Unit 8 – IMFS – GLUE INS

N29

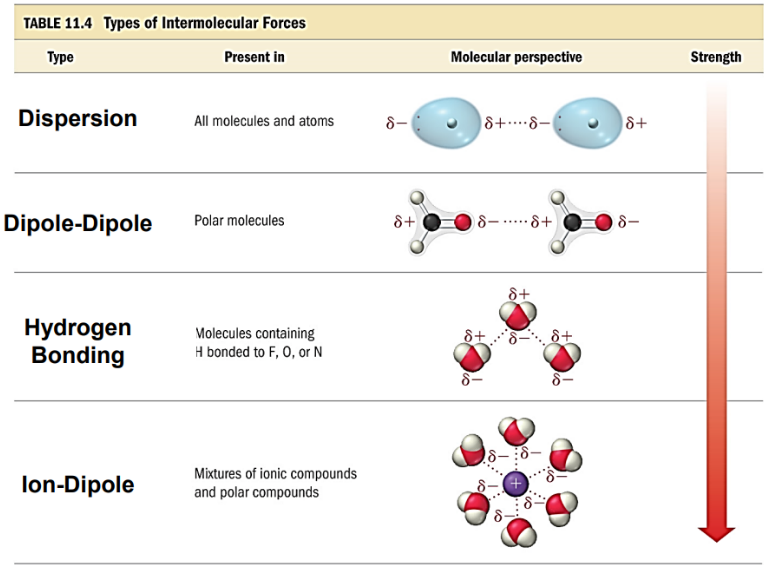
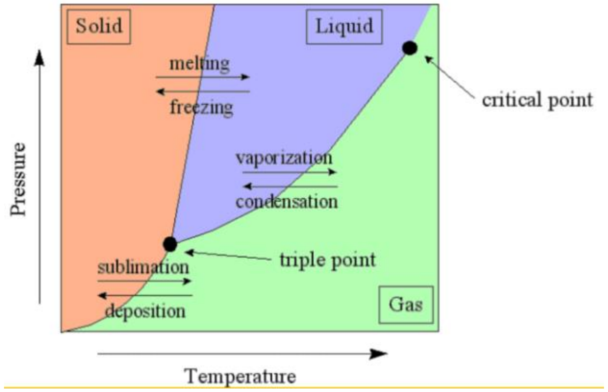


TABLE 11.4 Types of Intermolecular Forces

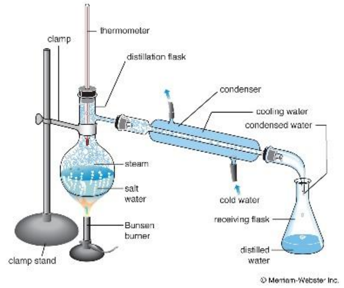
Type	Present in	Molecular perspective	Strength
Dispersion	All molecules and atoms	δ− δ+····δ− δ+	
Dipole-Dipole	Polar molecules	δ+ δ− ·····δ+ δ−	
Hydrogen Bonding	Molecules containing H bonded to F, O, or N	δ+ δ+ δ− δ+ δ− δ−	
Ion-Dipole	Mixtures of ionic compounds and polar compounds	δ− δ− δ− δ− δ− δ− +	

