

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

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Notes taken during two introductory chemistry courses (CHEM121 and CHEM122) at the New Mexico Institute of Mining and Technology Spring 2015.

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1 Chapter 1. Units and Significant Figures

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

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, μ 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.fig.s 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

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2.3 Naming	3
2.4 Alkanes and Alcohols	4

1. Dalton's atomic theory
2. Key experiments that led to discovery of atom/nucleus/electrons (Cathode ray, oil drop, α 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 β are negative, α are positive, and γ 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 α scattering most α 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

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3.2 Stoichiometry	4

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|---|---|--|
| 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

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4.5 Oxidation-Reduction Reactions	5

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|---|--|---|
| 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 ₃ ⁻		all following	unless with NH ₄ ⁺ , alkali metal
CH ₃ COO ⁻		CO ₃ ²⁻	
alkali metals		PO ₄ ³⁻	
all following	unless with Hg ₂ ²⁺ , Pb ²⁺	all following	unless with Ca ²⁺ , Sr ²⁺ , Ba ²⁺
Cl ⁻	unless with Ag ⁺	S ²⁻	
Br ⁻	unless with Ag ⁺	OH ⁻	
I ⁻	unless with Ag ⁺		
SO ₄ ²⁻	unless with Sr ²⁺ , Ba ²⁺		

4.2 Strong Acids and Bases

Strong acids HI, HBr, HCl, HClO₃, HClO₄, HNO₃, H₂SO₄ (first proton only)

Strong bases group 1A metal hydroxides KOH, group 2A heavy metal hydroxides (beginning at Ca(OH)₂)

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 K^{+} and $(\text{NO}_3)^{2-}$ as spectator ions.

4.4 Acid-Base Reactions

Acids form H⁺ in water

Bases form OH⁻ 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⁻, reduction is gain of e⁻
Oxidation number is an artificial (negated) e⁻ count.

O -2, except in O₂²⁺ 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

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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. ΔH from $\delta E, P\delta V$
6. relate q_p to ΔH . Signs indicate exo/endothermic
7. Relate ΔH 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 ΔH°

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 ΔE means system has gained energy, has received: it's endothermic.

Negative ΔE means system has lost energy, has given: it's exothermic.

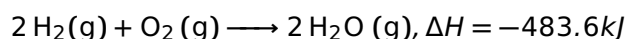
State function result depends only on present state

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 ΔH for a composite reaction is the sum of the ΔH for each component reaction.

5.5 Enthalpies of Formation

Enthalpy of formation ΔH_f° is the enthalpy required to **form** a substance in standard conditions, 25°C and 1 atm . Units: kJ/mol .

For stablest elementals at standard conditions, such as $\text{C}(\text{graphite})$, H_2 , 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^- s.

6.1 Energy of Light and Photons, Quantum Worries

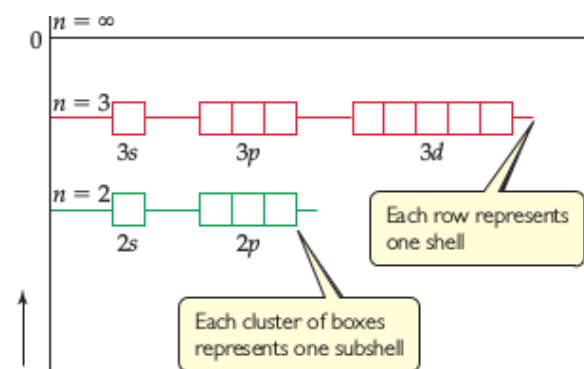
Properties of light speed of light $= c = 2.99 \cdot 10^8 \frac{m}{s} = \lambda \nu$ where λ is wavelength ν is frequency.

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^- '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^-) 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 $l \in 0 \dots n-1$

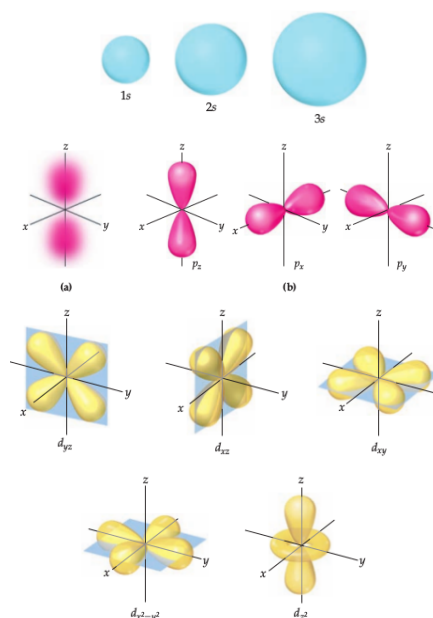
Magnetic quantum number a box, $m_s \in -l \dots l$

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

Subshell electrons share n, l

Pauli's exclusion principle all e^- in an atom have unique quantum numbers.

