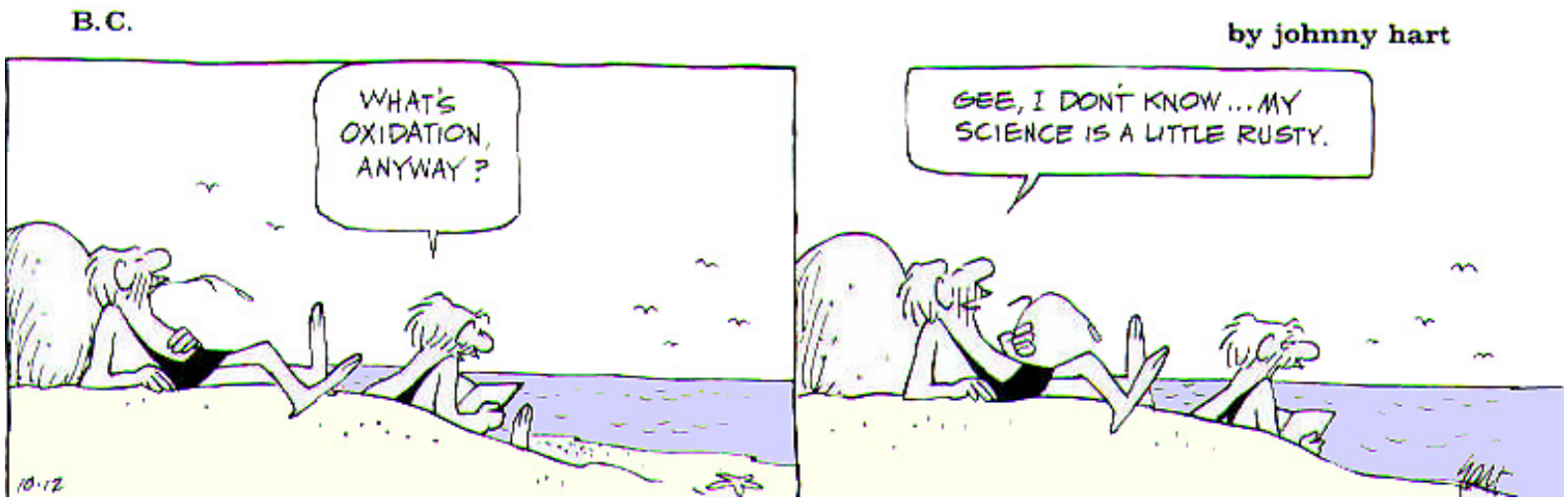
Electrochemistry – High Temperature Concepts

Nigel Sammes
POSTECH
South Korea

nsammes@postech.ac.kr

2nd Joint European Summer School on Fuel Cell and Hydrogen Technology

OK Let's Get Started



Introduction to Electrochemistry

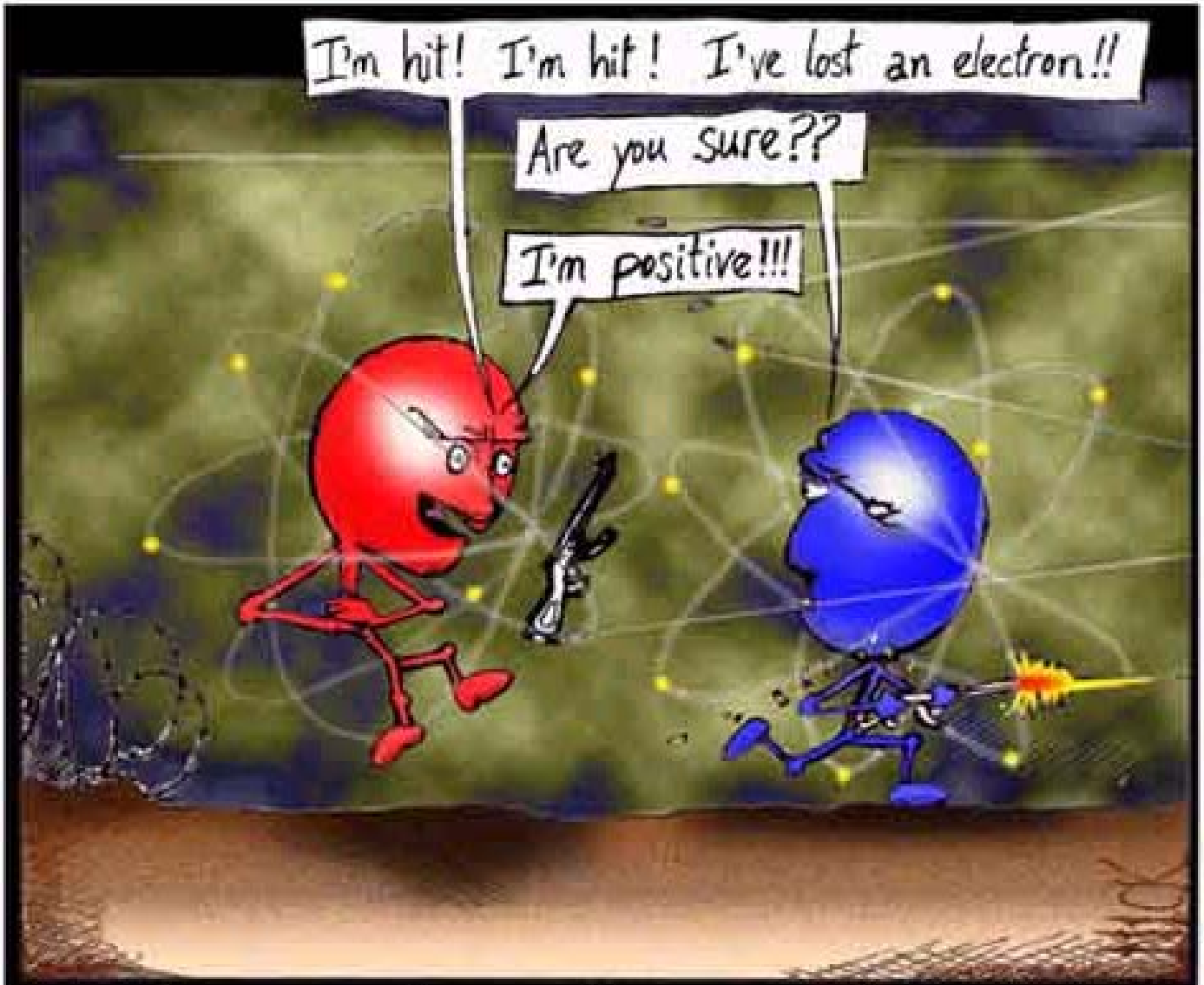
Electrochemistry is:

- Generation of electricity by realizing the energy from a spontaneous chemical reaction

OR

- using electricity to force a chemical reaction to occur

Electrochemistry is all about the concepts of "oxidation" and "reduction".



Another casualty in the War of the Atoms

Oxidation and Reduction

Oxidation is…

- the **loss** of electrons
- an **increase** in oxidation state
- the addition of oxygen
- the loss of hydrogen

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

magnesium is losing electrons

Reduction is…

- the **gain** of electrons
- a **decrease** in oxidation state
- the loss of oxygen
- the addition of hydrogen

$$MgO + H_2 \rightarrow Mg + H_2O$$

Mg^{2+} in MgO gains electrons

In Electrochemistry we get Redox Reactions

- Oxidation and reduction always occur together in a chemical reaction.
- For this reason, these reactions are called "**redox**" reactions.

Although there are different ways of identifying a redox reaction, the best is to look for a *change in oxidation state*:

$$2\ Fe^{3+} + 2\ I^{-} \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

$$2\ AgNO_3 + Cu \rightarrow 2\ Ag + Cu(NO_3)_2$$

$$HCl + AgNO_3 \rightarrow AgCl + HNO_3$$

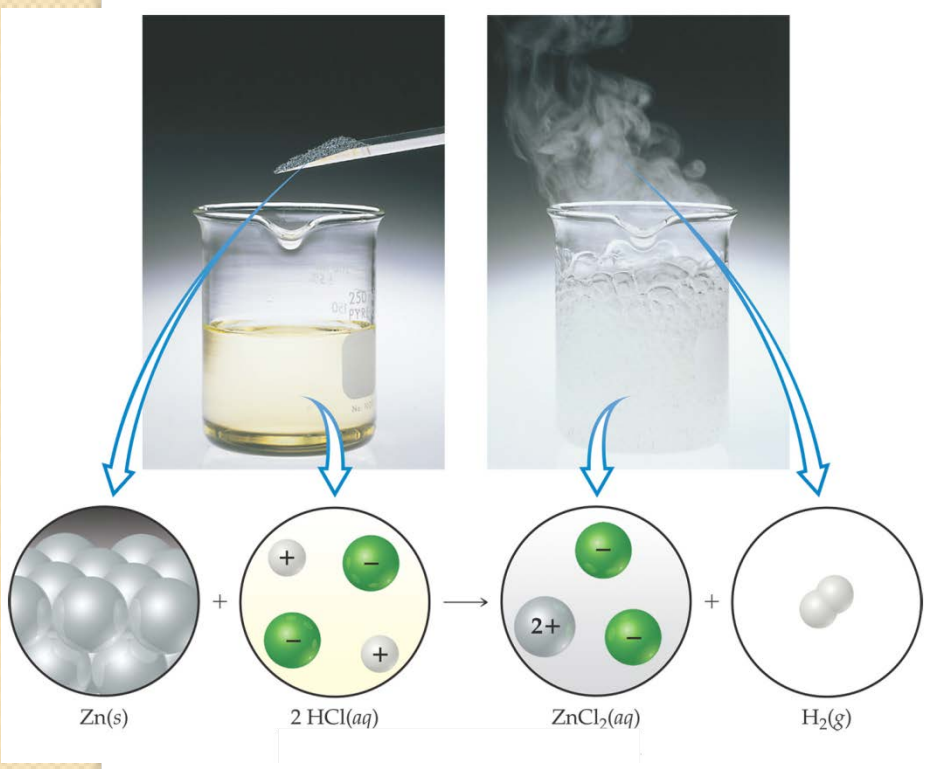
More Definitions

- **Oxidizing Agent**
  - the substance in a chemical reaction which causes another species to be oxidized.
  - the oxidizing agent always gets *reduced* in the reaction.
- **Reducing Agent**
  - the substance in a chemical reaction that causes another species to be reduced.
  - the reducing agent always gets *oxidized*!

Oxidation Numbers

$$Zn(s) + 2\,H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

0 +1 +2 0



In order to keep track of what loses electrons and what gains them, we assign oxidation numbers.

Oxidation and Reduction

$$\underset{0}{Zn}(s) + 2\,\underset{+1}{H^+}(aq) \longrightarrow \underset{+2}{Zn^{2+}}(aq) + \underset{0}{H_2}(g)$$

- A species is oxidized when it loses electrons.
  - Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.

Oxidation and Reduction

$$\underset{0}{Zn}(s) + 2\,\underset{+1}{H^+}(aq) \longrightarrow \underset{+2}{Zn^{2+}}(aq) + \underset{0}{H_2}(g)$$

- A species is reduced when it gains electrons.
  - Here, each of the H^+ gains an electron and they combine to form H_2.

Oxidation and Reduction

$$\underset{0}{Zn}(s) + 2\,\underset{+1}{H^+}(aq) \longrightarrow \underset{+2}{Zn^{2+}}(aq) + \underset{0}{H_2}(g)$$

- What is reduced is the oxidizing agent.
  - H^+ oxidizes Zn by taking electrons from it.
- What is oxidized is the reducing agent.
  - Zn reduces H^+ by giving it electrons.

Half-Reaction Method

Consider the reaction between MnO_4^- and $C_2O_4^{2-}$:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$$

Half-Reaction Method

First, we assign oxidation numbers.

$$\overset{+7}{MnO_4^-} + \overset{+3}{C_2O_4^{2-}} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{CO_2}$$

Since the manganese goes from +7 to +2, it is reduced.

Since the carbon goes from +3 to +4, it is oxidized.

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow CO_2$$

To balance the carbon, we add a coefficient of 2:

$$C_2O_4^{2-} \longrightarrow 2\ CO_2$$

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow 2\ CO_2$$

The oxygen is now balanced as well. To balance the charge, we must add 2 electrons to the right side.

$$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2\ e^-$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$

The manganese is balanced; to balance the oxygen, we must add 4 waters to the right side.

$$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To balance the hydrogen, we add 8 H^+ to the left side.

$$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Reduction Half-Reaction

$$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To balance the charge, we add 5 e^- to the left side.

$$5\ e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Combining the Half-Reactions

Now we evaluate the two half-reactions together:

$$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2\ e^-$$

$$5\ e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To attain the same number of electrons on each side, we will multiply the first reaction by 5 and the second by 2.

Combining the Half-Reactions

$$5\ C_2O_4^{2-} \longrightarrow 10\ CO_2 + 10\ e^-$$

$$10\ e^- + 16\ H^+ + 2\ MnO_4^- \longrightarrow 2\ Mn^{2+} + 8\ H_2O$$

When we add these together, we get:

$$10\ e^- + 16\ H^+ + 2\ MnO_4^- + 5\ C_2O_4^{2-} \longrightarrow$$
$$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ e^-$$

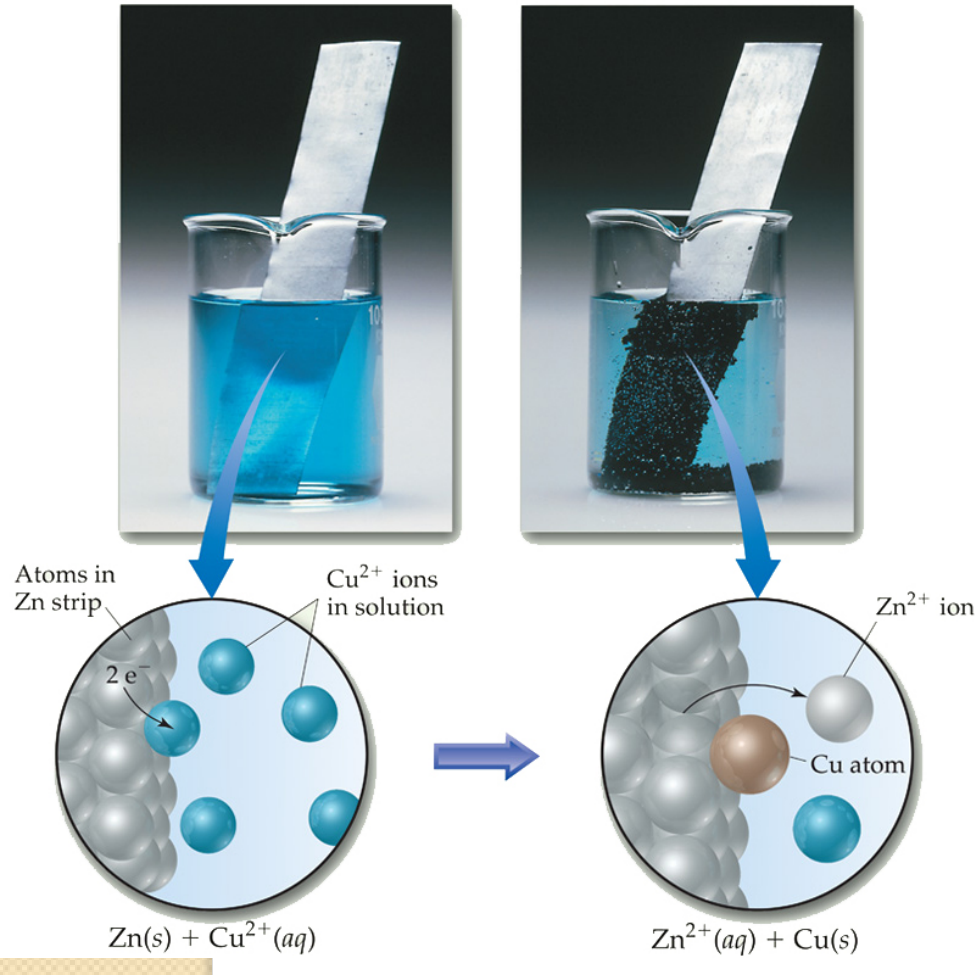
Combining the Half-Reactions

$$10\ e^- + 16\ H^+ + 2\ MnO_4^- + 5\ C_2O_4^{2-} \longrightarrow 2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ e^-$$

The only thing that appears on both sides are the electrons. Subtracting them, we are left with:

$$16\ H^+ + 2\ MnO_4^- + 5\ C_2O_4^{2-} \longrightarrow 2\ Mn^{2+} + 8\ H_2O + 10\ CO_2$$

Voltaic Cells

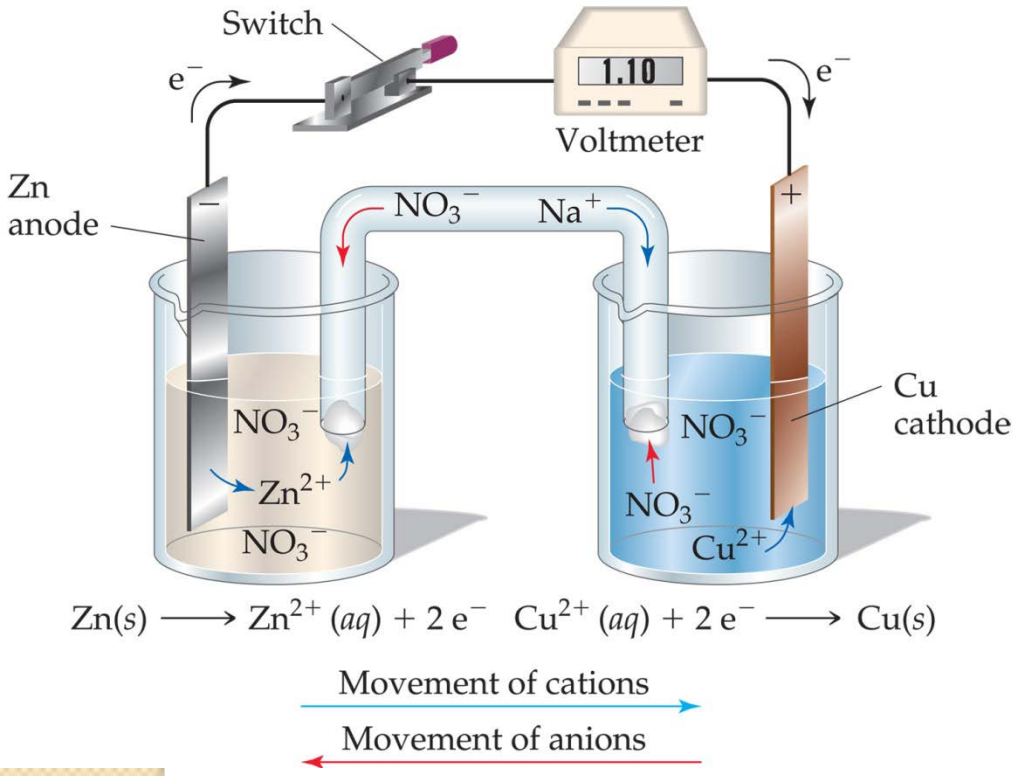


In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

Voltaic Cells

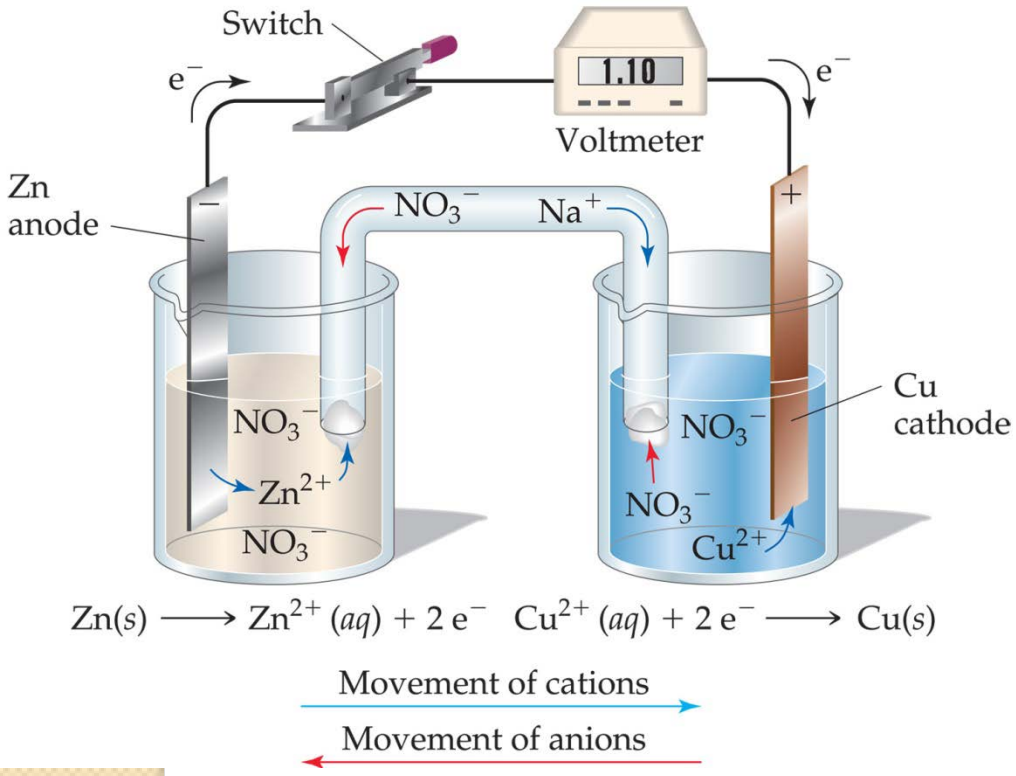
- We can use that energy to do work if we make the electrons flow through an external device.
- We call such a setup a voltaic cell.

Voltaic Cells



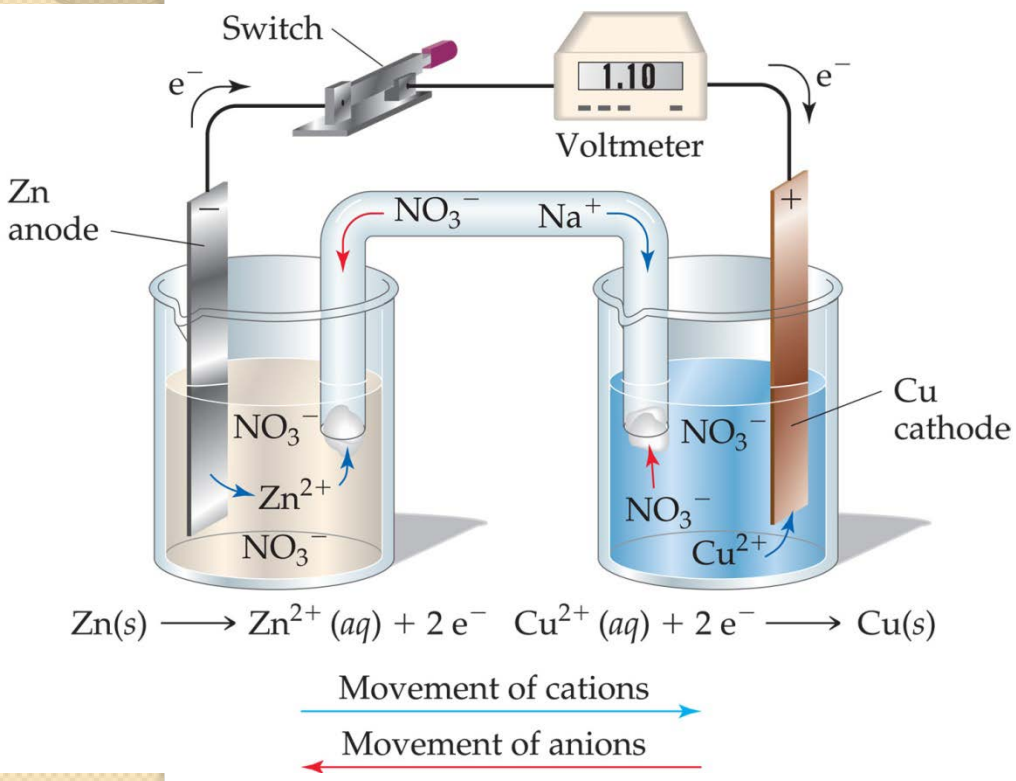
- A typical cell looks like this.
- The oxidation occurs at the anode.
- The reduction occurs at the cathode.

Voltaic Cells



Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.

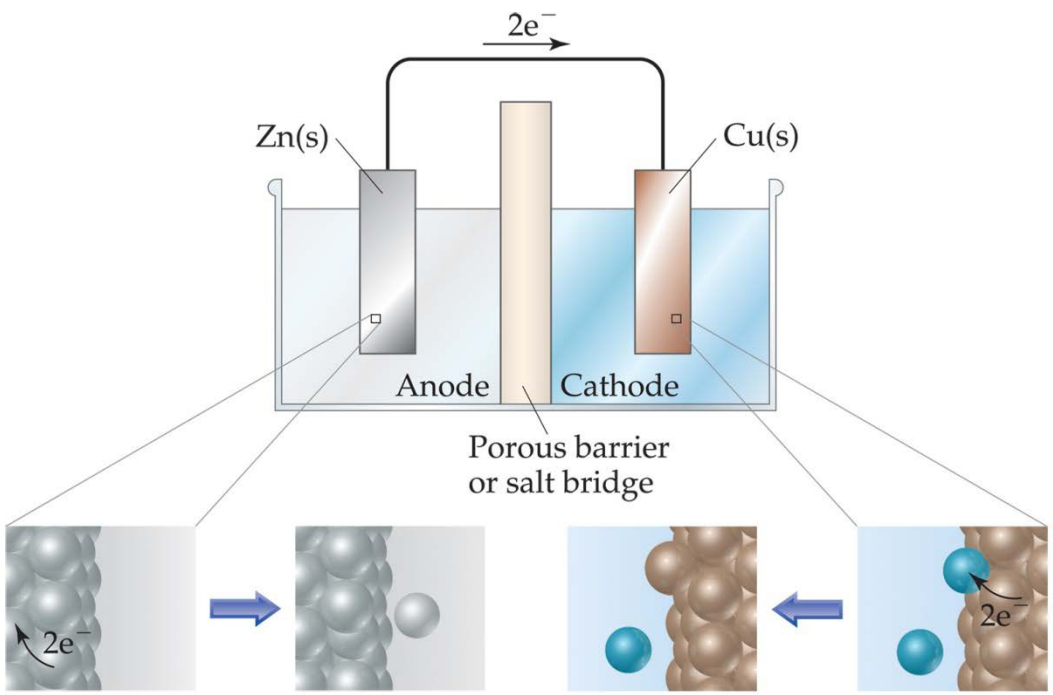
Voltaic Cells



- Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.
  - Cations move toward the cathode.
  - Anions move toward the anode.

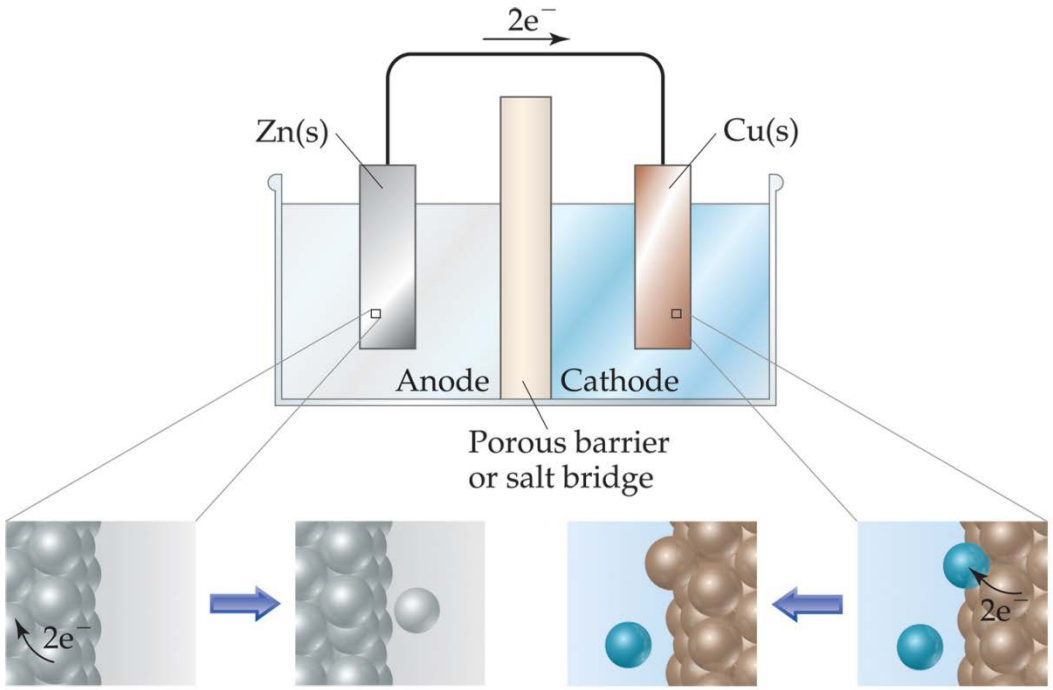
Voltaic Cells

- In the cell, then, electrons leave the anode and flow through the wire to the cathode.
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.

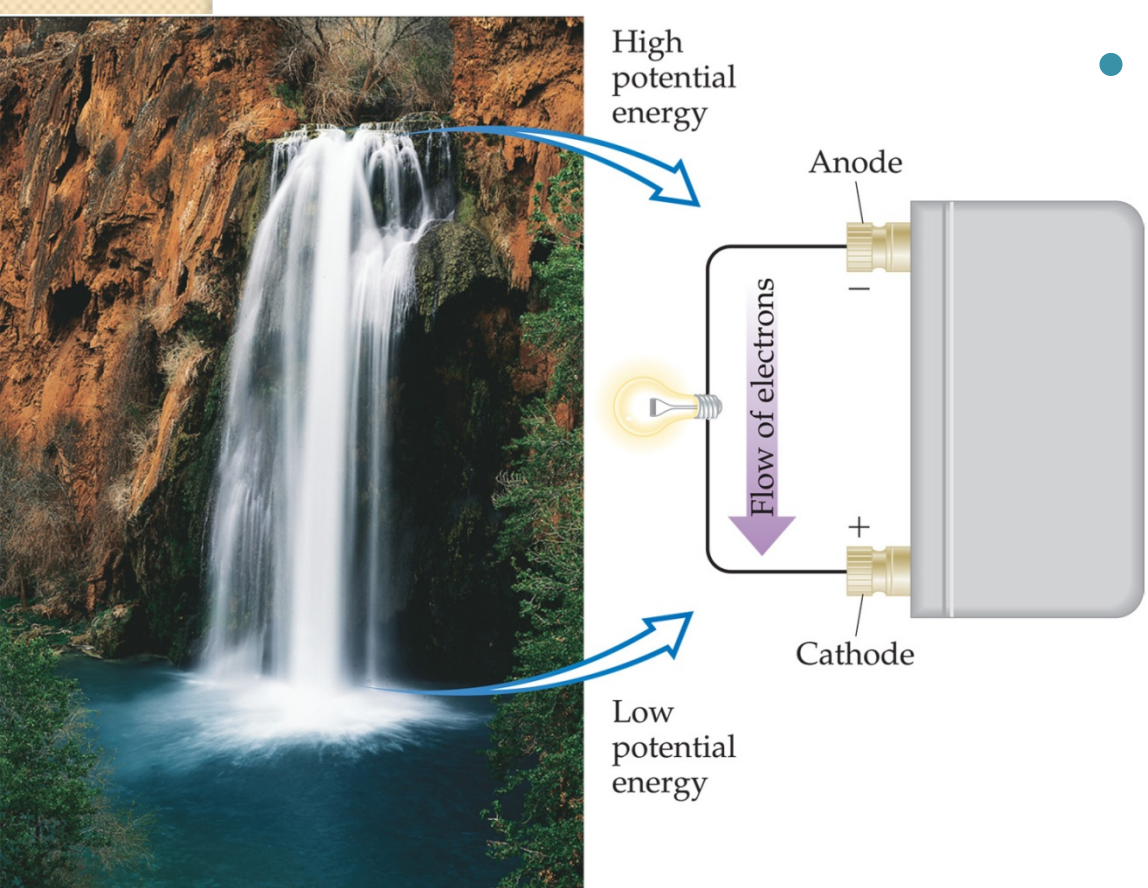


Voltaic Cells

- As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.
- The electrons are taken by the cation, and the neutral metal is deposited on the cathode.



Electromotive Force (emf)



- Water only spontaneously flows one way in a waterfall.
- Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.

Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the electromotive force (emf).
- It is also called the cell potential, and is designated E_{cell}.

Cell Potential

Cell potential is measured in volts (V).

$$1\,V = 1\,\frac{J}{C}$$

Standard Reduction Potentials

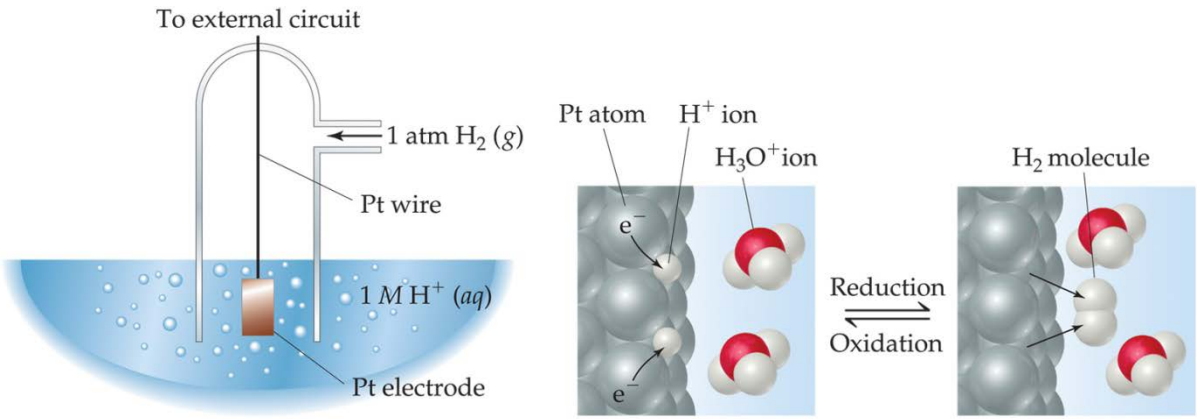
Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Reduction potentials for many electrodes have been measured and tabulated.

Standard Hydrogen Electrode

- Their values are referenced to a standard hydrogen electrode (SHE).
- By definition, the reduction potential for hydrogen is 0 V:

$$2\ H^+\ (aq, 1M) + 2\ e^- \longrightarrow H_2\ (g, 1\ \text{atm})$$



Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E^{\circ}_{cell} = E^{\circ}_{red}\,(\text{cathode}) - E^{\circ}_{red}(\text{anode})$$

Because cell potential is based on the potential energy per unit of charge, it is an intensive property.

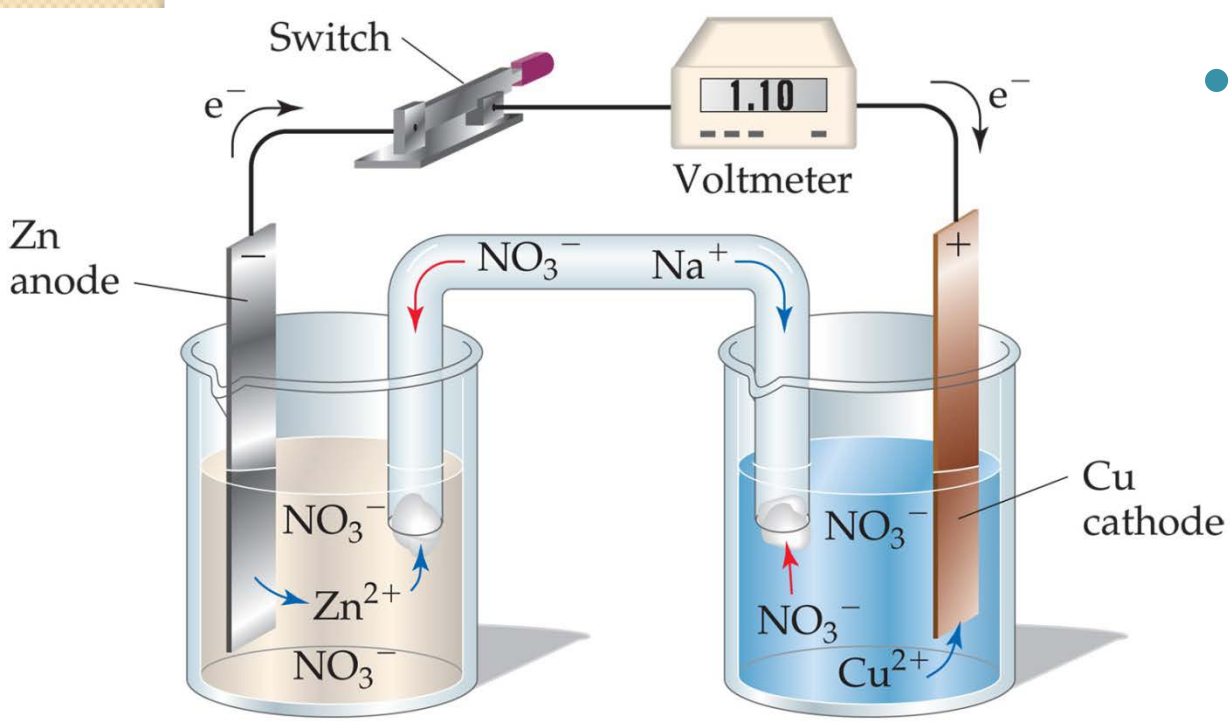
Cell Potentials

- For the oxidation in this cell,

$$E^{\circ}_{red} = -0.76\,V$$

- For the reduction,

$$E^{\circ}_{red} = +0.34\,V$$



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ $\quad Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Cell Potentials

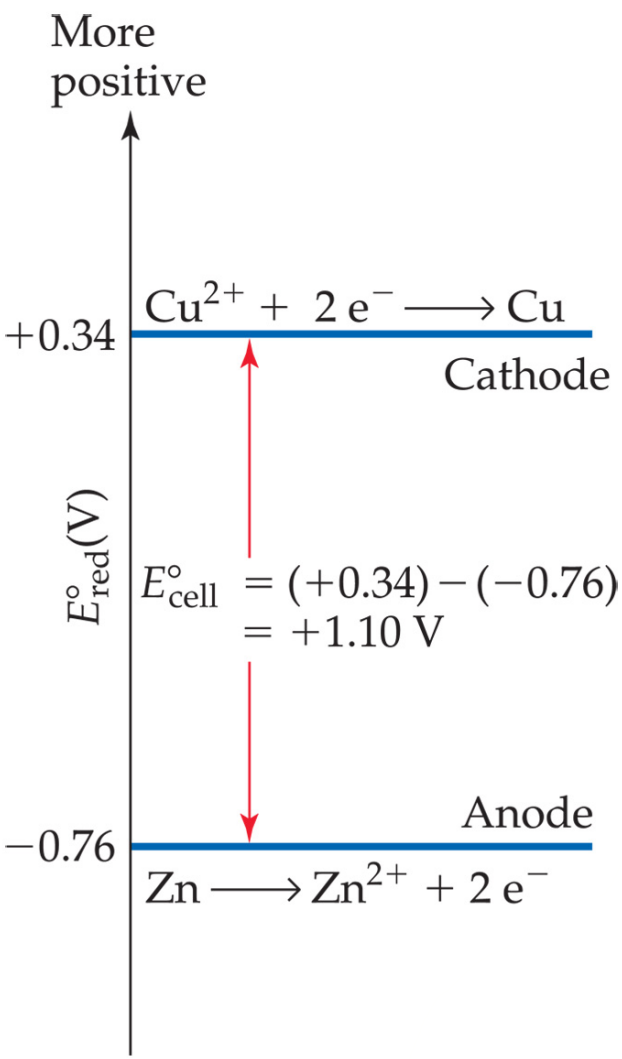
$$E^{\circ}_{cell} = E^{\circ}_{red}\ (\text{cathode}) - E^{\circ}_{red}\ (\text{anode})$$

$$= +0.34\,V - (-0.76\,V)$$

$$= +1.10\,V$$

Oxidizing and Reducing Agents

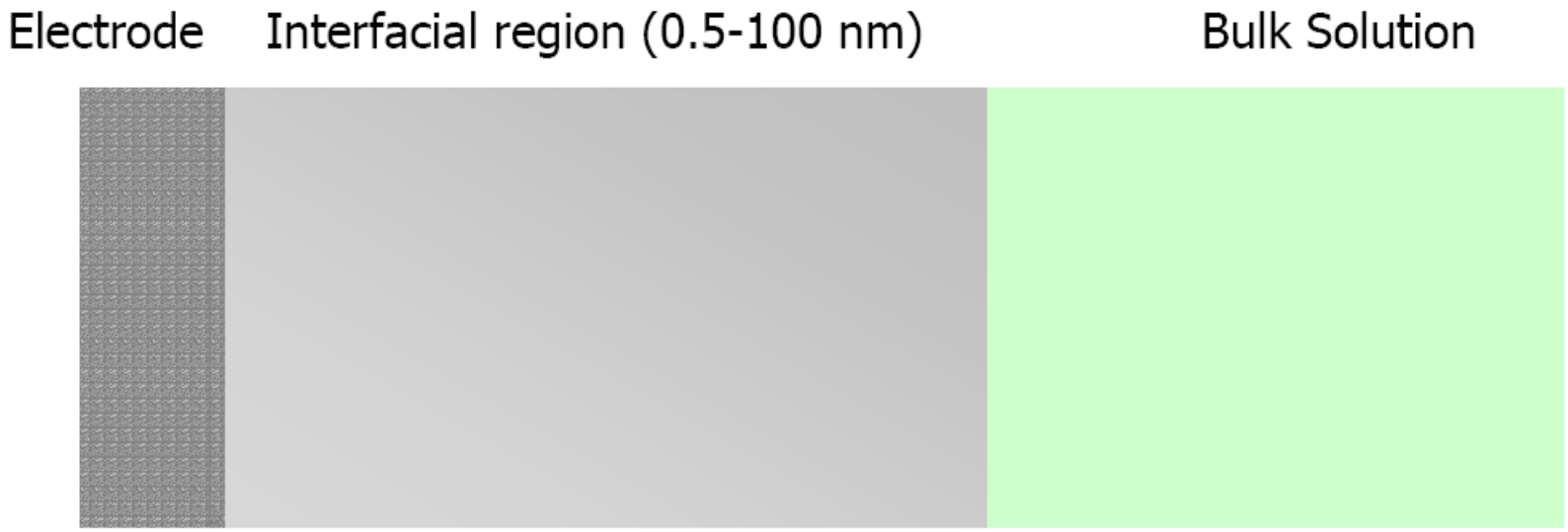
The greater the difference between the two, the greater the voltage of the cell.



