Le Chatelier's Principle:

1. An increase in concentration on one side of an equation favors or drives the reaction to the opposite side. adding reactants favors products
adding products favors reactants

2. An increase in temperature favors or drives an endothermic reaction forward to products.

3. An increase in temperature drives an exothermic reaction backwards to reactants.

4. An increase in pressure drives a reaction toward the side with fewer molecules (moles) of gas. The gas volume is smaller with fewer gas molecules.

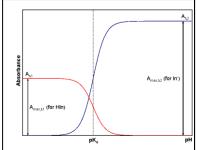5. Adding a catalyst does not alter the relative amounts of reactant and product. Forward reaction happens more easily and so does the reverse reaction. Equilibrium is only reached faster.

In the previous week, we qualitatively investigated how an equilibrium shifts in response to a stress to re-establish equilibrium. This week we will quantitatively assess the equilibrium constant for the same reaction: the reaction of iron(III) cation complexing with a thiocyanate anion (SCN−) to form the iron(III) thiocyanate complex, Fe(SCN)2+ (Equation 1). Its equilibrium expression is as shown in Equation 2.
Fe3+ (aq) + SCN (aq) Fe(SCN)2+ (aq)   Equation 1
Equation 2 2+ eq 3+ [Fe(SCN)] K = - [Fe][SCN]
If Keq is a large number (>1), then the chemical equilibrium favors the formation of product (large numerator). If Keq is a small number (<1) then the chemical equilibrium favors the formation of reactants (large denominator). In this experiment, several solutions of varying initial concentrations of the reactants are to be prepared. Despite the different concentrations, the equilibrium constants calculated from their equilibrium concentrations should be the same, as long as the temperature is kept constant.

Before we begin the study of the equilibrium concentrations, we must first prepare a standard curve to help us determine the concentration of Fe(SCN)2+ at equilibrium. Le Chatelier's Principle states that if at equilibrium a change is applied to a system, the species will react to offset the change so as to maintain the equilibrium. We will use this principle to aid in the preparation of the standard curve. In each solution, we will be adding to a much higher in excess concentration of the red (iron(III) thiocyanate complex, Fe(SCN)2+. If the concentration of the reactant, iron(III) nitrate, is increased (0.200 M), so as to become **much** larger than the thiocyanate anion concentration (0.00200M), then the reaction (Equation 1) will be forced almost completely to products. In this situation, the iron(III) concentration is 100 times that of the thiocyanate, therefore essentially all the red-colored thiocyanate must be composed of the red colored product, Fe(SCN)2+, equal to the limits of our detection apparatus, the final concentration of Fe(SCN)2+ is equal to the initial concentration of SCN−. The intensity of the red color will be measured spectrophotometrically and will be directly proportional to the equilibrium concentration of the Fe(SCN)2+ ion. (Review Beer's Law from Experiment 3.)

After a standard curve is produced, the conditions will be altered so that the concentrations of each of the two reacting species (Fe3+ and SCN−) will be the same order of magnitude (~0.00200 M each). Because the concentrations will be so similar, the system will no longer be forced all the way to the right (towards the products) and you will be able to determine an equilibrium constant from this data. The concentration of Fe(SCN)2+ at equilibrium will be determined spectrophotometrically according to its absorbance in the standard curve. Since for every mole of the red complex, Fe(SCN)2+ produced, one mole of Fe3+ and one mole of 78
EXPERIMENT 9: DETERMINATION OF AN EQUILIBRIUM CONSTANT

SCN − will have reacted, the equilibrium concentrations (unreacted species) of Fe3+ and SCN− can be determined by subtracting the concentration of Fe(SCN)2+ formed from the initial concentrations before the reaction took place. We can set up an "ICE" table, find the equilibrium concentrations for each of the three species, and solve for Keq.
Each of the initial solutions will be made up so as to contain 0.500 M H+. Therefore when mixing the solution of 0.00200 M Fe3+ made up in 0.500 M H+ and the solution of 0.00200 M SCN− made up in 0.500 M H+, no matter what the proportions, the 0.500 M H+ concentration will be constant. The reason for this is that the iron(III) thiocyanate formation reaction must be run around 0.5 M acid to prevent significant iron hydrolysis (Equation 3) that affects the concentration of iron(III) ions.
Fe3+(aq) + 3H2O (l) Fe(OH)3 (s) + 3H+ (aq) Equation 3
Also, the reaction must be run at a low enough pH because otherwise the acid reacts with the thiocyanate reducing the available SCN− as well (Equation 4).
H+(aq) + SCN−(aq) HSCN (aq) Equation 4
Each reagent is labeled with its concentration. However, once you mix reagents together, you will have diluted the concentration. The calculations that you use will need to account for these dilutions. An example is below:
Example 1: If 5.08 mL of 0.00200 M Fe(NO3)3 is mixed with 3.10 mL of 0.00200M KSCN and 2.00 mL of 0.500 M HNO3 , what is the final concentration of the Fe3+ ion?
1 1 2 2 2 3 3 1 1 2 2 3 3 2 MV = M V where V is the TOTAL volume in the final solution (0.00200 M Fe(NO)) (5.08 mL) M V M = = 0.000998 M Fe(NO) V 10.18 mL
= 9.98x10−4 M Fe3+
Check: Is the answer reasonable? M2 should be more dilute than M1.