Hund's rule the preferred e^- arrangement has maximum e^- with the same spin m_s



7 Chapter 7. Periodic Properties of the Elements

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7.5 Nonmetals	9
7.6 Noble Gases	9
7.7 Hydrogen	9
7.8 Oxygen group	9
7.9 Halogens	9

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|---|--|---|
| 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

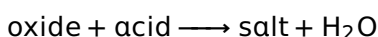
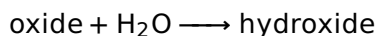
Solid conductors of both heat and electricity

Only one liquid at room temperature: Hg

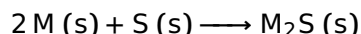
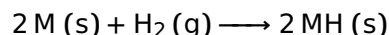
Form cations in aqueous solution, tend to make basic solutions.

Low first ionization energy I_1

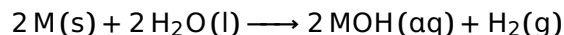
Common reactions



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: $\text{K} + \text{O}_2 \longrightarrow \text{KO}_2$

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

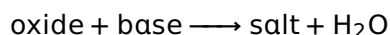
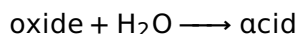
Usually brittle

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 $\text{XeF}_{2/4/6}$, KrF_2 , 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 H^+ present in water

7.8 Oxygen group

Atypical nonmetals

Oxygen stable as O_2

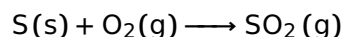
Peroxide O_2^{2-}

Superperoxide O_2^{2-}

Sulfur stable as 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

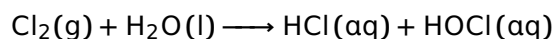
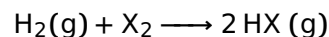
Very soluble, negative e^- affinity

Fluoride is extremely reactive

Diatomic molecules formed such as I_2 , Cl_2 , except F

Trend: melting, boiling points increase as elements get heavier

Common reactions



8 Chapter 8. Basic Concepts of Chemical Bonding

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8.2 Resonance structures	10
8.3 Exceptions to the Octet Rule	10
8.4 Ionic Bonds	10
8.5 Strengths and Lengths of Covalent Bonds	10
8.6 Bond Polarity and Electronegativity	11

1. Lewis symbols for atoms and ions
2. Lattice energy. Rank based on ion sizes and charges.
3. e^- config and octet rule to draw Lewis structure
4. Electronegativity differences and non-polar/polar covalent and ionic bonds
5. Charge separation in diatomic

6. molecules based on dipole moment and bond length
6. Formal charges, ID dominant Lewis structures
7. Recognize molecules where resonance structures are needed, draw dominant res. struct.
8. All exceptions to octet rule

9. Relationship between bond type (single, double, triple), bond strength/enthalpy, and bond length
10. Bond enthalpies to estimate enthalpy changes for gas-phase reactants and products

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.

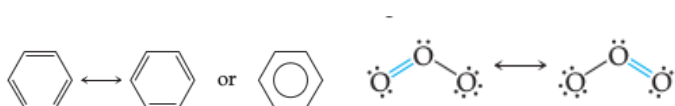
Formal Charge valence - $\frac{1}{2}$ bonding - non-bonding

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

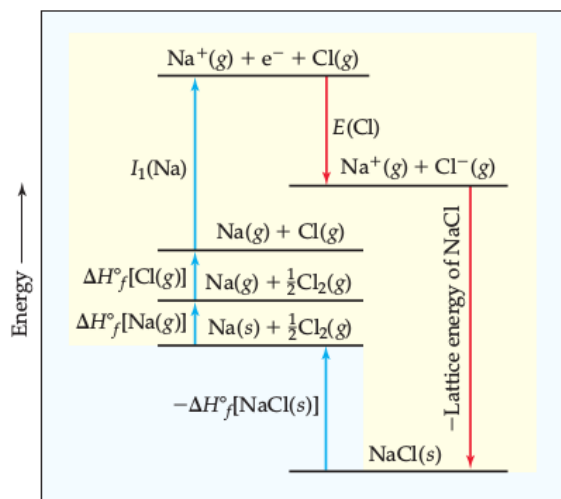
Bond enthalpy ΔH needed to break a bond in one mole of a gaseous substance: $Cl_2(g) \longrightarrow 2 Cl(g)$. Represented as $D(Cl-Cl)$

Enthalpies of Reactions can be determined using bond enthalpies, even if ΔH_f° 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 ΔH



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

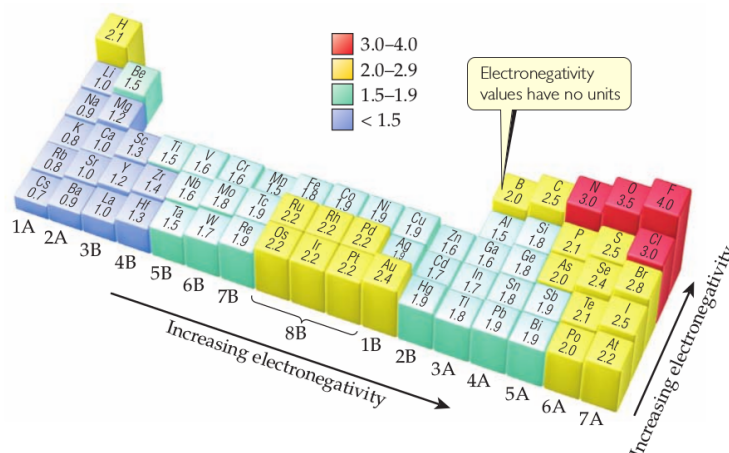
Nonpolar covalent equal electron sharing. Difference in e.neg = 0.

