Module 2, Lecture 7
Electron Transfer Reactions
Part 1

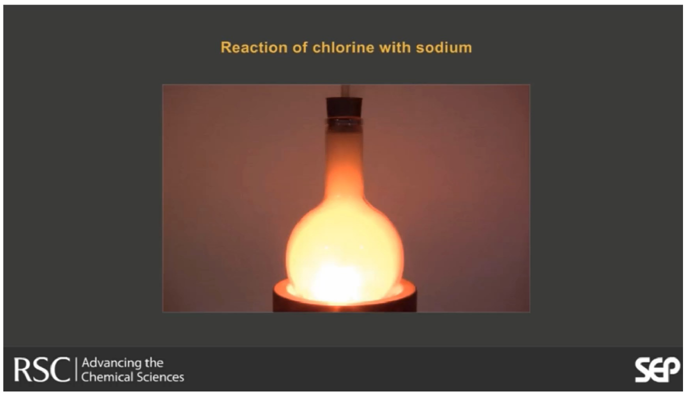
Learning Objectives:

- To describe reactions in terms of electron transfer between species and identify reduction and oxidation processes
- Identify oxidizing/reducing agents
- How to predict the potential energy of a spontaneous redox reaction
- Understand the concept of potential difference
- Understand how Galvanic cells allow the determination of standard reduction potentials and the importance of the Standard Hydrogen Electrode
- Correctly use $E^o_{cell} = E^o_{RHS} - E^o_{LHS}$

Textbook: Chapter 20

1

Reaction of sodium with chlorine



https://youtu.be/h5R6EMiqlUY

2

Reaction of sodium with chlorine

The reaction involves taking sodium atoms and reacting them with chlorine molecules. The product is two molecules of the ionic solid sodium chloride.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

We call the product an **ionic compound** because it is made up of two ions, a sodium cation, Na^+, and a chloride anion, Cl^-.

3

What happens to each species?

We can split the overall reaction up into two parts.

$$Na(s) \rightarrow Na^+$$

In this reaction, the sodium atoms must each lose 1 electron to change from a neutral atom to a positively charged **cation**
We could therefore write the equation as:

$$Na(s) \rightarrow Na^+ + e^-$$

Loss of an electron(s)
OXIDATION

$$Cl_2(g) \rightarrow 2Cl^-$$

In this reaction, the chlorine molecule must gain 2 electrons to change from a neutral molecule to two negatively charged **anions**
We could therefore write the equation as:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-$$

Gains of an electron(s)
REDUCTION

4

Oxidation numbers

A way of identifying oxidation and reduction.

1. **When atoms exist as elements, they have an oxidation number of zero**
   e.g. Na, Cl_2, C and He all have an oxidation number of zero

2. **The oxidation number of a monatomic (one atom) ion is the same as the charge on the ion.**
   e.g. Cu^{2+} has an oxidation number of +2, Cl^- has an oxidation number of -1

3. **Hydrogen in compounds has an oxidation number of +1** (except in metal hydrides, which we won't study)

5

Oxidation numbers

4. **Oxygen in compounds has an oxidation number of -2, except in hydrogen peroxide (H_2O_2) where it has an oxidation number of -1.**

5. **The sum of the oxidation numbers of atoms in a molecule is zero.**
   e.g. The sum of the ox. numbers for the atoms in H_2SO_4, H_2O and C_4H_{10} is zero.

6. **The sum of oxidation numbers of atoms in a polyatomic ion (ions containing more than one atom) is equal to the charge on the ion.**
   e.g. For NH_4^+, the oxidation numbers for the atoms add to +1
   For SO_4^{2-}, the oxidation numbers of the atoms add to -2

A **positive** change of an oxidation number indicate a **LOSS** of electrons. **Negative** change indicates a **GAIN** of electrons

6

Half equations

We call these component equations the **Reduction** and **Oxidation** **Half Equations**.

Adding them together gives the overall Reduction-Oxidation, or **Redox** reaction.

Note that when we add the half equations together we must ensure that they have the same numbers of electrons.

$2Na(s) \rightarrow 2Na^+ + 2e^-$	**Oxidation half equation**
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	**Reduction half equation**
$2Na(s) + Cl_2(g) + \cancel{2e^-} \rightarrow 2Na^+ + 2Cl^- + \cancel{2e^-}$	
$2Na(s) + Cl_2(g) \rightarrow 2Na^+ + 2Cl^-$	**Overall Redox equation**

7

Oxidising and reducing agents

When the sodium atoms lose their electrons (i.e. are oxidised), the $Cl_2(g)$ molecules take them– we therefore call the $Cl_2(g)$ the **oxidising agent/oxidant**.

The $Cl_2(g)$ molecules can gain electrons (i.e. are reduced) because the Na atoms lose them– we therefore call the Na(s) the **reducing agent/reductant**

$2e^-$

$$2Na(s) + Cl_2(g) \rightarrow 2Na^+ + 2Cl^-$$

Reducing agent
causes reduction and is **oxidised**

Oxidising agent
causes oxidation and is **reduced**

8

POP Quiz!!