The electron configuration or organization of electrons orbiting neutral atoms shows a recurring pattern or periodicity. The electrons occupy a series of electron shells (numbered shell 1, shell 2, and so on). Each shell consists of one or more subshells (named s, p, d, f and g). As atomic number increases, electrons progressively fill these shells and subshells more or less according to the Madelung rule or energy ordering rule, as shown in the diagram to the right. The electron configuration for neon, for example, is 1s² 2s² 2p⁶. With an atomic number of ten, neon has two electrons in the first shell, and eight electrons in the second shell—two in the s subshell and six in the p subshell. In periodic table terms, the first time an electron occupies a new shell corresponds to the start of each new period, these positions being occupied by hydrogen and the alkali metal

Since the properties of an element are mostly determined by its electron configuration, the properties of the elements likewise show recurring patterns or periodic behavior, some examples of which are shown in the diagram on the left. It is this periodicity of properties, manifestations of which were noticed well before the underlying theory was developed, that led to the establishment of the periodic law (the properties of the elements recur at varying intervals) and the formulation of the first periodic tables.

The electron affinity of an atom is the amount of energy released when an electron is added to a neutral atom to form a negative ion. Although electron affinity varies greatly, some patterns emerge. Generally, nonmetals have more positive electron affinity values than metals. Chlorine most strongly attracts an extra electron. The electron affinities of the noble gases have not been measured conclusively, so they may or may not have slightly negative values.

Electron affinity generally increases across a period. This is caused by the filling of the valence shell of the atom; a group 17 atom releases more energy than a group 1 atom on gaining an electron because it obtains a filled valence shell and is therefore more stable.
A trend of decreasing electron affinity going down groups would be expected. The additional electron will be entering an orbital farther away from the nucleus. As such this electron would be less attracted to the nucleus and would release less energy when added. However, in going down a group, around one-third of elements are anomalous, with heavier elements having higher electron affinities than their next lighter congeners. Largely, this is due to the poor shielding by d and f electrons. A uniform decrease in electron affinity only aoolies to group 1 atoms.

The lower the values of ionization energy, electronegativity and electron affinity the more **metallic character** the element has. Conversely, nonmetallic character increases with higher values of these properties. Given the periodic trends of these three properties, metallic character tends to decrease going across a period and, with some irregularities (mostly) due to poor screening of the nucleus by d and f electrons, and relativistic effects, tends to increase going down a group. Thus, the most metallic elements (such as caesium and francium) are found at the bottom left of traditional periodic tables and the most nonmetallic elements (oxygen, fluorine, chlorine) at the top right. The combination of horizontal and vertical trends in metallic character explains the stair-shaped dividing line between metals and nonmetals found on some periodic tables, and the practice of sometimes categorizing several elements adjacent to that line, or elements adjacent to those elements, as metalloids.

Beer-Lambert Law
A=εbc
Where A is absorbance (no units, since $A = log_{10} P_0/P$)
ε is the molar absorptivity with units of $L \, mol^{-1} \, cm^{-1}$
b is the path length of the sample - that is, the path length of the cuvette in which the sample is contained. We will express this measurement in centimetres.
c is the concentration of the compound in solution, expressed in mol L-1
Transmittance, $T = P/P_0$
%Transmittance, $\%T = 100 \, T$
Absorbance,
$A = log_{10} P_0/P$
$A = log_{10} 1/T$
$A = log_{10} 100 / \%T$
$A = 2 - log_{10} \%T$