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

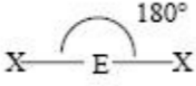
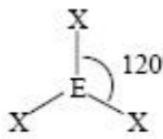
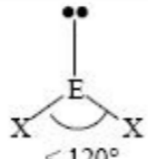
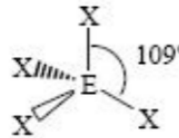
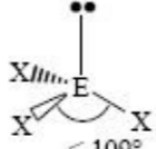

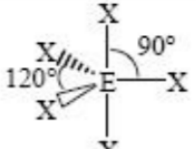
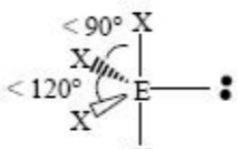
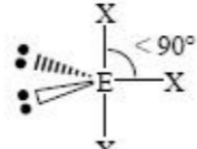
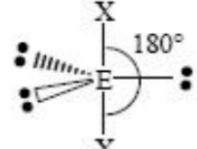

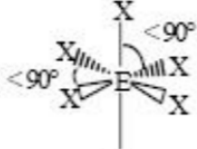
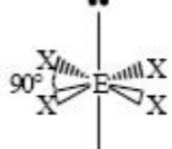
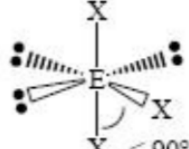
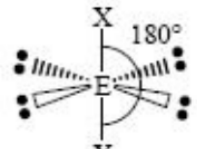
9.1 Molecular Shapes	12
9.2 VSEPR Model	12
9.3 Covalent Bonding, Orbital Overlap	13
9.4 Hybrid Orbitals	13
9.5 Multiple Bonds	13
9.6 Molecular Orbitals	14
9.7 Period 2 Diatomic Molecules	14

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 σ , π bonds.

6. Delocalized π bonds in molecules like Benzene
7. Count e^- in delocalized π system
8. Concept of bonding and antibonding MOs and draw examples of σ and π 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^- . CCl_2O has 3 domains about the central atom.

Nonbonding takes up more space

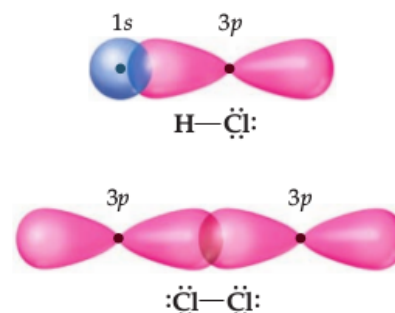
Multiple centers? just find the shape for each center

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.

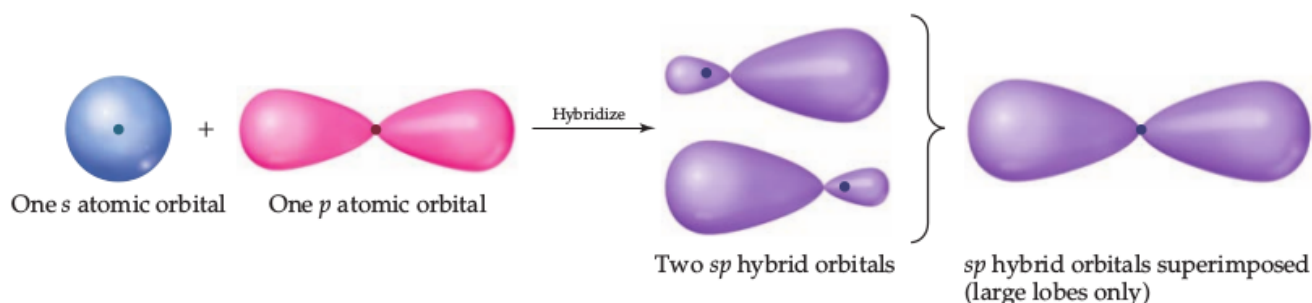
Linear 180° arrangement of domains implies sp hybridization.

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, NH_3 , H_2O have sp^3 orbitals.

