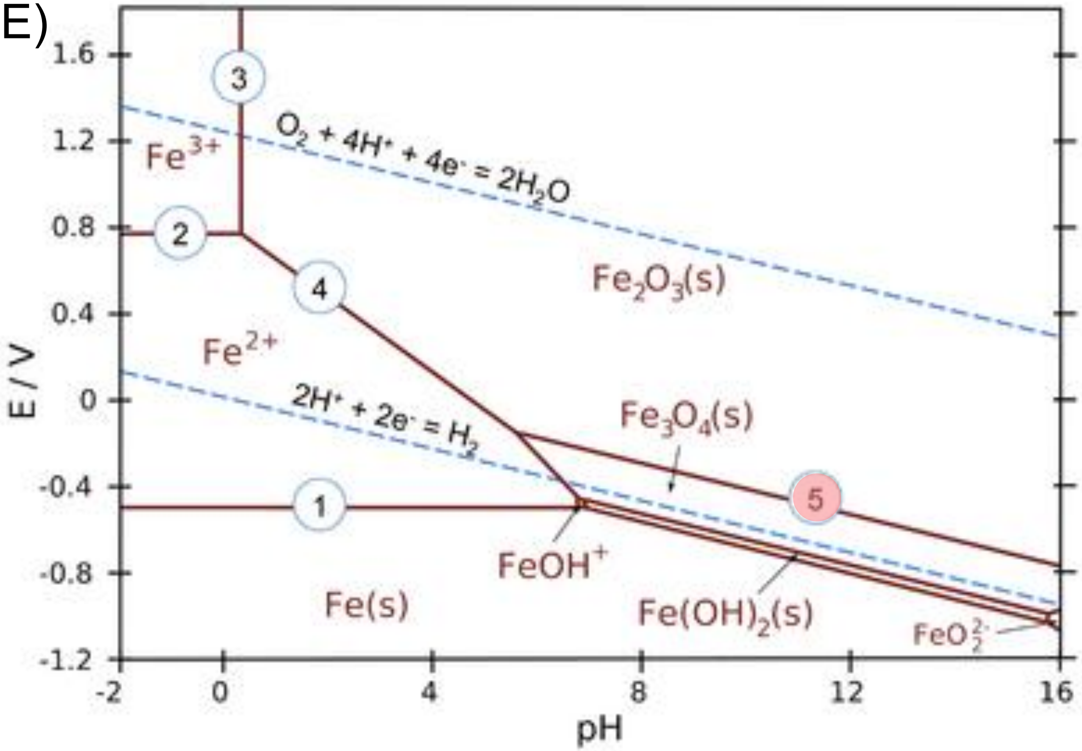
$$E = E^\circ - \frac{0.0592\ V}{n} \lg \frac{1}{(a_{H^+})^2}$$

$$= E^\circ - \frac{0.0592\ V}{n} \cdot 2 \lg \frac{1}{a_{H^+}}$$

$n = 2$

$$\boldsymbol{E = 0.220V - 0.0592\ V \cdot pH} \textbf{ (vs. SHE)}$$

Pourbaix diagram for Fe at 1.0 mM



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Gibbs Free Energy Change

Definition

- Under constant temperature and pressure, the main chemical parameter to determine whether a system is at equilibrium or if a process/reaction will proceed spontaneously (or not) is the Gibbs free change ΔG

$$\Delta G = G_{Final} - G_{Initial}$$

$$\underbrace{G}_{\text{Gibbs free energy}} = \underbrace{H}_{\text{Enthalpy}} - \underbrace{T}_{\text{Temperature}} \bullet \underbrace{S}_{\text{Entropy}}$$

