

Pauling Scale of Electronegativities for the Various Elements

1 H 2.1																				
3 Li 1.0	4 Be 1.5																	5 B 2.0		
11 Na 0.9	12 Mg 1.2																	13 Al 1.5		
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.8	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr 2.0			
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe 2.8			
55 Cs 0.7	56 Ba 0.9	57 La 1.1-1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn ---			
87 Fr 0.7	88 Ra 0.9	89-103 Ac 1.1-1.3	104 Ku ---	105 Ha ---																

PREDICTING PRODUCTS OF INORGANIC REACTIONS IN AQUEOUS SOLUTION

This handout organizes and summarizes sets of rules based on empirical inorganic chemistry which allow the following questions to be answered:

- I. Is a given compound soluble?
- II. Will a given compound dissociate?
- III. What are the products of a given reaction?
- IV. Will a given reaction occur?

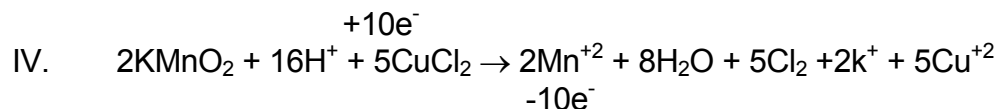
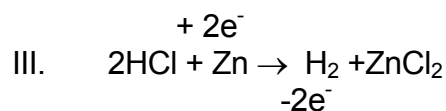
Suggested prerequisites for the material covered in this lab are: atomic structure, periodic properties, bonding, electronegativity, and inorganic nomenclature. Balancing chemical equations, a topic covered in most general chemistry textbooks, nicely complements the material covered in this lab, however, the goals of predicting products in chemical reactions and determining the major direction of reactions can be achieved without recourse to balance equations.

Inorganic chemical reactions can be broken into two broad classes: first, metathesis reactions (double displacement reactions) in which there are no changes in oxidation numbers; second, oxidation-reduction reactions in which there are changes in oxidation numbers (electrons are transferred from one atom, molecule or ion to another). The first part of this lab treats metathesis reactions; the second part treats oxidation-reduction reactions.

Balanced examples of metathesis reactions:

- I. $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{HNO}_3$
- II. $2\text{KOH} + \text{Pb}(\text{ClO}_3)_2 \rightarrow \text{Pb}(\text{OH})_2 + 2\text{KClO}_3$

Balanced examples of oxidation-reduction reactions include:



PART I: METATHESIS REACTIONS

The driving force for metathesis reactions is the removal of ions from solution. Therefore, to predict the direction of a metathesis reaction one simply determines the degree of removal of ions from solution by the reactants and products. Prediction products is trivial: cations and anions merely exchange as illustrated in Examples I and II. Note that electroneutrality is maintained. There are only two ways in which ions can be removed from solution: insolubility and degree of ionic association. Although qualitative (Handbook of Chemistry and Physics, The Chemical Rubber Co.) and quantitative (Handbook of Chemistry, Handbook Publishers, Inc., Sandusky Ohio, and International Critical Tables of Numerical Data, Physics, Chemistry and Technology, McGraw Hill Book Co., Inc., New York, NY) solubility data is available in the literature, in most cases the solubility of inorganic compounds in aqueous solutions can be predicted using the rules given in below.

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TABLE I

Rules for Predicting Solubility in Water

- I. Soluble compounds
 - A. All Na^+ , K^+ , and NH_4^+ compounds are soluble.
 - B. All NO_3^- , $\text{C}_10_4^-$, $\text{C}_10_3^-$, and $\text{C}_2\text{H}_3\text{O}_2^-$ compounds are soluble.
 - C. All SO_4^{2-} compounds are soluble except: Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{3+} .
 - D. All Cl^- , Br^- , and I^- compounds are soluble except: Ag^+ , Hg_2^{2+} , and Pb^{2+} .
- II. Insoluble compounds
All O^{2-} , OH^- , and S^{2-} compounds are insoluble except: Na^+ , K^+ , NH_4^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} . Metal sulfides are the least soluble followed by H_2S ; hydroxides are only slightly more soluble than sulfides.
- III. The compounds of anions not mentioned in any of the preceding rules are probably insoluble except when combined with Na^+ , K^+ , or NH_4^+ .

