

Previous Models

- 1) Bohr's model ← Atomic model of middle age
- 2) Newlands Octaves ← was average of left and right are
- 3) Mendeleev's Periodic table

had it in order of increasing mass, we now have it in order of increasing atomic number.

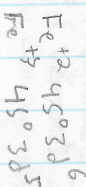
Max of e^- in an orbital =

$$2n^2$$

radii ↑
I.E. ↓
Metallic character ↑
electron affinity ↓
(becomes more true)

* e^- that are removed follow "last one in, first one out"

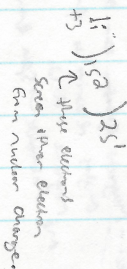
transition metals have exceptions



- Orbital Penetration of nucleus
↳ (getting close to nucleus)
s > p > d > f
↑ most often

Effective nuclear charge - nuclear charge felt most e^- on shell, electrons in lower orbitals on screen e^- from nucleus, weakening attraction to nucleus.

$$Z_{\text{eff}} = Z - V$$



(groups)

(1)

Alkali

Metals (2)

Alkaline earth metals

2s

Li Be

3s

Na Mg

4s

K Ca

transition metals

Sc Ti V Cr Mn Fe Co Ni Cu Zn

4s $3d^4 \rightarrow 4s^1 5$

4s $3d^9 \rightarrow 4s^1 10$

exceptions to Aufbau principle like e^- configurations that are "preferred" in nature.

Al Si P S Cl Ar

B C N O F Ne

He

Halogen

(3) (4) (5) (6) (7) (8)

Noble Gases

He

Ne

Ar

Kr

Xe

Rn

Fr

Ra

Ac

Th

Pa

U

Np

Pu

Am

Cm

Bk

Cf

Es

Fm

Md

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Forday $\rightarrow F = 96487 \text{ C/g}$

Crookes $\rightarrow$ Cathode ray tubes - Cathode rays were small negatively charged particles (e^-)

Thompson $\rightarrow$ Cathode ray electron $1.76 \times 10^{18} \text{ C/g}$

Millikan $\rightarrow$ Charge of electron $1.6 \times 10^{-19} \text{ C/electron}$

$\rightarrow$ Mass of electron $9.1 \times 10^{-31} \text{ g}$

Chadwick $\rightarrow$ identified Neutron from radioactive decay.

Rutherford $\rightarrow$ Solusystem model $\rightarrow$ Gold foil particle scattering

Planck $\rightarrow$ Energy only absorbed or emitted in quanta of magnitude $\Delta E = h\nu = \frac{hc}{\lambda}$ (relationship btw frequency of light and energy. (particularly thought to be amplitude))

Balmer $\rightarrow \frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ $n_f = 2, n_i = 3, 4, 5$

$\rightarrow$ Short light through slit and go through prism you get spectrum - certain wavelengths observed (violet)

Lyman $\rightarrow$ UV $n_f = 1, n_i = 2, 3, 4$

Paschen $\rightarrow$ IR $n_f = 3, n_i = 4, 5, 6$

$E = h\nu = hc/\lambda = hcR \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$
 $= 2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$

photoelectric effect

$E = h\nu \rightarrow K.E. = \frac{1}{2}mv^2$

$E = B.E. + K.E.$
 binding energy of nucleus
 of nucleus electron

$E = h\nu = \frac{hc}{\lambda} = h\nu_0 - \frac{1}{2}mv^2$

$\frac{1}{2}mv^2 = h\nu - h\nu_0$
 $\uparrow$ energy applied $\uparrow$ kinetic energy of electron

- Bohr Model - Coulombic forces of attraction

- Angular momentum $MUR = \frac{nh}{2\pi}$ is quantized

- Radius of atom - $r = \frac{a_0 n^2}{Z}$

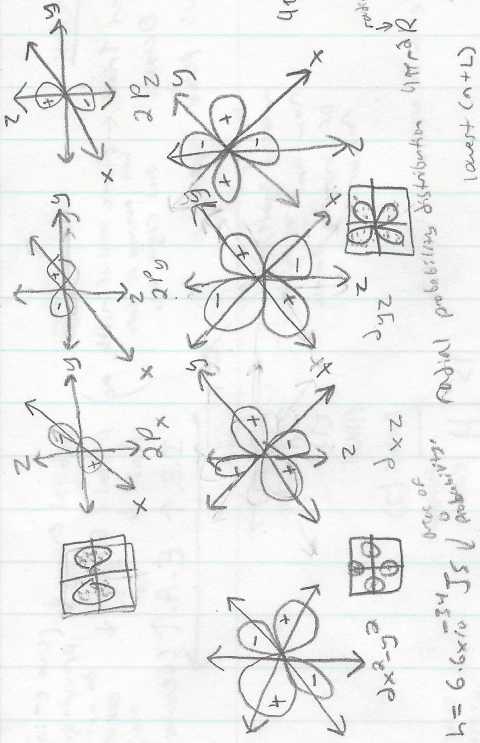
$\rightarrow -E \text{ of } e^- - E = K.E. + P.E. = \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r} \right) = \frac{Z^2 e^2}{8\pi\epsilon_0 r} - \frac{Z^2 e^2}{4\pi\epsilon_0 r} = -\frac{Z^2 e^2}{8\pi\epsilon_0 r}$

$\frac{Z^2 e^2}{4\pi\epsilon_0 r} = \frac{mv^2}{r}$ centrifugal force

$MUR = \frac{nh}{2\pi}$

$r = \frac{a_0 n^2}{Z}$

$\rightarrow -E \text{ of } e^- - E = K.E. + P.E. = \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r} \right) = \frac{Z^2 e^2}{8\pi\epsilon_0 r} - \frac{Z^2 e^2}{4\pi\epsilon_0 r} = -\frac{Z^2 e^2}{8\pi\epsilon_0 r}$



Radial probability distribution $4\pi r^2 R^2$

Angular momentum of e^- $L = \hbar \sqrt{l(l+1)}$

$\psi = R(r) \Theta(\theta) \Phi(\phi)$

Pauli exclusion - no more than 2 e^- in an orbital, no 2 e^- can have same quantum #s.

Heisenberg uncertainty principle $\Delta x \Delta p \geq \frac{h}{4\pi}$

Schrodinger equation $\hat{H}\psi = E\psi$

Uncertainty in position, momentum

Electron - atomic orbital

Probability of e^- distribution

More we know about one, less we know about the other.

Standing wave $n\lambda = 2\pi r$
 $m\nu\lambda = \frac{h}{\lambda}$
 $n\lambda = 2\pi r$
 $\frac{h}{m\nu} = \frac{h}{m\nu}$

DeBroglie $\rightarrow$ wave-particle duality of e^-

Planck $E = h\nu$
 Einstein $E = mc^2$
 $\frac{h\nu}{c} = mc^2$
 $\frac{h}{\lambda} = mc$
 $\frac{h}{\lambda} = \frac{h}{\lambda}$

Summerfield - elliptical orbits - Atoms with quantum numbers

Zeeman effect - Magnetic quantum m_l - orbit at certain angles relative to angle of applied magnetic field.

Goudmit and Goudmit $\rightarrow$ Spin quantum m_s

$\frac{e^2}{4\pi\epsilon_0 r} = \frac{Z^2 e^2}{8\pi\epsilon_0 r}$

$= -\frac{Z^2 e^2}{8\pi\epsilon_0 r}$

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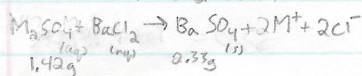
Coulomb's law - ↑ charge of species, stronger the force of attraction - closer they are.

Intermolecular attractors - ionic, polar, hydrogen, van der Waals
(depending on how big element is)

pure mixture - Homogeneous
element compound Heterogeneous

Quantitative } what exists?
Qualitative }

Find atomic mass of element

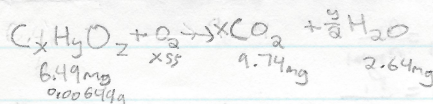


$$n_{BaSO_4(p)} = \frac{m}{M} = \frac{0.33g}{233g/mol} = 0.001416mol$$

$$1.42g M_2SO_4 = \text{mass of } 2M^+ + \text{mass of } SO_4$$

$$= 0.01(2M + 96)$$

$$M = 23g/mol \therefore M = Na$$



$$n = \frac{m}{M} \quad H = \frac{n}{M} \quad n = \frac{0.00264g}{18.02g/mol} = 0.0001465mol$$

$$n = \frac{0.00649g}{44g/mol} = 0.0001475mol$$

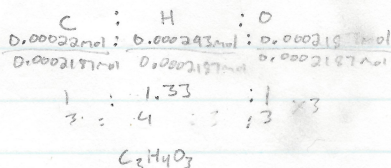
$$n = \frac{0.00974g}{18.02g/mol} = 0.0005405mol$$

$$M = nM \quad H_m = nM = 0.0005405mol(1.01) = 0.0005455g$$

$$M = (0.0001465mol)(12.01g/mol) = 0.001759g$$

$$M = 0.00264g - 0.001759g = 0.000881g$$

$$n_O = \frac{m}{M} = \frac{0.000881g}{16g/mol} = 0.0000551mol$$



Physical: %w/w g solute/100g soln
%w/v g solute/100mL soln
%v/v mL solute/100mL soln

Chemical: Molarity M $\frac{\text{moles of solute}}{\text{L of solution}}$
Molality, m $\frac{\text{moles of solute}}{\text{kg solvent}}$

Normality, N $\rightarrow$ amount of material that either produces or consumes 1 mol of H^+ or OH^-

$$M_1V_1 = M_2V_2 \rightarrow \text{true when } n \text{ is the same for both things that consume same } \# \text{ of } H^+$$

$$N_1V_1 = N_2V_2 \rightarrow \text{always true.}$$

$$\text{Mole fraction, } X = \frac{\text{moles of one component of soln}}{\text{total moles of all components of soln}}$$

Qualitatively $\rightarrow$ mixture either dilute or concentrated

Separation technology:

Crystallization $\rightarrow$ separate solids from liquid soln based on relative solubilities, put solids in hot solution, cool it down at point where one is less soluble than other.

