COURSE : CHEM 202 - SUMMER 2010
FINAL GRADE : 87

NOTE : This is not a 'complete' summary. I've only written what I judged important, with some tips ...
To do well you have to practice your knowledge in Problems

Done by ERIK VZ (you can add me on facebook, if you have questions ...)

Please visit the following blog www.blueaub.blogspot.com

I've taken some of my time to scan my notes and put them on goaub, It is your turn to "loose" 5 minutes of yours!

I hope it was helpful for you!

ENVIRONMENTAL CHEMISTRY

Chapter 1: Atmosphere

ATMOSPHERE

↑

Higher Atmosphere {
100Km Thermosphere T ↗

↑ Absorbs all wavelength $\lambda < 200$ nm

50 Km Mesosphere T ↘
}

↑ Absorbs 100% of UV $\lambda < 315$ nm

T ↗ −2°C (airplanes) ozone layer

Lower Atmosphere 99.9% of the total mass {
12 Km Stratosphere

↑ Absorbs of UV $\lambda < 400$ nm

0 Km Troposphere T ↘ −57°C
}

↑ 60 Km Ionosphere (region where e^- and ions are abundant)

MIXING RATIO

$$\xi_i = \frac{n_i}{n_{total}} = \frac{RT}{P} n_i$$

n_i → concentration mol/m³

$$n = \frac{m_i}{M_i}$$

(using $PV = nRT$)

Chapter 2: Stratospheric Chemistry

$$P_h = P^\circ e^{-\left(\frac{\bar{M}_a g h}{RT}\right)} \Rightarrow \text{Barometric law}$$

↳ pressure @ h above the sealevel in m

$\bar{M}_a$: avg molecular weight of air 0.02896 kg·mol⁻¹

Mass of the atmosphere

$$m_a = \frac{4\pi R^2 P_0}{g}$$

Mass of the atmosphere except the troposphere:

$$m = \frac{4\pi (R+15)^2 P_{h=15}}{g} < m_a$$

example:

$AB + h\nu \rightarrow A + B$

$\Delta H_f = \Delta H_f(A) + \Delta H_f(B) - \Delta H_f(AB)$

energy

1 mole of photon

$\Delta E = h\nu = \frac{hc}{\lambda}$ (reaction depends of radiation wavelength) — h → planck constant

$\Delta E = \frac{\Delta H_f}{N_A}$ (for one photon)

Free radicals → odd number of e^- in a molecule

Oxygen-only chemistry - formation and turnover of ozone

M = catalyst

Synthesis: $O_2 + h\nu(\lambda < 240\,nm) \rightarrow O + O$ Slow

$O + O_2 + M \rightarrow O_3 + M$ Fast

Decomposition:
null cycle

$O_3 + h\nu(\lambda \simeq 230-320\,nm) \rightarrow O_2^* + O^*$ Fast

$O + O_3 \rightarrow O_2 + O_2$ Slow

Catalytic decomposition processes of ozone

$X + O_3 \rightarrow XO + O_2$
$XO + O \rightarrow X + O_2$ } catalytic cycle

$O + O_3 \rightarrow 2O_2$

X { HO_x ($\cdot H$, $\cdot OH$, $HOO\cdot$) } natural
NO_x ($\cdot NO$, $\cdot NO_2$)
ClO_x ($\cdot Cl$, $ClO\cdot$) → Anthropogenic
Br
⋮

CFC - xyz

$n_C = x + 1$
$n_H = y - 1$
$n_F = z$

n_{Cl} to be found

CFC's undergo UV decomposition (liberates free radicals) } see holding cycles (reservoirs)

$k = Ae^{-\frac{E_a}{RT}}$

Chapter 4: Tropospheric Chemistry

N_2O fertilizer
NO (nitric oxide)

density $d = \frac{m}{V}$

Combustion:

a Hydrocarbure + bO_2 → cH_2O + dCO_2
a mol b mol ...