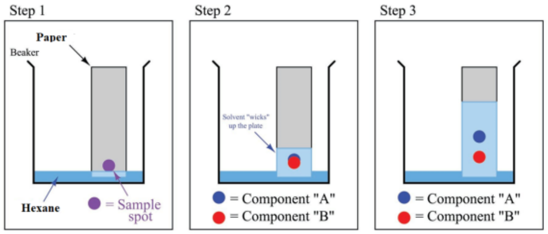
N30



Unit 9 – SOLUTIONS – GLUE INS

N31





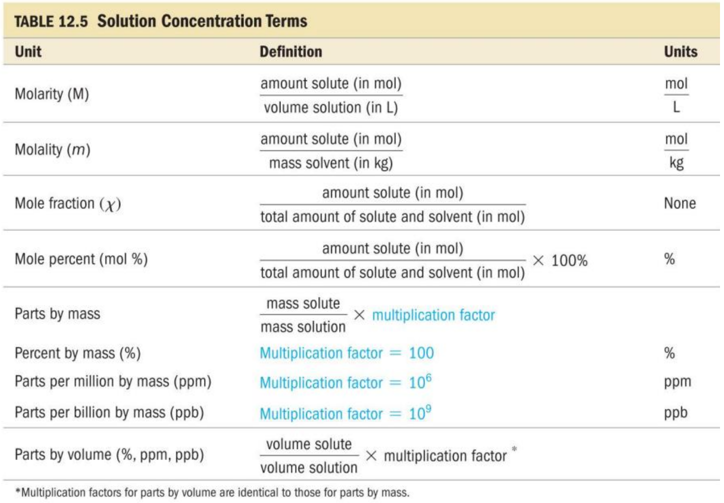


TABLE 12.5 Solution Concentration Terms

Unit	Definition	Units
Molarity (M)	$\frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$	$\frac{\text{mol}}{\text{L}}$
Molality (m)	$\frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$	$\frac{\text{mol}}{\text{kg}}$
Mole fraction (χ)	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}}$	None
Mole percent (mol %)	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} \times 100\%$	%
Parts by mass	$\frac{\text{mass solute}}{\text{mass solution}} \times$ multiplication factor	
Percent by mass (%)	Multiplication factor = 100	%
Parts per million by mass (ppm)	Multiplication factor = 10^6	ppm
Parts per billion by mass (ppb)	Multiplication factor = 10^9	ppb
Parts by volume (%, ppm, ppb)	$\frac{\text{volume solute}}{\text{volume solution}} \times$ multiplication factor*	

*Multiplication factors for parts by volume are identical to those for parts by mass.

N32

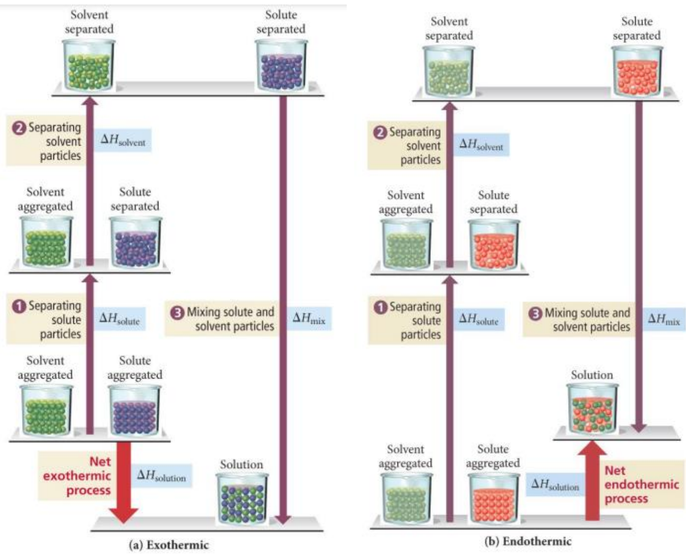
Energetics of Solution Formation: The Enthalpy of Solution

To make a solution you must

1. Overcome all attractions between the solute particles; therefore, ΔH_{solute} is endothermic. ΔH_1

2. Overcome some attractions between solvent molecules; therefore, $\Delta H_{solvent}$ is endothermic. ΔH_2

3. Form new attractions between solute particles and solvent molecules; therefore, ΔH_{mix} is exothermic. ΔH_3

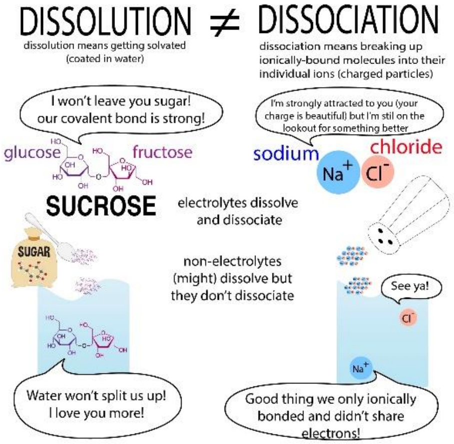


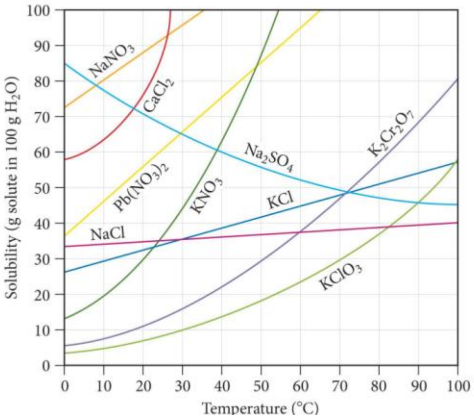
(a) Exothermic (b) Endothermic

TABLE 12.2 Relative Interactions and Solution Formation

Solvent-solute interactions	>	Solvent-solvent and solute-solute interactions	Solution forms
Solvent-solute interactions	=	Solvent-solvent and solute-solute interactions	Solution forms
Solvent-solute interactions	<	Solvent-solvent and solute-solute interactions	Solution may or may not form, depending on relative disparity