Distillation

Chromatography $\rightarrow$ place sample on absorbent paper, put in container with solvent, barely touching, let water rise up paper until different components of sample separated out.



Distillation $\rightarrow$ water is vaporized, heated until gaseous, undesirable elements do not vaporize.

$\rightarrow$ water vapor led into condenser, cooled down until returned to liquid state.

$\rightarrow$ separate 1 component of liquid from another based on boiling points.

Solvent Extraction - separate 1 component of liquid from another based upon solubility in another solvent.

- In a separating funnel, give it good shaking soln with dissolve in 1 solvent over the other; solvent cannot be soluble in each other.

- Atomic mass relative: based on carbon 12, assigned 12 amu
mass spectrometer - atoms or molecules passed through beam of high energy electrons, knocks off electrons making molecules into ions, magnetic field deflects ions, most deflected = lightest

Atomic mass = AVG mass of element based on isotopic composition.

$$\text{Mass\% element} = \frac{\text{element} \times 100\%}{\text{compound}}$$

$$\frac{\% \text{ of atoms}}{\frac{6.022 \times 10^{23} \text{ atoms}}{A - Avogadro's constant}} = n$$

$\rightarrow$ determining formula for compounds

- $\rightarrow$ Determine mass%
- $\rightarrow$ Determine $\#$ of moles in 100g compound using M
- $\rightarrow$ divide by smallest n
- $\rightarrow$ if not whole $\#$, multiply until whole $\#$.

acid produces H_3O^+ in H_2O , base produces OH^-

Titration is experimental procedure by which acids and bases (or oxidizing and reducing agents) are reacted for quantitative analysis.

equivalence point of an acid base titration is point when $\#$ of H^+ added from burette is $\#$ of moles of OH^- originally present in flask.

$\rightarrow$ Know b/c of indicator, titration ends at end point - when indicator changes colour (near equivalence point).

precipitation rxns - insoluble precipitate separates from liquid.
soluble salts of +1 cations, except Ba^{2+} , Hg^{2+} , and Pb^{2+} , ClO_4^-
 $\rightarrow$ and Pb^{2+} , except for: Ag^+ , Hg^+ and Pb^{2+}

insoluble
 $\rightarrow$ most OH^- and O^{2-} salts and most salts of CO_3^{2-} , S^{2-} , PO_4^{3-} , CrO_4^{2-} except those of group 1 cations and NH_4^+ .

Hilroy

balancing redox rxns: 1) assign oxidation #s

2) Identify half rxns

3) Balance elements in eq'n other than H and O (components of solvent)

4) Balance charges with H_3O^+ or OH^- (acidic or basic, respectively)

5) Balance O with H_2O

6) ensure # of e^- released in oxidation rxn = # of e^- gained in reduction rxn.

7) add half rxns together

8) Simplify where possible. (remove H_2O where possible)

only obeyed
at low
pressures,
called an
ideal
gas.

Boyles Law $\rightarrow P \propto \frac{1}{V}$

Charles Law $\rightarrow V \propto T$

Gay Lussac $\rightarrow V_T = V_0 \frac{V_{0C}}{V_{0C}}$

Avogadro's hypothesis $\rightarrow V \propto n$

Gay Lussac's law of combining volumes

Dalton's Law of Partial pressures

$$PV = nRT \leftarrow \text{ideal gas law}$$

$\uparrow$ 1L $\uparrow$ 273.15K
 $\downarrow$ 1atm $\downarrow$ 0.08206
 $\downarrow$ 760 mmHg $\downarrow$ 101.3 kPa
 $d = m/v$

$$STP = 1 \text{ atm}, 273 \text{ K}$$

$$P_i = X_i \cdot P_{\text{total}}$$

$$P_{\text{total}} = P_1 + P_2 \dots$$

partial pressure

- 1) volume of individual gases is unimportant
- 2) forces among particles are unimportant.

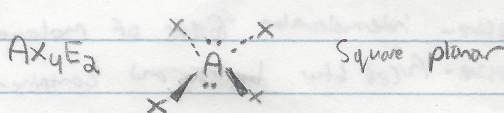
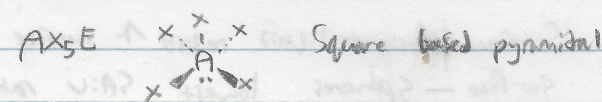
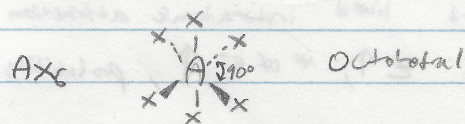
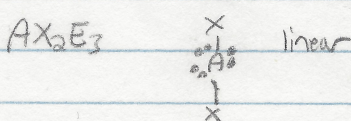
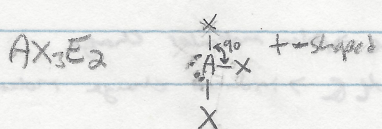
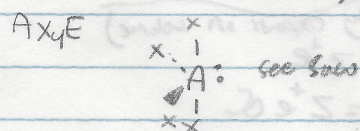
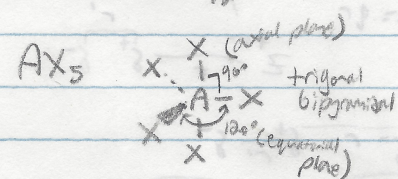
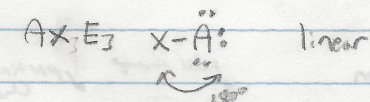
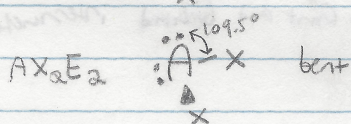
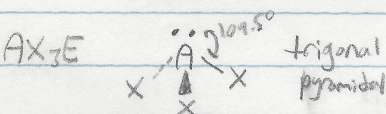
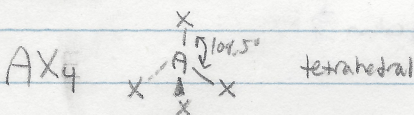
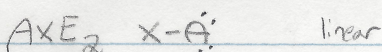
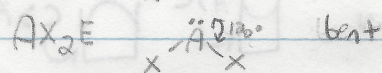
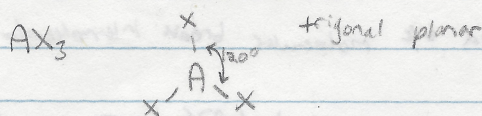
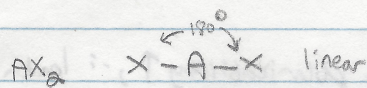
$$X_i = \frac{n_i}{n_{\text{total}}}$$

$$X_i = \frac{P_i}{P_{\text{total}}}$$

$$P_i = X_i \cdot P_{\text{total}}$$

VSEPR theory

- Central atom = LARGEST, Least electronegative; Never H.
- Satisfying Octet more important than resolving formal charge.
- repulsions: $lp-lp > lp-bp > bp-bp$
 $\rightarrow$ pairs of e^- repel each other, molecule wants to keep them apart



If ligand has

8e ⁻	not	2e ⁻
7e ⁻ or 1e ⁻		1e ⁻
6e ⁻		0e ⁻
5e ⁻		-1e ⁻
4e ⁻		-2e ⁻

radical $\rightarrow$ molecule w/ single unpaired $e^- \rightarrow$ will react readily

bond order $\uparrow$ as bond length $\downarrow$ as bond energy $\uparrow$

of bonds holding # of elements

delocalised $e^- \rightarrow$ entropy $\uparrow$ $\therefore$ $\uparrow$ bond energy

Electronegativity - ability of atom to attract e^- towards itself. Molecular not Atomic property.

$$|X_A - X_B| = 0.102 \Delta^{1/2}$$

= 0 pure covalent

= 70, < 1 polar covalent 2 different metals

= 1-2 polar covalent

Ionic

= > 2 Ionic

$\mu = qr$ dipole moment - polar molecules (Magnitude of net charge separation (ΔEN) in polar molecule, r = distance of separation)

μ not oxidation # or formal charge
(pure covalent) (pure ionic) $e^- = 1.6 \times 10^{-19} C$

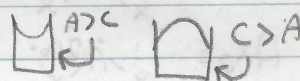
London dispersion forces - atoms develop temporary nonsymmetrical e^- distribution, causing a temporary, instantaneous dipole, inducing a dipole in neighbouring atoms, causing a weak and short lived interatomic attraction

as $Z \uparrow$, # of $e^- \uparrow$, probability of dipole $\uparrow$, polarizability $\uparrow$, $\therefore$ London dispersion forces $\uparrow$

Surface tension - liquids resist $\uparrow$ surface area b/c molecules break intermolecular bonds to reach surface - spheres lowest SA:V ratio

Cohesive - intermolecular forces of molecules of liquid

Adhesive - forces btw liquid and container



$$\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$P_{\text{atm}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

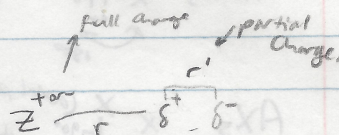
$$\ln \left(\frac{P_{\text{vap}}}{P_{\text{Ta}}} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

δ = electron density concentrated around internuclear axis
 π = electron density concentrated above and below or in front and behind internuclear axis (with nodal plane at the axis)

