

# CHEM 336/ TOX 336 Environmental Chemistry and Toxicology

Course Outline: Winter Semester 2005

**Instructor:** Dr. Kate Stuttaford  
**Office:** McN 129  
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**Office hours:** By appointment only  
**Meeting Times:** Tuesday/Thursday 8:30 to 9:50 in Axelrod 117

**Course Description:** The chemistry of the natural environment; the influence of pollutants upon the environment, including methods of introduction of pollutants to and removal of pollutants from the environment. Credit weighting = 0.50.

**Please note: students with standing in CHEM 131 should not take this course.**

**Required Text:** Environmental Chemistry, 2<sup>nd</sup> Ed., 1994 by Nigel J. Bunce, available at the UofG Bookstore. You may optionally purchase the Answer Guide to the problems. Copies of both books are on reserve at the library.

**Other References:** “Environmental Chemistry” C. Baird provides supplementary reading for some topics discussed in this course and is on reserve for 2-hour loan from the Library Reserve Desk.

The course website contains links to government and other environmental sites that can be useful in explaining certain subjects. The website can be found through the Chemistry and Biochemistry department site  
Please remember that information posted on the internet is not always reliable and that careful consideration must be given to the source.

<b>Evaluation:</b>	Two in-class tests (80 minutes each)	50%
	1 in-class assignment	10%
	1 take-home assignment	10%
	Final Examination (2 hours)	30%

**Problems:** Numerical problems will be assigned week by week. Most will be from the textbook. Where material has been added to the course, relevant problems will be provided. I strongly recommend working the problems in small groups; be sure to ask for help if you are having difficulty.

**Exams:** These will comprise a combination of short answer and numerical questions. It is highly recommended that you do the assigned problems as part of your study strategy for the exams. Attendance at review classes is also strongly recommended as part of a conscientious approach to study.

**Assignments:** Assignments will be further explained with a handout at the appropriate lecture. Late assignments will be accepted but with a 5% penalty per day.

**Lecture Schedule:**

<b>Date</b>	<b>Lecture topic</b>	<b>Chapter</b>
Jan 13	Introduction: review; the atmosphere; environmental cycles and residence times	1.1-1.2
Jan 18	Solar energy/ photochemistry; Greenhouse gases and climate change; Kyoto	1.3-1.5
Jan 20	Greenhouse gases and climate change class discussion; Ozone balance in the stratosphere	2.1-2.4
Jan 25	Montreal protocol; CFCs/ replacement compounds	2.5-2.8
Jan 27	Pollution in the troposphere; Formation of the hydroxyl radical; Photochemical smog	3.1-3.5
Feb 1	Secondary pollutants; air toxics; particulate matter in the lower atmosphere	3.6-3.9
Feb 3	Indoor air quality: occupational hygiene; Review for term test	4.1
<b>Feb 8</b>	<b>Term Test 1: Chapters 1-3</b>	
Feb 10	Indoor air emissions; radioisotopes in the environment	4.2
Feb 15	Dissolved gases in natural water; Henry's law	5.1
Feb 17	Dissolved solids in natural water: alkalinity and hardness; water softening <b>In-class assignment</b>	5.2
Feb 22	READING WEEK	
Feb 24	READING WEEK	
Mar 1	Acid rain: nitrogen and sulfur oxides in the atmosphere <b>Take-home assignment</b>	6.1-6.5
Mar 3	Acid rain: biological effects and abatement methods	6.6-6.8
Mar 8	Drinking water: chlorination; Review for term test	7.1-7.3
<b>Mar 10</b>	<b>Term Test 2: Chapters 4-6</b>	
Mar 15	Alternatives to chlorination; Sewage treatment	7.4-7.8, 8.1
Mar 17	Treatment of other wastes; Chlorine and its compounds	8.2-8.6, 9.1-9.4
Mar 22	PCBs and dioxins: chemistry and sources	9.5-9.7
Mar 24	PCBs and dioxins: toxicology, toxic equivalency factors, Phase I/ Phase II metabolism	9.5-9.7
Mar 29	Endocrine disrupting compounds; Pollution in the pulp and paper industry	
Mar 31	Mercury in the environment; Lead in the environment	10.1-10.3
Apr 5	Arsenic in the environment; Acid mine drainage	10.4-10.5
Apr 7	Catch-up and Review	
<b>Apr 19</b>	<b>Final Exam: whole course, emphasis on material covered since Term Test 2</b>	

