How does Environmental Chemistry Differ from Laboratory Chemistry?

Environmental	**Laboratory**
• open	• open, closed, or isolated
• Dynamic T, P , V, n	• Controlled T, P , V, n
• Multiphase	• Few reactions
• Observable, monitoring	• Reproducible experiments
• Dynamic	• Often equilibrated
• Missing information	
• Mismatched information	

Implications of Dynamic T and P

- Nonequilibrium
  - Constant changes of mass within volume
  - Barometric Changes
  - Air quality episodes
  - Meteorological Transport
  - Biological processes
  - Interfacial transport
  - Industrial Processes

Timescales of Environmental Processes

- Vary widely
    - Diurnal variation of solar radiation
    - Clouds, Fogs have a timescale of hours
    - Dissolution can take microseconds to hours
    - Phase transitions can take hours to weeks
    - Photolysis can take microseconds to hours
    - Temperature changes (daily, seasonal)

How Environmental Chemistry Connects to Other Areas of Chemistry

- General Chemistry
    - Prerequisite to this course

- Physical Chemistry
    - Thermodynamics
    - Kinetics
    - Photochemistry
    - Phase Transitions

- Organic Chemistry
    - Volatile organic carbon
    - Humus in soils
- Inorganic Chemistry
    - Metals
    - Chelation
    - Complexation
    - Speciation
- Biological Chemistry
    - Toxicity
    - Biodegradation
- Analytical Chemistry
    - Qualitative and quantitative analysis
    - Monitoring
    - Remediation
- Toxicology
    - Remediation
    - Toxicity
    - Pesticides, Herbicides, and Alternatives

Units for Environmental Chemistry

- Solutions
    - Molarity - moles/L solution
    - Molality - moles/kg solution
    - Normality - equivalents/L solution (context determines "equivalents")
    - Mole fraction
    - ppm - parts per million or mg/L
- Gas Phase
    - moles/L
    - moles/cm^3
    - molecules/cm^3
    - partial pressure expressed in atmospheres, torr, mm Hg, bars, or Pascals
    - mole fraction
    - ppm - parts per million

A Closer Look at ppm

- Defined differently in gas and aqueous phase
- In the **aqueous phase** 1 ppm is defined as 1 mg/L
  - Sometimes this is denoted as 1 ppm w/v (weight per volume)
  - 1 ppm w/w (weight per weight) is 1 mg/kg. (Recall that 1 L of water has a mass of 1 kg).
- In the **gas phase** 1 ppm can be considered as a mole fraction of 10^{-6}.

  $$1 \text{ ppm} = \frac{n_i}{n_{tot}} = 10^{-6}$$

  where n_i is the number of moles of the species of interest and n_{tot} is the total moles of gas in the system.
  - Note that this definition does not require constant T and P conditions.
  - At pressures typical of atmospheric pressure, the ideal gas law works reasonably well. Therefore:

    $$PV = nRT$$

$$P_i V = n_i RT$$
$$P_{tot} V = n_{tot} RT$$

and

$$1 \text{ ppm} = \frac{P_i}{P_{tot}} = 10^{-6}$$

Calculations involving ppm

- Aqueous phase examples:
  - Consider an isotonic saline solution with a concentration of 0.9 % w/v NaCl:

$$\frac{0.9 \text{ g NaCl}}{100 \text{ mL H}_2\text{O}}$$
$$= \frac{0.9 \text{ g} \times \ 1000 \text{ mg} \times \ 1000 \text{ mL}}{100 \text{ mL} \times 1 \text{ g} \times \ 1 \text{ L}}$$
$$= 9000 \text{ ppm}$$

  - Consider 0.1 M NH_3:

$$\frac{0.1 \text{ moles NH}_3}{1 \text{ L}} \times \frac{17\text{g NH}_3}{1 \text{ moles NH}_3} \times \frac{10^3 \text{ mg NH}_3}{1 \text{ g NH}_3}$$
$$= 1.7 \times 10^3 \text{ mg NH}_3/\text{L} = 1700 \text{ ppm}$$