Significance

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

Additional notes

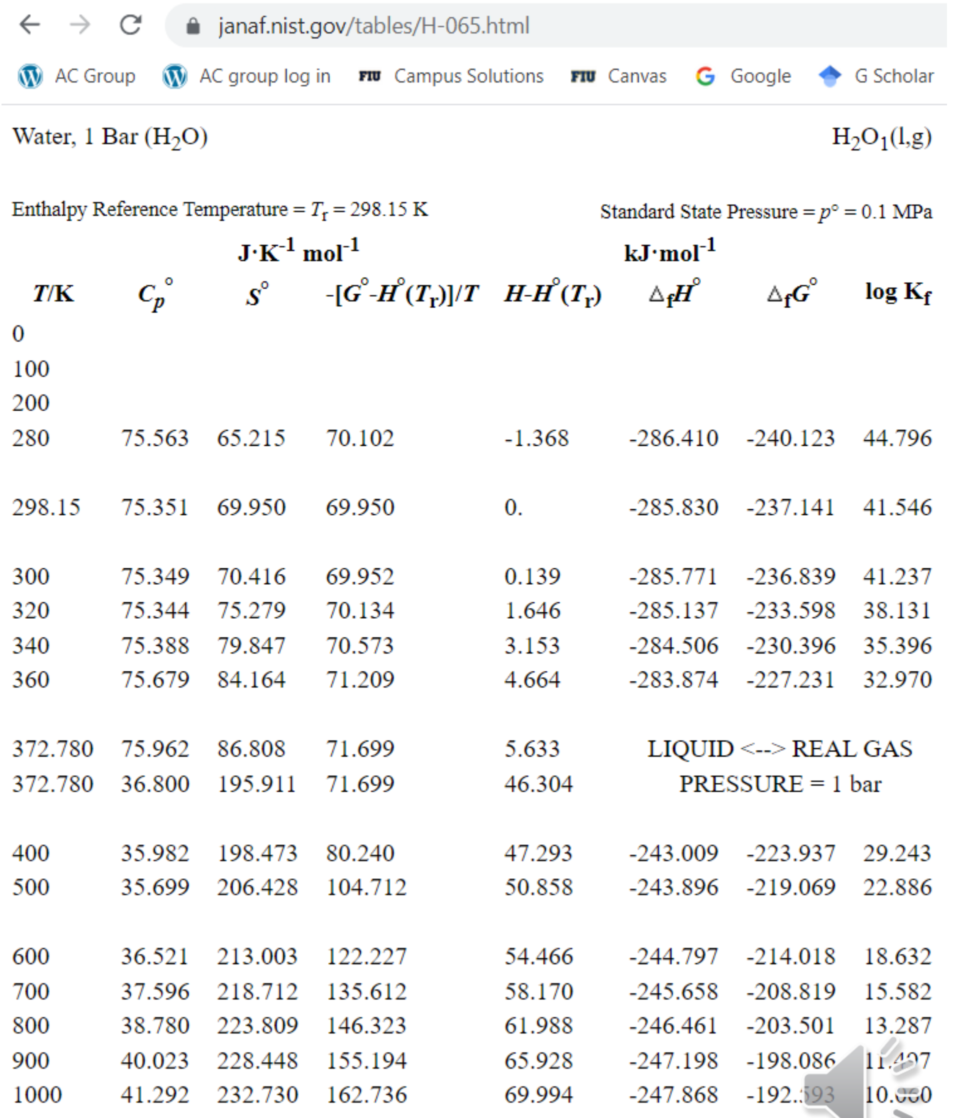
- ΔG depends only on the **difference** in Gibbs free energy of the final state and the initial state (or products and reactants) and is independent of the path of the transformation and related mechanism
- ΔG does NOT represent **rate** of a process/reaction

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

- **Definition**

  "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**
  - NIST – JANAF Thermo-chemical Tables, 4th Edition, Journal of Physical and Chemical Reference Data, 1998, https://janaf.nist.gov/
  - CRC Handbook of Chemistry and Physics https://hbcp.chemnetbase.com/
  - Others



