

# Chemistry Guide 2005

By Yaniv

## 5. GASES

$$1 \text{ torr} = 1 \text{ mm Hg}$$

$$1 \text{ atm} = 760 \text{ torr}$$

$$1 \text{ Pa} = 1 \text{ N} / \text{m}^2$$

// rarely used in USA

Ideal Gas Law:  $PV = nRT$   
in K}

{n = mols of gas; R = gas const. = 0.08206 L atm / K mol; T = temp.

STP: standard T and P: 273K, 1atm

- at STP, 1mol (g) = 22.42 L

$$n = \text{grams (g)} / \text{MW}$$

$$PV = nRT$$

$$PV = mRT / \text{MW}$$

{m = mass}

$$P = mRT / \text{MW} V$$

// since  $m/V = \text{density} \dots$

$$P = dRT / \text{MW}$$

{d = density}

Dalton's Law of Partial Pressures:

$$P_T = P_A + P_B + P_C$$

{ $P_T$  = total P;  $P_A$  = pressure due to gas A; etc.}

$$P_A = n_A RT / V; P_B = n_B RT / V; \text{ etc}$$

(n) Discussion on models is found on p. 175, the first half of the page

(n) Discussion on deriving the Ideal Gas Law is found on p. 175-6, bottom of page to most of the next

$$PV / n = (2/3) (KE)_{\text{AVG}} = RT$$

{ $(KE)_{\text{AVG}}$  = average Kinetic Energy}

// at ideal conditions we use R

$$(KE)_{\text{AVG}} = 3 RT / 2$$

// from the above, we derive this expression

$$(KE)_{\text{AVG}} = N_A (\overline{u^2})$$

{ $\overline{u^2}$  = average of the square of the velocities of the particles;  $N_A$  = Avogadro's #}

$$(KE)_{\text{AVG}} = 3 RT / 2$$

$$N_A (\overline{u^2}) = 3 RT / 2$$

$$\overline{u^2} = 3 RT / N_A m$$

$$\text{SQRT}(\overline{u^2}) = \text{SQRT}(3 RT / N_A m)$$

$$u_{\text{rms}} = \text{SQRT}(3 RT / N_A m) \quad \{u_{\text{rms}} = \text{root mean square velocity} = \text{SQRT}(\overline{u^2})\}$$

(d) Diffusion – describes the mixing of gases

(d) Effusion – describes the passage of a gas through a tiny orifice into an evacuated chamber

// Rates of effusion are inversely proportional to the mass of the particle

$$u_{\text{rms}}(1) = \frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\text{SQRT}(M_2)}{\text{SQRT}(M_1)} \quad \{M = \text{atomic or molecular weights of the gases}\}$$

$$u_{\text{rms}}(2) = \frac{\text{Rate of effusion for gas 2}}{\text{Rate of effusion for gas 1}} = \frac{\text{SQRT}(M_1)}{\text{SQRT}(M_2)}$$

// Distance traveled by a gas is also inversely proportional to the mass of the particle

$$u_{\text{rms}}(1) = \frac{\text{Distance traveled by gas 1}}{\text{Distance traveled by gas 2}} = \frac{\text{SQRT}(M_2)}{\text{SQRT}(M_1)}$$

$$u_{\text{rms}}(2) = \frac{\text{Distance traveled by gas 2}}{\text{Distance traveled by gas 1}} = \frac{\text{SQRT}(M_1)}{\text{SQRT}(M_2)}$$

// Johannes van der Waals developed an equation for real gases

$$V_{\text{obs}} = V - nb$$

{ $V_{\text{obs}}$  = observed V; b = empirical const.}

// the V takes into account the V of the gas

$P_{\text{obs}} = P$  – correction factor  
reduces the P

// the P takes into account the attractions between the particles that

$$P_{\text{obs}} = P - a(n/V)^2$$

{a = proportionality const.}

$$P_{\text{obs}} = nRT / (V - nb) - a(n/V)^2 \quad \text{// this rearranges to give the van der Waals equation}$$

$$[P_{\text{obs}} + a(n/V)^2](V - nb) = nRT \quad \text{// } P_{\text{obs}} \text{ is actually simply } P$$

(n) the values for a and b are found on p. 184, Table 5.3

\* 5.9

## 6. THERMOCHEMISTRY

First Law of Thermodynamics: “the energy of the universe is constant.”

(d) Potential Energy: energy due to position or composition.

(d) Kinetic Energy: energy due to the motion of the object that depends on its mass and velocity

(d) Work: force over a distance

(n) Heat involves a transfer of energy between objects of different temperatures

Energy is pathway independent (state function) since the same amount of potential energy will be lost despite the path or outcome while different amounts of heat and work can result from an amount of energy so these are pathway dependent (non-state functions)

(e) A ball rolling down a hill can roll down one side with a rough surface causing more energy to become heat and slowing the motion and preventing it from hitting another ball up a shorter hill.

- The second side can be smoother and would allow the first ball to achieve the necessary speed to hit the next one up the shorter hill.
- In both cases, the same amount of potential energy was lost since the ball moved position and ended in the same place, but different amounts of work and heat were produced from the different paths, so both work and heat are path dependent.

