

# Notes on “Chemistry: the Central Science (13th Edition)”

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## Contents

<b>1 Chapter 1. Units and Significant Figures</b>	<b>2</b>	<b>8 Chapter 8. Basic Concepts of Chemical Bonding</b>	<b>9</b>
<b>2 Chapter 2. Atoms, Molecules, Ions</b>	<b>2</b>	8.1 Lewis Structures . . . . .	10
2.1 Basics . . . . .	3	8.2 Resonance structures . . . . .	10
2.2 Dalton's Theory and its Development . . . . .	3	8.3 Exceptions to the Octet Rule . . . . .	10
2.3 Naming . . . . .	3	8.4 Ionic Bonds . . . . .	10
2.3.1 Cations . . . . .	3	8.5 Strengths and Lengths of Covalent Bonds . .	10
2.3.2 Anions . . . . .	3	8.6 Bond Polarity and Electronegativity . . . . .	11
2.3.3 Binary compound . . . . .	3	<b>9 Chapter 9. Molecular Geometry and Bonding Theories</b>	<b>11</b>
2.3.4 Acids . . . . .	3	9.1 Molecular Shapes . . . . .	12
2.4 Alkanes and Alcohols . . . . .	4	9.2 VSEPR Model . . . . .	12
<b>3 Chapter 3. Chemical Reactions and Reaction Stoichiometry</b>	<b>4</b>	9.3 Covalent Bonding, Orbital Overlap . . . . .	13
3.1 Chemical Equations and Reactions . . . . .	4	9.4 Hybrid Orbitals . . . . .	13
3.2 Stoichiometry . . . . .	4	9.5 Multiple Bonds . . . . .	13
<b>4 Chapter 4. Reactions in Aqueous Solution</b>	<b>4</b>	9.6 Molecular Orbitals . . . . .	14
4.1 Solubility Guidelines . . . . .	5	9.7 Period 2 Diatomic Molecules . . . . .	14
4.2 Strong Acids and Bases . . . . .	5	<b>10 Chapter 10. Gases</b>	<b>16</b>
4.3 Solution basics . . . . .	5	<b>11 Chapter 11. Liquids and IMFs</b>	<b>16</b>
4.4 Acid-Base Reactions . . . . .	5	11.1 Liquids . . . . .	16
4.5 Oxidation-Reduction Reactions . . . . .	5	11.2 Intermolecular Forces . . . . .	17
<b>5 Chapter 5. Thermochemistry</b>	<b>5</b>	<b>12 Chapter 12. Solids</b>	<b>18</b>
5.1 Energy . . . . .	6	12.1 Classification . . . . .	18
5.2 Enthalpy . . . . .	6	12.2 Structures . . . . .	19
5.3 Calorimetry . . . . .	6	12.3 Metallic solids . . . . .	19
5.4 Hess's law . . . . .	6	12.4 Metallic bonding . . . . .	19
5.5 Enthalpies of Formation . . . . .	6	12.5 Complex . . . . .	20
5.6 Foods and Fuels . . . . .	6	12.6 Ionic solids . . . . .	20
<b>6 Chapter 6. Electronic Structure of Atoms</b>	<b>6</b>	12.7 Molecular solids . . . . .	20
6.1 Energy of Light and Photons, Quantum Worries . . . . .	7	12.8 Covalent-network solids . . . . .	20
6.2 Electron Orbitals . . . . .	7	12.9 Semiconductors . . . . .	20
<b>7 Chapter 7. Periodic Properties of the Elements</b>	<b>7</b>	12.10 Polymers . . . . .	21
7.1 Periodic Properties of the Elements . . . . .	8	<b>13 Chapter 13. Properties of Solutions</b>	<b>21</b>
7.2 Metals . . . . .	8	13.1 Solution Process . . . . .	21
7.3 Alkali metals . . . . .	8	13.2 Saturated solutions and solubility . . . . .	22
7.4 Alkaline metals . . . . .	8	13.3 Factors affecting solubility . . . . .	22
7.5 Nonmetals . . . . .	9	13.4 Expressing solution concentrations . . . . .	22
7.6 Noble Gases . . . . .	9	13.5 Colligative Properties . . . . .	22
7.7 Hydrogen . . . . .	9	13.6 Colloids . . . . .	23
7.8 Oxygen group . . . . .	9		
7.9 Halogens . . . . .	9		

<b>14 Chapter 14. Chemical kinetics</b>	<b>23</b>	<b>17 Chapter 17. More Aspects of Aqueous Equilibria</b>	<b>30</b>
14.1 Reaction Rates . . . . .	23	17.1 Common-Ion Effect . . . . .	31
14.2 Rates and Concentration . . . . .	24	17.2 Buffers . . . . .	31
14.3 Concentration and Time . . . . .	24	17.3 Acid-Base Titrations . . . . .	31
14.4 The Effect of Temperature on Rates . . . . .	24	17.4 Solubility Equilibria . . . . .	32
14.5 Reaction Mechanisms . . . . .	25	17.5 Factors affecting solubility . . . . .	32
14.6 Catalysts . . . . .	25	17.6 Precipitation and Separation of Ions . . . . .	32
		17.7 Qualitative Analysis for Metallic Elements . . . . .	32
<b>15 Chapter 15. Chemical equilibrium</b>	<b>25</b>	<b>19 Chapter 19. Chemical Thermodynamics</b>	<b>32</b>
15.1 Rock bottom . . . . .	26	19.1 Spontaneous Processes . . . . .	33
15.2 Equilibrium constant . . . . .	26	19.2 Entropy and the Second Law . . . . .	33
15.3 Direction and Summation of Equations . . . . .	26	19.3 Molecular Interpretation of Entropy and the Third Law . . . . .	33
15.4 Heterogeneous Equilibrium . . . . .	26	19.4 Entropy Changes in Chemical Reactions . . . . .	33
15.5 Finding K from initial and equilibrium concentrations . . . . .	26	19.5 Gibbs Free Energy . . . . .	34
15.6 Applications of K . . . . .	27	19.6 Free Energy, Temperature, and Equilibrium Constant . . . . .	34
15.7 Le Châtelier's Principle . . . . .	27		
<b>16 Chapter 16. Acid-Base Equilibria</b>	<b>27</b>	<b>20 Chapter 20. Electrochemistry</b>	<b>34</b>
16.1 Arrhenius Acids and Bases . . . . .	28	20.1 Oxidation States and Redox . . . . .	34
16.2 Brønsted-Lowry Acids and Bases . . . . .	28	20.2 Balancing Redox . . . . .	35
16.3 Auto-ionization of Water . . . . .	28	20.3 voltaic cells . . . . .	35
16.4 pH and pOH Scale . . . . .	28	20.4 Voltage under Standard Conditions . . . . .	35
16.5 Strong acids and bases . . . . .	28	20.5 Free Energy and Redox Reactions . . . . .	35
16.6 Weak Acids and $K_a$ . . . . .	29	20.6 Voltage under Nonstandard Conditions . . . . .	35
16.7 Weak Bases and $K_b$ . . . . .	29	20.7 Batteries and Fuel Cells . . . . .	35
16.8 Acid-Base Properties of Salt Solutions . . . . .	29	20.8 Corrosion . . . . .	35
16.9 Acid-Base Behavior and Chemical Structure . . . . .	29	20.9 Electrolysis . . . . .	35
16.10 Lewis Acids and Bases . . . . .	30	<b>21 Chapter 21. Nuclear Chemistry</b>	<b>35</b>
		21.1 . . . . .	36

## 1 Chapter 1. Units and Significant Figures

- |                                                     |                                        |           |
|-----------------------------------------------------|----------------------------------------|-----------|
| 1. Elements, compounds, hetero/homogeneous mixtures | 3. Common prefixes                     | chemistry |
| 2. Common elements                                  | 4. Significant figures OHYEA           |           |
|                                                     | 5. SI units and non-SI units common in |           |

**Common elements** C, F, H, N, I, O, P, S, Al, Br, Ca, Cl, He, Li, Mg, Si, Cu, Fe, Pb, Hg, K, Ag, Na, Sn

**Common prefixes** Yocto (15), Tera, Giga, Mega, kilo, deci, centi, mill,  $\mu$ icro, nano, Ångstrom(-10, non-SI), p, femto (-15), atto, zepto (-21)

**SI units** kg, m, s or sec, K, mol, A, cd (candela)

**Common in chem:** L, 1000 cubic centimeters

**Sig.fig. addition** keep lowest decimal sig.fig.s. 1.0 +

$$221.31 = 222.3$$

**Sig.fig. multiplication** keep lowest sig.fig.s

**Sig.fig. logarithms** sig.figs of mantissa expressed in scientific notation equals the number of significant figures to the right of the decimal  
 $\log(2.7310^5) = \log(2.73) + \log(10^5) = 0.436 - 5.00000\dots$

## 2 Chapter 2. Atoms, Molecules, Ions

### Contents

<b>2.1 Basics</b> . . . . .	<b>3</b>
<b>2.2 Dalton's Theory and its Development</b> . . . . .	<b>3</b>
<b>2.3 Naming</b> . . . . .	<b>3</b>
<b>2.4 Alkanes and Alcohols</b> . . . . .	<b>4</b>

1. Dalton's atomic theory
2. Key experiments that led to discovery of atom/nucleus/electrons (Cathode ray, oil drop,  $\alpha$  scattering)
3. Electrical charge and relative masses of  $e^-$ ,  $p^+$ ,  $n$
4. Subatomic composition of isotopes
5. Atomic weight knowing natural abundances
6. Periodic table properties, metals/nonmetals
7. Molecular and ionic substances, in terms of their composition
8. Empirical/molecular formulas
9. Compositions expressed as molecular and structural formulas
10. Ions and the gain/loss of  $e^-$ , predict common charges
11. Write empirical formulas of ionic compounds given charges of component ions
12. Name ionic compounds
13. Name binary inorganic compounds and acids
14. Name alkanes and alcohols

## 2.1 Basics

**Empirical formula** extra information is needed to find chemical

formula  
**Mass of electron**  $9.10 \cdot 10^{-28}g$   
**Charge of electron**  $1.602 \cdot 10^{-19}C$

**Rays**  $\beta$  are negative,  $\alpha$  are positive, and  $\gamma$  are neutral.  
**Cations** positive. meow  
**Anions** negative.

## 2.2 Dalton's Theory and its Development

**Laws:** elements made of atoms, atoms are unique/exclusive to elements, atoms cannot be changed by chemistry, compounds have the same relative number and kinds of atoms, and the next law:

**Law of multiple proportions** elements  $A$  and  $B$  form two compounds  $C_1$  and  $C_2$ . This proportion will be a natural number:  $\frac{C_1 \cdot A}{C_2 \cdot A}$  where  $C_1$  is larger.

**Cathode rays** cathode rays are electrically charged

and negative. Determined by firing such a ray and manipulating its positive end using magnetic and electric fields

**Oil drop experiment** Rate of oil drops affects their rate of descent. Used to find ratio of electron's mass and charge.

**Rutherford's  $\alpha$  scattering** most  $\alpha$  particles went through a gold foil with little deflection, though some were greatly repelled.

## 2.3 Naming

Chromate is  $CrO_4^{2-}$  and Dichromate is  $Cr_2O_7^{2-}$ . Permanganate is  $MnO_4^-$ . Also, the only nonmetal cation encountered is Ammonium  $NH_4^+$ .

### 2.3.1 Cations

**Metal single charge** name ion

**Metal ambiguous charge** name (charge in Roman numerals) ion

### 2.3.2 Anions

**Single** name-ide

**Oxyanions normal sequence**  $CO_3^{2-}$ ,  $NO_3^-$ ,  $ClO_3^-$ ;  $PO_4^{3-}$ ,  $SO_4^{2-}$

**Oxyanions +1 O count** per-name-ate

**Oxyanions normal O count** name-ate

**Oxyanions -1 O count** name-ite

**Oxyanions -2 O count** hypo-name-ite

**Oxyanions with hydrogen** prepend "hydrogen" or "dihydrogen" to oxyanion name

### 2.3.3 Binary compound

**Greek prefix** to indicate atomic number, leave first alone if AN = 1

**Leftmost first** unless oxygen and a halogen, except F.

**Bottommost first**

**Suffix -ide** on second element

### 2.3.4 Acids

make  $H^+$  in water.

**name-ide is converted to** hydro-name-ic acid

**name-ate** is converted to name-ic acid

**name-ite** is converted to name-ous acid

## 2.4 Alkanes and Alcohols

**General formula**  $C_nH_{2n+2}$

**Naming sequence** methanol, ethanol, propanol, tetranol, pentanol, greek-prefix-nol.

**Alcohols** one of the H in the alkane replaced by a hydroxide OH.

droxide OH.

**Enantiomers** different structure (even if rotated) due to location of the hydroxide group. 1-propanol has OH on edge, 2-propanol has it in center

## 3 Chapter 3. Chemical Reactions and Reaction Stoichiometry

### Contents

<b>3.1 Chemical Equations and Reactions</b>	<b>4</b>
<b>3.2 Stoichiometry</b>	<b>4</b>

- |                                                     |                                                                               |                                                                |
|-----------------------------------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------|
| 1. Balance chemical equations                       | 4. Grams and moles                                                            | and MW                                                         |
| 2. Combination, decomposition, combustion reactions | 5. Avogadro's number                                                          | 7. ID limiting reactants and calculate amounts consumed/formed |
| 3. Formula weights                                  | 6. Empirical and molecular formulas of a compound from percentage composition | 8. Percent yield of a reaction                                 |

### 3.1 Chemical Equations and Reactions

**Unbalanced Formula**  $CH_4 + O_2 \longrightarrow CO_2 + H_2O$

**Balanced Formula**  $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

**State indicators** (s), (l), (g), (aq) indicates dissolution in water, others for different solvents

**Formula weight**  $\sum_{\text{Element}} \#E \cdot E \text{ atomic weight}$

**Elemental Composition**  $\frac{\# \text{ element} \cdot \text{weight of}}{\text{formula weight}}$

empirical formula weight divided by the molecular weight is always a natural number

**Combination reaction**  $A + B \longrightarrow C$

**Decomposition reaction**  $C \longrightarrow A + B$

**Limiting Reactants** test each reaction by moles until an obvious limit is found

**One AMU** is one  $\frac{g}{mol}$ .

### 3.2 Stoichiometry

**One mole** is equal to  $6.022 \cdot 10^{23}$  units.

**Stoichiometric Equivalence**  $A + 2B \longrightarrow 3C + 4D$   
one mole of A yields 3 moles of C, one mole of D must have consumed half a mole of B.

**Combustion analysis**  $\dots C \dots H \longrightarrow nCO_2 + mH_2O$

$\%C = \frac{C_{mol}}{X_{mol}}$   $\%H = \frac{H_{mol}}{X_{mol}}$ . Try different denominators X until all are natural numbers. Use algebra if another element involved.