Biomass: $\{CH_2O\}$
Gasoline: C_7H_{13}

1 mol air { 0.78 mol N_2, 0.21 mol O_2, 0.01 mol Ar }

SMOG
- NO_x → PAN's reservoir of NO_x
- VOC
- O_3

yields

Hydrocarbon reactivity increases with size and number of double bonds

Chapter 8: Global Warming

$m_{atm} = 5.27 \times 10^{18}$ Kg
$\bar{M}_a = 0.02896$ Kg. mol^{-1}

$n_{(mol\ total)} = \frac{m_{atm}}{\bar{M}_a}$

$P_{actual\ H_2O} = \frac{H_R}{100} P_V(H_2O)$

H_R → humidity level in atmosphere
$P_V(H_2O)$: partial pressure of H_2O → depends of T

→ $PV = nRT$

$F = \sigma T^4$

→ flux (energy emitted from $1 m^2$) earth/sun

σ: Stefan-Boltzmann constant
$\sigma = 5.67 \cdot 10^{-8}\ W m^{-2} K^{-4}$

N_2O Greenhouse gas
IR
nonsymetric molecules

Chapter 11: Gases in Water

Photosynthesis → biomass

$CO_2 + H_2O \rightarrow \{CH_2O\} + O_2$

Pure rain: $pH = 5.7$

Acidic rain $pH \simeq 5.0$

Toxic Metals

Some metals are essential for life
Other are dangerous

$Cr(VI)$ → carcinogen

$((CH_3)Hg^+$ → toxic
acid pH favorize its formation (lake acidification would increase mercury toxification)

Cd (similar to Zn)

Hg^0
Hg_2^{2+}
Hg^{2+}
} non toxic

Biological cycle
(plants, fish, ...)
↓ responsible for
long rang transportation of Hg

Danger: food chain / water

Chapter 11 : Acid Rain

$pH_{rain} = 5.7$

acid rain → $pH \approx 5.0$

Mass Balance

The mass of acetate (m_{Ac}) put into a solution must still be present even though it is now present as HAc and Ac^-. (same for concentrations).

Charge Balance

The total number of positive charges must equal the number of negative charges

$$[H^+] = [HSO_4^-] + 2[SO_4^{2-}] + [HO^-]$$

To predict how acidic the rain should be

1) Estimate how much CO_2 dissolves in the rain to give a solution of H_2CO_3 (use Henry's law P_{CO_2})
2) Explore the dissociation of the H_2CO_3 to release H_3O^+

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad K_H$$

Polyprotic Acid

$$H_2CO_3 \longrightarrow H^+ + HCO_3^- \qquad \log K_1 = -6.4$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.4}$$

$$\Rightarrow \log K_1 = \log \frac{[HCO_3^-]}{[H_2CO_3]} + \log[H^+]$$

$$pK_1 = -\log \frac{[HCO_3^-]}{[H_2CO_3]} + pH$$

$$pH = pK_1 - \log \frac{[H_2CO_3]}{[HCO_3^-]}$$

$$pH = pK - \log \frac{\text{reactive}}{\text{product}}$$

} determine predominant species !! (Very Important)

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9}$$ (solubility product)

↳ to calculate $[Ca^{2+}]$

Alkalinity (measure of the ability of a water body to neutralize acids)

$$\text{alkalinity} = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H_3O^+]$$

As $[HCO_3^-]$, $[CO_3^{2-}]$ ↗ the solution becomes basic, pH ↗

→ To calculate pressure due to water:

Find $V_{H_2O} \simeq m_{H_2O}$ (in Liter)

$F = mg$ = pressure

⇒ To determine $[HCO_3^-]$ and $[CO_3^{2-}]$

look at the pH and see which species is predominant (other are negligible)

Chapter 16: Water Pollution and Waste Water Treatment

Dissolved oxygen (DO) depends on temperature and altitude

Biological oxygen demand (BOD) = amount of O_2 (in mg) required to carry out the oxidation of organic carbon in one liter of water.

Plant Nutrients: C, N, P = 106 : 16 : 1

The shortage of one of these elements keeps the spread of vegetation under control.

