CHEM 304
SPRING 2012
EXAM 1 Review Sheet:

THEME: Atmospheric Chemistry: Fundamentals, Stratospheric and Tropospheric Chemistry.

SCOPE: Baird Chapters 1 – 3 & 5, HW #1 – #6, Lecture thru first part of M 3/5/12, & all handouts.

FORMAT: Expect a mix: short answer (reactions, "factoids", etc.), numerical problems, and a short essay – yes I said "essay": a long (1-page or so) coherently written statement or description of some key part of the material.

TERMS:

Pressure
Bar
millibar
atmospheres
Torr
Laspe Rate
Troposphere
Stratosphere
Mesosphere
Thermosphere
Tropopause
Stratopause
Mesopause
Free radical
Source
Reservoir
Sink
Mixing Ratio

ppm, ppb
Partial Pressure
Number Density
Free radical
Initiation
Propagation
Termination
ΔH (for a reaction)
Heat of formation
ΔG (for a reaction)
Free energy of formation
K (equilibrium constant)
"Disequilibrium"
Photochemistry
Photolysis
Electromagnetic radiation
Bond energy
Chemical kinetics
Rate Law
Rate Constant

Elementary Reaction
Catalyst
Intermediate
Lifetime
Ozone
Dobson Unit
Odd oxygen (Ox)
Chapman Mechanism/Cycle
Chemical Family
Null Cycle
Ozone Depletion Potential
Polar Stratospheric Cloud
Primary Pollutant
Secondary Pollutant
Thermal Inversion
Smog
Acid Rain
Aerosol

CONCEPTS:

<u>Fundamentals</u>

• Chemical Stability: What is the role that a stability of a given substance plays in environmental chemistry. What three ways do we assess stability? (empirical, intuitive, and quantitative).

• Physical and Chemical Structure of the atmosphere: Units for pressure. How does atm pressure vary with altitude? How does temperature vary with altitude? How does this distinguish atmospheric layers? Can you name the layers and the boundaries between them? What factors determine the lapse rate in the lowest two layers? Chemical composition of the atmosphere: What are the main components? What chemical characteristic must all the main chemical components share? Calculating and converting between the various ways of expressing concentrations of trace chemical species.

• Key Chemical Principles: Recognizing/classifying the three general types of free radical reactions. Disequilibrium: Calculating ΔG and K for a reaction, and equilibrium concentrations from K. What does ΔG (for a reaction) mean? What does K mean?

• Photochemistry: Characteristics of electromagnetic radiation: converting between frequency, wavelength and energy. Identifying regions by wavelength (and vice versa). Basic principles of photochemistry: what two criteria must be met for light to break a bond? Understanding/Interpreting an absorption spectrum and how this relates to photochemical stability.

• Chemical Kinetics: Factors that affect the rate of a reaction. Writing rate laws for elementary reactions. Calculating reaction rates. Calculating lifetimes.

Stratospheric Chemistry:

• Basics and Chapman Chemistry: What are the three functions of ozone in the atmosphere? What is the approximate altitude range of the ozone "layer"? What is the peak number density and or mixing ratio (i.e. is there a "layer" that is 100% ozone)? What is an average column thickness of ozone (in Dobson Units), and how much ozone is this at ambient temperature and 1 atm pressure? The Chapman mechanism reactions. The Ox family, and the main justification for this "family concept" (i.e. how long does O or O_3 live as compared to Ox collectively?). Rationalizing an ozone layer based on differential light penetration and abundance of O_2 and M vs. altitude. What wavelengths of light are available at various layers in the atmosphere? How does the ozone layer as predicted by Chapman chemistry differ from what is observed?

• Catalytic Ozone Loss: Three general reaction cycles (or "paths"): one catalytic loss path that requires O atoms, one that does not require O atoms, and one "null cycle". The three (or four if you include BrO_x) catalyst families (X=?). Which member of each is the most effective O_3 destroyer? Using rate laws (comparing rates) to gauge the effectiveness and/or relative significance of the various paths (e.g. path #1 vs. path #2 for X=OH, and how this varies with altitude, how the three paths compare with X=NO, etc.). Reservoirs: formation, decomposition, and "depth". What factor(s) affect depth? What are the main sources of "X"? What processes (mainly tropospheric) must these source species "dodge" to make it to the stratosphere? Why does it take so long for a substance to diffuse into the mid-ozone layer ? About how long does it take to cross the tropopause and subsequently diffuse to the mid-stratosphere (rough average ranges…)? What is the ramification in terms of how overall chemical stability relates to stratospheric pollution? (e.g. Why do HCFC's cause less O_3 depletion than CFC's?) What is the main sink process for "X"? Are the effects of adding X species to the stratosphere additive – why or why not?

• The Antarctic ozone "Hole": History: how was it discovered, and why wasn't it discovered earlier? When does it form? What dynamical/meteorological (i.e. non-chemical) factors facilitate ozone hole formation, and how does each of these factors contribute to the special chemistry? What is the chemical signature of this special chemistry? What *heterogeneous* reactions (non-gas phase, on surfaces) occur that cause this chemical signature? What is their effect on ClOx reservoirs and NOx levels? In the spring, when the light returns, do all wavelengths come back at the same time with equal intensity, or is there a systematic trend? If so, why? What effect does this have on the chemistry (in terms of liberating catalysts from reservoirs)? What is the reaction sequence that occurs that ultimately leads to substantial O_3 loss (3 reactions + 2x one more to balance the cycle)? How does it differ from "standard" (path #1) O_3 depletion? What X family is key to this chemistry? Is this a natural problem or one of human origin? Is this a local, regional, or global environmental problem?

Tropospheric Chemistry:

• General Features: What are the 5 main, general, tropospheric "disposal" processes? What is the main tropospheric oxidant? How is it formed? How is the ozone from which it is generated formed (natural path – while we are on the subject how does NOx pollution enhance this?)? What simple gasses are released by decay of biological wastes under aerobic and anaerobic conditions? What gas is released by decay of "biological waste"? What are the main primary air pollutants? Oxidation of CO. How does this (in turn) lead to the production of the main aqueous-phase oxidant? Oxidation of methane.

• Photochemical Smog: What are the "ingredients" for smog chemistry? What are their sources? Oxidation of hydrocarbons – know the reactions! Subsequent formation of PAN. How do thermal inversions enhance this chemistry? How/Why is NOx formed during hydrocarbon combustion?

• Acid and Aerosol Formation: How acidic is "natural" rainwater? How acidic is "acid rain" in regions where it is a problem? Where are these regions? What species cause this acidity? Calculating the pH of natural, "clean" rain water. Key reactions: Conversion of NO to HNO_3 to ammonium nitrate. SOx chemistry. SOx sources. Ket reactions: Conversion of SO_2 to H_2SO_4: (2 paths, one gas-phase one aqueous) to ammonium sulfate.