N33





N35

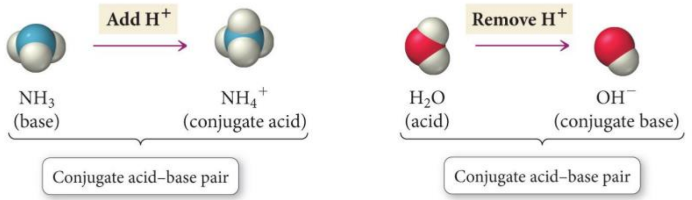
Will Something Precipitate?

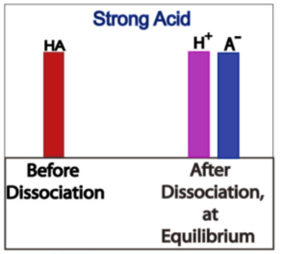
Q < K_{sp}	**No precipitate yet! The solution is unsaturated. All ions are still dissociated.**
Q = K_{sp}	**No precipitate yet! The solution is saturated. The maximum amount of ions are dissociated.**
Q > K_{sp}	**A precipitate will form! The maximum amount of ions are already dissociated, so the extra will "crash out" as a solid precipitate.**

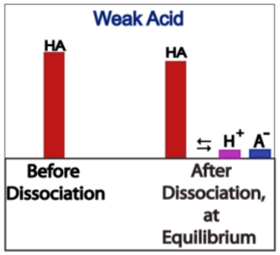
**Note* Supersaturated solutions have Q > K_{sp} but a ppt hasn't crashed out yet because it was made at a higher temperature and slowly cooled down. It is unstable and the ppt will crash out once the sol'n is disturbed.*

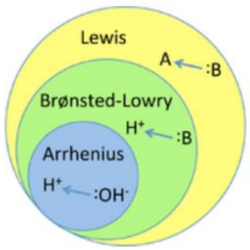
Unit 10 – ACID BASE – GLUE INS

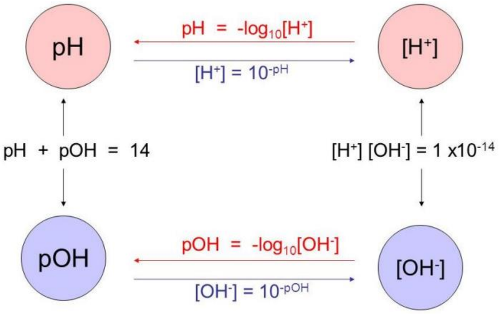
N36











N38

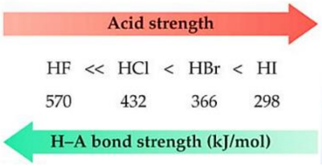
	Turns into a…	Hydrolyzes?
Strong Acid	Weaker conjugate base	No
Weak Acid	Stronger conjugate base	Yes
Strong Base	Weaker conjugate acid	No
Weak Base	Stronger conjugate acid	Yes

	Turns into a…	Hydrolyzes?	Ion makes sol'n
Strong Acid	**Weaker conjugate base**	No	Neutral
Weak Acid	**Stronger conjugate base**	Yes	Basic
Strong Base	**Weaker conjugate acid**	No	Neutral
Weak Base	**Stronger conjugate acid**	Yes	Acidic

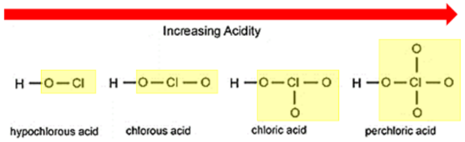
$Ka_{(ion)} > Kb_{(ion)}$	Acidic
$Ka_{(ion)} < Kb_{(ion)}$	Basic
$Ka_{(ion)} = Kb_{(ion)}$	Neutral

	Makes the solution…
Acidic + Neutral	Acidic
Basic + Neutral	Basic
Neutral + Neutral	Neutral
Acidic + Basic	Compare Ka and Kb to determine which "wins"

