

Chemistry 120

Reactions in Aqueous Solution

Solutions

- Homogenous Mixtures
- Composed of Two or More Components
 - *Solvent*: component present in greatest amount
 - *Solutes*: everything else that is *dissolved in the solvent*
- Solutions occur in any State of Matter
 - Atmosphere, alloys
 - Most have liquid solvents (H₂O)

Describing Solutions

- *Concentration*
 - Amount of solute per amount of solvent
- Behavior of Solutes in Solution based on Solution's Conductivity
 - *Non-electrolytes*
 - *Weak electrolytes*
 - *Strong electrolytes*
- *Solubility* of a Solute in a Solvent
 - Maximum amount of solute that will dissolve

Concentration

- Common Concentration Units
 - Molarity (M): moles of solute per liter of solution
 - Molality (m): moles of solute per kg solvent
 - Normality (N): equivalents of solute per liter of solution
 - % by weight: g solute per 100 g of solution
 - % by volume: mL solute per 100 mL solution
 - ppm: parts per million (e. g., mg/kg)

Calculating Concentrations

- A solution contains 50.0 g NaCl per 500.0 mL of the solution. What is the molarity of NaCl in the solution?

$$50.0 \text{ g NaCl} \left(\frac{1 \text{ mole NaCl}}{58.4425 \text{ g NaCl}} \right) = 0.855_s \text{ mole NaCl}$$

$$\frac{0.855_s \text{ mole NaCl}}{0.5000 \text{ L}} = 1.71 \text{ M NaCl}$$

Concentrations are written using "[]".
So you will often see: $[\text{NaCl}] = 1.71 \text{ M}$.

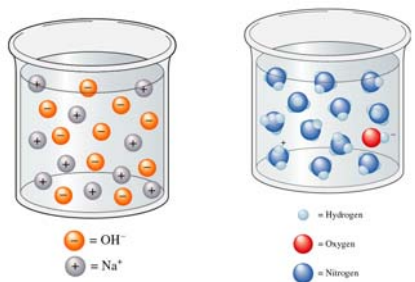
Describing Solute's Behavior

- Shown in Chemical Equation
- Non-Electrolytes
 - Do not break up into ions when dissolve
 - Mostly molecular compounds
 - Example: ethanol in water = $\text{C}_2\text{H}_5\text{OH} (\text{aq})$
- Strong Electrolytes
 - Break up into ions when dissolve
 - Mostly ionics with some molecular
 - Example: $\text{NaCl} (\text{aq}) = \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq})$

Describing Solute's Behavior

- Weak Electrolytes
 - Partially break up into ions when dissolve
 - Undissociated species still present
 - Usually molecular with some ionics
 - Example: $\text{H}_3\text{PO}_4(\text{aq}) = \text{H}_3\text{PO}_4(\text{aq}) + \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$
 - Example: $\text{NH}_3(\text{aq}) = \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - Amount of ions formed described by *equilibrium constant(s)*

Pictorial Representation



Strong Electrolyte

Weak Electrolyte

Ion Concentrations

- Strong Electrolytes completely dissociate
 - A 1.00 M NaCl solution has $[\text{Na}^+] = 1.00 \text{ M}$ and $[\text{Cl}^-] = 1.00 \text{ M}$
 - But in a 1.00 M Na_2SO_4 $[\text{Na}^+] = 2.00 \text{ M}$ and $[\text{SO}_4^{2-}] = 1.00 \text{ M}$
- Weak Electrolytes do not dissociate completely
 - Don't necessarily give ion concentrations
 - When ion concentrations needed, calculate from equilibrium constant(s)

Solubility

- Solids
 - Finite solubility in liquid and solid solvents
 - Some have higher solubility (*soluble*) than others (*insoluble* or *slightly soluble*)
- Liquids
 - Liquids that dissolve in each other are *miscible*
 - Liquids that do not are *immiscible*
- Gases
 - Finite solubilities in solids and liquids
 - Infinitely soluble in other gases

Methods of Preparing Solutions

- With a Solid Reagent
 - Concentration from mass and sol'n volume
 - Concentration to mass using sol'n volume
- With a Liquid Reagent
 - Either by mass or volume (density)
- From another Solution (*Dilution*)
 - Volume of *stock solution* from its concentration and new sol'n volume

Preparing Solution from Solid

- What amount of KMnO_4 (in grams) is needed to prepare 250.0 mL of a solution that has a $[\text{MnO}_4^-]$ of 0.110 M?