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



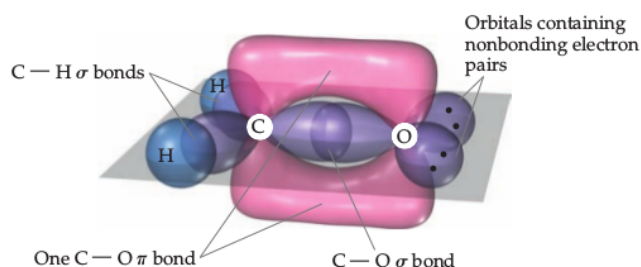
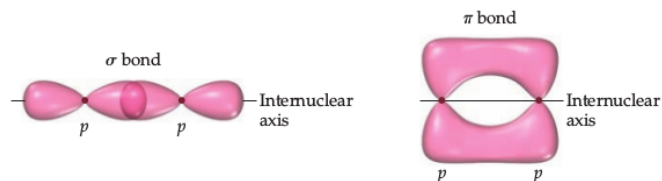
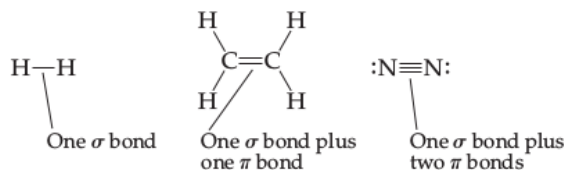
9.5 Multiple Bonds

Single bonds are called σ . Always local.

Triple and double bonds have one σ and two or one π bonds. Weaker – roundabout for e^- – but reduces rotation.

p_π orbital is the un-hybridized $2p$ orbital in an sp^2 that can be involved in forming a π 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

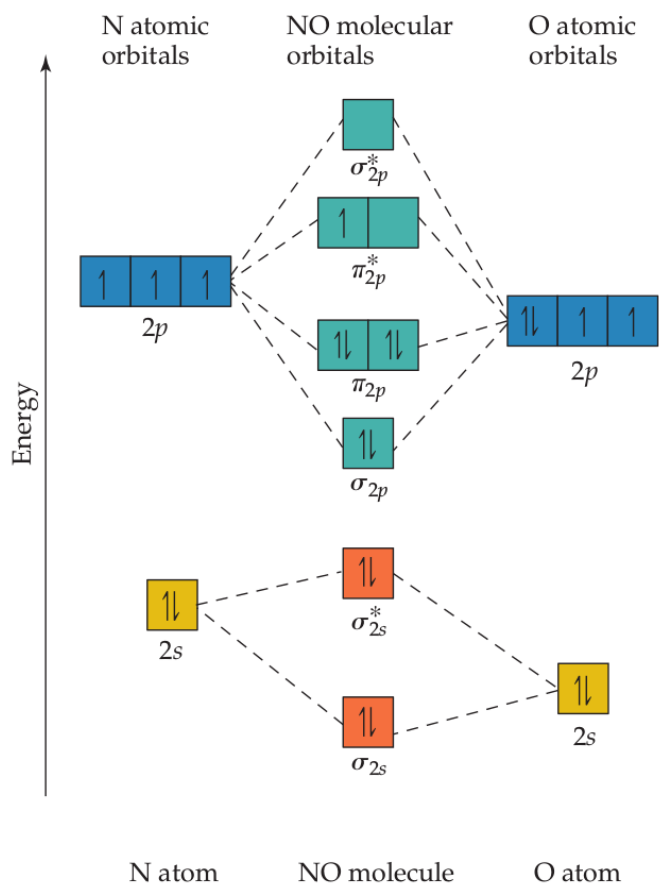
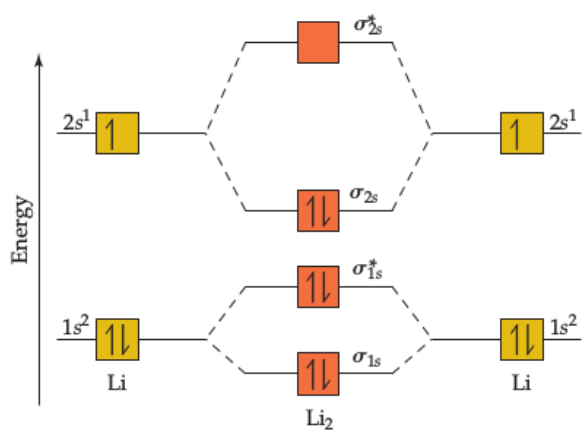
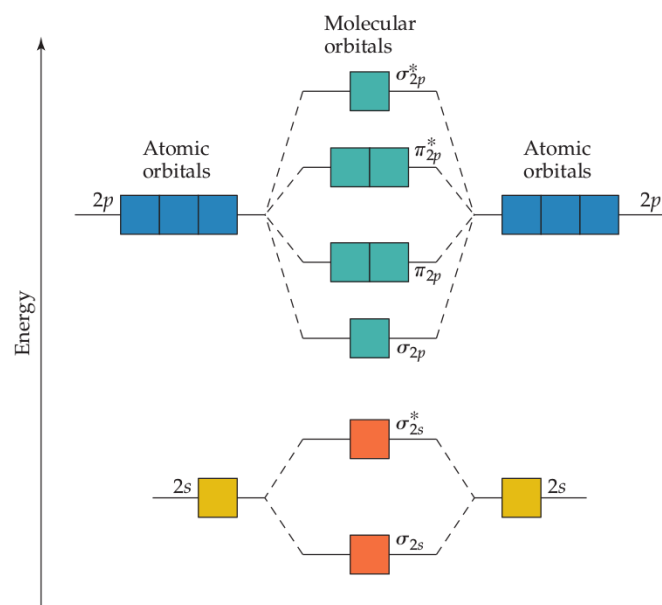
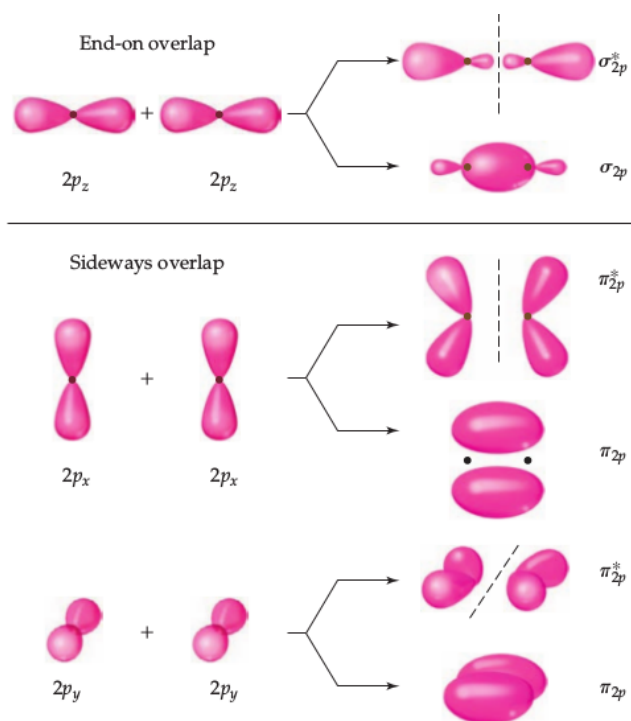
Homonuclear diatomic molecules (two identical)