Types of equilibrium
1.In the gas phase. Rocket engines[12]
2.The industrial synthesis such as ammonia in the Haber-Bosch process (depicted right) takes place through a succession of equilibrium steps including adsorption processes.
3.atmospheric chemistry
4.Seawater and other natural waters: Chemical oceanography
5.Distribution between two phases
-1.LogD-Distribution coefficient: Important for pharmaceuticals where lipophilicity is a significant property of a drug
-2.Liquid-liquid extraction, Ion exchange, Chromatography
-3.Solubility product
-4.Uptake and release of oxygen by haemoglobin in blood
6.Acid-base equilibria: Acid dissociation constant, hydrolysis, buffer solutions, indicators, acid-base homeostasis
7.Metal-ligand complexation: sequestering agents, chelation therapy, MRI contrast reagents, Schlenk equilibrium
8.Adduct formation: Host-guest chemistry, supramolecular chemistry, molecular recognition, dinitrogen tetroxide
9.In certain oscillating reactions, the approach to equilibrium is not asymptotically but in the form of a damped oscillation .[10]
10.The related Nernst equation in electrochemistry gives the difference in electrode potential as a function of redox concentrations.
11.When molecules on each side of the equilibrium are able to further react irreversibly in secondary reactions, the final product ratio is determined according to the Curtin-Hammett principle.

$Q>K \rightarrow$ delG<0 $\rightarrow$ Forward
$Q>K \rightarrow$ delG >0 $\rightarrow$ Reverse
K>1 $\rightarrow$ high product
K<1 $\rightarrow$ low product
Equilibrium is toward weaker acids/bases

Ion	Solubility	Exceptions
NO_3^-	soluble	none
ClO_4^-	soluble	none
Cl^-	soluble	except Ag^+, Hg_2^{2+}, *Pb^{2+}
I^-	soluble	except Ag^+, Hg_2^{2+}, Pb^{2+}
SO_4^{2-}	soluble	except Ca^{2+}, Ba^{2+}, Sr^{2+}, *Pb^{2+}, *Ag^+
CO_3^{2-}	insoluble	except Group IA and NH_4^+
PO_4^{3-}	insoluble	except Group IA and NH_4^+
^-OH	insoluble	except Group IA, *Ca^{2+}, Ba^{2+}, Sr^{2+}
S^{2-}	insoluble	except Group IA, IIA and NH_4^+
Na^+	soluble	none
NH_4^+	soluble	none
K^+	soluble	none

*slightly soluble

Electronegativity is the tendency of an atom to attract electrons. An atom's electronegativity is affected by both its atomic number and the distance between the valence electrons and the nucleus. The higher its electronegativity, the more an element attracts electrons. It was first proposed by Linus Pauling in 1932. In general, electronegativity increases on passing from left to right along a period, and decreases on descending a group. Hence, fluorine is the most electronegative of the elements,[n 3] while caesium is the least, at least of those elements for which substantial data is available.

There are some exceptions to this general rule. Gallium and germanium have higher electronegativities than aluminium and silicon respectively because of the d-block contraction. Elements of the fourth period immediately after the first row of the transition metals have unusually small atomic radii because the 3d-electrons are not effective at shielding the increased nuclear charge, and smaller atomic size correlates with higher electronegativity. The anomalously high electronegativity of lead, particular other than the Pauling method show the normal periodic trends for these elements.

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

$$\Delta_r G^\ominus = -RT \ln K$$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q_r$$