Find the number of moles MnO_4^- needed.

Convert moles MnO_4^- to grams KMnO_4 .

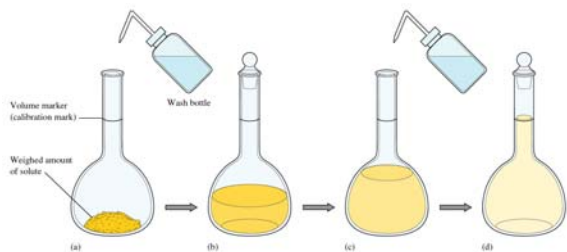
Preparing Solution from Solid

- Shortcut: can do Complete Calculation with Daisy-chained Conversion Factors

$$250.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.110 \text{ mole MnO}_4^-}{1 \text{ L}} \right) \left(\frac{1 \text{ mole KMnO}_4}{1 \text{ mole MnO}_4^-} \right) \left(\frac{158.03 \text{ g KMnO}_4}{1 \text{ mole KMnO}_4} \right) = 4.35 \text{ g KMnO}_4$$

Preparing Solution from Solid

- Precise Method with Volumetric Flask



Preparing Solution from a Solution

- How many mL of the 0.110 M MnO_4^- solution do we need to prepare 250.0 mL of a 0.0110 M MnO_4^- solution?

Calculate the number of moles needed.

And now the volume.

Preparing Solution from a Solution

- Shortcut: to determine the Volume (or Concentration) of a Solution involved in a Dilution use: $C_i \cdot V_i = C_d \cdot V_d$

$$C_i V_i = C_d V_d$$

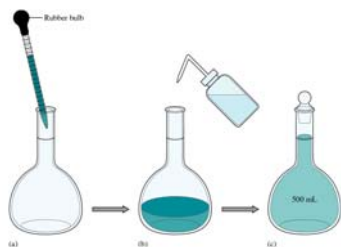
$$(0.110 \text{ M})V_i = (0.0110 \text{ M})(250.0 \text{ mL})$$

$$V_i = 25.0 \text{ mL}$$

When done this way, no need to convert mL to liters!

Preparing Solution from a Solution

- Precise Method using Volumetric Pipet



Serial Dilutions

- If 10.0 mL of a 0.110 M MnO_4^- solution is diluted to 100.0 mL and then 10.0 mL of the resulting solution is diluted to 100.0 mL, what is the final $[\text{MnO}_4^-]$?

Calculate the number of moles in 10.0 mL of solution.

Calculate the new concentration.

Serial Dilutions

Now repeat using 10.0 mL of new solution.

Calculate the new concentration.

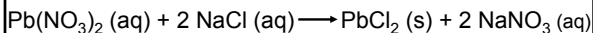
- Shortcut: multiply Initial Concentration by Ratio of each Dilution

$$\left(\frac{10.0 \text{ mL}}{100.0 \text{ mL}}\right) \left(\frac{10.0 \text{ mL}}{100.0 \text{ mL}}\right) \left(\frac{0.110 \text{ mole MnO}_4^-}{1 \text{ L}}\right) = 1.10 \times 10^{-3} \text{ M MnO}_4^-$$

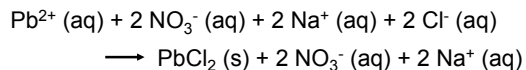
Writing Chemical Equations for Reactions in Solution

- Same as for other Reactions
 - Indicate in solution with (aq) (water solvent)
- For Reactions of Ionic Species can simplify Chemical Equation
 - *Net ionic equation*
 - *Spectator ions*
 - Weak electrolytes, non-electrolytes
 - Solids, liquids, gases
 - Charge balance

Net Ionic Equation Example

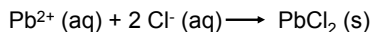


Write out everything as it actually exists.

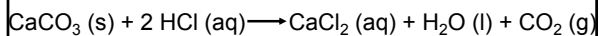


Note NO_3^- , Na^+ and Cl^- do not change.

So, "cancel" from both sides, leaving



Net Ionic Equation Example



Net ionic equation is a generalized chemical equation.