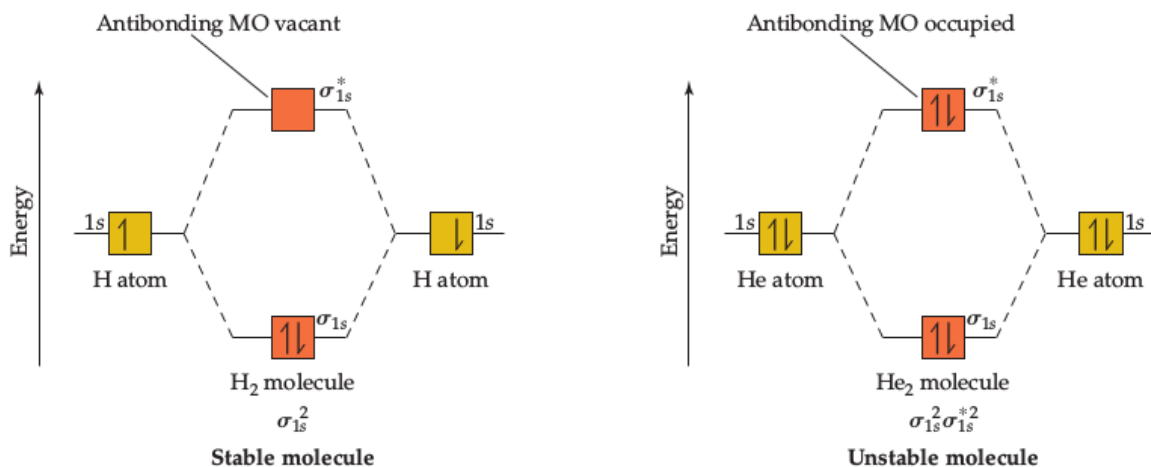
1. number of MO = number of AO combined
2. AO most effectively combined with other AO of similar energy
3. Effectiveness of combo relates to overlap.
4. MO can have two e^- with opposite spin (Pauli)
5. Hund's rule obeyed for same energy MOs

Heteronuclear diatomic similar to homo-nuclear, but an MO has a greater contribution from AO to which it is closer in energy. NO: σ_{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 = $1.0132 \cdot 10^5$ 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.