$$\Delta G = \Delta H - T\Delta S$$

21. Periodic Trends and the s-block elements
21.1 Overview of Periodic Trends
All periodic trends based on **effective nuclear charge Zeff.**
Unique chem of light elements: Second-period el. are different from congeners b/c: small radii, energetically unavailable d orbitals, tendency to form π bonds.
Small radii -> less negative EA b/c increased e-e repulsions; can't have more than 4 neighbors; high charge/radius ratio, so more covalent-nature ionic bonds.
Energetically unavailable d orbitals (would have to go to n=3 energy) -> can't have more than 4 e- pairs.
Smaller atoms -> more p-orbital overlap -> stronger π bonds -> more multiple bonds.
Inert Pair Effect: Heavier elements of Groups 13-17 often have oxy states are lower by 2 than max predicted. (b/c increased ionization energies, decreasing bond strengths)
IE increase b/c full (n-1)d or (n-2)f subshells poor at shielding ns el -> ns have high Zeff.
Larger atoms -> lower valence orbital overlap -> weaker bonds.
Combined -> net E from forming bonds < additional E to remove ns el.
21.2 The Chemistry of Hydrogen
Protium, Deuterium stable. Tritium radioactive. Forms H species in atms, rainfall to ocean.
D2O has b.p. of 101. -> evap or frac distillation to separate. More mass -> diffuses slow -> electrolysis makes more H2 gas than HD gas.
H can make compounds by (1) losing e to form H+, Lewis acid -> accept e to form e-pair bond. (2) Accept e to form hydride ion H-. Reacts with electron metals (g. 1&2) to form ionic hydrides. (3) Share e to form e-pair bond, cov. or polar cov.
Can act as bridge. H-bond bridges electron- atom and lone e-pair. Three-center bond: H- bridges 2 electron- atoms by minority sp3 orbitals -> 2 e holding 3 atoms -> e-deficient.)
To make H2 gas: M + dilute acid; M + v. strong base; MH + H2O.
Most el. form binary hydrides. Covalent: molecular sub, volatile, low m.p. Ionic: More electro+ M, nonvolatile, 3D lattice, upon heating decompose to H2 and M. Metallic: Less electro+ M, similar to M, H are interstitial impurities.
21.3 The Alkali Metals
Atomic and ionic radii increase smoothly from Li to Cs, first IE decreases. High EA b/c adding e- forms ns2 config. Densities increase down b/c mass increases faster than volume. Unusual: decrease in melting and boiling down. Li+ strongest reduc. Na weakest; b/c Li is small -> high hydration E.
All electro+, have ns1 config, form M+.
All react vigorously with G17 -> MX. All react w/ G16 -> M2Y. Excess G16 -> chain of G16 atoms (e.g. Na2S3)
O rxn depends on M:O ratio and M size. In air: Li2O, Na2O2, KO2, RbO2, CsO2. Size of M cat ~ size of O an. Spec cond make all M/O except LiO2. M perox, superox are strong oxy agents w/ redg. MOx + CO2 -> MCO3 + O2. MOx + CO2 + H2O -> MHCO3 + O2.
Only Li makes M3N, b/c small size -> stronger lattice. All react with P, As.
Variety of G14 react. KiSi4, Li2C2. Heavier G1 -> interacting w/ empty sp3 orbitals -> form e-pair bond, covalent. Li-C = very covalent.
Low charge, large l-radii -> weak lewis acids. Most sig for Li+. Electrostatic interaction -> crown ethers, cryptands (spherical crown ethers) surround G1, very selective.
G1 dissolve reversibly in liquid NH3. M + NH3 -> H2 + M+ + NH2- is slow, but can be very concentrated. Solutions of G1 in NH3, intense color & high conduct b/c solvated e- a- loosely bonded in NH3 cavity stabilized by H-bonds. 3M = blue, higher = bronze gold. NH3 solutions contain M+, M, M2, M-.
21.4 Alkaline Earth Metals
Prepped by electrolytic reduction of molten chlorides.
Atomic, ionic radii increase, IE decreases smoothly from Be to Ba. G2 IE >> G1 IE. BUT: Density Ca < Be, Mg; MG has lowest m.p, b.p Ba strongest redg. Be weakest; electrode potential Ca~Sr~Ba b/c IE, hydration energy cancel. G2 have almost no EA b/c would need to fill ns2 config.
G2 mostly ionic, but be small & high IE -> very covalent, some Mg2+ covalent character.
All react w/ G17 -> MX2. Ionic, except BeX2 -> covalent, polymeric halide-bridged structure, volatile -> linear XBeX, potent Lewis acids -> react w/ tetrahedral adducts.
All react w/ O -> MO, exc. BaO2 b/c larger O2(2-), Ba(2+). Be direct, others made MCO3 -> MO + CO2. Heavier G16 similar to G1 fors: binary + chains. BeO amphoteric, others form hydroxides. Be(OH)2. MCO3 + H+ -> M(2+) + CO2 + H2O. Lighter M(OH)2 insoluble, heavier soluble.
G2 w/ N opposite G1 rxn. Only Be3N doesn't form. High lattice E from high charged -> overcome N2 triple bond. All G2 rxn w/ heavier G15 -> M3Z2. G2(-Be) rxn w/ C -> MC2 -> BeZC (covalent).
G2(-Be) rxn direct w/ H2 -> MH2. Heavier G2 ionic, lighter polymeric & high covalent character. Heavier G2 ionic, lighter polymeric & high lattice E, decreasing hydration E.
G2 form more complexes w/ Lewis B than G1 b/c 2+ charge, small l-radii. Most important for Be, decreases rapidly down. Be(2+) chem dominated by Lewis acid behavior -> octet of e- around Be. Be(2+) salts dissolve in acidic, polarized H2O, tetrahedral [Be(H2O)4](2+). Strong base -> tetrahedral hydroxo [Be(OH)4](2-). -> BeO amphoteric. Also forms stable [BeF4](2-). Heavier alkalines form complex w/ cood # 6+.