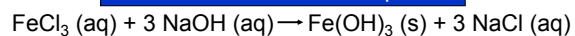
Solution Stoichiometry

- Same as for Reactions not in Solution
- Always convert from Laboratory-scale Measurement to Moles
- Ways of expressing Amount of Material
 - Mass (grams)
 - Volume (mL) and concentration (M)
 - Molarity most often used, but others are similar

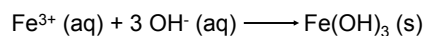
Solution Stoichiometry

- To 25.0 mL of 0.234 M FeCl_3 is added 42.5 mL of 0.435 M NaOH . What is the theoretical yield of $\text{Fe}(\text{OH})_3$?

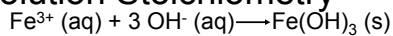
Write balanced chemical equation.



Or use the net ionic equation.



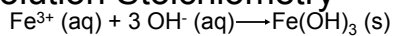
Solution Stoichiometry



volume	25.0	42.5	----
conc.	0.234	0.453	----
grams	----	----	?
molar mass	----	----	106.87
moles	5.85×10^{-3}	$1.92_5 \times 10^{-2}$	

Calculate moles of Fe^{3+} and moles OH^{-} .

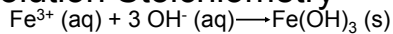
Solution Stoichiometry



volume	25.0	42.5	----
conc.	0.234	0.453	----
grams	----	----	?
molar mass	----	----	106.87
moles	5.85×10^{-3}	$1.92_5 \times 10^{-2}$	

Calculate limiting reagent

Solution Stoichiometry



volume	25.0	42.5	----
conc.	0.234	0.453	----
grams	----	----	0.625
molar mass	----	----	106.87
moles	5.85×10^{-3}	$1.92_5 \times 10^{-2}$	(5.85×10^{-3})

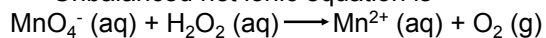
Titration

- Special Case where a *Stoichiometric Amount* of each Reactant is added
- One Reagent (*Titrant*) added to other Reactant in Solution until they have exactly reacted with each other
 - Process is called a *titration*
 - Volume of titrant where reactants exactly match is *equivalence point*

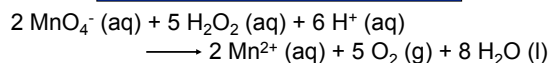
Titration Example

- An acidic aqueous solution contains an unknown amount of H_2O_2 . If it takes 15.01 mL of a 0.110 M KMnO_4 solution to reach the equivalence point, how many grams of H_2O_2 are in the solution?

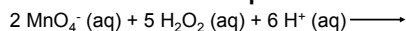
Unbalanced net ionic equation is



Write balanced chemical equation.



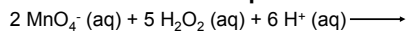
Titration Example



volume	15.01	----
conc.	0.110	----
grams	----	?
molar mass	----	34.01
moles	$1.65_1 \times 10^{-3}$	

Calculate moles of MnO_4^- .

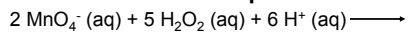
Titration Example



volume	15.01	----
conc.	0.110	----
grams	----	?
molar mass	----	34.01
moles	$1.65_1 \times 10^{-3}$	$4.12_8 \times 10^{-3}$

Calculate moles of H_2O_2 .

Titration Example



volume	15.01	----
conc.	0.110	----
grams	----	0.140
molar mass	----	34.01
moles	$1.65_1 \times 10^{-3}$	$4.12_8 \times 10^{-3}$

Calculate grams of H_2O_2 .

Final Word on Titrations

- Phrases that indicate Titrations
 - How much (what volume) _____ is needed to exactly react (react completely) with
 - Volume of _____ needed to reach (titrate to) the equivalence point
 - What is the concentration of _____ (how much _____ is present), given a volume and concentration of titrant
 - Is titrated with _____ to the equivalence point

Types of Reactions

- Precipitation Reactions
 - Solid (*precipitate*) forms when two solutions mixed
- Acid-Base Reactions
 - Also known as neutralization reactions
- Redox Reactions
 - Primarily involve movement of electrons
- Gas-forming Reactions
 - Gas formed when two solutions mixed