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

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

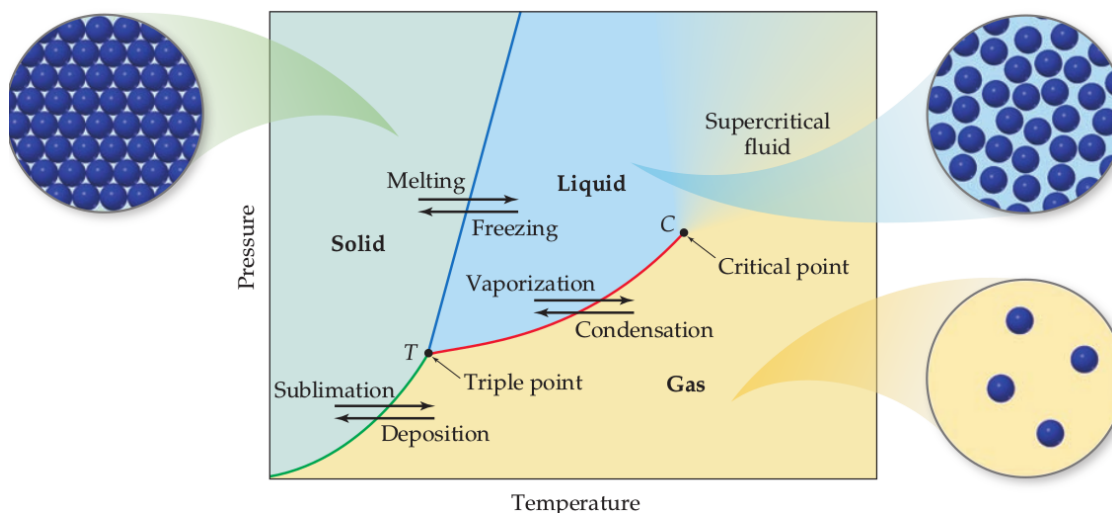
Capillary action rise of liquid up narrow tubes

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.

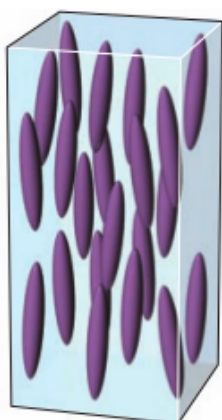
Volatile evaporate readily

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



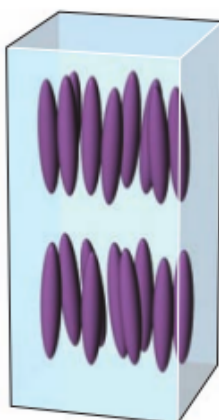
Liquid phase

Molecules arranged randomly



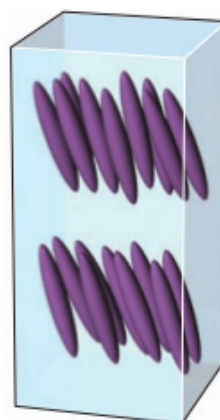
Nematic liquid crystalline phase

Long axes of molecules aligned, but ends are not aligned



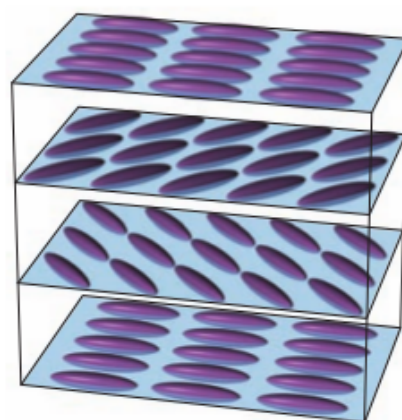
Smectic A liquid crystalline phase

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

12 Chapter 12. Solids

Contents

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12.4	Metallic bonding	19
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12.6	Ionic solids	20
12.7	Molecular solids	20
12.8	Covalent-network solids	20
12.9	Semiconductors	20
12.10	Polymers	21

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!

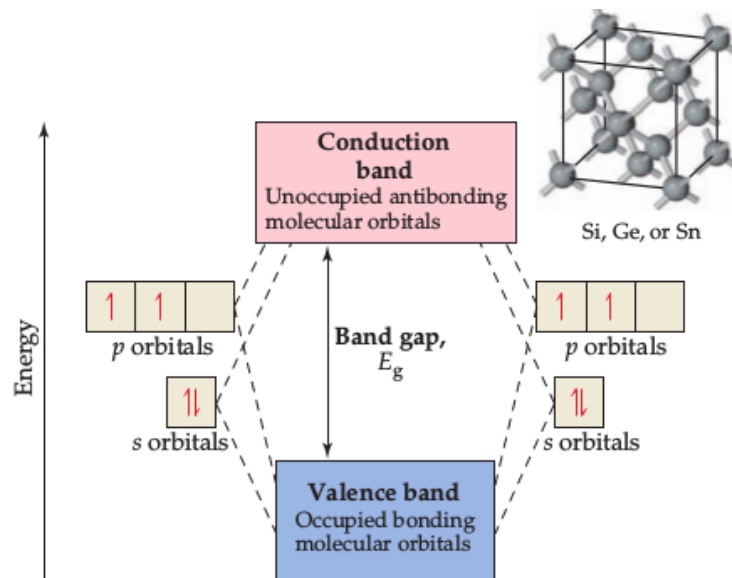
Molecular-orbit model, Band Structure Orbitals shared by entire metal. Fills low \rightarrow high. Bands are per-molecule in nonmetals. 3d band, 4s, 4d bands ...