(d) System: the part of the universe on which we wish to focus our attention

(d) Surroundings: everything else in the universe

(d) Exothermic: energy flows out of the system and into the surroundings (energy is a product)

(d) Endothermic: energy flows into the system and out of the surroundings (energy is a reactant)

Exothermic reactions derive the energy from the difference in PE (potential energy) between the reactants and products.

$$\Delta E = q + w \quad \{\Delta E = \text{change in PE of the system; } q = \text{heat; } w = \text{work}\}$$

// Energy, heat, and work are measured in Joules     $\{1\text{J} = 1\text{kg m}^2/\text{s}^2\}$

$\Delta E > 0$ , rx is endothermic

$\Delta E < 0$ , rx is exothermic

$$w = F d \quad \{d = \text{distance}\}$$

// work is defined as force over a distance

$$P = F / A \quad \{F = \text{force; } A = \text{area}\}$$

// Pressure is defined as force over an area

$$P\Delta V = F V / A \quad // V \text{ is } d \text{ raised to the third and } A \text{ is } d \text{ raised to the second}$$

$$P\Delta V = F d^3 / d^2 \quad // d^3 / d^2 \text{ cancel out}$$

$$P\Delta V = F d = w \quad // P\Delta V \text{ has the same formula as work and therefore change in volume is work}$$

$$w = -P\Delta V \quad // \text{negative is included to keep with the sign convention}$$

(d) Enthalpy: see p. 203 bottom through p. 204

$$\Delta H = q \quad \{H = \text{enthalpy}\}$$

// at constant pressure this is true as proven on the above mentioned pages

“At const. P, the  $\Delta H$  of the system is equal to the energy flow as heat”

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad // \text{if } \Delta H < 0, \text{ then exothermic}$$

// if  $\Delta H > 0$ , then endothermic

$$C = q / m \Delta T \quad \{C = \text{heat capacity; } m = \text{mass}\}$$

(d) Heat Capacity: a measure of a substance’s ability to absorb energy

$$\Delta H / \text{mol} = C m \Delta T / \text{mol} \quad // \text{used in a coffee cup calorimeter to determine energy released as heat}$$

// answers are usually given per mol of substance

// Const. V Calorimetry (bomb calorimeter)

$$\Delta E = q + w$$

$$\Delta E = q + P\Delta V, \Delta V = 0$$

$$\Delta E = q \quad // \text{ since the container is rigid and no work is done, energy is released only as heat}$$

$$q / \text{ mol} = \Delta T C / \text{ mol} \quad \{q = \text{heat evolved; } C = \text{heat capacity of calorimeter}\}$$

// answers are usually given per mol of substance

### Hess's Law

- Since all individuals of a compound have the same H despite how they were formed, H is a state function.
- Because this is true, one can add and subtract H's along with their reaction formulas to derive the  $\Delta H$  of a particular reaction. (see p. 209 for better description)
- Rules for using Hess's Law:
  - If a reaction is reversed (as in to cancel out a reactant with a product), the sign of the  $\Delta H$  is reversed.
  - If a reaction is multiplied by a coefficient, the  $\Delta H$  is also multiplied by the coefficient.

\*Standard Enthalpies of Formation

## 7. ATOMIC STRUCTURE AND PERIODICITY

Properties of an Electromagnetic Wave:

Frequency – number of wave cycles per second

Wavelength – distance between two consecutive crests or troughs of a wave

$$\lambda \nu = c \quad \{\lambda (\text{lambda}) = \text{wavelength in m; } \nu (\text{nu}) = \text{frequency in cycles per s; } c = 3.0 \cdot 10^8 = \text{light speed}\}$$

// in the SI system, frequency is measured in Hertz (Hz) which equals 1/s

German physicist Max Planck noticed that energy is quantized (it is absorbed or emitted in multiples of a specific qty)

$\Delta E$  can now be determined by:

$$\Delta E = nh\nu \quad \{n = \text{an integer; } h = \text{Plank's const} = 6.626 \cdot 10^{-34} \text{ Js}\}$$

Albert Einstein later discovered the particle description of energy (photon), which held a quantized amount of energy

$$E_{\text{photon}} = h\nu = hc / \lambda$$

French physicist Broglie questioned if mass has wavelike properties (since light was discovered to have particulate properties), and the following expression resulted:

$$m = h / \lambda \nu \quad \{\nu = \text{velocity of particle}\} \quad // \nu \text{ is not } \nu$$

$$\lambda = h / m\nu \quad // \text{ used to calculate wavelength for a particle}$$

White light emits a continuous spectrum of all the colors, which comprise it.

When white light is emitted through H gas, only specific wavelengths pass through.

This indicates that, "only certain energies are allowed for the electron in the hydrogen atom," since the energy of the electron in the atom is quantized.

With the discovery of quantized electron energy, Neils Bohr developed the Bohr model that depicts the atom with the nucleus in the center and electrons revolving around it.

// This model is clearly inaccurate since a charged particle under acceleration should radiate energy, so if true, the electron would spend its energy and fall into the nucleus.

// The most important expression to come from the Bohr model is for the energy levels available to the electron in the hydrogen atom:

$$E = - (2\pi^2 m e^4 / h^2) (Z^2 / n^2) \quad \{m = \text{mass of } (-e); Z = \text{nuclear charge; } n = (-e) \text{ orbital \#}\}$$

$$E = -2.178 \cdot 10^{-18} \text{ J } (Z^2 / n^2) \quad // \text{ since this equation is only accurate with Hydrogen, it can be simplified}$$

$E = -2.178 \times 10^{-18} \text{ J } (Z^2 / \infty) = 0$  // the negative accounts for the fact that a liberated (-e) has more energy than one still in the atom

$\Delta E = E \text{ of final state} - E \text{ of original state}$  // used to calculate  $\Delta E$  when an (-e) changes energy level

$\Delta E = h (c/\lambda)$

$\lambda = hc / \Delta E$  // used to calculate the  $\lambda$  of the emitted or absorbed photon  
(n) the absolute value of  $\Delta E$  is used to keep the wavelength value positive as well

After the Bohr model proved unworkable for neither real mapping of the atom nor calculations in atoms other than H, efforts were made to describe the electrons as standing waves. The result concluded that one cannot know where an atom is positioned. From this, Werner Heisenberg developed his uncertainty principle:

$\Delta x \Delta(mv) \geq h/4\pi$  { $\Delta x$  = uncertainty in a particle's position;  $\Delta(mv)$  = uncertainty in a particle's momentum}

Since the uncertainty principle stresses that one can not know the precise position of a particle, this then leads to the probability distribution of electrons around an atom. One can simply know the likelihood of finding an electron at a point compared to that of another point.