Examples: CrO_4^{2-} , CO_3^{2-} , PO_2^- , PO_3^- , AsO_3^- , SO_3^{2-} , etc.
- IV. Covalent compounds are generally insoluble, water is an exception.

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Once the solubilities of the reactants and products of a particular reaction are known, the degree of ion formation must be predicted. This can be accomplished using the rules listed in Table II.



TABLE II

Rules for Predicting Ion Formation

- I. All salts dissociate nearly 100% in dilute solution.
- II. All strong acids and strong bases dissociate 100%.
 - A. Acids (proton sources)
 1. Strong acids are:
Binary - HCl, HBr, HI
Ternary - H_nXO_{n+2} and H_nXO_{n+3} (X being any element other than H or O)

Example: H_2SO_4 , HNO_3 , $HClO_4$ are all strong acids.
 2. Other common acids are weak and dissociate much less than 100%.
 - B. Bases (hydroxide sources)
 1. Strong bases are:

 $M(OH)_n$ when the cation (M^{+n}) comes from Groups IA or IIA, except Li^+ , Be^{2+} , and Mg^{2+} .
 2. Other common bases are weak and dissociate much less than 100%.
- III. Binary covalent compounds such as CO_2 , NO, etc. do not dissociate in water.



Table III summarizes the abbreviations used throughout this paper to describe the behavior of reactants and products in aqueous solution. When applicable, abbreviations consistent with those found in the Handbook of Chemistry and Physics are used.



TABLE III

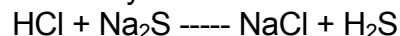
Abbreviations

SA - strong acid	<i>s</i> - slightly soluble
SB - strong base	i - insoluble
WA - weak acid	hd - highly dissociates
WB - weak base	sd - slightly dissociated
S - salt	OA - oxidizing agent
s - soluble	RA - reducing agent

Three examples illustrate the application of the solubility and ion formation rules.

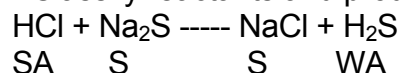
Example I: Predict the products and direction of reaction for: $\text{HCl} + \text{Na}_2\text{S}$

Step 1: Predict products by exchanging cations and anions while maintaining electroneutrality.

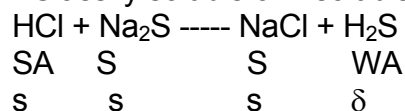


Notice that the direction of the reaction has not been indicated and the reaction is not balanced.

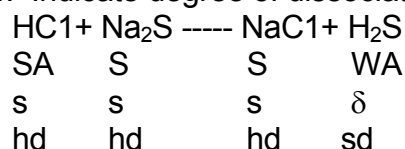
Step 2: Classify reactants and products



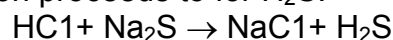
Step 3: Classify soluble or insoluble



Step 4: Indicate degree of dissociation



Step 5: Based on the previous 3 steps, indicate the major direction of the reaction. H_2S is the only substance removing ions from solution; therefore, the reaction proceeds to form H_2S .



In examples II and III, Steps 1, 2, 3 and 4 have been condensed.