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. 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

$$\frac{\text{Cations per formula unit}}{\frac{\text{anions per formula unit}}{\text{anion coord number}}}$$
 is equal to $\frac{\text{cation coord number}}{\text{anion coord number}}$
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 CH_2 units.

13 Chapter 13. Properties of Solutions

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13.2 Saturated solutions and solubility	22
13.3 Factors affecting solubility	22
13.4 Expressing solution concentrations	22
13.5 Colligative Properties	22
13.6 Colloids	23

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| 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 ΔH_{solute}
 $\text{solvent}_m \rightleftharpoons m \text{ solvent}$ takes $\Delta H_{solvent}$ $n \text{ solute} + m \text{ solvent} \rightleftharpoons \text{solution}$ takes ΔH_{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 $\frac{\text{mass of component in soln}}{\text{total soln mass}} \cdot 10^6$

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

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14.3	Concentration and Time	24
14.4	The Effect of Temperature on Rates	24
14.5	Reaction Mechanisms	25
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| 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 ΔH , 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 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!

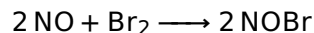
Rate-determining step is the slowest. If initial, likely that its rate law will govern that of the overall.

Slow initial step the rate is usually equal to the rate

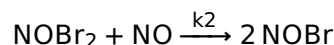
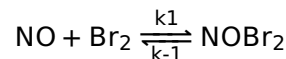
of the initial step.

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 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

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15.7 Le Châtelier's Principle	27

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

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 1atm . $A = CM/1M$ 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.

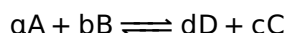
Converting $K_p = K_c(RT)^{\Delta n}$ where Δn = moles of gaseous product – moles of gaseous reactant.

15.3 Direction and Summation of Equations

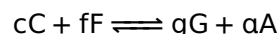
Reaction written backwards $K_{rev} = \frac{1}{K}$

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

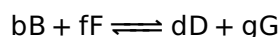
Reactions added simply multiply all K s involved. Adding the two equations:



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 Δconc is known.

If initial and another Δconc 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 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

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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 dissolved: $B + H_2O(l) \longrightarrow BH^+(aq) + OH^-(aq)$

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. H_2SO_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 NH_3 is replaced with N-C.

Second category anions of weak acids. The acid NaClO has the conjugate base 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 H^+ or OH^- .

An anion can be considered the conjugate base of an acid 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. NaCl , $\text{Ba}(\text{NO}_3)_2$, RbClO_4
2. Anion produces hydroxide ions, cation doesn't react (from weak acid, strong base)? pH should be basic. NaClO , RbF , BaSO_3
3. Cation produces hydronium ions, anion doesn't react (from weak base, strong acid)? pH should be acidic. NH_4NO_3 , 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. NH_4ClO , $\text{Al}(\text{CH}_3\text{COO})_3$, 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. HBr is very strong
3. The greater the stability of the conjugate base A^- , the stronger the acid.

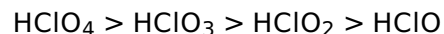
Binary acids bond strength decreases and acidity and size increase down a group.

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

OH bond: acid or base as the electro-negativity of Y in 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 (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 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 CH_3COOH , Benzoic acid (benzene and carboxyl), Formic acid 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

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|---|--|---|
| 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 .

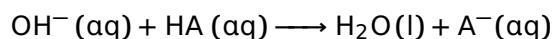
Composition method 2 make conjugate acid/base from weak soln by adding strong acid/base. Example: CH_3COOH and add $NaOH$ neutralize half of the acetic acid.

Any pH can be chosen for a buffer

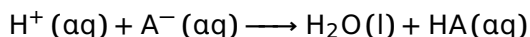
Buffer capacity how much intruding acid/base can be tolerated without straying from **pH range**

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 $[H^+]$

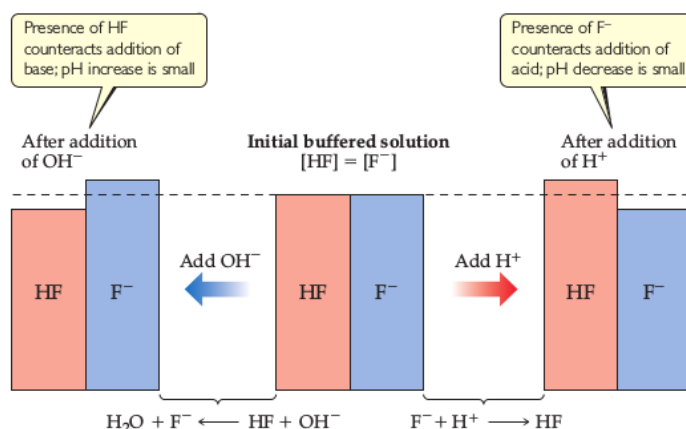
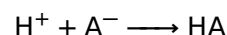
Henderson-Hasselbalch equation for conjugate acid-base pairs: $pH = pK_a + \log \frac{base}{acid}$ where K_a of the acid is used and the two conc.s are at equilibrium. Can use initial conc.s – easier – but use this assumption with care.