Precipitation Reactions

- Formation of Precipitate depends on Solubility of Product(s)
 - Balance of forces holding particles in solid state versus those present in solution
- Most Molecular Compounds are insoluble in Water
 - Exceptions: HX (X=halogen), NH₃, methanol, ethanol, etc.
- Many Ionic Compounds are soluble

Solubility of Ionic Compounds

- Two Groupings
 - Those that dissolve well in water (*soluble*): NaCl, KCl, KOH, etc.
 - Those whose water solubility is very small (*insoluble*): BaSO₄, PbCl₂, Fe(OH)₃, etc.
- Most are strong Electrolytes despite Solubility
 - Insoluble ionics are still strong electrolytes
 - Total number of ions present small

General Rules for Solubility

Generally Soluble Compounds

<i>Compound Type</i>	<i>Exceptions</i>
Salts of Na ⁺ , K ⁺ , NH ₄ ⁺	KClO ₄
All salts of Cl ⁻ , Br ⁻ , I ⁻	Ag ⁺ , Hg ₂ ²⁺ , Pb ²⁺ , HgI ₂
Salts containing F ⁻	MgF ₂ , CaF ₂ , SrF ₂ , BaF ₂ , PbF ₂
Salts of NO ₃ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , C ₂ H ₃ O ₂ ⁻	KClO ₄ , AgC ₂ H ₃ O ₂ , Hg ₂ (C ₂ H ₃ O ₂) ₂
Compounds containing SO ₄ ²⁻	SrSO ₄ , BaSO ₄ , PbSO ₄
Most SO ₃ ²⁻ salts	

General Rules for Solubility

Generally Insoluble Compounds

<i>Compound Type</i>	<i>Exceptions</i>
All salts of CO ₃ ²⁻ , PO ₄ ³⁻ , C ₂ O ₄ ²⁻ , CrO ₄ ²⁻ , S ²⁻	Compounds of NH ₄ ⁺ and alkali metal cations
Most compounds of metal ions with O ²⁻ and OH ⁻	NH ₄ ⁺ and alkali metal cations, Sr(OH) ₂ and Ba(OH) ₂ are fairly soluble

Predict Solubilities

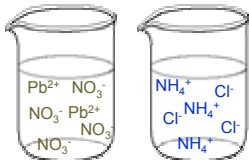
Compound	Soluble ?	Compound	Soluble ?
NaCl		Ba(OH) ₂	
BaSO ₄		CaF ₂	
Mg ₃ (PO ₄) ₂		AgNO ₃	
PbS		NH ₄ C ₂ H ₃ O ₂	
Fe(OH) ₃		KMnO ₄	
KOH		MnO ₂	
MgSO ₄		Ag ₂ SO ₄	

Using Solubility Rules to predict Precipitation Reactions

- What happens when Aqueous Solution of NH_4Cl and an Aqueous Solution of $\text{Pb}(\text{NO}_3)_2$ are mixed?

– Both compounds are ionic and are strong electrolytes

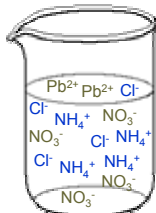
Both are completely dissociated!



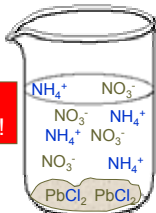
Using Solubility Rules to predict Precipitation Reactions

Do we get this?

We get this.



No! Consider solubility rules!



The dissociated ions coexisting in the solution.

PbCl_2 is insoluble and precipitates from solution.

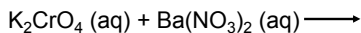
Using Solubility Rules to predict Precipitation Reactions

- Know Solubility Rules
- Take Ions present in Solution initially
 - Look for a Combination that is insoluble
 - Switch partners
- No insoluble combination = no reaction
- Determine other Product(s) from Spectator Ions
- Balance

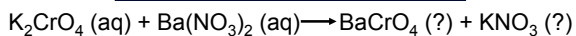
Using Solubility Rules to predict Precipitation Reactions

- Write the balanced Chemical Equation for what happens when an aqueous K_2CrO_4 solution is mixed with an aqueous $Ba(NO_3)_2$ solution.

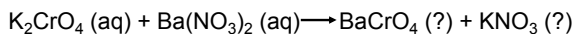
Write reactants.



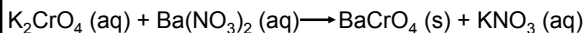
Switch partners to form products.