Example II: $\text{Fe}(\text{OH})_3 + \text{NaCl}$

Step 1: $\text{Fe}(\text{OH})_3 + \text{NaCl} \rightarrow \text{FeCl}_3 + \text{NaOH}$

Step 2: WB S S SB

Step 3: i s s s

Step 4: sd hd hd hd

In this example $\text{Fe}(\text{OH})_3$ is the only species capable of removing ions from solution: therefore, the major direction for the reaction is toward the $\text{Fe}(\text{OH})_3$ (from right to left)

Step 5: $\text{Fe}(\text{OH})_3 + \text{NaCl} \rightarrow \text{FeCl}_3 + \text{NaOH}$

Example III: $(\text{NH}_4)_2\text{CO}_3 + \text{Mg}(\text{OH})_2$

Step 1: $(\text{NH}_4)_2\text{CO}_3 + \text{Mg}(\text{OH})_2 \rightarrow \text{NH}_4\text{OH} + \text{MgCO}_3$

Step 2: S WB WB S

Step 3: s i s i

Step 4: hd sd sd hd

In this example, more information is needed before predicting the direction of reaction. Does the insoluble $\text{Mg}(\text{OH})_2$ remove more ions than the slightly dissociated NH_4OH and insoluble MgCO_3 ?

PART II: OXIDATION-REDUCTION REACTIONS

The driving force for redox reactions is the increased stability of the substances being formed. Predicting products is more complicated than it was for metathesis reactions, and the statement of exact rules must wait until electrochemistry and certain other concepts have been mastered. However, some qualitative rules of great assistance in predicting product formation and direction of reaction are listed in Tables IV and V.



TABLE IV

Rules for Assigning Oxidation Numbers

- I. All free elements are at oxidation number zero (0).
- II. Group A elements of the periodic table:
 - A. Metals in Group A have one positive oxidation number equal to the group number (ex. Mg(GP IIA) has 0 and +2).
 - B. Nonmetals in Group A have one negative oxidation number equal to their (group number -8) and positive oxidation numbers equaling their group number, (group number -2), (group number -4) . . . [example C1 (Gp VIIA) has -1; 0; +7, +5, +3, +1].
 - C. In aqueous solution nonmetals at negative oxidation numbers exist as simple anions while those with positive oxidation number exist normally as oxyanions or binary covalent oxides.
- III. Group B elements of the periodic table:
 - A. Group elements may have either "metallic oxidation numbers" (+1, +2, +3) or "nonmetallic oxidation numbers" (+4 → +7). Oxidation numbers of these elements must be memorized. There are no simple rules to aid in predicting their values.
 - B. During reaction, acidic solution favors change to a more metallic oxidation number; basic solution favors change to a less metallic (more nonmetallic) oxidation number.
 - C. In aqueous solution Group B elements at metallic oxidation numbers exist as simple cations while those with nonmetal oxidation numbers normally exist as oxyanions or binary covalent oxides.





TABLE V

Rules for Predicting Products of Oxidation Reduction Reactions in Aqueous Solution

- I. Assign oxidation numbers using the rules in Table III.
- II. Label oxidizing and reducing agents. Elements at their highest oxidation number must be oxidizing agents (they can only accept electrons). Elements at their lowest oxidation number must be reducing agents (they can only donate electrons). Elements at an intermediate oxidation number may be either oxidizing or reducing agents.
- III. Assign Pauling electronegativities to each element.
 - A. If the oxidation number is positive, increase the Pauling electronegativity by 0.1 for each unit increase in oxidation number (example Al is 2.0; Al^{+3} is 2.3).
 - B. If the oxidation number is negative, decrease the electronegativity by 0.1 for each unit decrease in oxidation number. (example S is 2.5; S^{2-} is 2.3)
 - C. Changes in a few of the Pauling electronegativities improve predictions.
 1. Change Cu from 1.9 to 2.3.
 2. When a transition element is at a nonmetal oxidation number (+4 \rightarrow +7) increase its electronegativity by 1.1 units before adding .1 for each unit increase in oxidation number. (example Cr^{+6} is $1.6 + 1.1 + 0.6 = 3.3$).
- IV. For a reaction to take place the oxidizing agent must have a higher electronegativity than the reducing agent. The reducing agent's oxidation number will increase to the first stable oxidation number. The oxidizing agent's oxidation number will decrease to the first stable oxidation number.
- V. In oxidation reduction reactions involving a ternary acid, where both the hydrogen ion and the central element may act as the oxidizing agent, the concentration of the acid determines whether the major reaction involves the hydrogen ion or the central element. Concentrated solutions favor reaction of the central element; dilute solutions favor reaction of the proton.
- VI. Oxygen at oxidation number -2 almost never acts as a reducing agent and can usually be ignored in aqueous redox reactions.