## **Review - Atmospheric Chemistry**

### **Gas Chemistry Review**

The Gaseous State: our atmosphere consists of gases

Confined only by gravity

- force of gas on a unit area is due to the mass alone
- that force will ↓ as altitude ↑, since gas density ↓

Atmospheric Pressure

force / area = pressure exerted by the atmosphere  
= ATMOSPHERIC PRESSURE

### Dalton's Law of Partial Pressures

Each gas of a mixture exerts its own pressure independent of the other gases in the mixture. This is known as its PARTIAL PRESSURE.

$$\text{Total pressure (mixture)} = \sum \text{partial pressures}$$
$$P_T = P_A + P_B + P_C \dots P_i$$

### Boyle's Law

The volume of a given quantity of gas varies inversely with the pressure of the gas, at a constant temperature.

$$P_1 V_1 = P_2 V_2 = \text{a constant}$$

## Charles' Law

The volume of a given quantity of gas at constant pressure varies directly with the absolute temperature.

- gas volume increases as temperature increases but not proportionally to °C
- introducing  $K = °C + 273.16$   
= absolute temperature
- Temperature expressed in  $K = T$

$$T_1/T_2 = V_1/V_2$$

## Avogadro's Principle

One mole of all gases at standard temperature and pressure occupy the same volume.

$$= 22.414 \text{ L}$$

$$V \propto n \text{ (P, T constant)}$$

## Combined Gas Law

By combining each of these laws we get:

$$V \propto nT / P$$

$$PV / nT = R \text{ (a constant)}$$

$$PV = nRT \text{ (you've seen this before!)}$$

For one mole of gas under standard conditions:

$$R = P_o V_o / T_o$$

$$\begin{aligned} R &= \frac{1 \text{ atm} \times 22.414 \text{ L/mole}}{273.16 \text{ K}} = \frac{82.06 \text{ cm}^3 \text{ atm}}{\text{mole K}} \\ &= 0.082 \text{ L atm / mole K} \\ &= 8.314 \times 10^7 \text{ ergs/ mole K} \\ &= 1.987 \text{ kcal/ mole K} \end{aligned}$$

Using  $PV = nRT$  for mixtures of gases

$$\begin{aligned} P_T &= n_T RT / V \\ P_T &= \frac{RT}{V} \sum n_i \end{aligned}$$

Mole fraction

= mole fraction of one gaseous species in a mixture

$$= n_i / n_T$$

**sum of mole fractions = 1**

## Problem #1

If 10 g H<sub>2</sub> and 64 g O<sub>2</sub> are contained in a 10L flask at 200° C, calculate the total pressure of the mixture.

$$m = 10 \text{ g and MW} = 2 \text{ g/mol}$$

$$n = \frac{10 \text{ g}}{2 \text{ g/mol}} = 5 \text{ mol of H}_2 \text{ gas}$$

$$m = 64 \text{ g O}_2 \text{ and MW} = 32 \text{ g/mol}$$

$$n = 2 \text{ mol O}_2 \text{ gas}$$

$$n(\text{H}_2) = 5 \text{ mol, } n(\text{O}_2) = 2 \text{ mol}$$

$$V = 10 \text{ L}$$

$$T = 200^\circ \text{ C} = 473.16 \text{ K}$$

$$P_T = \frac{RT}{V} \sum n_i$$

$$= 0.082 \text{ L atm/mole K} \times 473.16 \text{ K} \times (5+2) \text{ mol} / 10 \text{ L}$$

$$= 27.2 \text{ atm}$$

Upon sparking, what is the final pressure in the container?