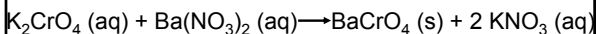
Using Solubility Rules to predict Precipitation Reactions



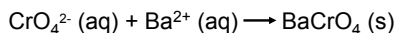
Use solubility rules to predict whether precipitate forms.



Balance.



What is net ionic equation?



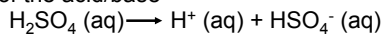
Acids and Bases

- Special Families of Electrolytes
 - *Acids* increase the amount of $H^+(aq)$
 - Examples: HCl , H_2SO_4 , $HC_2H_3O_2$
 - *Bases* increase the amount of $OH^-(aq)$
 - Examples: KOH , $Mg(OH)_2$, NH_3
- Further Classification
 - *Strong* fully dissociate in solution
 - *Weak* don't fully dissociate in solution
- Weak/Strong is independent of Amount!

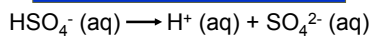
Special Acids and Bases

- Polyprotic Acids/Bases

- Add more than one mole H^+/OH^- per mole of the acid/base

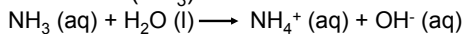


100% dissociated strong acid



<100% dissociated weak acid

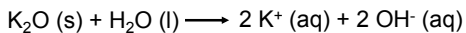
- Ammonia (NH_3) is a Weak Base



Even though NH_3 contains no OH^- it is a base.

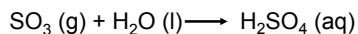
Special Acids and Bases

- Metal Oxides are Basic



Note that $K^+(aq) + OH^-(aq) = KOH(aq)$

- Non-Metal Oxides are Acidic



Note that $H_2SO_4(aq) = H^+(aq) + HSO_4^-(aq)$

General Rules for Acid/Base Strength

- Most Acids are Weak

- Except mineral acids: HCl , HNO_3 , HBr , HI , $HClO_4$, $HClO_3$, H_2SO_4 (first H^+ only)

- Anions formed from Polyprotic Acids are Weak Acids

- Examples: HSO_4^- , HCO_3^- , $H_2PO_4^{2-}$

- Group 1 and 2 Hydroxides are Strong Bases

- Exception: $Be(OH)_2$

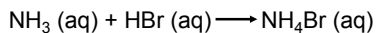
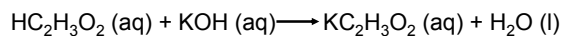
Reactions of Strong Acids and Bases

- Strong Acids and Bases react to form H_2O and a Salt
 $KOH(aq) + HCl(aq) \longrightarrow KCl(aq) + H_2O(l)$
- Net Ionic Equation
 $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$
Remember $KOH(aq) = K^+(aq) + OH^-(aq)$
and $HCl(aq) = H^+(aq) + Cl^-(aq)$
- Weak Acids and Bases reactions are similar, but more Complicated

Reactions of Weak Acids and Bases

- Remember Weak Acids/Bases do not dissociate Completely
 - Have molecules and ions in solution
 - Who reacts?
- Overall the Reaction is the Same
 - Acid + base gives a salt and water
 - Watch out for the net ionic equation!
 - Watch out for NH_3 !

Net Ionic Equations involving Weak Acids and Bases



Oxidation-Reduction Reactions

- Reactions predominantly involve only moving Electrons (*Electron Transfer*)
 - Some will also move atoms
- *Oxidation* is loss of electrons (or gaining oxygen atoms)
- *Reduction* is gain of electrons (or losing oxygen atoms)
- Need Way to track Electrons
 - *Oxidation numbers*

Rules for Oxidation Numbers

- Elements have oxidation numbers of “0”
- Oxidation number of monatomic ion = charge
- F is always “-1” when combined
- Cl, Br and I are “-1” except with O or F
- H is usually “+1” except with metal then “-1”
- O is usually “-2” except in peroxides where “-1”
- Sum of oxidation numbers must equal charge on the species