### Quantum Numbers:

Principal quantum number (n)

- can have values of any integer greater than 0
- as n increases, the orbital becomes larger and (-e)'s spend more time further from the nucleus
- as n increases, the energy is less negative and the (-e) is less tightly bound to the nucleus

Azimuthal quantum number (l)

- Can have integral values from 0 to n-1 for each value of n
- Relates to the shape of the atomic orbital (s, l = 0; p, l = 1; ...)
- Sometimes called a subshell (number of subshells is the number of l's possible)

Magnetic quantum number (ml)

- Can have integral values between l and -l including zero
- Relates to the orientation of the orbital in space relative to the other orbitals in the atom

see pages 256 and 257 for orbital shapes

For the H atom, the energy of an orbital is determined by n, so all orbitals with the same value of n have the same energy and are referred to as degenerate. At its most stable state, the electron in H remains in the 1s orbital, but energy can excite the atom and raise the electron to a higher state. The size of an orbital is arbitrarily defined as the volume that contains 90% of the total (-e) probability.

The Pauli exclusion principle provides for the Electron spin quantum number ( $m_s$ ) that can only have two values (+1/2 and -1/2). The principle states that no two electrons can have the same quantum numbers and the final values provide a distinction between the last pair.

The two electrons sharing a shell spin in opposite directions in order to have opposite magnetic field orientation and to help them overcome the (-e)/(-e) repulsion.

See pages 261 – 2 for a history of the periodic table

Look through pages 263 – 270 for The Aufbau Principle and the Periodic Table (recommended)

$Z_{\text{eff}}$  is determined experimentally by solving the following equation for Z:

$$E = -(Z_{\text{eff}}^2 / n^2)(1312 \text{ kJ / mol}) \quad \{E = \text{energy of ionization}\}$$

If asked to explain why some electrons are ionized with less energy, note the (-e) configuration and look for (-e)/(-e) repulsion and/or shielding / penetration (occurs to electrons further from the nucleus that are shielded from the

(+) charge of the nucleus). The electrons with higher n values experience most shielding or least penetration of (+) charge.

Electrons in the same type of orbital are not very effective at shielding each other, however they do shield electrons in outer shells.

Ionization energy is the energy needed to liberate the highest energy (-e) from an atom. One will notice a considerable rise in ionization energy for a second electron in a shell is removed since it no longer experiences the (-e) / (-e) repulsion.

The trend for ionization energy is an increase across the periodic table and a decrease in descending the table. This is because as more shells are added, the outer shells are more shielded but not enough to overcome the added proton, and as a new energy levels begin in going down the table, the added electrons are well shielded from the nuclear charge.

The trend for radius is a decrease across the table and an increase in descending the table. This is understandable since the greater outer electrons in an atom to the right of the table creates a smaller atom as the electrons are held tighter to the nucleus, but as a new level is filled, the electrons are shielded enough to overcome the nuclear charge

\*\* Alkali metals\*\*

## 8. BONDING – GENERAL CONCEPTS

Coulomb's Law:

$$E = 2.31 \cdot 10^4 \text{ J nm } (Q_1 Q_2 / r) \quad \left\{ \begin{array}{l} Q_1 \text{ \& } Q_2 = \text{numerical charges; } r = \text{distance between nuclei} \\ // \text{ if charges are opposite, then } (Q_1 \cdot Q_2) = -1 \text{ since atoms are more stable} \\ // \text{ if charges are same, then } (Q_1 \cdot Q_2) = +1 \text{ since atoms are less stable} \end{array} \right.$$

(n) bonds are formed if it lowers the energy of the particles and makes them more stable // in other words, if

the rx is

exotherm.

(d) Covalent bond: bond in which the electrons are shared between atoms.

(d) Polar covalent bond: covalent bond in which the electrons are not shared equally creating polarity within the (m).

The polarity of a (m) is usually determined by the method developed by Linus Pauling. In a hypothetical (m) HX, the electro negativity is calculated by finding the difference between the hypothetical (determined by the average of the H-H bond and the X-X bond) and actual bond energy. The formula is as follows:

$$\Delta = (\text{H-X actual energy}) - (\text{H-H energy} + \text{X-X energy}) / 2$$

If the change is near 0, then there is little polarity; otherwise the more electronegative (a) gets the (-) charge. One can identify the electro(-) (a) by the periodic table trends (see ch.7)

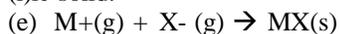
(d) Ionic bond: electrons are passed between atoms and the charges hold them together.

In an (i)ic bond, the atoms try to fill their valence shell of electrons, and they do so by receiving the appropriate number of electrons from another atom which needs to give the same amount to empty the valence shell so that the outermost shell is filled.