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

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.

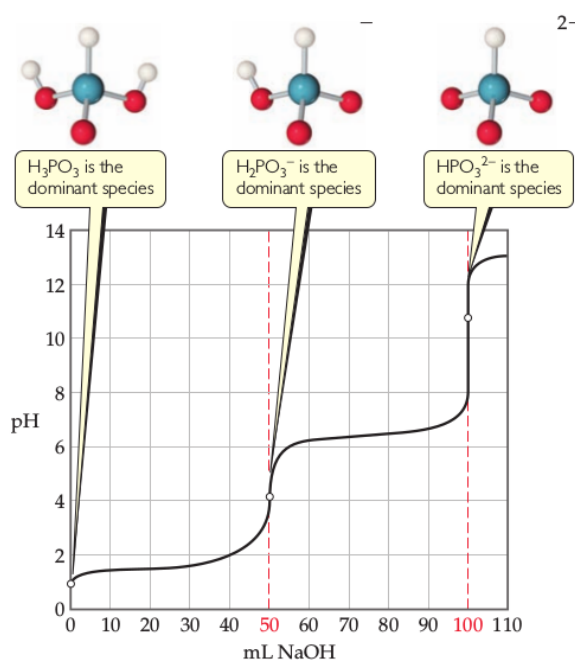
Strong acid titrates strong weak pH lowers, same as base titrating acid.

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. 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 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. CuS $K_{sp} = 6 \cdot 10^{-37}$, ZnS $K_{sp} = 2 \cdot 10^{-25}$. CuS will precipitate with pH around 1, 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

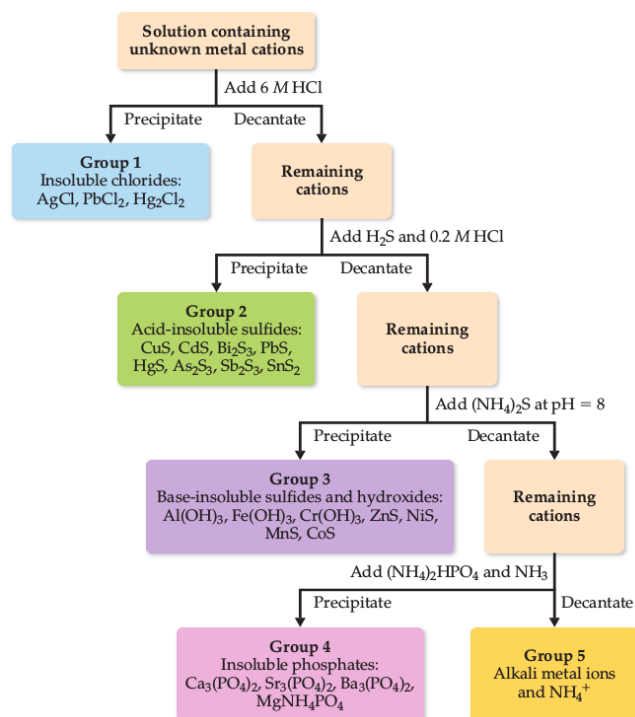
Common 5 group scheme **Group 1** insoluble chlorides, add HCl, precipitates AgCl , Hg_2Cl_2 , PbCl_2

Group 2 acid-insoluble sulfides, soln. now acidic, H_2S is added, precipitates CuS , Bi_2S_3 , CdS , PbS , HgS , Ag_2S_3 , Sb_2S_3 , 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 Al^{3+} , Cr^{3+} , Fe^{3+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+}

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

Group 5 alkali metal, NH_4^+ flame test, other individual tests.



19 Chapter 19. Chemical Thermodynamics

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19.4 Entropy Changes in Chemical Reactions	33
19.5 Gibbs Free Energy	34
19.6 Free Energy, Temperature, and Equilibrium Constant	34

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|---|--|--|
| 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 ΔH and ΔS |
| 3. Entropy and micro-states | 8. Entropy changes for an isothermal process | 13. ΔG under nonstandard conditions |
| 4. Possible molecular motions | 9. Gibbs free energy from enthalpy change | 14. ΔG° and equilibrium constant |
| 5. Predict sign of ΔS 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° 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 ΔS° 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 ΔG 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 ΔG_f° 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 ΔG° .

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

19.6 Free Energy, Temperature, and Equilibrium Constant

temperature doesn't affect ΔH and ΔS of a process very much. ΔG 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

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20.2Balancing Redox	35
20.3voltaic cells	35
20.4Voltage under Standard Conditions	35
20.5Free Energy and Redox Reactions	35
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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} , ΔG° to equilibrium constants
7. Calculate emf under nonstandard conditions
8. ID components of common batteries
9. Construction, explanation of lithium-ion

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 ΔG

$$\Delta G = -nFE$$

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

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.