  - 5 ppm ClO_2 solution:

    $$\frac{5 \text{ mg ClO}_2}{1 \text{ L}} = 5 \times 10^{-3} \text{g ClO}_2/\text{L}$$

    $$\frac{5 \times 10^{-3} \text{ g ClO}_2}{\text{L}} \times \frac{1 \text{ mol ClO}_2}{67.5 \text{ g}}$$

    $$= 7.4 \times 10^{-5} \text{ M ClO}_2$$

- Gas phase examples:
  - H_2S at 1ppb
  - To convert to a pressure or a density requires information about total pressure and temperature.
  - If values are not given, reasonable values may be assumed.
  - In this case, assume:

    $$P_{tot} = 100.10 \text{ kPa; } T = 0.1°\text{C} = 273.35 \text{ K}$$

    Therefore:

    $$P(H_2S) = 10^{-9} \times 100.10 \text{ kPa}$$

    $$= 1.001 \times 10^{-7} \text{ kPa} = 1.001 \times 10^{-4} \text{ Pa}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.001 \times 10^{-4}\ \text{Pa}}{8.31441\ \text{J mol}^{-1}\ \text{K}^{-1} \times 273.25\ \text{K}}$$

$$= 4.41 \times 10^{-11}\ \text{mol m}^{-3}$$

$$= 2.65 \times 10^{13}\ \text{molec m}^{-3}$$

$$= 2.65 \times 10^{7}\ \text{molec cm}^{-3}$$

Note that:

$$1\ \text{atm} = 101.325\ \text{kPa} = 101325\ \text{Pa}$$

$$1\ \text{m}^3 = 10^3\ \text{L} = 10^6\ \text{cm}^3$$

- O_3 at 0.2 mg m^{-3}

$$\frac{0.2\ \text{mg}}{1\ \text{m}^3} \times \frac{1\ \text{mol}}{48\ \text{g}} \times \frac{10^{-3}\ \text{g}}{1\ \text{mg}} = 4.167 \times 10^{-3}\ \text{mol/m}^3$$

$$P = \frac{n}{V}RT = 4.167 \times 10^{-3}\ \text{mol/m}^3$$

$$\times 8.31441\ \text{J mol}^{-1}\ \text{K}^{-1} \times 293\ \text{K}$$

$$= 10.15\ \text{Pa}$$

$$P_{tot} = 1\ \text{atm} = 101.325\ \text{kPa}$$

$$\frac{P}{P_{tot}} = \frac{10.15\ \text{Pa}}{101.325 \times 10^3\ \text{Pa}} = 1 \times 10^{-4}$$

$$1 \times 10^{-4} \times \frac{1\ \text{ppm}}{10^{-6}} = 100\ \text{ppm}$$

Indoor Air Quality

(See Chapter 4 of Bunce)

- Consideration of indoor air quality involves a (relatively) simple scenario that illustrates some of the key concepts of environmental chemistry.
- This also uses a bit of calculus which we will use more than once.

$$\int_{x_1}^{x_2} \frac{dx}{x} = \ln x \Big|_{x_1}^{x_2} = \ln x_2 - \ln x_1 = \ln \frac{x_2}{x_1}$$

  - In indoor air quality problems this can appear as an integral of this form:

$$\int_{x_1}^{x_2} \frac{dx}{a - x}$$

    where x_1 and x_2 are, respectively, the initial and final concentrations.