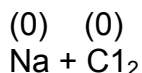


In complicated reactions, it is often worthwhile to write the reaction as two or more half reactions. The following examples illustrate the application of the rules for predicting products of oxidation reduction reactions.

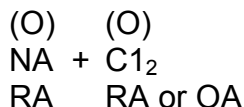
Three examples illustrate the application of the rules for product formation.

Example I: Na + Cl

Step 1: Assign oxidation numbers. These are written in parentheses above the element.

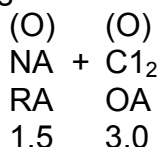


Step 2: Identify oxidizing agents (OA) and reducing agents (RA) directly below the elements.

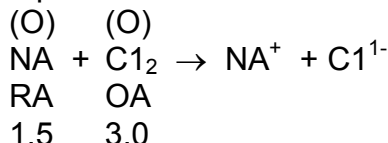


(Cl₂ must be the oxidizing agent for a reaction to take place.)

Step 3: Assign electronegativities.



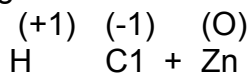
Step 4: Determine if a reaction will take place and use the oxidation number rules to predict products.



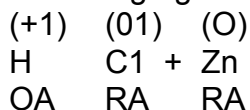
Because electronegativity of the oxidizing agent is greater than that of the reducing agent, a reaction will take place. Note that sodium has only one positive oxidation number, while chlorine has one negative oxidation number.

Example II: HCl + Zn

Step 1: Assign oxidation numbers

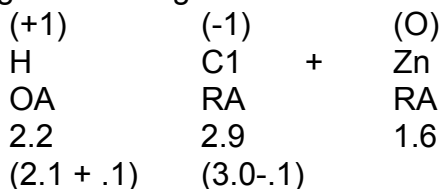


Step 2: Label oxidizing agents and reducing agents.

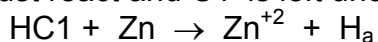


Hydrogen at +1 is at its highest oxidation number, therefore, it must be the oxidizing agent. Chlorine at -1 and zinc at 0 are at their lowest oxidation numbers, therefore, they must be reducing agents.

Step 3: Assign electronegativities.



Step 4: Determine if a reaction will take place. Remember the oxidizing agent must have a higher electronegativity than the reducing agent. Thus, in this case, H⁺ and Zn must react and Cl⁻ is left unchanged.



Zinc, being the reducing agent is oxidized to its only positive oxidation number (+2). Hydrogen, the oxidizing is reduced to oxidation number zero, which is its first stable oxidation number lower than +1.

Example III: $\text{KMnO}_4 + \text{Cl}_2$

Step 1: (+1) (+7) (-2) (0)
 K Mn O₄ + Cl₂

Step 2: OA OA RA OA or RA

Remember, oxygen at oxidation number -2 almost never acts as a reducing agent; therefore, it can be ignored throughout the remainder of this problem. Because the potassium (K^{+2}) and manganese (Mn^{+7}) can only behave as oxidizing agents, Cl₁ must be the reducing agent.

Step 3: K Mn O₄ + Cl₂
 OA OA RA
 (.8 + .1) (1.5 + 1.1 + .7) 3.0

The potassium ion can not be the oxidizing agent because the oxidizing agent must have a higher electronegativity than reducing agent.

Therefore, only manganese and chlorine need any additional attention.

Treating the half reactions individually simplifies the problem.

Step 4a: (0) (+5)
 Cl₂ → Cl

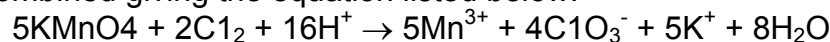
At +5 Cl, a nonmetal, is at a nonmetallic valence, but ions with a charge of greater than +3 must exist as the oxy anion of a ternary compound or as a binary covalent oxide.