(e) Na gives an (-e) to Cl so that both Cl's and Na's shell has 8 (-e)s. Na<sup>+</sup> attracts Cl<sup>-</sup> and the (m) exhibits polarity.  
 $\text{Na} + \text{Cl} \rightarrow \text{NaCl} \quad \text{Na} \rightarrow \text{Na}^+ + e^-$

Ions also have different sizes than their parent atom. (-)(i)s are larger due to the added shell and repulsion within the shells. (+)(i)s are smaller since the nucleus holds the smaller # of (-e)s more tightly.

(d) Lattice energy: the change in energy that takes place when separated gaseous (i)s are packed together to form an (i)ic solid.



See page 308 for an example problem (highly recommended)

Lattice  $E = k (Q_1 Q_2 / r)$  { $k =$  proportionality const.} // Lattice  $E$  can also be represented by Coulomb's Law

See page 310-11 (first half) to understand the significance of charge in representing lattice  $E$  from the above equation (optional).

Since there is no solid difference between (i)ic and polar covalent bonds (electrons are shared to an extent even in (i) bonds), there is only percent (i)ic character which is calculated as follows:

% (i)ic character of a bond = (measured dipole moment of X-Y / calc. Dipole moment of X+Y-) \*100

(n) any compound that will conduct an electric current when dissolved in water can be considered (i)ic.

Bond Energy Notes:

- Double and triple bonds hold atoms closer together
- Some bond energies are somewhat sensitive to the environment so the energies differ from (m) to (m).

Bond energies can be used to estimate the energy changes of reactions. The energy of making new bonds is subtracted from the energy released in breaking old bonds to give the change in energy.

$\Delta H = \sum D$  (bonds broken) -  $\sum D$  (bonds formed) { $D =$  bond energy / mol of bonds (is always positive)}

Although the molecular orbital (MO) model is the more accurate, it becomes too complicated when dealing with complex (m)s, so we will use the localized electron (LE) model. This model assumes that, "a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms." The MO model provides many more quantitative values unlike the LE model.

Lewis Structures:

To create a Lewis structure, find the valence electrons of each atom by the (-e) configuration and organize the atoms with bonding pairs and lone pairs of electrons so that the following rules are met and the amount of valence electrons is maintained.

Duet Rule - a complete shell for first row elements have 2 (-e)s.

Octet Rule - a complete shell for all other elements have 8 (-e)s.

Exceptions to the octet rule occur in Period 3 and beyond where more than 8 (-e)s can exist in the valence shell. If one cannot determine which element deserves the extra electrons, they should be placed on the middle (a).

A molecule exhibits resonance if there are multiple ways to position electrons. Place all structures alongside one another and place double arrows pointing to each other. This does not necessarily mean that in actuality, there are multiple ways the atom can exist since in reality, electrons are not localized, so the double bond would in stead exist partially in every bond. (p. 329 has illustrations for resonance).

## 9. COVALENT BONDING: ORBITALS

## 10. LIQUIDS AND SOLIDS

Forces in (s)s and (l)s.

(d) Dipole-Dipole Forces: Intermolecular bond caused by attractions between polar (m)s. Only 1% as strong as covalent or (i)ic bonds.

(d) Hydrogen Bonds: a type of dipole-dipole bond caused by H atoms. It is several times as strong as other dipole bonds.

(d) London Dispersion Forces: Intermolecular bond caused by an instantaneous dipole in one (m) which then polarizes nearby (m)s. It is much weaker than any other bond.

Liquids

(d) Surface tension: "the resistance of a liquid to an increase in its surface area."

This is increased in molecules with strong inter(m) bonds.

(d) Capillary action: "the spontaneous rising of a liquid in a narrow tube."

(d) Adhesive forces: “the forces between the liquid (m)s and their container.”

(d) Cohesive forces: “the forces between the liquid (m)s.”

Adhesive and cohesive forces can cause liquid (m)s to pull each other up a narrow tube.

(d) Viscosity: “the measure of a liquid’s resistance to flow.”

Liquids with large molecular forces such as H bonding and liquids of complex molecules that can become entangled among each other have a high viscosity.

### Structures and Types of Solids

2 categories:

(d) Crystalline: those with a highly regular arrangement of their components.

(d) Amorphous: those with considerable disorder in their structure.

“The positions of the components in a crystalline solid are usually represented by a lattice made up by repeating unit cells.” (see p. 391 for images of lattices and units)

### **\*\*Bragg Equation\*\***

Solids are also divided into (i) ionic solids and molecular solids. Ionic solids are those which dissolve in water as (i)s and conduct electricity. Molecular solids dissolve as neutral (m)s and do not conduct electricity. A third type is an atomic solid in which the solid is made up of atoms of one element covalently bonded to one another (e.g. graphite and diamond).

### Metals

“Metals are characterized by high thermal and electrical conductivity, malleability, and ductility.”

The structure of a metal solid follows the closest packing model (see p.395 for picture)

### **\*\*Density\*\***

The electron sea model in which the atoms and electrons are tightly bound by the bond but can move within the solid best explains the properties of a metal, so if a metal is hit with a hammer, it bends instead of breaking.

## **11. PROPERTIES OF SOLUTIONS**

### **12. CHEMICAL KINETICS**

(d) Reaction Rate: “the change in concentration of a reactant or product per unit of time.”

Rate =  $\Delta[A] / \Delta t$       {[A] = concentration of reactant or product; t = time}

// If the [ ] is of a reactant, then the [ ] decreases so a (-) is placed in front of the equation

to

keep it positive.

Since the rate of the reaction is not constant (it changes as the [ ]s change), the data provided by the above formula is not an accurate way to determine the initial rate. It is impossible to find the slope of the reaction exactly at 0s with this formula because the  $\Delta t$  would be 0, an impossible mathematical operation.