  - This integral may be evaluated by the substitution method.
  - Let:

$$u = a - x;\ du = -dx$$

$$u_1 = a - x_1;\ u_2 = a - x_2$$

  - Thus:

$$\begin{aligned}\int_{x_1}^{x_2} \frac{dx}{a-x} &= -\int_{u_1}^{u_2} \frac{du}{u} \\ &= -\ln u\Big|_{u_1}^{u_2} = -\ln\frac{u_2}{u_1} = \ln\frac{u_1}{u_2} \\ &= \ln\frac{a-x_1}{a-x_2}\end{aligned}$$

- What are the characteristics of an indoor air situation?
  - Fixed volume
  - Relatively constant $T,\ V,\ P$.
  - The role of chemical reactions are usually minor.
- Sources of substances in indoor air:
  - Emissions
  - Respiration
  - Air Handling System
  - Infiltration
  - Combustion
  - Smoking

- Sinks of substances in indoor air:
    - Surfaces
    - Respiration
    - Air handling system (filters, traps)
    - Combustion processes
    - Industrial processes
- Indoor air pollution and indoor air quality
    - Have become issues over the past 30 years.
    - Oil crisis of the mid-1970's led to a sharp increase in the prices of petrochemical products.
    - The "first world" nations consume more oil than they produce.
    - Energy conservation and efficiency became major public issues.
    - In buildings, efforts to control heating costs focussed on reducing the number of air changes per hour.
    - Indoor air contaminants are often emitted at a constant rate.

  - With fewer air changes, these contaminants do not get diluted and may rise to concentrations in excess of safe levels.

What is Safe?

- Often if is difficult to give a clear answer
  - There is a wide variability of human response and sensitivities.
  - Toxic effects may not be immediately apparent.
  - Response may be nonlinear.
  - There may be synergisms among contaminants.

Threshold Limit Values (TLV)

- Used in many jurisdictions to provide guidance for permissible exposure to substances in the workplace.
  - Usually included in Material Safety Data Sheets (MSDS).
  - Represents an assessment of the safe level of exposure

- TLVs are based on:
  - Experience
  - Biological Trials
  - Human Trials
  - Toxicology

- TLV's represent guidelines, not firm limits, because of issues such as:
  - variablity of human response
  - modes of toxicity
  - nonlinear dose response

- Substances may have more than one TLV depending on type of exposure

- Time weighted average TLV (also known as TWA) based on an eight hour day, five day week.

$$\frac{\sum \mathrm{time_i\ c_i}}{\sum \mathrm{time_i}}$$

- Short term exposure limit TLV

- In the absence of other information, one-fifth of the short term TLV is used as the long term TLV.
- Ceiling TLV should not be exceeded at any time
- Cumulative exposures sometimes need to be considered. (i.e. exposure level × exposure time).
  - Usually tracked with a badge monitor.

Modes of Toxicity

- Irritants
- Carcinogens
- Asphyxiants (Displace O_2)
- Hemoglobin Binding
- Narcotic
- Neurotoxin
- Oxidants
- Reactive Compounds
- Often there is exposure to more than one substance at a time

  - Modes of toxicity of each substance must be considered to determine whether the TLV is exceeded.
- The effects of toxic substances may be:
  - Additive
  - Synergistic
  - Antagonistic
  - Independent
- Substances with dissimilar modes of toxicity
  - CO (binds hemoglobin) and HCl (irritant)
  - diethyl ether (narcotic) and toluenediisocyanate (reacts with OH and NH_2 groups)
  - O_3 (oxidant) and Hg (neurotoxin)
  - To determine whether TLV is exceeded, consider each the exposure of each substance relative to its TLV separately.
- Substances with similar modes of toxicity
  - Usually chemically similar substances have similar modes of toxicity.
  - HCl and HBr are both irritants.

  - Acetone and ethyl acetate are both narcotic solvents.
  - Ammonia and ethylamine are both bases.
  - CO and HCN both interfere with oxygen uptake by tissues.
  - To determine whether TLV is exceeded, compare each exposure level to its TLV, i.e.

    $$\frac{c_i}{\mathrm{TLV}_i}$$

    then sum

    $$\sum \frac{c_i}{\mathrm{TLV}_i}$$

    If the sum exceeds 1, then the exposure is unsafe.