T is 473.16 K  $\gg$  373.16 K which is the boiling pt of water, so product is water vapour not liquid.

$$\text{So } \sum n = 4 + 1 = 5$$

$$\begin{aligned} P_T &= 0.082 \text{ L atm/mole K} \times 473.16 \text{ K} \times 5 \text{ mol} / 10 \text{ L} \\ &= 19.4 \text{ atm} \end{aligned}$$

## Problem #2

Seven grams of nitrogen, 16 g oxygen and 3.03 g hydrogen are introduced into an evacuated container of 80 L capacity at 50 °C. What is the partial pressure of each gas in the mixture?

$$\begin{array}{ll} 7\text{g N}_2, \text{MW} = 28 \text{ g/mol} & n = 7 \text{ g} / 28 \text{ g/mol} = 0.25 \text{ mol N}_2 \\ 16\text{g O}_2, \text{MW} = 32 \text{ g/mol} & n = 16 \text{ g} / 32 \text{ g/mol} = 0.50 \text{ mol O}_2 \\ 3.03\text{g H}_2, \text{MW} = 2 \text{ g/mol} & n = 3.03 \text{ g} / 2 \text{ g/mol} = 1.5 \text{ mol H}_2 \end{array}$$

$$n_T = 0.25 + 0.5 + 1.5 = 2.25 \text{ mol}$$

$$\begin{aligned} P_T &= n_T RT/V \\ &= 2.25 \times 0.082 \times (50+273.16)/80 \\ &= 0.64 \text{ atm} \end{aligned}$$

$$P_N = 0.25/2.25 \times 0.64 = 0.071$$

$$P_O = 0.5/2.25 \times 0.64 = 0.14$$

$$P_H = 1.5/2.25 \times 0.64 = 0.43$$

$$0.071 + 0.14 + 0.43 = 0.64 \text{ atm total!}$$

## Review - General Thermodynamics

- the relationship between the energy changes that occur in chemical or physical processes.
- how much "work" is done, energy added or released.

### First Law of Thermodynamics

Energy is neither created nor destroyed.

$$\Delta H = \Delta E + \Delta nRT \text{ (for constant PV)}$$

(page 9 of the textbook)

$\Delta E$  = change in internal energy

$\Delta n$  = #moles gaseous product - #moles gaseous reactants

Example: vaporization of a liquid

- vapour has to do work against a constant P
- is a reversible reaction,  $P_{\text{vapour}} = P_{\text{atmosphere}}$

$$w = P \Delta V = P(V_v - V_l)$$

but  $V_l$  is negligible compared to  $V_v$

- so (if vapour behaves as an ideal gas):

$$V_v = nRT/P$$

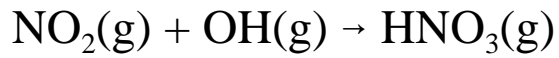
and  $w = PV_v = P (nRT/P) = nRT$

therefore work of vaporization depends ONLY on temperature

Standard enthalpy of formation and Hess's law:

$$\Delta H^\circ = \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactants})$$

i.e.



$$\Delta H^\circ = \Delta H^\circ_f (\text{HNO}_3, \text{g}) - \Delta H^\circ_f (\text{OH}, \text{g}) - \Delta H^\circ_f (\text{NO}_2, \text{g})$$

## Review - Kinetics

### Rate Laws:

Rates are always measured in units of concentration/unit time  
i.e.  $\text{mol L}^{-1} \text{s}^{-1}$ ,  $\text{atm s}^{-1}$

### First order rate of reaction:

$A \rightarrow \text{products}$

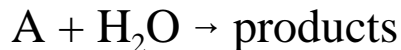
rate:	$-\text{d}A/\text{d}t = k[A]$
integrated rate law:	$[A] = [A]_0 e^{-kt}$ $\ln[A]/[A]_0 = -kt$
units of rate constant:	$\text{s}^{-1}$
half-life:	$t^{1/2} = \ln 2/k = 0.693/k$

### Second order rate of reaction:

$2A \rightarrow \text{products}$

rate:	$-\text{d}A/\text{d}t = k[A]^2$
integrated rate law:	$1/[A] = 1/[A]_0 + kt$
units of rate constant:	$\text{L mol}^{-1} \text{s}^{-1}$
half-life:	$t^{1/2} = 1/k[A]_0$