Eutrophication = excessive plant growth (algae population explodes)

Primary water treatment (sedimentation process)

$$3\,Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4$$

Treatment of phosphorus

$$Al^{3+}(aq) + PO_4^{3-}(aq) \rightarrow AlPO_4(s)$$

Any excess Al^{3+}:

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

Biological process to remove ammonium

$$NH_4^+(aq) + 2O_2(aq) + H_2O \rightarrow NO_3^-(aq) + 2H_3O^+(aq)$$

Organic matter

Presence of O_2:

$$\{CH_2O\} + O_{2(g)} \rightarrow CO_2(g) + H_2O$$

Absence of O_2:

$$2\{CH_2O\} \rightarrow CO_{2(g)} + CH_{4(g)}$$

→ Total carbonate species remains constant (important when we have other reactions)

Molecular Structure : VSEPR

$AX_m E_n$ (m → bonding pairs, n → lone pairs)

1- Draw the lewis structure of the atom
2- Count the number of effective pairs
(geometry that guarantee them to be the farthest possible from each other)

e⁻ arrangement:
- 2 pairs → Linear
- 3 pairs → Trigonal planar
- 4 pairs → Tetrahedral
- 5 pairs → Trigonal bipyramidal
- 6 pairs → Octahedral

Geometry (depends on X)

4 pairs of e⁻:
- AX_4E_0 → tetrahedral
- AX_3E_1 → trigonal pyramidal
- AX_2E_2 → V-shaped (bent)

5 pairs:
- AX_5E_0 → Trigonal bipyramidal
- AX_4E_1 → See-Saw
- AX_3E_2 → T-structure
- AX_2E_3 → Linear

6 pairs:
- AX_6E_0 → Octahedral
- AX_5E_1 → Square Pyramidal
- AX_4E_2 → Square Planar

AX_2E_1 → bent

Chapter 8: Chemical Bonding

Electronegativity (EN) → x ↑ priority
(and ionization energy)

similar to distance from the nucleus to the outer shell (the smallest)

Octet rule (only for the first two periods of the periodic table).

Depicting molecules and ions with Lewis structure:

1- place atom with lowest EN at the center
2- draw single bonds btw atoms after summing the Valence e^- and substract $2e^-$ for each bond from this sum
3- Complete with the remaining e^- (sometimes add bonds)

when two or more different lewis structures are possible for a molecule, they are termed resonance hybrid.

Formal Charges (for each atom separately) = Number of Ve^- in free atom − Number of bonds − Number of nonbonding electrons

In a molecule, we try to obtain the lowest formal charge

ΔEm = difference in electronegativity ($\delta-$) more electronegative | ~~more~~ less electronegative ($\delta+$)

as $\Delta Em \nearrow$, bonds become more polar

⚠ ~~Irons~~ Ions

$Fe: [Ar]\ 4s^2\ 3d^6$
$Fe^{2+}: [Ar]\ 3d^6$

} because the 4^{th} level ($n=4$) is the outershell

Size of Atoms

Cu, Cu^+, Cu^{2+}

$Cu^{2+} < Cu^+ < Cu$

(less e^-, more attraction)
size = distance from the nucleus to the outer shell

EN(S) < EN(N)

⚠ Elements in period 1, 2
They CAN'T exceed the octet

Most stable structure

Resonance structures with:

1 - lowest formal charges
2 - unlike charges on adjacent atoms
3 - a more negative formal charge on more E.N. atom

Acids and Bases

Acid : produces hydrogen ions (H^+) in aqueous solution
Base : produces hydroxide (OH^-) ions

$$H^+(aq) + H_2O(l) = H_3O^+(aq)$$

General Reaction

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate base}}{A^-(aq)} + \underset{\text{conjugate acid}}{H_3O^+(aq)}$$

$$Ka_{eq} = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

Ka is the acid dissociation constant

$$HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$$

Strong acid : high Ka (dissociates completely)
Weak acid : low Ka (dissociates partially)