Water, 1 Bar (H_2O) H_2O_1(l,g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1} mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
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
340	75.388	79.847	70.573	3.153	-284.506	-230.396	35.396
360	75.679	84.164	71.209	4.664	-283.874	-227.231	32.970
372.780	75.962	86.808	71.699	5.633	LIQUID <--> REAL GAS		
372.780	36.800	195.911	71.699	46.304	PRESSURE = 1 bar		
400	35.982	198.473	80.240	47.293	-243.009	-223.937	29.243
500	35.699	206.428	104.712	50.858	-243.896	-219.069	22.886
600	36.521	213.003	122.227	54.466	-244.797	-214.018	18.632
700	37.596	218.712	135.612	58.170	-245.658	-208.819	15.582
800	38.780	223.809	146.323	61.988	-246.461	-203.501	13.287
900	40.023	228.448	155.194	65.928	-247.198	-198.086	11.497
1000	41.292	232.730	162.736	69.994	-247.868	-192.593	10.060

Reaction Gibbs Free Energy Change ($\Delta_\mathrm{r} G$)

- **For a chemical reaction, the Gibbs free energy change is the difference in the Gibbs free energy between final products and initial reactants**

$$\boldsymbol{\Delta_\mathrm{r} G = G_{Final} - G_{Initial}}$$

- **Practical calculation of** $\Delta_\mathrm{r} G$

$$\Delta_\mathrm{r} G = \Delta_\mathrm{r} G^\circ + RT \ln k$$

R	Ideal gas constant = 8.314 J/(mol·K)
T	Absolute temperature in K
k	Reaction constant
$\Delta_\mathrm{r} G^\circ$	Standard Gibbs free energy change - the Gibbs free energy change at standard condition (1 bar), often calculated by:

$$\Delta_\mathrm{r} G^\circ = \sum n_i \Delta_\mathrm{f} G^\circ(products) - \sum n_j \Delta_\mathrm{f} G^\circ(reactants)$$

- **Example**

$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D$$

$$\Delta_\mathrm{r} G^\circ = [\gamma \Delta_\mathrm{f} G^\circ(C) + \delta \Delta_\mathrm{f} G^\circ(D)] - [\alpha \Delta_\mathrm{f} G^\circ(A) + \beta \Delta_\mathrm{f} G^\circ(B)]$$

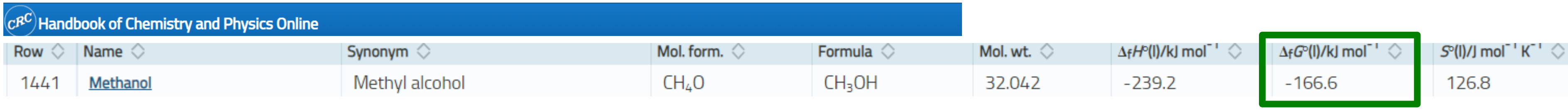
Example - $\Delta_r G°$ for Methanol Fuel Cell

Calculate $\Delta_f G°$ for methanol oxidation (in a methanol fuel cell) at 25°C

$$2CH_3OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 4H_2O_{(l)}$$

Look up Gibbs formation energy data from thermochemistry references

- CRC Handbook of Chemistry and Physics at https://hbcp.chemnetbase.com/



Handbook of Chemistry and Physics Online

Row	Name	Synonym	Mol. form.	Formula	Mol. wt.	$\Delta_f H°$(l)/kJ mol⁻¹	$\Delta_f G°$(l)/kJ mol⁻¹	$S°$(l)/J mol⁻¹ K⁻¹
1441	Methanol	Methyl alcohol	CH_4O	CH_3OH	32.042	-239.2	-166.6	126.8

At 25°C, $\Delta_f G°$:		
	$CH_3OH_{(l)}$	-166.6 kJ/mol
	$O_{2\,(g)}$	0 kJ/mol
	$CO_{2\,(g)}$	-394.4 kJ/mol
	$H_2O_{(l)}$	-237.1 kJ/mol