## Pseudo first order rate of reaction:



(or replace H<sub>2</sub>O with any substance at such a high conc. the reaction does little to change it)

rate 
$$-dA/dt = k'[A][H_2O]$$

reaction is technically second order, but set  $k = k'[H_2O]$  and it appears to be first order

rate 
$$-dA/dt = k[A]$$

## Arrhenius Equation

- used to find activation energy, given rate constants at different temperatures:

$$k = Ae^{-E_a/RT}$$

- a plot of  $\ln k$  vs  $1/T$  gives slope =  $-E_a/R$  and intercept  $\ln A$
- Note: T must be in Kelvin

# Atmospheric Chemistry

## Atmospheric composition

### Major components

- N<sub>2</sub> 78%
- O<sub>2</sub> 21%  
(Unique property of earth's atmosphere; biological processes)
- Ar ~1%

### "Medium" components

- CO<sub>2</sub> 336 ppmv
- CH<sub>4</sub> 1700 ppbv
- H<sub>2</sub>O variable  
(range ~ 0 to 0.4% (0.004 atm))

### Definitions: *ppmv and ppbv*

ppmv =  $10^{-6} \times P_T$  - varies with altitude because  $P_T$  varies

### Trace components

- H<sub>2</sub> 600 ppbv
- N<sub>2</sub>O 310 ppbv
- CO ~100 ppbv
- O<sub>3</sub> <30 ppbv (clean troposphere)  
→ 80 ppbv (Canadian guideline)
- some hydrocarbons low ppbv
- NO<sub>x</sub> low pptv 10 ppbv
- SO<sub>2</sub> <1 ppbv

## Regions of the atmosphere and environmental problems

- Troposphere (lower atmosphere, to ~ 15 km)
- Stratosphere (~ 15 - 50 km)
- Mesosphere (~ 50 - 90 km)
- Thermosphere (>90 km)

Most of the mass of the atmosphere ( $\sim 5 \times 10^{15}$  tonnes) is present in the troposphere ( $\sim 99\%$  below 30 km)

- beyond 150 km is essentially a vacuum,  $P_T \sim 10^{-9}$  atm

### Tropospheric problems

- Greenhouse warming
- Photochemical smog
- Particulates
- Acid precipitation

### Stratospheric problems

- Ozone depletion

## Residence Times

$$\tau = \frac{\text{amount of substance in a "reservoir"}}{\text{rate of inflow to, or outflow from a reservoir}}$$