Electrochemical Cells

- We are interested in the process that affects the transport of charge at the interface
  - Electrode charge is carried by electrons
  - Electrolyte charge is carried by ions
- An electrochemical cell typically consists of two electrodes

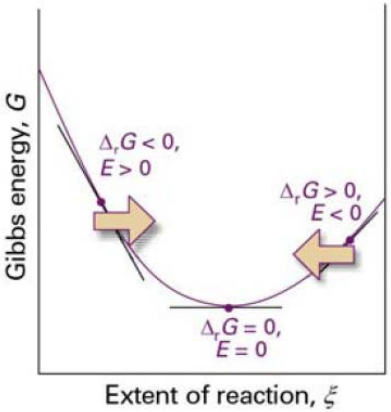
Many events occur at and near electrodes



- Faradic electron transfer at electrode surface
- Non-Faradic
  Ionic concentrations different from the bulk solution because of polarization effects and production of a double layer
  This affects currents and cell potentials
- mass transfer from bulk solution to electrode.

  Kinetics governed by diffusion and convection

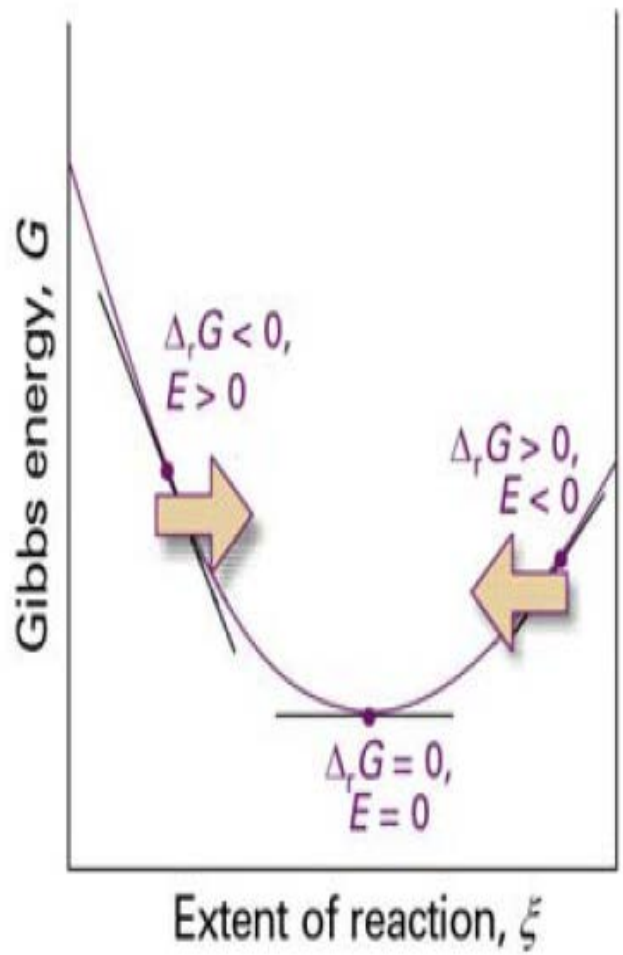
How does the relate to ΔG?



- $\Delta G° = -nFE°$
- *Where:*
  - ΔG = free energy
  - n = number of moles of electron
  - *F* = Faraday's constant (9.65×10^4 J/V•mol)
  - E^o= standard redox potential
- If at nonstandard state: $\Delta G = -nFE$

Gibbs Free Energy

- A cell in which the overall cell reaction is NOT in equilibrium can generate electrical work
- The cell potential is related to the magnitude of this work
- Thus the E_{cell} is also known as the EMF
- For spontaneous reaction, the cell potential should be positive



Electrochemical Cells under Non-standard Conditions

- Remember, the standard cell potential, E° is measured under standard conditions (298 K, 1 atm, and 1.0 M).
- If we are not under standard conditions, we have to solve for *E* under non-standard conditions
- Use the Nernst Equation (where Q is the electrochemical cell reaction):

$$E_{cell} = E^{\theta}_{cell} - \frac{RT}{nF}\ln(Q)$$

Cells at Equilibrium

- The minimum on the curve is at equilibrium

- The Gibbs Free Energy is zero, and thus the cell cannot do external work
- Thus: Q = K; the equilibrium constant for the cell reaction

$$\ln K = \frac{nFE^{\theta}_{cell}}{RT}$$

Cells at Equilibrium

- Thus we can get the standard potential of the cell

Structure of the Double Layer – Interface Role

- Electrode Kinetics are governed by the potential difference across a thin layer adjacent to the electrode surface
- This layer is called the double layer
- Potential difference across the thin layer is about 0.1V
- Large electric field (10^6 V/cm)

Structure of the Double Layer – Interface Role

- Large driving force for the electrode reaction
- Because of the large electric field we will have charge separation in the double layer
- Electroneutrality will not apply to the double layer region
- At equilibrium no current is applied (use thermodynamics)
- When have current – deviate from equilibrium
- Difference between the potential and the equilibrium potential is called the **OVERPOTENTIAL**

Structure of the Double Layer – Interface Role

- The surface overpotential is given by:

$$\eta_s = \phi - \phi^o$$

Where:

η_s is the surface overpotential

ϕ is the potential due to the current

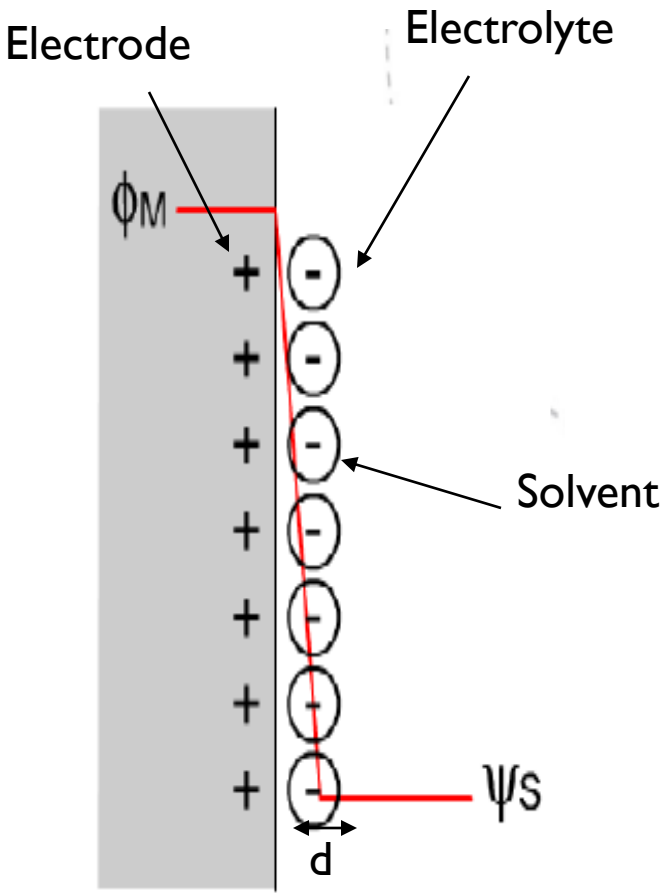
ϕ^0 is the equilibrium potential

Structure of the Double Layer

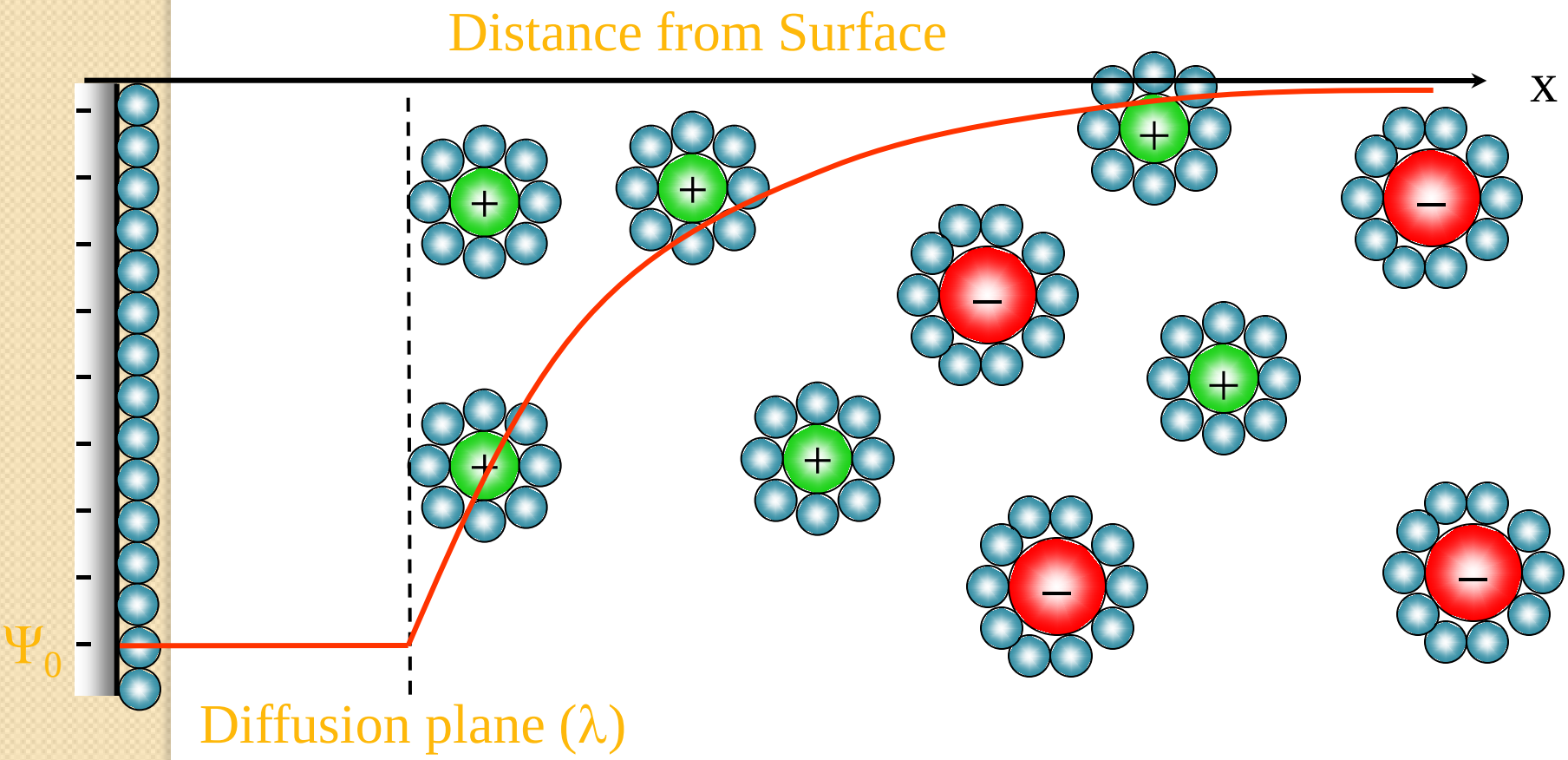
- When we apply a potential to an electrode, the charges that accumulate at the surface attract opposite charges from the electrolyte
- We have a distribution of charges to balance
- There are a number of different models to determine this effect (of the double layer):
  - Helmholtz model
  - Gouy and Chapman model
  - Stern model

Helmholtz model

- Developed in 1879
- Simplest
- Two parallel layers of charges separated by solvent molecules
- Distance (d) represents the outer Helmholtz layer
- Fixed distribution of layer



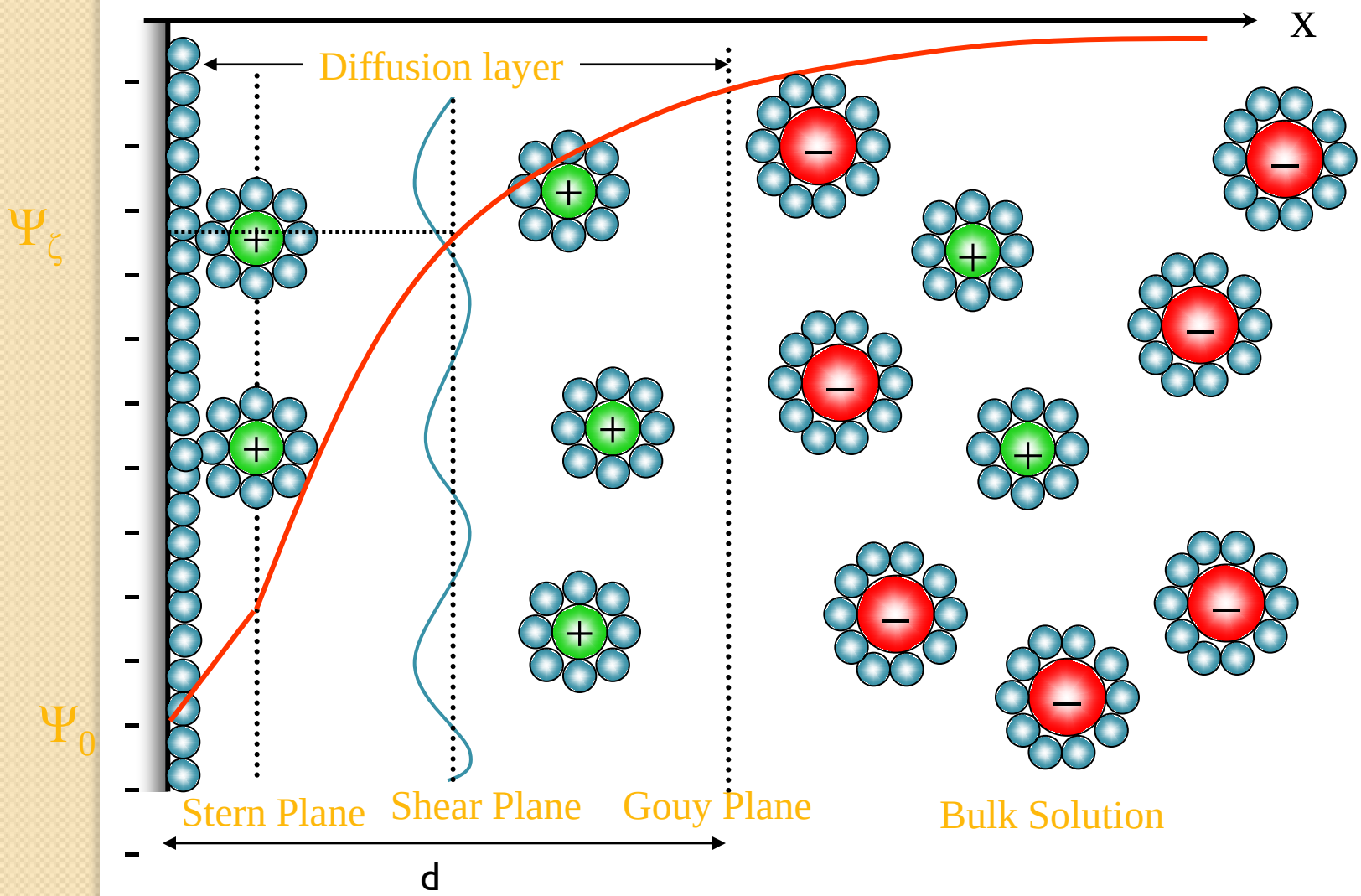
Gouy-Chapman Model



Gouy-Chapman Model

- Assumed Poisson-Boltzmann distribution of ions from surface
  - ions are point charges
  - ions do not interact with each other
  - no fixed charges
- Assumed that diffuse layer begins at some distance from the surface (λ)

Stern Model


x
Diffusion layer
Ψ_ζ
Ψ_0
Stern Plane
Shear Plane
Gouy Plane
Bulk Solution
d

Stern Model

- This combines the Helmholtz and the Gouy-Chapman
- Some of the charge is fixed (d region) and some is diffuse (or spread out)
- The total length of the boundary is given by the fixed region plus the diffuse region

Consequences of the Double-Layer

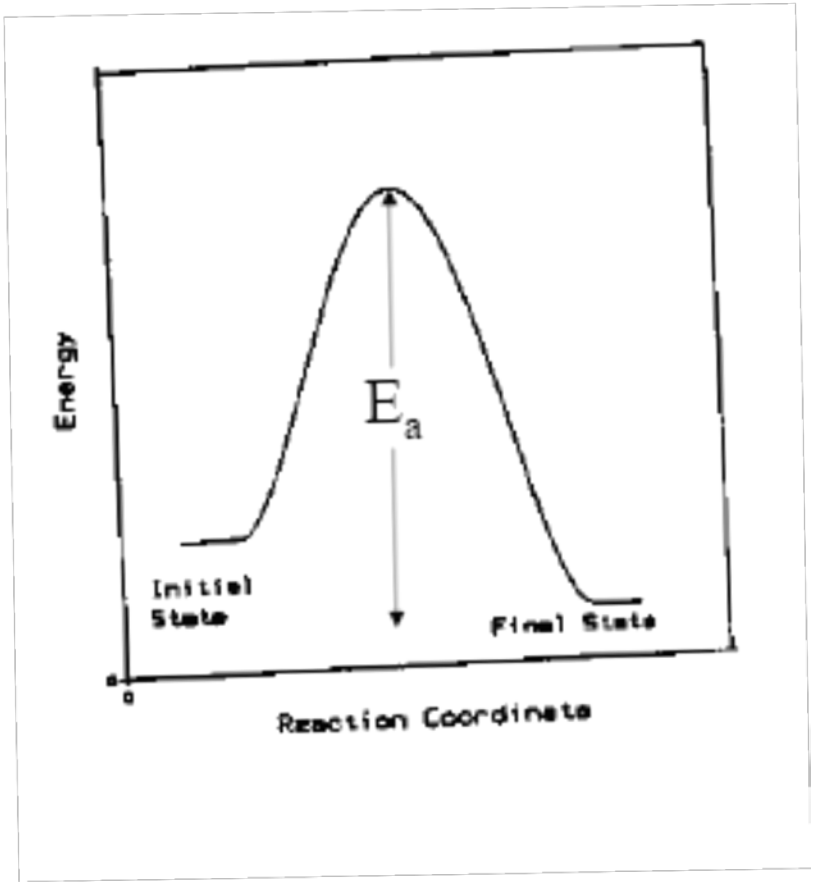
- Species outside the Helmholtz region are too distant to react.
- The driving force for the reaction is the potential drop across the Helmholtz region, rather than the potential drop across the whole double layer.
- Concentration at the bulk is different to the concentration at the surface of the electrode.

Consequences of the Double-Layer

- When we study the kinetics (next) we need only the intrinsic effect of kinetics (need to eliminate the effect of the double layer):
  - Add a non-reacting supporting electrolyte to the solution (if liquid);
  - This can increase the $C_{G\text{-}C}$, then the overall capacitance can be approximated by C_H.

Electrode Kinetics

- In ordinary (by that I mean in a typical reaction) we express the progress of a reaction by plotting the reaction co-ordinate versus the energy



Electrode Kinetics

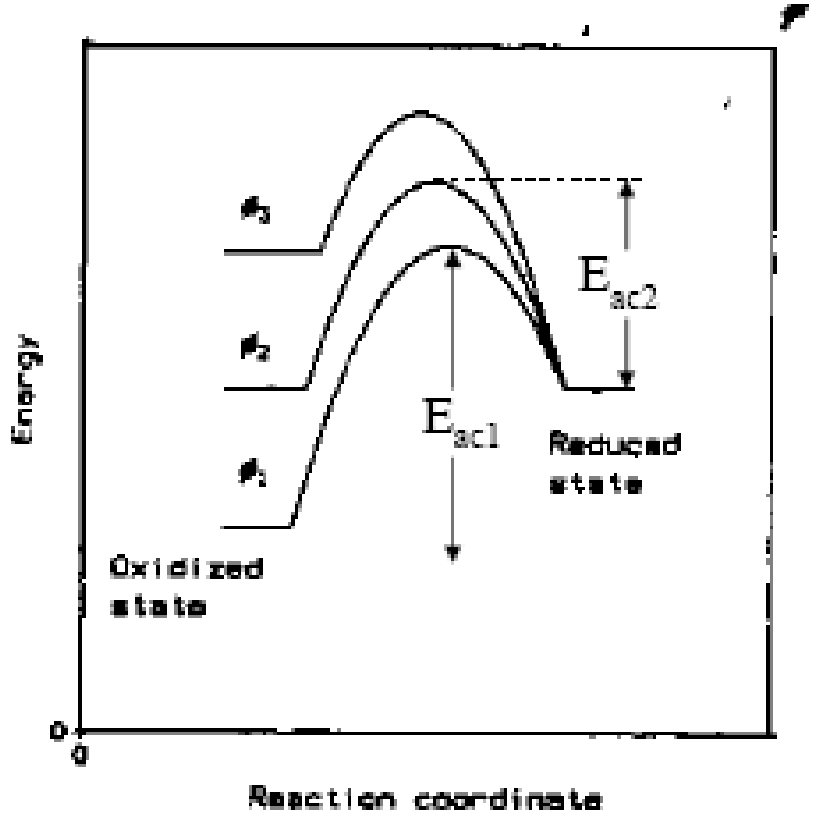
- Now, let us consider one elementary step electrochemical reaction:

$$O^{+} + e^{-} \underset{k_a}{\overset{k_c}{\Leftrightarrow}} R$$

- Where:
  - O^{+} is the oxidized species
  - R is the reduced species
  - k_c is the cathodic reaction rate constant
  - k_a is the anodic reaction rate constant

Electrode Kinetics

- A more negative potential (more positive energy) tends to promote reduction
- At progressively more negative potential, the energy of the oxidized species is increased
  - ϕ_3: reduction is favored
  - ϕ_1: oxidation is favored
  - ϕ_2: equilibrium potential; no net reaction takes place



Electrode Kinetics

- Consider the case where we start an experiment at the potential ϕ_1 and we reduce it to ϕ_2.
- The activation energy for the first process (E_{act1}) is higher than that for the second process (E_{act2})
- We can express the activation energy for the second process as a function of the first:

$$G_{C2} = G_{C1} + \beta nF(\phi_2 - \phi_1)$$

Electrode Kinetics

- Where β is the symmetry factor (transfer coefficient) which represents the fraction of energy that has been used to reduce the activation energy of the reaction.
- Similarly, the activation energy for the anodic process (which increases) can be expressed by:

$$G_{a2} = G_{a1} - (1-\beta)nF(\phi_2 - \phi_1)$$

- n is the number of electrons transferred in the reaction (n is 1 most of the time, unusual to have more than 1 in an elementary step)

Electrode Kinetics

- The form of our kinetic expression is the same as that for chemical reactions (Arrhenius relationship)

$$k = k' \exp\left(\frac{-G}{RT}\right)$$

- Where:
  - k' is a rate constant (cm/s)
  - G is the free energy of activation

Electrode Kinetics

- The rate of electrochemical reaction is directly proportional to the current density

$$r = i/nF = k'c\exp\left(\frac{-G}{RT}\right)$$

- r is the reaction rate (mol/s cm^2)
- i is the current density (A/cm^2)
- c is the reactant concentration (mol/cm^3)

Electrode Kinetics

- For the general anodic reaction again:

$$O^{+} + e^{-} \underset{k_a}{\overset{k_c}{\Leftrightarrow}} R$$

- We can substitute

$$G_{a2} = G_{a1} - (1-\beta)nF(\phi_2 - \phi_1)$$

- Into

$$r = {}^{i}\!/_{nF} = k^{'} c \exp\left(\frac{-G}{RT}\right)$$

Electrode Kinetics

- And assuming that we have a reference electrode (ie drop the subscripts) we get:

$$r_a = \frac{i_a}{nF} = k_a^{'} c_R \exp\left\{ -\frac{G_a - (1-\beta)nF\phi}{RT} \right\}$$

Electrode Kinetics

- We can redefine the reaction constant to include the activation energy at our reference potential:
- This is from substituting

$$k = k' \exp\left(\frac{-G}{RT}\right)$$

- Into the last equation, giving:

$$r_a = \frac{i_a}{nF} = k_a c_R \exp\left\{\frac{(1-\beta)nF\phi}{RT}\right\}$$

Electrode Kinetics

- Similarly for the cathodic reaction:

$$r_c = \frac{i_c}{nF} = k_c c_o \exp\left\{\frac{-\beta nF\phi}{RT}\right\}$$

- The NET current density ($i=i_a=i_c$) is the difference between the anodic and cathodic current densities

$$r = r_a = r_c = \frac{i}{nF} = k_a c_R \exp\left\{\frac{(1-\beta)nF\phi}{RT}\right\} - k_c c_o \exp\left\{\frac{-\beta nF\phi}{RT}\right\}$$

Electrode Kinetics

- At equilibrium the net current density is ZERO
- However, the rates of the anodic and cathodic reaction are NOT ZERO
- The magnitude of both (i_a and i_c) are the same
- This is called the EXCHANGE CURRENT DENSITY (i_o)

Electrode Kinetics

- If we designate the equilibrium potential as ϕ° then

$$\frac{i_0}{nF} = k_a c_R \exp\left\{\frac{(1-\beta)nF\phi^0}{RT}\right\} - k_c c_o \exp\left\{\frac{-\beta nF\phi^0}{RT}\right\}$$

- Taking the logs of the equation above and we get:

$$\phi^0 = \frac{RT}{nF}\ln\left(\frac{k_c}{k_a}\right) - \frac{RT}{nF}\ln\left(\frac{C_R}{C_o}\right)$$

Electrode Kinetics

- Now, if we substitute this equation

$$\phi^0 = \frac{RT}{nF}\ln\left(\frac{k_c}{k_a}\right) - \frac{RT}{nF}\ln\left(\frac{C_R}{C_o}\right)$$

- into

$$r = r_a = r_c = \frac{i}{nF} = k_a c_R \exp\left\{\frac{(1-\beta)nF\phi}{RT}\right\} - k_c c_o \exp\left\{\frac{-\beta nF\phi}{RT}\right\}$$

Electrode Kinetics

- We Get (assuming that we use the definition of overpotential)

$$\eta_s = \phi - \phi^o$$

where, η_s is the surface potential, ϕ is the potential due to the current, and ϕ^0 is the equilibrium potential

$$\frac{i}{nF} = k_a c_R \exp\left\{\frac{(1-\beta)nF}{RT}\left(\eta_s + \frac{RT}{nF}\ln\frac{k_c}{k_a} + \frac{RT}{nF}\ln\frac{C_o}{C_R}\right)\right\}$$

$$-k_c c_o \exp\left\{\frac{-\beta nF}{RT}\left(\eta_s + \frac{RT}{nF}\ln\frac{k_c}{k_a} + \frac{RT}{nF}\ln\frac{C_o}{C_R}\right)\right\}$$

Electrode Kinetics

- Rearranging this equation gives:

$$i = nFk_c^{1-\beta}k_a^{-\beta}c_o^{1-\beta}c_R^{-\beta}\left[\exp\left\{\frac{(1-\beta)nF}{RT}\eta_s\right\} - \exp\left\{\frac{-\beta nF}{RT}\eta_s\right\}\right]$$

- This is the general kinetics expression for the first order elementary step given in

$$O^+ + e^- \underset{k_a}{\overset{k_c}{\Leftrightarrow}} R$$

Electrode Kinetics

- The concentration of the reactants are at the surface of the electrode
- The cathodic and anodic kinetic constants can be evaluated at equilibrium from the exchange current density

$$k_c = \frac{i_o}{nFC_o^0} \text{ and } k_a = \frac{i_o}{nFC_R^0}$$

- Where the superscript (0) represents equilibrium conditions

Electrode Kinetics

- Substituting the kinetic constants into the general expression given earlier, we get:

$$i = i_o \left(\frac{c_o}{c_o^0} \right)^{1-\beta} \left(\frac{c_R}{c_R^0} \right)^{\beta} \left[\exp\left\{ \frac{(1-\beta)nF}{RT} \eta_s \right\} - \exp\left\{ \frac{-\beta nF}{RT} \eta_s \right\} \right]$$

Butler-Volmer Equation

- Redefining the transfer coefficents for the anodic and cathodic components as:

$$\alpha_a = (1-\beta)n$$

$$\alpha_c = \beta n$$

- And assuming the concentration at the surface is equal to the concentration at the bulk which will be the case under equilibrium conditions, then we get

Butler-Volmer Equation

- We get

$$i = i_o\left[\exp\left\{\frac{\alpha_a F}{RT}\eta_s\right\} - \exp\left\{\frac{-\alpha_c F}{RT}\eta_s\right\}\right]$$

- This is known as the Butler-Volmer Equation
- Thus there are three variables (α_a, α_c and i_0) that need to be determined to use a Butler-Volmer equation

Butler-Volmer Equation

- B-V equations give a good representation of experimental data for many systems
- The exchange current density is a strong function of temperature
- When the exchange current density is very large, the reactions are said to be REVERSIBLE

Butler-Volmer Equation

- When TWO reactions take place simultaneously, on the same electrode surface, we can use the BV equation for both of them
- We will have to determine the individual parameters for both reactions

Linear Form of the Butler-Volmer Equation

- One of the disadvantages of the BV equation is that the overpotential cannot be expressed implicitly
- To study this, two approximations have been made:
  - Small surface overpotential
  - Large surface overpotential

Linear Form of the Butler-Volmer Equation

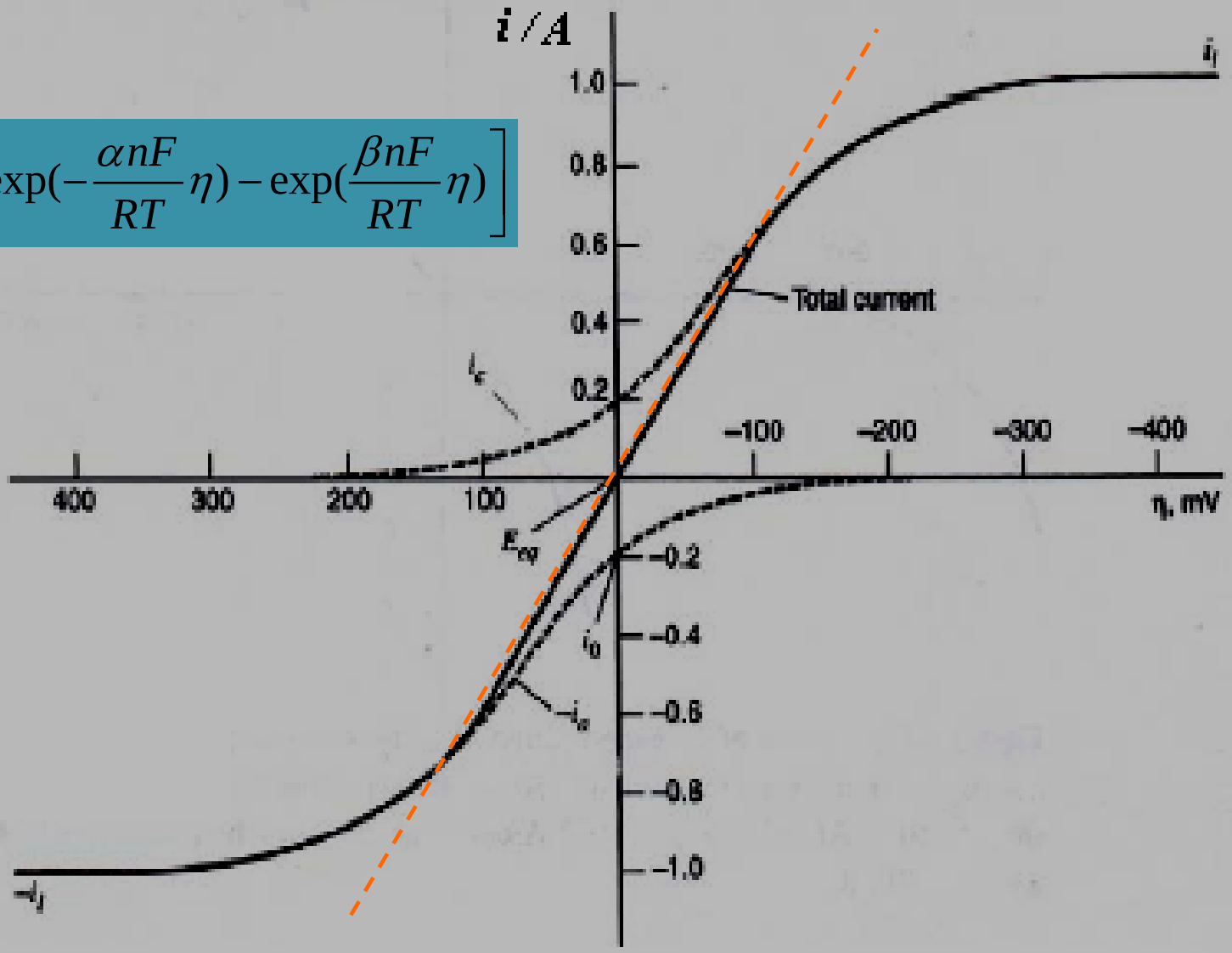
- When the overpotential is very small, the exponential term in the BV equation

$$i = i_o\left[\exp\left\{\frac{\alpha_a F}{RT}\eta_s\right\} - \exp\left\{\frac{-\alpha_c F}{RT}\eta_s\right\}\right]$$

- Can be expanded using the Maclaurin series, neglecting some of the terms in the series:

$$i = \frac{i_o(\alpha_a + \alpha_c)F}{RT}\eta_s$$

$$i = i_0\left[\exp(-\frac{\alpha nF}{RT}\eta) - \exp(\frac{\beta nF}{RT}\eta)\right]$$



Current-overpotential curves for the system O + $e \rightleftharpoons$ R with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

Linear Form of the Butler-Volmer Equation

- This is a linear form of the BV equation
- The current density is a function of only one parameter (i_o and the transfer coefficients can be defined as one constant)
- It is used to model systems operating at low current densities
- Often used when the overpotential is 10 mV or less

Tafel Equation

- If the overpotential is large and positive, the second term in the BV equation can be neglected

$$i = i_o\left[\exp\left\{\frac{\alpha_a F}{RT}\eta_s\right\} - \exp\left\{\frac{-\alpha_c F}{RT}\eta_s\right\}\right]$$

- Thus:

$$i = i_o \exp\left\{\frac{\alpha_a F}{RT}\eta_s\right\}$$

- If the overpotential is large and negative, then the first term can be ignored:

$$i = -i_o \exp\left\{-\frac{\alpha_c F}{RT}\eta_s\right\}$$

Tafel Equation

- These are known as TAFEL EQUATIONS
- Take the logs of $$i = i_o \exp\left\{\frac{\alpha_a F}{RT}\eta_s\right\}$$

$$\eta_s = B\log|i| - A$$

$$B = \frac{2.303RT}{\alpha_a F}$$

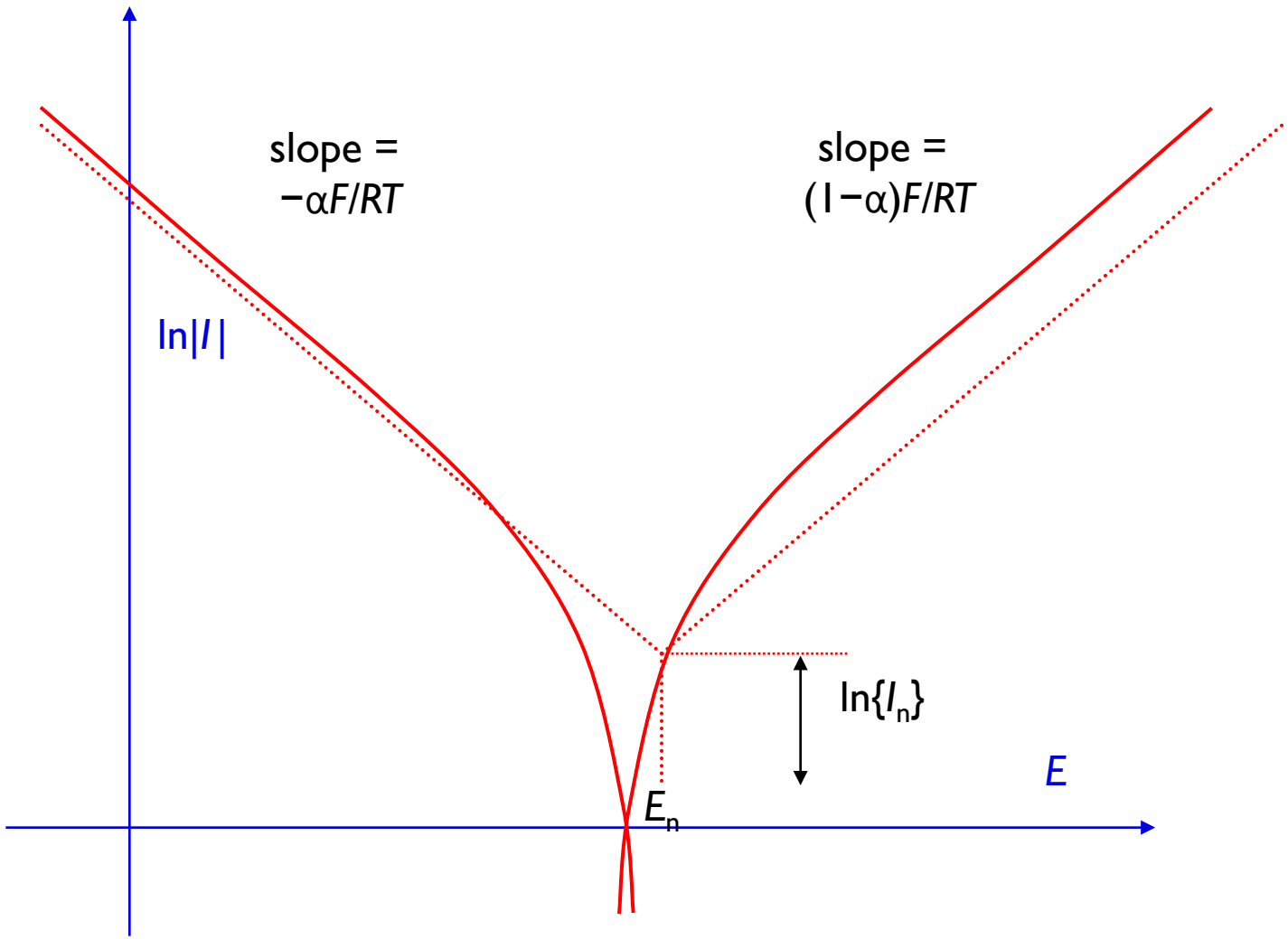
$$A = \frac{2.303RT}{\alpha_a F}\log i_o$$

- The constant B is called the TAFEL SLOPE
- Use of the Tafel approximation depends On the error that can be tolerated
- It is generally used when the overpotential Is at least 50 to 100 mV
- The Tafel slope varies between 30 to 300 mV/decade

Tafel Equation

- Values of the exchange current density and the transfer coefficient are obtained experimentally
- Plot overpotential versus log(i).
- The slope of the line will give the transfer coefficient, and the intercept will give the exchange current density
- We will come back to this later…so please try and remember!!!