In the following redox equation what is being oxidized and what is being reduced?

$$Fe^{2+}(aq) + Au^{3+}(aq) \rightarrow Au^{+}(aq) + Fe^{3+}(aq)$$

9

POP Quiz!!

In the following redox equation what is being oxidized and what is being reduced?

$$Fe^{2+}(aq) + Au^{3+}(aq) \rightarrow Au^{+}(aq) + Fe^{3+}(aq)$$

Reduction is gain of electrons:
Au^{3+}(aq) gains electron (goes from +3 to +1 so gains 2 electrons)

Oxidation is loss of electrons:
Fe^{2+}(aq) loses electrons (goes from +2 to +3 so loses 1 electron)

10

Another example

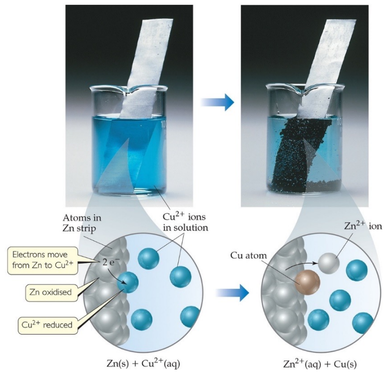
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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

Oxidation half equation,
Zn(s) is the **reducing agent**

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

Reduction half equation,
$Cu^{2+}(aq)$ is the **oxidising agent**



11

Does electron transfer always occur?

Consider the reverse process from previous slide

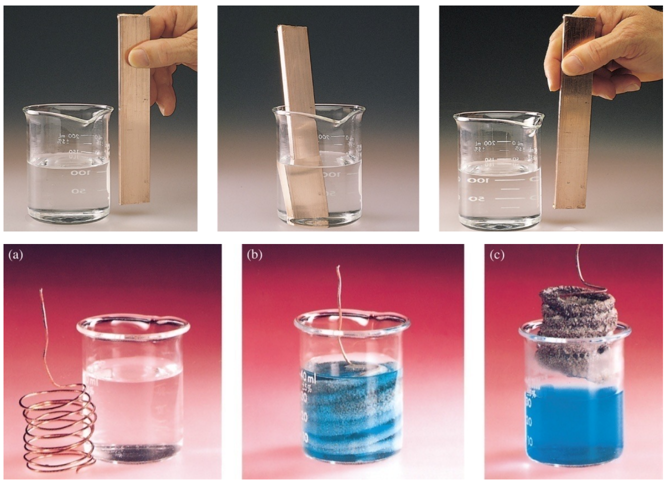
$Cu(s) + Zn^{2+}$

no reaction

But Cu(s) reacts with silver ions….

$Cu(s) + Ag^+$

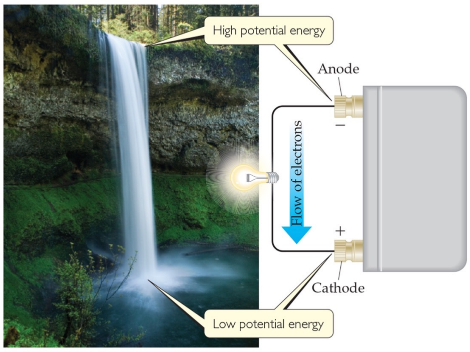
reaction



12

Driving force for e^- transfer

If electron transfer occurs then a **driving force** or **potential difference** must exist
units of potential difference are $V = J\ C^{-1}$ – energy per unit charge



We are going to think of the potentials involved as being the **potential for the gain of electrons** (called the **reduction potential**)

13

Reduction potentials

These can be thought of as the energy change when a substance gains electrons. **The biggest change in energy wins**.

In a reaction the substance with the highest potential energy (**highest reduction potential**) will **attract the electrons the most**, while the substance with the lowest potential will lose electrons.

"A tug of war for the electrons"

Careful Highest means "most positive", not necessarily "biggest number"…

14

Example

Predict the reaction that will occur when Ni(s) and Fe(s) is added to a solution containing 1.0 mol L^{-1} Ni^{2+}(aq) and 1.0 mol L^{-1} Fe^{2+}(aq).

$E^o(Ni^{2+}/Ni) = -0.25$ V $\qquad E^o(Fe^{2+}/Fe) = -0.44$ V

The values show us that the **reduction potential for Ni^{2+}/Ni is the more positive** so the reaction with nickel will involve the gain of electrons: Ni^{2+} will become Ni(s).

We say that Ni^{2+} will be reduced in the spontaneous reaction so is a stronger oxidising agent than Fe^{2+}:

$$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$$
$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e$$
$$\overline{Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)}$$

15

Potential difference

The overall potential difference for the reaction can be found using:

$$E^o_{reaction} = E^o_{reduction\ process} - E^o_{oxidation\ process}$$

From previous slide:

$E^o_{reaction} = E^o_{reduction\ process} - E^o_{oxidation\ process}$

the Ni^{2+}/Ni reduction potential is the most positive value

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

$= (-0.25\ V) - (-0.44\ V)$

$=$ **+0.19 V**

$E^o_{reaction}$ is always **positive** for a **spontaneous** reaction

16

POP Quiz!!