**Percentage yield** actual yield divided by theoretical yield.

## 4 Chapter 4. Reactions in Aqueous Solution

### Contents

<b>4.1 Solubility Guidelines</b>	<b>5</b>
<b>4.2 Strong Acids and Bases</b>	<b>5</b>
<b>4.3 Solution basics</b>	<b>5</b>
<b>4.4 Acid-Base Reactions</b>	<b>5</b>
<b>4.5 Oxidation-Reduction Reactions</b>	<b>5</b>

- |                                                                                 |                                                        |                                                 |
|---------------------------------------------------------------------------------|--------------------------------------------------------|-------------------------------------------------|
| 1. ID compounds as acids or bases, strong weak or non-electrolyte?              | reactions                                              | solution                                        |
| 2. Recognize reaction types, simple acid-base, precipitation and redox (OILRIG) | 3. Calculate molarity, use it to find volume and moles | 5. Perform and interpret results of a titration |
|                                                                                 | 4. Carry out a dilution to achieve a desired           |                                                 |

## 4.1 Solubility Guidelines

soluble	exceptions	insoluble	exceptions
NO <sub>3</sub> <sup>-</sup>		all following	unless with NH <sub>4</sub> <sup>+</sup> , alkali metal
CH <sub>3</sub> COO <sup>-</sup>		CO <sub>3</sub> <sup>2-</sup>	
alkali metals		PO <sub>4</sub> <sup>3-</sup>	
all following	unless with Hg <sub>2</sub> <sup>2+</sup> , Pb <sup>2+</sup>	all following	unless with Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup>
Cl <sup>-</sup>	unless with Ag <sup>+</sup>	S <sup>2-</sup>	
Br <sup>-</sup>	unless with Ag <sup>+</sup>	OH <sup>-</sup>	
I <sup>-</sup>	unless with Ag <sup>+</sup>		
SO <sub>4</sub> <sup>2-</sup>	unless with Sr <sup>2+</sup> , Ba <sup>2+</sup>		

## 4.2 Strong Acids and Bases

**Strong acids** HI, HBr, HCl, HClO<sub>3</sub>, HClO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> (first proton only)

**Strong bases** group 1A metal hydroxides KOH, group 2A heavy metal hydroxides (beginning at Ca(OH)<sub>2</sub>)

**Weak acids, bases** all else

## 4.3 Solution basics

**Solvent** more of this

**Solute** dissolved in solvent

**Molarity** moles per Litre

**Dilution**  $M_{\text{conc}}V_{\text{conc}} = M_{\text{dilute}}V_{\text{dilute}}$

**Electrolyte** fancy for salt. Forms ions in water by dissociating.

**Weak electrolytes** oscillate, only a fraction of itself is dissociated.

**Precipitation** pairs of oppositely charged ions attract each other to form a solid (salt). Look for any

insoluble products. A type **metathesis** reaction  
 $AX + BY \longrightarrow AY + BX$

**Ionic equation** Split any dissociated (aq) molecules into ions. Cancel out ions present on both sides of equation, these are **spectator ions**.

**Example ionic equation**  $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KI}(\text{aq}) \longrightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$  can be converted to  $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow \text{PbI}_2(\text{s})$  with  $\text{K}^{+}$  and  $(\text{NO}_3)^{2-}$  as spectator ions.

## 4.4 Acid-Base Reactions

**Acids** form H<sup>+</sup> in water

**Bases** form OH<sup>-</sup> in water

**Acids and Bases** combined  $\text{HA} + \text{BOH} \longrightarrow \text{H}_2\text{O} + \text{AB}$

**Gas formation** is possible  $2\text{HCl}(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \longrightarrow \text{H}_2\text{S}(\text{g}) + 2\text{NaCl}(\text{aq})$

## 4.5 Oxidation-Reduction Reactions

**Metal activity** increases to the top-left. Higher means easier to oxidize.

**OIL-RIG** oxidation is loss of e<sup>-</sup>, reduction is gain of e<sup>-</sup>  
**Oxidation number** is an artificial (negated) e<sup>-</sup> count.

**O** -2, except in O<sub>2</sub><sup>2+</sup> where each O has -1.

**H** +1 with metals, -1 with nonmetals

**F** -1

**other halogens** -1, can be positive with oxygen  
**elemental** 0

**monatomic ion** charge

**polyatomic ion** sum of oxidation numbers is charge

# 5 Chapter 5. Thermochemistry

## Contents

5.1 Energy . . . . .	6
5.2 Enthalpy . . . . .	6
5.3 Calorimetry . . . . .	6
5.4 Hess's law . . . . .	6
5.5 Enthalpies of Formation . . . . .	6

1. Interconvert energy units
2. System vs surroundings in thermodynamics
3. Internal energy from heat and work. Sign conventions
4. Concept of a state function, examples
5.  $\Delta H$  from  $\delta E, P\delta V$
6. relate  $q_p$  to  $\Delta H$ . Signs indicate exo/endothermic
7. Relate  $\Delta H$  at constant pressure and the amount of substance involved
8. Heat transferred using temperature measurements and heat capacities/specific heats (calorimetry)
9. Hess' law to determine enthalpy changes
10. Standard enthalpies of formation to calculate  $\Delta H^\circ$

## 5.1 Energy

**Kinetic energy**  $\frac{mv^2}{2}$

**Electrostatic energy** between two points, charges  $Q$ , distance  $d$ ,  $k = 8.99E9 Jm/C^2$ ;  $\frac{kQ_1Q_2}{d}$

**1 calorie** 4.184 Joules

**System** area singled out for study

**Surroundings** all else

**Work**  $F \times d$

**First Law of Thermodynamics** energy cannot be created or destroyed

## 5.2 Enthalpy

**Internal energy**  $E$  is the sum of kinetic and potential energies.

**Change**  $\Delta E = E_{\text{final}} - E_{\text{initial}}$

**Change and Work**  $\Delta E = q + w$  heat + work.

**Positive**  $q$  endothermic, **negative**  $q$  exothermic.

**Positive**  $\Delta E$  means system has gained energy, has received: it's endothermic.

**Negative**  $\Delta E$  means system has lost energy, has given: it's exothermic.

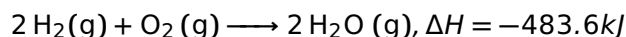
**State function** result depends only on present state

**Enthalpy**  $H = E + PV$  where  $P$  is pressure and  $V$  is volume. All three terms are state functions.

**Change in Enthalpy**  $\Delta H = H_{\text{products}} - H_{\text{reactants}} = q +$

$w - w = q$  equal to heat at constant pressure. **Extensive** property (depends on amount). Depends on states of substances. Units:  $kJ$

**Example**



## 5.3 Calorimetry

Specific heat of substance mass (units  $\frac{J}{\text{molK}}$ ), range and change in temperature can be used to find the heat released or absorbed during a change.

$$Q = C_s m \Delta T$$

## 5.4 Hess's law

**Composite reaction** can be split into other, sometimes simpler, reactions which add to form it

**Hess's law** indicates the  $\Delta H$  for a composite reaction is the sum of the  $\Delta H$  for each component reaction.

## 5.5 Enthalpies of Formation

**Enthalpy of formation**  $\Delta H_f^\circ$  is the enthalpy required to **form** a substance in standard conditions,  $25^\circ\text{C}$  and  $1 \text{ atm}$ . Units:  $kJ/mol$ .

**For stablest elementals** at standard conditions, such as  $\text{C}(\text{graphite})$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\Delta H_f^\circ = 0$ .

**Example** for diamond  $\text{C}(\text{s})$   $\Delta H_f^\circ = 1.88 \text{ kJ/mol}$ . For water vapor  $\Delta H_f^\circ = -241.8 \text{ kJ/mol}$

## 5.6 Foods and Fuels

Proteins	17
Fats	38
Carbohydrates	17

Wood, pine	18
Charcoal	34
Texas Crude Oil	45
Hydrogen	142

Non-renewable fuels are fucked, renewable fuels not used enough.

# 6 Chapter 6. Electronic Structure of Atoms

## Contents

- |                                                                        |                                                                       |                                                                                                         |
|------------------------------------------------------------------------|-----------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| 1. Wavelength and frequency of electromagnetic radiation               | 6. Uncertainty principle and what it limits                           | bitals in a many-electron atom, use Pauli exclusion principle and Hund's rule                           |
| 2. Order the common kinds of radiation according to wavelengths/energy | 7. Quantum numbers to the number and type of orbitals, orbital shapes |                                                                                                         |
| 3. Photons and their energy                                            | 8. Radial probability function graphs                                 |                                                                                                         |
| 4. Line spectra, relate to quantized energy                            | 9. Hydrogen atom orbitals vs other atoms' orbitals                    |                                                                                                         |
| 5. Wavelength of a moving object                                       | 10. Draw energy-level diagram for the or-                             |                                                                                                         |
|                                                                        |                                                                       | 11. Using periodic table, write condensed electron configurations. Number of unpaired e <sup>-</sup> s. |

## 6.1 Energy of Light and Photons, Quantum Worries

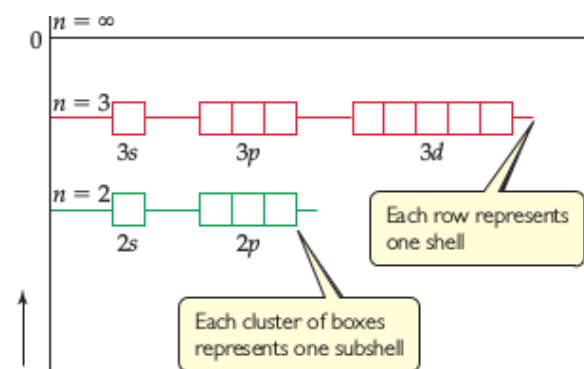
**Properties of light** speed of light =  $c = 2.99 \cdot 10^8 \frac{m}{s} = \lambda \nu$  where  $\lambda$  is wavelength  $\nu$  is frequency.

**Energy of single photon**  $E_p = h\nu$  where Planck's constant  $h = 6.62E-43 J \cdot s$

**Wavelength of matter**  $\lambda = h/mv$  related to mass and velocity.

**Heisenberg's uncertainty principle**  $\Delta x \Delta(mv) \geq h/4\pi$  Position and momentum cannot be known perfectly.

## 6.2 Electron Orbitals



**Electrons positioned** by using a probability distribution which depends on their energy level.

### Line spectrum

**Spectral lines of Hydrogen** energy must be absorbed to emit an electron. Wavelength of each spectra line:

$$\lambda = R_H(1/n_1^2 - 1/n_2^2)$$

### Energy of hydrogen emissions

$$\Delta E = -2.18 \cdot 10^{-18} J (1/n_f^2 - n_i^2)$$

**Orbital diagram** visualization of each e<sup>-</sup>'s quantum numbers in an atom or molecule. Row of boxes, one box holds at most a pair of arrows pointing in opposite directions (e<sup>-</sup>) and groups of boxes are

slightly separated to indicate different orbitals p, s, d, f.

**Electron Quantum Numbers**  $n, l, m_l, m_s$

**Energy level**  $n \in N^+$

**Orbitals** p, s, d, f  $l \in 0 \dots n-1$

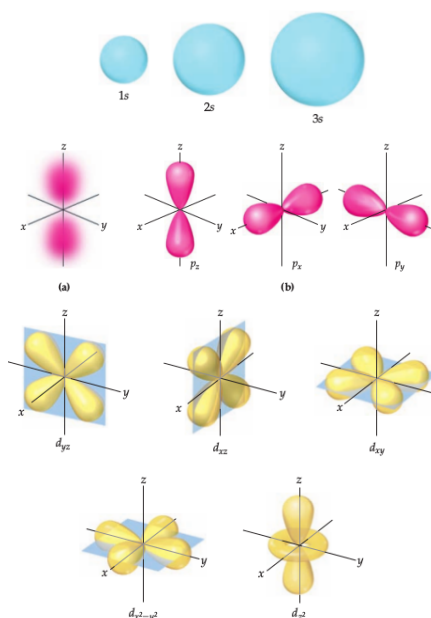
**Magnetic quantum number** a box,  $m_s \in -l \dots l$

**Spin magnetic quantum number** up/down,  $m_l = \pm 1/2$

**Subshell** electrons share  $n, l$

**Pauli's exclusion principle** all e<sup>-</sup> in an atom have unique quantum numbers.

**Hund's rule** the preferred e<sup>-</sup> arrangement has maximum e<sup>-</sup> with the same spin  $m_s$



## 7 Chapter 7. Periodic Properties of the Elements

### Contents

<b>7.1 Periodic Properties of the Elements</b>	<b>8</b>
<b>7.2 Metals</b>	<b>8</b>
<b>7.3 Alkali metals</b>	<b>8</b>
<b>7.4 Alkaline metals</b>	<b>8</b>
<b>7.5 Nonmetals</b>	<b>9</b>
<b>7.6 Noble Gases</b>	<b>9</b>
<b>7.7 Hydrogen</b>	<b>9</b>
<b>7.8 Oxygen group</b>	<b>9</b>
<b>7.9 Halogens</b>	<b>9</b>

- |                                                                                         |                                                                                                |                                                                                               |
|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| 1. Explain effective nuclear charge $Z_{eff}$                                           | 6. Irregularities in periodic table, electron affinity and configuration                       | groups 1A and 2A with water, oxygen, hydrogen and halogens                                    |
| 2. Trends in atomic/ionic radii, ionization energy, electron affinity                   | 7. Differences in metals and nonmetals (basicity of metal oxides, acidity of non-metal oxides) | 10. Unique properties of hydrogen                                                             |
| 3. Radius change on loss or gain of $e^-$                                               | 8. Correlate atomic properties with electron configuration                                     | 11. Atomic properties of groups 6A 7A and 8A with chemical reactivity and physical properties |
| 4. Electron configuration of ions                                                       | 9. Balanced equations for reactions of                                                         |                                                                                               |
| 5. Change in ionization energy as $e^-$ are added or removed, especially core electrons |                                                                                                |                                                                                               |

## 7.1 Periodic Properties of the Elements

**Effective nuclear charge**  $Z_{eff}$  roughly equal to  $Z - S$  = number of protons - number of nonvalence  $e^-$ . The 1s orbital acts as a "lampshade" to the 2s, 2p orbitals, and so on... **Trend:** increases to the right.

**Ionization energy** It becomes harder to remove successive  $e^-$ .  $I = X(g) \longrightarrow X^+(g) + e^-$ .  $I_2 = X^+(g) \longrightarrow X^{2+}(g) + e^-$ . **Trend:** increases to the top-right.

**Electron Affinity** Energy for reaction  $X(g) + e^- \longrightarrow$

$X^-(g)$ . If positive, ions are unstable. **Trend:** increases to the top-right. F and Cl have the highest.

**Atomic radius** Cations are smaller, anions are larger. **Trend:** increases to the bottom-left.

**Isoelectric series radius** same charge ions? Size decreases as atomic number increases:  $O^{2-} > Br^- > F^- > Al^{3+}$

**$e^-$  configuration of ions** Add or remove  $e^-$  from the highest n, then l.

## 7.2 Metals

**Trend:** metallic character increases to the bottom-left.

**Shiny** silver

**Malleable and ductile** can be hammered into sheets and stretched into wires

**Compounds** usually ionic

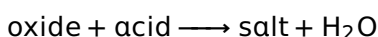
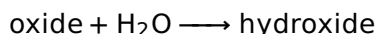
**Solid conductors** of both heat and electricity

**Only one liquid** at room temperature: Hg

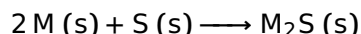
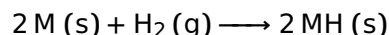
**Form cations** in aqueous solution, tend to make basic solutions.

**Low first** ionization energy  $I_1$

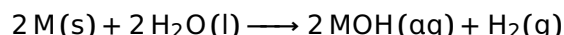
**Common reactions**



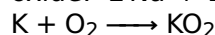
**Common reactions**



Vigorous reaction in water:



**Special with Oxygen** can coerce oxygen to form peroxide:  $2 \text{Na} + 2 \text{O} \longrightarrow \text{Na}_2\text{O}_2$  or super peroxide:



## 7.4 Alkaline metals

**Solid** release colorful flame when burned

**Compared to Alkali metals** harder, denser, less reactive

**Water reactions** Be inert; Mg slowly, faster with steam; all others react slowly with water

**Tend to lose** their two outer s  $e^-$ .

## 7.3 Alkali metals

**Soft solids** naturally present only in compounds

**Good conductors**

**Low** densities, melting points

**Very** reactive, colorful flames when burned

Metalloids in between.