Coulombs law $F = \frac{q_1 q_2}{r^2}$

Ion pair $\Rightarrow E = \frac{Z^+ Z^-}{4\pi\epsilon_0 r}$
 $\rightarrow$ charge or 1 electron
 $\rightarrow$ dipole moment = $q \cdot r$

ion-dipole $\rightarrow E = \frac{-|Z^{+or-}| e \mu}{4\pi\epsilon_0 r^2}$



dipole-dipole $\rightarrow E = \frac{-2\mu\mu}{4\pi\epsilon_0 r^3}$
 $\rightarrow$ polarizability (depends on volume)
 $q_1 = Z^+ e$
 $q_2 = Z^- e \alpha$

Ion-induced dipole $E = -\frac{1}{2} \frac{|Z^{+or-}| e \alpha}{4\pi\epsilon_0 r^4}$

dipole-induced dipole $E = \frac{-\mu^2 \alpha}{4\pi\epsilon_0 r^6}$
 $q_1 = \mu \rightarrow$ polar molecules charge
 $q_2 = \mu \alpha \rightarrow$ induced charge molecule and its polarizability

Induced dipole-induced dipole $E = \frac{-3I^2 \alpha^2}{4\pi\epsilon_0 r^6}$
 $\rightarrow$ ionization energy

$\hookrightarrow$ London dispersion or van der Waals forces

Electronegativity - ability of atom in bond to attract e^- towards itself

Pauling

$$|X_A - X_B| = 0.102 \Delta^{1/2}$$

↑ electronegativity of A

$$D_{AB} \approx (D_{AA} \times D_{BB})^{1/2} \rightarrow \text{pure covalent}$$

$$D_{AB} = (D_{AA} \times D_{BB})^{1/2} + \Delta \rightarrow \text{polar covalent}$$

↑ bond dissociation energy

↑ E to distort polar to non-polar (asymmetrical to symmetrical)

↑ breaking pure covalent bond

$\Delta = 0 \rightarrow$ pure covalent
 $\Delta > 0, < 1 \rightarrow$ polar covalent, 2 different nonmetals
 $\Delta = 1-2 \rightarrow$ polar covalent / ionic
 $\Delta > 2 \rightarrow$ ionic

Mulliken

$$X = (I.E. + E.A.) / 2$$

Rochow

$$X = 3590 (Z_{eff} / r_{cov}^2) + 0.744$$

↑ effective nuclear charge ↑ radius

Dipole Moment - 2 atoms w/ diff. EN then polar bond.

$$\mu = q \cdot r$$

↑ dipole moment ↓ distance of separation

↑ magnitude of charge separation ↓ charge (charge of e^- alone)

London dispersion forces - atoms develop nonsymmetrical e^- configurations, causing temporary dipole and temporary intermolecular attraction.

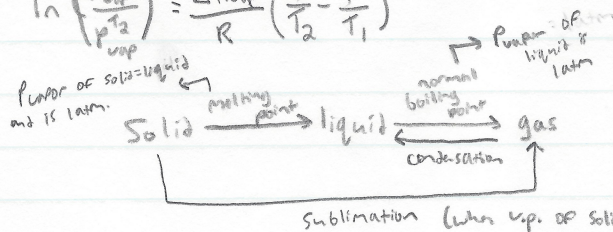
as mass ↑, $Z \uparrow$, # of $e^- \uparrow$, probability of dipole ↑, polarizability ↑, ∴ London dispersion forces ↑

vapor pressure $\Rightarrow P = P_{\text{vapor}} + P_{\text{Hg column}} \rightarrow$ vapor present at equilibrium

volatile = evaporates readily $\rightarrow$ liquids w/ high vapor pressure
 ↑ vapor pressure, ↓ intermolecular forces, ↑ temperature.

$$\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\ln \left(\frac{P_{T_2}^{\text{vap}}}{P_{T_1}^{\text{vap}}} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



— endothermic —

$$F = \frac{q_1 q_2}{4\pi \epsilon_0 r^2}$$

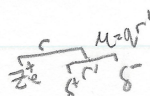
Coulombs law

e^- - charge of e^-

$Z^{\text{+or-}}$ - ionic charge

$\mu = q \cdot r$ = dipole moment

α - polarizability depends on volume ($4\pi r^3$) $\rightarrow$ how easy cloud can be distorted, depends on volume

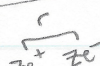


$$E = \frac{Z^+ Z^-}{4\pi \epsilon_0 r}$$

1) ion-ion pair

$$E = \frac{-|Z^{\text{+or-}}| e \mu}{4\pi \epsilon_0 r^2}$$

2) ion-dipole



$$E = \frac{-2 q_1 q_2}{4\pi \epsilon_0 r^3}$$

3) dipole-dipole

$$E = \frac{-1}{2} \frac{|Z^{\text{+or-}}|^2 e^2 \alpha}{4\pi \epsilon_0 r^4}$$

4) ion-induced dipole

$$q_1 = Z e^+ \quad q_2 = Z e^- \alpha$$

↑ depends on charge of first one + α induce dipole shift.

$$E = \frac{-\mu^2 \alpha}{4\pi \epsilon_0 r^6}$$

5) dipole-induced dipole

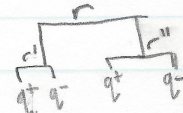
↳ dipole molecule w/ dipole moment approaches a dipole

$$q_1 = \mu \quad q_2 = \mu \alpha$$

↳ London dispersion forces

$$E = \frac{-3 I^2 \alpha^2}{4\pi \epsilon_0 r^6}$$

weakest attraction, b/c 2 smaller molecules, 1 may become polar for short time and induce a dipole. Protons attracted b/c they have many induced dipoles - induced dipole bonds, even for each one weak.



polarity $\uparrow$ = hydration (attraction to water) $\uparrow$

H-bond = special dipole-dipole bonds $\rightarrow$ stronger than dipole-dipole attractions.

Colligative properties - affected by # of particles dissolved in solution, nature of solvent and concentration

$V_{\text{soln}} = X_{\text{solvent}} V_{\text{solvent}}$ Solute is non-volatile so $v.p.$ solute is negligible.

$\Delta T_{b.p.} = i m K_{b.p.}$
 molarity

$\Delta T_{f.p.} = i m K_{f.p.}$
 boiling/freezing point constant for solvents

$\pi = i M R T = \frac{i n R T}{V}$
 osmotic pressure

$V_{\text{soln}} < V_{\text{solvent}}$

$T_{bp \text{ soln}} > T_{bp \text{ solvent}}$

$T_{ap \text{ soln}} < T_{ap \text{ solvent}}$

$p = K_H X$
 partial pressure of gas
 Henry law constant
 mole fraction

$S_{\text{gas}} > S_{\text{solution liquid}} > S_{\text{solvent liquid}} > S_{\text{solid}}$

$\Delta S > 0$

$\text{liquid} \rightarrow \text{gas } T_{bp} \quad \Delta H > 0$
 $\text{solid} \rightarrow \text{liquid } T_{fp} \quad \text{endothermic}$

$i = \text{Van't Hoff factor} = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$

$\Delta G = \Delta H - T \Delta S \rightarrow$ more entropy means T can be lower while still making ΔG < 0 and thus spontaneous.

Schrodinger derivation

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

$$\frac{d\psi}{dx} = \left(A \cos \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right) \rightarrow \psi$$

$$\frac{d^2\psi}{dx^2} = \left(-\frac{2\pi}{\lambda} A \sin \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right)$$

$$\frac{d^2\psi}{dx^2} = \left(-\frac{2\pi}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right) \psi$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi}{\lambda^2} = 0$$

$$v = \frac{h}{m\lambda} \leftarrow \frac{h}{\lambda} = mv$$

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}m \frac{h^2}{m^2\lambda^2} \Rightarrow K.E. = \frac{h^2}{2m\lambda^2} \Rightarrow \frac{1}{\lambda^2} = \frac{2m K.E.}{h^2}$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi}{\lambda^2} = \frac{2m K.E.}{h^2}$$

$$= \frac{-Ze^2}{4\pi\epsilon_0 r}$$

$$E = K.E. + P.E. \Rightarrow K.E. = E - P.E. \Rightarrow K.E. = E + \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} \psi \left(E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) = 0$$

one dimensional Schrodinger wave equation.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2} \psi \left(E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) = 0$$

3 dimensional Schrodinger wave equation

$$\nabla^2\psi + \frac{8\pi^2m}{h^2} \psi \left(E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) = 0$$

$$\frac{8\pi^2m}{h^2} \left(E\psi + \frac{Ze^2\psi}{4\pi\epsilon_0 r} \right) = -\nabla^2\psi$$

$$E\psi + \frac{Ze^2\psi}{4\pi\epsilon_0 r} = \frac{-\nabla^2\psi h^2}{8\pi^2m}$$

$$E\psi = \frac{-\nabla^2\psi h^2}{8\pi^2m} - \frac{Ze^2\psi}{4\pi\epsilon_0 r}$$

$$E\psi = H\psi$$

steric factor = fraction of collisions with effective orientations.
 $\downarrow$ by $\uparrow$ temp, $\uparrow$ proportion of molecules that have the EA to pass the energy barrier to react.
 $\downarrow$ diameter of molecule

$$K = PZ e^{-E_a/RT}$$

$Z = \frac{\pi d^2 \bar{v} N_c}{\sqrt{2}}$ Collision frequency
 $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$ temperature energy
 N_c concentration (mol/L)
 $\downarrow$ Avogadro's # (atoms/mol)

$$K = PZ e^{-E_a/RT}$$

$$\ln K = \ln PZ - \frac{E_a}{RT}$$

Slope = $-\frac{E_a}{R}$

$$\frac{K_{T_1}}{K_{T_2}} = \frac{(PZ)_{T_1} e^{-E_a/RT_1}}{(PZ)_{T_2} e^{-E_a/RT_2}} = \frac{e^{-E_a/RT_1}}{e^{-E_a/RT_2}} = e^{\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})}$$