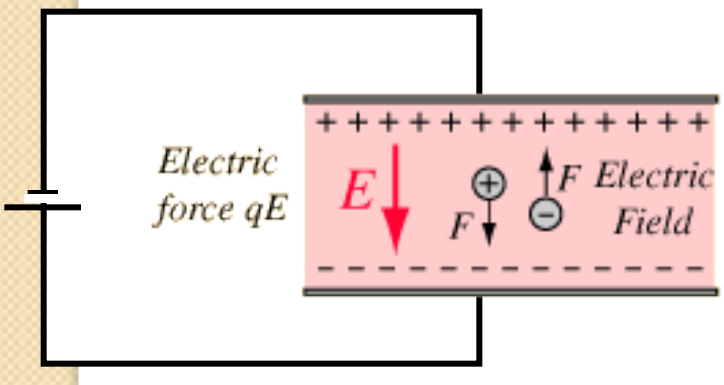
Tafel Slope

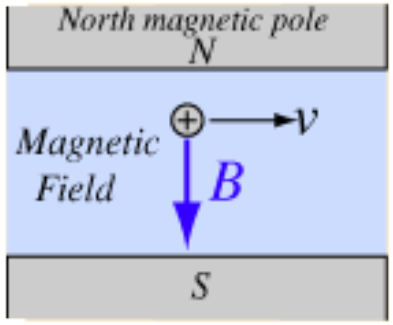


Driving force for conduction

Lorentz Force Law $\vec{F} = q\vec{E} + q\vec{v} \times \vec{B}$

Electric force *Magnetic force*





Magnetic force of magnitude qvBsinθ perpendicular to both v and B, away from viewer.

Driving force for conduction

current density

electrical field

$$J = \sigma E$$

electrical conductivity

By the way: also Ohm's Law!

Terms for electronic conduction

- Resistance $V = I \times R$
- Resistivity $\rho = RA/l$

- Conductance $G = \sigma l/A$
- Conductiviy $J = \sigma E$

conductivity *charge per electron*

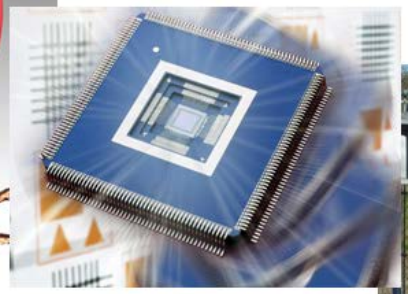
$$\sigma = n_e q_e \mu_e$$

1/[Ωm] or S/m

number of electrons *electron mobility*

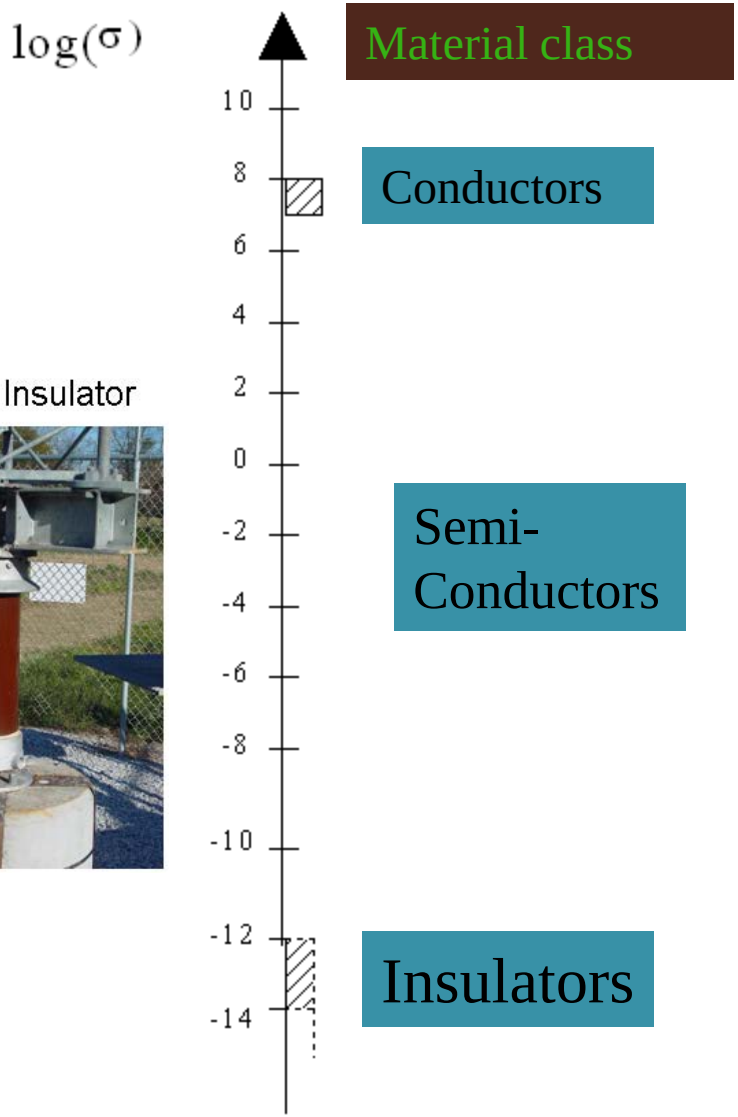
Classification

Conductor



Semi-conductor

Insulator



Ionic Conduction

- This is due to the crystal structure
- Electronic conduction is primarily due to the electronic band gap
- Can vary from highly ionic conduction (almost no electronic) to quasi-metallic

Defects in Non-stochiometric Binary Compounds

- We have:
  - Intrinsic defects
  - Extrinsic defects (dopants/impurity)
- Intrinsic defects fall into two main categories (see later):
  - Schottky Defects
  - Frenkel Defects

Potential Gradients as Driving Force

- Usually driving force for diffusion is the chemical potential of the particles
- Thus driving force for transport of electrical charge is the electrical potential gradient
- Let us consider transport of particles "i" under force "F"

$$j_i\,(\text{moles or particles/cm}^2\,\text{sec}) = c_i\,(\text{moles or particles/cm}^3).v_i\,(cm/s)$$

Potential Gradients as Driving Force

- Drift velocity v_i is proportional to the driving force, F

$$v_i = B_i F_i$$

- B is the proportionality factor (Beweglichkeit) – it is the average drift velocity per unit driving force
- and

$$F_i = -\frac{dP_i}{dx}$$

- Where P is the potential

Potential Gradients as Driving Force

- Thus,

$$j_i = c_i v_i = -c_i B_i \frac{dP_i}{dx}$$

Now, we can say μ_i is related to chemical activity a_i

where, $\mu_i = \mu_i^o + kT \ln a_i$

Where, $a_i = \frac{c_i}{c_i^o}\left(\frac{\text{conc}}{\text{reference conc}}\right)$

Potential Gradients as Driving Force

- Thus,

$$\frac{d\mu_i}{dx} = kT\frac{d\ln c_i}{dx} = \frac{kT}{c_i}\frac{dc_i}{dx}$$

$$\text{Thus, } j_i = -c_i B_i \frac{d\mu_i}{dx} = -B_i kT\frac{dc_i}{dx}$$

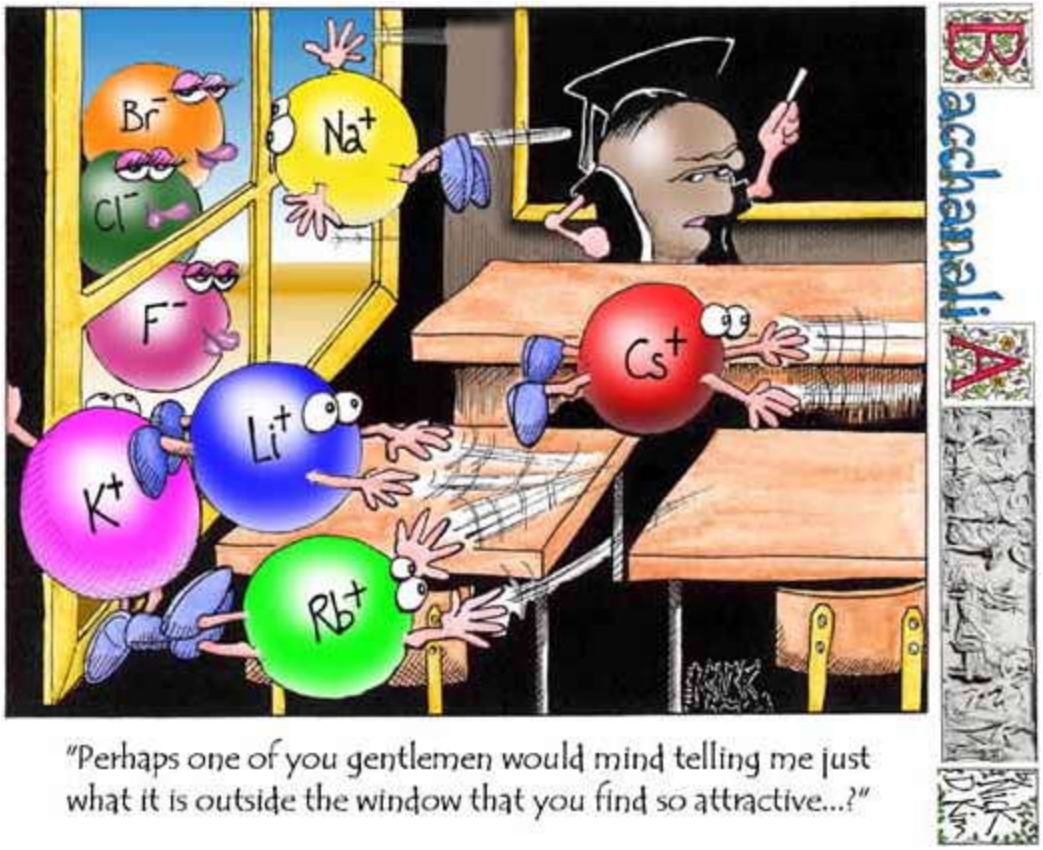
$$\text{Now, } D_i = B_i kT = \text{Diff Coeft.}$$

$$\text{Thus, } j_i = -D_i \frac{dc_i}{dx}$$

This is only valid for neutral particles

Diffusion

- Before we go any further let us look at the concept of diffusion



"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?"

The Solid State

- Solid State Electrochemistry can be split into 2 main fields:
  - Ionics – Properties of the electrolyte
  - Electrodics – Electrode reactions

Brief history of structure, stoichiometry, and defects

- Early chemistry had no concept of stoichiometry or structure.
- The finding that compounds generally contained elements in ratios of small integer numbers was a great breakthrough!
- Understanding that external geometry often reflected atomic structure.
- Perfectness ruled. Non-stoichiometry was out.
- Intermetallic compounds forced re-acceptance of non-stoichiometry.
- But real understanding of defect chemistry of compounds is less than 100 years old.

Introduction

- Classical chemistry and crystallography gave an idealized picture of the composition and crystal structure of inorganic compounds.
- It was not until the 1930's when Wagner and Schottky (1930) showed, through statistical thermodynamic treatment of mixed phases that crystal structures are not ideal.
- Some lattice sites will be empty (vacant) and extra atoms may occupy the interstitial space between the atoms on the lattice sites. The empty lattice sites are termed vacancies and the extra atoms, interstitial atoms.

C. Wagner and W. Schottky, Theorie der geordneten Mischphasen, *Z. Phys. Chem.*, Vol 11, 1930, p 163

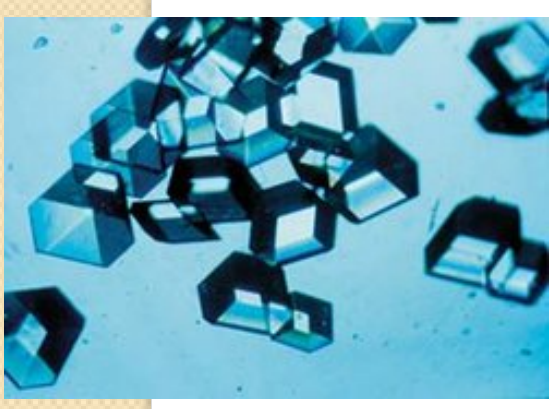
Introduction

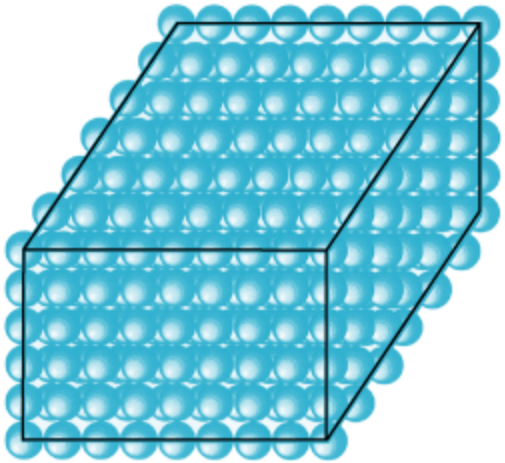
- Following Wagner and Schottky all crystalline solids will at any temperature contain vacancies and extra atoms and will as such exhibit deviations from the ideal structure.
- Furthermore, all inorganic compounds may in principle have variable composition and thus be nonstoichiometric.
- These deviations or imperfections are called *defects*. The reason for this is that by convention *the ideal structure is used as the reference state*, and *any deviation from this ideal state is termed a defect.*

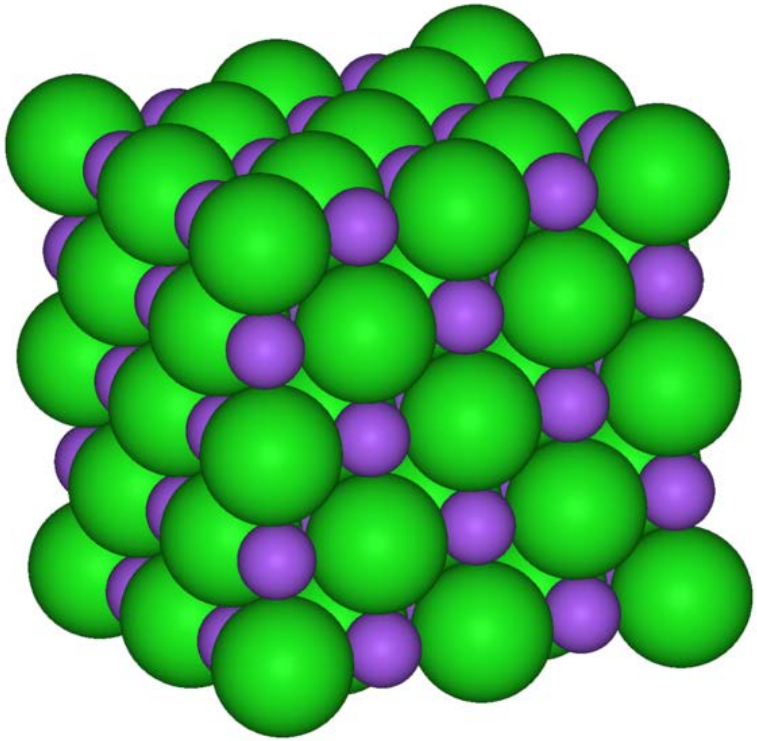
Perfect Crystal

- Our course in defects takes the perfect structure as starting point.

- This can be seen as the ideally defect-free interior of a single crystal or large crystallite grain at 0 K.





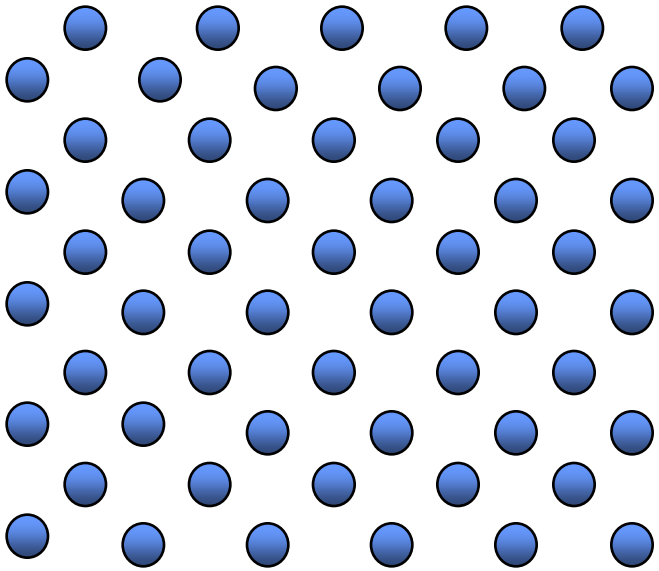


Some simple classes of oxide structures

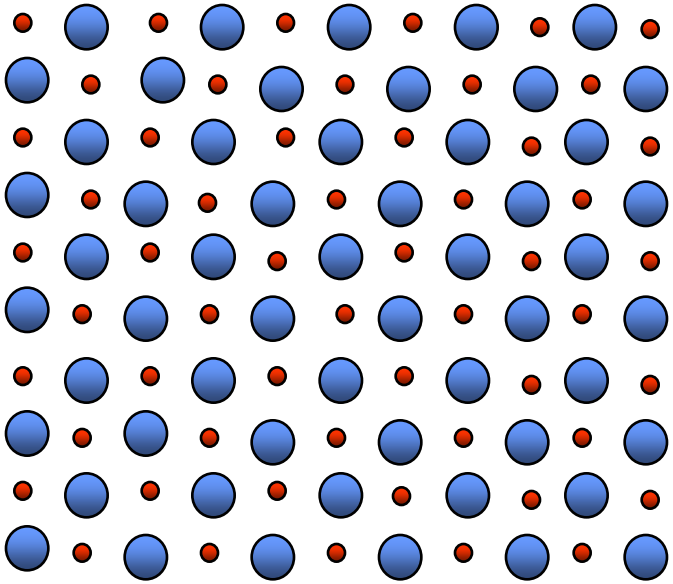
Formula	Cation:anion coordination	Type and number of occupied interstices	fcc of anions	hcp of anions
MO	**6:6**	**1/1 of octahedral sites**	**NaCl, MgO, CaO, CoO, NiO, FeO a.o.**	**FeS, NiS**
MO	**4:4**	**1/2 of tetrahedral sites**	**Zinc blende: ZnS**	**Wurtzite: ZnS, BeO, ZnO**
M_2O	**8:4**	**1/1 of tetrahedral sites occupied**	**Anti-fluorite: Li_2O, Na_2O a.o.**	
M_2O_3, ABO_3	**6:4**	**2/3 of octahedral sites**		**Corundum: Al_2O_3, Fe_2O_3, Cr_2O_3 a.o. Ilmenite: $FeTiO_3$**
MO_2	**6:3**	**½ of octahedral sites**		**Rutile: TiO_2, SnO_2**
AB_2O_4		**1/8 of tetrahedral and 1/2 of octahedral sites**	**Spinel: $MgAl_2O_4$ Inverse spinel: Fe_3O_4**	

We shall use 2-dimensional structures for our schematic representations of defects

- Elemental solid



- Ionic compound

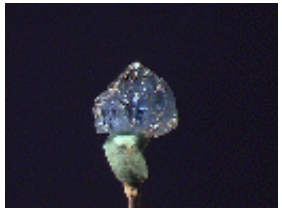


Perfect vs defective structure

- Perfect structure (ideally exists only at 0K)
- No mass transport or ionic conductivity
- No electronic conductivity in ionic materials and semiconductors;

- Defects introduce mass transport and electronic transport; diffusion, conductivity…
- New electrical, optical, magnetic, mechanical properties

- Defect-dependent properties



Kröger-Vink notation for 0-dimensional defects

- Point defects
  - Vacancies
  - Interstitials
  - Substitutional defects
- Electronic defects
  - Delocalised
    - electrons
    - electron holes
  - Valence defects
    - Trapped electrons
    - Trapped holes
- Cluster/associated defects

- Kröger-Vink-notation

$$A_s^c$$

A = chemical species
or v (vacancy)

s = site; lattice position
or i (interstitial)

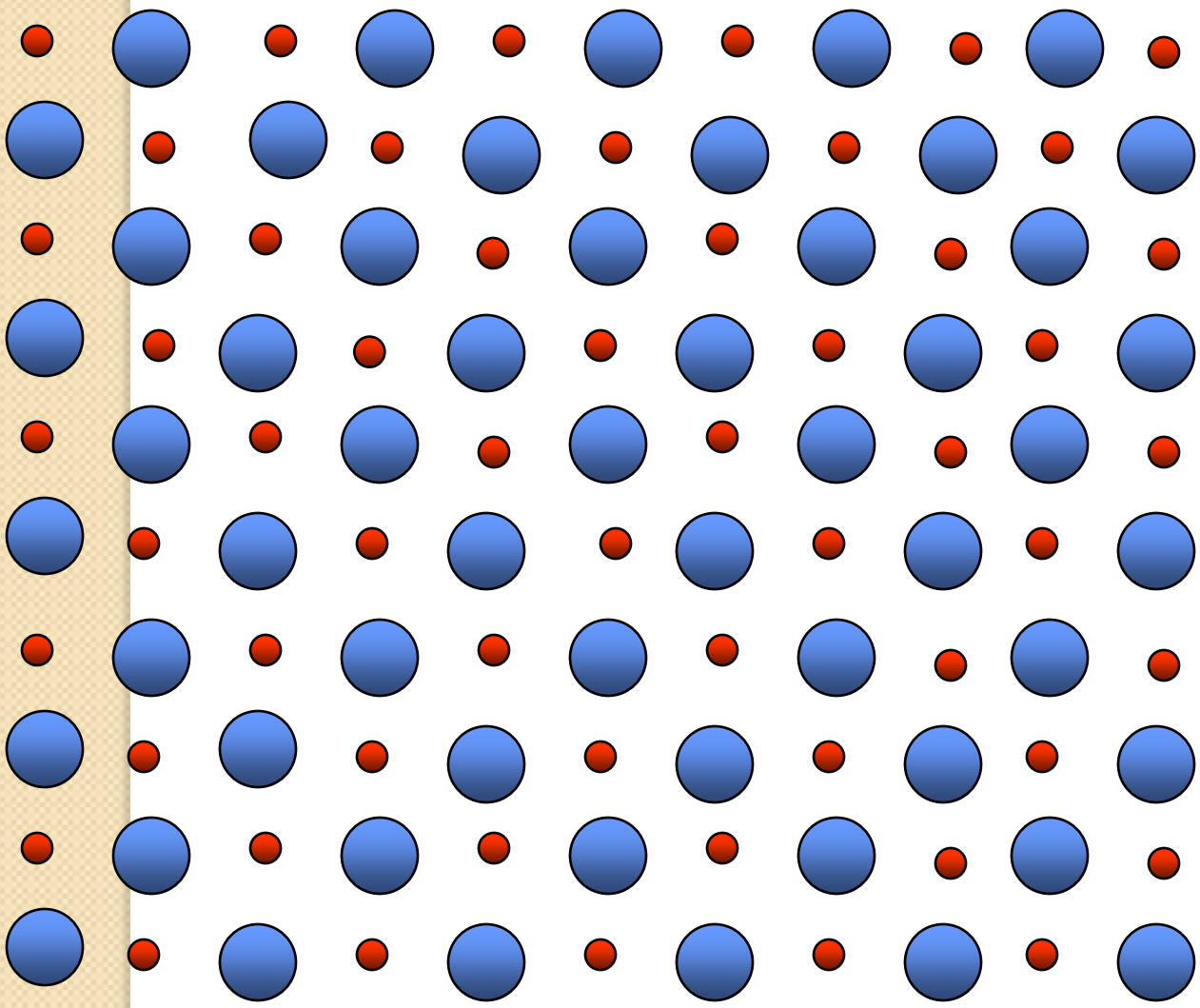
c = charge

Effective charge = Real charge on site minus charge site would have in perfect lattice

Notation for effective charge:

•	positive	
/	negative	
×	neutral	(optional)

Perfect lattice of MX, e.g. ZnO



Zn_{Zn}^{2+}

Zn_{Zn}^{x}

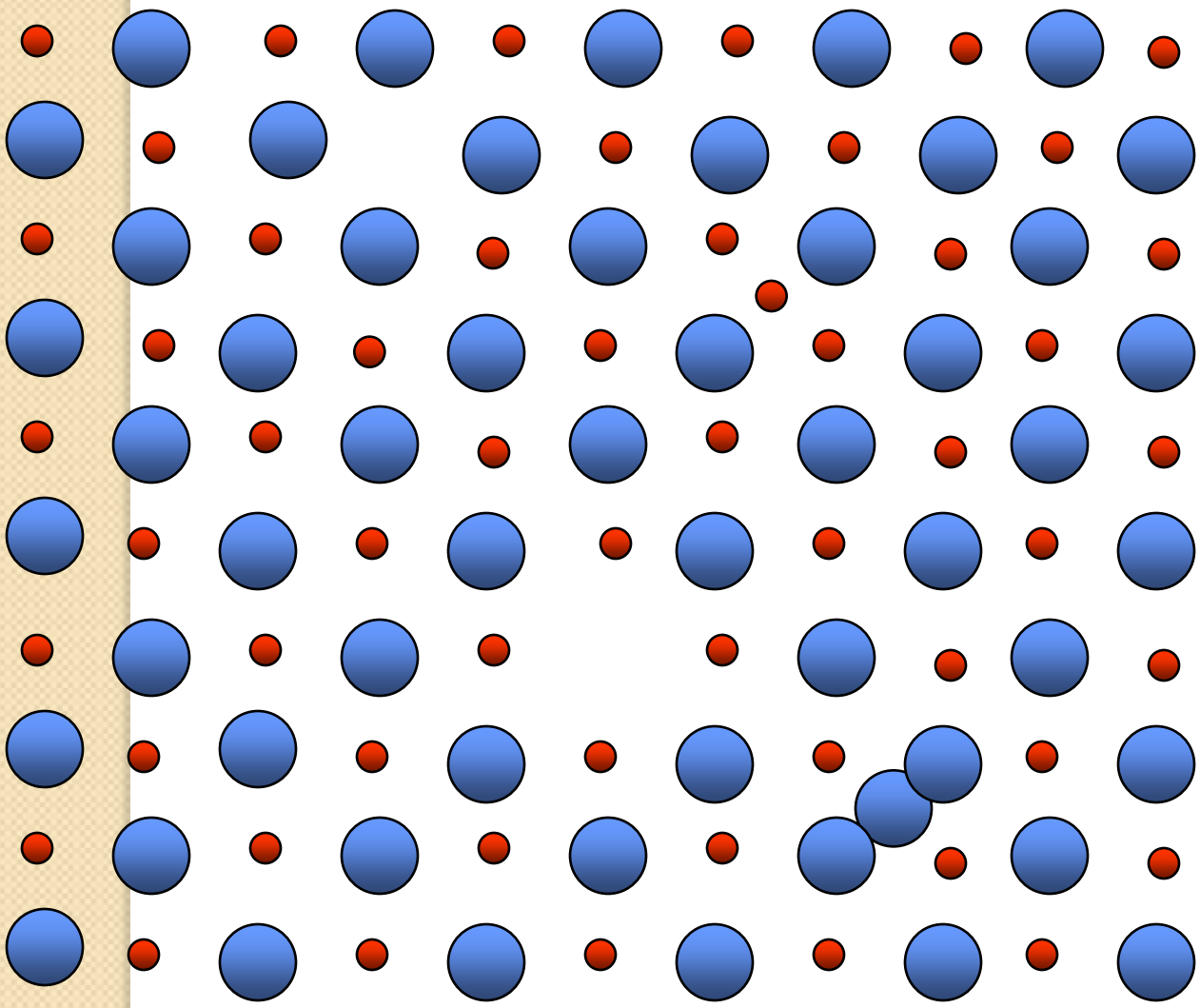
O_{O}^{2-}

O_{O}^{x}

v_i

v_i^x

Vacancies and interstitials



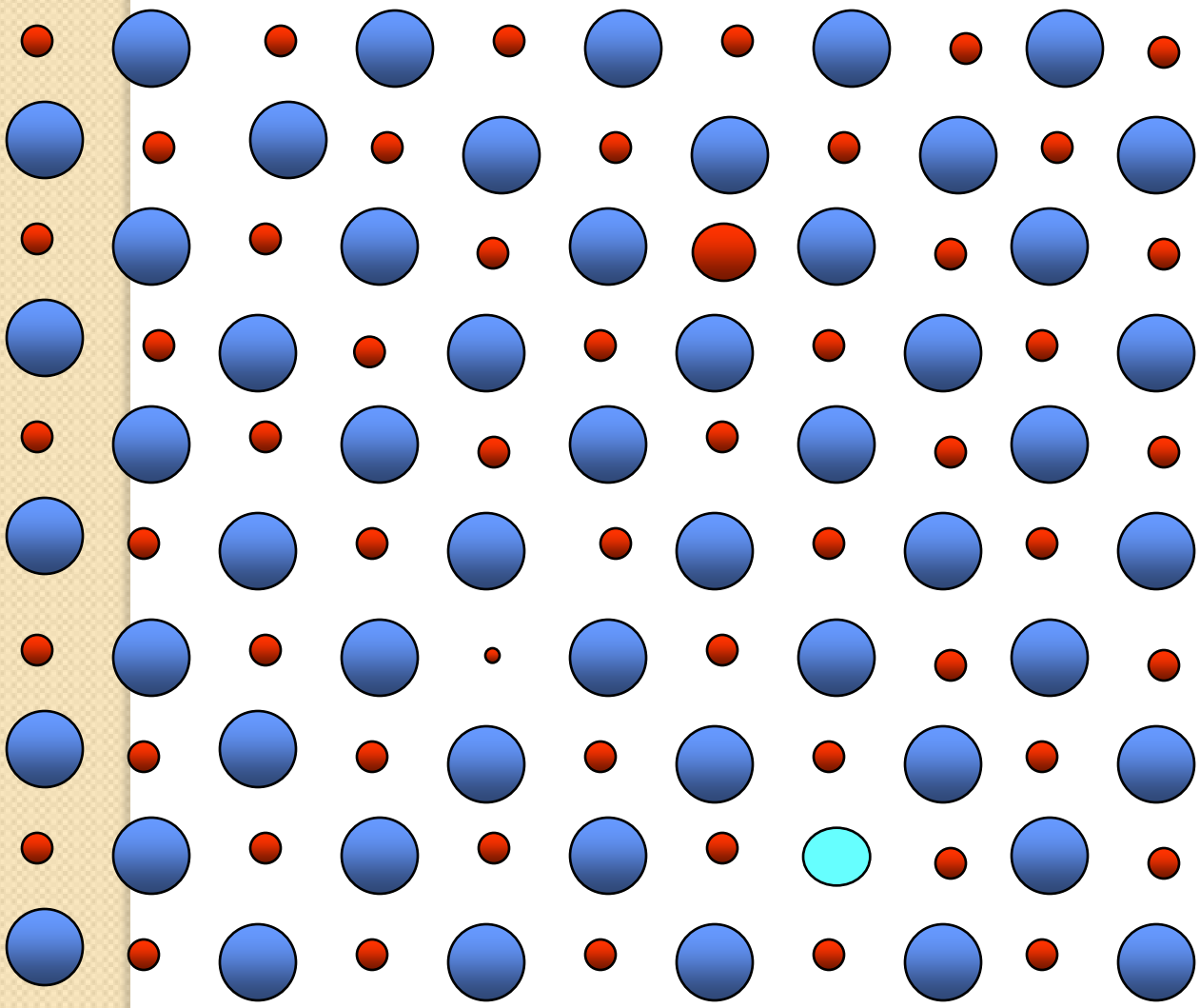
$v_{Zn}^{//}$

$Zn_i^{\bullet\bullet}$

$v_O^{\bullet\bullet}$

$O_i^{//}$

Electronic defects



e'

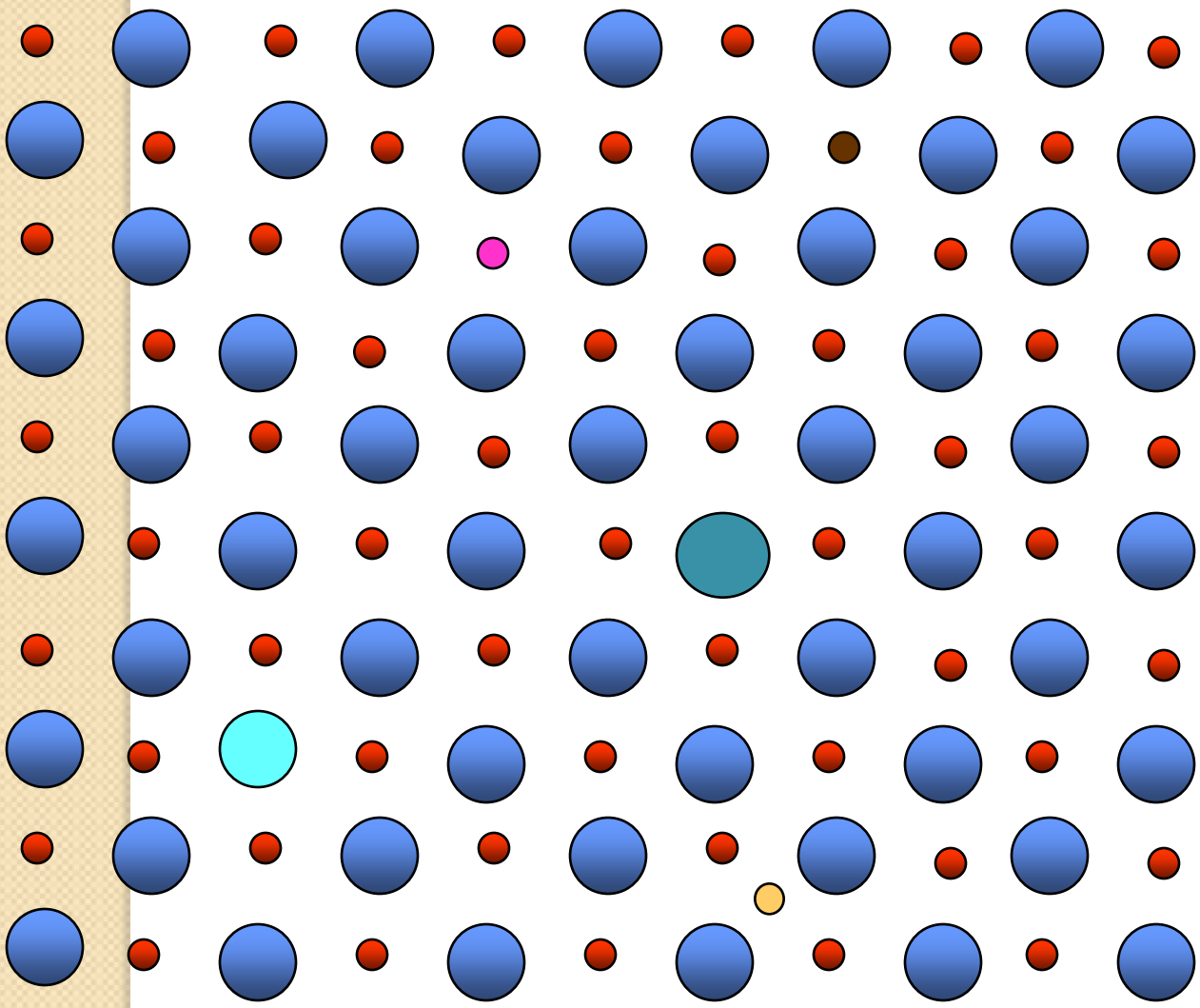
Zn'_{Zn}

$h^{\bullet}$

$Zn^{\bullet}_{Zn}$

$O^{\bullet}_{O}$

Foreign species



Ag'_{Zn}

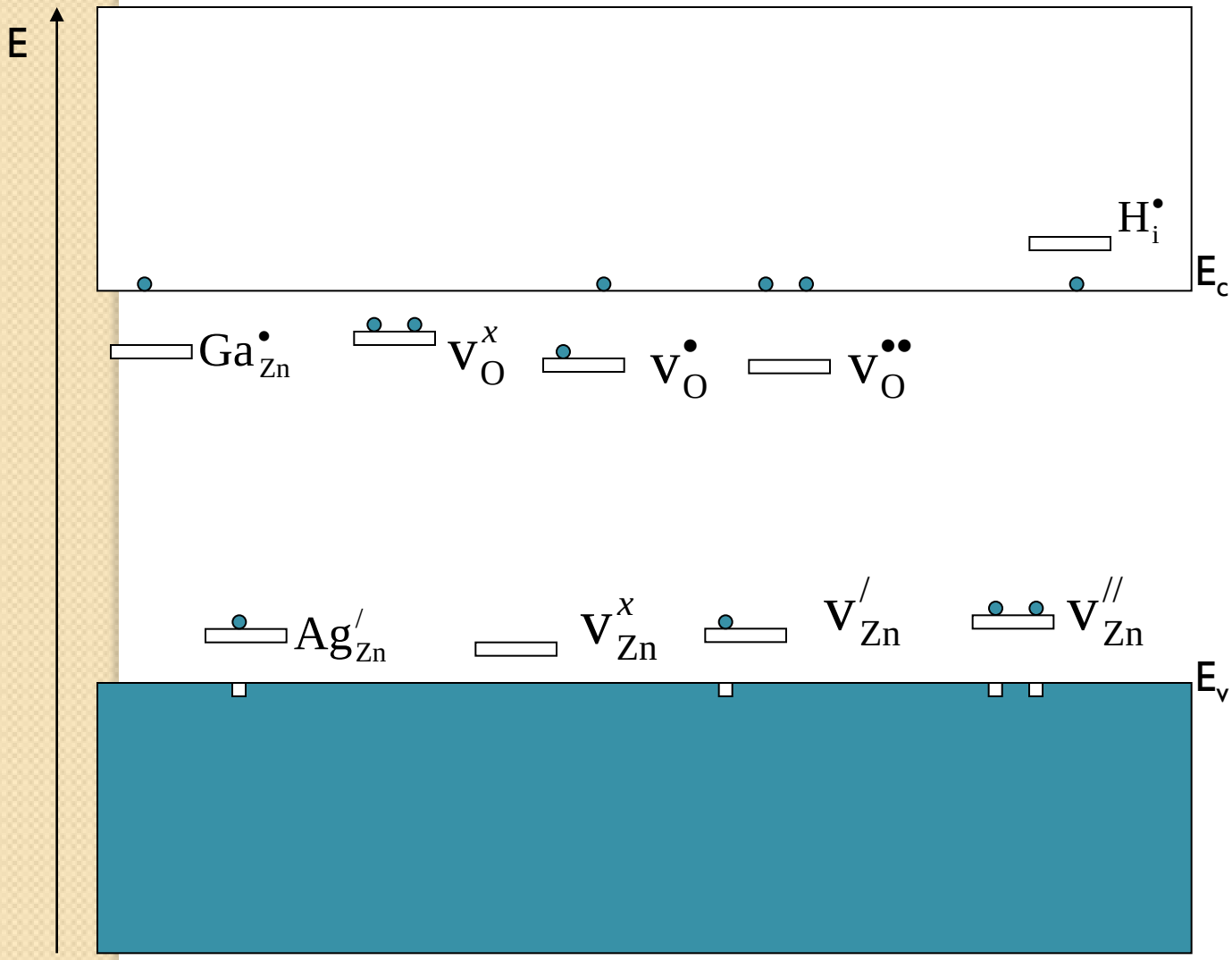
$Ga^{\bullet}_{Zn}$

N'_{O}

$F^{\bullet}_{O}$

$Li^{\bullet}_{i}$

Defects are donors and acceptors



Ionic Conduction

- This is due to the crystal structure
- Electronic conduction is primarily due to the electronic band gap
- Can vary from highly ionic conduction (almost no electronic) to quasi-metallic

Defects in Non-stochiometric Binary Compounds

- We have:
  - Intrinsic defects
  - Extrinsic defects (dopants/impurity)
- Intrinsic defects predominantly fall into two main categories:
  - Schottky Defects
  - Frenkel Defects

Lattice Defects

The concept of a perfect lattice is adequate for explaining *structure-insensitive* properties (esp. for metals).