## 7.5 Nonmetals

**Many colors** but no luster

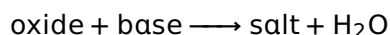
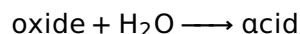
**Usually brittle**

**Poor conductors** heat and electricity

**Nonmetal oxides** molecules. Form acidic solutions.

**High first** ionization energy  $I_1$

**Common reactions**



## 7.6 Noble Gases

**Monatomic** almost no reactions

**Filled** s and p orbitals

**Possible compounds** exist in rare, laboratory conditions  $\text{XeF}_{2/4/6}$ ,  $\text{KrF}_2$ ,  $\text{HArF}$

## 7.7 Hydrogen

**Resembles a** nonmetal more than an Alkali.

**Preserves**  $e^-$ , tends to covalent bonds

**Most stable**  $\text{H}_2(\text{g})$

**Proton**  $\text{H}^+$  present in water

## 7.8 Oxygen group

**Atypical nonmetals**

**Oxygen stable as**  $\text{O}_2$

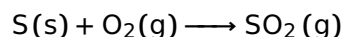
**Peroxide**  $\text{O}_2^{2-}$

**Superperoxide**  $\text{O}_2^{2-}$

**Sulfur stable as**  $\text{S}_8$

**Stability of water-like**  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

**Possible reaction** air pollutant:



## 7.9 Halogens

**Typical** nonmetals

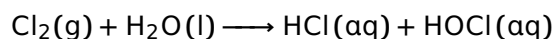
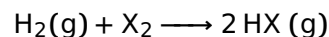
**Very** soluble, negative  $e^-$  affinity

**Fluoride** is extremely reactive

**Diatomic** molecules formed such as  $\text{I}_2$ ,  $\text{Cl}_2$ , except F

**Trend:** melting, boiling points increase as elements get heavier

**Common reactions**



# 8 Chapter 8. Basic Concepts of Chemical Bonding

## Contents

<b>8.1 Lewis Structures</b> . . . . .	<b>10</b>
<b>8.2 Resonance structures</b> . . . . .	<b>10</b>
<b>8.3 Exceptions to the Octet Rule</b> . . . . .	<b>10</b>
<b>8.4 Ionic Bonds</b> . . . . .	<b>10</b>
<b>8.5 Strengths and Lengths of Covalent Bonds</b> . . . . .	<b>10</b>
<b>8.6 Bond Polarity and Electronegativity</b> . . . . .	<b>11</b>

- |                                                                               |                                                                                          |                                                                                                     |
|-------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| 1. Lewis symbols for atoms and ions                                           | molecules based on dipole moment and bond length                                         | 9. Relationship between bond type (single, double, triple), bond strength/enthalpy, and bond length |
| 2. Lattice energy. Rank based on ion sizes and charges.                       | 6. Formal charges, ID dominant Lewis structures                                          | 10. Bond enthalpies to estimate enthalpy changes for gas-phase reactants and products               |
| 3. $e^-$ config and octet rule to draw Lewis structure                        | 7. Recognize molecules where resonance structures are needed, draw dominant res. struct. |                                                                                                     |
| 4. Electronegativity differences and non-polar/polar covalent and ionic bonds | 8. All exceptions to octet rule                                                          |                                                                                                     |
| 5. Charge separation in diatomic                                              |                                                                                          |                                                                                                     |

## 8.1 Lewis Structures

**Representation** of electron arrangement and bonds. Valence  $e^-$  are drawn as dots around atom, shared pairs are lines between atoms. Most atoms require 8 valence  $e^-$ , H needs 2.

**Electron Config of Ions** remove or add  $e^-$  to highest  $n$ , then  $l$ .

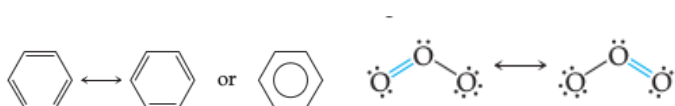
**Formal Charge** valence -  $\frac{1}{2}$  bonding - non-bonding

**Most common Lewis structure** has the lowest formal charge

**Not enough valence** electrons could cause a multiple bond.

## 8.2 Resonance structures

The actual bonds of a substance with multiple valid bonding schemes cannot be modeled using a single Lewis structure. Examples, Benzene and  $O_3$ :



Benzene's arrangement confers special stability to molecules.

## 8.3 Exceptions to the Octet Rule

**Odd number of  $e^-$**   $BF_3$  has resonance and six valence around Boron, NO has 11 valence electrons

**Hypervalent** molecule or ion has more than an octet around central atom Only period 3+ , due to larger size.

**Octet gives unfavorable** distribution.

**Large atom** unsurrounded by large number of small electronegative atoms, enough to overpower the octet rule.

**Electron configuration** shows distribution of  $e^-$  in orbitals. F:  $[He]2s^2 2p^5$

1A	Li	$[He]2s^1$	$Li \cdot$
2A	Be	$[He]2s^2$	$\cdot Be \cdot$
3A	B	$[He]2s^2 2p^1$	$\cdot \dot{B} \cdot$
4A	C	$[He]2s^2 2p^2$	$\cdot \dot{C} \cdot$
5A	N	$[He]2s^2 2p^3$	$\cdot \dot{N} \cdot$
6A	O	$[He]2s^2 2p^4$	$\cdot \dot{O} \cdot$
7A	F	$[He]2s^2 2p^5$	$\cdot \dot{F} \cdot$
8A	Ne	$[He]2s^2 2p^6$	$:\ddot{Ne}:$

## 8.4 Ionic Bonds

**Lattice energy** indicates energy needed to separate an ionic substance into its gaseous components:  
 $AB \longrightarrow A^+(g) + B^-(g)$

**Related** to Coulomb's law for particles.

**Born-Haber cycle** Used to calculate the elusive lattice energy using several known energies and Hess's law.

## 8.5 Strengths and Lengths of Covalent Bonds

**Strength** is determined by energy needed to break the bond

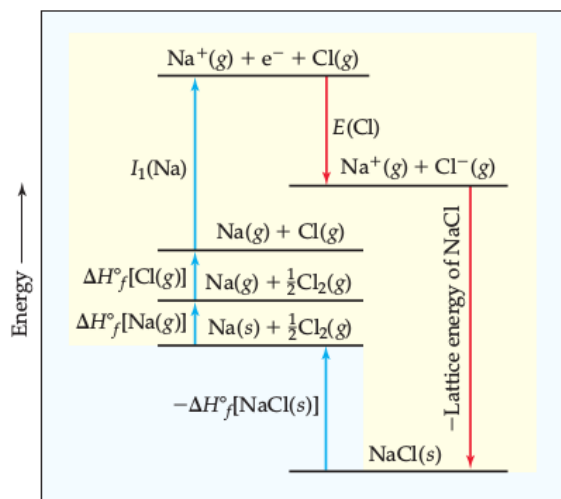
**Bond enthalpy**  $\Delta H$  needed to break a bond in one mole of a gaseous substance:  $Cl_2(g) \longrightarrow 2 Cl(g)$ . Represented as  $D(Cl-Cl)$

**Enthalpies of Reactions** can be determined using bond enthalpies, even if  $\Delta H_f^\circ$  are not known for all involved. Imagine two steps: energy to break

all bonds as needed, energy to form new bonds.

**Bond length** decreases with increasing number of bonds between two atoms.

**Smaller bond length** larger  $\Delta H$



## 8.6 Bond Polarity and Electronegativity

**Electronegativity** ability of an atom in a molecule to attract  $e^-$ . Based on ionization energy, electron affinity and other properties. **Trend:** increases to the top-right

**Bond polarity** equality of  $e^-$  distribution in covalent bond

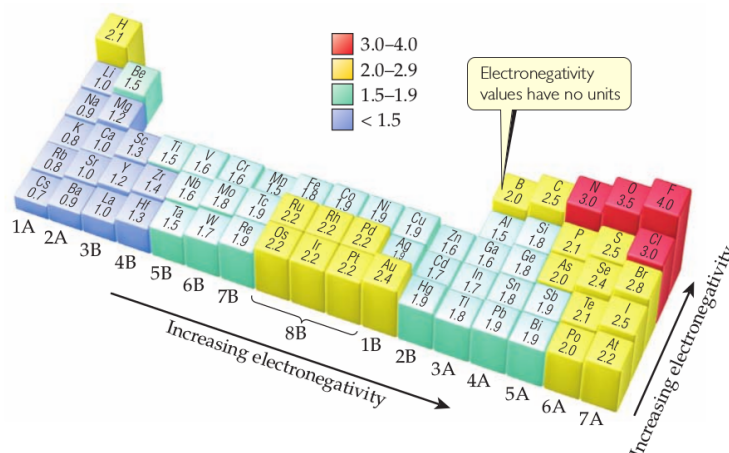
**Nonpolar covalent** equal electron sharing. Difference in e.neg = 0.

**Polar covalent** not equal electron sharing. Partial charge represented as  $\delta+$  and  $\delta-$ . In HF, H has partial positive, in  $H_2O$  H has partial negative. Difference in e.neg about 0.5.

**Ionic bonds** very unequal electron sharing. Difference in e.neg  $\gg 0.5$ .

**Dipole moment** indicates direction and magnitude of partial charge. Relates to charge and radius:

$$\mu = Q \cdot r.$$



## 9 Chapter 9. Molecular Geometry and Bonding Theories

### Contents

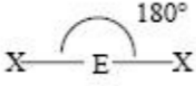
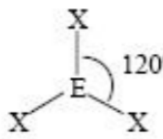
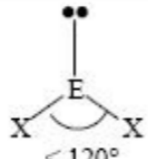
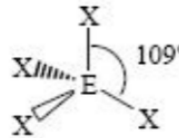
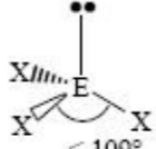

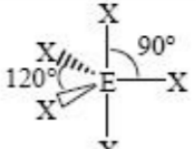
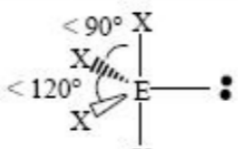
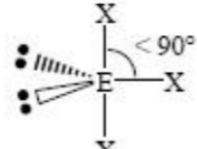
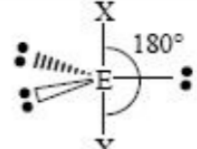

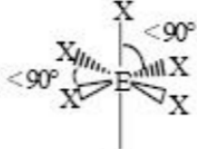
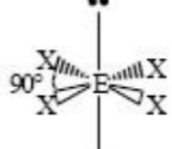
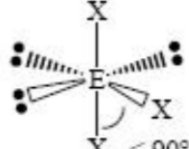
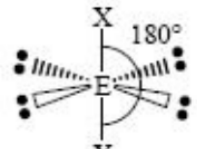
9.1 Molecular Shapes . . . . .	12
9.2 VSEPR Model . . . . .	12
9.3 Covalent Bonding, Orbital Overlap . . . . .	13
9.4 Hybrid Orbitals . . . . .	13
9.5 Multiple Bonds . . . . .	13
9.6 Molecular Orbitals . . . . .	14
9.7 Period 2 Diatomic Molecules . . . . .	14

1. Predict 3D shapes using VSEPR model
2. Polar or nonpolar based on geometry and individual dipole moments
3. Orbital overlap and covalent bonds
4. Hybridization atoms in molecules based on molec structures
5. Overlap and  $\sigma$ ,  $\pi$  bonds.

6. Delocalized  $\pi$  bonds in molecules like Benzene
7. Count  $e^-$  in delocalized  $\pi$  system
8. Concept of bonding and antibonding MOs and draw examples of  $\sigma$  and  $\pi$  MOs.
9. MO energy-level diagram. Place  $e^-$  to obtain bond orders and  $e^-$  configura-

- tions of diatomic molecules.
10. Correlate bond order, bond strength/enthalpy, bond length, magnetic properties with MO descriptions of molecules.

## 9.1 Molecular Shapes

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramidal	 Bent or Angular		
5	 Trigonal Bipyramidal	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

## 9.2 VSEPR Model

**Shapes minimize** electron repulsion

**Electron Domain** a bonding pair, a multiple bond, or a non-bonding  $e^-$ .  $\text{CCl}_2\text{O}$  has 3 domains about the central atom.

**Nonbonding** takes up more space

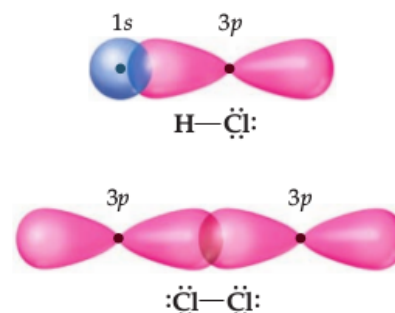
**Multiple centers?** just find the shape for each center

**For 6 domains:** octahedral arrangement is the stablest

## 9.3 Covalent Bonding, Orbital Overlap

**Overall Polarity** of a covalent molecule. Consider the shape and each dipole, they may cancel each other out, if they don't then the molecule is indeed polar.

**Combining VSEPR with Lewis** structures suggests covalent bonds form by the intersection of two non-bonding orbitals.



## 9.4 Hybrid Orbitals

**Hybrid orbitals** combined atomic orbitals, have different shapes

**Hybridization** mixing orbitals, although number of orbitals must remain constant.

**Hypervalent** central atoms aren't generally hybridized.

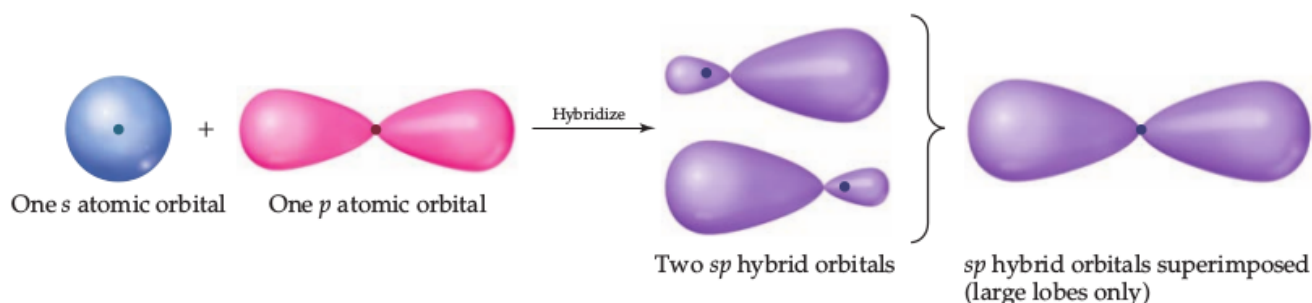
**Linear** 180° arrangement of domains implies  $sp$  hybridization.

**Triangular** 120° arrangement implies  $sp^2$  hybridization, total 3.

**Tetrahedral** 109.5° arrangement implies  $sp^3$  hybridization, total 4.

**Not all orbitals** need  $s$  contact, can also be non-bonding,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  have  $sp^3$  orbitals.