Standard reaction Gibbs free energy change

$$\Delta_r G° = \sum n_i \Delta_f G°(product) - \sum n_j \Delta_f G°(reactants)$$

$$\begin{aligned}\Delta_r G° &= [2\Delta_f G°(CO_{2\,(g)}) + 4\Delta_f G°(H_2O_{(l)})] - [2\Delta_f G°(CH_3OH_{(l)}) + 3\Delta_f G°(O_{2\,(g)})] \\ &= [2(-394.4\text{ kJ/mol}) + 4(-237.1\text{ kJ/mol})] - [2(-166.6\text{ kJ/mol}) + 3(0\text{ kJ/mol})] \\ &= \mathbf{-1404\text{ kJ/mol of progression (NOT oxidation of 1 mole methanol!)}}\end{aligned}$$

Spontaneous process with very large driving force due to large negative $\Delta_r G°$

Cell Potential E and $\Delta_r G$

For an electrochemical cell with one mole of **progression**, maximum (electrical) work that can be produced:

$$W_{max} = E \bullet Q = E \bullet nF$$

n	mole of electron transferred per mole of progression
F	Faraday constant - 96485 C/mol
W_{max}	A positive number because it is done by the system onto its surroundings

From energy conservation, the work done by the system to its environment equals the reaction Gibbs free energy change or change (reduction) in system Gibbs free energy:

$$\Delta G = -W_{max}$$

Therefore,

$$\Delta G = -nFE$$

- Connects cell potential & change in system thermodynamic properties
- A spontaneous process/reaction is characterized by negative ΔG and positive E
- When all reactants and products in their standard states, $\Delta G° = -nFE°$

Example – Standard Cell Potential for Methanol Fuel Cell

Calculate standard cell potential E° for methanol complete oxidation as in a methanol fuel cell at 25°C

$$\mathbf{2CH_3OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 4H_2O_{(l)}}$$

From earlier, $\Delta_r G^\circ = -1404$ kJ/mol

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

$$E^0 = -\frac{\Delta_r G^\circ}{nF}$$

For this reaction, $n = 12$ (6 oxygen, each from 0 valence to -2 valence → 6 x 2 = 12)

$$E^0 = -\frac{-1404 \times 1000\, J/mol}{12 \times 96485\, C/mol} = \mathbf{1.21V}$$

At 25°C, the reaction between (near) pure CH_3OH and 1 bar O_2 producing 1 bar CO_2 and near pure H_2O gives a cell potential (emf) of 1.21 V, *under idealist condition*

Cathodic/reduction half cell: $3O_{2\,(g)} + 12e^- + 12H^+_{(aq)} \rightarrow 6H_2O_{(l)}$

$O_{2\,(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}$

Anodic/oxidation half cell: $2CH_3OH_{(l)} + 2H_2O_{(l)} \rightarrow 2CO_{2\,(g)} + 12H^+_{(aq)} + 12e^-$

Cell Potential to Gibbs Free Energy Example

Using standard electrode potential data to calculate the standard Gibbs formation energy $\Delta_f G°$ for liquid water at 298.15 K

Consider water formation reaction from pure elements in standard states:

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{\,(l)}$$

Anodic reaction: $H_{2\,(g)} \rightarrow 2H^+_{(aq)} + 2e^-$ $E°(H^+/H_2) = 0.000$ V

Cathodic reaction: $O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightarrow H_2O_{(l)}$ $E°(O_2/H_2O) = 1.229$V

Overall or full cell: $E° = E°_{cat} - E°_{an} = 1.229\text{ V} - 0.000\text{ V} = \mathbf{1.229\text{ V}}$

Therefore,

$$\Delta_r G° = -nFE° = -4 \times 96485 \frac{C}{mol} \times 1.229\, V = -474.32 \text{ kJ/mol}$$