But, to understand *structure-sensitive* properties, it is necessary to consider numerous lattice defects.

Practically all mechanical properties are structure-sensitive properties.

(almost) structure-insensitive	*structure-sensitive*
elastic constants	Electrical conductivity
Melting points	Semiconducting properties
density	Yield stress
Specific heat	Fracture strength
coefficient of thermal expansion	Creep strength

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations
  Edges, Screws, Mixed

Line defects

- Grain Boundaries
- Stacking Faults
- Anti-Phase and Twin Boundaries

Area/Planar defects

Length Scale of Imperfections

point, line, planar, and volumetric defects

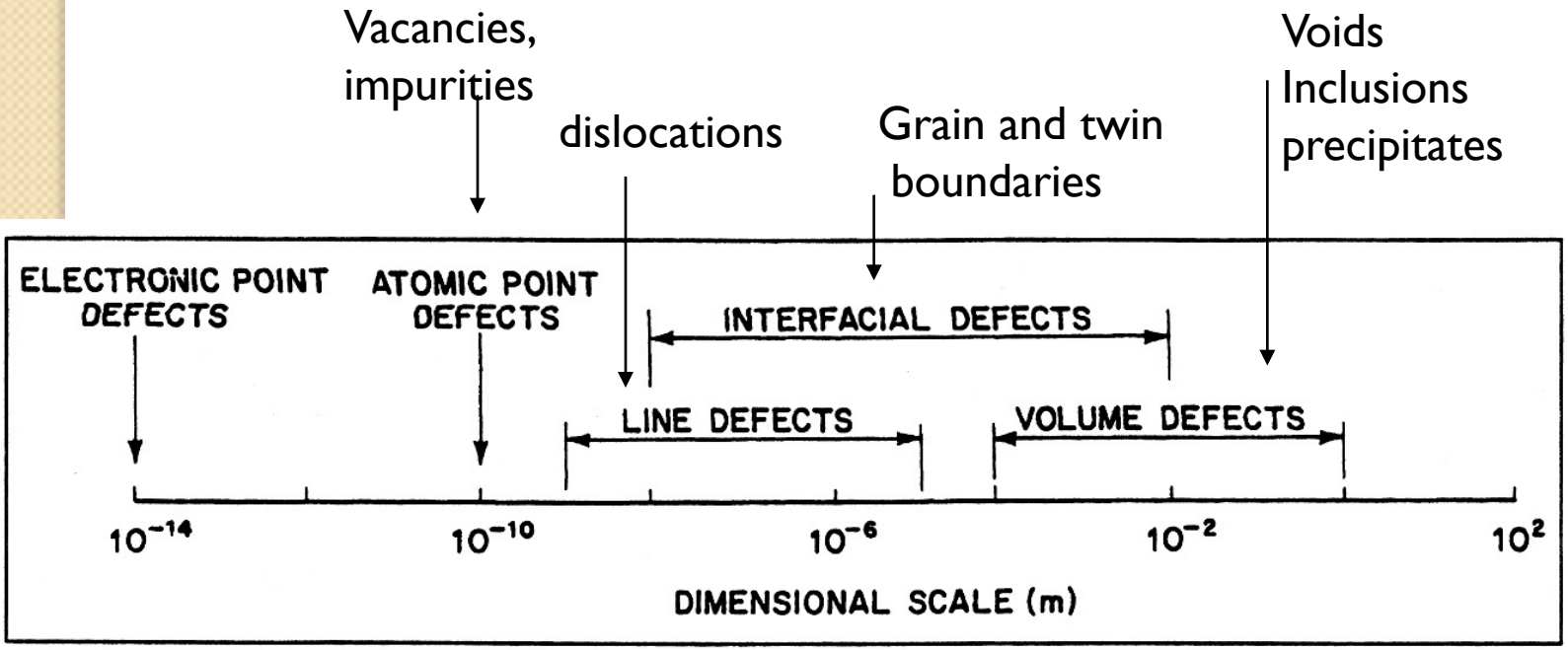
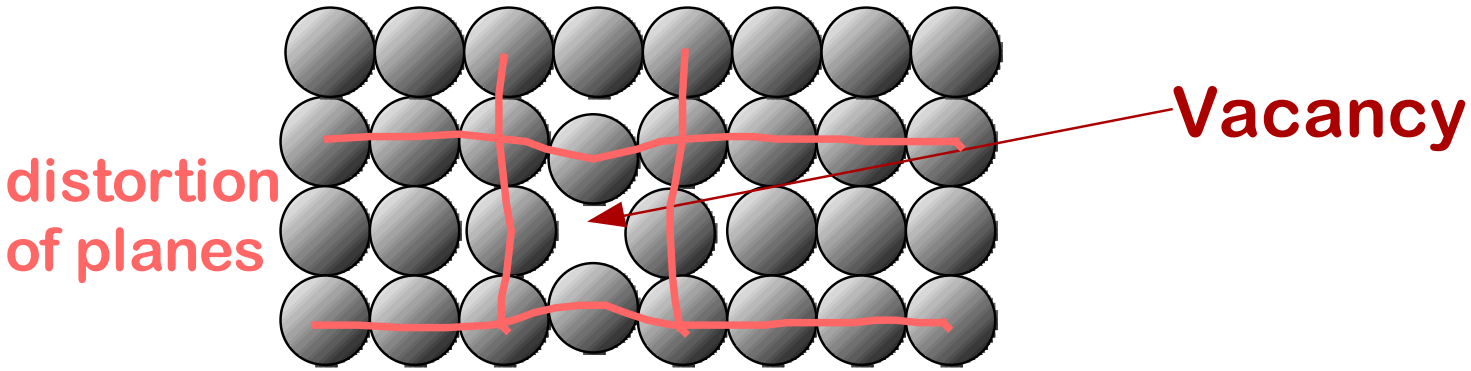


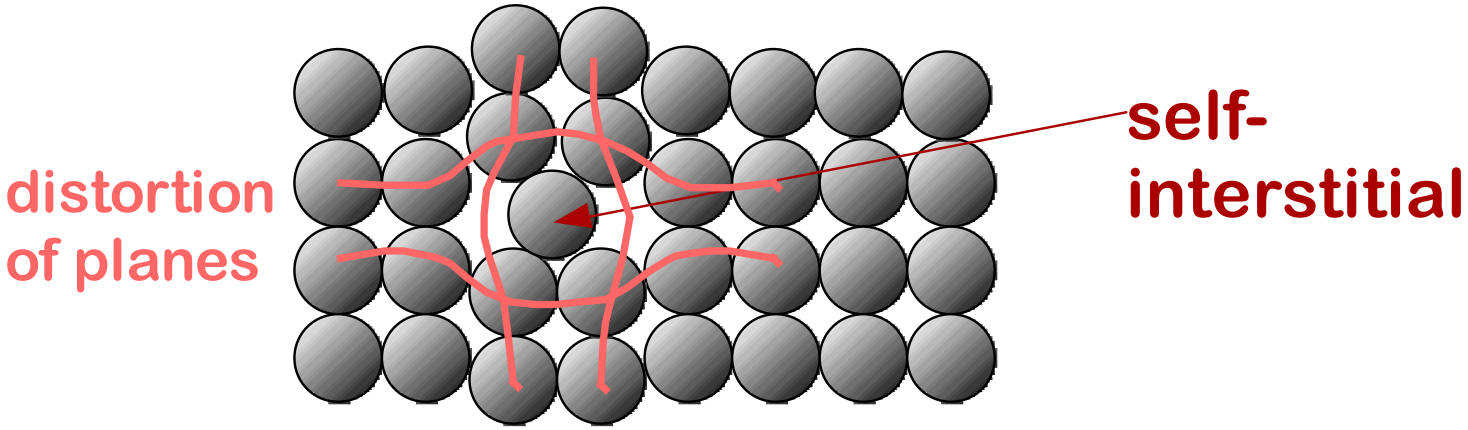
Figure 4.1 Dimensional ranges of different classes of defects.

Point Defects

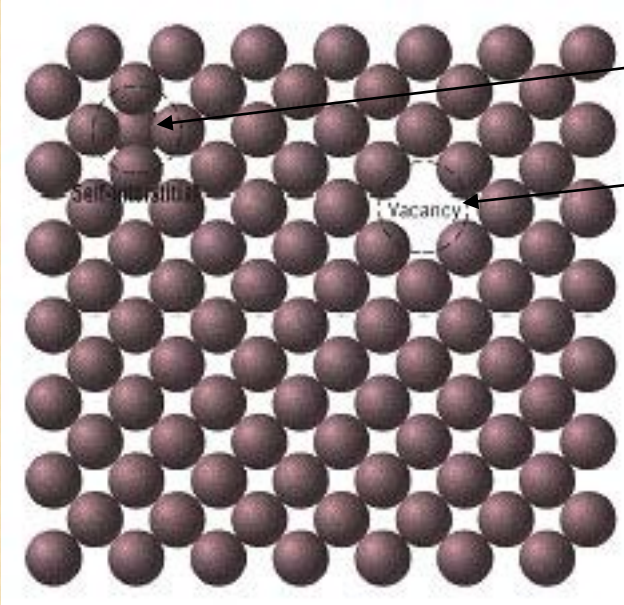
- **Vacancies**: vacant atomic sites in a structure.



- **Self-Interstitials**: "extra" atoms in between atomic sites.



Point Defects



Self-interstitial: atom crowded in 'holes'

Vacancy: a vacant lattice site

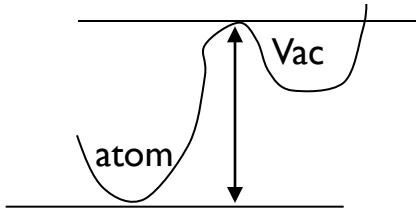
It is not possible to create a crystal free of vacancies. About 1 out of 10,000 sites are vacant near melting.

Self-interstitials are much less likely in metals, e.g.,, as it is hard to get big atom into small hole - there is large distortions in lattice required that costs energy.

Thermodynamics (temperature and counting) provides an expression for

Vacancy Concentration:
(see handout)

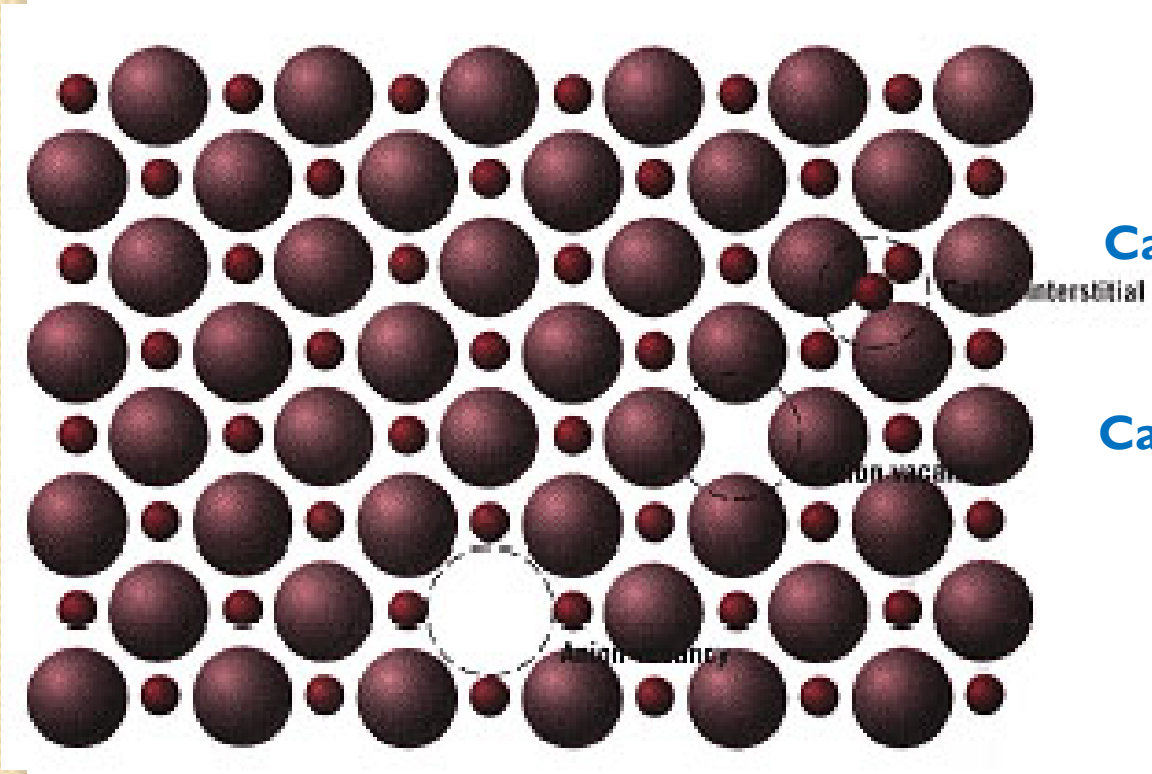
$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{k_B T}\right)$$



Q_v=vacancy formation energy
k_B= 1.38 x 10^{-23} J/atom-K = 8.62 x 10^{-5} eV/atom-K
k_B/mole = R = 1.987 cal/mol-K

Defects ALWAYS cost energy!

Point Defects in Ceramics



Cation Interstitial

Cation Vacancy

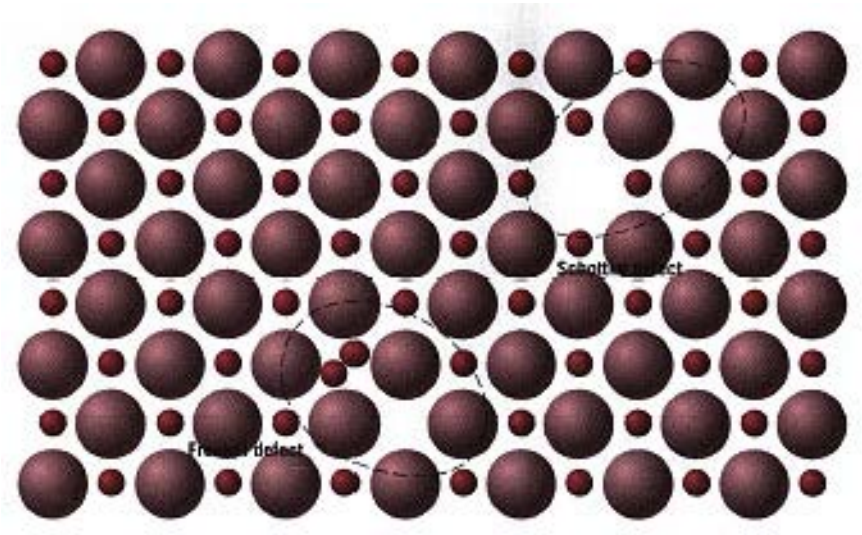
Anion Vacancy

Frenkel and Schottky Defects: paired anions and cations

- Electronic neutrality *must be maintained* in crystal.
- Defects must come in pairs to maintain $\Delta Q=0$.

- Cation-vacancy + Cation-interstitial = Frenkel Defect ($\Delta Q=0$)

- In AX-type crystals,
  Cation-vacancy + Anion-vacancy = Schottky Defect ($\Delta Q=0$)



Schottky

Frenkel

Schottky Disorder

- Given by:

$$M_M^X + O_O^X \Leftrightarrow V_M^{''} + V_O^{\cdot\cdot} + (MO)_{defect}$$

$$\text{Where, } K_S = \left[V_M^{''}\right]\left[V_O^{\cdot\cdot}\right]$$

Frenkel Disorder

- This is less common, except for the latter case of Anti-Frenkel (AF) disorder
- Frenkel disorder is given by

$$M_M^X + V_i^X \leftrightarrow M_i^{\cdot\cdot} + V_M^{''}$$

$$\text{Where, } K_F = \left[M_i^{\cdot\cdot}\right]\left[V_M^{''}\right]$$

$$\text{Anti Frenkel:}$$

$$O_O^X + V_i^X \leftrightarrow O_i^{''} + V_O^{\cdot\cdot}$$

$$\text{Where, } K_{AF} = \left[O_i^{''}\right]\left[V_O^{\cdot\cdot}\right]$$

Temperature Dependence of Schottky Defect

- Here

$$\left[V_M^{''}\right] = \left[V_O^{\cdot\cdot}\right] = n_s = N \exp\left[\frac{-\Delta H_f}{2kT}\right]$$

- N_s = number of Schottky defects/m^3
- T = temperature
- N = number of cations/anions/m^3
- ΔH_f = enthalpy of formation

Temperature Dependence of Schottky Defect

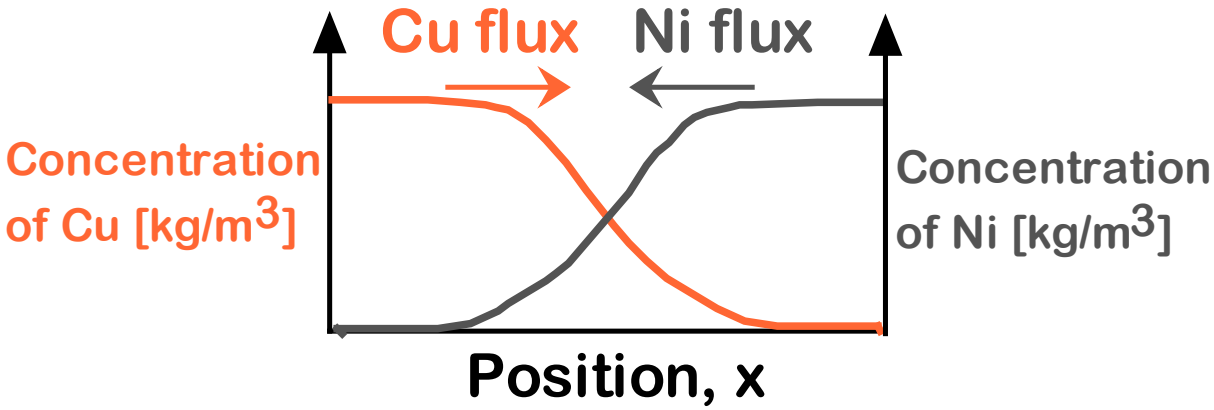
- For alkali and lead halides
  - $\Delta H_f \approx 2.14 \times 10^{-3} T_m$
- For oxides, there is no such approximation
- Influence of dopant (eg MF_2 in MO, and Me_2O in MO)

$$MF_2^{\circ} \rightarrow M_M^X + 2F_O^{\cdot} + V_M^{''}$$

$$Me_2O \rightarrow 2Me_M^{\cdot} + O_O^X + V_O^{\cdot\cdot}$$

Steady-state Diffusion: J ~ gradient of c

- Concentration Profile, C(x): [kg/m^3]



- Fick's First Law: D is a constant!

flux in x-dir. [kg/m^2-s]

Diffusion coefficient [m^2/s]

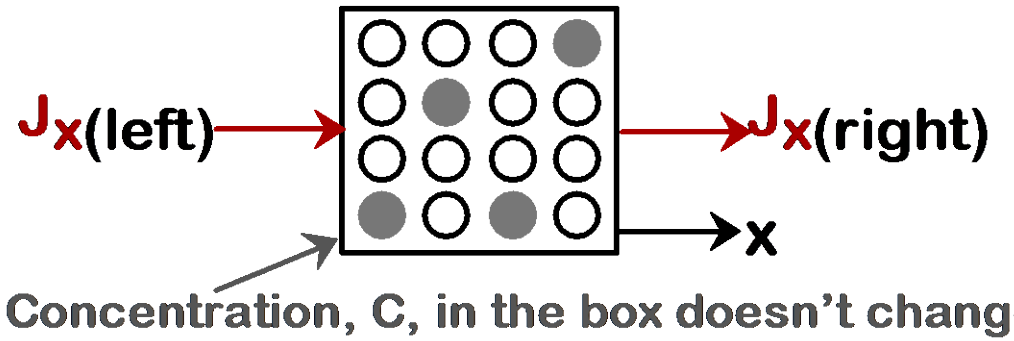
$$J_x = -D \frac{dC}{dx}$$

concentration gradient [kg/m^4]

- The steeper the concentration profile, the greater the flux!

Steady-State Diffusion

- Steady State: concentration profile not changing with time.



Steady State:

$J_x(\text{left}) = J_x(\text{right})$

- Apply Fick's First Law:

$$J_x = -D\frac{dC}{dx}$$

- If Jx)left = Jx)right , then

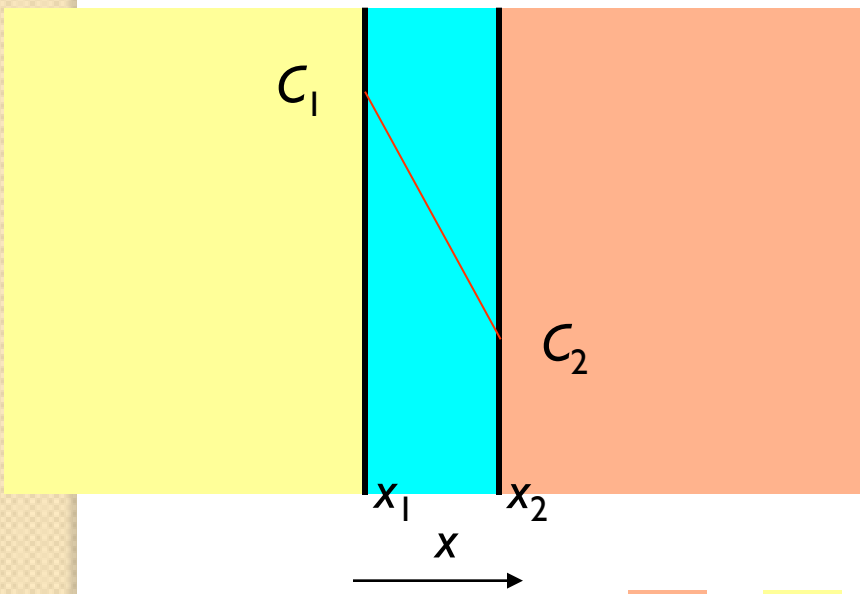
$$\left(\frac{dC}{dx}\right)_{\text{left}} = \left(\frac{dC}{dx}\right)_{\text{right}}$$

- Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!

Steady-State Diffusion

Rate of diffusion independent of time

$$J \sim \frac{dC}{dx}$$



Fick's first law of diffusion

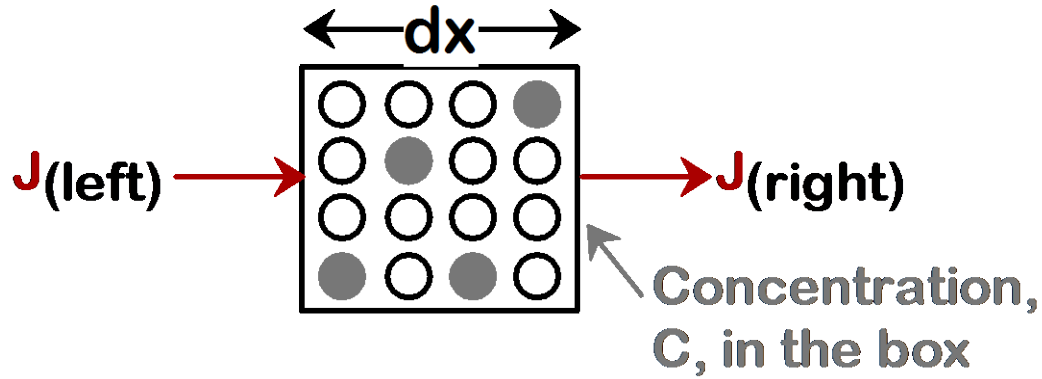
$$\boxed{J = -D\frac{dC}{dx}}$$

$D \equiv$ diffusion coefficient

if linear $\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$

Non-Steady-State Diffusion

- Concentration profile, C(x), changes w/ time.



- To conserve matter:

$$\frac{J(\text{right}) - J(\text{left})}{dx} = -\frac{dC}{dt}$$

$$\frac{dJ}{dx} = -\frac{dC}{dt}$$

- Fick's First Law:

$$J = -D\frac{dC}{dx} \quad \text{or}$$

$$\frac{dJ}{dx} = -D\frac{d^2C}{dx^2} \quad \text{(if D does not vary with x)}$$

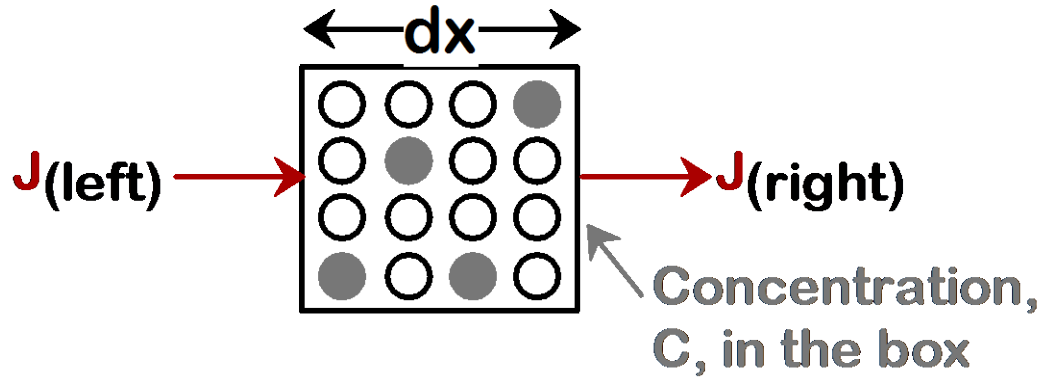
equate

- Governing Eqn.:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Non-Steady-State Diffusion: another look

- Concentration profile, C(x), changes w/ time.



- Rate of accumulation C(x)

$$\frac{\partial C}{\partial t}dx = J_x - J_{x+dx}$$

$$\rightarrow \quad \frac{\partial C}{\partial t}dx = J_x - (J_x + \frac{\partial J_x}{\partial x}dx) = -\frac{\partial J_x}{\partial x}dx$$

- Using Fick's Law:

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x} = -\frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right)$$

Fick's 2nd Law

- If D is constant:

Fick's Second "Law" $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \approx \left(D\frac{\partial c^2}{\partial x^2}\right)$

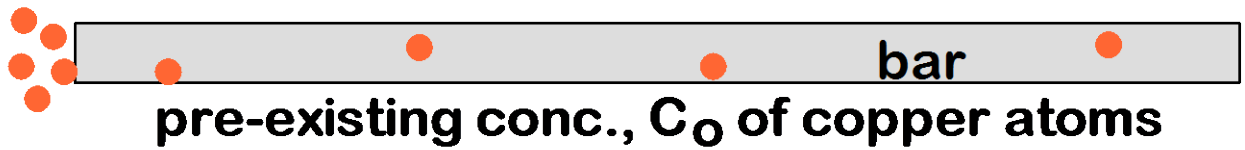
Non-Steady-State Diffusion: C = c(x,t)

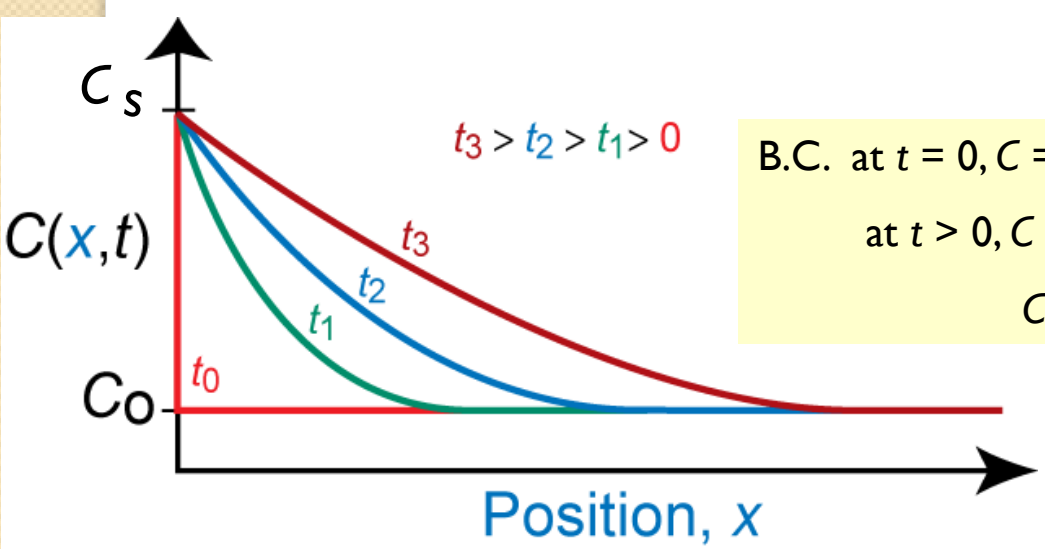
concentration of diffusing species is a function of both time and position

Fick's Second "Law" $\frac{\partial c}{\partial t} \approx \left(D \frac{\partial c^2}{\partial x^2} \right)$

- Copper diffuses into a bar of aluminum.

Surface conc., C_S of Cu atoms





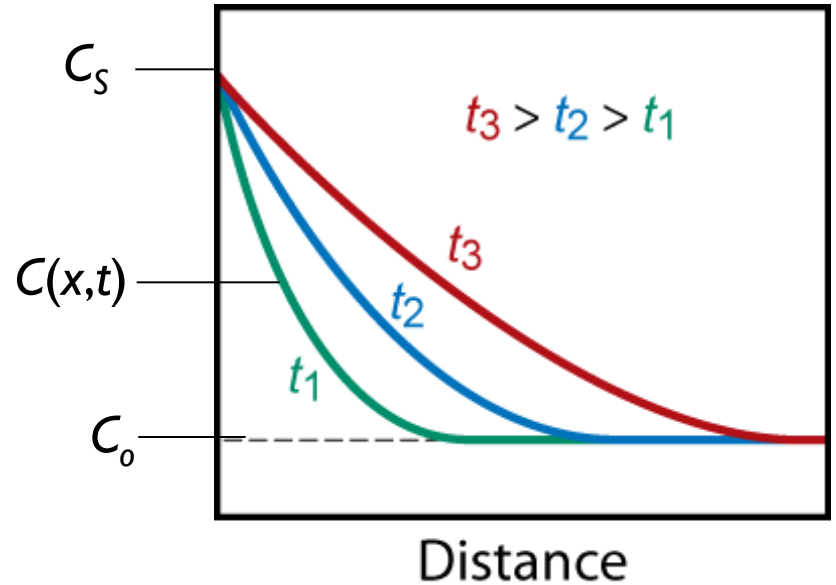
B.C. at $t = 0, C = C_o$ for $0 \leq x \leq \infty$

at $t > 0, C = C_S$ for $x = 0$ (fixed surface conc.)

$C = C_o$ for $x = \infty$

Non-Steady-State Diffusion

- Cu diffuses into a bar of Al.



Fick's Second "Law": $\frac{\partial c}{\partial t} \approx \left(D \frac{\partial c^2}{\partial x^2} \right)$

- Solution:

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}} \right)$$

"error function"

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

Potential Gradients as Driving Force

- Usually driving force for diffusion is the chemical potential of the particles
- Thus driving force for transport of electrical charge is the electrical potential gradient
- Let us consider transport of particles "i" under force "F"

$$j_i\,(\text{moles or particles/cm}^2\,\text{sec}) = c_i\,(\text{moles or particles/cm}^3).v_i\,(cm/s)$$

Potential Gradients as Driving Force

- Drift velocity v_i is proportional to the driving force, F

$$v_i = B_i F_i$$

- B is the proportionality factor (Beweglichkeit) – it is the average drift velocity per unit driving force
- and

$$F_i = -\frac{dP_i}{dx}$$

- Where P is the potential

Potential Gradients as Driving Force

- Thus,

$$j_i = c_i v_i = -c_i B_i \frac{dP_i}{dx}$$

Now, we can say μ_i is related to chemical activity a_i

where, $\mu_i = \mu_i^o + kT \ln a_i$

Where, $a_i = \frac{c_i}{c_i^o}\left(\frac{\text{conc}}{\text{reference conc}}\right)$

Potential Gradients as Driving Force

- Thus,

$$\frac{d\mu_i}{dx} = kT\frac{d\ln c_i}{dx} = \frac{kT}{c_i}\frac{dc_i}{dx}$$

$$\text{Thus, } j_i = -c_i B_i \frac{d\mu_i}{dx} = -B_i kT\frac{dc_i}{dx}$$

$$\text{Now, } D_i = B_i kT = \text{Diff Coeft.}$$

$$\text{Thus, } j_i = -D_i \frac{dc_i}{dx}$$

This is only valid for neutral particles

Simplified Model for One-Dimensional Diffusion

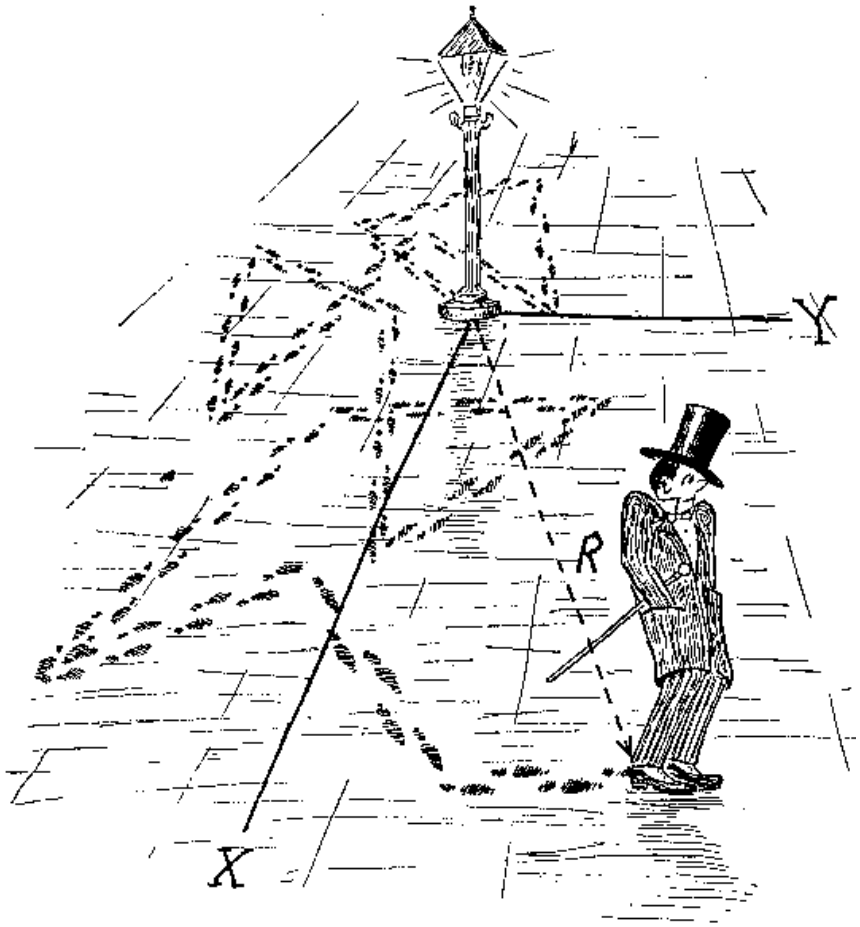
- From,

$$j_i = -D_i \frac{dc_i}{dx}$$

- And, let us consider a 1D model where the particles jump between parallel planes separated by distance s.