- Many well-defined industrial mixtures have established effective TLVs.
  - Consider the fraction f_i of each component in the defined mixture. The effective TLV is:

    $$\mathrm{TLV(mixture)} = \frac{1}{\sum \frac{f_i}{\mathrm{TLV_i}}}$$

Synergism

- Toxic effect of combined exposure is greater than predicted on the basis of individual exposures.
- Examples of synergism frequently found in pharmacology.
  - One drug enhances the effect of another.
  - Many chemotheraphy protocols are based on synergism.

Antagonism

- Toxic effect of combined exposure is less than predicted on the basis of individual exposures.
- Also may be used to describe substances that react with one another, in which case, one may need to be concerned with the outcome of the reaction.
  - Is heat released?
  - What are the products?
- Many examples in pharmacology:

  - Fe^{2+} and Vitamin C can bind each other and be excreted.
  - Metal antidotes are often chelation agents (for example a raw egg).
  - Many poison control strategies involve antagonisms.
- Often there is not information available on whether various combinations of environmental contaminants are synergistic or antagonistic.

Monitoring Exposure

- Raises many issues involving human and technological factors.
- What does the monitoring result mean in light of:
  - Individual variations in sensitivities
  - Allergies
  - Metabolism
  - Medications
  - Individual health status

- Exposure away from the workplace:
    - Solvents
    - Paints
    - Adhesives
    - Particulates
- Privacy issues
    - Blood tests
    - Urine samples
    - Multiple sources of metabolites
    - Unauthorized use of samples (AIDS testing, DNA analysis, forensic matching, drugs and alcohol).

Calculations about Air Quality

- Useful in:
    - assessing safe conditions
    - designing mitigation strategies
    - assessing impact of HVAC (heating, ventilation, and air conditioning) decisions.

- Introduces a number of concepts that can be carried into other contexts.
- Information involved includes:
  - Ambient Level
  - Source terms
  - Sink terms
- Consider first a steady-state situation. (We will later consider a situation where things are changing).
- In a steady state situation, the concentration is constant:

  $$\frac{d[c_i]}{dt} = 0$$

  where $[c_i]$ is the concentration of the substance of interest in the units of interest such as ppm or mg/m^3.
  - In a steady-state, the rate of appearance is balanced by the rate of disappearance. (See 4.2 p 114 in Bunce.)
- What affects the rate of appearance?
  - i.e. What are the sources?

  - Indoor emissions
  - Outdoor concentrations brought in with air changes.
- What affects the rate of disappearance?
  - i.e. What are the sinks?
  - Air changes
  - Filters, air cleaners
- A Closer Look at Indoor Sources
  - Emission rate in units such as mg h^{-1}.
  - Mixing Volume (usually room size) in units such as m^3.
  - These are combined to give a source term of the form:

$$\frac{R}{V} \quad \frac{\mathrm{mg\ h}^{-1}}{\mathrm{m}^3}$$

- The air change rate, k, is usually given as air changes per hour or ach.
  - k has units such as h^{-1}.
  - The volume of air associated with an air change is the mixing volume, V.

- Outdoor air is brought in with each air change
    - May contain the substance of interest with concentration $[c_o]$
- Air changes give rise to source and sink terms:
    - Source term is $k[c_o]$.
    - Sink term is $k[c_i]$.
- At a steady state, the source terms equal the sink terms:

$$\frac{R}{V} + k[c_o] = k[c_i]$$

    - Must ensure that everything is in compatible units for calculations.
    - It is possible to rearrange this equation algebraically:

$$R + k[c_o]V = k[c_i]V$$

$$[c_i] = \frac{R}{kV} + [c_o]$$

    - This equation is valid **only** for steady state conditions.