**To find** draw Lewis structure, find shapes, any  $s$  orbitals? Must be hybrid.



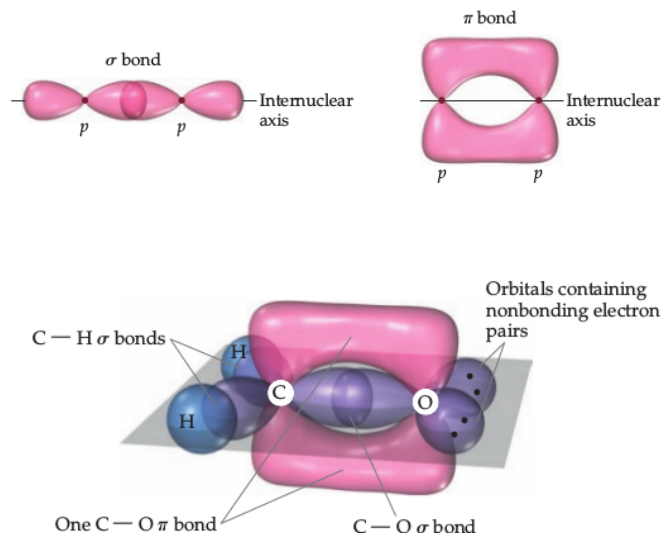
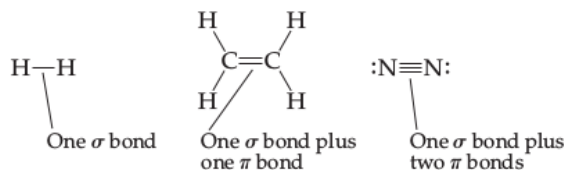
## 9.5 Multiple Bonds

**Single bonds** are called  $\sigma$ . Always local.

**Triple and double bonds** have one  $\sigma$  and two or one  $\pi$  bonds. Weaker – roundabout for  $e^-$  – but reduces rotation.

**$p_\pi$  orbital** is the un-hybridized  $2p$  orbital in an  $sp^2$  that can be involved in forming a  $\pi$  orbital.

**Benzene** rigid thanks to the **delocalized** (floating)  $e^-$  in double bonds.



## 9.6 Molecular Orbitals

**Molecular orbital** wave functions describing  $e^-$ . Orbitals combine to cover the whole molecule. MO can have 0, 1 or 2  $e^-$

**Number of MO** number of atomic orbitals combining to make MOs.

**Bonding MO** waves add constructively to form mighty bond

**Anti-Bonding MO** waves add destructively,  $e^-$  repelled.

**Bond order**  $\frac{1}{2}$  (bonding  $e^-$  - anti-bonding  $e^-$ ).

**Trend:** as bond order increases, bond enthalpy increases and bond distance decreases

**Electrons arranged** according to Hund's Rule and Pauli's E. Principle.

**Core electrons** do not contribute to molecular bonding much

## 9.7 Period 2 Diatomic Molecules

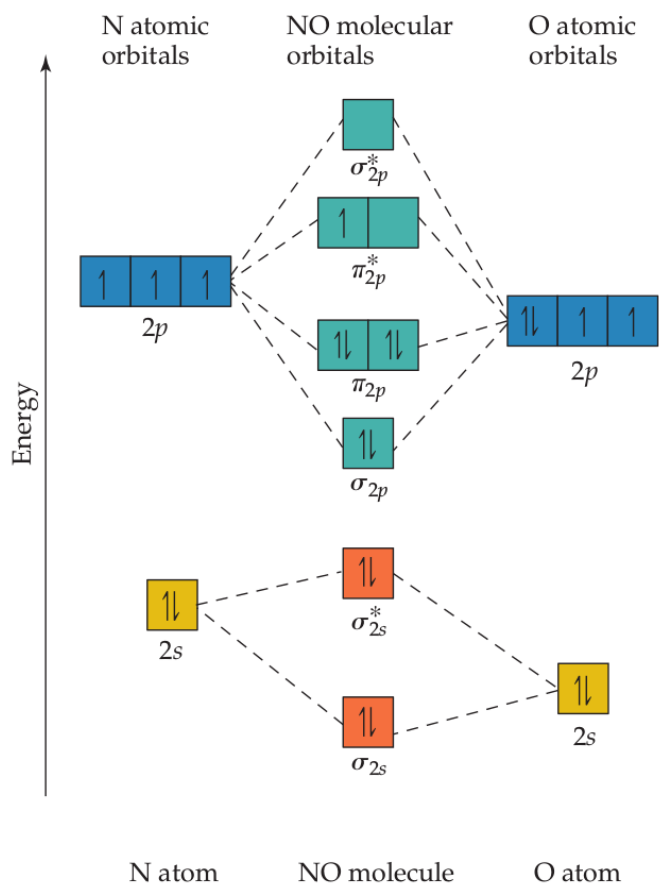
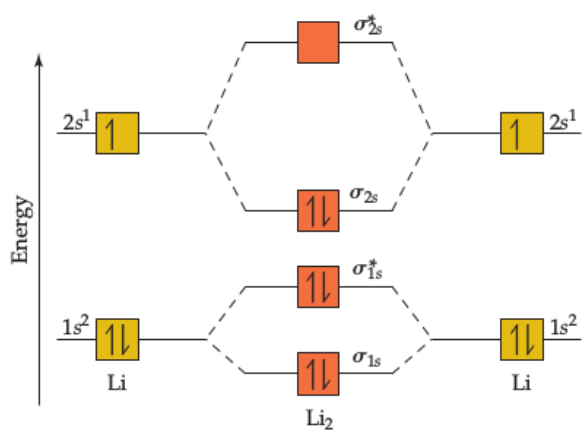
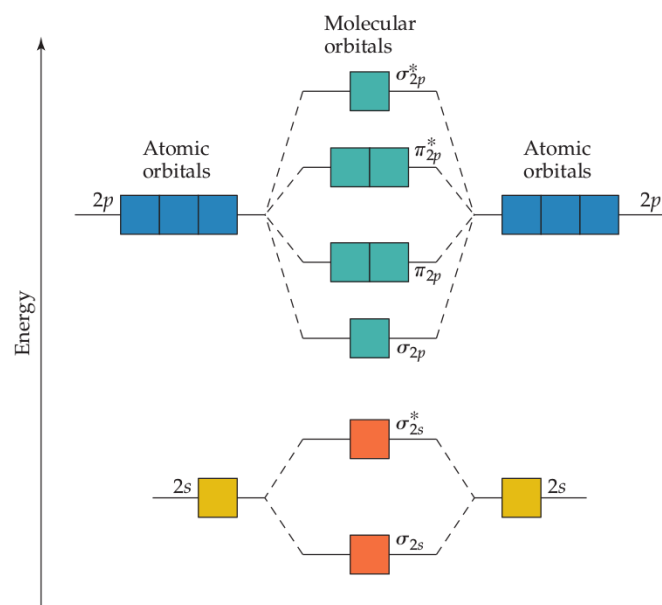
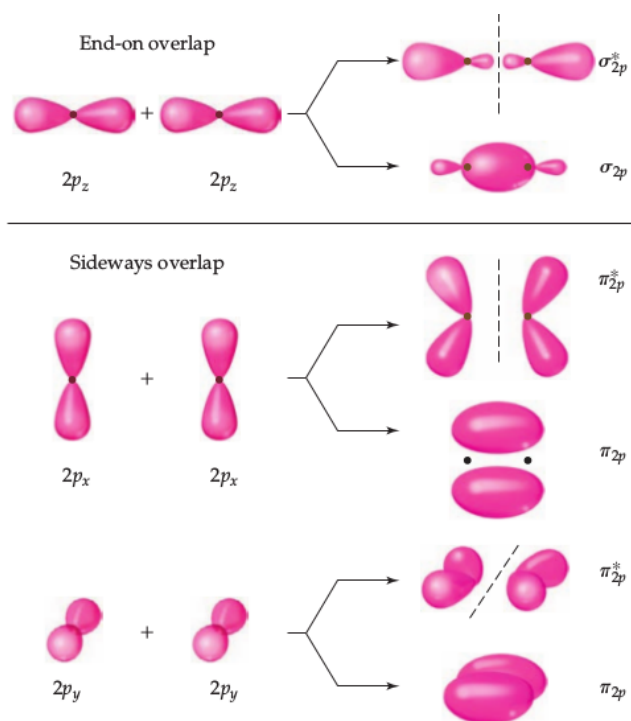
**Homonuclear diatomic** molecules (two identical)

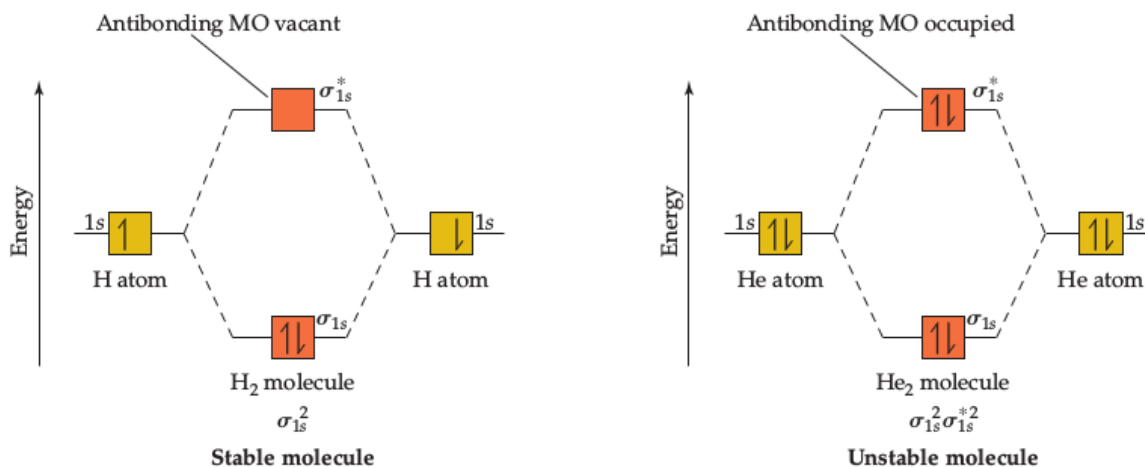
1. number of MO = number of AO combined
2. AO most effectively combined with other AO of similar energy
3. Effectiveness of combo relates to overlap.
4. MO can have two  $e^-$  with opposite spin (Pauli)
5. Hund's rule obeyed for same energy MOs

**Heteronuclear diatomic** similar to homo-nuclear, but an MO has a greater contribution from AO to which it is closer in energy. NO:  $\sigma_{2s}$  is closer to the O 2s than to the N 2s, thus the sigma has greater contribution from O than N.

**Paramagnetism** unpaired  $e^-$  cause magnetic attraction

**Diamagnetism** no unpaired  $e^-$  weak magnetic repulsion





## 10 Chapter 10. Gases

- Convert between pressure units, mostly torr and atm
- Calculate P, V, n, or T
- Explain how gas laws relate to ideal-gas equation
- Density or MW of a gas
- Volume of gas consumed/formed
- Total pressure of a gas mixture given partial pressures
- Kinetic molecular theory of gases: gas laws, rates of effusion/diffusion
- Explain why volumes, intermolecular attractions cause gases deviate from ideal gas laws

**Units** 1 atm = 760 torr = 1.0132 · 10<sup>5</sup> Pascals

**Charles' law** V/T is constant

**Boyle's law** PV is constant

**Ideal gas law** PV = nRT where R = 0.08205  $\frac{\text{Latm}}{\text{molK}}$

**Van der Waal's equation** for non-ideal gases, some corrections must be made. a, b are gas specific. Larger gas molecules are less ideal.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

**RMS speed** of molecules  $\sqrt{\frac{3RT}{M}}$

**Rate of effusion** lighter gases effuse faster  $\frac{r_1}{r_2} =$

$$\sqrt{\frac{M_2}{M_1}}$$

**Density of a gas**  $\frac{PM}{RT}$

**Partial pressure**  $p_{\text{total}} = \sum \text{each gas } p$

**Mole fraction**  $X = \frac{P_1}{P_t} = \frac{n_1}{n_t}$  moles of gas and total moles, total pressure and partial pressure.  $P_1 = \frac{n_1}{n_2} P_t = X_1 P_t$ .

## 11 Chapter 11. Liquids and IMFs

### Contents

11.1 Liquids	16
11.2 Intermolecular Forces	17

- IMFs: dispersion, dipole-dipole, hydrogen bonding, ion-dipole
- Explain polarizability, relate to dispersion forces
- Explain viscosity, surface tension, capillary action
- Names of state changes, exo or endothermic?
- Interpret heating curves, get enthalpy changes (temp/phase)
- Critical pressure, crit temperature, vapor pressure, normal boiling/melting points, critical point, triple point
- Sketch phase diagrams, water's = special
- Molecular arrangements and characteristics of nematic, smectic, cholesteric liquid crystals. Features of those that favor liquid crystalline phases

### 11.1 Liquids

**Viscosity** ease of molecule motion relative to each other. **Trend:** decreases with size.

**Surface tension** net inward force that must be countered to expand the surface area of a liquid.

**Cohesive forces** molecules bind to each other

**Adhesive forces** bind to surface



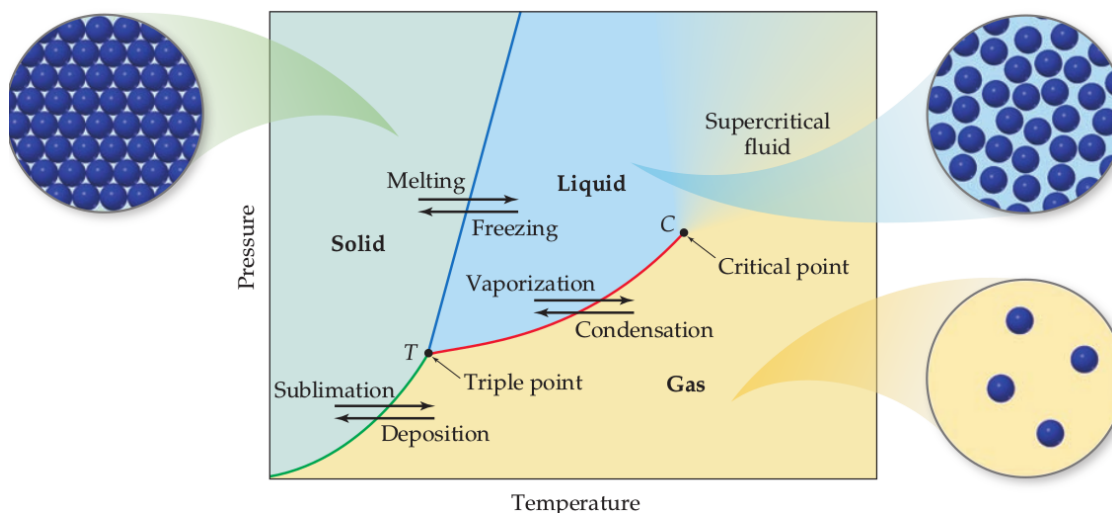
**Capillary action** rise of liquid up narrow tubes

**Heat of sublimation** energy needed to move solid directly to gas phase. Equal to  $\Delta H_{fus} + \Delta H_{vap}$ .

**Vapor pressure** pressure exerted by the substance's vapor above the surface of a liquid. There's always some vaporization.