$$\tau = 1 / \sum k'$$

- where  $k'$  is the rate constant for loss of the substance from the reservoir

Definitions: *reservoir, sources, sinks*

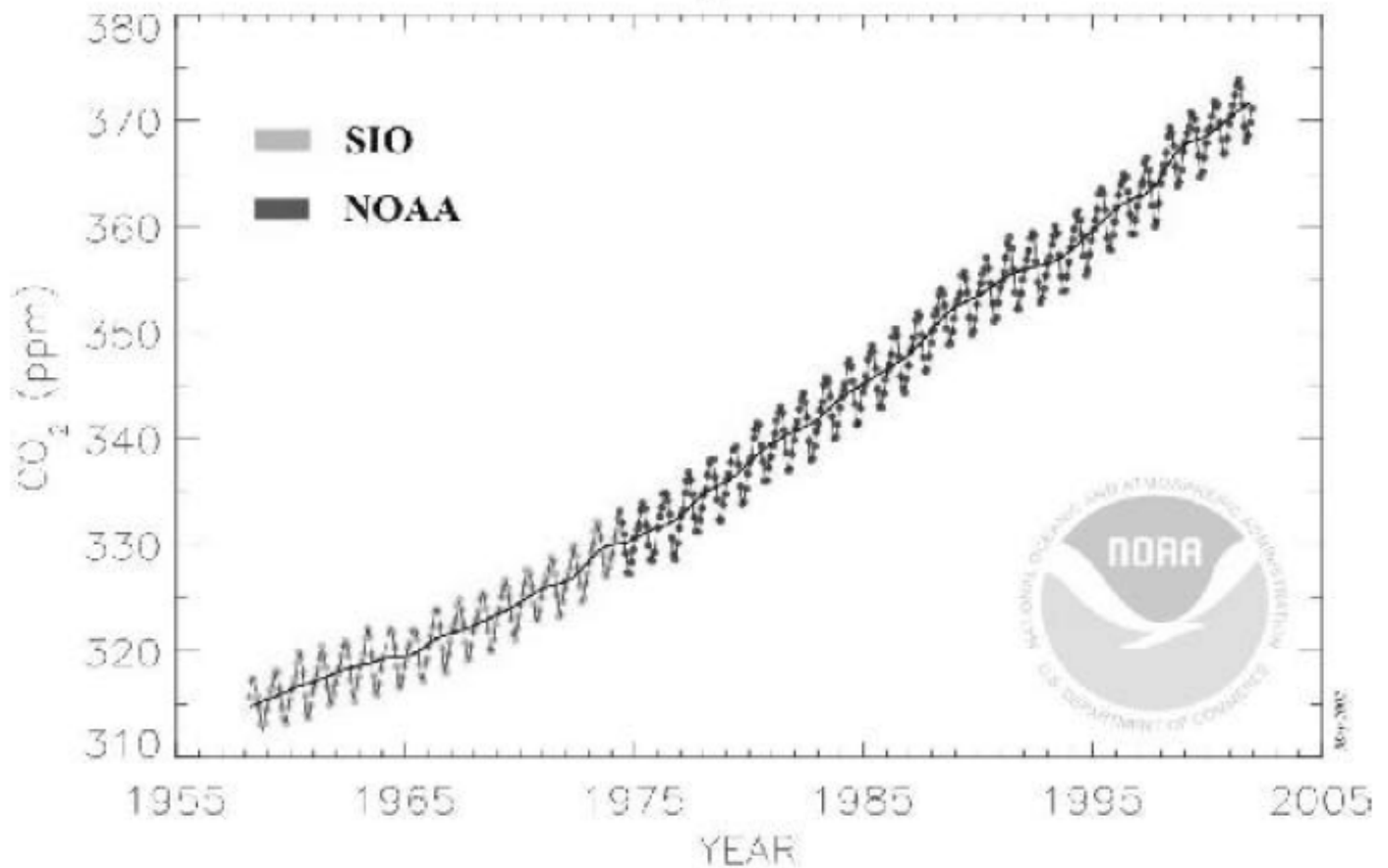
- complete mixing of a substance throughout the troposphere takes several years
- substances with long residence times (compared to the mixing time)
  - will be widely distributed throughout the reservoir
  - will represent global pollution problems
  - e.g. chlorofluorocarbons
- substances with short residence times (compared to the mixing time)
  - will not be widely distributed throughout the reservoir
  - will represent regional pollution problems
  - e.g. acid rain

## Residence Times

- Residence times of atmospheric gases - mostly biologically regulated
- $O_2$  ( $1.2 \times 10^{15}$  t) / ( $4.0 \times 10^{11}$  t / yr) =  $3.0 \times 10^3$  yr
  - sinks: respiration, decay, combustion, weathering
  - source: photosynthesis
- $N_2$  ( $3.9 \times 10^{15}$  t) / ( $3 \times 10^8$  t / yr) =  $1 \times 10^7$  yr
  - sinks: N fixation, lightening and combustion, industrial (Haber process)
  - sources: bacterial denitrification and decay

- $\text{CO}_2$  ( $6.2 \times 10^{11} \text{ t}$ ) / ( $3.7 \times 10^{11} \text{ t / yr}$ ) = 1.7 yr
  - sinks: photosynthesis, ocean (not well understood)
  - sources: respiration, combustion, decay
  - pronounced 1 year cycle:  $\text{CO}_2$  is removed faster than added in summer; reverse trend in winter
  - rate of increase  $\sim 1.5 \text{ ppmv / yr}$