Strength of Binary Acids



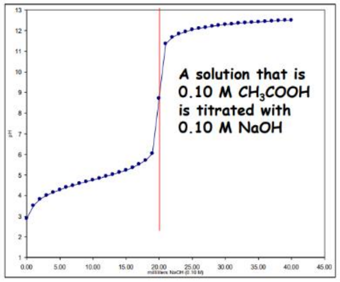
Strength of Oxyacids (and other similar)



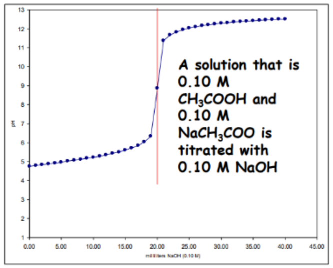
High electronegativity of the *side group* pulls electron density AWAY from the bond involving Hydrogen. Bond is therefore weakened so it breaks more easily, therefore more acidic.

N39

Weak Acid	Formula of the acid	Example of a salt of the weak acid
Hydrofluoric	HF	KF – Potassium fluoride
Formic	HCOOH	KHCOO – Potassium formate
Benzoic	C_6H_5COOH	NaC_6H_5COO – Sodium benzoate
Acetic	CH_3COOH	NaH_3COO – Sodium acetate
Carbonic	H_2CO_3	$NaHCO_3$ - Sodium bicarbonate
Propanoic	$HC_3H_5O_2$	$NaC_3H_5O_2$ - Sodium propanoate
Hydrocyanic	HCN	KCN - potassium cyanide


A solution that is 0.10 M CH_3COOH is titrated with 0.10 M NaOH

Weak Base	Formula of the base	Example of a salt of the weak acid
Ammonia	NH_3	NH_4Cl - ammonium chloride
Methylamine	CH_3NH_2	CH_3NH_3Cl – methylammonium chloride
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3NO_3$ - ethylammonium nitrate
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3Cl$ – aniline hydrochloride
Pyridine	C_5H_5N	C_5H_5NHCl – pyridine hydrochloride

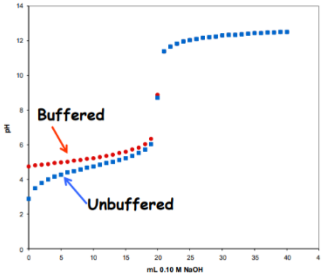

A solution that is 0.10 M CH_3COOH and 0.10 M $NaCH_3COO$ is titrated with 0.10 M NaOH

One way of doing these calculations

Rearrange your Law of Mass Action:

$$Ka = \frac{[H^+][A^-]}{[HA]} \rightarrow [H^+] = Ka\frac{[HA]}{[A^-]} \rightarrow = Ka\frac{[Acid]}{\underset{salt}{[conj.Base]}}$$

$$Kb = \frac{[BH^+][OH^-]}{[B]} \rightarrow [OH^-] = Kb\frac{[B]}{[BH^+]} \rightarrow = Kb\frac{[Base]}{\underset{salt}{[conj.Acid]}}$$



Henderson-Hasselbalch Equation

$$pH = pK_a + log\left(\frac{A^-}{HA}\right) \quad = pK_a + log\left(\frac{[Base]}{[Acid]}\right)$$

$$pOH = pK_b + log\left(\frac{BH^+}{B}\right) = pK_b + log\left(\frac{[Acid]}{[Base]}\right)$$

pKa = -log(Ka)
pKb = -log(Kb)

Just like pH = -log[H⁺]

The acids or bases may be conjugates from the salt!

Other ways to think about He-Ha

Acid with a buffer:

$$pH = pK_a + log\left(\frac{[salt]}{[Acid]}\right) = pK_a + log\left(\frac{[conj.Base]}{[Acid]}\right)$$

Base with a buffer:

$$pOH = pK_b + log\left(\frac{[salt]}{[Base]}\right) = pKb + log\left(\frac{[conj.Acid]}{[Base]}\right)$$

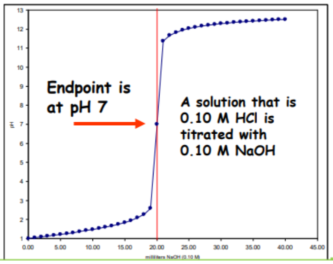
Suggestions…

Pick a method and stick to it. They all have pros and cons.