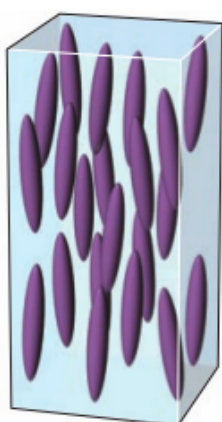
**Volatile** evaporate readily

**Boiling point** vapor pressure = external pressure. Molecules can break free of their neighbors



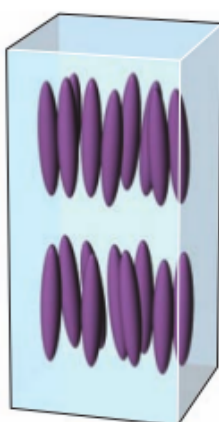
**Liquid phase**

Molecules arranged randomly



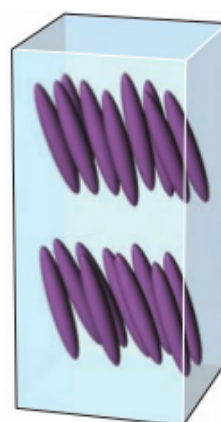
**Nematic liquid crystalline phase**

Long axes of molecules aligned, but ends are not aligned



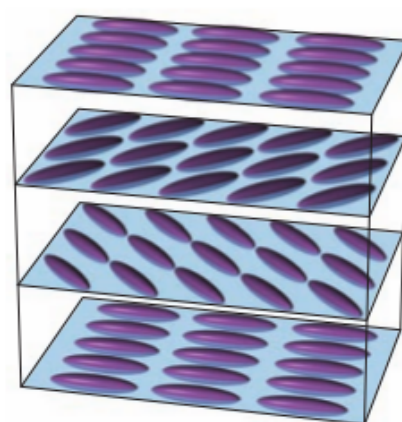
**Smectic A liquid crystalline phase**

Molecules aligned in layers, long axes perpendicular to layer planes



**Smectic C liquid crystalline phase**

Molecules aligned in layers, long axes of molecules inclined with respect to layer planes



**Cholesteric liquid crystalline phase**

Molecules pack into layers, long axes of molecules in one layer rotated relative to the long axes in the layer above it

## 11.2 Intermolecular Forces

Stronger IMFs mean higher viscosity, surface tension (maintain surface area) and capillary action. For molecules of approximately equal mass and size, **the strength of intermolecular attractions increases with increasing polarity.**

Name	strength	description	
<b>Dispersion</b>	weakest	instantaneous $e^-$ imbalance disrupt neighbors	all molecules do it, oblong, heavier = stronger
<b>Dipole-dipole</b>	weak	between dipoles	only between polar molecules
<b>Van der Waal's</b>	weak group	includes dispersion, dipole-dipole. Short range	repulsive/attractive, stronger = higher BP
<b>Hydrogen bonding</b>	strong	10% covalent, mostly electrostatic	molecules with NH, OH, HF groups
<b>Ion-dipole</b>	strongest	between polar group and ion	example: $H_2O$ and an ion

## 12 Chapter 12. Solids

### Contents

<b>12.1</b>	<b>Classification</b>	<b>18</b>
<b>12.2</b>	<b>Structures</b>	<b>19</b>
<b>12.3</b>	<b>Metallic solids</b>	<b>19</b>
<b>12.4</b>	<b>Metallic bonding</b>	<b>19</b>
<b>12.5</b>	<b>Complex</b>	<b>20</b>
<b>12.6</b>	<b>Ionic solids</b>	<b>20</b>
<b>12.7</b>	<b>Molecular solids</b>	<b>20</b>
<b>12.8</b>	<b>Covalent-network solids</b>	<b>20</b>
<b>12.9</b>	<b>Semiconductors</b>	<b>20</b>
<b>12.10</b>	<b>Polymers</b>	<b>21</b>

1. classify solids based on bonding/IMFs
2. differences between crystalline and amorphous solids (crystal lattice, unit cells, etc)
3. why are there a limited number of lattices? 5 2D and 7 3D primitive lattices
4. characteristics/properties of metals
5. empirical formula and density of ionic/metallic solid given a unit cell. estimate length of a cubic unit cell from radii of atoms present
6. homogeneous/heterogeneous alloys
7. electron-sea model of metallic bonding
8. MO model of metallic bonding to generate electronic band structure of metals, qualitatively predict MP & BP, hardness
9. predict structures of ionic solids given radii and empirical formula
10. MP & BP in terms of IMF and crystalline forces
11. valence/conduction bands. band gap, holes, semiconductor and insulator
12. account for relative band gap energies of semiconductors through periodic trends
13. n-type and p-type doping to control conductivity
14. plastic, thermoplastic, thermosetting plastic, elastomer, copolymers, and cross-linking
15. polymers formed from monomers, what features allow this?
16. polymer chain interactions impact physical properties
17. properties of semicond. and metals change with nanometer crystals
18. structure/properties of fullerenes, carbon nanotubes and graphene

### 12.1 Classification

#### Types of kinetic energy

translational, rotational, vibrational.

**solids** lowest energy phase, mostly vibrational energy  
Atoms packed tight. It is surfaces of solids that react.

**metallic solids** held together by delocalized sea of valence  $e^-$

**ionic solids** mutual attraction between anions/cations

**covalent-network solids** extended network of covalent

bonds

**molecular solids** weak IMFs

**polymers** long chains of atoms, covalent

**nanomaterials** individual crystals are 1-100nm.

## 12.2 Structures

**crystalline solids** regularly repeating pattern, usually flat faces, specific angles

**amorphous solids** no long-range order

**unit cell** smallest repeating unit

**crystal lattice** geometrical pattern of points where unit cells go. *N-dimensional* lattices can be defined with *n* vectors

**motif**, group of atoms, associated with each *lattice point*

**primitives** 5 2D lattices, 7 3D lattices

**square**  $a = b, \gamma = 90$

**rect**  $a \neq b, \gamma = 90$

**hex**  $a = b, \gamma = 120$

**rhombic**  $a = b$

**oblique**  $a \neq b$

**cubic**  $a = b = c, \alpha = \beta = \gamma = 90$

**tetra**  $a = b \neq c, \alpha = \beta = \gamma = 90$

**hexa**  $a = b \neq c, \alpha = \beta = 90, \gamma = 120$

**rhombohedral**  $a = b \neq c, \alpha = \beta =$

$\gamma \neq 90$

**orthorhombic**  $a \neq b \neq c, \alpha = \beta = \gamma = 90$

**monoclinic**  $a \neq b \neq c, \alpha = \beta = 90, \gamma \neq 90$

**triclinic**  $a \neq b \neq c, \alpha \neq \beta \neq \gamma$

**body-centered cubic** additional point at center of such a cell

**face-centered** additional points at the faces of a cell

## 12.3 Metallic solids

**Metallic solids** good conductors of electricity and heat, malleable (sheets), ductile (wires)

**Structure** usually simple, just need one atom on each lattice point.

**Primitive** 1 atom per unit cell.

**Body-centered** 2 atoms per.

**Face-centered** 4 atoms per.

**Tight packing** is favorable if  $e^-$  are shared. **Hexagonal close packing** hcp, **Cubic** ccp.

**Coordination number** 12 for hcp

and ccp. In both, each sphere has 12 equidistant neighbors. Any immediate neighbors.

**Alloy** material that contains more than one element and behaves like a metal.

**Substitutional alloy** two metallic components have similar radii and bonding characteristics. Less typical if radii differ > 15%.

**Interstitial alloy** solute atoms must have smaller bonding

radii than solvent. Extra bonds mean stronger/harder/less ductile.

**Heterogeneous alloy** components are not dispersed uniformly. Properties depend on both composition and the manner in which the solid was formed from molten mixture (ex: cooled fast/slow?).

**Inter-metallic compounds** not mixtures. Definite properties.

## 12.4 Metallic bonding

**Electron-sea model** metal = array of metal cations in a sea of valence electrons. Electrons migrate to positive end. Also, their motion facilitates transfer of kinetic energy (heat). Not enough  $e^-$  on each atom, must share!

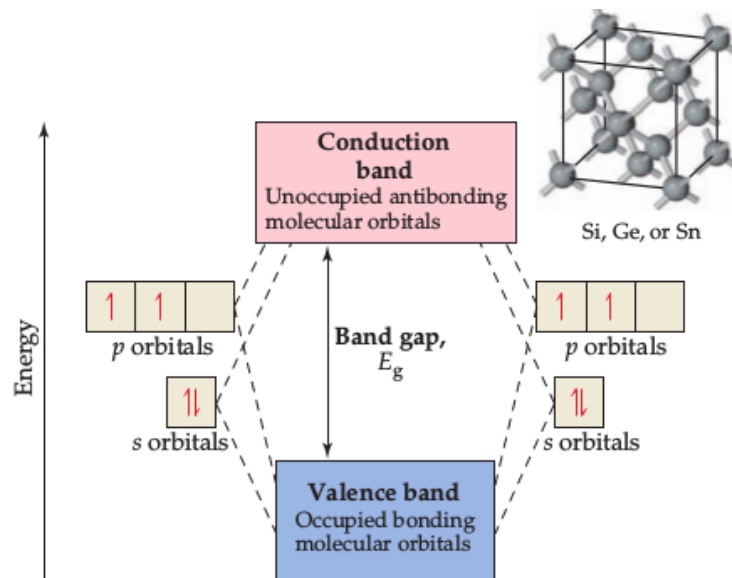
**Molecular-orbit model, Band Structure** Orbitals shared by entire metal. Fills low  $\rightarrow$  high. Bands are per-molecule in nonmetals. 3d band, 4s, 4d bands ...

**Conduction band** easy to remove  $e^-$  from here, the top.

**Valence band**  $e^-$  stick to here, closest to nucleus.

**Stronger bonds** mean higher boiling/melting points, heats of fusion, hardness, and so forth.

**Group 6B** middle, highest strength. More does not always mean more strength, repulsion in antibonding MOs can ruin it. Recall bond order  $\frac{1}{2}$  (bonding  $-$  antibonding  $e^-$ )



## 12.5 Complex

**Color** caused by  $e^-$  shuffling about the d-orbital.  $\text{TiO}_2$  has no electrons in the d-orbital and is colorless.

## 12.6 Ionic solids

**Ionic solids** electrostatic attraction between cations and anions. Interactions increase as charges of ions increases (lattice energy++).

**Structures** cations are usually much smaller than anions.  
**Coordination number** smaller than metals. Close packing is prohibited by repulsive forces.

**Formula from structure**  

$$\frac{\text{Cations per formula unit}}{\frac{\text{anion coord number}}{\text{cation coord number}}}$$
 is equal to  
**No conduction** as solids! Molten salt can conduct.

## 12.7 Molecular solids

**Molecular solids** atoms/neutral molecules held by dipole-dipole, dispersion, and/or hydrogen bonds.

**Weak bonds** low BP, MP (below 200 Celsius), soft. More symmetry means tighter packing,

stronger bonds.

## 12.8 Covalent-network solids

**Strong bonds** covalent bonds beat IMFs. Diamond, quartz.

## 12.9 Semiconductors

**Semiconductors** harder for  $e^-$  to move between levels because of a "band gap" separating valence/conduction bands. Typically group 4 (C, Si, Ge, Sn). Band gap ++, conduction --  
**large band gap** no conduction!

## 12.10 Polymers

**Polymers** chains or branched structures composed of monomers.

**Addition Polymerization** two monomers added to each other, double bond between is eliminated.

**Condensation Polymerization** condensing two monomers to-

gether, getting rid of intermediate small molecule once they are linked.

**Chain initiation** a free radical initiator possessing an unstable unpaired electron attacks a monomer unit to cause it to expose another unstable  $e^-$ .

**Chain propagation** this unit at-

tacks other monomers, forming an ever growing chain.

**Polymer crosslinks** produce harder substances with less flexibility.

**Commercial example** polyethylene chains contain between  $10^3$  and  $10^5$   $\text{CH}_2$  units.

## 13 Chapter 13. Properties of Solutions

### Contents

<b>13.1</b>	<b>Solution Process</b>	<b>21</b>
<b>13.2</b>	<b>Saturated solutions and solubility</b>	<b>22</b>
<b>13.3</b>	<b>Factors affecting solubility</b>	<b>22</b>
<b>13.4</b>	<b>Expressing solution concentrations</b>	<b>22</b>
<b>13.5</b>	<b>Colligative Properties</b>	<b>22</b>
<b>13.6</b>	<b>Colloids</b>	<b>23</b>

- |                                                                |                                                                                |                                                                                           |
|----------------------------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| 1. Enthalpy/entropy changes affect solution formation          | 5. Partial pressure of a gas and its solubility                                | 10. Osmotic pressure of a solution                                                        |
| 2. IMFs and solubility, like dissolves like                    | 6. Molarity, molality, mole fraction, percent composition, ppm, inter-convert! | 11. Solution vs colloid                                                                   |
| 3. Equilibrium in the solution process, solubility of a solute | 7. Colligative property? How do non-electrolytes and electrolytes affect?      | 12. Similarities between motions of gas molecules and the motions of colloids in a liquid |
| 4. Temperature and solid, liquid or gas solubility             | 8. Vapor pressure of a solvent over soln                                       |                                                                                           |
|                                                                | 9. BP elevation, FP depression                                                 |                                                                                           |

### 13.1 Solution Process

**Natural tendency** formation of solutions is favored by the increase in entropy that accompanies mixing.

**Intermolecular interactions** solute-solute, solvent-solvent, solvent-solute. The first two must be defeated to disperse and make room.

**Solvation** when ions/molecules of solute are split and surrounded by solvent.

**Solvation** solute is surrounded by solvent molecules.

**Hydration** solvation with water as solvent

**Energy cost** Solute and solvent must break down,

then they must be mixed.  $\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$

Think:  $\text{solute}_n \rightleftharpoons n \text{ solute}$  takes  $\Delta H_{solute}$   
 $\text{solvent}_m \rightleftharpoons m \text{ solvent}$  takes  $\Delta H_{solvent}$   $n \text{ solute} + m \text{ solvent} \rightleftharpoons \text{solution}$  takes  $\Delta H_{mix}$

**Exothermic**  $\Delta H_{mix} < 0$

**Endothermic**  $\Delta H_{solvent/solute} > 0$  need energy.

**Spontaneity** If overall exothermic, solvation occurs spontaneously. Explains why **likes dissolve likes**. Similar IMFs have similar costs.

## 13.2 Saturated solutions and solubility

**Equilibrium** solute + solvent  $\rightleftharpoons$  solution

**Crystallization** when solute is reverted to original state. "Undissolved." Happens at the same time as solvation. Visible when solvent is spent and cannot maintain solvation interactions with enough solute.

**Saturation** Equilibrium with undissolved solute. Additional solute will not dissolve (unless you add heat!). **Make a super-saturated:** add heat, lower heat, creates unstable solution.

**Solubility** how much solute an amount of solvent can dissolve.

## 13.3 Factors affecting solubility

**Like dissolves like** the stronger the interactions between solvent and solute, the greater the solubility. Polar dissolves polar; non-polar, non-polar.

**Miscible** liquids that mix in all proportions. May be **immiscible**.

**Pressure** liquid and solid solubilities are unaffected. Gas solubility is related to its partial pressure above liquid.

**Henry's law** molarity of gas = constant  $\cdot$  partial pressure  $S_g = kP_g$ . Constant  $k$  depends on temperature, solute and solvent.

**Temperature** increase increases solubility of most **solids** in water. There are exceptions  $\text{Ce}_2(\text{SO}_4)_3$

**Temperature** increase decreases solubility of most **gases** in water

## 13.4 Expressing solution concentrations

**Mass percentage**  $\frac{\text{mass of component in soln}}{\text{total soln mass}} \cdot 100\%$

**Parts per million/billion**  $\frac{\text{mg}}{\text{kg}}$ , also  $\frac{\text{mass of component in soln}}{\text{total soln mass}}$ .

$10^6$

**Mole fraction**  $\frac{\text{moles of component in soln}}{\text{total moles}}$

**Molality** Commonly used, independent of temperature!  $\frac{\text{moles of solute}}{\text{kg of solvent}}$ , little m.