(n) In our studies, we are only to deal with initial rates, so the rate is only dependant on the [ ]s of the reactants.

To find the initial rate, we use the rate law which calculates the rate based on the [ ] of reactants.

Rate =  $k[A]^n$       {k = rate const.; A = reactant; n = order of the reactant (can be (+) or (-) integer or fraction}

// n must be determined by experiment. The coefficient from the balanced equation is not n.

(n) In our studies, the order will generally be (+) integers.

To determine the order of a reaction by experiment, the initial [ ]s are charted along with the initial rates. The order is found by comparing the effect of the concentration of a reactant on the rate. If a double in the [ ] doubles the rate, it is first order. If a double in the [ ] quadruples the rate it is second order (since  $2^2$  is 4). The order is the exponent on the number which multiplies the [ ] that multiplies the rate

### The First Order Rate Laws:

For a general reaction involving one reactant,  $A \rightarrow$  products which is first order in A, the rate law is:

$$\ln[A] = -kt + \ln[A]_0 \quad // \text{ This rate law is only for first order reactions and is of the form } y = mx + b.$$

is  
always a straight line

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \quad // \text{ The integrated rate law can also be expressed in this equation.}$$

$$\ln \left( \frac{2[A]}{[A]_0} \right) = kt_{1/2} \quad // \text{ The half-life of a first order reaction can be determined by the integrated rate law by}$$
$$\ln(2) = kt_{1/2} \quad \text{solving for time when the initial concentration is substituted by 2 times the current [ ].}$$
$$t_{1/2} = \ln(2) / k$$

### The Second Order Rate Laws:

For a general reaction involving one reactant,  $A \rightarrow$  products which is second order in A, the rate law is:

$$\text{Rate} = k[A]^2$$

$$1/[A] = kt + (1/[A]_0) \quad // \text{ This is the integrated rate law for a second order rx in } y = mx + b \text{ form.}$$

// To test for a second order rx, we plot  $1/[A]$  against  $t$  and the slope will be  $k$  throughout.

$$2/[A]_0 = kt_{1/2} + 1/[A]_0 \quad // \text{ The half-life can be calculated by substituting } [A] = [A]_0 / 2$$

$$(2/[A]_0) - (1/[A]_0) = kt_{1/2}$$

$$1/[A]_0 = kt_{1/2}$$

$$t_{1/2} = 1/(k [A]_0)$$

### Zero Order Rate Laws:

In a zero order reaction, the rate is constant and does not depend on the [ ]s of reactants.

$$\text{Rate} = k[A]^0 = k \quad // \text{ The concentration to the 0 power is 1, so it does not affect the rate.}$$

$$[A] = -kt + [A]_0 \quad // \text{ This is the integrated rate law for zero order reactions in } y = mx + b \text{ form.}$$

// To test for 0 order reactions, we plot  $[A]$  against  $t$  and the slope will be  $-k$  throughout.

Zero order reactions usually occur “when a substance such as a metal surface or an enzyme is required for the reaction to occur.” In both of these cases a constant factor controls the rate (either the surface area of the metal or the [ ] of enzyme).

Reactions with more than one reactant require plotting values on a graph to determine the order.

If it is 0 order  $[A]$  plotted against time will be linear.

If it is 1<sup>st</sup> order,  $\ln[A]$  plotted against time will be linear.

If it is 2<sup>nd</sup> order,  $1/[A]$  against time will be linear.

In many reactions, the reactants and products do not precisely describe the mechanism of the reaction.

(d) Intermediate: a species that is created and then used by a reaction sequence

(d) Elementary step: a reaction whose rate law can be written from its balanced equation because it accurately describes the mechanism of the reaction (often several elementary steps make up a reaction sequence).

(d) Unimolecular step: a reaction with only one reactant

(d) Bimolecular step: a reaction with two colliding molecules

(d) Termolecular step: a reaction with the collision of three molecules (very rare and very slow)

Requirements for a reaction sequence are:

1. “The sum of the elementary steps must give the overall balanced equation for the reaction.”
2. “The mechanism must agree with the experimentally determined rate law.”

(d) Rate-determining step: the rate of a reaction is dependent on the rate of the slowest step – the rate-determining step.

It is from this step that the rate law can be determined from the balanced equation, but this is unrealistic since the rate law is necessary for proposing a mechanism. The determination of a mechanism from the rate law is very

difficult and requires more skill and experience than is expected from us. We will mostly be expected to determine if a proposed mechanism is acceptable (not necessarily correct since “a mechanism can never be proved absolutely”).

If the rate-determining step is not the first step, there is a chance it contains an intermediate. In order to remove it, one must substitute it with another value as follows:

Find the step where the intermediate is created. Set the rate laws for the forward and reverse reactions of that step equal to each other (the rates are equal), and solve for the [ ] of the intermediate. Use this value to replace the intermediate in the rate law and the ks (constants) cancel out to form a new rate constant (a constant divided or multiplied by other constants is still constant since none of the values that make it up ever change).

The collision model, which follows the idea that, “molecules must collide to react,” is true and has been proven so. But when calculated, the number of collisions is much greater than the rate of the reaction. Svante Arrhenius who proposed the existence of activation energy that, “must be overcome to produce a chemical reaction” first addressed this. This is explained by the need of energy to break old bonds before they can be rearranged to new molecules (or simply left as free-standing atoms).  
(diagram for activation energy is located on p. 499)

Total # of collisions with necessary  $E_a$   
= (Total # of collisions)  $e^{-(E_a / RT)}$  {e = fraction of particles with necessary  $E_a$ }

Even the  $E_a$  does not account for all the unsuccessful collisions because in many collisions, the molecules are not properly oriented to react (See images on p. 501).