Drunkard's walk

from G. GAMOW



Random Diffusion

- Let us consider jumps of the atoms are random
- We have, after a starting point, the displacement of a diffusing atom R_n (after n jumps)

$$\vec{R}_n = \vec{s}_1 + \vec{s}_2 + \ldots\ldots s_n = \sum_{j=1}^{n} \vec{s}_j$$

- To obtain a value for the magnitude of the sum, simply square R_n

Random Diffusion

- Thus,

$$R_n^2 = \vec{R}_n^{\,2} = \sum_{j=1}^{n} \vec{s}_j^{\,2} + 2\sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \vec{s}_j \, \vec{s}_k$$

- If, as above, the jump vectors are equal, ie $s_1 = s_2 \ldots = s_j = s$ (as for the cubic system)
- And if they are random and uncorrelated, then the 2nd term on the RHS will approach zero for large numbers of jumps, as on an average s_j and s_k have an equal chance of being +ve or –ve.

Random Diffusion

$$ns^2 = 6Dt$$

- Thus, $R_n^2 = \sum_{j=1}^{n} \vec{s}_j^{\,2} = ns^2$

$$\text{Thus, } R_n = \sqrt{ns} = \text{mean displacement}$$

- Thus, the mean displacement is proportional to the √ of the number of jumps X individual jump distance
- By combining the equation above and
- we can express the random diffusion in terms of D
- Thus, $R_n^2 = ns^2 = 6D_r t$ (r refers to random walk)

  $\text{or, } R_n = \sqrt{6D_r t}$ t is the time which the mean square Displacement takes place

Random Diffusion

- Let us consider the displacement in a single dimension (eg x-direction)
- From simple geometry, we have

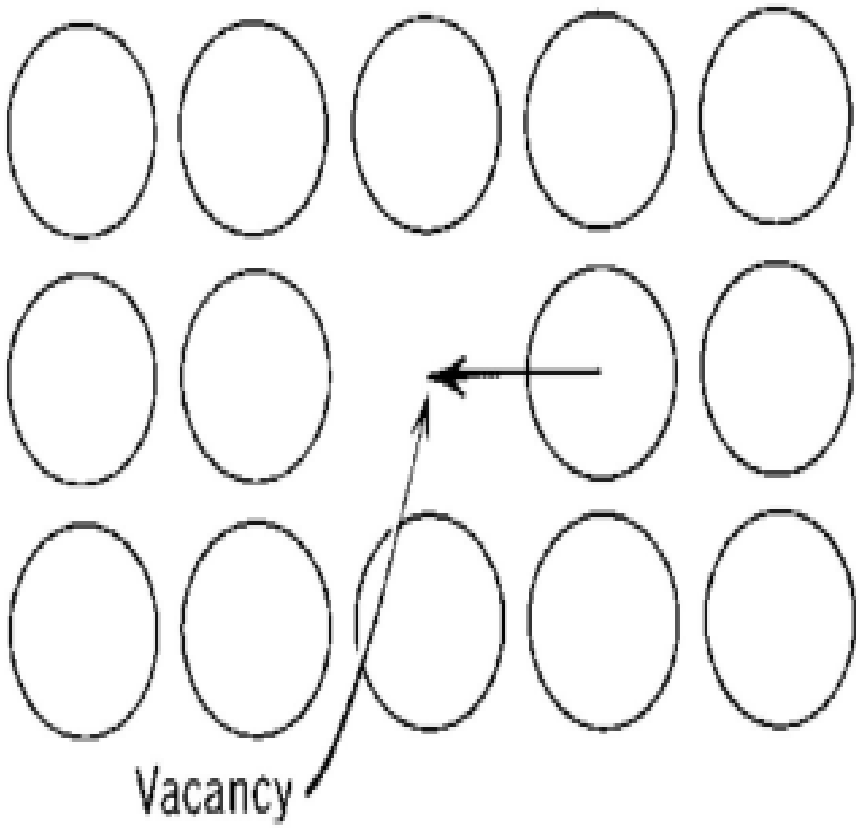
$$R_n^2 = 3x^2$$

where x^2 is the mean square displacement in each orthogonal direction (for a cubic system)

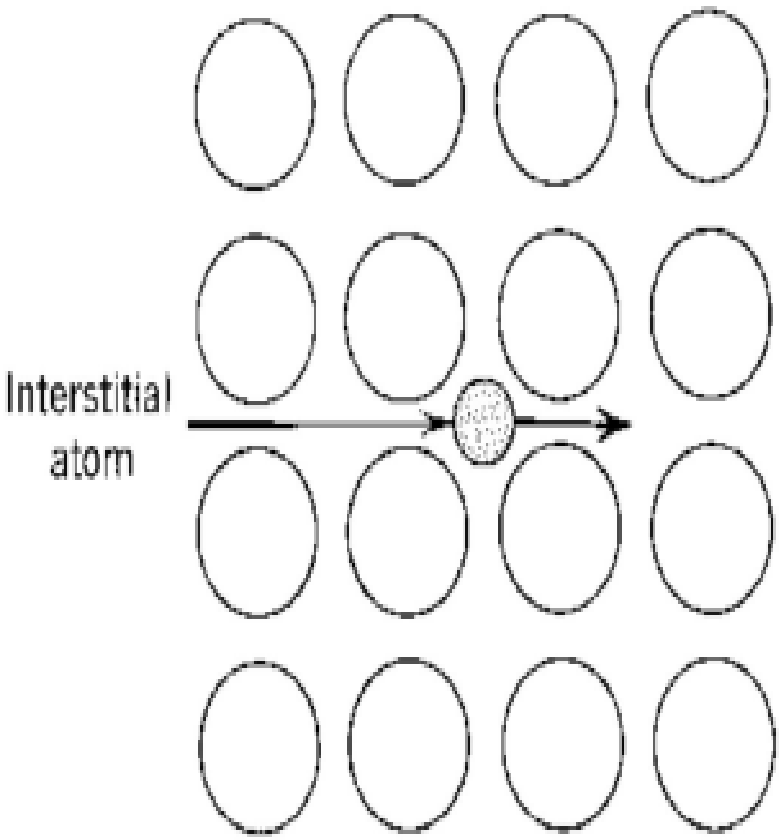
$$x = \sqrt{2D_r t}$$

- This gives the mean diffusion length in one direction in a 3D cubic crystal

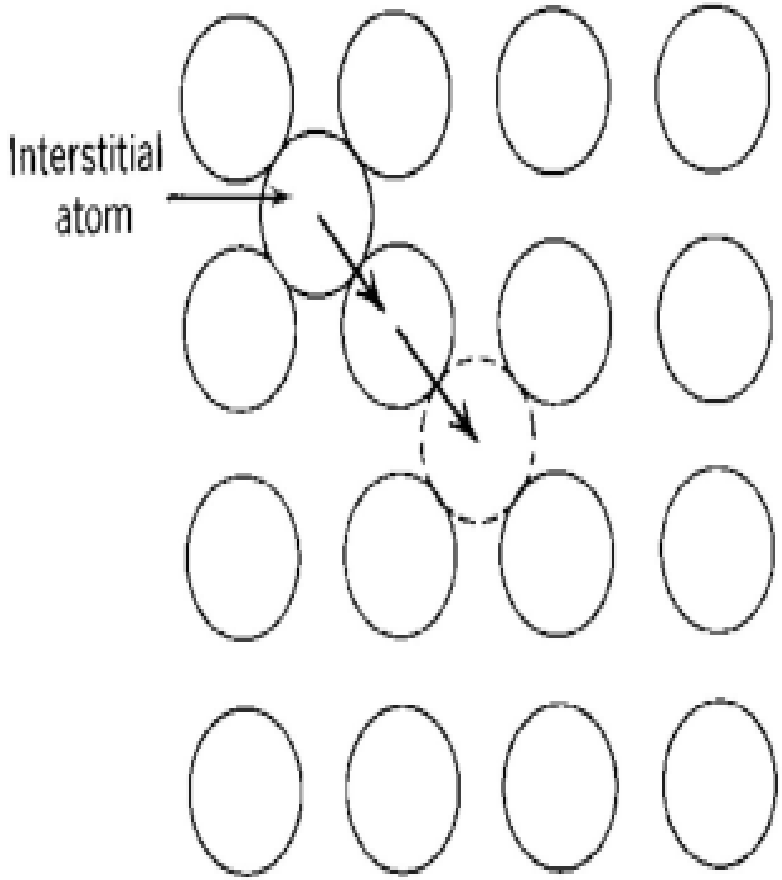
Diffusion Mechanisms – Vacancy Mechanism



Diffusion Mechanisms – Interstitial Mechanism



Diffusion Mechanisms – Interstitialalcy Mechanism



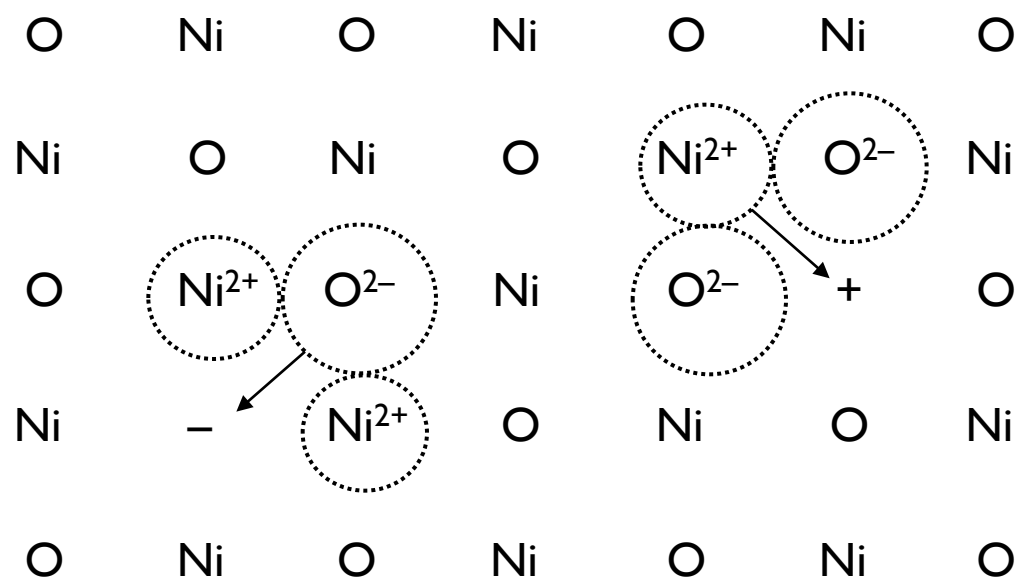
Other Mechanisms

- These include:
  - Crowdian
  - Ring Mechanism (more common in metals)

Diffusion in Compounds: Ionic Conductors

- **Unlike diffusion in metals, diffusion in compounds involves second-neighbor migration.**
- **Since the activation energies are high, the D's are low unless vacancies are present from *non-stoichiometric ratios* of atoms.**

e.g., NiO
There are
Schottky defects



- **The two vacancies cannot accept neighbors because they have wrong charge, and ion diffusion needs 2nd neighbors with high barriers (activation energies).**

Diffusion in Compounds: Ionic Conductors

- D's in an ionic compound are seldom comparable because of size, change and/or structural differences.
- Two sources of conduction: ion diffusion and via e^- hopping from ions of variable valency, e.g., Fe^{2+} to Fe^{3+}, in applied electric field.

e.g., ionic

- In NaCl at 1000 K, $D_{Na+} \sim 5D_{Cl-}$,whereas at 825 K $D_{Na+} \sim 50D_{Cl-}$!
- This is primarily due to size r_{Na+} = 1 A vs r_{Cl-}=1.8 A.

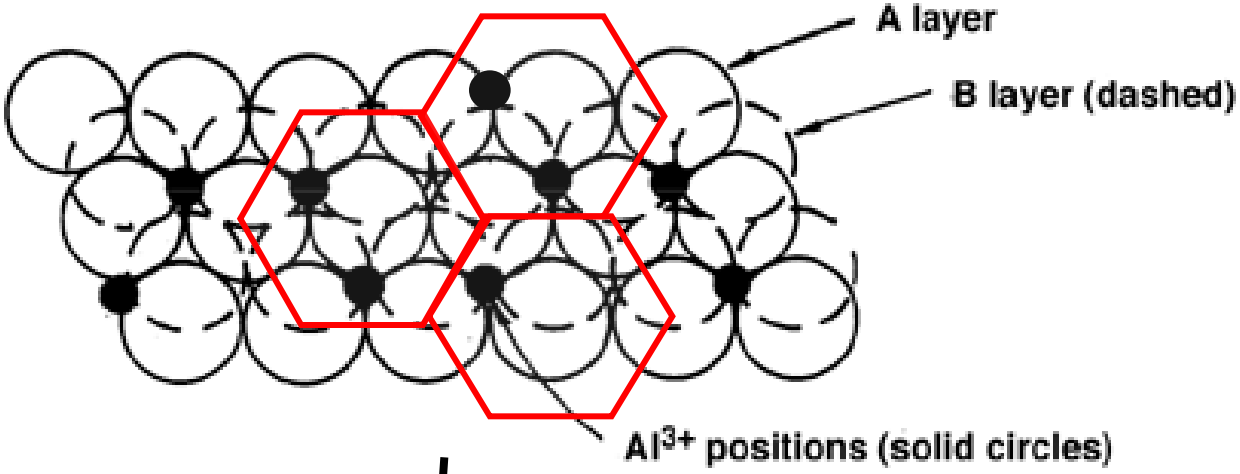
e.g., oxides

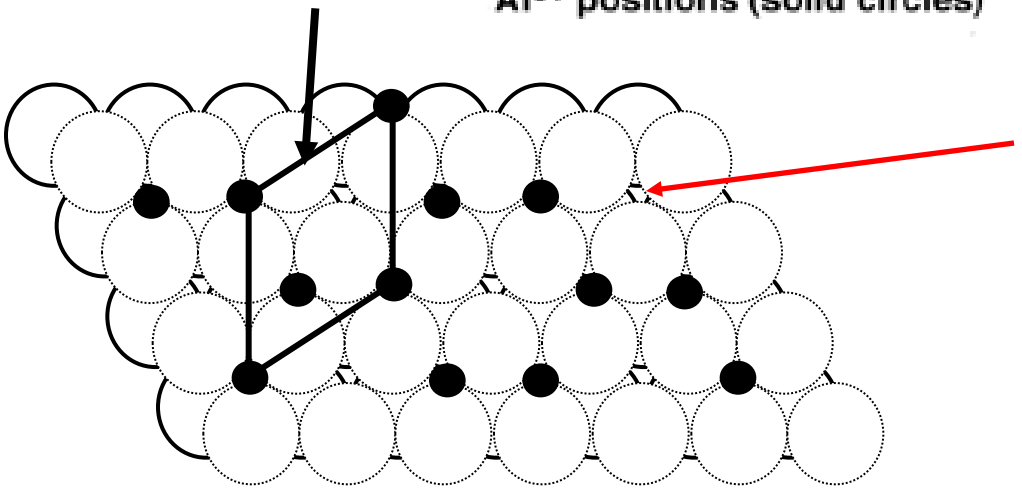
- In uranium oxide, $U^{4+}(O^{2-})_2$, at 1000 K (extrapolated), $D_O \sim 10^7 D_U$.
- This is mostly due to charge, i.e. more energy to activate 4+ U ion.
- Also, UO is not stoichiometric, having U^{3+} ions to give UO_{2-x}, so that the anion vacancies significantly increase O^{2-} mobility.

e.g., solid-solutions of oxides (leads to defects, e.g., vacancies)

- If $Fe_{1-x}O$ (x=2.5-4% at 1500 K, $3Fe^{2+} \rightarrow 2Fe^{3+}$ + vac.) is dissolved in MgO under reducing conditions, then Mg^{2+} diffusion increases.
- If MgF_2 is dissolved in LiF ($2Li^+ \rightarrow Mg^{2+}$ + vac.), then Li^+ diffusion increases. All due to additional vacancies.

Ceramic Compounds: Al_2O_3





Unit cell defined by Al ions: 2 Al + 3 O

Summary: Structure and Diffusion

Diffusion FASTER for...

- open crystal structures
- lower melting T materials
- materials w/secondary bonding
- smaller diffusing atoms
- cations
- lower density materials

Diffusion SLOWER for...

- close-packed structures
- higher melting T materials
- materials w/covalent bonding
- larger diffusing atoms
- anions
- higher density materials

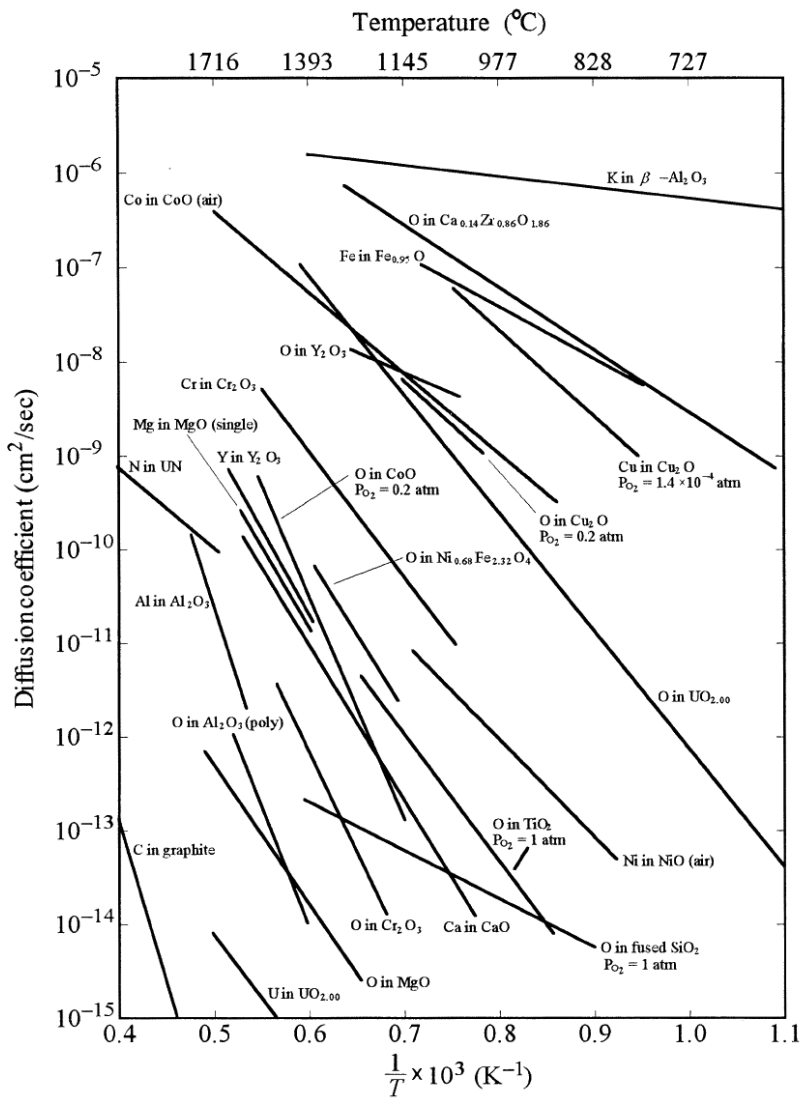


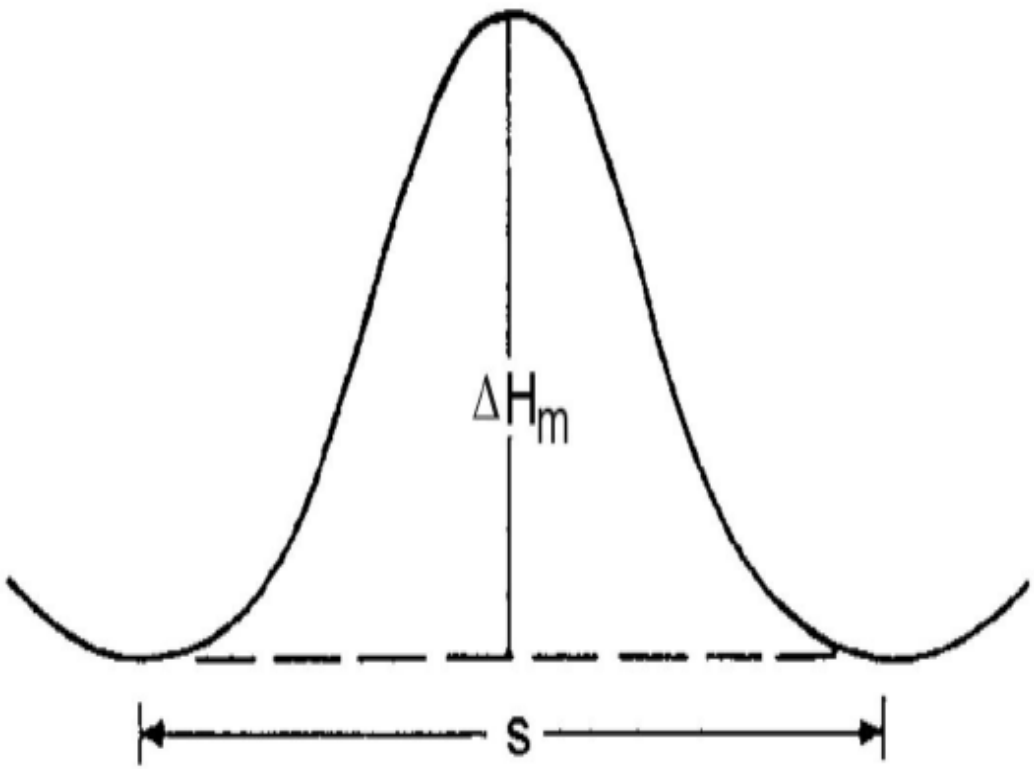
Figure 7.2 Temperature dependence of diffusion coefficients for some common ceramic oxides.[88]

[88] Adapted from W. D. Kingery, H. K. Bowen and D. R. Uhlmann, *Introduction to Ceramics*, 2nd ed., Wiley, New York, 1976. Reprinted with permission.

Temperature Dependence of Attempt Frequency ω

- For atoms to jump, they have barriers
- Large part of the barrier is strain energy required to DISPLACE neighboring atoms to create a sufficiently large opening to allow atoms to jump
- See figure over showing potential energy barrier

Potential Energy of atom diffusing in a solid



Temperature Dependence of Attempt Frequency ω

- Potential height is ΔH_m (activation energy to jump)
- Each atom vibrates in its position and during a fraction of time given by Boltzmann distribution factor (exp(-ΔH_m/RT))
- It possesses sufficient energy to overcome the barrier
- Thus, $$\omega \alpha \exp\left(-\frac{\Delta H_M}{RT}\right)$$

Temperature Dependence of Attempt Frequency ω

- Zenner (1951/52) considered the system/atom in its initial equilibrium condition and in its activated state at the top of the potential barrier
- He found:

$$\omega = \nu \exp\left(-\frac{\Delta G_M}{RT}\right) = \nu \exp\left(\frac{\Delta S_M}{R}\right) \exp\left(-\frac{\Delta H_M}{RT}\right)$$

  - v is the vibrational frequency (assumed to be approx. the Debye frequency of 10^{13} Hz

Resulting Analysis of Diffusion Coefficient D_r

- From the above:

$$D_r = \alpha a_o^2 \nu \exp\left(\frac{(\Delta S_d + \Delta S_M)}{R}\right)\exp\left(-\frac{(\Delta H_d + \Delta H_M)}{RT}\right)$$

Typically, $D = D_o \exp(-Q/RT)$

D_o is the pre-exponential factor, and Q is the activation energy

Thus, $Q = \Delta H_d + \Delta H_M$

and $D_o = \alpha a_o^2 \nu \exp\dfrac{\Delta S_d + \Delta S_M}{R}$

If N_d is a constant and independent of temperature (ie frozen in)

$$D_r = \alpha a_o^2 \nu N_{d,frozen} \exp\left(\frac{\Delta S_M}{R}\right)\exp\left(-\frac{\Delta H_M}{RT}\right) = D_o \exp\left(-\frac{\Delta H_M}{RT}\right)$$

and $Q = \Delta H_M$

Oxygen Vacancy Diffusion in Oxygen Deficient Oxides

- Here, oxygen vacancies predominate
- Thus,

$$D_r = \alpha a_o^2 \nu \left(\frac{1}{4}\right)^{1/3} Po_2^{-1/6} \exp\left(\frac{\frac{\Delta S_{V\ddot{o}}}{3} + \Delta S_M}{R}\right) \exp\left(\frac{-\left(\frac{\Delta H_{V\ddot{o}}}{3} + \Delta H_M\right)}{RT}\right)$$

D_r increases as oxygen partial pressure decreases

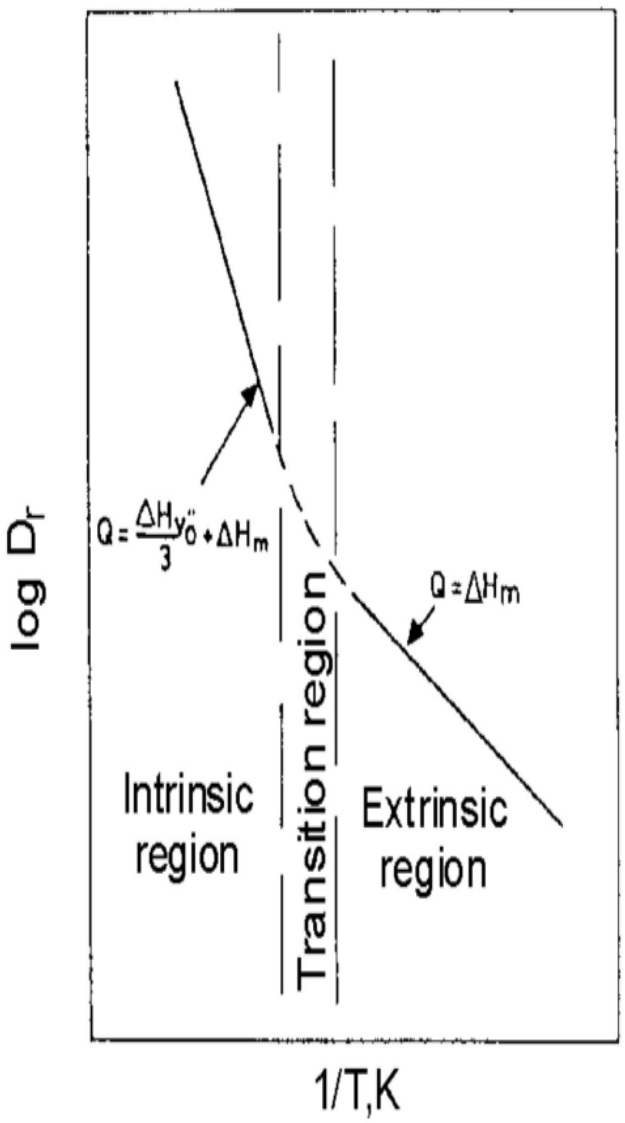
and, $Q = \frac{\Delta H_{V\ddot{o}}}{3} + \Delta H_M$

If concentration of oxygen vacancies determined by lower valent impurities

$$D_r = \alpha a_o^2 \nu \left[A_M^{''}\right] \exp\left(\frac{\Delta S_M}{R}\right) \exp\left(-\frac{\Delta H_M}{RT}\right)$$

and get $Q = \Delta H_M$, thus get transition from intrinsic to extrinsic...see over

Diffusion Coefficient for Oxygen Diffusion by Vacancy Mechanism in Oxygen Deficient Solid



- As T decreases, defect interactions become more important

Interstitial Diffusion

- Here diffusion occurs by solute atoms jumping from one interstitial site to another.
- Much simpler
- The expression for interstitial diffusion is simpler that that for substitutional.

$$D = \alpha a^2 p \nu \exp^{-\Delta F_m / RT}$$

$$\mathrm{p} = \text{number of nearest interstitial sites}$$

$$\mathrm{a} = \text{lattice parameter}, \alpha = \text{geometric factor}$$

$$\nu = \text{vibrational frequency}$$

$$\Delta \mathrm{F_m} = \text{free energy per mole for jumping}$$

Interstitial Diffusion

- Thus only contains one free energy term
- Not dependant upon presence of vacancies

Because, $\Delta F = Q - T\Delta S$

$$D = \alpha a^2 p \nu \exp^{+\Delta S_m / R} \exp^{-Q_m / RT}$$

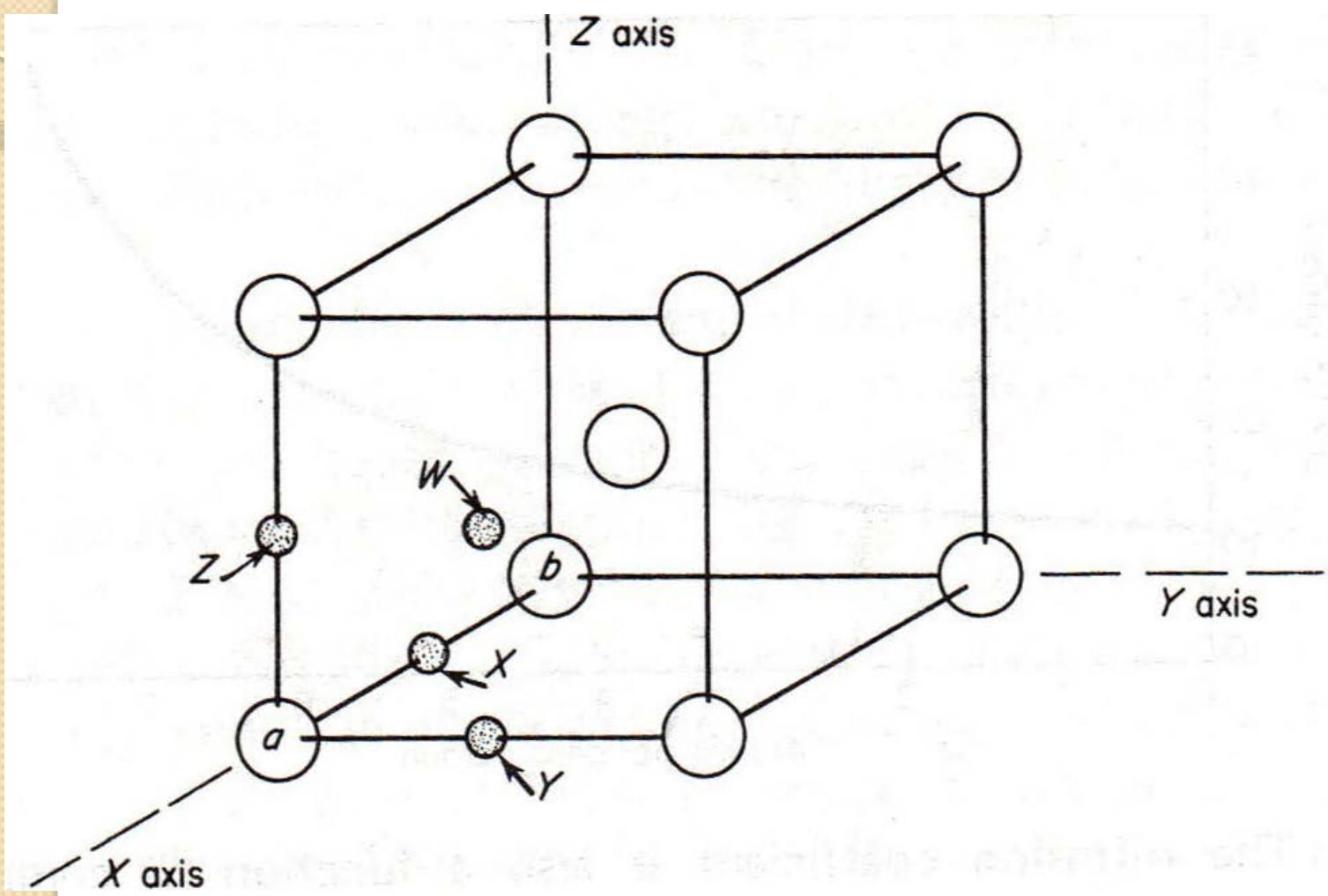
ΔS_m = entropy change of the lattice

Q_m = work associated with jumping across the activation energy

Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- The study of interstitial diffusion by internal-friction.
- In a BCC like iron, interstitial atoms sit on the centers of the cube edges or at the centers of the cube faces.
- See figure over
- An interstitial atom at either x or w would lie between two iron atoms aligned in a <100> direction.

Nature of the sites that interstitial carbon atoms occupy in BBC Fe



Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- The occupancy of one of these, pushes apart the two solvent atoms (a and b)
- An atom at x or w increases the length of the crystal in the [100] direction.
- An atom at y or z in the [010] and [001] respectively
- Thus, if an external force is applied to the crystal (as is the case here), so that it produces a state of tensile stress parallel to the [100] axis, it will strain the lattice and those sites with axes parallel to [100] will have their openings enlarged (closed in axes normal to stress).

Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- If applied stress is small, and strain is small, the number of excess solute atoms per unit volume that are in interstitial sites is small.
- Thus the number of sites is directly proportional to the stress

$$\Delta n_p = K s_n$$

Δn_p = additional number of solute atoms in preferred positions,

K is a proportionality constant

s_n = tensile stress

Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- Each of the additional solute atoms adds a small increment to the length.
- The total strain of the metal consists of two parts:
  - Normal elastic strain (ε_{el})
  - Anelastic strain (ε_{an}) – which is caused by the movement of solute atoms into sites with axes parallel to the stress axis

$$\varepsilon = \varepsilon_{el} + \varepsilon_{an}$$

Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- When a stress is suddenly applied, the elastic component can be considered to develop instantly.
- The anelastic strain, however, is time dependent, and does not appear instantly.
- The sudden application of a stress places the solute atoms in a non-equilibrium distribution
- Equilibrium now corresponds to an excess of solute atoms, Δn_p, in sites with axes parallel to the stress

Measurement of Interstitial Diffusion Coefficients – The Snoek Effect

- Equilibrium occurs due to thermal movement – eventually
- The net effect of the stress is to cause a slightly greater number of jumps
- However, at equilibrium this number will be the same.
- The rate at which the number of additional atoms in preferred sites grows, depends on the number of the excess sites that are still unoccupied

Diffusion along Grain Boundaries and Free Surfaces

- Atom movement not only in bulk of crystals
- Can occur along surfaces and grain boundaries
- Experimental measurements have shown that surface and gb forms are:

$$D_S = D_{S_o} e^{-Q_S / RT}$$

$$D_b = D_{b_o} e^{-Q_b / RT}$$

D_{S_o} and D_{b_o} are the constants of the diffusion coeffients

Q is the activation energy

Diffusion along Grain Boundaries and Free Surfaces

- It has been shown that diffusion is more rapid along gbs than in the interior.
- Free surface rates are larger than both
- Surface diffusion is very important in metallurgical processes
- However, gbs are also very important as they form a network, and there are more of them
- They also cause large errors in calculations of diffusion in crystals

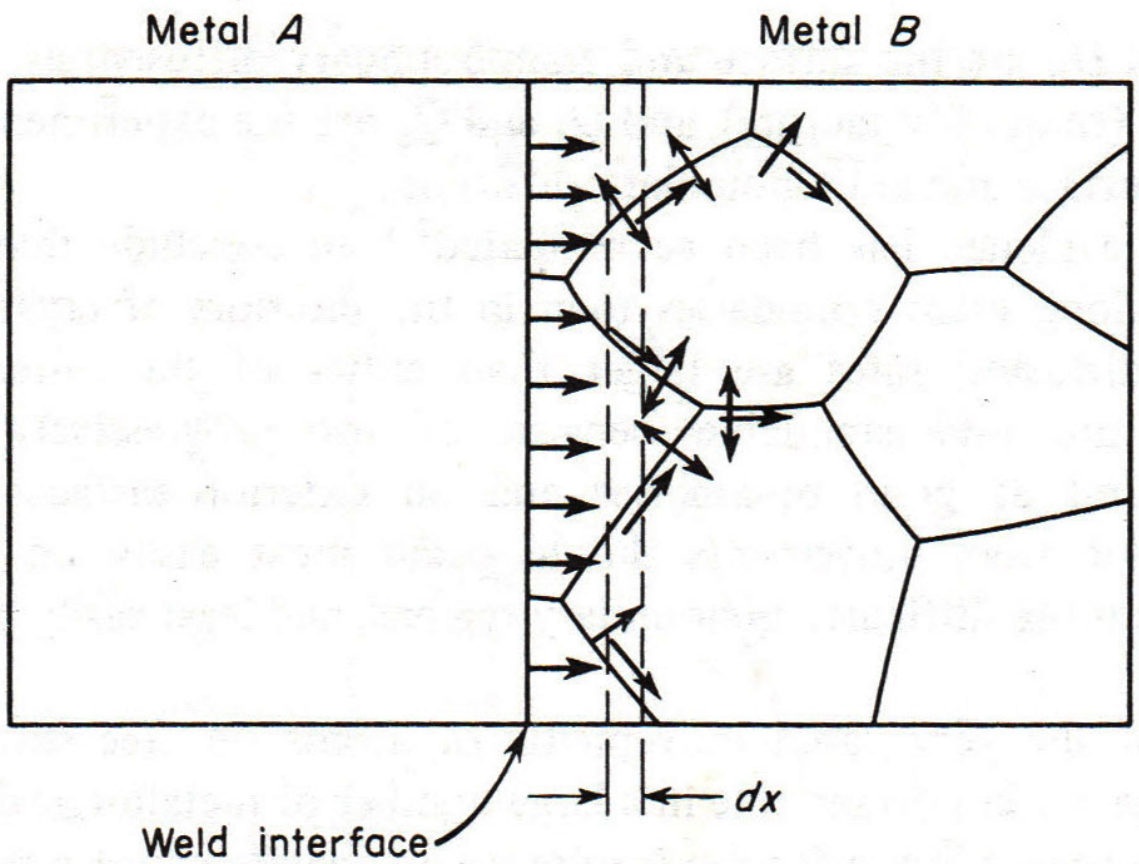
Diffusion along Grain Boundaries and Free Surfaces

- When we measure the diffusion coefficient of a polycrystal, the value is the combined effect of volume and grain boundary.
- What is obtained is an apparent diffusivity (D_{ap})
- The diffusion is not simply the summation.
- Grain Boundary diffusion is faster than bulk.
- However, as the grain boundaries "fill up", loss of diffusion occurs

Diffusion along Grain Boundaries and Free Surfaces

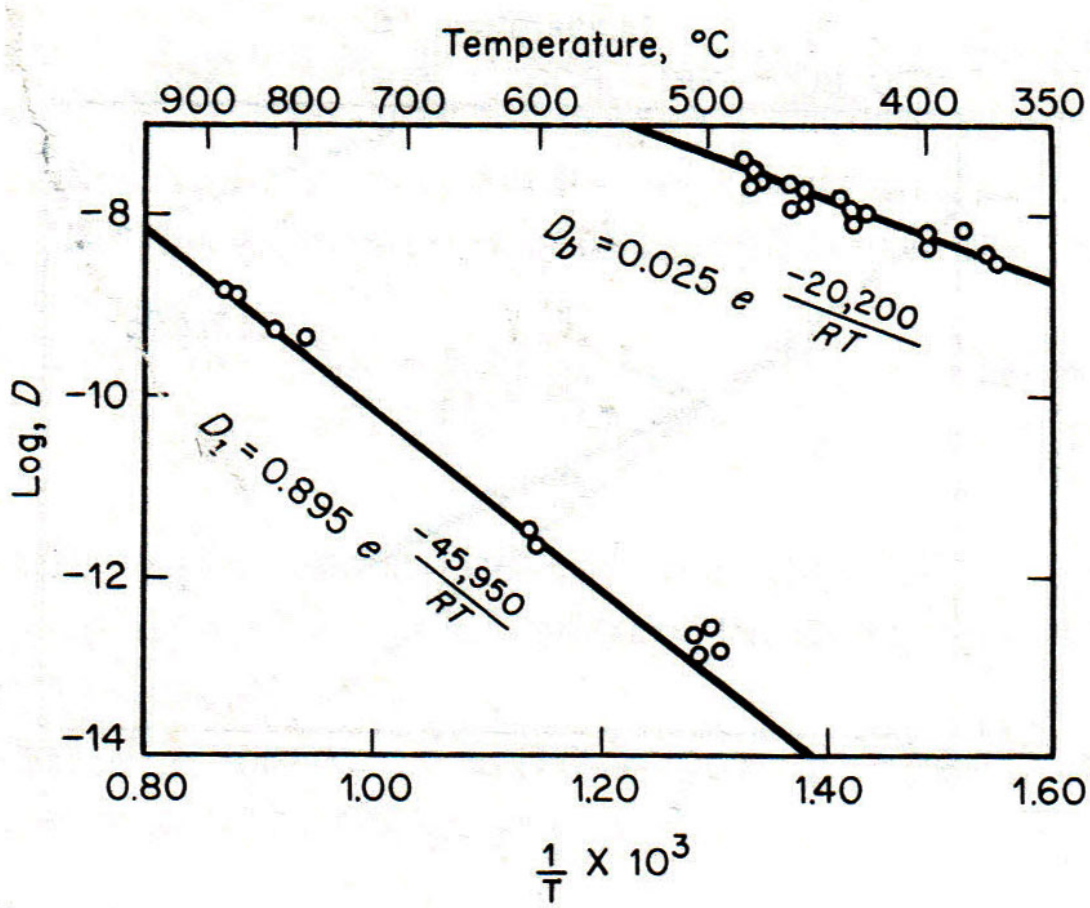
- See figure over
- This represents a diffusion couple composed of metals A and B
- Both are polycrystalline
- Grain boundaries only on RHS
- Arrows show A into B
- To study this we remove thin layers and analyze at a distance (dx)

Combined effect of gb and bulk diffusion



- The problem is complex.
- For a given ratio of D_{gb}/D_b the relative number of A atoms that reach dx is a function of grain size.
- The smaller the grain size, the greater the total grain-boundary are available, and thus the more significant they become.
- Fig shows gb and bulk diffusion for Ag in Ag

Bulk and gb diffusion for Ag



Diffusion along Grain Boundaries and Free Surfaces

- Both types of diffusion show a straight line relationship on the log D-1/T system
- For grain boundary diffusion, the equation of the line is $(D_b)D_{gb} = 0.025\ e^{-20,200/RT}$
- For bulk diffusion it is $(D_l)D_b = 0.895\ e^{-45,950/RT}$
- Thus:
  - Diffusion easier along gb
  - Different effects of T on gb and bulk

Diffusion along Grain Boundaries and Free Surfaces

- Thus, at high temperatures diffusion through the bulk overpowers the gb diffusion.
- At low temperatures, gb dominates.