**Molarity**  $\frac{\text{moles of solute}}{\text{litres of soln}}$ , big M.

## 13.5 Colligative Properties

**Colligative property** depend on concentration of solute, type of solvent. Not on the type of solute.

**Raoult's law, vapor pressure depression** Applies to *nonvolatile solute*

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}$$

$$\Delta P = X_{\text{solute}} P_{\text{solvent}}$$

$$X_y = \frac{\text{moles of y}}{\text{total moles}}$$

**Solutions w/ two or more volatile** components, the vapor pressure of the solution is the sum of the vapor pressure of each component as calculated by Raoult's law.

**Ideal solution** obey Raoult's law. Solute-solute, solvent-solvent and solute-solvent interactions all equal.

**Molal boiling point elevation constant** BP of a solution is higher than that of the solvent.  $m$  is molality.

$$\Delta T_b = T_{b(\text{solution})} - T_{b(\text{solvent})} = iK_b m$$

**Molal freezing point depression constant** FP of a solution is lower than that of the solvent.  $m$  is molality.

$$\Delta T_f = T_{f(\text{solution})} - T_{f(\text{solvent})} = -iK_f m$$

**van't Hoff Factor** number of fragments a solute breaks up into for that particular solvent. Usually anion/cation dissociated.

**True van't Hoff Factor**  $i = \frac{\Delta T_{f(\text{measured})}}{\Delta T_{f(\text{theoretical})}}$

**Osmosis** Solvent molecules pass through semipermeable membrane between two solutions of differing concentration. Solvent always goes to solution with lower solvent concentration. Want equilibrium (isotonic). Hypotonic: lower osmotic pressure, hypertonic: more concentrated.

**Osmotic pressure**  $\Pi = i\left(\frac{n}{V_{\text{soln}}}\right)RT = iM_{\text{molarity}}RT$

## 13.6 Colloids

Some mixtures appear to initially dissolve, but gravity separates solute from solvent.

**Colloids** between homogeneous mixtures and true solutions. Large solvent molecules/particles.

**Tyndall effect** Large enough to **scatter light**, Tyndall effect.

**Hydrophilic** folds to keep hydrophobic groups away from water. Polar groups go to surface. Usually have N or O and a charge.

**Hydrophobic** can only be dispersed if stabilized. Oth-

erwise, they run away. One method is via adsorption of ions to the surface. This repels particles from each other and causes interactions with the water.

**Emulsion** a suspension of one liquid in another, like Milk.

**Adsorption** think adhesion. Sticking stuff to surface.

**Brownian motion** collisions cause colloid particles to exhibit random motion

## 14 Chapter 14. Chemical kinetics

### Contents

<b>14.1</b>	<b>Reaction Rates</b>	<b>23</b>
<b>14.2</b>	<b>Rates and Concentration</b>	<b>24</b>
<b>14.3</b>	<b>Concentration and Time</b>	<b>24</b>
<b>14.4</b>	<b>The Effect of Temperature on Rates</b>	<b>24</b>
<b>14.5</b>	<b>Reaction Mechanisms</b>	<b>25</b>
<b>14.6</b>	<b>Catalysts</b>	<b>25</b>

- |                                                                                                  |                                                                           |                                                                 |
|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-----------------------------------------------------------------|
| 1. Factors affecting rate of reactions                                                           | 4. Explain form and meaning of a rate law (reaction order, rate constant) | 1st order and half-life                                         |
| 2. Rate of reaction given time and concentration                                                 | 5. Determine these given measure rates for various concentrations         | 8. Activation energy affects a rate, Arrhenius equation         |
| 3. Relate rates of product formation and reactant disappearance given balanced chemical equation | 6. Integrate rate laws                                                    | 9. Predict rate law for a multi-step mechanism given each step. |
|                                                                                                  | 7. Relationship between rate constant of                                  | 10. Explain principles of catalysis                             |

### 14.1 Reaction Rates

**Chemical kinetics** concerned with rates of reaction

**Reaction rates** affected by physical states the more readily collisions occur, the more rapidly goes the reaction. Affected by reaction concentrations and

temperature. Catalysts increase reaction rates by affecting activation rates.

**homogeneous** same phase

**heterogeneous** different phases

## 14.2 Rates and Concentration

Rate is typically measured in molarity per second, change in concentration, (M/s).

**Average rate** of disappearance of A =  $\frac{\Delta[A]}{\Delta t}$

**Instantaneous rate** concentrations can be measured using **spectroscopy**.

**Beer's law** concentration, c is directly proportional to absorbance, A.  $A = \epsilon bc$ , b is path length.

**Stoichiometry** In reaction  $A \longrightarrow B$  the rate of appearance of product is the rate of disappearance of reactant.

**Relative rates** In reaction  $aA + bB \longrightarrow cC + dD$ , the rates are  $-\frac{1}{a} \frac{\Delta A}{\Delta t} = -\frac{1}{b} \frac{\Delta B}{\Delta t} = \frac{1}{c} \frac{\Delta C}{\Delta t} = \frac{1}{d} \frac{\Delta D}{\Delta t}$ . This does not hold true if intermediate substances are

formed in significant amounts.

**Rates are positive** by convention  
**(Differential) Rate Law** Typically of form  $R = -k[A]^m[B]^n$

**Rate constant**  $k :: M^{-m-n+1}s^{-1}$ . Different for every reaction and temperature;  $> 10^9$  means fast,  $< 10$  means slow.

**Reaction orders**  $m, n$  usually 0, 1, 2. Can be negative or fractional.

**Overall reaction order**  $n + m$

**Rate law from Initial rates**  $n = \frac{\ln \frac{Rate_1}{Rate_2}}{\ln \frac{[A]_1}{[A]_2}}$

## 14.3 Concentration and Time

Integrated, linear rate laws for the first order reaction  $A \longrightarrow \dots$

**First-order reaction**  $\ln[A]_t = \ln[A]_0 - kt$ .

**Second order reaction**  $\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$ .

**Zero-order reaction**  $[A]_t = [A]_0 - kt$

**Half life** of a first-order depends only on  $k$ .  $t_{1/2} = -\frac{\ln 1/2}{k}$

## 14.4 The Effect of Temperature on Rates

**Collision model** based on kinetic molecular theory. Molecules must collide to react, so goes the theory. More energy/temp means more collisions, faster rate. Molecules must be aligned correctly on impact.

**Activation energy**,  $E_a$  needs to be achieved. Must also be moving fast enough and in the correct orientation. Lower  $E_a$  means faster reactions. Never negative.

**Rate does not depend on  $\Delta H$** , only on  $E_a$

**Activated complex/transition state** Enough energy in the right direction, now the molecules

may react together. Highest potential energy. It's all downhill from here!

**Arrhenius equation** Rate constant incorporates all of these:  $k = Ae^{-E_a/RT}$ . A is the **frequency factor**, constant as temperature is varied. Can be used to find different  $k$ s.  $R = 8.314 J \cdot mol^{-1} \cdot K^{-1} = 0.082057 L \cdot atm \cdot K^{-1} \cdot mol^{-1}$

**Solve for  $k$**  at different temperatures. A and  $E_a$  remain constant:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{A} (1/T_2 - 1/T_1)$$



## 14.5 Reaction Mechanisms

**Reaction mechanism** Steps which constitute a reaction. Order in which bonds are modified. And change in relative positions.

**Elementary reactions** Single step. Defined by # of molecules colliding: **uni/bi/termolecular**. > 3 molecules colliding is improbable.

**Intermediate**  $\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$  is actually  $\text{NO}_2 + \text{NO}_2 \longrightarrow \text{NO}_3 + \text{NO}$  then  $\text{NO}_3 + \text{CO} \longrightarrow \text{NO}_2 + \text{CO}_2$  Together:  $2\text{NO}_2 + \text{NO}_3 + \text{CO} \longrightarrow \text{NO}_2 + \text{NO}_3 + \text{NO} + \text{CO}_2$  Thus  $\text{NO}_3$  is an intermediate, common in both sides of the addition. Multi-step reactions have one or more such substances.

**Rate laws** of elementary reactions have an overall reaction order equal to the number of molecules involved. Termolecular,  $n+m=3$ . A single chemical equation cannot tell us if a reaction is elementary!

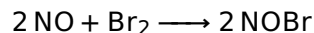
**Rate-determining step** is the slowest. If initial, likely that its rate law will govern that of the overall.

**Slow initial step** the rate is usually equal to the rate

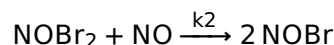
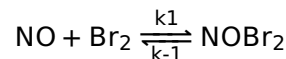
of the initial step.

If the initial step is fast, the rate law may be derived by assuming equilibrium and solving the  $k_1$  and  $k_{-1}$  to get rid of the intermediate substance  $\text{NOBr}_2$ .

Example:



could be a termolecular reaction, or the fast equilibrium step and a slow final step



$k_1, k_{-1}$  reach equilibrium meaning rate of (forward = reverse) and the total rate constant  $k = k_2 \frac{k_1}{k_{-1}}$ . Two steps, but only uni/bi molecular is more likely. 35 or more steps are sometimes derived!

## 14.6 Catalysts

**Catalyst** changes the speed of (initial) activation of a reaction without being changed itself Usually done by lowering  $E_a$ . Opposite = inhibitor.

**Homogeneous catalyst** same phase as reactants. Not so for a **Heterogeneous catalyst** (first step usually adsorption of reactants)

**Adsorption** (think adhesion), how fast a substance is bound to a surface.

**Enzymes** marvelously efficient biological catalysts.

Usually huge proteins, kilo to mega amu. Very selective. Faster than nonbiologicals,  $10^3 - 10^7$  reactions per molecule per second (turnover number).

**Substrates** substances reacting at the active site

**Active site** location of catalysis.

**Lock-and-key model** Explanation for specificity of an enzyme.

# 15 Chapter 15. Chemical equilibrium

## Contents

15.1 Rock bottom . . . . .	26
15.2 Equilibrium constant . . . . .	26
15.3 Direction and Summation of Equations . . . . .	26
15.4 Heterogeneous Equilibrium . . . . .	26
15.5 Finding K from initial and equilibrium concentrations . . . . .	26
15.6 Applications of K . . . . .	27
15.7 Le Châtelier's Principle . . . . .	27

1. What is meant by equilibrium, relate to rates
2. Write equilibrium-constant expression for any reaction
3. Inter-convert  $K_c$  and  $K_p$
4. Magnitude of equilibrium constant and relative amounts of reactants and products
5. Manipulate constant to reflect changes in chemical equation
6. Heterogeneous reaction equilibrium constant (EC)
7. Calculate EC from concentration measurements
8. Predict direction of a reaction given EC and conc.s
9. Calculate concentrations given EC and one equi. conc.
10. Calculate equi. conc.s given EC and starting conc.s
11. Le Châtelier's principle to predict how conc.s, volume or temperature of system at equilibrium affects the equilibrium position

## 15.1 Rock bottom

**Dynamic equilibrium** two opposing events have the same rate, no net change occurs.

**Vapor pressure** rate of molecules leaving the liquid near the surface is equal to the rate of their return to liquid state

**Chemical equilibrium** opposing reactions with the same rate.

**Example**  $\text{N}_2\text{O}_4(\text{g}) (\text{colorless}) \rightleftharpoons 2\text{NO}_2(\text{g}) (\text{brown})$ .

The equilibrium constant is

$$K = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

**At equilibrium** concentrations do not change and products/reactants cannot escape system.

**For equilibrium** to occur, both reactions must be able to occur.

## 15.2 Equilibrium constant

**Unique to an equilibrium** even if initial concentrations change

**law of mass action** consider the general equilibrium equation  $aA + bB \rightleftharpoons dD + eE$ . The equilibrium expression is

$$K_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b}$$

**No units**  $K_c$  is unitless because another method of measuring it ends up unitless.

**Activity** of a substance in an ideal mixture is the ratio of  $C$  or  $P$  to a reference like  $1M$  or  $1\text{atm}$ .  $A = CM/1M$  thus, no units

**Solids and Liquids** activity is unity.

**Depends on order** of the equilibrium reaction, even though they are naturally order-less. Thus, in a way  $K_c = \frac{1}{K_c}$ .

**Can use partial pressure** instead of concentrations for gaseous reactions.

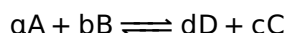
**Converting**  $K_p = K_c(RT)^{\Delta n}$  where  $\Delta n$  = moles of gaseous product – moles of gaseous reactant.

## 15.3 Direction and Summation of Equations

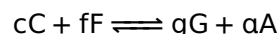
**Reaction written backwards**  $K_{rev} = \frac{1}{K}$

**Reaction multiplied** by a constant  $n$ ,  $K_n = K^n$ .

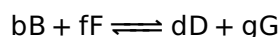
**Reactions added** simply multiply all  $K$ s involved. Adding the two equations:



with  $K_0$  and



with  $K_1$  will give



with  $K_0K_1$ .

## 15.4 Heterogeneous Equilibrium

**homogeneous** all involved substances in same phase

**heterogeneous** involved substances in different

phases

**liquid or solid** substances have an activity equal to unity. Ratio of their mass to volume is constant.

## 15.5 Finding K from initial and equilibrium concentrations

**If initial and final known** then  $\Delta\text{conc}$  is known.

**If initial and another  $\Delta\text{conc}$  known** use coefficients in balanced reaction to relate change in the known with the current unknown.

**If initial and change known** just add!

**Use an ICE table** Initial, Change in, and Equilibrium concentrations.

**Example** Key steps: finding change in  $\text{conc}$  knowing only  $\Delta\text{conc}_{\text{HI}}$ .

$$(1.87 \cdot 10^{-3}) \left( \frac{1\text{molH}_2}{2\text{molHI}} \right) = 0.935 \cdot 10^{-3}$$

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
Initial	$1.00 \cdot 10^{-3}$		$2.00 \cdot 10^{-3}$		0.00
Change	$-0.935 \cdot 10^{-3}$		$-0.935 \cdot 10^{-3}$		$+1.87 \cdot 10^{-3}$
Final	$0.065 \cdot 10^{-3}$		$1.065 \cdot 10^{-3}$		$1.87 \cdot 10^{-3}$

## 15.6 Applications of K

**Predicting the Direction of Reaction** If  $Q < K$  then more products will be needed, if  $Q > K$  then more reactants needed.

**Reaction quotient** Calculated like  $K$ , but for concen-

trations or partial pressures at any point in the reaction.

**Calculating equilibrium concentrations** just solve for unknowns using known equilibrium concentrations.

## 15.7 Le Châtelier's Principle

**Le Châtelier's Principle** if equilibrium is disturbed in any way, the system will shift its position to counteract. "le-SHOT-lee-ay."

**Lies to the right** lots of "product"

**Lies to the left** lots of "reactant"

**Concentration of reactants increased** increases concentration of products

**Pressure change** by changing volume, if increased in gaseous equilibrium the system will want to min-

imize the number of moles of gas. Constant temperature.

**Volume change** same as pressure change

**Temperature change** If reaction is endothermic, increasing  $T$  increases  $K$ . If reaction is exothermic, increasing  $T$  decreases  $K$ .