$\uparrow$ assume T doesn't affect PZ

$$\ln\left(\frac{K_{T_1}}{K_{T_2}}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_{T_1}}{K_{T_2}}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

rate (based on collisions) = $\frac{K_{col}}{K_{obs}} = \frac{PZ e^{-0/RT}}{PZ e^{-E_a/RT}} = \frac{1}{PZ e^{-E_a/RT}}$

$\downarrow$ assume $E_a = 0$; based only on collisions

$$\text{rate}_F = K_F [R] = K_b [P] = \text{rate}_b$$

(at equilibrium)

$$K = \frac{K_F}{K_b} = \frac{[P]}{[R]}$$

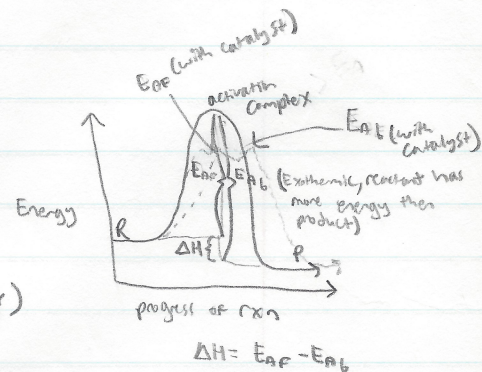
$$\frac{K_F}{K_b} = \frac{(PZ)_F e^{-E_{aF}/RT}}{(PZ)_b e^{-E_{ab}/RT}} = \frac{(PZ)_F}{(PZ)_b} e^{\frac{-E_{aF} + E_{ab}}{RT}} = \frac{(PZ)_F}{(PZ)_b} e^{-\Delta H^\circ/RT}$$

$$\ln\left(\frac{K_F}{K_b}\right) = \ln\left(\frac{(PZ)_F}{(PZ)_b}\right) + \frac{\Delta H^\circ}{RT}$$

Van't Hoff

$$\left\{ \ln(K) = \ln\left(\frac{PZ_F}{PZ_b}\right) - \frac{\Delta H^\circ}{RT} \right.$$

$$\ln\left(\frac{(PZ)_F}{(PZ)_b}\right) \approx \frac{\Delta S^\circ}{R} \text{ if } PZ_F > PZ_b, \text{ (reactants more ordered than products)}$$



* Fast initial step / slow intermediate Step = use steady state approximation

decay

1st order $t_{1/2} = 0.693/K \Rightarrow \frac{\ln 2}{K}$

0 order $t_{1/2} = [R_0]/2K$

2nd order $t_{1/2} = \frac{1}{K[R_0]}$

Half life

1; 2

20; 20

20; 10

20; 40

$$H = E + PV$$

$$\Delta G = H - TS$$

$$G = E + PV - TS$$

$$\Delta G = dE + dPV + dW - Tds - sdT$$

$$\Delta G = dq + dW + dPV + dW - Tds - sdT$$

$$\Delta G = Tds + dW + dPV + dW - Tds - sdT$$

$$\Delta G = dW + dPV + dW - Tds - sdT$$

$$\Delta G = (dW_{elec} - dPV) + dPV$$

$$\Delta G = dW_{elec}$$

$$\Delta G = -nFE$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = nFE^\circ$$

$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ = nF \frac{\partial E^\circ}{\partial T}$$

$$\Delta S^\circ = nF \frac{\partial E^\circ}{\partial T}$$

$$\Delta H^\circ = G^\circ + T\Delta S^\circ$$

$$\Delta H^\circ = -nFE^\circ + TnF \frac{\partial E^\circ}{\partial T}$$

$$\Delta H^\circ = nF \left(T \frac{\partial E^\circ}{\partial T} - E^\circ \right)$$

$$\Delta G = -nFE$$

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

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\text{at } Q=K; \Delta G=0 \quad E=0$$

$$E^\circ = \frac{RT}{nF} \ln(K)$$

Concentration cell - higher concentration = Cathode

lower concentration = anode - donates its e^- to Cathode to lower its concentration

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[M_{anode}]}{[M_{cathode}]} \right)$$

$\rightarrow 0$ since same species.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

most elect-negative

$$F_2 + 2e^- \rightleftharpoons 2F^-$$

$$\frac{E^\circ(V)}{= 2.87}$$

$$W = -qE$$

$$(J) \quad (C) \quad (V = J/C)$$



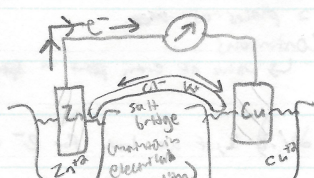
$$\Delta G_3^\circ = 2\Delta G_2^\circ - \Delta G_1^\circ \quad \text{but } \Delta G^\circ = -nFE^\circ$$

$$= 2(-1FE_2^\circ) - (-2FE_1^\circ)$$

$$= 2F(E_2^\circ - E_1^\circ)$$

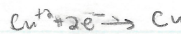
$$= -2FE^\circ_{cell}$$

$$= -nFE^\circ_{cell}$$



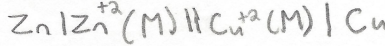
Oxidation occurs

anode (reducing agent)



reduction occurs

cathode (oxidizing agent)



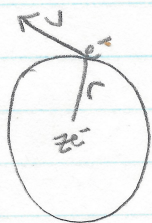
$$E = h\nu = hc\bar{\nu} = hcR\left(\frac{1}{n^2}\right) \\ = 2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_F^2} - \frac{1}{n_I^2} \right)$$

$$J = K_g m^2 s^{-2}$$

$$E = \text{B.E.} + \text{K.E.}$$

binding energy of e^- to surface kinetic energy of ejected e^-

$$\frac{hc}{\lambda} = h\nu = h\nu_0 + \frac{1}{2}mv^2 \Rightarrow \frac{1}{2}mv^2 = h\nu - h\nu_0 \\ v = \frac{c}{\lambda}$$



Bohr Model

$$\frac{Ze^-}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

Coulombic forces of attraction Centrifugal force
2 opposing forces

$$E = \text{K.E.} + \text{P.E.} = \frac{1}{2}mv^2 + \left(\frac{-Ze^2}{4\pi\epsilon_0 r} \right)$$

$$= \frac{1}{2} r \frac{Ze^-}{4\pi\epsilon_0 r^2} + \frac{-Ze^2}{4\pi\epsilon_0 r}$$

→ converts $\frac{F}{\text{length}}$ to charge

$$= \frac{Ze^-}{8\pi\epsilon_0 r} + \frac{-Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{-Ze^-}{8\pi\epsilon_0 r}$$

$$r = \frac{\epsilon_0 n^2 h^2}{Ze^2 \pi m}$$

$$= \frac{-Ze^4 m}{8n^2 h^2 \epsilon_0^2}$$

$$= -2.178 \times 10^{-18} \left(\frac{1}{n^2} \right)$$

Wave-Particle Duality

$$E = h\nu$$

$$E = mc^2$$

$$h\nu = \frac{hc}{\lambda} = mc^2$$

$$\frac{h}{\lambda} = mc$$

photons

radius of circle.
 $n\lambda = 2\pi r \rightarrow$ Standing wave

$$mvr = \frac{nh}{2\pi}$$

$$2\pi r = n\lambda = \frac{nh}{mv}$$

$$mvr = nh$$

$$mv = \frac{nh}{n\lambda}$$

$$mv = \frac{h}{\lambda}$$

(electrons)

Aufbau = e^- seek minimum energy state ($n+1$)

Pauli exclusion = No 2 e^- can have 4 quantum #s the same.

Hund's rule = e^- enter separate orbitals singly if possible. ↳ orbital w/ same energy.

Heisenberg Uncertainty Principle

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

↑ increasing in position ↑ uncertainty in velocity

* where e^- is most likely to be

if so we wouldn't know where e^- is..

↑ e^- can't be in 2 places at once.

finite, single valued, continuous

↳ value at every point in space

ψ = wavefunction, e^- orbital - must be

ψ^2 = intensity of e^- distribution

$\int \psi^2 dV = 1$ (probability of finding e^- within certain volume element, dV is 1, if we look for e^- we will find it.)