22.1 The Elements of Group 13
Except B, relatively electro+. B behaves like nonmetal, Al metal. All have ns2np1 config, lose all 3 e to form +3 oxy state. Heavier el. forms +1 oxy, lose np e. All compounds moderately strong Lewis A. No consistent trend in IE, EA, red potential, electro- increases from Al to Tl. Increase in Zeff from Ga, In, Tl b/c poor shielding of d, f subshells -> IE(Tl)>IE(In).
B has high IE, low EA, small size -> does not form metallic lattice, instead multicenter bonds. Elemental B has B12 icosahedron -> poor packing = low density. Reacts with many nonmetals -> binary compounds (BN, B2O3, BX3). BN3 similar to el. C. B-N nonelectronic w/ B-C; similar to graphite (B3N3 ring layers). High pressure -> cubic similar to diamond. B2O3 has layers of trigonal planar BO3 groups w/ O bridging 2 B atoms. Diborane many metal+nonmetal oxides(SiO2) -> borosilicate glasses. Co -> blue. At high T, B reacts with all M to give metal borides w/ 3D clusters of B atoms. B Hydrides (B2H6) has multicenter bonds. Carboranes contain both CH and BH units. B&H have identical electro- -> rxn dictated by minor diff in distro of e- density. E-rich (BH4-) act as redg, e-deficient (B2H6) act as oxyg.
All 4 heavy G13 react w/ G17 -> MX3 or M2X6. Tl w/ I exception -> Thallium (I) Triodide. I not powerful enough oxyg to get Tl to +3 state. Of halides, only F- typical ionic: high melting (>950), low solubility in nonpolar. Trichlorides, tribromides, triiodides are more covalent -> G17-bridged dimers. Unlike B2H6, e-pair bonds, not delocalized e-deficient bonds. Bridging G17 poor e-pair donors -> potent Lewis A. MX3 + H2O -> M(OH)3 + 3HX. Halides of heavier G17 less reactive b/c low charge/radius ratio -> form [M(H2O)6](3+). M + O2 -> M2O3 w/ high T, excess O (Tl2O3 unstable). All O dissolve in dilute acid, but Al2O3 & Ga2O3 amphoteric. Al, Ga, In rxn w/ G16 -> M2Y3. Tl(III) strong oxyg -> Tl2Y. AlN direct, GaN & InN indirect. All G13 (-Tl) rxn w/ heavy G15 form III-V (GaAs) semiconductors. Unlike B, heavy G13 no rxn direct w/ H. AlH3 indirect: insoluble, polymeric, rapidly decomposed by H2O. GaH3 indirect, unstable.
B limited tendency to form complexes, b/c small size. In form many. Simplest hydrated G16 -> strong B-L acids. G13 also form complex w/ species containing 2 or more -- charged groups.
22.2 The Elements of Group 14
All G14 form compounds w/ +4 or +2 oxy state. Down -> increasing atomic size & heavy have high Zeff, IE -> relative stability of +2 oxy increases from C to Pb. C makes multi bonds from π overlap of 2p orbitals, others less so. Catenation decreases rapidly down G14 b/c decreasing bond energies b/c less overlap. C different, Si & Ge similar, reversal in trends b/w Sn & Pb b/c d,f subshells.
Allotropes of C are simple e-pair bonds. CX4 all known, but indirect: CH4 + X2 -> CX4 + HX. C-F more stable than C-H. C-F O -> CO2 or CO. CO + X2 -> X2C--O. CO2 +H2O -> H2CO3. C=S -> S2, C=Se -> CSe2. Both linear, vile smelling, volatile liquids. CS, CSe unstable b/c very weak triple bond from poor π overlap. C = less electro-. C+ electro+ (G1, G2, Al) -> ionic carbides: discrete cations, anions. Small make C(4-) methides, large make C2(2-) acetylides. C+ TransM + high T -> interstitial carbides: Less electron - C covalent C M -> conduct e-. high m.p., very hard. C + similar electro- -> covalent carbides (SiC, B4C): hard, high m.p., chem inert.
Si dissolves in base -> H2 + SiO4, in HF -> SiF6(2-). Ge more metallic, dissolves in hot oxy acids (NO3, SO4), but w/o oxyg -> not in aq base. Sn more metallic, but Pb only el. purely like M. Heavier G14 ionic, heavier G16 ionic b/c thin layer of Pb(2+) salt like PbSO4.
All G14 dichlorides known, but increase stable dramatically down. All (-Pb) form MX4, only F gives PbF4. Si,GeX4 -> MO2 + HX. Sn,PbX4 -> M(aq). Pb(2+) stable -> PbO, PbS. Others MO2, MS2. Down > more stable, Si-O bond VERY strong -b/c low-E, empty d orbitals on Si, nonbonding e-pairs in p orr spot of O -> partial π double bond.
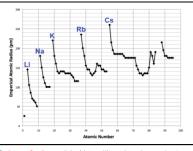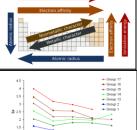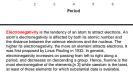
22.3 The Elements of Group 15
N,P like nonmetal; As,Sb semimetal; Bi metal. All form +3, lighter form +5, lightest form -3. Tend to behave like Lewis B.
N forms multibonds. N-N triple bond so thermodynamically favored that virtually all single N-N compounds potentially explosive. Few binary compounds of N formed by direct reaction: LiN only. At high temps -> NO, NO2, NH3, NCCN. NH3 + X2 -> NX3. Electro+ -> Li3N, Ca3N2. Less electro+ -> interstitial. Covalent bonding w/ semimetals.
Heavier G15 form catenation w/ only single bonds, stability decreases down the group. Reactivity of G15 decreases down the group. P has greatest ability to form p bonds w/ el such as O, N,C. Thermal stability of organic or organometallic compounds of G15 decreases down the group b/c decreasing strength of pπ-co-E bond.
22.4 The Elements of Group 16
G16 is the first group in p block containing no stable metallic elements. O has greatest tendency to form multi bonds. Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, oxides of el in or near semimetal band tend to be amphoteric.
Going down G16, catenation, strength of single bonds, reactivity decrease. Stability of highest oxidation state decreases down the column. Dioxides of G16 become increasingly basic and co-od # steadily goes down.
22.5 The Elements of Group 17
Because the halogens are highly reactive, none is found in nature as the free element. Electrostatic repulsions b/w lone pairs of e- on adjacent atoms cause single bonds to be weaker than expected. B/c IE decrease down the column, the heavier G17 form compounds in positive oxy states (+1,+3,+5,+7).
As oxy state of metal increases, the % covalent character of corresponding metal halides also increases due to polarization of M-X bond. Down columnb, both acid strength and oxy power of G17 oxoacids decrease. All G17 el exc F form compounds in odd oxidation states, but the importance of the higher oxy states generally decreases down.
22.6 The Elements of Group 18
The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known. Clathrates. Xe has a high affinity for both F and O. Formation of stable ionic lattice, high co-od # of Xe protect central atom from attack by other species.