**Effects of catalysts** activation energies are lowered, but  $K$  is not changed. Equilibrium will be reached faster.

# 16 Chapter 16. Acid-Base Equilibria

## Contents

16.1Arrhenius Acids and Bases . . . . .	28
16.2Brønsted-Lowry Acids and Bases . . . . .	28
16.3Auto-ionization of Water . . . . .	28
16.4pH and pOH Scale . . . . .	28
16.5Strong acids and bases . . . . .	28
16.6Weak Acids and $K_a$ . . . . .	29
16.7Weak Bases and $K_b$ . . . . .	29
16.8Acid-Base Properties of Salt Solutions . . . . .	29
16.9Acid-Base Behavior and Chemical Structure . . . . .	29
16.10Lewis Acids and Bases . . . . .	30

1. ID Arrhenius acids and bases
2. Describe nature of hydrated proton, either  $H^+$  (aq) or  $H_3O^+$  (aq)
3. ID Brønsted-Lowry acids and bases and ID conjugate acid-base pairs
4. Correlate the strength of an acid to the strength of its conjugate base
5. Equilibrium position of a proton-transfer relates to the strengths of acids and

- bases involved
6. Auto-ionization of water and explain how  $[H_3O^+]$  and  $[OH^-]$  are related by  $K_w$
7. Calculate the pH given  $[H_3O^+]$  and  $[OH^-]$
8. Calculate the pH of a strong acid or base given its concentration
9. Relate  $K_a$  and/or  $K_b$  for a weak acid/base and its concentration and the pH

10. Calculate  $K_b$  for a weak base given  $K_a$  of its conjugate acid and vice versa
11. Predict whether an aqueous solution of a salt will be acidic, basic or neutral
12. Predict the relative strength of a series of acids from their molecular structures
13. ID Lewis acids and bases

## 16.1 Arrhenius Acids and Bases

**Acid** increases concentration of  $H^+$  ions.

**Bases** increase the concentration of  $OH^-$  ions

**Examples**  $HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)$

$NaOH \longrightarrow Na^+(aq) + OH^-(aq)$

## 16.2 Brønsted-Lowry Acids and Bases

**Acid-base reactions** involve the transfer of protons from one substance to another

**Acid** donates a proton to another substance

**Base** receives a proton

**Hydronium ion** closer to the reality of aqueous solutions.

**Used interchangeably**  $H^+(aq)$  and  $H_3O^+(aq)$

**Water acts like** a Brønsted-Lowry base when a Brønsted-Lowry acid is dissolved:  $HA + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$ .

**Water also acts like** a Brønsted-Lowry acid when a Brønsted-Lowry base is dissolve:  $B + H_2O(l) \longrightarrow BH^+(aq) + OH^-(aq)$

**Amphoteric** substances can behave as either acids

and bases. Basic if in the presence of something more acidic, acidic if the other is more basic.

**Amphiprotic** Either a proton acceptor or donor. Although an amphiprotic species must be amphoteric, the converse is not true.

**Amphiprotic**  $HCO_3^-$ ,  $HS^-$ ,  $HPO_4^{2-}$ ,  $HF$ ,  $H_2O$

**Conjugate acid** every base converts into one.  $H_3O^+$  is the c.a. of  $H_2O$

**Conjugate base** every acid converts into one.  $OH^-$  is the c.b. of  $H_2O$

**Relative Strengths of Acids and Bases** The stronger the acid/base, the weaker its conjugate base/acid.

1. Strong acid's conjugate base shows negligible basicity
2. Weak acid's conjugate base is a weak base
3. Negligibly acidic substance's conjugate is a strong base

**Leveling effect** Stronger acids react with water to produce  $H_3O^+$  and stronger bases react to produce  $OH^-$ . These are the strongest acids and bases that can exist in water.

**Equilibrium favors** transfer of protons to form weaker acids and bases.

## 16.3 Auto-ionization of Water

**Autoionization**  $H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$

**Ion-product constant** the equilibrium constant for water  $k_w = 1 \cdot 10^{-14}$  at 25 degrees Celsius.

**Neutral solution**  $[H^+] = [OH^-]$

## 16.4 pH and pOH Scale

**pH** is equal to  $-\log_{10}[H^+]$

**pOH** is equal to  $-\log_{10}[OH^-]$

**pH + pOH** at 25 degrees Celsius is always 14.

**Negative pH** indicates a very strong acid

**pH greater than 14** indicates a very strong base

**pH may be measured** by detecting trace electric charge

**pH depends on** concentration of the acid or base

## 16.5 Strong acids and bases

**Most common strong acids** six mono-protic: ( $HClO_3$ ,  $HClO_4$ ,  $HCl$ ),  $HBr$ ,  $HI$ ,  $HNO_3$ , and one diprotic:  $H_2SO_4$  but only with the first proton

**Strong:** no equilibrium, balance lies entirely to the

right

**Most common strong bases** ionic hydroxides of the alkali metals, and of the heavier alkaline earth metals (Calcium++). The latter are limited in solubility.

$$K_a K_b = K_w$$

## 16.6 Weak Acids and $K_a$

**Equilibrium constant for acids** is called the acid-dissociation constant  $K_a$ . Larger means stronger. Need not be aqueous. Example for  $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

**Percent ionization for acids** Larger also means stronger.

$$\frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}}$$

**Polyprotic acids** can undergo more than one dissociation.  $\text{H}_2\text{SO}_3$  has two protons to give away. It is always easier to remove the first proton.

$\text{p}K_a$  is equal to  $-\log_{10} K_a$

## 16.7 Weak Bases and $K_b$

**Equilibrium constant for bases** is called the base-dissociation constant  $K_b$ . Larger means stronger. Only for water based! Example for  $\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq})$ :

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

**Category One** neutral substances that have an atom with a non-bonding pair of electrons that can accept a proton. Most have Nitrogen. Includes Ammonia and Amines.

**Amines** at least one N-H bond in  $\text{NH}_3$  is replaced with N-C.

**Second category** anions of weak acids. The acid  $\text{NaClO}$  has the conjugate base  $\text{ClO}^-$ .

$\text{p}K_b$  is equal to  $-\log_{10} K_b$

## 16.8 Acid-Base Properties of Salt Solutions

**Nearly all salts are strong electrolytes** their acid-base properties are due to their cations and anions

**Hydrolysis** ions react with water to generate  $\text{H}^+$  or  $\text{OH}^-$ .

**An anion can be considered** the conjugate base of an acid  $\text{A}^-$ . If it is not a strong acid, it is a weak acid.

**Polyatomic cations with one or more protons** can be considered the conjugate acids of weak bases.

**The larger the charge on the metal ion** the stronger the interaction between ion and oxy-

gen of its hydrating water molecules. Facilitates proton transfer.

**Combined effect of cation and anion :**

1. Anion and cation don't react with water (both from strong a/b)? pH should be neutral.  $\text{NaCl}$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{RbClO}_4$
2. Anion produces hydroxide ions, cation doesn't react (from weak acid, strong base)? pH should be basic.  $\text{NaClO}$ ,  $\text{RbF}$ ,  $\text{BaSO}_3$
3. Cation produces hydronium ions, anion doesn't react (from weak base, strong acid)? pH should be acidic.  $\text{NH}_4\text{NO}_3$ ,  $\text{AlCl}_3$ ,  $\text{Fe}(\text{NO}_3)_3$
4. Both anion and cation react in water (both from weak)? The pH of the solution depends on the relative abilities of the ions to react.  $\text{NH}_4\text{ClO}$ ,  $\text{Al}(\text{CH}_3\text{COO})_3$ ,  $\text{CrF}_3$

## 16.9 Acid-Base Behavior and Chemical Structure

**Strength of the H-A bond** is the greatest indicator of acid strength

**Acid Strength** 1. stronger partial charges on H in H bonds. If non-polar, the bond is neither acidic nor basic

2. bond strength, increases as you move to the left-bottom.  $\text{HBr}$  is very strong

3. The greater the stability of the conjugate base  $\text{A}^-$ , the stronger the acid.

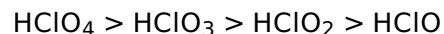
**Binary acids** bond strength decreases and acidity and size increase down a group.

**Oxyacids** O-H bonds present, but the compound is an acid

**OH bond: acid or base** as the electro-negativity of Y in  $\text{Y-O-H}$  increases, so does the acidity. Electron density is drawn to Y so the O-H bond becomes

weaker and more polar. Also, the stability of the conjugate base ( $\text{YO}^-$ ) increases with the electronegativity of Y.

**Acid strength increases** as additional electronegative atoms bond to the central atom Y.



**Carboxylic Acids** Contain the carboxyl group  $\text{COOH}$

$\begin{array}{c} \text{O}^- \\ || \\ \text{C} - \text{O} - \text{H} \end{array}$  Largest group of organic acids. The conjugate base is stabilized by resonance between the two oxygens, spreads negative charge. Also the non O-H oxygen draws electron density from the broken bond, increases polarity.

**Carboxylic acid examples**  $\text{CH}_3\text{COOH}$ , Benzoic acid (benzene and carboxyl), Formic acid  $\text{HCOOH}$ .

## 16.10 Lewis Acids and Bases

**Lewis acids and bases** is a general definition of acids and bases.

**Lewis Acid** electron-pair acceptor

**Lewis Base** electron-pair donor

**Water** is not required. A wider variety of reactions

may be treated, including acid-base reactions (no proton transfer).

**Strength of electrostatic** interactions

**The interaction of lone pairs** on one molecule with vacant orbitals on another is one of the most important concepts in chemistry.

# 17 Chapter 17. More Aspects of Aqueous Equilibria

## Contents

<b>17.1</b>	<b>Common-Ion Effect</b>	<b>31</b>
<b>17.2</b>	<b>Buffers</b>	<b>31</b>
<b>17.3</b>	<b>Acid-Base Titrations</b>	<b>31</b>
<b>17.4</b>	<b>Solubility Equilibria</b>	<b>32</b>
<b>17.5</b>	<b>Factors affecting solubility</b>	<b>32</b>
<b>17.6</b>	<b>Precipitation and Separation of Ions</b>	<b>32</b>
<b>17.7</b>	<b>Qualitative Analysis for Metallic Elements</b>	<b>32</b>

- |                                                                     |                                                                            |                                                                         |
|---------------------------------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 1. The Common-ion effect                                            | base/acid titration                                                        | 13. Precipitate when soln.s mixed by comparing $Q$ and $K_{sp}$         |
| 2. How does a buffer function?                                      | 8. Differences in the prev two titration curves?                           | 14. Ion concentrations needed to begin precipitation                    |
| 3. Calculate the pH of a buffered solution                          | 9. Estimate $pK_a$ for mono/polyprotic acids form titration curves         | 15. Effect of complex-ion formation on solubility                       |
| 4. Same, after adding small amounts of strong acid/base             | 10. $K_{sp}$ , molar solubility, mass solubility, solve for one using two. | 16. Logic of ID of metal ions in aqueous soln by a series of reactions. |
| 5. Calculate appropriate quantities to make buffer for certain pH   | 11. Molar solubility in presence of common ion                             |                                                                         |
| 6. Calculate pH at any point in a strong acid-strong base titration | 12. Effect of pH on solubility                                             |                                                                         |
| 7. Same, but for weak-strong acid/base or                           |                                                                            |                                                                         |

## 17.1 Common-Ion Effect

Solution with weak acid/base and a soluble substance containing that acid/base **shifts the equilibrium to the left** concentrations lowering  $H^+$ . Example: adding  $CH_3COONa(aq)$  salt to a solution of  $CH_3COOH(aq)$  or adding  $NH_4Cl$  electrolyte to solution of  $NH_3(aq)$

## 17.2 Buffers

**Buffered solution** small amount of strong acid/base. Resists changes in pH by neutralizing any  $H^+$  or  $OH^-$ .

**Composition example** buffer pair  $CH_3COOH/CH_3COO^-$

**Composition method 1** mix a weak acid/base with a salt of that acid/base. Example: adding  $CH_3COONa$  to soln of  $CH_3COOH$ .

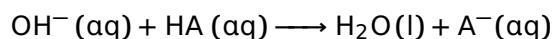
**Composition method 2** make conjugate acid/base from weak soln by adding strong acid/base. Example:  $CH_3COOH$  and add  $NaOH$  neutralize half of the acetic acid.

**Any pH** can be chosen for a buffer

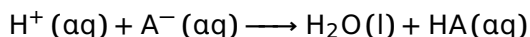
**Buffer capacity** how much intruding acid/base can be tolerated without straying from **pH range**

**pH Range** usually in range  $pK_a \pm 1$ . Work best when  $[HA] = [A^-]$ .

**Add  $OH^-$  ions** acid takes over



**Add  $H^+$  ions** base takes over



**pH of a Buffer** Use an ICE table. Cancel out spectator ions. Find  $[H^+]$

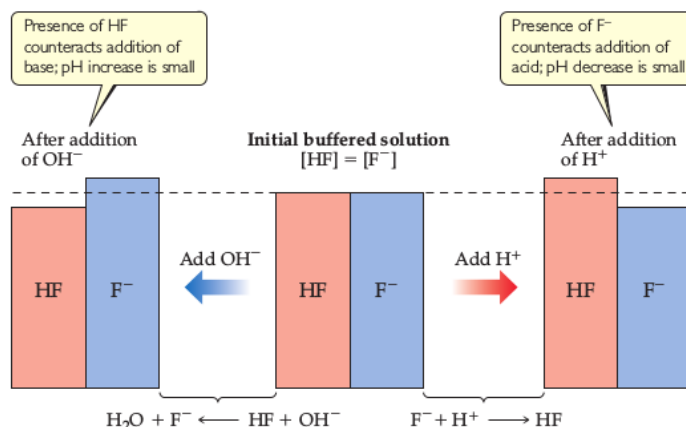
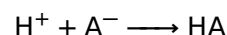
**Henderson-Hasselbalch equation** for conjugate acid-base pairs:  $pH = pK_a + \log \frac{base}{acid}$  where  $K_a$  of the acid is used and the two conc.s are at equilibrium. Can use initial conc.s – easier – but use this assumption with care.

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

**Adding a strong acid/base** Strong acid/base always neutralized completely with weak base/acid (water's  $1/k_w = 10^{14}$ ). To calculate pH of buffer after addition:

1. Find limiting reactant in the acid-base neutralization reaction ( $OH^-$  or  $H^+$  into ICE table)
2. Use new values of  $HA$ ,  $A^-$  and  $k_a$  to find  $[H^+]$

Balance:



## 17.3 Acid-Base Titrations

**pH titration curve** indicates pH as the titration progresses. See initial, equivalence and post-equivalence values.

**Equivalence point** moles of acid = moles of base

**Strong base titrates strong acid** pH rises from about 0 to about 14; equivalence point 7.

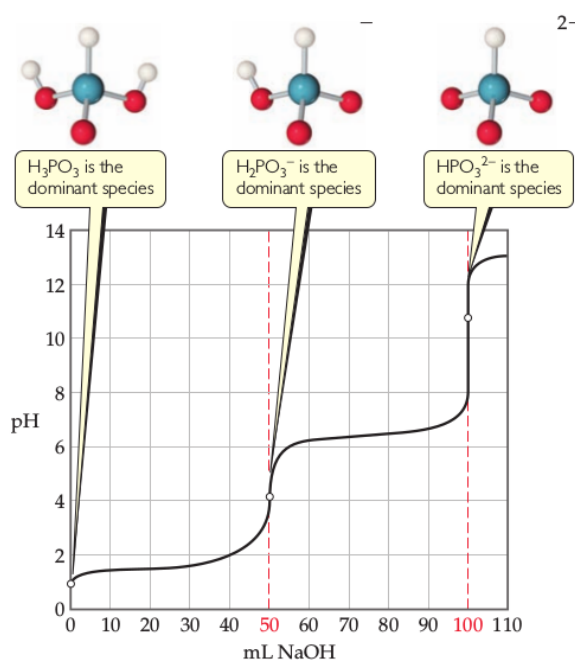
**Strong acid titrates strong weak** pH lowers, same as base titrating acid.