↳ AKA normalization.

$$G = H - TS \quad H = E + PV$$

$$G = E + PV - TS$$

$$\Delta G = \Delta E + P\Delta V + V\Delta P - T\Delta S - S\Delta T \quad dE = dq + dw$$

$$\Delta G = dq + dw + p\Delta V + V\Delta P - T\Delta S - S\Delta T \quad dq = T\Delta S$$

$$\Delta G = dw + p\Delta V + \underbrace{V\Delta P - S\Delta T}_{\text{both } = 0} \quad \text{Constant } T \text{ and } P.$$

$$\Delta G = dw + p\Delta V$$

$$\Delta G = (dw_{\text{elec}} - p\Delta V) + p\Delta V \quad \text{System}$$

$$= dw_{\text{elec}}$$

dw = total work that can be done, not just expansion or retraction of

dw = expansion work + electrical work

$$\Delta G = W_{\text{electrical}}$$

$$\Delta G = -nF\mathcal{E}$$

$\mathcal{E}$ = electrical potential
 n = no. of mol of e^- transferred.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -nF\mathcal{E}^\circ$$

$$\frac{\partial \Delta G}{\partial T} = -\Delta S^\circ = nF \frac{\partial \mathcal{E}^\circ}{\partial T}$$

$$\Delta S^\circ = nF \frac{\partial \mathcal{E}^\circ}{\partial T}$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

$$\Delta H^\circ = -nF\mathcal{E}^\circ + TnF \frac{\partial \mathcal{E}^\circ}{\partial T}$$

$$\Delta H^\circ = nF \left(T \frac{\partial \mathcal{E}^\circ}{\partial T} - \mathcal{E}^\circ \right)$$

$$\Delta G = -nF\mathcal{E}$$

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

$$-nF\mathcal{E} = -nF\mathcal{E}^\circ + RT \ln Q$$

$$\mathcal{E} = -\mathcal{E}^\circ + \frac{RT}{nF} \ln Q \quad \text{Nernst equation}$$

At equilibrium $Q=K$, $\Delta G=0$, $\mathcal{E}=0$

$$\mathcal{E}^\circ = \frac{RT}{nF} \ln K$$

$$\mathcal{E} = \frac{RT}{nF} \ln \left(\frac{M_{\text{anode}}}{M_{\text{cathode}}} \right) \quad \text{Since in concentration cell } \mathcal{E}^\circ = 0$$

Chapter 5

5.6

Kinetic molecular theory: molecules in gas are far apart, most of volume is empty & negligible

U_{RMS} → root mean square velocity

↳ average of the squares of the particle velocities

U_{mp} = velocity possessed by the greatest # of gas particles

U_{avg} = average velocity of particles

- Molecules in constant random motion, moving in straight line until collision, when it changes direction (still straight line).

- Molecules exert no force on each other except during collisions.

- Average kinetic energy depends on temperature.

→ as temp ↑, pressure ↑, velocity ↑ (constant V)

→ as temp ↑, volume ↑, pressure ↑ then ↓ (variable V)

→ as temp ↓, volume ↓

5.7

Diffusion - One gas mixes with another

Effusion - a gas escapes from a small opening 

→ Avg kinetic energy, velocity constant (constant temperature)

→ individual molecules have varied kinetic energies

→ Avg velocity depends on relative masses $\frac{V_1}{V_2} = \sqrt{\frac{M_2}{M_1}}$ Graham's law

→ effusion rate < diffusion rate < velocity (very high for gasses)

5.8

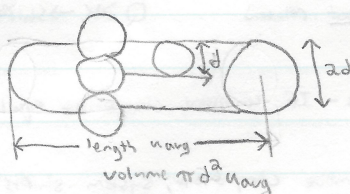
Z = collision rate (per second) of the gas particles with a section of the wall that has area A .

5.9

↳ influenced by: Avg velocity of gas molecules
Size of area being observed
of particles in container

5.9

Intermolecular collision frequency



Mean free path, λ → distance molecule can go without hitting other atoms

5.10

At pressures higher than 1 atm, deviations from ideal behavior: $PV = nRT$

↳ van der Waals eqn $(P + \frac{a}{V^2})(V - b) = RT$

↳ intermolecular attraction factor

↳ molecules attracted to each other do not hit wall.

↳ excluded volume/mol

↳ area occupied by molecules volume or restricted from their shape.

$$PV = P_b + \frac{aV}{V^2} - \frac{ab}{V^2} = RT$$

$$P(V-b) + \frac{a}{V}(V-b) = RT$$

$$PV(V-b) + \frac{a}{V}(V-b) = VRT \quad \times V$$

$$PV + \frac{a}{V} = \frac{VRT}{(V-b)} \quad \div (V-b)$$

$$\frac{PV}{RT} + \frac{a}{RT} \cdot \frac{1}{V} = \frac{V}{(V-b)} \quad \div (RT)$$

$$\frac{PV}{RT} = \frac{V}{(V-b)} - \frac{a}{VRT}$$

$$\frac{PV}{RT} = 1 + \frac{b}{V} - \frac{a}{VRT}$$

$$\frac{bVRT}{V} = a$$

$$bRT = a$$

$T = a/bR \rightarrow$ Boyle's Temp → temperature where gas behaves ideally.

At low P, $\frac{V}{V-b} \approx 1$

$$\frac{b}{V} \approx \frac{a}{VRT} \approx 0$$

At high T, $\frac{a}{VRT} \approx 0$

Compressibility Coefficient

$$Z = \frac{PV}{RT} \text{ for } n=1$$

$Z=1 \Rightarrow$ ideal behavior. extent Z deviates from 1 measures how non ideal gas is.

Chapter 6

6.1 dynamic equilibrium - rxn hasn't stopped, both forward and backward remains the same.
- affected by: initial concentrations, relative energies of reactants and products, degree of organization of reactants and products

6.2 law of mass action $A + KB \rightleftharpoons IC + nD$ equilibrium expression $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
 $\rightarrow$ if balanced eqn raised to the n , K^n
 $\rightarrow$ not applicable to concentrated aq. soln or gasses at high pressure

$K_{obs} \rightarrow$ calculated from observed values, not corrected for the effects of non-ideality
 $\rightarrow$ only K_{obs} has units
 $\rightarrow$ depends on ratio of concentrations.

6.3 $K_p = K_c (RT)^{\Delta n}$

6.4 Equilibrium Constant expression is ratio of equilibrium concentrations/pressures for a given substance to a reference concentration/pressure.
 reference for $K_p = 1.0 \text{ atm}$
 $K_c = 1.0 \text{ mol/L} = K$

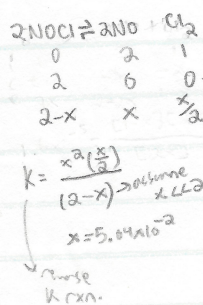
6.5 Homogeneous equilibria - reactants and products in gas phase
 Heterogeneous equilibria - equilibria involving more than 1 phase
 $\rightarrow$ activity of pure solid/liquid = 1
 $\rightarrow$ concentration not in equilibrium expression, activity is

6.6 large $K \rightarrow$ far to right
 small $K \rightarrow$ far to left
 Size of K and time not related
 reaction quotient (Q) - determines direction towards equilibrium
 $Q > K \rightarrow$ shift left, $Q = K \rightarrow$ at equilibrium, $Q < K$ shift right

6.8 Le Chatelier's principle - If conditions change at equilibrium, the equilibrium position will shift in a direction that reduces change.

$\rightarrow$ Concentration - add/remove component, system shifts away/toward side with component
 $\rightarrow$ Pressure - adding/removing gasses at constant volume
 $\rightarrow$ $\uparrow, \downarrow$ volume
 $\rightarrow$ add inert gas at constant volume $\rightarrow$ assume real gas behavior so gas doesn't have to be noble gas
 IF volume reduced, system shifts to reduce its own volume $V \propto n$
 $\rightarrow$ Temperature - value of K changes w/ temp.
 $\rightarrow$ exothermic - shift left if energy added.
 $\rightarrow$ endothermic - shift right if energy added.

6.9 $p^{obs} < p^{ideal}$ for real gasses above 1 atm



$K^{obs} \uparrow$ w/ pressure
 $\rightarrow$ power in denominator amplifies error compared to power in numerator
 $1 \text{ atm} < K_p$ 1% K_p^{obs}
 $1 \text{ atm} > K_p$ deviations severe

Finding one K from others

If rxns are

reversed

Multiplied by factor

added

Subtracted

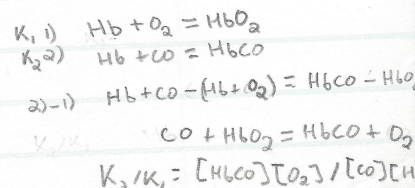
inverted

raised to the power of the factor

Multiplied

Divided

$K_1 = [C] / [A][B]$ $\frac{1}{K_1} = [A][B] / [C]$
 $K_4 = [E] / [D]$
 $K_1 K_4 = [C][E] / [A][B][D]$



weak base $\rightarrow$ NH_3 (ammonia), NH_4OH (ammonium hydroxide)
 Strong base $\rightarrow$ KOH , $\text{Ba}(\text{OH})_2$, NaOH
 weak acid $\rightarrow$ HF , H_2S , HCN
 Strong acid $\rightarrow$ HCl , HBr , HNO_3
 amphoteric/amphiprotic - H_2O , Al_2O_3

Chapter 7

Electrolyte strength
 $\rightarrow$ extent to which it
 produces ion in solution.

acids and bases

- 1) Arrhenius - acid donates H^+ , base receives H^+
- 2) Bronsted Lowry - acid donates proton, base receives proton
- 3) Lewis - acid donates pair of electrons, base receives pair of electrons.

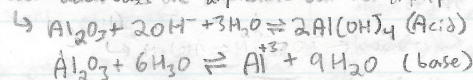
- Solvent may not always be in water $\rightarrow$ acid generates cationic form of solvent (for H_2O its H_3O^+)
 base generates anionic form of solvent (for H_2O its OH^-)

Factors affecting strength - relative electronegativities
 - bond polarity and energy
 - interaction w/ solvent
 - stability of products

Amphiprotic - Substance can both donate or accept a proton (H^+) $\rightarrow$ all amphiprotic substances are amphoteric

Amphoteric - (more general) Substance can act like an acid or a base $\rightarrow$ Lewis acids/bases are amphoteric but not amphiprotic

$\rightarrow$ H_2O is both amphiprotic and amphoteric



Concentration = * moles dissolved in solvent

Electrolyte = how much * moles ionizes (electron attractiveness)

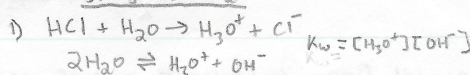
$\rightarrow$ depends on: relative electronegativities * as electronegativity of central atom $\uparrow$,
 bond polarity and energy strength of acid $\uparrow$,
 interaction w/ solvent
 stability of products

$\rightarrow$ Strongest acid that can exist in H_2O is H_3O^+ , Strongest base is OH^- . Anything higher dissociates to form H_3O^+ or OH^- .