// We can now represent k as follows.

$k = zpe^{-(E_a / RT)}$  {z = collision freq.; p = steric factor (always <1) = ratio of collisions w/ proper orientation}

$k = Ae^{-(E_a / RT)}$  {A = freq. factor = zp} // The above expression then becomes the Arrhenius equation.

// most rate const.s have been proven to follow this equation.

$\ln(k) = -(E_a/R)(1/T) + \ln(A)$  // taking the natural log of each sides gives this  $y = mx + b$  form equation, and from

this we can approximate the  $E_a$  and A of a rx by plotting  $\ln(k)$  against  $1/T$ .

// This equation can then derive another to calculate  $E_a$  by using two experimentally obtained rate constants of the same rx at two different Ts. (One can find the method for deriving this on page 503 – recommended.)

$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$

(d) Catalyst: “a substance that speeds up a reaction without being consumed.”

A catalyst changes the mechanism of the rx thereby lowering the  $E_a$ .

(d) Homogeneous catalyst: “is present in the same phase [(g), (l), (s)] as the reacting molecules.”

(d) Heterogeneous catalyst: exists in a different phase than that of the reacting (m)s.

(d) Adsorption: the collection of one substance on the surface of another.

An example of a heterogeneous catalyst is a metal surface used for hydrogenation (see p. 506).

(n) A catalyst can react in the reaction but the reaction must produce the chemical again by the end of the rx in the same numbers as it was consumed in.

### 13. CHEMICAL EQUILIBRIUM

As explained in the previous chapter, rate of rx usually changes due to the [ ] of the reactants. At some point during the rx, the rates are equal and therefore result in no net change (see graphs on page 522-3).

Based on observations of many chemical reactions, Norwegian chemists, Guldberg and Waage proposed the *law of mass action*. This stated that for a reaction of formula  $jA + kB \leftrightarrow lC + mD$  the equilibrium expression is as follows:

$K = ([C]^l[D]^m) / ([A]^j[B]^k)$  {A-D = chemical species; j-m = coefficients; K = equilibrium const.}

If the reactants are gases, then  $K_p$  replaces  $K$  (or  $K_c$ ). The new equilibrium constant follows the same formula as the one above with the replacement of  $[ ]$  by partial pressures.

\*\*Concentrations for gases

(d) Heterogeneous Equilibria: Equilibrium reactions which contain species of more than one phase ((g), (l), (s)). In reactions in which certain products or reactants are solids or liquids, they are raised to the power of 0 because they do not affect the equilibrium.

(n) If  $K > 1$ , then in the end, there is more product than reactant (the rx lies to the right). If  $K < 1$ , then in the end there is more reactant than product (the rx lies to the left).

$$Q = \frac{[C]^n[D]^m}{[A]^j[B]^k} \quad \{Q = \text{rx quotient (usually used for initial [ ]s or Ps)}\}$$

The rx quotient is useful in determining if an rx will shift left or right from its initial  $[ ]$ s.

If  $Q < K$  then the rx will shift to the right.

If  $Q > K$  then the rx will shift to the left.

After finding  $Q$ , it is not recommended to go towards equilibrium from the middle of the rx. Instead one should run the problem to the stoichiometric finish or beginning and then proceed to find an unknown  $[ ]$ .

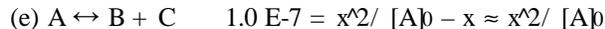
To find the equilibrium concentrations of the species in a rx (from a stoichiometric beginning or finish), identify the rx by writing the formula and then write equilibrium expression. Substitute the equilibrium  $[ ]$ s with the initial  $[ ]$  and a change factor of  $x$  which adds to the  $[ ]$  of the products and subtracts from the reactants.

(n) Do not forget to multiply the change factor by the appropriate coefficient of the species it modifies.



One must then solve for  $x$  and from  $x$  attain the necessary  $[ ]$ s.

It becomes difficult to find equilibrium  $[ ]$ s when the equation is quadratic, but if the  $K$  is small enough (less than  $10^{-5}$  is usually considered small), then one may ignore the effect of  $x$  in adding or subtracting because it is too insignificant.



$$x = (1.0 \times 10^{-7} * [A]_0)^{1/2}$$

#### Le Chatelier's Principle:

"If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change."

- If more of one species of the reaction is added, then the equilibrium will shift to the side opposite of that particular species. (e)  $A \leftrightarrow B$  adding more of  $B$  will shift the equilibrium to the left

- If the pressure is increased, then the equilibrium will shift to the side with fewer moles of gas.

(e)  $A(g) \leftrightarrow 2B(g)$  increasing  $P$  will shift the equilibrium to the left

- If the  $T$  is increased, then the equilibrium will shift away from the side where heat is a reactant. If  $T$  is decreased, then the equilibrium will shift towards the side where heat is a reactant. (e)  $A \leftrightarrow B + \text{heat}$  increasing temperature will shift the equilibrium to the left.

## 14. ACIDS AND BASES

## 15. APPLICATIONS OF AQUEOUS EQUILIBRIA

## 16. SPONTANEITY, ENTROPY, AND FREE ENERGY

(d) Spontaneous process: occurs without outside intervention

Although exothermicity explains most reactions, it does not explain some (e) the spontaneous melting of water (an endothermic process that absorbs energy).

(d) Entropy: a measure of disorder.

It has been concluded, "The driving force for a spontaneous process is an increase in the entropy of the universe."

An example of the spontaneous tendencies of the universe is the organization of a deck of cards where there are many orders in which the cards can exist but only one organized fashion.