- **Ice tables**
  Pro = familiar Con = takes forever, lots of steps
- **He-Ha**
  Pro = fast, on the AP eq. sheet Con = Have to recognize to use it, not always solving for pH
- **Rearranging Law of Mass Action**
  Pro = simple Con = Have to recognize to use it, extra step to get to pH or pOH

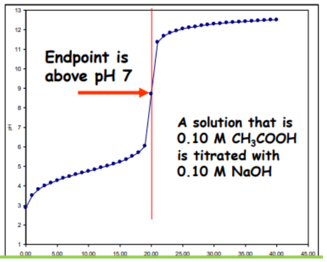
N41

Strong Acid/Strong Base Titration


Endpoint is at pH 7

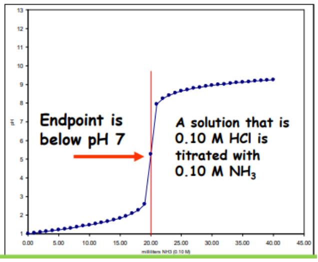
A solution that is 0.10 M HCl is titrated with 0.10 M NaOH

Weak Acid/Strong Base Titration


Endpoint is above pH 7

A solution that is 0.10 M CH_3COOH is titrated with 0.10 M NaOH

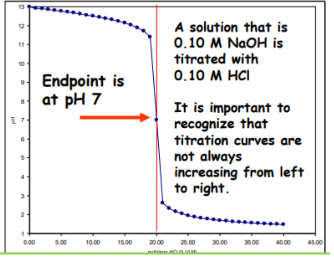
Strong Acid/Weak Base Titration



Endpoint is below pH 7

A solution that is 0.10 M HCl is titrated with 0.10 M NH_3

Strong Acid/Strong Base Titration



Endpoint is at pH 7

A solution that is 0.10 M NaOH is titrated with 0.10 M HCl

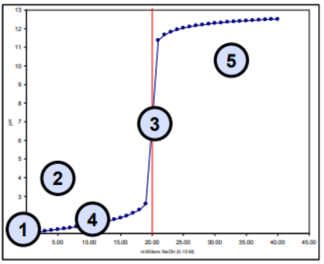
It is important to recognize that titration curves are not always increasing from left to right.

Titration Calculations…

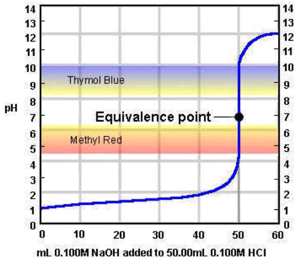
1. **Starting pH**
   - ICE table then pH
2. **Early on during titration**
   - Stoich then He-Ha
3. **Equivalence Point**
   - mol acid = mol base
   - No more buffer! Reverse rxn
   - Calc new K value - ICE then pH
4. **½ Way Point**
   - ½ moles @ eq.pt
   - pH = pKa
5. **Towards end of titration**
   - Extra titrant left over
   - Stoich then simple pH

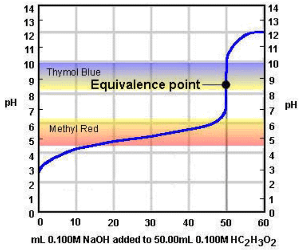
Calculations to Plot a Titration Curve

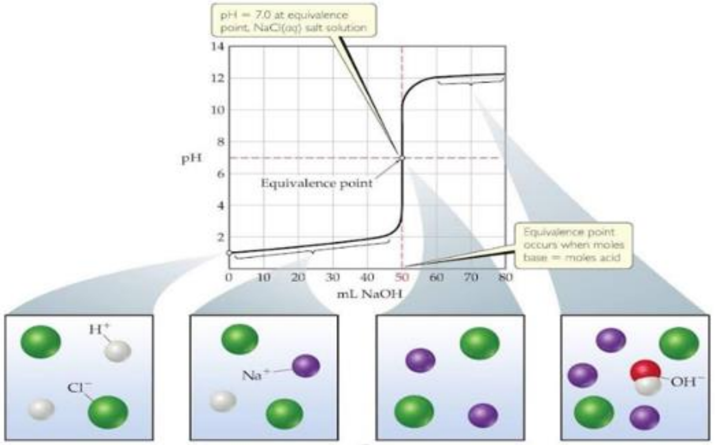
1. **Starting pH**
   - ICE table then pH
2. **Early on during titration**
   - Stoich then He-Ha
3. **Equivalence Point**
   - mol acid = mol base
   - No more buffer! Reverse rxn
   - Calc new K value - ICE then pH
4. **½ Way Point**
   - ½ moles @ eq.pt
   - pH = pKa
5. **Towards end of titration**
   - Extra titrant left over
   - Stoich then simple pH