Remember

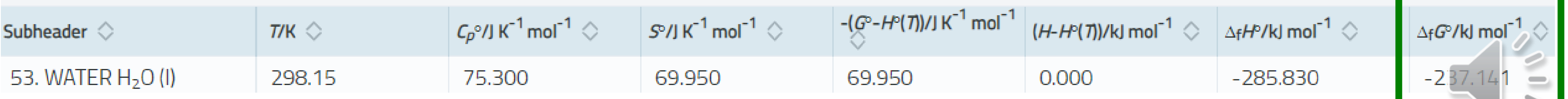
$$\Delta_r G° = 2\Delta_f G°(H_2O_{(l)}) - [2\Delta_f G°(H_{2\,(g)}) + \Delta_f G°(O_{2\,(g)})] = 2\Delta_f G°(H_2O_{(l)})$$

Therefore,

$$2\Delta_f G°(H_2O_{(l)}) = -474.32 \text{ kJ/mol}$$

$$\Delta_f G°(H_2O_{(l)}) = \mathbf{-237.16\ kJ/mol}$$

Check - CRC Handbook Standard Thermodynamic Properties of Chemical Substances



Subheader	T/K	$C_p°$/J K^{-1} mol^{-1}	$S°$/J K^{-1} mol^{-1}	$-(G°-H°(T))$/J K^{-1} mol^{-1}	$(H-H°(T))$/kJ mol^{-1}	$\Delta_f H°$/kJ mol^{-1}	$\Delta_f G°$/kJ mol^{-1}
53. WATER H_2O (l)	298.15	75.300	69.950	69.950	0.000	-285.830	-237.141

Gibbs Free Energy to Cell Potential Example

Using the Gibbs formation energy data from CRC Handbook to calculate standard cell potential for the following reaction:

$$\mathbf{Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}}$$

Check CRC Handbook - Thermodynamic Properties of **Aqueous Ions**
https://hbcp.chemnetbase.com/faces/documents/05_04/05_04_0001.xhtml

At 25°C, $\Delta_f G°(Cu^{2+}) = 65.5\ \mathrm{kJ/mol}$, $\Delta_f G°(Zn^{2+}) = -147.1\ \mathrm{kJ/mol}$

Therefore, $\Delta_r G° = [\Delta_f G°(\mathrm{Cu}) + \Delta_f G°(\mathrm{Zn^{2+}})] - [\Delta_f G°(\mathrm{Cu^{2+}}) + \Delta_f G°(\mathrm{Zn})]$

$$\Delta_r G° = [0\ \mathrm{kJ/mol} + (-147.1\ \mathrm{kJ/mol})] - [65.5\ \mathrm{kJ/mol} + 0\ \mathrm{kJ/mol}] = -212.6\ \mathrm{kJ/mol}$$

$$\Delta_r G° = -nFE° \qquad E° = -\frac{\Delta_r G°}{nF} = -\frac{-212.6 \times 1000\ J/mol}{2 \times 96485\ C/mol} = \mathbf{1.10\ V}$$

Check using standard electrode potential data

Anodic/oxidation: Zn (s) → Zn^{2+} (aq) + 2e- $E°(Zn^{2+}/Zn) = -0.762$ V

Cathodic/reduction: Cu^{2+} (aq) + 2e- → Cu (s) $E°(Cu^{2+}/Cu) = 0.337$ V

Overall: $E° = E^o_{cat} - E^o_{an} = 0.337\mathrm{V} - (-0.762\mathrm{V}) = \mathbf{1.10\ V}$

Example at Non-Standard Condition

For a reaction $\Delta_r G = \Delta_r G^\circ + RT\ln k = -nFE$

Cell potential $E = -\frac{\Delta_r G}{nF} = -\frac{\Delta_r G^\circ}{nF} - \frac{RT}{nF}\ln k = E^\circ - \frac{RT}{nF}\ln Q$