This is connected to spontaneity in the example of effusion of a gas. As the number of (m)s of (g) increase, the probability of a position of having all (or most) of the molecules exist in one chamber increases exponentially (see charts on page 681). This explains that the phenomenon of spontaneity is explained simply as having a greater probability of a process to take place.

The Second Law of Thermodynamics: "In any spontaneous process there is always an increase in the entropy of the universe."

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad \{S = \text{entropy; univ} = \text{universe; sys} = \text{system; surr} = \text{surroundings}\}$$

A rx is spontaneous if  $\Delta S_{\text{univ}}$  is (+), and is spontaneous in the other direction if (-).

### The Effect of Temperature on Spontaneity

Considering the boiling of water, the system gains entropy because the (g) phase occupies much more space and therefore can exist in many more configurations than the (l) phase and therefore the rx is favored. The surroundings, however, loses heat and therefore the entropy decreases, so the  $\Delta S_{\text{univ}}$  depends on the magnitude of the two  $\Delta S$  values. The spontaneity of the rx is now determined by the T (remember that S is directly related to T). In the case of boiling water, it is only spontaneous when the T of the surroundings is greater than 100°C. This makes sense in the above equation because the  $\Delta S_{\text{surr}}$  value would be relatively small if the temperature were above this point (the change in temperature would be small because the loss of energy to the system does not greatly affect the relatively high T of the surroundings). At a lower temperature, the lost energy would change  $\Delta S$  for the surroundings enough to make  $\Delta S_{\text{univ}}$  (-). This concept is illustrated in the following expression:

$$\Delta S_{\text{univ}} = -\Delta H / T \quad // \text{ as the T increases, the } \Delta S_{\text{univ}} \text{ decreases because it is less affected by the } \Delta H \\ // \text{ the (-) sign keeps with the sign convention}$$

(n) As the above example has a (+)  $\Delta S_{\text{sys}}$  and (-)  $\Delta S_{\text{univ}}$  so it is favored at high T, the opposite is true for rxs with a (-)  $\Delta S_{\text{sys}}$  and (+)  $\Delta S_{\text{univ}}$ .

### Free Energy

Besides  $\Delta S_{\text{univ}}$ , free energy is also used to predict spontaneity.

$$G = H - TS \quad \{G = \text{free energy}\} \quad // \text{ when no subscript is included, it is of the system}$$

The following proves this:

$$\begin{aligned} -(\Delta G / T) &= -(\Delta H / T) + \Delta S && // \text{ dividing both sides by T gives the following} \\ -(\Delta G / T) &= \Delta S_{\text{surr}} + \Delta S && // \text{ recall that at const T, } \Delta S_{\text{univ}} = -\Delta H / T \\ -(\Delta G / T) &= \Delta S_{\text{univ}} && // \text{ therefore if } \Delta G \text{ is (-) then } \Delta S \text{ is (+) and the rx is spontaneous} \end{aligned}$$

$\Delta S_{\text{univ}}$  can predict the spontaneity of any rx while  $\Delta G$  predicts that of those at const T and P. Since many rxs occur under the latter conditions,  $\Delta G$  is usually used.

(n) If  $\Delta G = 0$ , then the two states coexist.

### Entropy Changes in Chemical Reactions

Since more positions are possible when more moles of gas exist, a reaction in which the number of moles of gas usually increases has increased entropy. (n) This does not mean that the rx is spontaneous.

Since complex (m)s (especially those with non-linear shapes) have more "rotational and vibrational motions," they have a higher entropy as well because there are more possible positions for them (see illustrations for H<sub>2</sub>O on page 695).

$$\Delta S^{\circ}_{\text{rx}} = \sum S^{\circ}_{\text{prod}} - \sum S^{\circ}_{\text{reactants}} \quad // \text{ Entropy values can be determined by the following expression} \\ \text{because it is a state function, meaning that any particle at the same T and P} \\ \text{(despite its path of formation) has the same S value.}$$

// Since entropy is an extensive property, any coefficients of a rx species must be also multiply the S values.

(d) Extensive property: "depends on the amount of substance present."

(n) According to the Third Law of Thermodynamics, the entropy value of a perfect crystal at 0 K is zero (see illustration on page 693).

### Free Energy and Chemical Reactions

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \{\Delta G^\circ = \text{standard free energy change}\}$$

(d) Standard free energy change = "The change in free energy that will occur if the reactants in their standard states are converted to products in their standard states."

$$\Delta G^\circ_{rx} = \sum G^\circ_{prod} - \sum G^\circ_{reactants} \quad // \text{ Since all are state functions, this equation works to calculate S, G, and H.}$$

$$\Delta H^\circ_{rx} = \sum H^\circ_{prod} - \sum H^\circ_{reactants} \quad // \text{ Also note that all are extensive properties.}$$

### Dependency of Free Energy on Pressure

For an ideal gas, G is not P dependent because there are no inter (m) forces and the (m)s occupy no volume.

S large V > S small V // This is true because (m)s can occupy more different positions in large Vs.

S low P > S high P // This is true because (m)s can move more freely and occupy more different positions in low P

$$G = G^\circ + RT \ln(P) \quad \{G = \text{free energy at P pressure; } G^\circ = \text{standard free energy}\}$$

(n) Derivation not available

$$\Delta G = \Delta G^\circ + RT \ln(Q) \quad \{Q = \text{rx quotient}\}$$

$$0 = \Delta G^\circ + RT \ln(K) \quad // \text{ The above equation becomes this when } Q = K.$$

$$\Delta G^\circ = -RT \ln(K) \quad // \text{ Therefore this equation can be derived.}$$

When  $\Delta G^\circ = 0$ , the rx is at equilibrium when the reactants and products are each at the standard state (1 atm and 25°C).