$\rightarrow$ don't include H_2O b/c concentration is constant (55.5M)

Strong acid in H_2O

pH of 10^{-8} HCl
 $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
 $\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$
 $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
 $\text{H}^+_{\text{total}} = [\text{H}^+]_{\text{from HCl}} + [\text{H}^+]_{\text{from H}_2\text{O}}$
 $\text{pH} = -\log[\text{H}^+]_{\text{total}}$
 Since HCl is small, $[\text{H}^+]_{\text{from HCl}} \gg [\text{H}^+]_{\text{from H}_2\text{O}}$



2) Species existing: H_2O^+ , Cl^- , H_2O , OH^-

3) Charge balance: $[\text{H}_3\text{O}^+] = [\text{Cl}^-] + [\text{OH}^-]$

4) Mass balance: $C_a = [\text{Cl}^-] = 10^{-8}$ (given $[\text{HCl}]$ initially)

5) Solve for H_3O^+
 $[\text{H}_3\text{O}^+] = C_a + \frac{K_w}{[\text{H}_3\text{O}^+]}$
 $[\text{H}_3\text{O}^+] = 10^{-8} + \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$

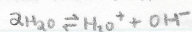
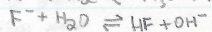
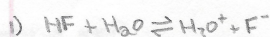
$$[\text{H}_3\text{O}^+] - 10^{-8} = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+]^2 - 10^{-8}[\text{H}_3\text{O}^+] - 1.0 \times 10^{-14} = 0$$

If $[\text{H}^+] > 10^{-6}$ then autoionization of water does not need to be taken into account.

$\therefore [\text{HCl}] < 10^{-6}$, pH not $-\log[\text{HCl}]$

Weak acid in water



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4} \text{ M}$$

$$K_b = \frac{[\text{F}^-][\text{OH}^-]}{[\text{HF}]} = \frac{K_w}{K_a} = 1.38 \times 10^{-11} \text{ M}$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1 \times 10^{-14} \text{ M}$$

2) Species H_3O^+ , F^- , HF , OH^-

3) Charge balance $[\text{H}_3\text{O}^+] = [\text{F}^-] + [\text{OH}^-]$

4) Mass balance $C_a = [\text{HF}] + [\text{F}^-] = 10^{-2} \text{ M}$

5) Solve

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

$$[\text{F}^-] = [\text{H}_3\text{O}^+] - [\text{OH}^-]$$

$$[\text{HF}] = C_a - ([\text{H}_3\text{O}^+] - [\text{OH}^-]) = 10^{-2} - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}$$

$$7.2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]([\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]})}{10^{-2} - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}}$$

Semi exact assumption

assume $[\text{OH}^-] \ll [\text{H}_3\text{O}^+]$ since K_b is small.

$$7.2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]^2}{10^{-2} - [\text{H}_3\text{O}^+]}$$

$$7.2 \times 10^{-6} - 7.2 \times 10^{-4}[\text{H}_3\text{O}^+] - [\text{H}_3\text{O}^+]^2 = 0$$

$$= 2.68 \times 10^{-3}$$

$$\frac{[\text{OH}^-]}{[\text{H}_3\text{O}^+]} = \frac{[3.73 \times 10^{-3}]}{[2.68 \times 10^{-3}]} \times 100\%$$

$$= 1.39 \times 10^{-13} \ll 5\%$$

check

Semi exact weak acid assumption

assume $C_a \gg [\text{H}_3\text{O}^+]$ since K_a is small

$$7.2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]^2}{10^{-2}}$$

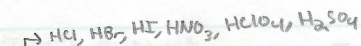
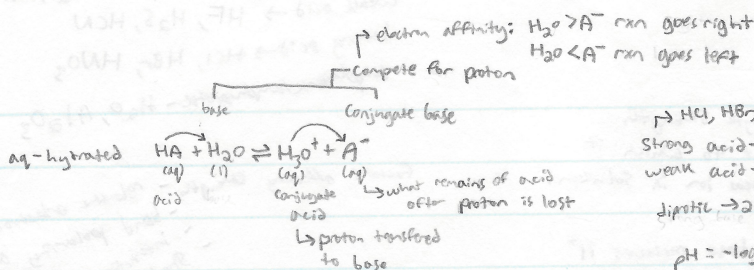
$$[\text{H}_3\text{O}^+] = 0.0023$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+]}{10^{-2} - [\text{H}_3\text{O}^+]} \cdot 100\%$$

$$= \frac{0.0023}{10^{-2} - 0.0023} \cdot 100\%$$

$$5\% < 29.8\% =$$

Hibroy



Strong acid $\rightarrow K_a$ large $\rightarrow$ conjugate base much weaker than H_2O
 weak acid $\rightarrow K_a$ small $\rightarrow$ stronger conjugate base
 diprotic $\rightarrow$ 2 acidic protons, monoprotic $\rightarrow$ 1 acidic proton

$pH = -\log[H^+]$ $pK = -\log K$

$\rightarrow$ 2 decimal (ie 7.00) $\rightarrow$ 2 sig figs (1.0 x 10⁻⁷ M)

K_b = rxn of base w/ H_2O to form conjugate acid and OH^- ion

polyprotic - can dissociate more than one proton per molecule,

in stepwise manner, 1 proton at a time.

$\rightarrow$ usually only 1st K_a is significant when determining pH

$\rightarrow H_2SO_4 \rightarrow$ unique, strong acid in first dissociation, weak acid in second dissociation step.

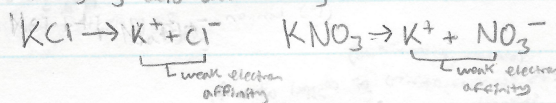
$\rightarrow$ only in dilute soln of H_2SO_4 does the second dissociation step contribute significantly to the $[H^+]$.

$K_a > K_b \rightarrow$ acidic

$K_a < K_b \rightarrow$ basic

$K_a = K_b \rightarrow$ neutral

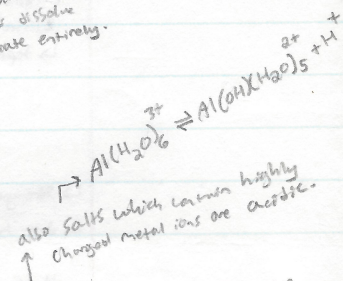
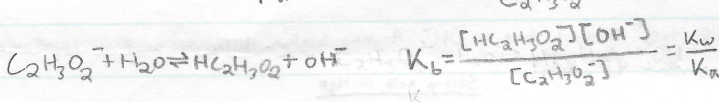
Salts - Salt of strong acid and strong base $\rightarrow$ pH 7. (neutral)



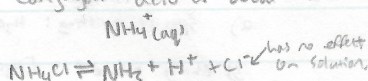
ionize readily in H_2O . Salts may be insoluble in water, won't dissolve much but what does dissolve will dissociate entirely.

ion w/ Cation of strong base + anion of weak acid $\rightarrow$ pH > 7 (basic)

Na^+ CH_3COO^-



ion w/ Cation is conjugate acid of weak base + anion of strong acid/base $\rightarrow$ pH < 7 (acidic)



$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$

chapter 8

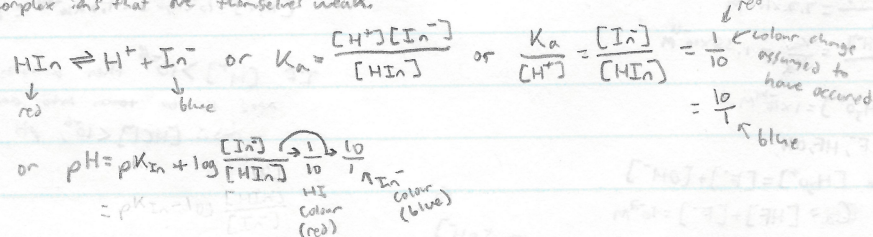
8.7

Determine equivalence in a titration

1) use pH meter, plot titration curve

2) Acid-base indicator - changes colour at endpoints, should be near equivalence point.

$\rightarrow$ complex ions that are themselves weak.



Strong acid/base $\rightarrow$ steep titration curve

weak acid/base $\rightarrow$ the weaker they are the smaller the vertical area around the equivalence point

$\rightarrow$ less flexibility in choosing indicator.

$\rightarrow$ must choose indicator whose useful pH range has midpoint as close as possible to the pH of equivalence points

universal indicator - mixture of 5 different indicators which each have 2 forms and change colours over different pH's.

Intensive properties are intensive
Extensive properties are extensive

Chapter 9

9.1

Energy - the capacity of a system to do work or to produce heat

1st law of thermodynamics

Law of Conservation of energy - energy cannot be created or destroyed, but transferred from 1 form to another.

Intensive $\rightarrow T, D, P, C, C_p/C_v$

$\rightarrow$ value doesn't depend on amount of substance

Extensive $\rightarrow E, S, G, M, n, V$

$\rightarrow$ depends on amount of substance.

$$0.08206 \frac{\text{Latm}}{\text{K mol}}$$

$$8.3145 \frac{\text{J}}{\text{K mol}}$$

$$101.3 \text{ J/Latm}$$

$$J = \frac{\text{kg m}^2}{\text{s}^2}$$

potential energy - energy due to position or composition b/c of attractive and repulsive forces

kinetic energy - due to motion of the object $KE = \frac{1}{2}mv^2$

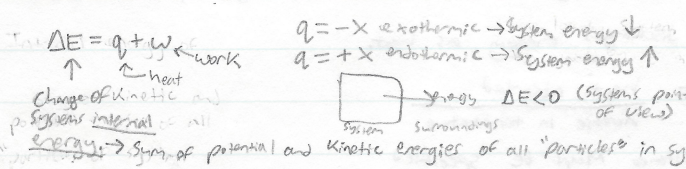
pathway - work and heat dependent on the pathway, energy is not.