Example: Gibbs free energy change and cell potential for the following reaction at 25^{o}C

$$\mathbf{Al_{(s)}|Al^{3+}{}_{(aq,\ 0.15\ M)}||Cu^{2+}{}_{(aq,\ 0.025\ M)}|Cu_{(s)}}$$

Anodic/oxidation: $Al_{(s)} \rightarrow Al^{3+}{}_{(aq,\ 0.15\ M)} + 3e^-$ $E^\circ(Al^{3+}/Al) = -1.66\ V$

Cathodic/reduction: $Cu^{2+}{}_{(aq,\ 0.025\ M)} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ(Cu^{2+}/Cu) = 0.337\ V$

Overall or full cell: 2An + 3Cat $2Al_{(s)} + 3Cu^{2+}{}_{(aq,\ 0.025\ M)} \rightarrow 2Al^{3+}{}_{(aq,\ 0.15\ M)} + 3Cu_{(s)}$

$E^\circ = E^o{}_{cat} - E^o{}_{an} = 0.337V - (-1.66V) = 1.997\ V$

$n = 6$; $Q = k = (c_{Al3+}/c^o)^2/(c_{Cu3+}/c^o)^3 = 0.15^2/0.025^3 = 1440$

$E = E^\circ - (0.0592V/n)\lg Q = 1.997\ V - 0.0592\ V/6 \times \lg 1440 =$ **1.97 V**

On the other hand, using standard Gibbs formation energy data from CRC Handbook:

$\Delta_r G^\circ = [2\Delta_f G^\circ(Al^{3+}{}_{aq}) + 3\Delta_f G^\circ(Cu)] - [2\Delta_f G^\circ(Al) + 3\Delta_f G^\circ(Cu^{2+}{}_{aq})]$

$= [2(-485.0) + 3\times 0] - [2(0) + 3(65.5)]$ kJ/mol = - 1166.5 kJ/mol

$\Delta_r G = \Delta_r G^\circ + RT\ln Q = -1166.5\text{kJ/mol} + 8.314\text{J/(mol•K)}\cdot 298.15\text{K}\cdot\ln 1440 = -1148\text{kJ/mol}$

Therefore, $E = -\Delta_r G/nF = -(-1148\ \text{kJ/mol})/(6\times 96485\ \text{C/mol}) =$ **1.98 V** - very close

Equilibrium Constant (K_{eq})

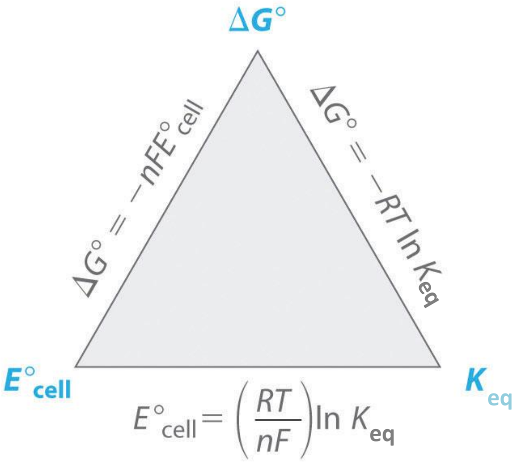
❑Definition

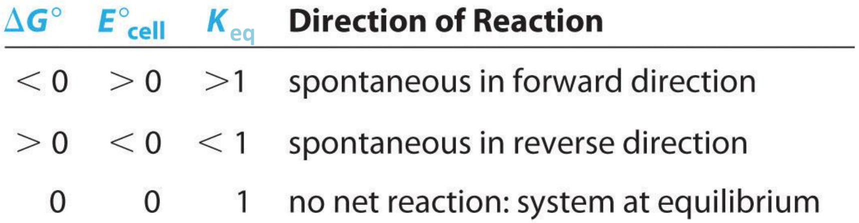
The equilibrium constant of a chemical reaction is the value of the **reaction quotient** when the reaction reaches **equilibrium**. It is **independent** of the actual concentrations of the reactant and product species, but depends on *T*, *P*.