23. Transition Metals
All trans-metal cations have d^n electron config, the ns e- are always lost first. The highest possible oxy state, corresponding to the formal loss of all valence e-, decreases in stability from G3 to G8, not observed in later groups. In trans M, the stability of higher oxy states increases down a group.
Left-Right / Top-Down: Increase electro-, decreasing magnitude of cation, decreasing enthalpy of hydration.
Chem of G3 metals almost exclusively M(3+) ions. Chem of G4 metals dominated by +4 oxy state. Only Ti has an extensive chemistry in lower oxy states. Chem of two heavy G5 metals (Nb, Ta) dominated by +5 oxy state. The chem of light element (V) dom by lower oxy states, esp +3. Chem of G6 (Mo+W) dom by +6 oxy state.
Chem of light (Cr) dom by lower states, esp +3. Chem of G7 (Mn, Tc,Re) dom by lower oxy states. Compounds in max possible oxy state, +7, are readily reduced. The most important oxy states are +2 and +3 for G8, +3 for G9, +2 and +4 for G10. Most important for G11 is +1, G12 is +2.
Metallurgy depends on separation of a metal compound from its ore and reduction to the metal at high temperature (pyrometallurgy) or in aqueous solution (hydrometallurgy).
Hard acids prefer hard bases, soft acids prefer soft bases . Ligands that are strong bases form the most stable complexes with hard metals. Chelate complexes are more stable than the analogous complexes w/ monodentate ligands.
Crystal field splitting does not change the total energy of the d orbitals. The largest crystal field splittin energies are found in complexes of metal ions from the 3rd row of the transition metals, that have charges of at least +3 and ligands that have localized lone pairs of e-. Octahedral d3 and d8 complexes and low-spin d6,d5,d7,d4 complexes exhibit large crystal field stabilization energies. Jahn-Teller distortions (degenerate -> asymmetrical) most important for d9 and high-spin d4 complexes.