### Mauna Loa Monthly Mean Carbon Dioxide

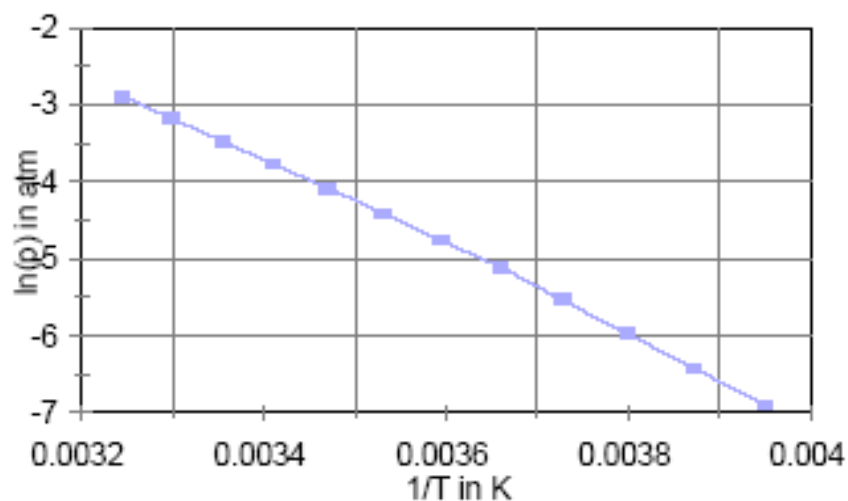
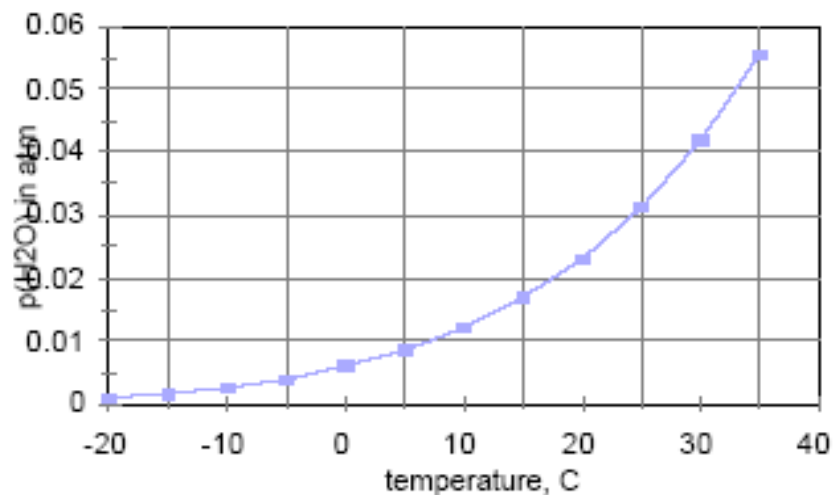


- $\text{H}_2\text{O}$  ( $1.3 \times 10^{10}$  t) / ( $4.3 \times 10^{11}$  t/ yr) =  $3.0 \times 10^{-2}$  yr = 10 d

Definition: *Relative humidity*

- $P(\text{H}_2\text{O})$  expressed as a percent of the Saturation or Equilibrium Vapour Pressure for a given temperature
  - eg. 80% relative humidity at  $0^\circ\text{C}$  = 0.0048 atm
  - 80% relative humidity at  $25^\circ\text{C}$  = 0.025 atm

Vapour pressure of water as  $f(\text{temperature})$



### Question #1

Consider all the sulfur compounds in the troposphere, under steady state conditions. If the mixing ratio is 1 ppb by mass what is the mass of sulfur compounds in the troposphere.

(mass of troposphere =  $4 \times 10^{21}$  g)

Answer:

$$1 \text{ ppb} = 1 \times 10^{-9}$$

$$4 \times 10^{21} \text{ g} \times 1 \times 10^{-9} = 4 \times 10^{12} \text{ g}$$

If the total natural and anthropogenic production is equal to  $200 \times 10^{12}$  g per year, what would the residence time be assuming steady-state conditions?

$$\begin{aligned} \text{Answer: } \quad \tau &= 4 \times 10^{12} \text{ g} / 200 \times 10^{12} \text{ g per year} \\ &= 0.02 \text{ year, or about 1 week} \end{aligned}$$