Diffusion Coefficient of Point Defects

- Sometimes we can consider diffusion of vacancies themselves
- The vacancy can theoretically jump to any one of the occupied nearest neighbors
- Thus, $D_v = \alpha a_o^2 \omega N$

  N is the fraction of occupied sites

  In dilute solutions, N is approx 1

  Thus, D is NOT dependent on N_d

  Thus, $D_r N = D_V N_d$

  General Form of the Equation

  $D_r N = D_d N_d$

  D_d = defect diffusion coefficient

Overview

- Now, for a fixed particle, i, with charge $Z_i e$

$$F = -Z_i e \frac{d\phi}{dx} = -Z_i e E$$

ϕ is the electrical potential

$$E = -\frac{d\phi}{dx}$$

The flux of i $j_i = c_i B_i F$

Concentration

Mobility

Overview

- Thus,

$$j_i = Z_i e c_i B_i E$$

Thus, $\mathrm{i_i}$ = current density x flux x charge

$$i_i = Z_i e j_i$$

$$= \left(Z_i e\right)^2 B_i c_i E$$

$$u_i = \text{charge mobility} = \mathrm{Z_i} e B_i$$

Therfore, $i_i = Z_i e c_i u_i E$ = conductivity x E

Overview

- Where, $\sigma_i = Z_i e c_i u_i = \text{conductivity (s/cm)}$
- Total electrical conductivity, σ, is the sum of the partial conductivities, σ_i of different charge carriers
- $$\sigma = \sum_i \sigma_i$$

$$\text{where, } t_i = \frac{\sigma_i}{\sigma}$$

Charge Carriers in Ionic Compounds

- Now,

$$\sigma = \sigma_c + \sigma_a + \sigma_n + \sigma_p$$

$$\text{or}, \sigma_c = t_c\sigma, \sigma_a = t_a\sigma, \sigma_n = t_n\sigma, \sigma_p = t_p\sigma$$

$$\sigma = \sigma\left(t_c + t_a + t_n + t_p\right)$$

$$\text{and } t_c + t_a + t_n + t_p = 1$$

$$\sigma_{ion} = \sigma_c + \sigma_a$$

$$\sigma_{elec} = \sigma_n + \sigma_p$$

$$\sigma = \sigma_{ion} + \sigma_{elec}$$

Nernst-Einstein Relation

- Now,

$$D_i = kTB_i$$

But, by calculating this with

$u_i = Z_i e B_i$ and

$$i_i = Z_i e c_i u_i E = \sigma_i E$$

Then, $D_i = kTB_i = u_i \dfrac{kT}{Z_i e} = \sigma_i \dfrac{kT}{c_i Z_i^2 e^2}$

- This is the Nernst-Einstein Relation
- Consider 1D system with a series of parallel planes separated by a distance s

Nernst-Einstein Relation

- Assume homogeneous
- Volume concentration in the planes is c_i
- Equal probability of jumping to neighboring planes
- Number of particles which jump from plane 1 to 2, and 2 to 1 per unit time is equal and opposite
- And

$$= 1/2\omega c_i s$$

Nernst-Einstein Relation

- And,

$$\omega_{reverse} = \nu \exp\left(\frac{\Delta S_m}{k}\right)\exp\left(-\frac{\Delta H_m + \frac{Z_i eSE}{2}}{kT}\right)$$

$$\text{Thus, } j_i = 1/2 c_i s \omega \left\{\exp\left(\frac{Z_i esE}{2kT}\right) - \exp\left(-\frac{Z_i esE}{2kT}\right)\right\}$$

$$\text{where, } \omega = \nu \exp\left(\frac{\Delta \mathrm{S_m}}{\mathrm{k}}\right)\exp\left(-\frac{\Delta H_m}{kT}\right)$$

Nernst-Einstein Relation

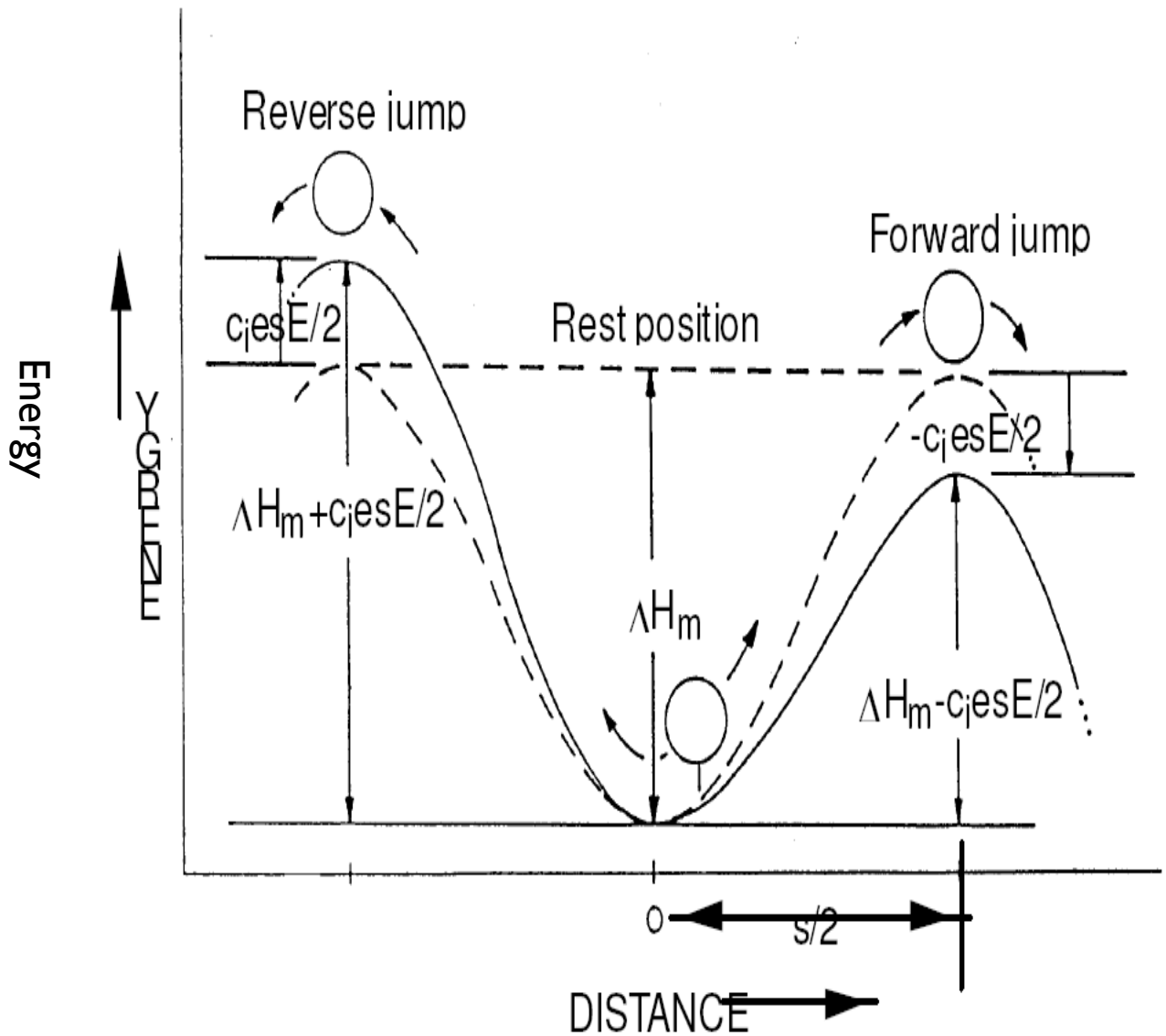
- With no electric field, the activation energy is ΔH_m
- When apply and electric field, E, jump frequency in positive direction is increased, and in negative direction is decreased
- In forward direction, the activation energy is REDUCED to:

$$\Delta H_m - 1/2 Z_i esE$$

In the negative direction, it is increased to

$$\Delta H_m + 1/2 Z_i esE$$

Electric Field on Migration



Nernst-Einstein Relation

- The net particle flux is the difference between the number of jumps in the forward and reverse directions

$$j_i = 1/2 c_i s\left(\omega_{forward} - \omega_{reverse}\right)$$

$$\text{where, } \omega_{forward} = \nu \exp\left(\frac{\Delta S_m}{k}\right)\exp\left(-\frac{\Delta H_m - \frac{Z_i eSE}{2}}{kT}\right)$$

Nernst-Einstein Relation

- When,

$$Z_i esE << 2kT$$

We can write that $j_i = 1/2\omega s^2 c_i \dfrac{Z_i eE}{kT}$

If, $D_i = 1/2\omega s^2$

Then, $j_i = D_i \dfrac{c_i Z_i eE}{kT}$

Now, we know that

$$j_i = Z_i e c_i B_i E = c_i u_i E = \frac{\sigma_i E}{Z_i e}$$

Thus, $D_i = B_i kT = u_i \dfrac{kT}{Z_i e} = \sigma_i \dfrac{kT}{c_i Z_i^2 e^2}$

Nernst-Einstein Relation

- Or Rearranged

$$\sigma_i = \frac{(Z_i e)^2 c_i D_i}{kT}$$

Ionic Conduction: related to fuel cells

- Molten salts and aqueous electrolytes conduct charge when placed in electric field, +q and –q move in opposite directions.

- The same occurs in solids although at much slower rate.
  - Each ion has charge of Ze (e = 1.6 x 10^{-19} amp*sec),
    so ion movement induces ionic conduction
  - Conductivity $\sigma = n\mu Ze$ is related to mobility, μ, which is related to D via the Einstein equations: $\mu = ZeD / k_B T$
  - Hence

$$\sigma_{ionic} = \frac{nZ^2e^2}{k_BT} D = \frac{nZ^2e^2}{k_BT} D_o e^{-Q/RT}$$

$$\log_{10} \sigma_{ionic} \sim \ln\left(\frac{nZ^2e^2}{k_BT} D_o\right) - \frac{Q}{2.3RT}$$

So, electrical conduction can be used determine diffusion data in ionic solids.

e.g., What conductivity results by Ca^{2+} diffusion in CaO at 2000 K?

- **CaO has NaCl structure with a= 4.81 A, with D(2000 K)~10^{-14} m^2/s, and Z=2.**

$$n_{Ca^{2+}} = \frac{4}{cell} \frac{cell}{(4.81x10^{-10} m)^3} = 3.59x10^{28} / m^3$$

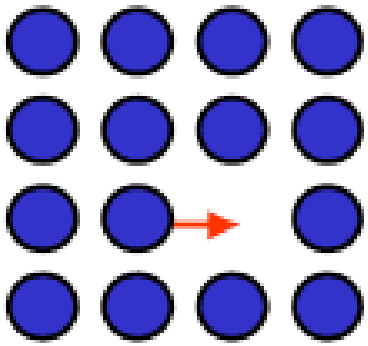
$$\sigma = \frac{nZ^2e^2}{k_BT} D \sim \frac{1.3x10^{-5}}{ohm - cm}$$

For Ionic Conductivity to occur

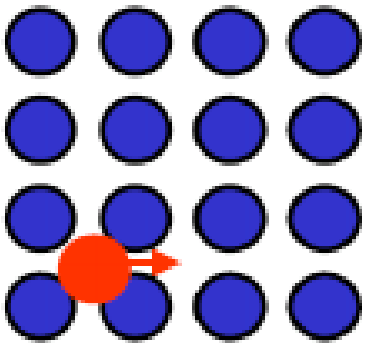
there are vacant atom sites in which an adjacent ions can move (or hop) into vacancies (to leave their own site vacant)

OR

There are some ions in interstital sites which can hop into adjacent interstital sites



Vacancy mechanism



Interstitial mechanism

Possible mechanism of motion: **hopping model**

Conductivity in MO

- Electronic Conductivity
- Here,

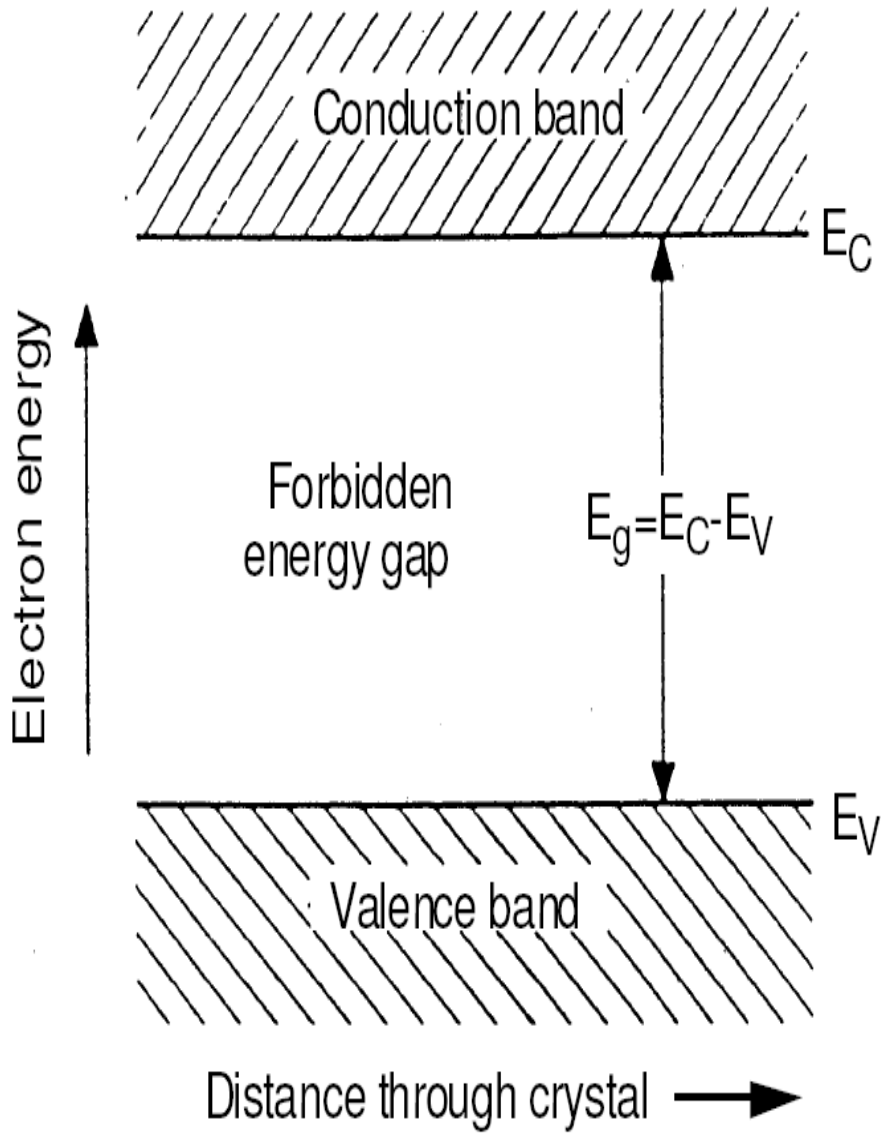
$$\sigma_{el} = \sigma_n + \sigma_p = en\mu_n + ep\mu_p$$

$$\text{Now, } E_g = 2(E_s - c)(eV)$$

$$E_g = \text{size of band gap, } \mathrm{E_s} = E_{at} / equiv, \mathrm{c} = \text{constant}$$

Drift or carrier mobilities

Energy Band


Conduction band
E_C
Electron energy
Forbidden
energy gap
$E_g=E_C-E_V$
E_V
Valence band
Distance through crystal

Intrinsic

- As T increases, electrons can be excited across the forbidden band into conduction band – intrinsic ionization
- Using classical statistics
- $$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right)$$

$$p = N_v \exp\left(-\frac{E_F - E_v}{kT}\right)$$

Intrinsic

- N_c and N_v are number of available states/density of states in conduction and valence bands
- E_c is the lowest energy level in conduction band
- E_v is highest level in the valence band
- E_F is the Fermi level

Intrinsic

- Now, the defect equilibrium is

$$O = e^{-} + h^{\cdot}$$

and, $K_i = np$

Thus, $K_i = np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$

If number of electrons and holes are equal (as in an intrinsic semiconductor), then

$$n = p = K_i^{1/2} = \left(N_c N_v\right)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

Intrinsic

- Thus,

$$\sigma_{elec} = \sigma_n + \sigma_p = en\mu_n + ep\mu_p =$$

$$e\left(N_c N_v\right)^{1/2}\left(\mu_n + \mu_p\right)\exp\left(-\frac{E_g}{2kT}\right)$$

Often written as

$$\sigma_{elec} = CONST.\exp\left(-\frac{E_g}{2kT}\right)$$

Intrinsic

- Thus, intrinsic electronic conductivity INCREASES with DECREASING energy gap

Extrinsic

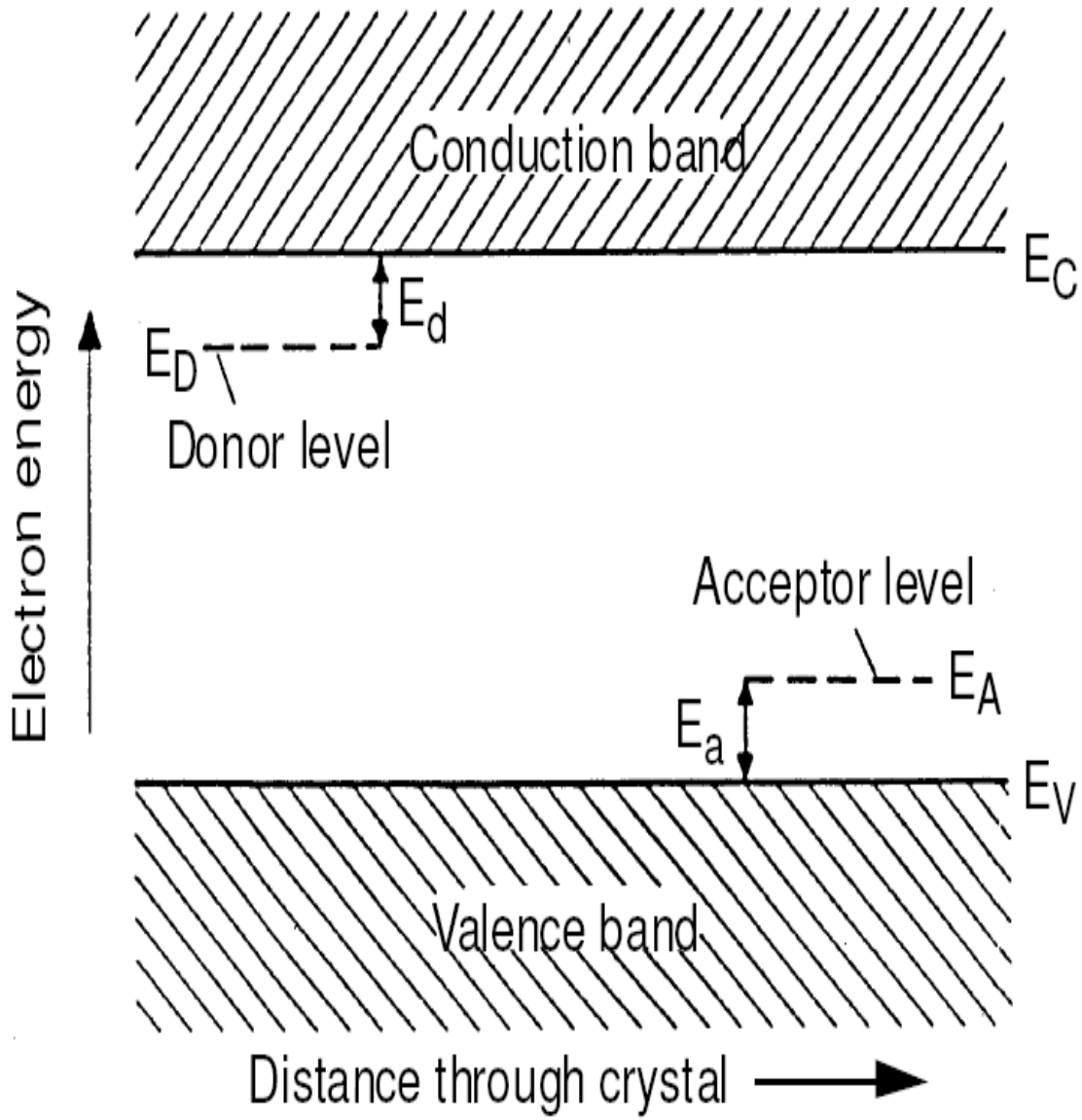
- This is summarized in the Figure over
- The Donor Effect
  - The ionization of a Donor D^x may be

$$D^x = D^{\cdot} + e^-$$

$$\text{Thus, } K_D = \frac{[D^{\cdot}]n}{[D^x]}$$

$$\text{and } \mathrm{N_D} = \text{total number of donors} = [D^{\cdot}] + [D^x]$$

Doped System



- η_Ω is the resistance to ionic movement (given as the conductivity of the electrolyte material; this is typically given as approximately 1S/cm at 1000°C)
- We also must consider the ionic transport number of the material (t_i) which is given as:
- $t_i = \sigma_i/\sigma_{total}$ (approximately 1 for doped-ZrO_2)

Methods for Measuring Partial Ionic and Electronic Conductivities

- We will look at the specific measurements of partial conductivities, before looking at how to measure ionic conductivity in general.
- There are a number of methods that one can consider:
  - Hebb-Wagner Polarization Method (electronic or ionic)
  - Short Circuiting Method
  - Simultaneous Measurement of electronic and ionic conductivity
  - Tubandt/Hittorf Method
  - EMF Measurements
  - Other lesser techniques

General Techniques

Time domain (*incomplete!*):

- Polarisation, $(V - I)$ — steady state
- Potential Step, $(\Delta V - I(t))$ — relaxation
- Cyclic Voltammetry, $(V_{f(t)} - I(V))$ — dynamic
- Coulometric Titration, $(\Delta V - \int I \, dt)$ — relaxation
- Galvanostatic Intermittent Titration $(\Delta Q - V(t))$ — transient

Next slide

Frequency domain:

- Electrochemical Impedance Spectroscopy (EIS) — perturbation of equilibrium state

Advantages of EIS

System in thermodynamic equilibrium

Measurement is small perturbation (approximately linear)

Different processes have different time constants

Large frequency range, μHz to GHz (and up)

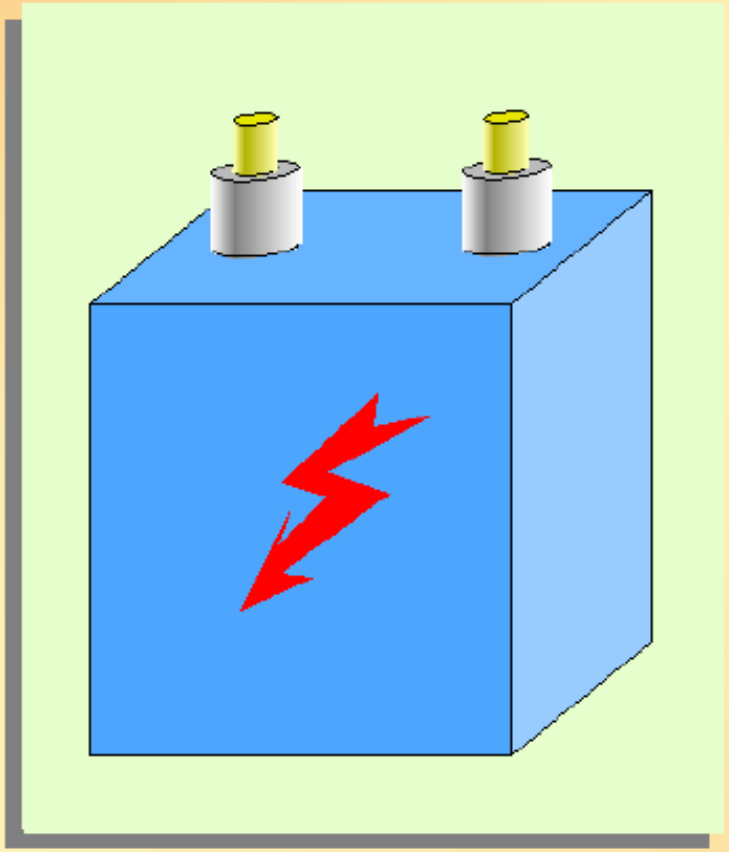
- Generally analytical models available
- Evaluation of model with 'Complex Nonlinear Least Squares' (CNLS) analysis procedures (later).
- Pre-analysis (subtraction procedure) leads to plausible model and starting values (also later)

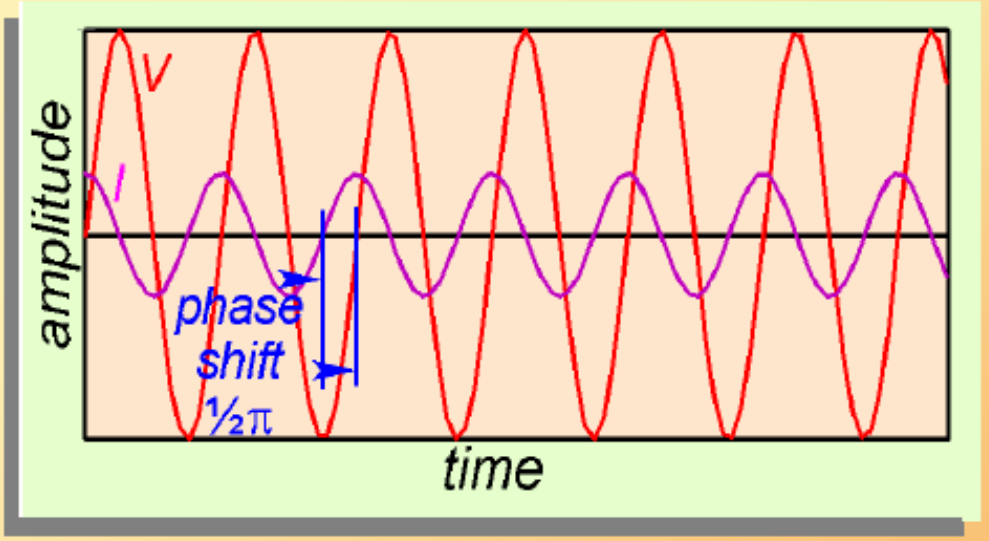
Disadvantage: rather expensive equipment,
low frequencies difficult to measure

Assume a Black Box Approach

Assume a black box with two terminals (electric connections).

One applies a voltage and measures the current response (or visa versa). Signal can be dc or periodic with frequency f, or angular frequency $\omega=2\pi f$,
with: $0 \leq \omega < \infty$





Phase shift and amplitude changes with ω!

So, What is EIS???

Probing an electrochemical system with a small ac-perturbation, $V_0 \cdot e^{j\omega t}$, over a range of frequencies.

The **impedance** (resistance) is given by:

$\omega = 2\pi f$

$j = \sqrt{-1}$

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_0 \quad e^{j\omega t}}{I_0 \quad e^{j(\omega t + \varphi)}} = \frac{V_0}{I_0}\left[\cos\varphi - j\sin\varphi\right]$$

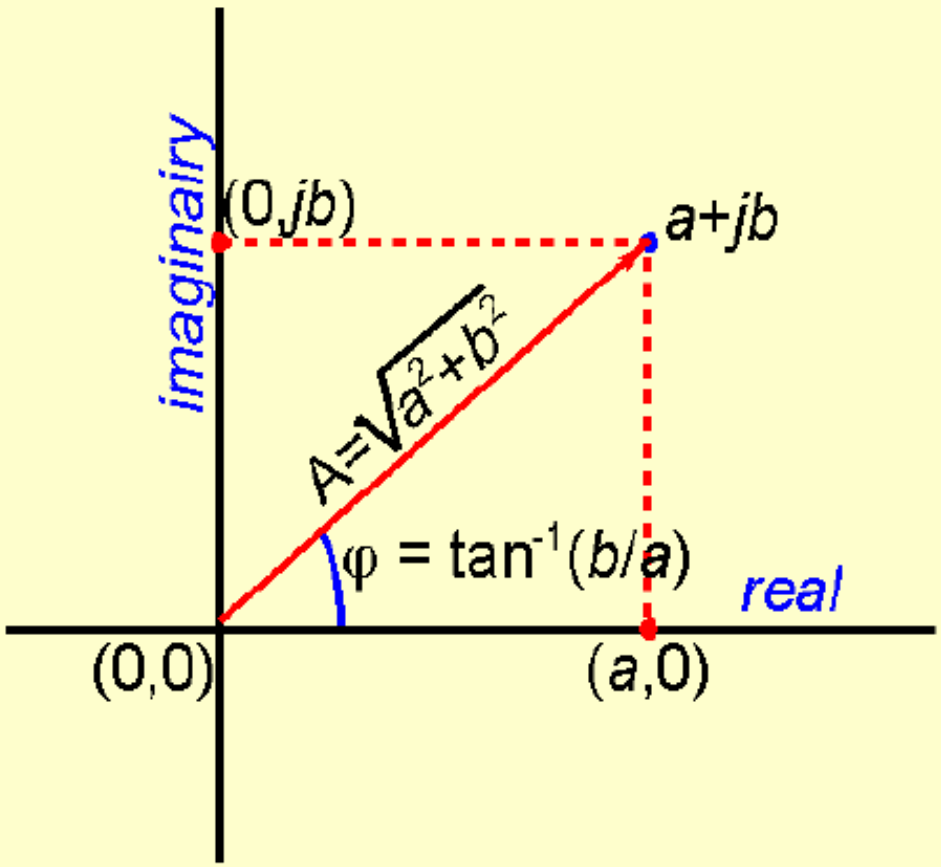
The magnitude and phase shift depend on frequency.