7. Periodic Table and Periodic Trends
7.2 Sizes of Atoms & Ions
Atomic Radii: Decrease from L->R, increase from T->B. Zeff matters most. e- in same principle shell not as effective at shielding each other. Higher n-> bigger orbitals (but must account for Zeff). e-in filled inner shells are very effective at shielding e- in outer shells from Z-charge.
Ionic Radii: Internuke d = Sum (r_cat + r_anion). Cation always smaller, Anion always larger for parent atom. When e- removed: 1. Rep b/w e- in same shell decreases. 2. Zeff increases b/c of fewer e- to shield. Going T->B increases. Isoelectronic -> greatest charge = smallest; least charge = greatest.
7.3 Energetics of Ion Formation
Ionization Energy I: E(g) -> E(+)(g) + e- . 1 eV/ atom = 96.49 kJ/mol. I_n > I_n-1 b/c 1. Coulumb's Law (removing from a stronger charge). 2. Reduces repulsive force -> >Zeff.
I required to remove e- from a filled core is prohibitively large. B/Al lower b/c 3s2 better at screening 3p1 than eachother. O/S lower b/c starting to fill spin states - more e- repulsion.
Electron Affinity: (EA) E(g) +e- -> E-(g)
N has EA ~0+. Generally EA becomes more negative L-R, less neg T-B.
Exception: 1. B-F less than E below. Increased e-e repulsive overcome e-nucleus attraction at short nuclear distances -> 3rd row has most negative EA. Going down, attraction b/w nucleus & new e- decreases, but also e-e repulsions -> tend to cancel out -> Groups have similar EA. 2. EA becomes more neg from Be->Ba b/c energy separation b/w filled ns2 and empty np subshells decreases with n.
G2, G18 have filled subshells -> new e- must enter new subshell -> very + EA. G15 less neg b/c of Hund's rule. Second EA are always positive.
Electronegativity: χ = (I + |EA|) / 2. Mulliken = Atoms; Pauling = Molecular measurements.
High χ -> Tend to acquire e- (Top Right). Low χ -> tend to lose e- (Lower Left). χ > 2.2 nonmetal. χ ~ 2 semimetal. χ<=1.8 Metal.

Atomic radii vary in a predictable and explainable manner across the periodic table. For instance, the radii generally decrease along each period of the table, from the alkali metals to the noble gases; and increase down each group. The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. These trends of the atomic radii (and of various other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom; they provided important evidence for the development and confirmation of quantum theory
The electrons in the 4f-subshell, which is progressively filled from cerium (Z = 58) to lutetium (Z = 71), are not particularly effective at shielding the increasing nuclear charge from the sub-shells further out. The elements immediately following the lanthanides have atomic radii which are smaller than would be expected and which are almost identical to the atomic radii of the elements immediately above them. Hence hafnium has virtually the same atomic radius (and chemistry) as zirconium, and tantalum has an atomic radius similar to niobium, and so forth. This is known as the lanthanide contraction. The effect of the lanthanide contraction is noticeable up to platinum (Z = 78), after which it is masked by a relativistic effect known as the inert pair effect. The d-block contraction, which is similar effect between the d-block and p-block, is less pronounced than the lanthanide contraction but arises from a similar cause.

The first **ionization energy** is the energy it takes to remove one electron from an atom, the second ionization energy is the energy it takes to remove a second electron from the atom, and so on. For a given atom, successive ionization energies increase with the degree of ionization. For magnesium as an example, the first ionization energy is 738 kJ/mol and the second is 1450 kJ/mol. Electrons in the closer orbitals experience greater forces of electrostatic attraction; thus, their removal requires increasingly more energy. Ionization energy becomes greater up and to the right of the periodic table.