Indicator	pH Range in which Color Change Occurs	Color Change as pH Increases
Crystal violet	0.0 - 1.6	yellow to blue
Thymol blue	1.2 - 2.8	red to yellow
Orange IV	1.4 - 2.8	red to yellow
Methyl orange	3.2 - 4.4	red to yellow
Bromcresol green	3.8 - 5.4	yellow to blue
Methyl red	4.8 - 6.2	red to yellow
Chlorophenol red	5.2 - 6.8	yellow to red
Bromthymol blue	6.0 - 7.6	yellow to blue
Phenol red	6.6 - 8.0	yellow to red
Neutral red	6.8 - 8.0	red to amber
Thymol blue	8.0 - 9.6	yellow to blue
Phenolphthalein	8.2 - 10.0	colourless to pink
Thymolphthalein	9.4 - 10.6	colourless to blue
Alizarin yellow	10.1 - 12.0	yellow to blue
Indigo carmine	11.4 - 13.0	blue to yellow







pH = 7.0 at equivalence point. NaCl(aq) salt solution

Equivalence point occurs when moles base = moles acid

Only HCl(aq) present before titration

H^+ consumed as OH^- added, forming H_2O. Still have HCl. Some conjugate is formed. BUFFER

H^+ completely neutralized by OH^-. Only conjugate left

No H^+ left to react with excess OH^-, now there is conjugate and excess OH^-

N40

[14] When solid BaF_2 is added to H_2O the following equilibrium is established.

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,F^-(aq) \quad K_{sp} = 1.5\times10^{-6} \text{ at } 25\ °C$$

a. Calculate the molar solubility of barium fluoride at 25 °C.

b. Explain how adding each of the following substances affects the solubility of BaF_2 in water.
   i. 0.10 M $Ba(NO_3)_2$
   ii. 0.10 M HNO_3

c. In an experiment to determine the K_{sp} of PbF_2 a student starts with 0.10 M $Pb(NO_3)_2$ and 0.10 M KF and uses the method of serial dilutions to find the lowest $[Pb^{2+}]$ and $[F^-]$ that form a precipitate when mixed. If the student uses the concentration of the ions in the combined solution to determine K_{sp}, will the value of K_{sp} calculated be too large, too small or just right? Explain.
   K_{sp} for $PbF_2 = 4.0 \times 10^{-8}$

d. i. In a solution of 0.010 M barium nitrate and 0.010 M lead(II) nitrate, which will precipitate first, BaF_2 or PbF_2, as NaF(s) is added? Assume volume changes are negligible. Explain (support your answer with calculations).
   ii. When the more soluble fluoride begins to precipitate, what is the concentration of the cation for the less soluble fluoride that remains in solution?

Unit 11– ELECTROCHEMISTRY – GLUE INS

N42

Rules for Assigning Oxidation Numbers

1. Any uncombined element is 0.
2. Monatomic ion equals the charge on the ion.
3. The more-electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.
4. Fluorine in a compound is always -1
5. Oxygen is -2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is -1
6. Hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is -1
7. In compounds, the elements of groups 1 and 2 as well as aluminum have oxidation numbers +1, +2 and +3 respectively.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals charge of the ion.

$$1\,A = \frac{1\ Coulomb}{1\ second} = \frac{6.242 \times 10^{18} e^-}{1\ second}$$

$$1\ Volt = \frac{1\ Joule}{1\ Coulomb}$$

$$1\ Faraday = \frac{96,500\ Coulombs}{1\ mol\ e^-}$$

Balancing Redox Equations

More complicated than balancing normal reactions.

You have to balance the electrons, not just the atoms!

Steps

1. Assign oxidation numbers to determine which things are oxidized and which are reduced.
2. Split the rxn into two halves – oxidation half and reduction half. Include electrons.
3. Balance the atoms.
4. Balance the charge by balancing the number of electrons.
5. Add half reactions back together, simplify, and CHECK.

Mnemonics

LEO goes GER
Loss of Electrons is Oxidation
Gain of Electrons is Reduction

OIL RIG
Oxidation is Loss of Electrons
Reduction is Gain of Electrons

Anode is Oxidation

Reduction at the Cathode

Anode The electrode where oxidation occurs

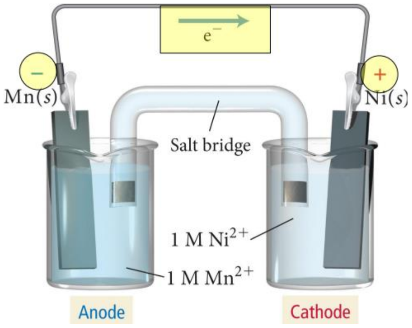
Cathode The electrode where reduction occurs

Oxidation and Reduction Recap

Oxidation is the process that occurs when
- the oxidation number of an element increases,
- an element loses electrons,
- a compound adds oxygen,
- a compound loses hydrogen, or
- a half-reaction has electrons as products.