Also: **admittance** (conductance), inverse of impedance:

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{I_0\, e^{j(\omega t + \varphi)}}{V_0\, e^{j\omega t}} = \frac{I_0}{V_0}\left[\cos\varphi + j\sin\varphi\right]$$

"real + j imaginary"

Complex Plane



Impedance ≡ 'resistance'

Admittance ≡ 'conductance':

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{Z_{re} - jZ_{im}}{Z_{re}^2 + Z_{im}^2}$$

hence:

$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{Y_{re} - jY_{im}}{Y_{re}^2 + Y_{im}^2}$$

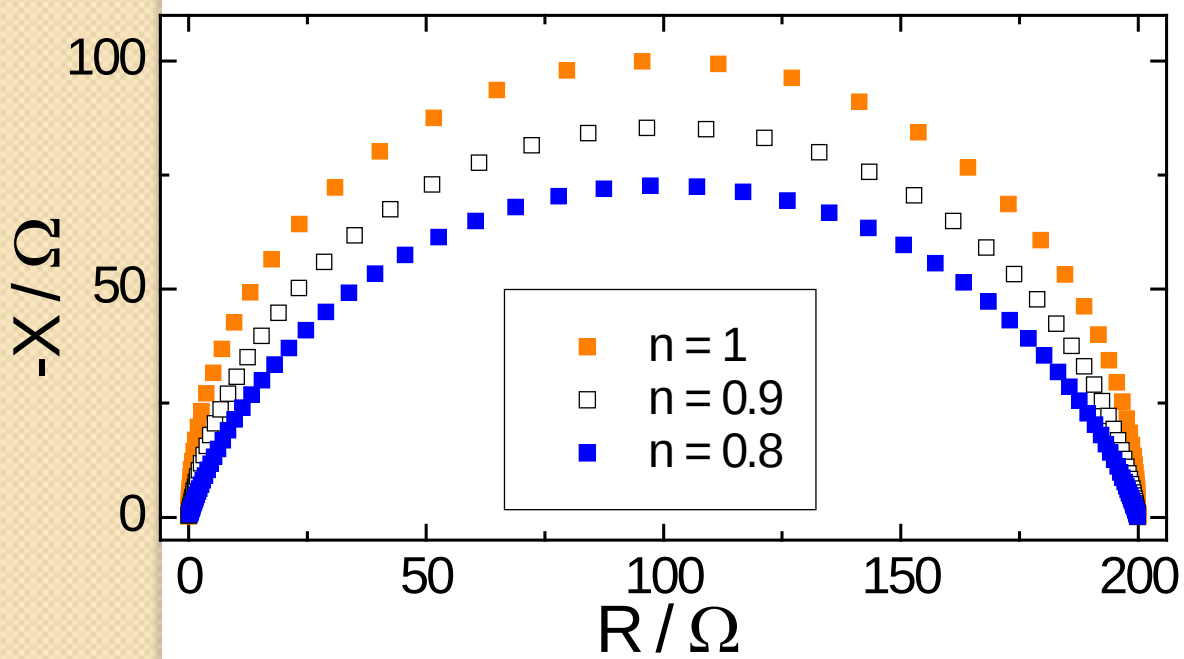
Representation of impedance value, $Z = a + jb$, in the complex plane

The (RC) Circuit - Remember

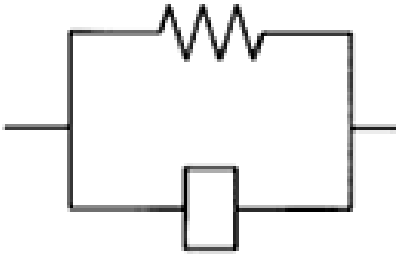
- Constant phase elements (CPE) may be regarded as non-ideal capacitors defined by the constants Y and n, and their impedance is given according to

$$Z_Q = \left[Y(j\omega)^n\right]^{-1}$$

- The CPE is very versatile ("a very general dispersion formula"):
  - If n = 1, the CPE represents an ideal capacitor
  - If n = 0, the CPE represents a resistor
  - If n = -1, the CPE represents an inductor
  - If n = 0.5 the CPE represents a Warburg element



Peak frequency: $\omega_0 = (RC)^{-1}$



Constant phase element

Impedance Spectroscopy in Solid State Ionics

- What: A technique for studying the conductivity of ionic conductors, mixed conductors, electrode kinetics and related phenomena

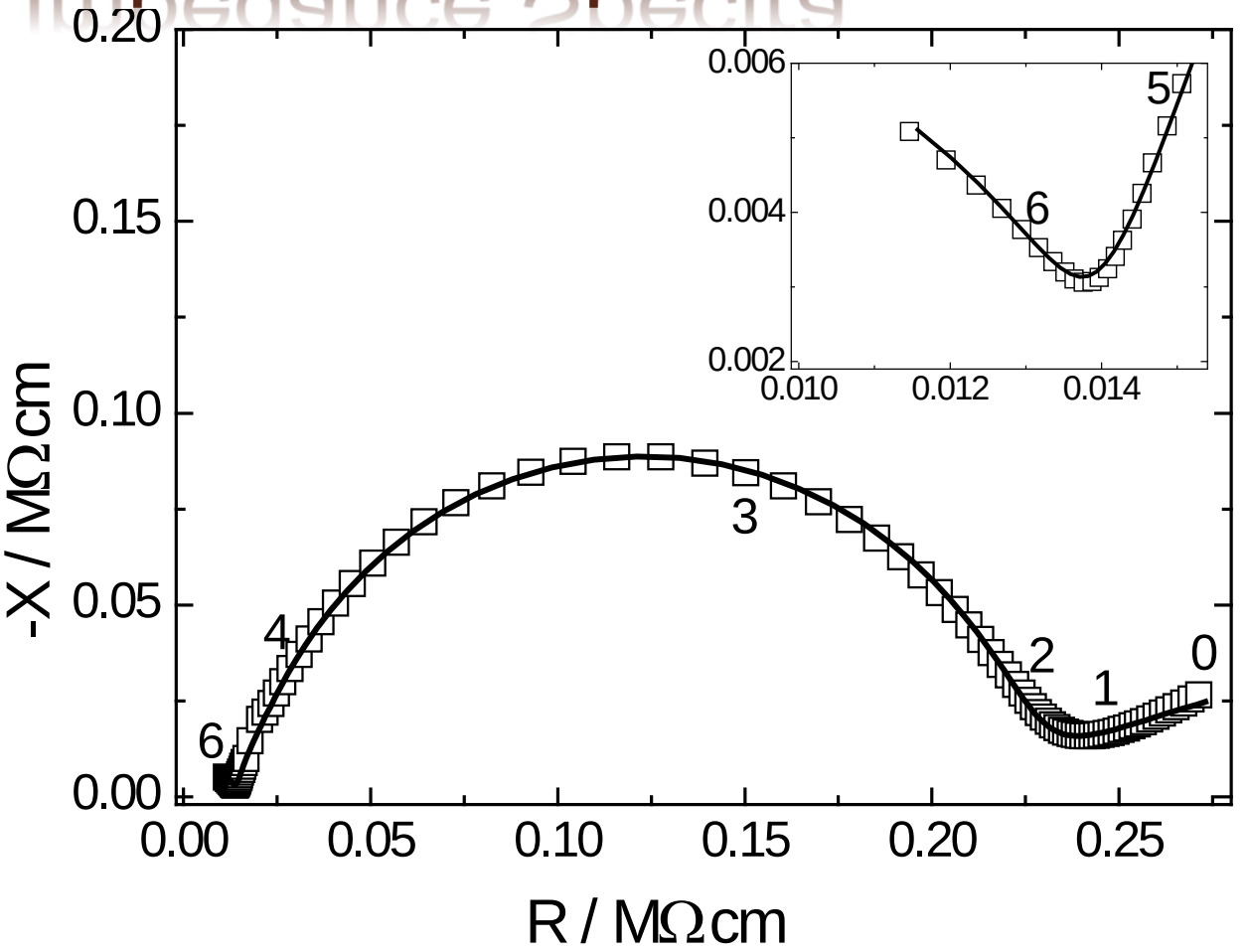
Features:

- Eliminates the need for non-blocking electrodes
- The impedance due to grain interiors, grain boundaries and different electrode properties can be measured independently

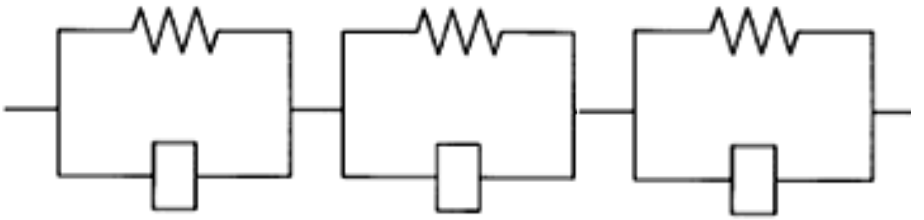
How:

- A small AC voltage (e.g. 10 mV – 1 V) is imposed on the sample over a wide range of frequencies (e.g. 1 MHz – 0.1 Hz), and the complex impedance is measured

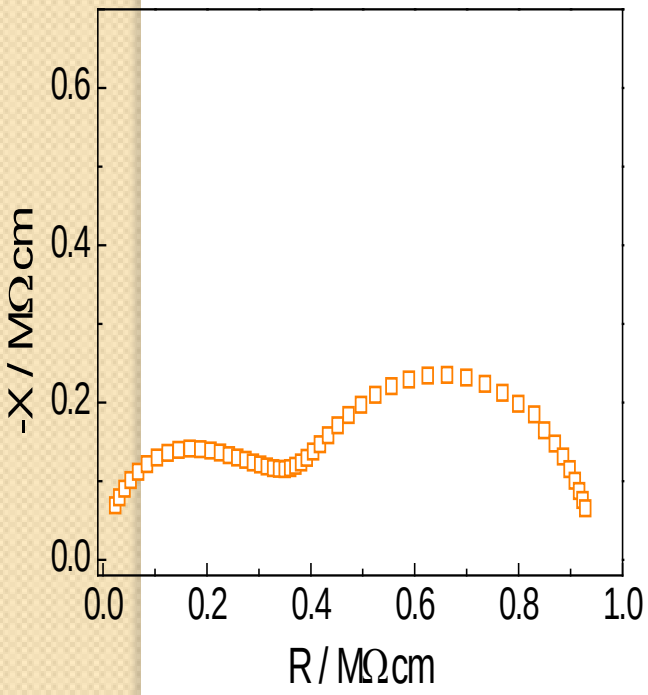
Real Impedance Spectra



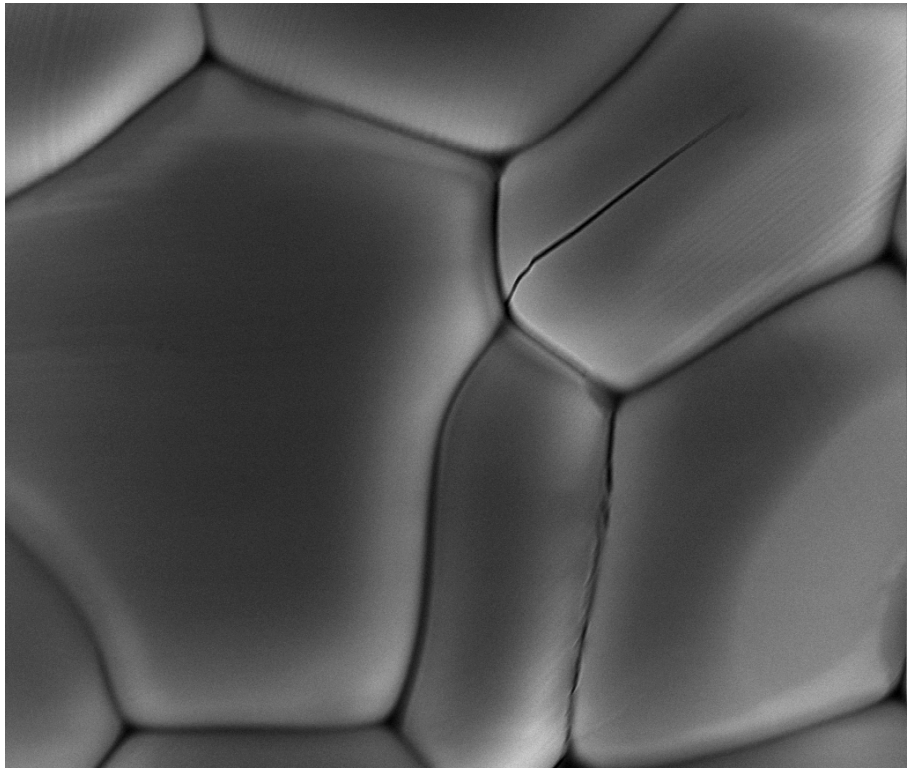
The spectrum can be fitted by using:



CONDUCTIVITY



GRAINS

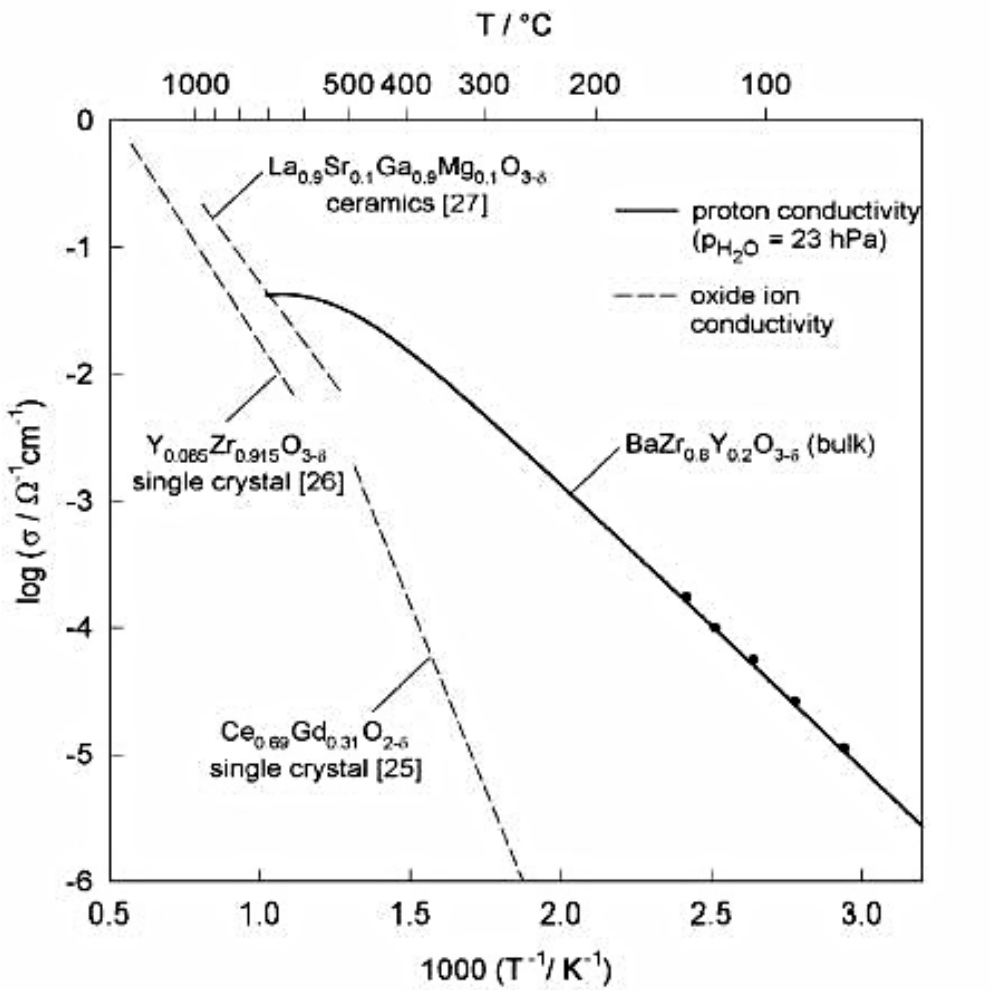


Grain Boundaries in Ionic Conductors

Key requirements for the SOFC electrolyte:

- Good ionic conduction
- No electronic conduction
- Control of concentration and mobility of ionic and electronic species

Conductivity as a function of T

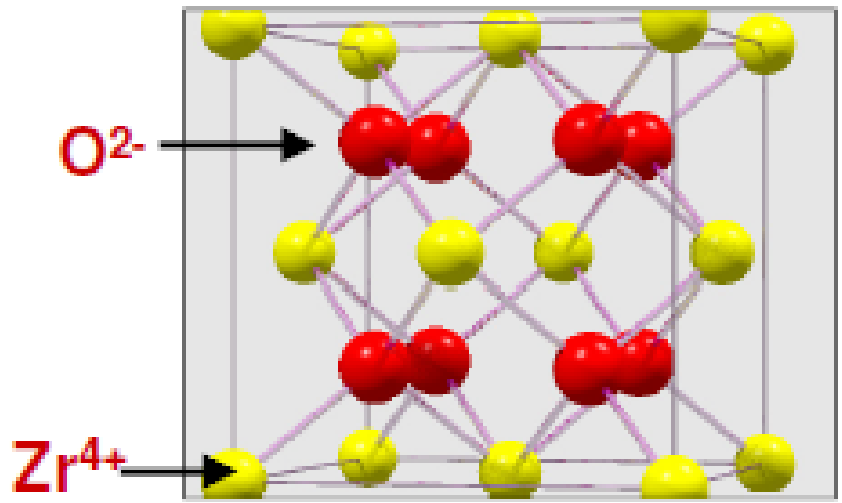


Conductivity in Zirconia (as an example)

- ZrO_2 with cubic structure

- Has fluorite structure (CaF_2)
- CCP of Zr^{4+} with O^{2-} in all tetrahedral holes

- Cubic ZrO_2 is NOT stable at room temperature



If the Zr site is partially substituted with either Y^{3+} (Y_2O_3 stabilised ZrO_2, YSZ) or Ca^{2+} (CaO lime-stabilised ZrO_2), then $Zr_{1-x}A_xO_2$ is stable at room temperature

($A = Y^{3+}$ or Ca^{2+})

Stabilized Zirconia

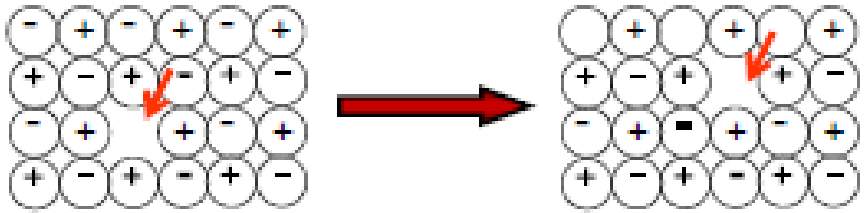
Mechanism of anion vacancy creation

The substituting cation (Ca^{2+}) has a lower charge than that of the replaceable cation (Zr^{4+}).

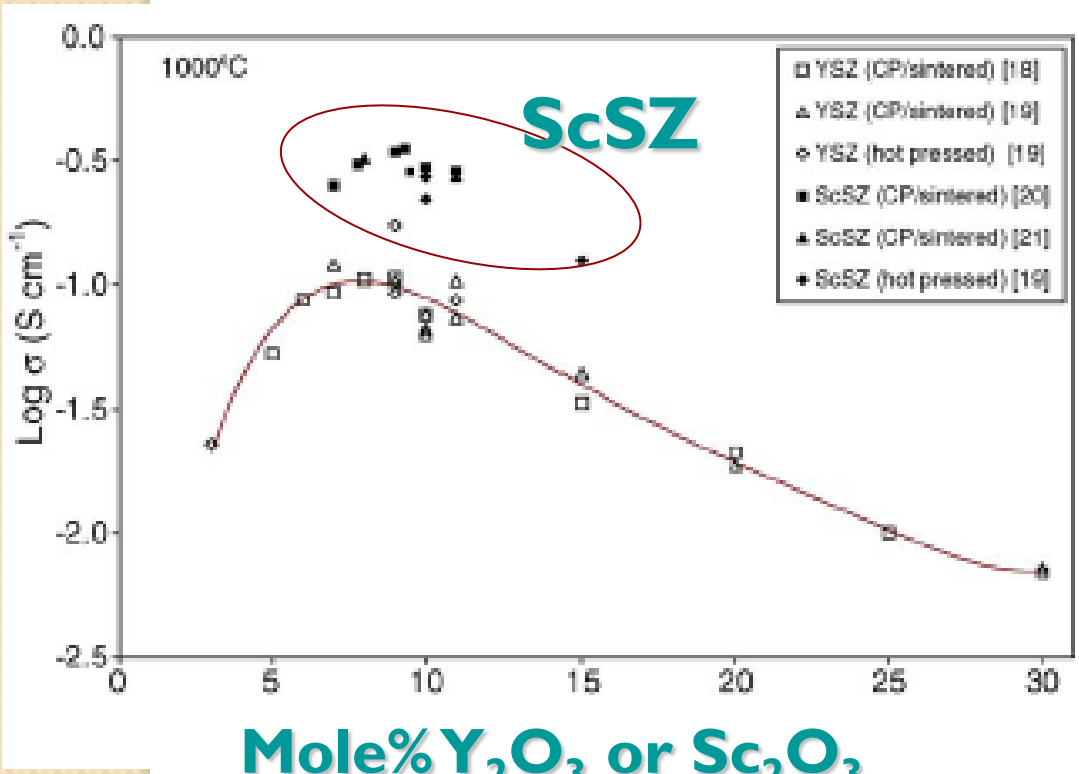
Anion vacancies are created to maintain charge neutrality in the ionic compound:

$$ZrO_2 \xrightarrow{Ca^{2+}/Zr^{4+}} Zr_{1-x}Ca_xO_{2-x} \qquad 0.1 \leq x \leq 0.2$$

"Lime-stabilised zirconia" is a good ***oxide ion conductor*** at ~ 600℃



Zirconates (zirconia based materials, Y or Sc doped zirconia)



- Structure: Cubic fluorite
- Oxygen conductivity
- Electronic conductivity

Fergus, Journal of Power Sources, Available online (2006)

Favored Materials (SOFC)

Cathode (Air Electrode)

- **$(La_{1-x}Ca_x)MnO_3$ (Perovskite)**
  - **$(La_{1-x}Sr_x)(Co_{1-x}Fe_x)O_3$** (Perovskite)
  - **$(Sm_{1-x}Sr_x)CoO_3$** (Perovskite)
  - **$(Pr_{1-x}Sr_x)(Co_{1-x}Mn_x)O_3$** (Perovskite)

Anode (H_2/CO Electrode)

- **$Ni/Zr_{1-x}Y_xO_2$ Composites**

Electrolyte (Air Electrode)

- **$Zr_{1-x}Y_xO_2$ (Fluorite)**
  - **$Ce_{1-x}R_xO_2$, R = Rare Earth Ion (Fluorite)**
  - **$Bi_{2-x}R_xO_3$, R = Rare Earth Ion (Defect Fluorite)**
  - **$Gd_{1.9}Ca_{0.1}Ti_2O_{6.95}$ (Pyrochlore)**
  - **$(La,Nd)_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (Perovskite)**

Interconnect (between Cathode and Anode)

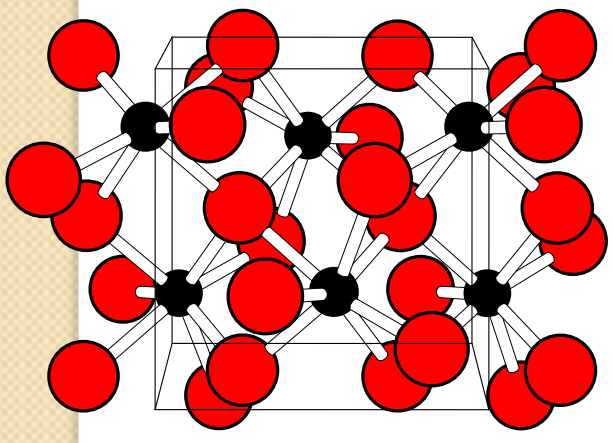
- **$La_{1-x}Sr_xCrO_3$ (Perovskite)**

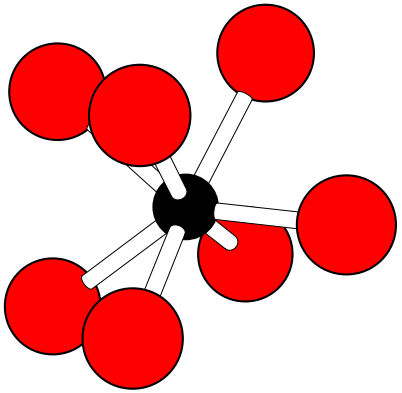
Design Principles: O^{2-} Conductors

- **High concentration of anion vacancies**
  - necessary for O^{2-} hopping to occur
- **High Symmetry**
  - provides equivalent potentials between occupied and vacant sites
- **High Specific Free Volume (Free Volume/Total Volume)**
  - void space/vacancies provide diffusion pathways for O^{2-} ions
- **Polarizable cations (including cations with stereoactive lone pairs)**
  - polarizable cations can deform during hopping, which lowers the activation energy
- **Favorable chemical stability, cost and thermal expansion characteristics**
  - for commercial applications

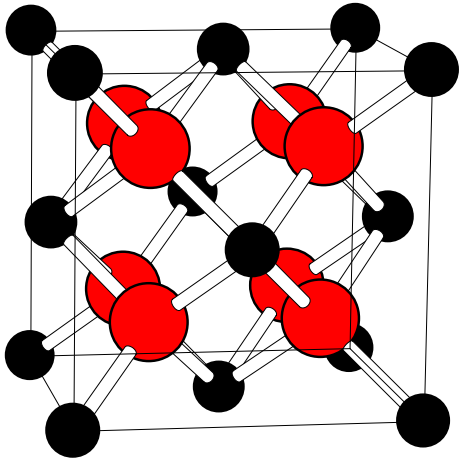
Phase Transitions in ZrO_2

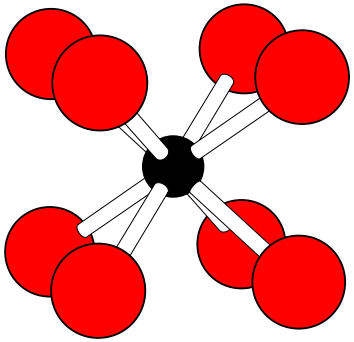
Room Temperature
Monoclinic ($P2_1/c$)
7 coordinate Zr
4 coord. + 3 coord. O^{2-}





High Temperature
Cubic (Fm3m)
cubic coordination for Zr
tetrahedral coord. for O^{2-}





Effect of Dopants: ZrO_2, CeO_2

- Doping ZrO_2 ($Zr_{1-x}Y_xO_{2-x/2}$, $Zr_{1-x}Ca_xO_{2-x}$) fulfills two purposes
  - Introduces anion vacancies (lower valent cation needed)
  - Stabilizes the high symmetry cubic structure (larger cations are most effective)

- We can also consider replacing Zr with a larger cation (i.e. Ce^{4+}) in order to stabilize the cubic fluorite structure, or with a lower valent cation (i.e. Bi^{3+}) to increase the vacancy concentration.

Compound	r^{4+} (Angstroms)	Specific Free Volume	Conductivity @ 800 °C
$Zr_{0.8}Y_{0.2}O_{1.9}$	0.86	0.31	0.03 S/cm
$Ce_{0.8}Gd_{0.2}O_{1.9}$	1.01	0.38	0.15 S/cm
δ-Bi_2O_3	1.17	0.50	1.0 S/cm (730 C)

Bi_2O_3 is only cubic from 730 °C to it's melting point of 830 °C. Doping is necessary to stabilize the cubic structure to lower temps.

Here we have the case of an Oxygen Deficient Oxides with Lower Valent Dopant Cations

eg ZrO_2 with Y'_{Zr} or Ca''_{Zr}

$$ZrO_2 + 2Y_Y^0 = V_O^{\cdot\cdot} + 2Y'_{Zr}$$

Look at the case of Y'_{Zr}

Defect equilibrium between vacancies and electrons will be

$$O_O^X = V_O^{\cdot\cdot} + 2e' + 1/2O_2$$

$$K_{VO} = \frac{[V_O^{\cdot\cdot}]}{[O_O^X]} n^2 Po_2^{1/2}$$

Electroneutrality will be :

$$2[V_O^{\cdot\cdot}] = [Y'_{Zr}] + n$$

Oxygen Deficient Oxides with Lower Valent Dopant Cations

- There will be 2 conditions:
  - If $2[V\ddot{o}] \approx n >> [Y_{Zr}^{'}]$
    - The foreign cations do not affect the defect equilibrium
    - The electrons and oxygen vacancy concentrations are given by their own equilibrium and are proportional to $Po_2^{-1/4}$ (see earlier)
  - If $2[V\ddot{o}] \approx [Y_{Zr}^{'}] >> n$
    - Oxygen vacancy concentration is determined and fixed by the dopant content
    - This is the Extrinsic Region

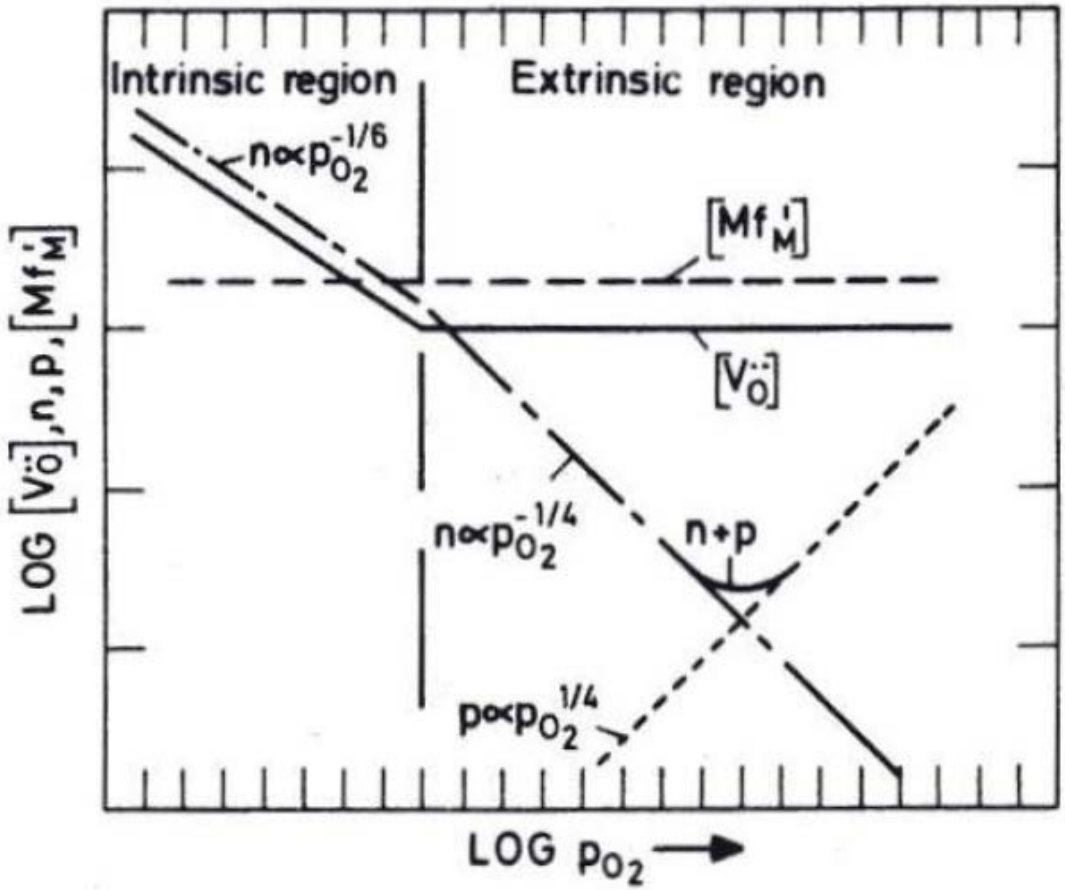
Oxygen Deficient Oxides with Lower Valent Dopant Cations

- The concentration of the minority defect, n, is given by:

$$n = \left(2K_{VO}\right)^{1/2}\left[Y'_{Zr}\right]^{-1/2} Po_2^{-1/4}$$

- Now, n and p are related by $K_i = np$
- p increases in the extrinsic region as Po_2 increases
- See Figure over

Conc. Of defects as a function of oxygen partial pressure in an oxygen deficient oxide containing oxygen vacancies



SOFC anode: one phase vs. two phase materials. Mixed conductivity.

1.2.1. Cermets: Ni-YSZ

1.2.2. Perovskite-related structures: Doped titanates ($SrTiO_3$), chromites, vanadates, ferrites; cerates –are stable in reducing atmospheres

1.2.3. Cubic fluorite structures: Zr and Ce-based materials (Y-Ti-Zr oxides; YTZ)

1.2.4. Pyrochlores: $Gd_2Ti_2O_7$

1.2.5. Spinel related materials (Mg_2TiO_4)

1.2.6. Bismuth oxide

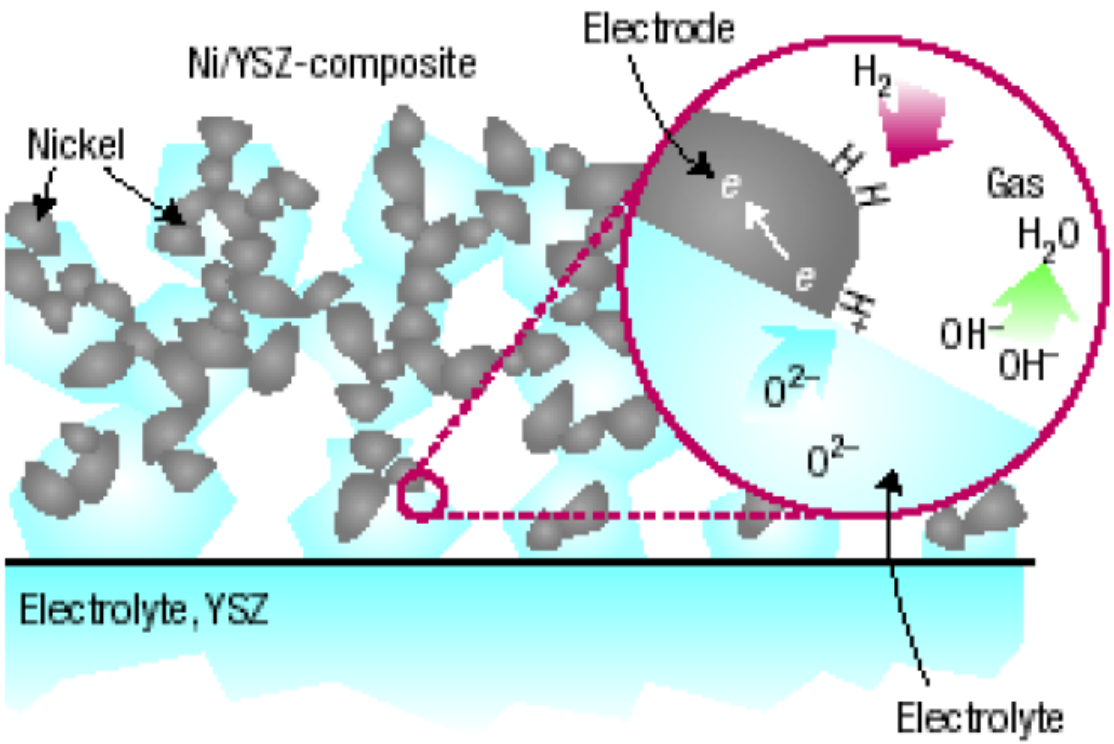
i) CERMETS-mixture of metals and oxide ceramics

Function of Metal Phase:

- Works as a catalyst
- Possesses electronic conductivity

Function of Ceramic Oxide Phase:

- Preserve porous structure
- Eliminates mass transport limitations
- Matches TEC

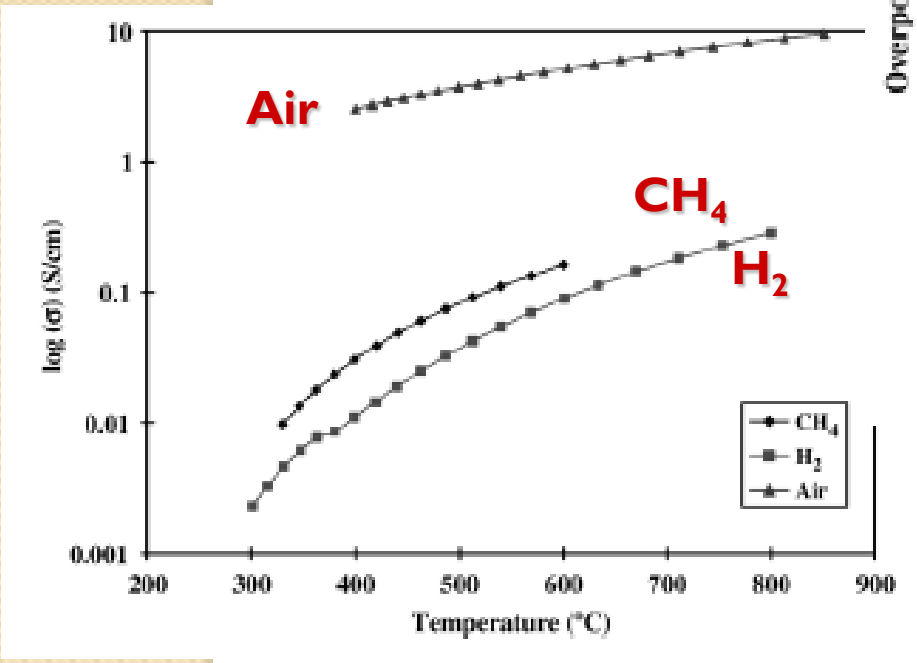


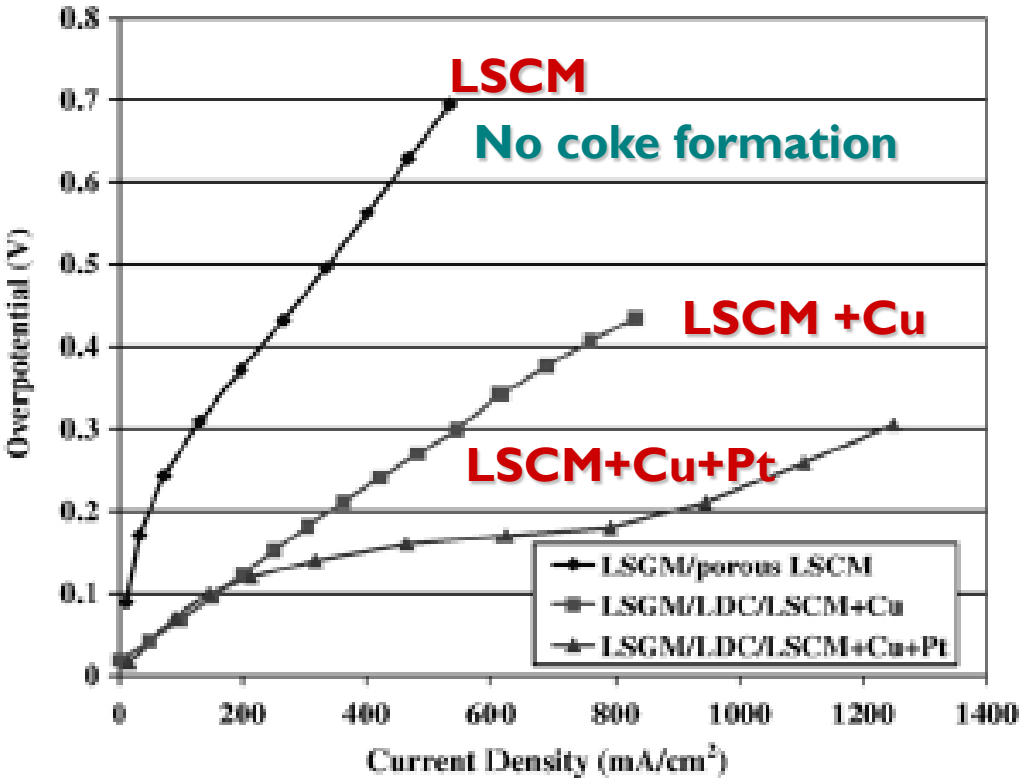
Why Ni?