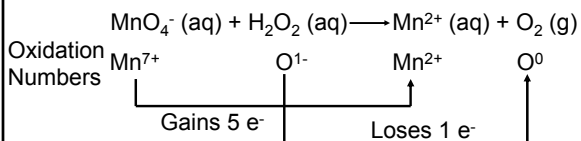
Determine Oxidation Numbers

Species	Oxid. Num.	Species	Oxid. Num.
N ₂		CO ₂	
NaH		CO	
KCl		V ₂ O ₃	
ClO ₄ ⁻		CoCl ₂	
O ₂		H ₂ O ₂	
Hg ₂ ²⁺		K ₂ Cr ₂ O ₇	
PF ₆ ⁻		LiAlH ₄	

Oxidation-Reduction Reactions

- Must have an *Oxidant* and a *Reductant*
- Oxidant
 - Causes *something else* to be oxidized
 - It is reduced (gains electrons)
 - Its oxidation number becomes more negative
- Reductant
 - Causes *something else* to be reduced
 - It is oxidized (loses electrons)
 - Its oxidation number becomes more positive

Identifying Oxidants and Reductants



MnO₄⁻ gains 5 e⁻, and is reduced. It is the oxidant.

H₂O₂ loses 2 e⁻, and is oxidized. It is the reductant.

Balancing Redox Reactions

- Can't Simply Balance Atoms, Electrons gained/lost must also be Balanced
- Balancing a Redox Reaction will depend on whether the Reaction is run under Acidic or Basic Conditions
- First Step is always to separate Overall Reaction into Two Half-Reactions
 - One is reduction, other oxidation

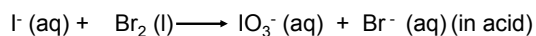
Balancing Redox

- Recognize Redox
- Separate into Half-Reactions
- Balance each Half-Reaction for Mass
 - Add H₂O to side deficient in oxygen, add H⁺ to other side to balance
- Balance Half-Reactions for Charge by adding Electrons to one Side
- Balance Electrons by Multiplying each Half-Reaction by Integers

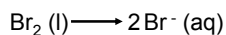
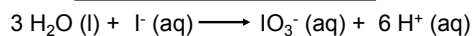
Balancing Redox

- Add the Half Reactions
- Simplify by Removing Species that appear on Both Sides
- Check that Equation is Balanced
 - If in acidic solution, done
 - In basic solution “neutralize” by adding OH⁻ to both sides equal to number of H⁺ in equation

Balancing Redox



Separate into half-reactions.

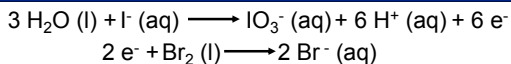


Balance half-reactions for mass.

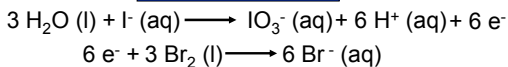
Add H₂O to side of each half-reaction that is deficient in O, and H⁺ to other side to balance.

Balancing Redox

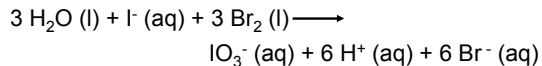
Balance half-reactions for charge by adding electrons.



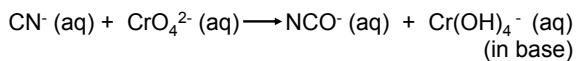
Balance electrons.



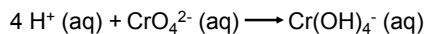
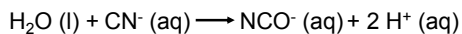
Add half-reactions and simplify.



Balancing Redox



Separate into half-reactions.

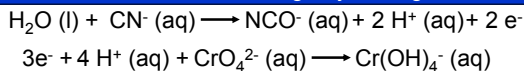


Balance half-reactions for mass.

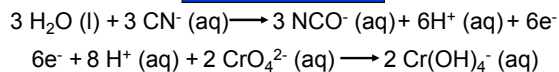
Add H^+ and H_2O as appropriate.

Balancing Redox

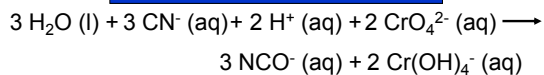
Balance half-reactions for charge by adding electrons.



Balance electrons.

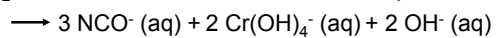
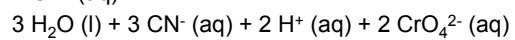
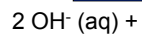


Add half-reactions and simplify.



Balancing Redox

Since this reaction is in base, add OH^- .



Combine H^+ and OH^- to form H_2O , and simplify.