For a general chemical reaction: $\alpha A + \beta B \leftrightarrow \gamma C + \delta D$

$$K_{eq} = \left[\frac{\prod_j^{product}\left(a_j\right)^{v_j}}{\prod_i^{reactant}\left(a_i\right)^{v_i}}\right]_{eq} = \left[\frac{(a_C)^{\gamma}\cdot(a_D)^{\delta}}{(a_A)^{\alpha}\cdot(a_B)^{\beta}}\right]_{eq}$$

❑Relation between ΔG°, E°, and K_{eq}





ΔG°	E°_{cell}	K_{eq}	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

https://chem.libretexts.org w/ modification

Example of *E* Dependence on Temperature

Using Gibbs formation energy data to calculate standard potential of hydrogen fuel cell at different temperature

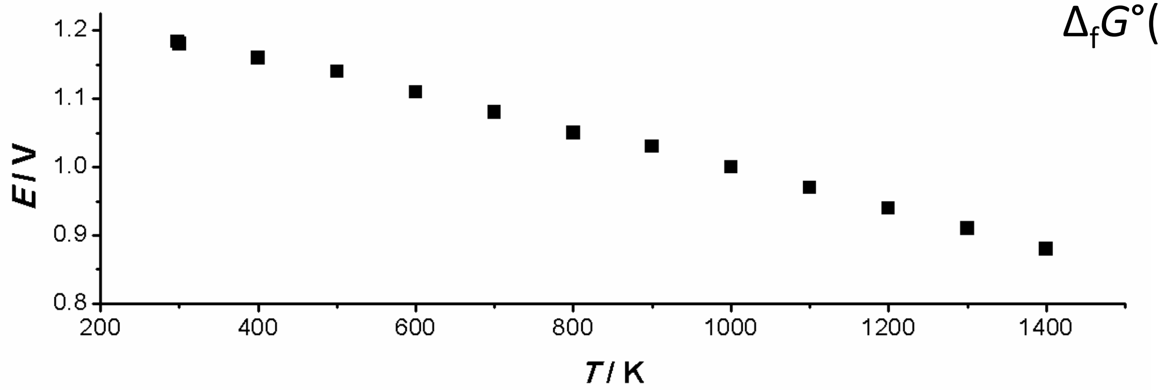
$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{\,(g)}$$

$\Delta_r G° = 2\Delta_f G°(H_2O_{(g)}) - [2\Delta f G°(H_{2\,(g)}) + \Delta f G°(O_{2\,(g)})] = 2\Delta_f G°(H_2O_{(g)})$

Therefore, standard cell potential $E° = -\Delta_r G°/nF = 2\Delta_f G°(H_2O_{(g)})/(4\times 96485\ C/mol)$

$E° = -\Delta_f G°(H_2O_{(g)})/(2\times 96485\ C/mol)$

T (K)	400	500	600	700	800	900	1000
$-\Delta_f G°(H_2O_{(g)})$ (kJ/mol)	223.9	219.0	214.0	208.8	203.5	198.1	192.6
E^o (V)	1.16	1.14	1.11	1.08	1.06	1.03	1.00



$\Delta_f G°(H_2O_{\,(g)})$ from https://janaf.nist.gov/

Homework

- ❑ **Read textbook chapter 2 and give an honor statement confirm reading**

- ❑ **Raise THREE (3) question that you don't understand for lecture videos**

  In case you have understood everything and don't have that many questions, please give corresponding number of multiple-choice problem (together with your answer) that you feel can be used to check a student's understanding.

  An example multiple-choice problem could be:
  Which of the units below can be the unit for current density j?
  a) A
  b) A/cm^2 (Answer)
  c) V
  d) C

- ❑ **Problems**
  - **Textbook** 2.1, 2.2, 2.3, 2.4, 2.5, 2.7, 2.9, 2.11, 2.16, 2.18, 2.20