If  $\Delta G^\circ$  is (+) then the rx lies to the left ( $K < 0$ ). If  $\Delta G^\circ$  is (-) then the rx lies to the right ( $K > 0$ ).

Regarding work, simply know that  $\Delta G$  equals the maximum amount of work that the rx can perform (only hypothetically, in reality energy would be lost because efficiency is never 100%)

## **17. ELECTRO CHEMISTRY**

A redox rx involves the exchange of (-e)s. An electric current can be generated by passing the electrons of a redox rx through a wire (metal is a good conductor because of the (-e) sea model in which the (-e)s are delocalized and move freely throughout the solid. This setup is not sufficient though because as the electrons move from one half cell to the other, the (-e) -receiving side will become too (-) while the other half cell will be too (+), and a charge difference like this takes more energy to create than the electricity produced. To overcome this problem, a salt bridge between the half-cells provides for the neutralization of the charges of either cell (a porous-disk can supplement the salt bridge).

(d) Galvanic cell: "a device in which chemical energy is changed to electrical energy."

(d) Anode: the electrode at which oxidation takes place.

(d) Cathode: the electrode at which reduction takes place.

The cell potential, or electromotive force, is the measure of the pull exerted by the reacting species to move the (-e)s between the cells. Cell potential is measured in volts, which equals one joule per coulomb ( $1V = 1J/C$ ) (a coulomb is a unit of charge).

Standard reduction potential (potential at standard conditions) is most useful when measured for half rxs that can later be applied to a number of half-cell combinations. By arbitrarily setting the potential of H to zero, the table of reduction potentials was obtained experimentally.

To find the potential for a galvanic cell, the sum of potentials for the two half rxs is added.

(n) The overall rx must be a redox, so one species must be reduced and the other oxidized. One half rx produces (-e)s and the other consumes them. A half rx can be reversed, but the sign must also change. Also note that reduction potential is an intensive property, so one must not multiply it by the coefficient required to balance the equation.

(d) Intensive property: property which does not depend on how many times the rx occurs.

In order to properly align the half rxs so that the electrons are produced by one rx and consumed by the other, and so that the reduction potential will be one that creates an electrical current, (clearly not every conceivable rx will create an electric current since this would mean that the current can flow both ways resulting in no flow) one must compare the cell potentials of each half-rx and reverse the most negative half rx so that the sum is positive.

$$\epsilon = -w / q \quad \{\epsilon = \text{cell potential}; w = \text{work}; q = \text{charge}\} \quad // \text{cell potential equals work done on the unit of charge transferred}$$

// Since the sign convention holds that work on the surroundings is (-), the sign is changed

$$-w = q \epsilon \quad // \text{This shows that the largest amt of work is from a cell with highest cell potential.}$$

(n) The work potential for a cell is never realized however because energy is always lost to friction.

$$1F = 96500 \text{ C / mol } (-e) \quad \{F = \text{faraday} = \text{coulombs per mole of } (-e)s\}$$

$$q = n F \quad \{n = \text{moles of } (-e) \text{ in the balanced equation}\} \quad // \text{This equation can then be derived.}$$

$$-w = n F \epsilon$$

Efficiency =  $w / w_{\text{max}}$  // the efficiency of a cell is calculated by dividing the theoretical work produced by the rx divided by the experimental voltage.

$$w_{\text{max}} = \Delta G \quad // \text{as seen in Ch.16, the maximum attainable work equals free energy at const T and P}$$

$$-n F \epsilon = \Delta G \quad // \text{work can then be replaced, deriving this expression.}$$

Since Le Chatalier's principle (see chapter 13) applies to these rxs, the [ ]s of the cells can affect the cell potential by shifting the rx to the left or right. From this principle, a concentration cell can be created by using a solution of the same particle in both the reduced and oxidized state at different [ ]s in each cell. This causes the rx to run until equilibrium and produces an electric current.

(n) Concentration cells have very small cell potentials because the sum of the half-cell potentials is close to 0.

#### The Nernst Equation

// the Nernst Equation is derived as follows

$$\Delta G = \Delta G^\circ + RT \ln(Q) \quad // \text{recall this expression from chapter 16.}$$

$$-nF\epsilon = -nF\epsilon^\circ + RT \ln(Q) \quad // \text{replace } \Delta G \text{ with } -nF\epsilon \text{ (proven above).}$$

$$\epsilon = \epsilon^\circ - (RT / nF) \ln(Q) \quad // \text{dividing both sides by } -nF \text{ results in this expression.}$$

$$\epsilon = \epsilon^\circ - (0.0592 / n) \ln(Q) \quad // \text{at } 25^\circ\text{C, } RT/F = 0.0592$$

When the galvanic cell dies (battery runs out),  $Q = K$  (the rx is at equilibrium) and  $\epsilon_{\text{cell}} = 0$ . In order to calculate the K of a rx, replace Q with K and  $\epsilon$  with 0 and solve for K in the Nernst equation.

(d) Electrolysis: forcing a current through a cell to produce a chemical change for which the potential is negative. In electrolysis, electrical energy becomes chemical energy.

$$1A = 1C / s \quad // \text{To determine the moles or grams of a reduced or oxidized species, use the ampere (amp) (A) as a conversion factor. Perform a stoichiometry problem by dividing and multiplying by conversion factors until the desired value is attained.}$$

In a mixture of ions, the (i) with the highest (most (+)) reduction potential will be reduced first.