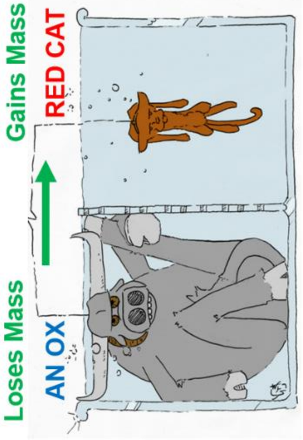
Reduction is the process that occurs when
- the oxidation number of an element decreases,
- an element gains electrons,
- a compound loses oxygen,
- a compound gains hydrogen, or
- a half-reaction has electrons as reactants.

N44



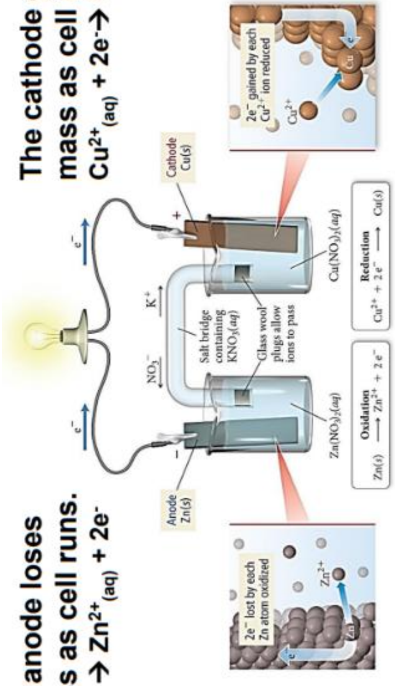
Galvanic
- Converts chemical energy into electrical energy.
- Positive cell potential, $E°_{cell}$ = +
- Spontaneous, negative free energy difference, ΔG = -
- Anode = - and Cathode = +
- Electrons supplied by the chemical being oxidized.
- Electrons flow from anode to cathode.

Electrolytic
- Converts electrical energy into chemical energy
- Negative cell potential, $E°_{cell}$ = -
- NOT spontaneous, positive free energy difference, ΔG = +
- Anode = + and Cathode = -
- Electrons supplied by an external source
- Electrons enter from the cathode and come out at the anode.



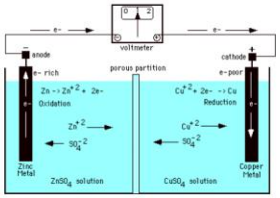
a RED CAT gains, what AN OX loses

The cathode gains mass as cell runs.
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$



The anode loses mass as cell runs.
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Line Notation



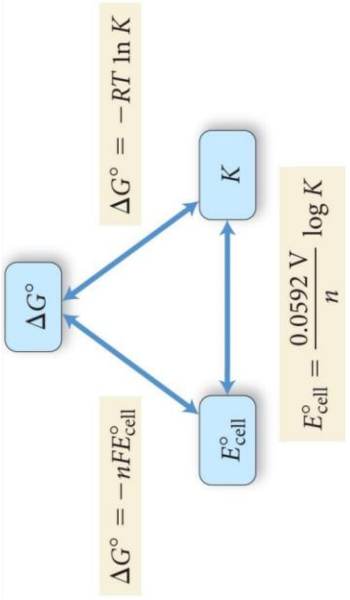
Zn(*s*) | Zn^{2+}(*aq*) || Cu^{2+}(*aq*) | Cu(*s*)

Anode material	|	Anode solution	||	Cathode solution	|	Cathode material

Requirements for Drawing/Labeling a Cell

- ☐ Determine what is reduced vs. oxidized ($E°_{cell}$ values, OR told which rxn to do)
- ☐ Beaker/container for anode and cathode AND liquid line drawn for each beaker
- ☐ Anode/cathode metal strips drawn submerged in liquid
- ☐ Label which solution/ions are in each beaker
- ☐ Label which beaker is anode and cathode
- ☐ Label anode/cathode strips with which solid metal each is
- ☐ Label anode and cathode with correct -/+ depending on if it is a galvanic cell (A-/C+) or electrolytic cell (A+/C-).
- ☐ Write the half reactions for each beaker
- ☐ Wire connecting anode/cathode strips together
- ☐ Label direction of e- flow along wire at top of drawing (anode → cathode always)
- ☐ Salt bridge submerged in liquid on both sides
- ☐ Label direction of ion flow inside salt bridge (anions flowing to anode, cations flowing to cathode)