State function (or state property) refers to a property of the system that depends only on its present state.

energy is a state function - heat and work are not.

System - part of universe on which we focus attention

Surroundings - everything else in universe



exothermic - heat flows out of system
endothermic - heat flows into system

heat comes from difference in potential energy between products and reactants.

exothermic rxn - potential energy stored in chemical bonds released as thermal energy via heat.

work done by system
work flows into surroundings

$\Delta V > 0, w < 0$ - expanding gas

$\Delta V < 0, w > 0$ - condensing gas

energy flows into system
surroundings work on system

$q > 0$ - system absorbed heat
 $q < 0$ - system gave off heat

Standard conditions = 298K, 1 atm, pH=7

9.2

Enthalpy $H = E + PV$

$\rightarrow$ pressure and volume of system.

internal energy of system

Enthalpy is a state function since E, P and V are too

$$\Delta E = q_p + w$$

$$\Delta E = q_p - P\Delta V \rightarrow w = -P\Delta V$$

$$q_p = \Delta E + P\Delta V = \Delta H$$

$$\Delta H = \Delta E + P\Delta V \rightarrow \text{if pressure is constant}$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P\Delta V \rightarrow \text{if pressure is constant}$$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H = \Delta E + P\Delta V \rightarrow \text{if pressure is constant}$$

$\Delta H_f^\circ = 8.314 \text{ J/K mol}$

(n gaseous products - n gaseous reactants)

Standard temp = 298K

solids or liquids!

at constant pressure (only work allowed is that from a volume change (PV)), the ΔH of the system is equal to the energy flow as heat.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$\Delta H > 0$ endothermic $\rightarrow$ products have more enthalpy so heat is absorbed by system

$\Delta H < 0$ exothermic $\rightarrow$ reactants have more enthalpy, decrease in enthalpy achieved by generation of heat.

9.3

Molar heat capacity of an ideal gas at constant volume $C_v = \frac{3}{2}R$

heat req. to change temp. of 1 mol of gas by 1K at constant temp.

Molar heat capacity of an ideal gas at constant pressure $C_p = C_v + R$

for monoatomic gases (consist of single atoms)

polyatomic gases $C_v > \frac{3}{2}R$ $\rightarrow$ polyatomic molecules absorb energy to excite rotational and vibrational motions and to move through space at higher speeds $\rightarrow$ structure causes them to absorb energy for processes other than translational motion.

$C_p = C_v + R$ for all gases that obey ideal gas law.

$$\Delta E = \frac{3}{2}nRT = nC_v\Delta T$$

For ideal gas $PV = nRT$
 $-P\Delta V = -nRT = w$
 $\rightarrow$ Boltzmann constant = 8.314 J

$\Delta E = \frac{3}{2} nRT = nC_v \Delta T$

"Heat" required = $q_p = nC_p \Delta T$

$H = E + PV$

$\Delta H = \Delta E + P\Delta V$

$\Delta H = Q - P\Delta V + P\Delta V$

$\Delta H = Q$ iff $-P\Delta V = \Delta PV$

$= Q_p$ (Constant pressure)
 $\rightarrow$ constant pressure

$\Delta PV = nR\Delta T$

$\frac{\Delta PV}{nR} = T$

$= (P_2 V_2 - P_1 V_1)$

$q = nC_v \Delta T$
 $\rightarrow$ using C_v or C_p

$q_v = \Delta E \Delta T$
 $\rightarrow$ constant volume

$= nC_v \Delta T$

$q_p = \Delta H \Delta T$
 $\rightarrow$ constant pressure

$= nC_p \Delta T$

$q_p = n(C_v + R) \Delta T$

$q_p = \underbrace{nC_v \Delta T}_{\Delta E} + \underbrace{nR \Delta T}_{P\Delta V = \text{work required}}$

$q_p = \Delta H = nC_p \Delta T \rightarrow$ for an ideal gas regardless of pressure or volume.

for ideal gas $E \propto T$, $H \propto T$ directly on temperature.

$q = nC_v \Delta T$

$\Delta H = nC_p \Delta T$

$\Delta E = nC_v \Delta T$ for ideal gas regardless of constant P or V for temperature change.

9.4

Calorimetry - the science of measuring heat, based on observing temperature the temp. change when a body absorbs or discharges energy as heat.

energy released =
 energy absorbed by soln =

heat capacity = $C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$

Specific heat capacity $\times$

Mass of Solution $\times$
 increase in temperature

$\rightarrow \Delta H = mC_p \Delta T$

Heat lost by

Chemical = heat
 gained by solution

Energy released =
 temp. increase $\times$
 energy required to
 change temperature
 by 1°C

$\rightarrow E = \Delta T C$

$\rightarrow$ amount of substance must be specified

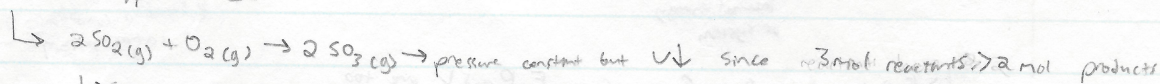
$\rightarrow$ Specific heat capacity $\text{J/K}\cdot\text{g}$ or $\text{J}/^\circ\text{C}\cdot\text{g} \rightarrow$ energy req. to raise temp. of 1g of substance
 $\rightarrow$ Molar heat capacity $\text{J/K}\cdot\text{mol}$ or $\text{J}/^\circ\text{C}\cdot\text{mol}$ by 1°C .

Constant pressure calorimetry - pressure remains constant through process.

$\rightarrow$ So... $\Delta H = q_p$

$\rightarrow$ Since $\Delta V = P\Delta V = 0$ so no work occurs ($w=0$) So... $\Delta E = q_p + w = \Delta H + 0$

$\rightarrow$ So $q_p = \Delta H = \Delta E$



$\rightarrow$ So... $w = -P\Delta V \rightarrow (V_{\text{final}} - V_{\text{initial}})$

work flows into system, $\Delta E = q + w$

$\rightarrow \Delta H = q_p$ at constant P

$\rightarrow \Delta E = q_p + w = \Delta H + w$; if $w \neq 0$ then $\Delta E \neq \Delta H$

$\rightarrow$ Calorimetry can be done at constant volume.

$\rightarrow$ bomb calorimeter $\Delta E = q + w = q = q_v$ (constant volume)

9.5

Hess' law - in going from a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

$\rightarrow$ If a rxn is reversed, sign of ΔH is also reversed, if multiplied by integer n , then $n\Delta H$

$\rightarrow$ Magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction.

If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

9.6

Standard enthalpy of formation ΔH_f° - the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in their standard states.

$\Delta H_{\text{reaction}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$

$\rightarrow$ elements in their standard states have $\Delta H_f^\circ = 0$, they are not included in

$\Delta H_{\text{reaction}}^\circ$ calculations.

$\rightarrow$ gas $\rightarrow P = 1 \text{ atm}$

$\rightarrow$ aq. $\rightarrow 1 \text{ M}, 1 \text{ atm}$

$\rightarrow$ S, L $\rightarrow$ is the pure solid or liquid

$\rightarrow$ element $\rightarrow$ form the element exists in (most stable) at 1 atm and 25°C

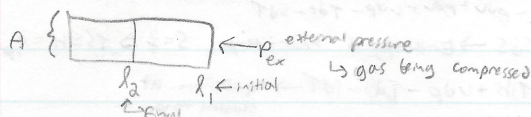
Chapter 10

$\Delta S_{\text{universe}} > 0$ for all spontaneous processes

$$\Delta G_{\text{system}} = -T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

$S = k \ln w \rightarrow$ # of ways system can be arranged

$\rightarrow w=0$ for perfect crystal $\Rightarrow$ must exist in 1 form only. $\Rightarrow$ OK no molecular motion



$$w = -f_{\text{ex}} (\lambda_2 - \lambda_1) A = -p_{\text{ex}} \Delta V$$

$$\Delta E = q - p \Delta V = q + w$$

q_v = heat transferred when v is constant

$q_v = \Delta E$ if v is constant ($v_2 - v_1 = 0$)

$\rightarrow \Delta E = q - 0 \Rightarrow w = 0 \Rightarrow p \Delta V = 0 \Rightarrow \Delta V = 0$

q_p = heat transferred at constant pressure

$$q = \Delta E + w \Rightarrow \Delta E = q + w$$

$$q_p = \Delta E + p \Delta V$$

$$= E_2 + pV_2 - E_1 - pV_1$$

let $H = E + pV$

$\rightarrow$ Enthalpy

$H_2 - H_1 = \Delta H \rightarrow$ enthalpy is heat absorbed by system at constant volume

$$\Delta H = \Delta E + p \Delta V = \Delta E + \Delta nRT \text{ (ideal)}$$

$$q_v = \Delta E = C_v \Delta T$$

$$\frac{\Delta E}{\Delta T} = C_v$$

$$q_p = \Delta H = C_p \Delta T$$

$$\frac{\Delta H}{\Delta T} = C_p$$

$$= \frac{\Delta E}{\Delta T} + \frac{p \Delta V}{\Delta T}$$

thermodynamics Standard conditions $\rightarrow 25^\circ\text{C}$ and 1 atm

bond energy - energy in a bond - C-H bonds have $\sim 400 \text{ kJ/mol}$

3rd law of thermodynamics

For a perfect crystal at 0K , $w=1 \therefore S=0 \rightarrow$ only 1 way atoms can be arranged

$\rightarrow$ establishes a 0 on the Kelvin scale

$S = k \ln w \rightarrow$ microscopic ways of obtaining macroscopically defined state

$\rightarrow$ Boltzmann constant R/N

$\rightarrow$ depends on physical state of matter $\rightarrow S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

$\rightarrow$ Solid dissolved in liquid $\uparrow S$, gas dissolved in liquid $\downarrow S$.