A strong acid yields a weak conjugate base.
(and vice versa)

$K_w = 1.0 . 10^{-14}\ mol^2/L^2$

Neutral Solution $[H^+] = [OH^-]$
Acidic Solution $[H^+] > [OH^-]$
Basic Solution $[H^+] < [OH^-]$

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

pH ↘ as $[H^+]$ ↗

% dissociation is greater in dilute solutions

Polyprotic Acids

Contain more than one acidic proton per molecule.
(H_2SO_4 , H_3PO_4 , H_2CO_3)

Stepwise dissociation

Only the 1st dissociation step is important in determining the pH

$Ka_1 > Ka_2 > Ka_3$

Only in dilute solutions does the 2nd dissociation step contribute significantly to $[H^+]$.

CHEMICAL KINETICS

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} = \frac{\Delta C}{\Delta t} \quad (mol.L^{-1}.s^{-1})$$

rate of reaction = rate of disappearance of reactants

$$= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

= rate of appearance of products

$$= \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Rate law (effect of concentration on reaction rates)

$$r = k[A]^m[B]^n \ldots$$

k ↓ rate constant

0 order reaction:

$r = k$ $\quad m + n + \cdots = 0$.

$$[A]_t = [A]_0 - kt$$

1st order reaction:

$r = k[A]$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$\boxed{t_{\frac{1}{2}} = \frac{\ln 2}{k}}$$

2nd order reaction:

$m + n + \cdots = 2$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Testing for a Rate law

Plot $[A]$ vs t
$\ln[A]$ vs t
$\frac{1}{[A]}$ vs t

} the straight line ⟺ order

Activation Energy

The minimum energy above the average kinetic energy that molecules must bring to their collisions for a chemical reaction to occur.

$$k = Ae^{-\frac{E_a}{RT}}$$

- E_a → activation energy
- T → temperature
- R → perfect gas constant
- k → rate constant
- A → constant

$$\Rightarrow \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

Slow step followed by fast step

we consider the slow one

Determine order of reaction?

- initial rates
- graph (straight line)

Rate Constant?

- slope of the graph
- formula ([illegible])
- use activation [illegible]

Reaction Mechanisms

(intermediates, balanced equation)

$$r = k[A]^a [B]^b$$

usually,

$$r = k[A][B]$$

Atomic Structure and Periodicity

$c = \lambda \nu$

$c = 3.10^8 m/s$

Bohr Model (Valid only for atoms with $1e^-$)

$$\Delta E = R_H \left(\frac{Z^2}{n_f^2} - \frac{Z^2}{n_i^2} \right)$$

if $n_2 > n_1$
$\Delta E_2 > \Delta E_1$

$R_H = 2.18 \cdot 10^{-18}$

$$\Delta E = h\nu = h \frac{c}{\lambda}$$

$h = 6.6261 \cdot 10^{-34}$

Heisenberg uncertainty principle

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

De Broglie

$$p = \frac{h}{\lambda} = m\nu$$

p → linear momentum; ν → velocity

$$\lambda = \frac{h}{m v_e}$$

Number of orbitals in one atom $= n^2$

$l = 0, 1, 2, \ldots, n-1$

$m_l = -l, \ldots, -1, 0, 1, \ldots, +l$

$n = 1/2/\ldots$

$m_s = -\frac{1}{2}$ or $+\frac{1}{2}$

$l = 0 \rightarrow s^2$
$l = 1 \rightarrow p^6$
$l = 2 \rightarrow d^{10}$
$l = 3 \rightarrow f^{14}$

($2l+1$ orbitals in each subshell) $\times 2e^-$

Aufbau process (build up and minimize energy)

Pauli exclusion principle (no $2e^-$ can have all four quantum numbers alike)

Probability of finding an e-
wave function
(Probabilities (0 at nodes)

num of nodes :
- radial nodes = $n - l - 1$
- angular nodes = l
Total number of nodes = $n - 1$

Done by Erik. VZ.

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