Cl₂ → Cl₃¹⁻

Step 4b: In KMnO_4 manganese is at oxidation number +7 and will be reduced. If the solution is acidic, the Mn will go to a metallic oxidation number (+3 or +2). If the solution is basic, it goes to a nonmetallic oxidation number (+4, +6 or +7).

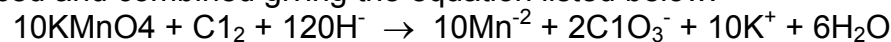
In acid: H⁺
 $\text{KMnO}_4 \rightarrow \text{Mn}^{3+}$

(+3 is the first stable oxidation number that manganese reaches at it is reduced in acid solution.) To complete this problem, the two half reactions are balanced and combined giving the equation listed below.



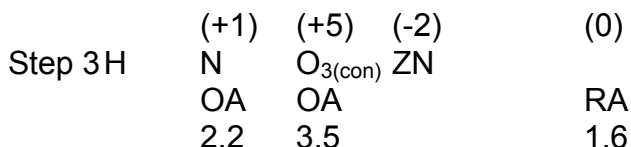
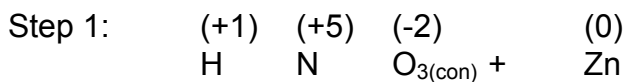
In base: OH⁻
 $\text{KMnO}_4 \rightarrow \text{MnO}_4^{-2}$

When MnO_4 is reduced under basic conditions, the first stable oxidation number reached by manganese is +6. Because manganese is a B group element at a nonmetallic valence, it is combined with oxygen and exists as MnO_4^{-2} . To complete the problem assuming basic conditions, the two half reactions are balanced and combined giving the equation listed below.

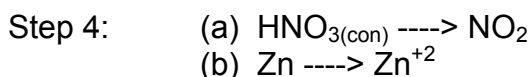


Example IV: Concentrated HNO_3 + Zn.

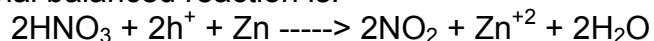
This example will be given in abbreviated form because the fundamental principles have already been demonstrated.



Since both H and N are oxidizing agents and both have electronegativities greater than that of Zn, either H or N could react with Zn. However, because the reaction conditions specify concentrated HNO_3 , reaction with the central element, N, is favored. The binary covalent oxide NO_2 is the predicted product.



The final balanced reaction is:



Worked study sets and practice problems are given below.

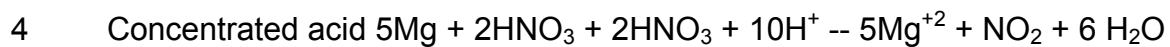
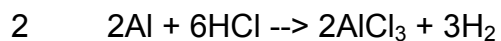
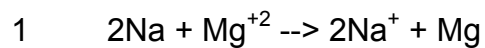
Metathesis Study Set

- 1 $\text{Pb}(\text{NO}_3)_2 + 2\text{HCl} \text{ --> } \text{PbCl}_2 + 2\text{HNO}_3$
- 2 $\text{H}_2\text{SO}_4 + 2\text{NaCN} \text{ --> } \text{Na}_2\text{SO}_4 + 2\text{HCN}$
- 3 $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \text{ --> } \text{BaSO}_4 + 2\text{NaCl}$

Metathesis Problem Set

- 1 aluminum nitrate + hydrochloric acid
- 2 cupric chloride + hydrogen sulfide
- 3 silver nitrate + ammonium chloride
- 4 barium chloride + sulfuric acid
- 5 hydrochloric acid + potassium nitrite
- 6 lead nitrate + hydrochloric acid
- 7 cadmium sulfide + hydrochloric acid
- 8 hydrochloric acid + ammonium hydroxide

Redox Study Set



Redox Problem Set