**Strong titrates weak** sudden change in pH, but equivalence point is closer. May not be 7 due to conjugate base/acid. Equivalence point pH increases as  $k_a$  decreases, closer to titrator's side.

**Acid-base indicator** can be used instead of pH meter. It must have an activation range near the equivalence point. Phenolphthalein range 8.3 to 10.0, Methyl red ranges from 4.2 to 6.0.

**Polyprotic acids** curve with two equivalence points.

**Half-equivalence point**  $pH = pK_a$



## 17.4 Solubility Equilibria

**Heterogeneous solubility** Species in different phases. Dissolution, precipitation of ionic compounds.

**Solubility-Product constant**  $K_{sp}$  solubility of solid in water.  $K_{sp}$  = product of concentrations of ions, raised to power of its equilibrium coefficient.  $\text{CaF}_2$  gives  $K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$ . Small means it doesn't dissolve much.

**Solubility** is quantity that dissolves to form saturated

soln, very volatile.  $K_{sp}$  measures how much solid dissolves, one for each temperature (extreme accuracy? consider concentration).

**Solubility from  $K_{sp}$**  ICE table for dissolved ions, their initial conc.s are 0 unless otherwise noted. Only if no other important equilibria affecting solubility.

Units:  $\frac{\text{g}}{\text{L soln}}$ ,  $\frac{\text{mol}}{\text{L soln}}$ .

**Deviations** caused by electrostatic between ions, ignoring acid-base equilibria, incomplete dissociation (like  $\text{MgF}^+$  ions)

## 17.5 Factors affecting solubility

**Common-ion effect** generally, solubility of a slightly soluble salt decreased by common-ion. Shift left.

**pH affects solubility**, increases for basic anions. Can dissolve completely in very acidic solution. Example:  $\text{Mg}(\text{OH})_2(\text{s})$  usually pH = 10.52  $[\text{Mg}^{2+}]$

= 0.00017, if pH is buffered to 9 and  $K_{sp} = 1.8 \cdot 10^{-11}$  then  $[\text{Mg}^{2+}] = 0.18\text{M}$ .

**Complex ion** very soluble in water. ...

**Formation of Complex ions**

**Formation constant**

**Amphoterism**

## 17.6 Precipitation and Separation of Ions

**Q for solubility**  $K_{sp}$ , but not necessarily at equilibrium. Can use same as Q in Chapter 15 to find direction of the reaction.

**Q =  $K_{sp}$**  solution is saturated, no precipitate

**Q <  $K_{sp}$**  reaction proceeds to the right, no precipitate

**Q >  $K_{sp}$**  reaction proceeds to the left, precipitate

**Selective precipitation** ions can be separated based on solubilities of salts. Sulfide ion is commonly used, sulfide salts span wide range.  $\text{CuS}$   $K_{sp} = 6 \cdot 10^{-37}$ ,  $\text{ZnS}$   $K_{sp} = 2 \cdot 10^{-25}$ .  $\text{CuS}$  will precipitate with pH around 1,  $\text{ZnS}$  will precipitate at higher pH.

## 17.7 Qualitative Analysis for Metallic Elements

**Metals vary** in their salt solubility, acid-base, complex ions. These differences can be used to separate and detect presence of metal ions.

**Qualitative analysis** presence/absence of species

**Quantitative analysis** quantity of species

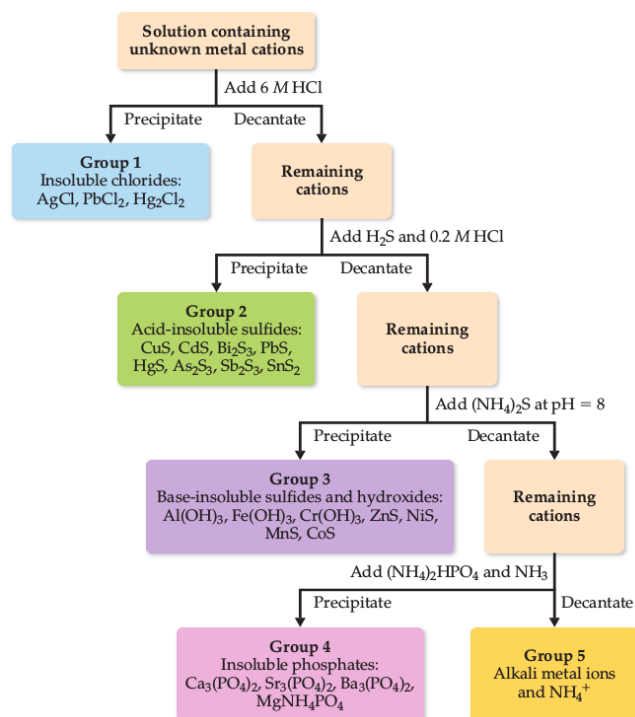
**Common 5 group scheme** **Group 1** insoluble chlorides, add HCl, precipitates  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PbCl}_2$

**Group 2** acid-insoluble sulfides, soln. now acidic,  $\text{H}_2\text{S}$  is added, precipitates  $\text{CuS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{PbS}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ . These have low  $K_{sp}$

**Group 3** base-insoluble sulfides and hydroxides, soln made basic,  $(\text{NH}_4)_2\text{S}$  added, precipitates  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$

**Group 4** insoluble phosphates,  $(\text{NH}_4)_2\text{HPO}_4$  precipitates  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$

**Group 5** alkali metal,  $\text{NH}_4^+$  flame test, other individual tests.



# 19 Chapter 19. Chemical Thermodynamics

## Contents



<b>19.1 Spontaneous Processes</b>	<b>33</b>
<b>19.2 Entropy and the Second Law</b>	<b>33</b>
<b>19.3 Molecular Interpretation of Entropy and the Third Law</b>	<b>33</b>
<b>19.4 Entropy Changes in Chemical Reactions</b>	<b>33</b>
<b>19.5 Gibbs Free Energy</b>	<b>34</b>
<b>19.6 Free Energy, Temperature, and Equilibrium Constant</b>	<b>34</b>

- |                                                                   |                                                            |                                                                          |
|-------------------------------------------------------------------|------------------------------------------------------------|--------------------------------------------------------------------------|
| 1. Spontaneous, reversible, irreversible and isothermal processes | 6. The Third law                                           | 11. Free-energy changes to predict if spontaneous                        |
| 2. Entropy and the Second law                                     | 7. Standard entropy changes using standard molar entropies | 12. Effect of temperature on spontaneity given $\Delta H$ and $\Delta S$ |
| 3. Entropy and micro-states                                       | 8. Entropy changes for an isothermal process               | 13. $\Delta G$ under nonstandard conditions                              |
| 4. Possible molecular motions                                     | 9. Gibbs free energy from enthalpy change                  | 14. $\Delta G^\circ$ and equilibrium constant                            |
| 5. Predict sign of $\Delta S$ for physical and chemical           | 10. Entropy change at a temperature                        |                                                                          |

## 19.1 Spontaneous Processes

**the first law** helps us keep track of heat changes, but does not tell us whether a process is favored because of anything we did to the system.  $\Delta H = q + w$ .

**thermodynamics** all about direction and extent of a reaction, not about rate.

**spontaneous** inherently directional process. Related to thermodynamic path from start to end states.

**example** ice melts to water spontaneously at a high enough temperature.

**reversible process** system and surroundings can return to original state by an exact reversal. Truly, they must occur with infinitesimally small units of heat occurring infinitesimally slowly.

**irreversible process** system cannot return to original state without permanent change in surroundings

**isothermal** process occurs at same temperature

## 19.2 Entropy and the Second Law

**entropy** denoted  $S$ , at constant temperature  $\Delta S = q_{rev}/T$  where  $q_{rev}$  is the heat the process would absorb if it was reversible. Units  $J/K$ . State function.

**for any process**  $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur}$

**for phase changes**  $\Delta q_{rev} = \Delta H_{fusion}$ .

**isothermic gas expansion**  $w_{rev} = -nRT \ln \frac{V_2}{V_1}$

**the second law**  $\Delta S_{univ} = 0$  for reversible processes and  $\Delta S_{univ} > 0$  for irreversible processes.

## 19.3 Molecular Interpretation of Entropy and the Third Law

**microstate** combination of motions and locations of atoms.

**Boltzmann's**  $S = k \ln W$  where  $k$  is B's constant

**entropy** randomness or disorder of a system. Related to number of microstates.

**translational motion** entire molecule moves. Kinetic energy.

**vibration motion** periodic molecular motion. "ac-

dion" bonds

**rotational motion** molecule spins like a top

**entropy increases** with increase in volume, temperature, motion of molecules, increase of motions and locations of molecules.

**entropy increases** solid dissolves, phase change  $(s) \rightarrow (l) \rightarrow (g)$  or increase in molecules.

**the third law** entropy of a pure crystalline solid at 0K is zero.  $W = 1$ . No motion, absolute zero, no entropy.

## 19.4 Entropy Changes in Chemical Reactions

**standard molar entropy** denoted  $S^\circ$  is entropy of a mole of substance at standard conditions.

**general observations** Not the same as enthalpies of formation! Elements at reference temperature are not zero. Increase with increasing molar mass,

or increasing number of atoms in formula. Gases greater than liquids or solids.

**tabulated**  $\Delta S^\circ$  can be used to calculate entropy change of any reaction.  $\Delta S^\circ = \sum_{products} nS^\circ - \sum_{reactants} mS^\circ$

**entropy change in surroundings** for isothermal process is  $\Delta S = -\Delta H/T = k \ln \frac{W_2}{W_1}$ .

## 19.5 Gibbs Free Energy

**Gibbs free energy** thermodynamic state function combining two state functions  $G = H - TS$ . For isothermal processes:  $\Delta G = \Delta H - T\Delta S$ .

**Gibbs at constant** temperature and pressure indicates spontaneity. Negative  $\Delta G$  means spontaneous, positive means nonspontaneous but reverse process is spontaneous.

**Equilibrium**  $\Delta G = 0$ . A spontaneous process.

**maximum level of work** that can be performed by

system indicated by the free energy.  $\Delta G = -W_{max}$ .

**standard free energies of formation**  $\Delta G_f^\circ$  defined just like standard enthalpies of formation. Defined zero for a pure element in standard state (convention, we only care about changes). Can be used to find standard free-energy change  $\Delta G^\circ$ .

$$\Delta G^\circ = \sum_{products} n\Delta G_f^\circ - \sum_{reactants} m\Delta G_f^\circ$$

## 19.6 Free Energy, Temperature, and Equilibrium Constant

**temperature doesn't affect**  $\Delta H$  and  $\Delta S$  of a process very much.  $\Delta G$  is governed by temperature.

**entropy term**  $-T\Delta S$  has greater effect on temperature dependence. Process with both  $\Delta H > 0$  and  $\Delta S > 0$  can be nonspontaneous at low temperatures but spontaneous at high temperatures. Example: ice.

**at equilibrium**  $\Delta G = 0, Q = K$  thus this equation:  $\Delta G = \Delta G^\circ + RT \ln Q$  turns into equation directly dependant on temperature and standard free-energy change

$$\Delta G^\circ = -RT \ln K$$

$$K = e^{-\Delta G^\circ/RT}$$

$$\Delta G = \Delta G^\circ + RT \ln K$$

# 20 Chapter 20. Electrochemistry

## Contents

20.1Oxidation States and Redox . . . . .	34
20.2Balancing Redox . . . . .	35
20.3voltaic cells . . . . .	35
20.4Voltage under Standard Conditions . . . . .	35
20.5Free Energy and Redox Reactions . . . . .	35
20.6Voltage under Nonstandard Conditions . . . . .	35
20.7Batteries and Fuel Cells . . . . .	35
20.8Corrosion . . . . .	35
20.9Electrolysis . . . . .	35

1. ID oxidation, reduction, oxidizing agent, reducing agent
2. Complete, balance redox equations using half-reactions
3. Sketch voltaic cells, ID cathode, anode, direction of  $e^-$  motion
4. Standard emfs from standard reduction potential

5. Reduction potentials to predict if redox is spontaneous
6. Relate  $E_{cell}^\circ, \Delta G^\circ$  to equilibrium constants
7. Calculate emf under nonstandard conditions
8. ID components of common batteries
9. Construction, explanation of lithium-ion

- battery
10. Construction, explanation of fuel cell
11. Corrosion, prevent with cathode protection
12. Reactions in electrolytic cells
13. Amount of products, reactants in redox and electric charge

## 20.1 Oxidation States and Redox

**electrochemistry** study of electricity and chemical reactions

**OIL RIG** oxidized is loss of electrons, reduction is gain-

ing electrons.

**reducing agent** causes reduction, it is oxidized to accomplish this

**oxidizing agent** causes oxidization, it is reduced to accomplish this

## 20.2 Balancing Redox

**half-reactions** a redox can be split into a reducing and into an oxidizing equation:

*sonofbitch*

**steps to balance in aqueous** 1.

**balance in basic aqueous**

**adding half-reactions** electrons should cancel to reveal the balanced equation

## 20.3 voltaic cells

### 20.4 Voltage under Standard Conditions

**standard conditions** 298K, 1atm, 1M

### 20.5 Free Energy and Redox Reactions

**Free energy**  $\Delta G$

$$\Delta G = -nFE$$

**Faraday constant**  $F = 96,485 \text{ C/mol}$

**Positive E** spontaneous

**Negative E** non-spontaneous

**1 Watt (W)** 1 J/s

### 20.6 Voltage under Nonstandard Conditions

**emf varies** with temperature and concentrations

**Nernst equation** Let  $n$  be the moles of  $e^-$  exchanged and  $Q$  be calculated similar to equil. constant  $k$  (use atm pressure without conversion):

$$E = E^\circ - (RT/nF) \ln Q$$

**At 298K**

$$E = E^\circ - (0.0592/n) \ln Q$$

### 20.7 Batteries and Fuel Cells

**battery** self contained electrochemical power source. Based on a variety of redox reactions.

**Primary cells** cannot be recharged

**Secondary cells** can be

**Common primary cell** alkaline dry cell

**Common secondary cells** Lead-acid, Ni-Cd, Nickel-metal hydride and Lithium-ion.

**Fuel cells** voltaic cells that need to be continuously supplied with reactants (such as  $H_2$ ) for a redox

reaction.

### 20.8 Corrosion

**corrosion** undesirable redox reaction.

**cathodic protection** protecting a metal by covering it using another that more readily undergoes oxidation.

**example** galvanized steel is Fe covered in Zn, a sacrificial anode in the redox reaction.

### 20.9 Electrolysis

**electrolysis reaction**

**electrolytic cell**

**current carrying medium** molten salt or electrolyte solution

**predict products** by comparing potentials of the red. and oxi. processes.

**active electrodes** are involved in the reaction

**quantity of substance formed** related to total current.  $1 \frac{C}{s} = 1A$

## 21 Chapter 21. Nuclear Chemistry

1. Balanced nuclear equations
2. Nuclear stability, decay from neutron-to-proton ratio of isotope
3. Balanced nuclear equations for nuclear transmutations

4. Ages of objects, amount of radionuclide remaining after time using half-life
5. Mass and energy changes for nuclear reactions
6. Binding energies for nuclei

7. Difference between fission and fusion
8. Power plant operation, differences
9. Units of radiation dosage
10. Biological effects of radiation

## 21.1

Minor

**description** item or whatevs

*Notes may be incomplete. Based on "Chemistry: The Central Science (13th Edition)" by Theodore E. Brown, H. Eugene LeMay, Bruce E. Bursten, Catherine Murphy, Patrick Woodward, and Matthew E. Stoltzfus.*