Large jumps in the successive molar ionization energies occur when removing an electron from a noble gas (complete electron shell) configuration. For magnesium again, the first two molar ionization energies of magnesium given above correspond to removing the two 3s electrons, and the third ionization energy is a much larger 7730 kJ/mol, for the removal of a 2p electron from the very stable neon-like configuration of Mg2+. Similar jumps occur in the ionization energies of other third-row atoms.

Titration of weak acid
The pH of a weak acid solution being titrated with a strong base solution can be found at different points along the way. These points fall into one of four categories [2]:
1.initial pH
2.pH before the equivalence point
3.pH at the equivalence point
4.pH after the equivalence point

1. The initial pH is approximated for a weak acid solution in water using the equation
$$pH = -\log\sqrt{K_a F}$$
where Ka is the dissociation constant and F is the concentration of the acid.

2. The pH before the equivalence point depends on the amount of weak acid remaining and the amount of conjugate base formed. The pH can be calculated by the following formula (which is a variation of the Henderson-Hasselbalch equation):
$$pH = pK_a + \log\left(\frac{n_{OH-added}}{n_{HAinitial} - n_{OH-added}}\right)$$
where:

pKa is the negative log of the acid dissociation constant of the weak acid.
nOH- added is the number of moles of added strong base in the solution.
nHA initial is the number of moles the weak acid initially present.
When the numerator of the log term equals the denominator (), then the ratio goes to 1 and the log term goes to zero. Thus the pH will equal the pKa which occurs half-way to the equivalence point.

3. At the equivalence point, the weak acid is consumed and converted to its weak conjugate base. The pH will be greater than 7 and can be calculated from an equation derived from the following relationships:
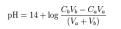
-1.pH + pOH = 14
-2.KaKb = 10^-14
-3.at equivalence CaVa = CbVb

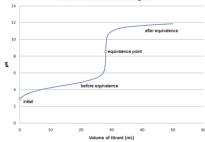The previous 3 relationships are used to generate the equivalence point pH formula below:
$$pH = 14 + \log\sqrt{\frac{C_b C_a K_w}{(C_a + C_b) K_a}}$$

Ca = concentration of acid and Cb = concentration of base
Kw = dissociation constant for water and Ka = for the acid
Note that when an acid neutralizes a base, the pH may or may not be neutral (pH = 7). The pH depends on the strengths of the acid and base.

4. After the equivalence point, the solution will contain two bases: the conjugate base of the acid and the strong base of the titrant. However, the base of the titrant is stronger than the conjugate base of the acid. Therefore, the pH in this region is controlled by the strong base. As such the pH can be found using the following:
$$pH = 14 + \log\frac{C_b V_b - C_a V_a}{(V_a + V_b)}$$

8. Structure and Bonding I
8.1 Overview
1. Atoms interact to form stable arrangements.
2. Energy required to dissociate bonded atoms/ions to isolation. Ion: **Lattice Energy.** Covalent: **Bond Energy.**
3. Optimal internuclear distance r_0 = bond distance.
8.3 Lattice Energies
U = -K" * (Q1 Q2)/(r0). K" depends on arrangement of ions; valence e- config.
High U: High m.p., high hardness, low solubility. **Born Haber Cycle.** (Hess' Law) Lattice energy most important factor in determining the stability of an ionic compound.
8.5: Formal Charge = Valence e- (free atom) - [nonbonding e- + (bonding e- / 2)] (in Lewis structure)
8.7: Lewis Base: Donates a pair of e-. **Lewis Acid:** Accepts a pair of e-. **e-deficient molecules** (BCl3) = Lewis A. Acid
Base Added: BF3 : NH3 (NH3 = Lewis Base; :is Co-od cov bond)
Molecules w/ multiple bonds can act like lewis A.
8.8 Properties of Covalent Bonds.
Bond Order: (# of bonding e - # antibonding e)/ 2. Higher bond order -> stronger, shorter bonds.
1. Bonds b/w M and atoms in a group decrease in strength down b/c region of space shared by e- b/w atoms gets proportionally smaller.
2. Bonds b/w like atoms usually weaker down. Same Reason as above. *N,O,F unusually weak single bonds b/c of lone-pair repulsions. Cl-Cl>Br>F>H>I.
3. Elements in periods 3,4 have VERY weak multi-bonds w/ eachother
4. Multi bonds b/w C,O,N and Per 3 elements unusually strong.
About a 10% discrepancy b/w ΔH_rxn (Bond energies) and ΔH_f