Look at these reduction potentials.

In each example which species will gain electrons and which will lose them?

i.	$E^o(Fe^{3+}/Fe^{2+}) = 0.77$ V	$E^o(Au^{3+}/Au^{+}) = 1.41$ V
ii.	$E^o(F_2/F^{-}) = 2.89$ V	$E^o(Na^{+}/Na) = -2.71$ V
iii.	$E^o(Zn^{2+}/Zn) = -0.76$ V	$E^o(H^{+}/H_2) = 0.00$ V
iv.	$E^o(Cu^{+}/Cu) = 0.52$ V	$E^o(Cu^{2+}/Cu^{+}) = 0.16$ V

17

POP Quiz!!

Look at these reduction potentials.

In each example which species will gain electrons and which will lose them?

i.	$E^o(Fe^{3+}/Fe^{2+}) = 0.77$ V	$E^o(Au^{3+}/Au^{+}) = 1.41$ V
ii.	$E^o(F_2/F^{-}) = 2.89$ V	$E^o(Na^{+}/Na) = -2.71$ V
iii.	$E^o(Zn^{2+}/Zn) = -0.76$ V	$E^o(H^{+}/H_2) = 0.00$ V
iv.	$E^o(Cu^{+}/Cu) = 0.52$ V	$E^o(Cu^{2+}/Cu^{+}) = 0.16$ V

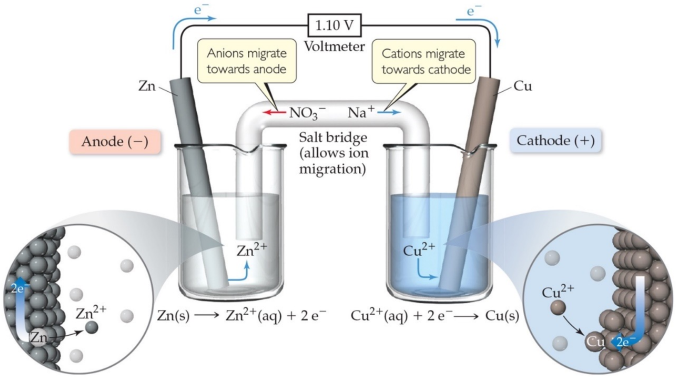
Oxidising agents-gain electrons - in most positive reduction half equation

Reducing agents-lose electrons - in least positive reduction half equation

18

Galvanic cells

- How do we determine the magnitude of the potential difference?
- Can't look at the direct electron transfer – too fast
- Instead separate half reactions and measure the potential difference – make a **Galvanic cell**



19

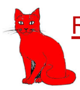
Cell potential, E^o_{cell}

E^o_{cell} measures the difference between how much each side wants to gain electrons.

We can therefore write $E^o_{cell} = E^o_{RHS} - E^o_{LHS}$

E^o_{RHS} and E^o_{LHS} are the **standard reduction potentials** for each of the half cells.

Reduction always occurs at the **CATHODE**
Oxidation always occurs at the **ANODE**



Red CAT

The sign of E^o_{cell} indicates which electrode has the reduction process:
- A positive value indicates reduction is occurring on the RHS electrode
- A negative value indicates reduction is occurring on the LHS electrode.

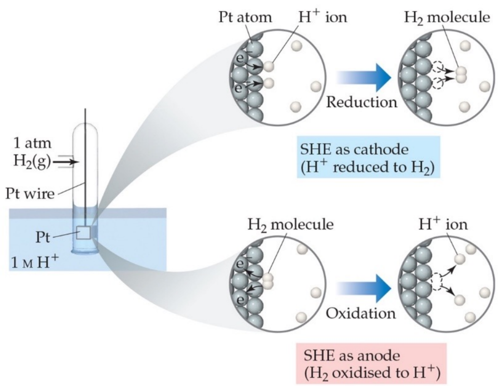
20

Standard hydrogen electrode (SHE)

This reference electrode is used to find the sign and magnitude of individual reduction potentials

We define this half cell to have a standard reduction potential of zero

i.e. $E^o(H^+/H_2) = 0.00$ V



21

Standard hydrogen electrode (SHE)

Like any other electrode the SHE can act as either the

ANODE $H_2(g, p^o) \rightarrow 2H^+(aq, c^o) + 2e^-$

CATHODE $2H^+(aq, c^o) + 2e^- \rightarrow H_2(g, p^o)$

Because we are comparing the other electrodes with it they can either be stronger or weaker oxidizing agents therefore we can find the **sign AND the value of their reduction potentials**.

22

✱ Homework ✱

Chemistry – the central science 15th Ed

Brown *et al.*

Problems 20.1 20.2 and 20.19

Answers on Blackboard

23