N45

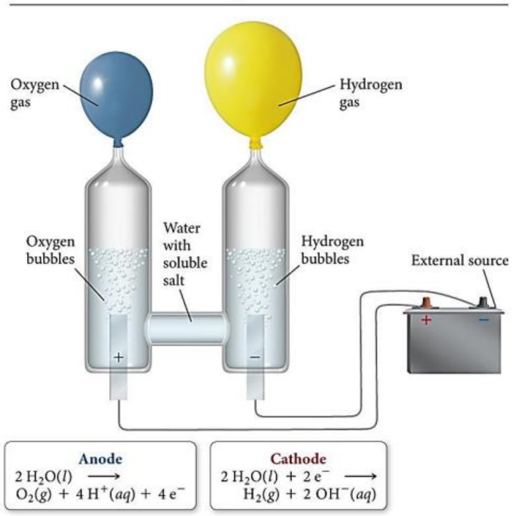


$$\Delta G° = -RT \ln K$$

$$E°_{cell} = \frac{0.0592\ V}{n} \log K$$

$$\Delta G° = -nFE°_{cell}$$

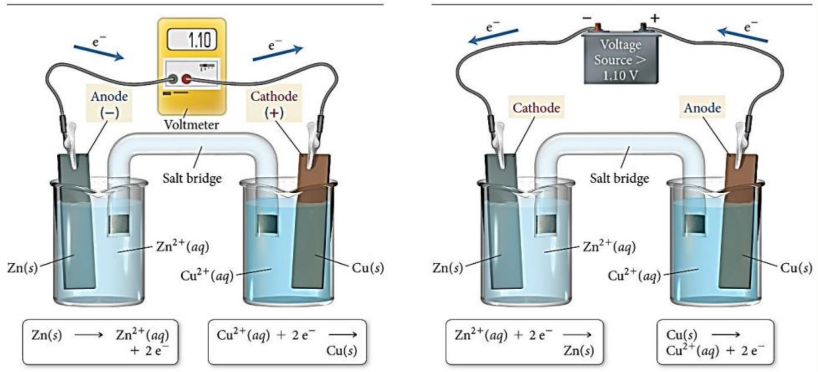
Electrolysis of Water



Voltaic versus Electrolytic Cells

Voltaic Cell

Electrolytic Cell



In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.

In voltaic cells

- Anode is the source of electrons and has a (−) charge.
- Cathode draws electrons and has a (+) charge.

In electrolytic cells

- Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
- Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery.

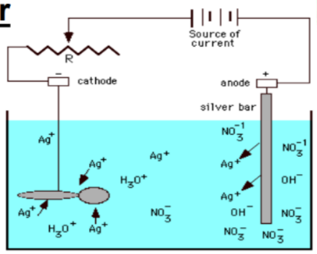
Standard Conditions and Nonstandard Conditions for the Zn/Cu Galvanic Cell

Equation	$E°$	$\Delta G°$	K
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	+1.10 V	−212 kJ/mol	1.5×10^{37}

$$E = E° - \frac{RT}{nF} \ln Q \qquad Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Farther Away From Equilibrium than Standard Conditions	Standard Conditions	Closer To Equilibrium than Standard Conditions	At Equilibrium The cell is "dead"
$Q < 1$	$Q = 1$	$Q > 1$	$Q = K = 1.5 \times 10^{37}$
$E > E°$	$E = E°$	$E < E°$	E = zero
$[Zn^{2+}] < [Cu^{2+}]$	$[Zn^{2+}] = [Cu^{2+}]$	$[Zn^{2+}] > [Cu^{2+}]$	$[Zn^{2+}] >> [Cu^{2+}]$
decreased [product] or increased [reactant] compared to standard conditions	[product] = [reactant]	increased [product] or decreased [reactant] compared to standard conditions	

Electroplating of Silver



Anode reaction:

$Ag \rightarrow Ag^+ + e^-$

Cathode reaction:

$Ag^+ + e^- \rightarrow Ag$

Electroplating requirements:

1. **Solution of the plating metal**
2. **Anode made of the plating metal**
3. **Cathode with the object to be plated**
4. **Source of current**