$\rightarrow$ ionizing $\uparrow$
Combinations

$\rightarrow$ bonds btw gas and water restricts molecules.

$\rightarrow \uparrow$ mass, $\uparrow$ complexity $= \uparrow$ entropy

Second law of thermodynamics

Process depends on the balance btw the change in enthalpy and the change in entropy to determine if anything happens $\rightarrow$ for any process that occurs in the universe, it is ΔG that determines if the process can occur spontaneously.

$\rightarrow \Delta H_{\text{sys}} < 0$, then $\Delta H_{\text{surr}} > 0$ so that $\Delta H_{\text{sys}} + \Delta H_{\text{surr}} = 0$

$\rightarrow$ energy cannot be created or destroyed

$\rightarrow$ If $\Delta H_{\text{sys}} < 0$, heat transferred to surroundings and $\Delta S_{\text{surr}} > 0 = -\Delta H_{\text{sys}}/T$

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$$

$\rightarrow$ expressed in system being observed

$$-T\Delta S_{\text{uni}} = -T\Delta S_{\text{sys}} = \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = \Delta G_{\text{sys}}$$

$$\Delta S_{\text{hot object}} = \frac{\Delta H}{T_{\text{hot object}}} \rightarrow \text{hot object loses heat}$$

$$\Delta S_{\text{cold object}} = \frac{\Delta H}{T_{\text{cold object}}} \rightarrow \text{cold object gains heat}$$

Chapter 13.8 $\rightarrow \Delta H = \sum \text{bonds broken} - \sum \text{bonds formed}$

C-H bonds not all same ΔH , we take average. (they change based on environment)

energy req. always the energy released

Spontaneity	$\Delta H < 0$	$\Delta S > 0$	$\Delta G < 0$
1)	-ve	+ve	-ve
2)	-ve	-ve	-ve low temp, +ve at high temp.
3)	+ve	+ve	+ve at low temp, -ve at high temp.
4)	+ve	-ve	+ve

Coulombs law:

$$E \propto \frac{q_1 q_2}{r^2}$$

MgO bond 4x stronger than NaCl bond. $\therefore$ MgO is insoluble in water but NaCl is...

K favors side with lowest G

Reactants $\leftrightarrow$ products

$$\frac{\Delta G^\circ}{RT} = \ln K$$

$= 0 \Rightarrow 1$
 $< 0 \Rightarrow < 1$
 $> 0 \Rightarrow > 1$

$G^\circ_{\text{reactants}} < G^\circ_{\text{products}}$

Since $G^\circ_P - G^\circ_R = +ve$

reaction will shift left b/c reactants have less free energy.

$$q_p = \Delta H$$

$$q_p = T \Delta S$$

S increases through diffusion

$$\Delta S = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

($\times$ of moles)(S°) + ...

$$\Delta S_{T_1 \rightarrow T_2} = n C \ln \left(\frac{T_2}{T_1} \right)$$

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H^\circ}{R(T_2 - T_1)}$$

S dependent on positional probability

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

boiling points $\Delta G = 0$

Solubility

$\rightarrow$ NaCl is soluble in H₂O at 25°C

$\rightarrow$ ionic bonds break - require energy
 $\rightarrow$ H-bonds break - require energy
 $\rightarrow$ make ion-dipole attractions - exothermic

$\Delta H > 0 \Rightarrow$ entropy must drive this reaction, $\Delta S > 0$
 bond breaking always endothermic
 bond making always exothermic

$\Delta H_{\text{sys}} + \Delta H_{\text{surr}} = 0 \rightarrow$ 1st law of thermodynamics
 $\Delta H_{\text{sys}} < 0 \Rightarrow \Delta H_{\text{surr}} > 0 \rightarrow$ heat transferred from system to surroundings

$$\Delta S_{\text{surr}} > 0 = -\Delta H_{\text{sys}} / T$$

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{uni}} = \frac{-\Delta H_{\text{sys}}}{T} + \Delta S_{\text{sys}}$$

$$T \Delta S_{\text{uni}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}$$

all determined by system being observed.

$$-T \Delta S_{\text{uni}} = -T \Delta S + \Delta H_{\text{sys}} = \Delta G_{\text{sys}}$$

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S \rightarrow \text{Constant temperature.}$$

ATP $\rightarrow$ enthalpy of P-O bond is regular but entropy is high, which is why there's high K value (rxn proceeds to the right spontaneously), despite bond breaking being endothermic process.

assume ΔH° and ΔS° are constant so ΔS° term subtracted.

+ve exothermic
 -ve endothermic

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

$\uparrow$ with respect to surroundings
 $\downarrow$ with respect to system

Von Hoff equation derivation $\rightarrow$ relating free energy changes to equilibrium constant...

$$G = H - TS \quad H = E + PV \rightarrow \Delta E = q_p + w \Rightarrow q_p = \Delta E - w \Rightarrow q_p = \Delta E + P \Delta V = H$$

Free energy $\leftarrow$ Entropy $\rightarrow$ equation is in terms of system observed.

$$G = E + PV - TS \rightarrow \text{everything } (\Delta = \text{change of infinitesimal size}) \rightarrow \Delta G = \Delta E + P \Delta V + V \Delta P - T \Delta S - S \Delta T$$

1st law of thermodynamics $= \Delta E = dq + dw = dq - P \Delta V$

$$\Delta G = dq - P \Delta V + P \Delta V + V \Delta P - T \Delta S - S \Delta T$$

$$dq = T \Delta S \rightarrow \text{Entropy is heat} \div \text{temp. } S = \frac{H}{T} \Rightarrow TS = H = q_p$$

$$\Delta G = T \Delta S + V \Delta P - T \Delta S - S \Delta T \rightarrow \text{equilibrium at standard temp.}$$

$$\Delta G = V \Delta P = RT \Delta P$$

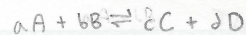
For ideal gas and $n=1$

$$\text{Integrate eqn} = RT \ln \frac{P}{P^\circ} = RT \ln P \text{ since } P^\circ = 1 \text{ atm}$$

$$G = G^\circ + RT \ln P \text{ and for } n \text{ mol}$$

$$nG = nG^\circ + nRT \ln P$$

Free energy in standard state $\leftarrow$ correction factor since temp might not be in standard state.



$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

$$= cG(C) + dG(D) - aG(A) - bG(B)$$

$$= cG^\circ(C) + cRT \ln P_C + dG^\circ(D) + dRT \ln P_D - aG^\circ(A) - aRT \ln P_A - bG^\circ(B) - bRT \ln P_B$$

$$= \Delta G^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Standard conditions (Exptl)

$$Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

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

at equilibrium $Q = K$ and $\Delta G = 0$

$\rightarrow$ At equilibrium, products and reactants have equal ability to do work, so no net work can be done.

$$\Delta G = 0 = \Delta G^\circ + RT \ln K$$

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

$\Delta G^\circ < 0$ rxn to right spontaneous, $K > 1$
 $\Delta G^\circ = 0$ equilibrium, $K = 1$
 $\Delta G^\circ > 0$ rxn to left spontaneous, $K < 1$

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

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

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

$$\Delta H^\circ - T \Delta S^\circ = -RT \ln K$$

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Von Hoff equation

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

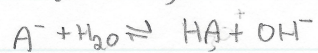
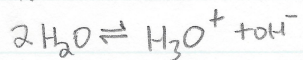
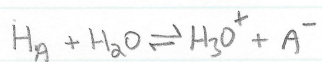
$$\Delta G^\circ = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = -RT \ln \left(\frac{P_2}{P_1} \right)$$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_2}{P_1} \right)$$

$\Delta S_{\text{surr}} \rightarrow$ sign depends on direction of heat flow
 $\rightarrow$ Exothermic rxns $\uparrow \Delta S_{\text{surr}}$ most important as a driving force at low temp.
 $\rightarrow$ rxns try to achieve lowest possible energy by transferring heat to surroundings. Reach equilibrium when $\Delta G = 0 \rightarrow$ lowest possible free energy.
 $\rightarrow$ magnitude depends on T.
 $\rightarrow$ heat transferred $\uparrow \Delta S$ more in low temperatures than high temperatures.

at equivalence point $C_a V_a = C_b V_b$



5 species $HA, A^-, H_3O^+, OH^-, Na^+$

$$1) K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$[A^-] + [OH^-] = [Na^+][H_3O^+]$$

$$C_b = Na^+$$

$$C_a = [HA] + [A^-]$$

$$K_w = [H_3O^+][OH^-]$$

$$K_a = \frac{[H_3O^+](C_b + [H_3O^+] - \frac{K_w}{[H_3O^+]})}{C_a - (C_b + [H_3O^+] + \frac{K_w}{[H_3O^+]})}$$

at equivalence point assume

$$[OH^-] \gg [H_3O^+]$$

$$[HA] \gg [A^-]$$

$$C_a V_a = C_b V_b \quad (\text{at 75\% point})$$

$$C_a \left(\frac{C_a}{\left(\frac{75}{100} \right)} \right) = C_b V_b$$

$$K_a = \frac{[OH^-]^2}{C_b - [OH^-]} = \frac{K_w}{K_a}$$