- High catalytic activity
- Low cost

ii) Perovskite oxides for anodes operating on hydrocarbon fuels : LSCM ($La_{0.75}Sr_{0.75}Cr_{0.5}Mn_{0.5}O_3$)

1. Stable; form single phase
2. Conductivity in reducing atmosphere is low (0.1-0.3 S/cm) $Mn^{4+}/Mn^{3+} \rightarrow Mn^{3+}/Mn^{2+}$

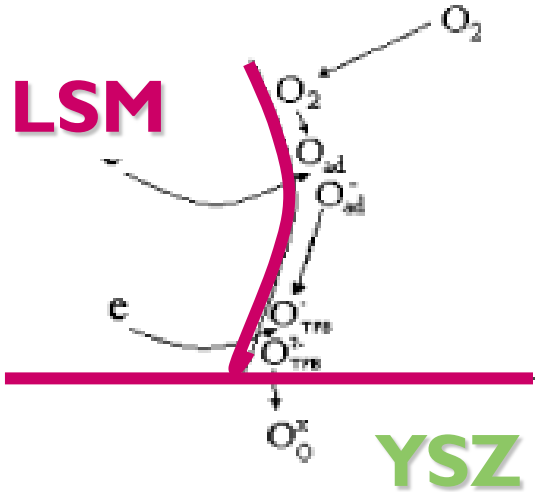




Anode Overpotentilal at 800oC in dry CH_4

Goodenough et al. Solid State Ionics 177 (2006) 1211-1217

Oxygen reduction on the LSM cathode



LIMITING STEPS

$$O_2(\text{bulk}) \rightarrow O_2(\text{interface})$$

$$O_2(\text{interface}) \rightarrow 2O_{ad}$$

$$O_{ad} + e^- \rightarrow O^-_{ad}$$

$$O^-_{ad} \rightarrow O^-_{TPB}$$

$$O^-_{TPB} + e^- \rightarrow O^{2-}_{TPB}$$

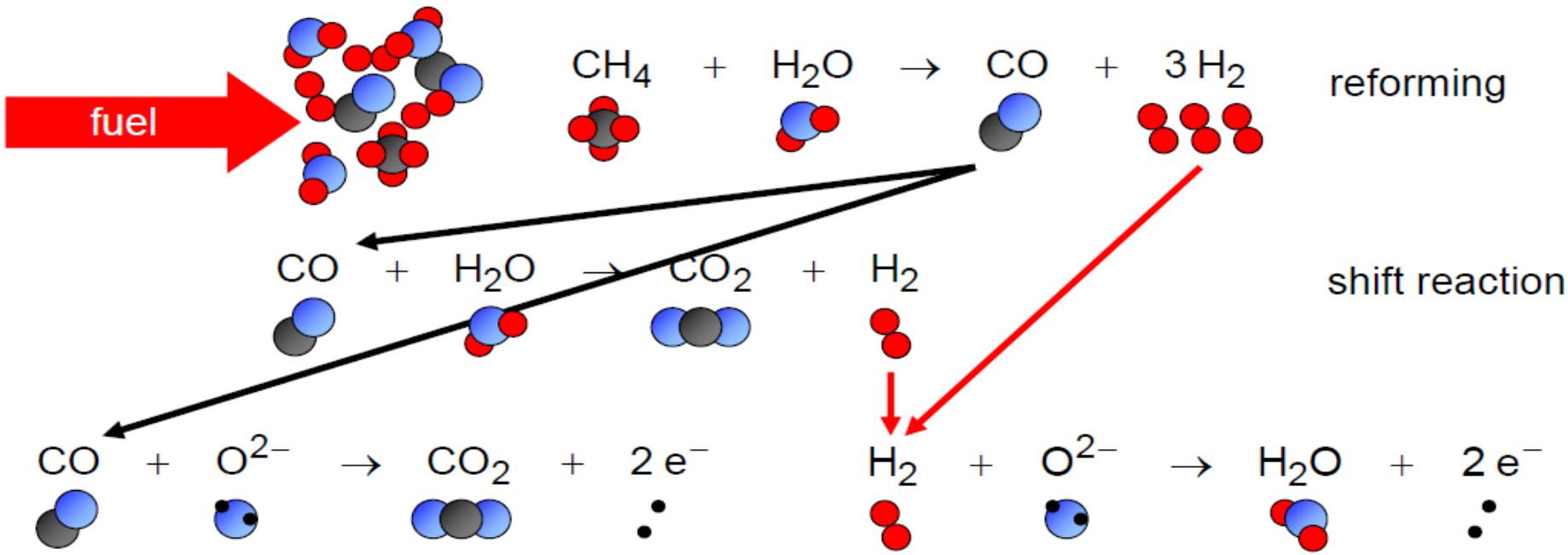
$$O^{2-}_{TPB,LSM} + V_{O,YSZ} \Rightarrow O^x_{O,YSZ}$$

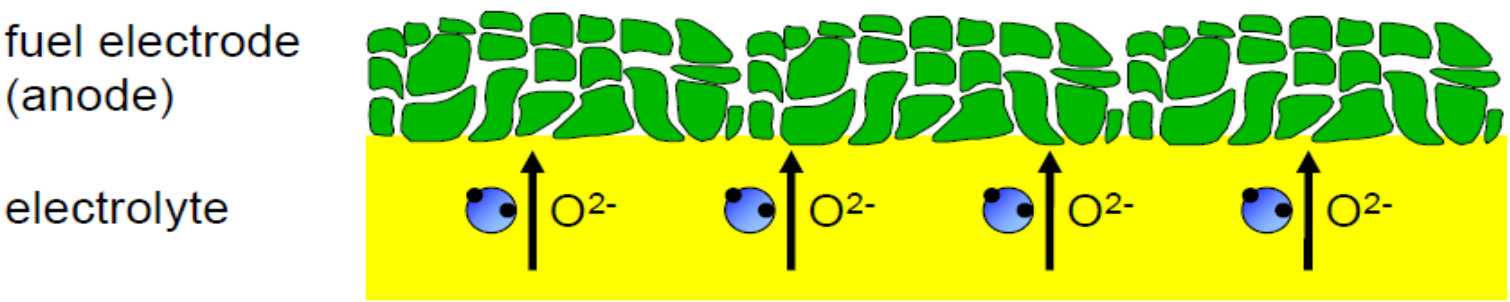
1. Gas diffusion
2. Adsorption
3. Charge transfer reaction (1)
4. Surface diffusion
5. Charge transfer reaction (2)
6. Incorporation of oxygen ions into electrolyte lattice

At high temperatures >900°C YSZ and LSM can react to form pyrochlore $La_2Zr_2O_7$ or/and perovskite $SrZrO_3$

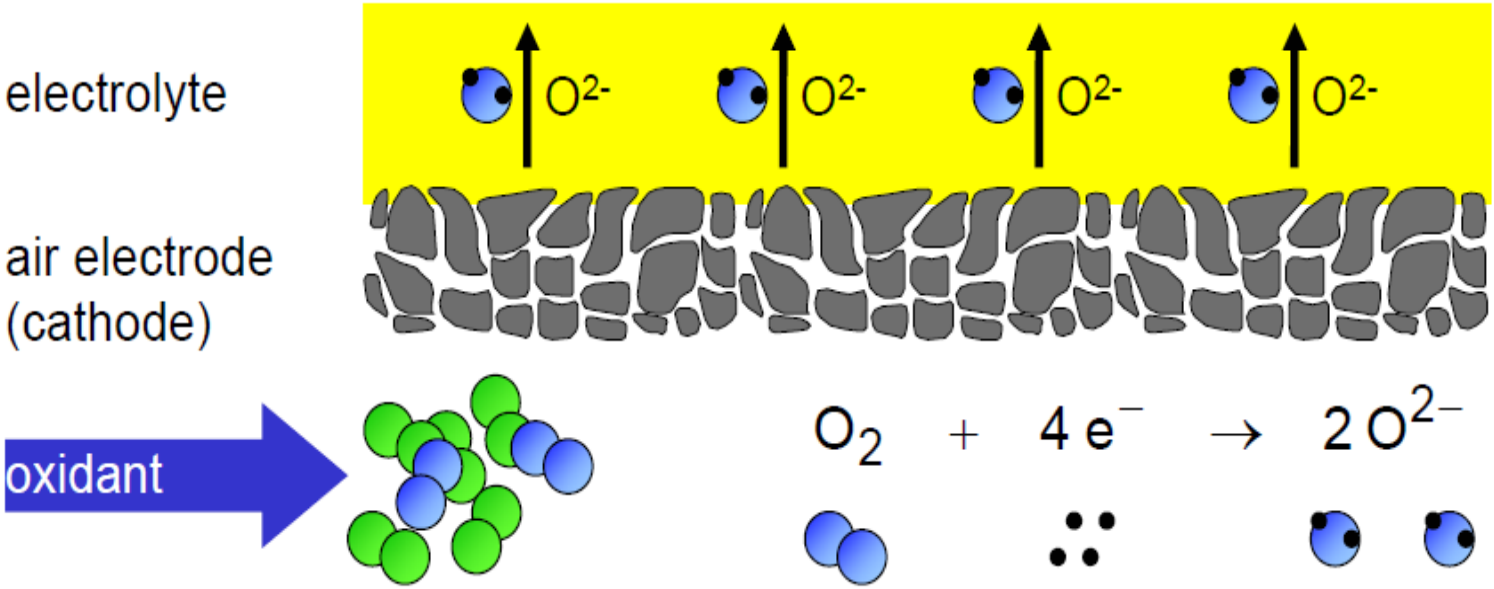
Chen et al. Journal of Power Sources 123 (2006) 17-25

Anode Reactions





Cathode Reactions



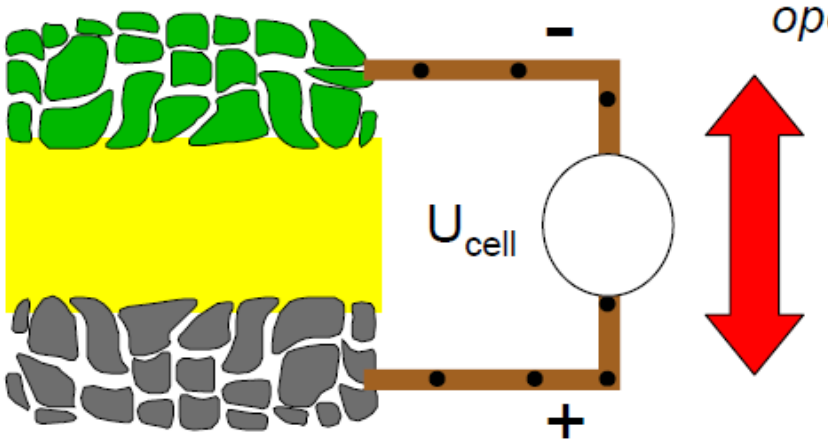
$$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$$

reduction

Open Circuit Voltage (OCV)

oxygen partial pressure

$p_{O_2,a(node)}$ ~ 10^{-15} bar



oxygen partial pressure

$p_{O_2,c(athode)}$ 0,21 bar

at open current (i=0; no consumer)

open cell voltage or Nernst voltage

open circuit voltage - OCV or U_{OCV}

$$U_{OCV} = \frac{RT}{nF} \ln \frac{p_{O_2,K(athode)}}{p_{O_2,A(node)}}$$

with R = gas constant
T = temperature
F = Faraday constant
n = amount of electrones taking part at the reaction (here n=4)

Cell Voltage

$$U_{OCV} = \frac{RT}{nF} \ln \frac{p_{O_2,c(athode)}}{p_{O_2,a(node)}}$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

$$K_{H_2/H_2O} = \frac{p_{H_2O,A}}{p_{H_2,A}\, p_{O_2,A}^{1/2}}$$

$$U_{OCV} = \frac{RT}{2F} \ln \frac{p_{O_2,K}^{1/2}\, p_{H_2,A}\, K_{H_2/H_2O}}{p_{H_2O,A}}$$

$$= \frac{RT}{2F} \ln K_{H_2/H_2O} + \frac{RT}{2F} \ln \frac{p_{O_2,K}^{1/2}\, p_{H_2,A}}{p_{H_2O,A}}$$

$$\Delta G_T^0 = -RT \ln K_{H_2/H_2O}$$

standard potential $U^0 = -\frac{\Delta G_T^0}{2F}$

standard Gibbs free energy $= \frac{RT}{2F} \ln K_{H_2/H_2O}$

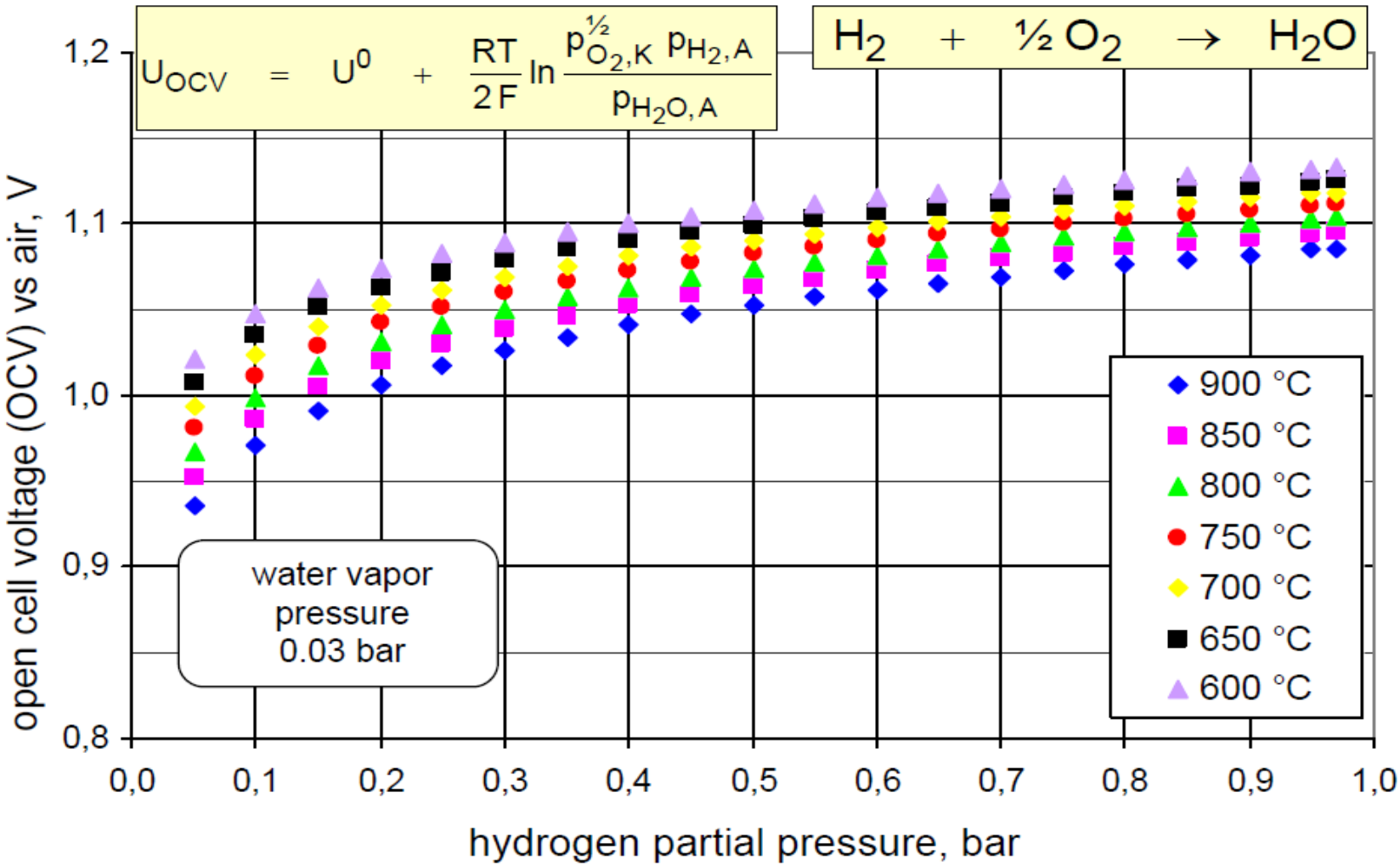
Cell Voltage

$$U_{OCV} = U^0 + \frac{RT}{2F} \ln \frac{p_{O_2,K}^{1/2}\, p_{H_2,A}}{p_{H_2O,A}}$$

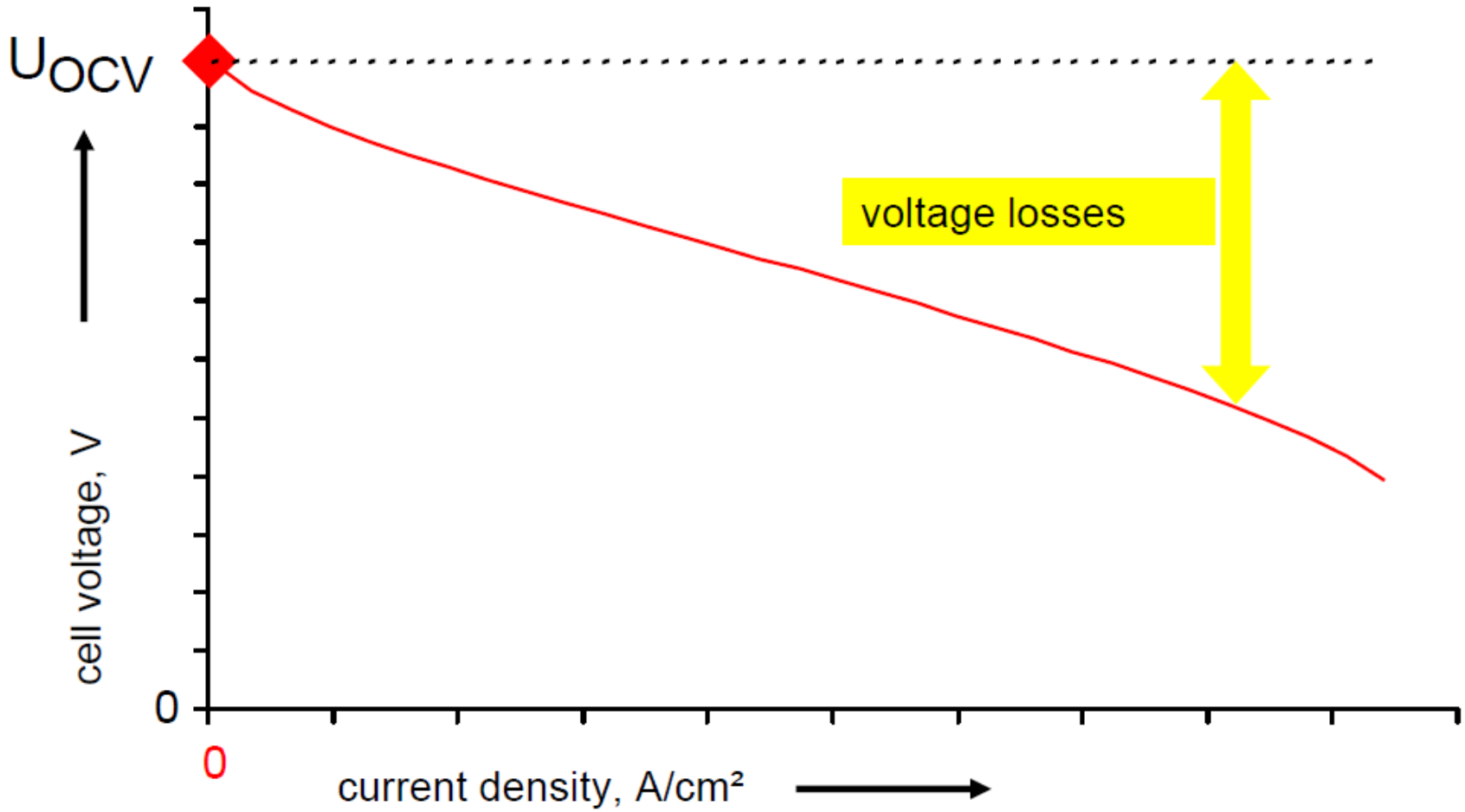
Nernst equation

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

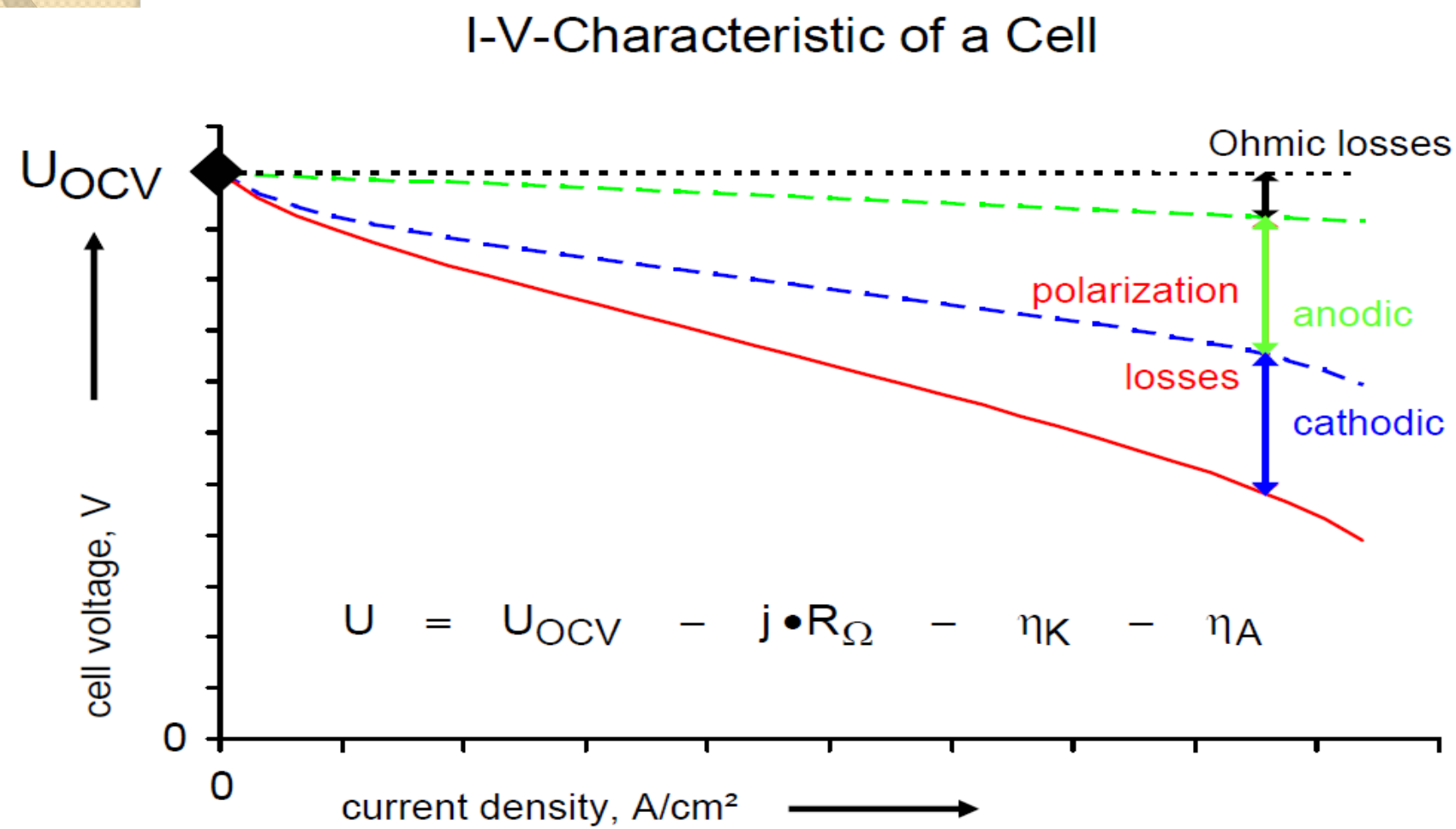
OCV as a Function of Hydrogen Partial Pressure



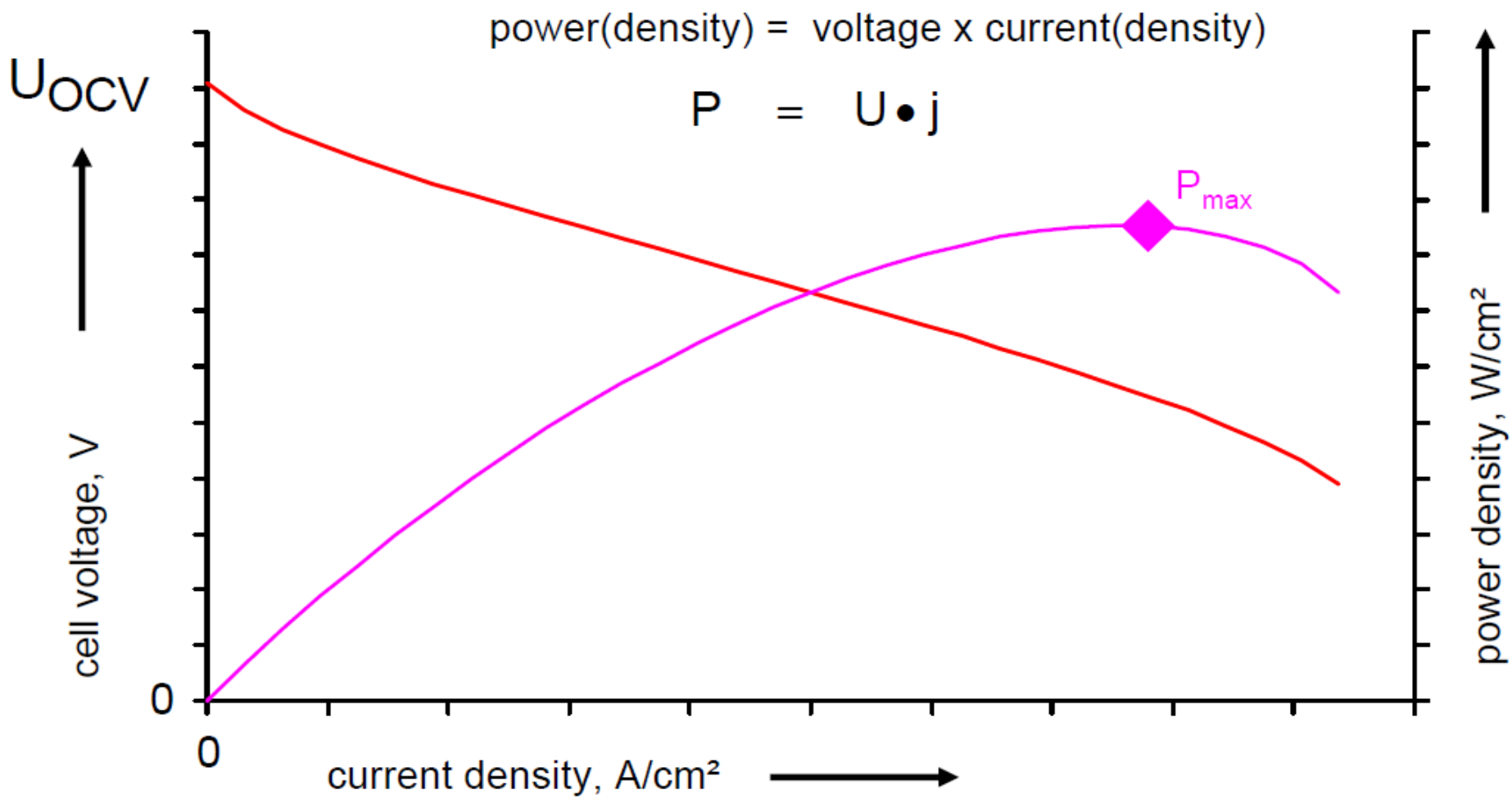
I-V Characteristics of a Cell



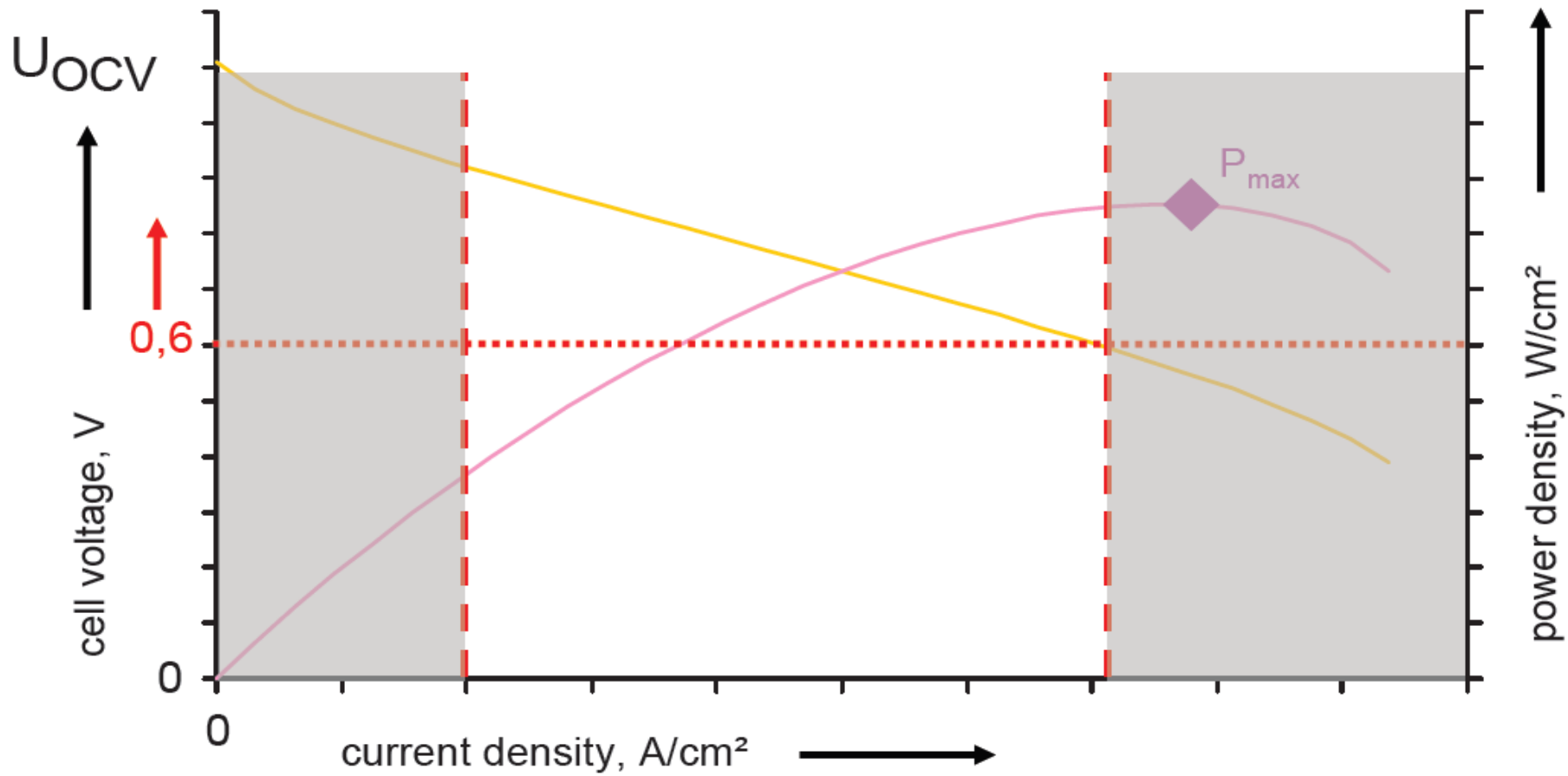
The Losses


I-V-Characteristic of a Cell
U_{OCV}
Ohmic losses
polarization
losses
anodic
cathodic
cell voltage, V
0
0
current density, A/cm²
$U = U_{OCV} - j \bullet R_{\Omega} - \eta_K - \eta_A$

I-V Characteristics of a Cell

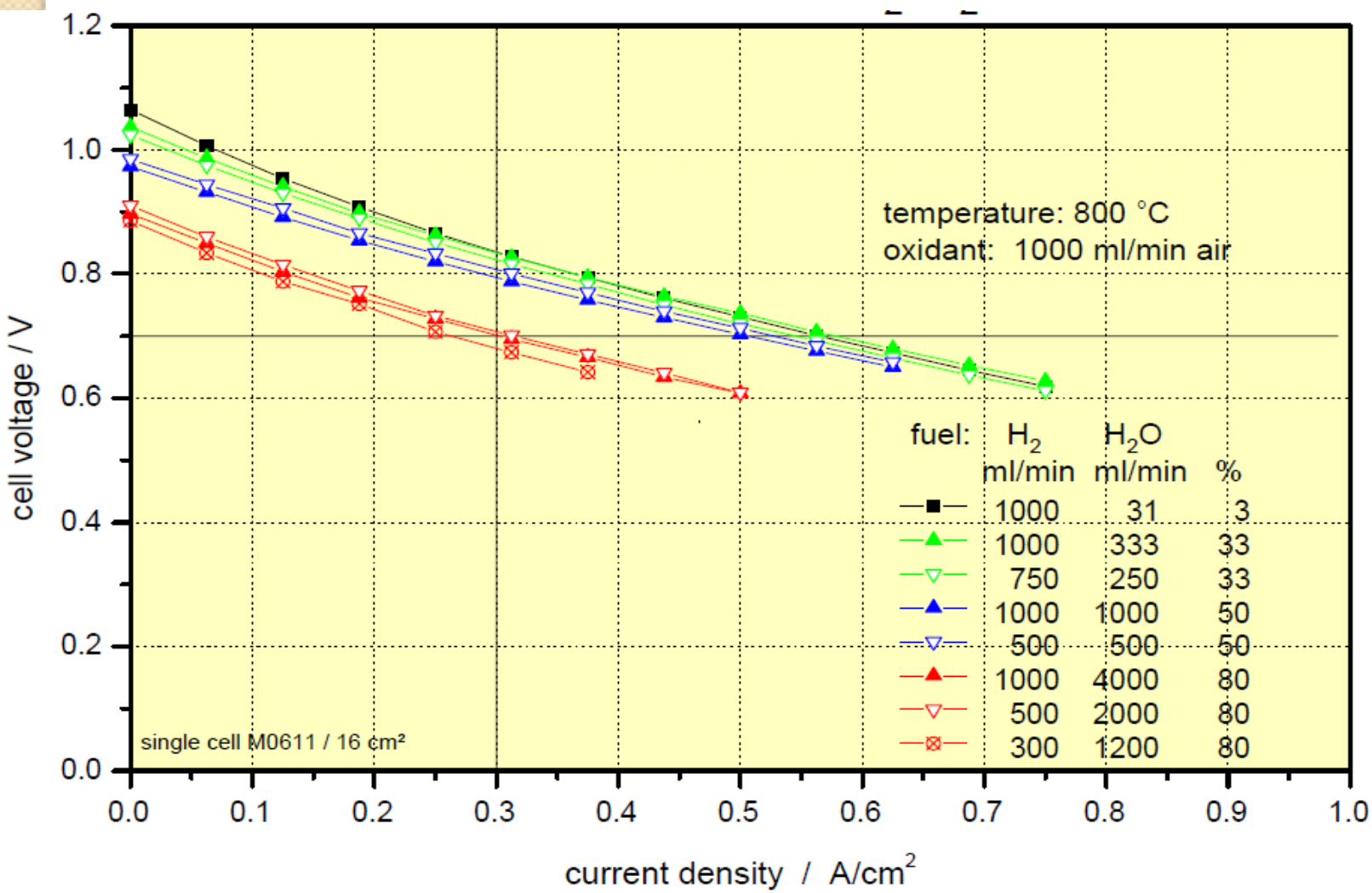


Operation of a SOFC



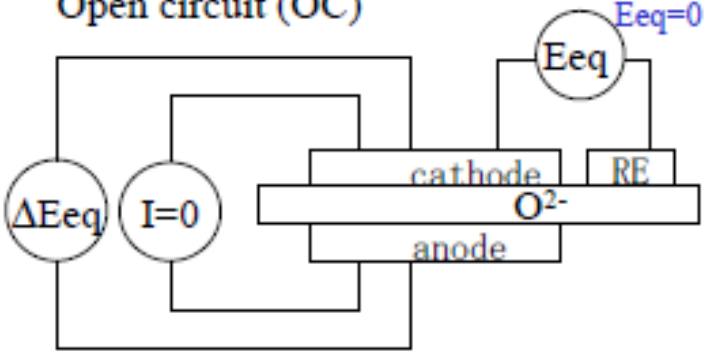
fuel cells are not operated at p_{max}!

Single Cell performance for Selected H_2/H_20 Ratios at 800 °C

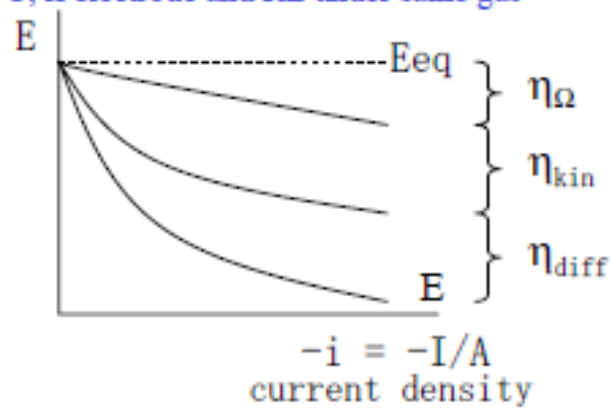


Losses in SOFC – First let us look at a 3-electrode system

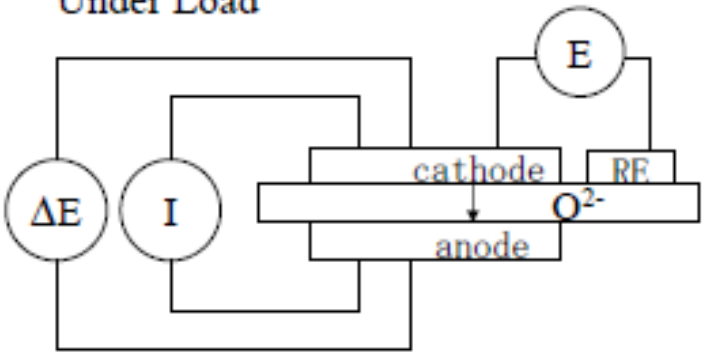
Open circuit (OC)



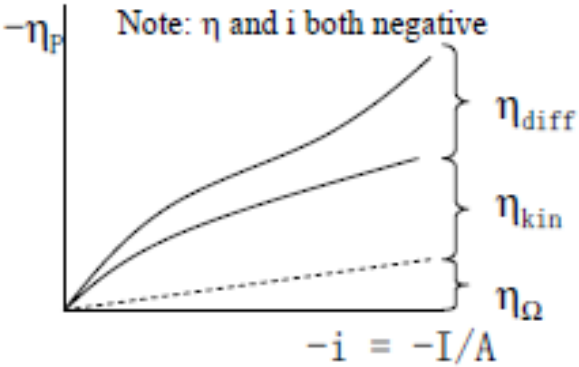
Eeq=0 at OC, if electrode and RE under same gas



Under Load



$E-Eeq=\eta=$ "polarization"



Polarization or Overpotential

- This is the potential driving force for the reaction:
  - In anodic direction (current and overpotential both positive)
  - In cathodic direction (both negative)
- For each electrode

$$\eta = E - E^o$$

$$\text{where, } \eta = \eta_{kin} + \eta_{dif} + \eta_{\Omega}$$

Ohmic

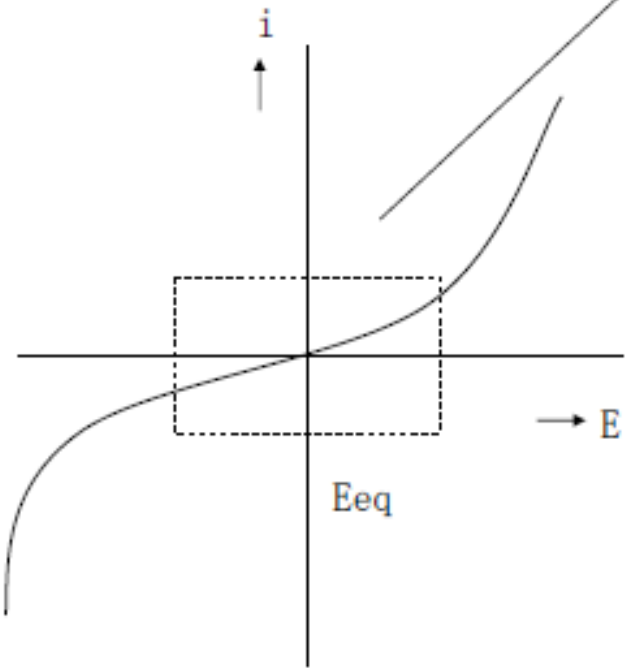
Kinetic (surface)

Diffusion (mass transfer, concn.)

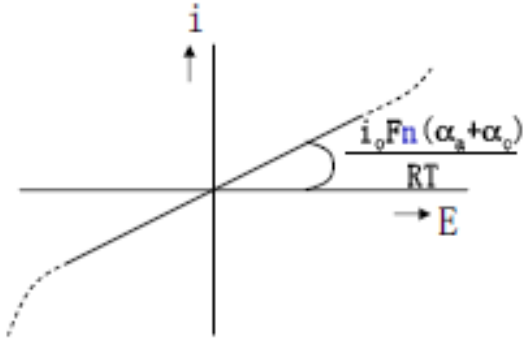
Kinetic Component

η_{kin} represents
ELECTRODE KINETIC
rate limitation

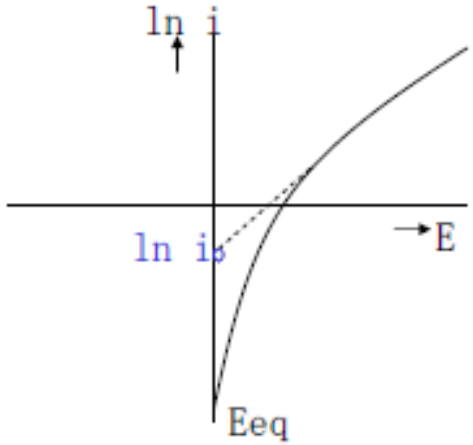
Butler-Volmer equation



Linear equation



Tafel equation (anodic branch)



Diffusion Component

- Due to diffusion resistance:
  - Gas phase diffusion resistance
  - Surface diffusion resistance (of electroactive species)
  - Not easy to distinguish from kinetic resistance

Overpotential

- It is a local quantity (for each electrode/electrolyte interface)
- Varies from point to point
- Due to non-uniform current distribution