- Steady state calculations are often of interest in industrial hygiene situations is the relationship between $[c_i]$ and k.
- Consider the case where $[c_o] = 0$
  - The equation becomes:

    $$[c_i] = \frac{R}{kV}$$

    and the indoor concentration is inversely proportional to the air change rate, k.
  - Minimum k can be determined for the desired maximum value of $[c_i]$.
  - The value of $[c_i]$ approaches 0 asymptotically.
- Consider the case where $[c_o] \neq 0$
  - The equation of interest is:

    $$[c_i] = \frac{R}{kV} + [c_o]$$

    Graphically this corresponds to shifting the $[c_i]$ axis by $[c_o]$.
  - $[c_i]$ can never be less than $[c_o]$.
  - The value of $[c_i]$ approaches $[c_o]$ asymptotically.

Nonsteady State Situations

- Examples:
  - Spill - sudden increase in R.
  - Fumehood - variable R and k.
  - Opening a door or window - discontinuous change in k.
- Must use equation in differential form:

$$\frac{d[c_i]}{dt} = \frac{R}{V} + k[c_o] - k[c_i]$$

  - If the source terms are less than the sink terms, then
  $$\frac{d[c_i]}{dt} < 0$$
  and $[c_i]$ will decrease with time.
  - If the source terms are greater than the sink terms, then
  $$\frac{d[c_i]}{dt} > 0$$
  and $[c_i]$ will increase with time.
  - For example, during an outdoor pollution episode, the $[c_i]$ will increase to the value of $[c_o]$.

- This equation has an exact analytic solution if R, V , $[c_o]$ and k are constant.
- Step 1: Separate variables.

$$\frac{d[c_i]}{\frac{R}{V} + k[c_o] - k[c_i]} = dt$$

$$\int_{[c_i(0)]}^{[c_i(t)]} \frac{d[c_i]}{\frac{R}{V} + k[c_o] - k[c_i]} = \int_0^t dt$$

- Step 2: Rearrange to isolate integration variable in denominator.

$$\int_{[c_i(0)]}^{[c_i(t)]} \frac{d[c_i]}{\frac{R}{kV} + [c_o] - [c_i]} = \int_0^t k\ dt$$

- Step 3: Recognize form of integral and integrate by substitution.

$$\int_{x_1}^{x_2} \frac{dx}{a-x} = -\ln(a-x)\Big|_{x_1}^{x_2} = \ln\frac{a-x_1}{a-x_2}$$

where

$$x = [c_i]; \quad a = \frac{R}{kV} + [c_o]$$

$$x_1 = [c_i(0)]; \quad x_2 = [c_i(t)]$$

- Step 4: Back substitute original variables into integrated form.

$$\ln \frac{\frac{R}{kV} + [c_o] - [c_i(0)]}{\frac{R}{kV} + [c_o] - [c_i(t)]} = k\ t$$

or:

$$-\frac{1}{k} \ln \frac{\frac{R}{kV} + [c_o] - [c_i(t)]}{\frac{R}{kV} + [c_o] - [c_i(0)]} = t$$

- From this, can evaluate how long it takes for an indoor air contaminant to decrease (or increase) from one level to another.
  - Comparison of the initial values of the sink and source terms permit assessment of direction of change.
- Isolate $[c_i(t)]$ to obtain another useful form of the equation:
  - Start with:

$$\ln \frac{\frac{R}{kV} + [c_o] - [c_i(t)]}{\frac{R}{kV} + [c_o] - [c_i(0)]} = -k\ t$$

Rearrange to:

$$\frac{\frac{R}{kV} + [c_o] - [c_i(t)]}{\frac{R}{kV} + [c_o] - [c_i(0)]} = e^{-kt}$$

$$\frac{R}{kV} + [c_o] - [c_i(t)] = e^{-kt}\left(\frac{R}{kV} + [c_o] - [c_i(0)]\right)$$

$$\frac{R}{kV} + [c_o] - e^{-kt}\left(\frac{R}{kV} + [c_o] - [c_i(0)]\right) = [c_i(t)]$$

- As $t \rightarrow \infty$, $e^{-kt} \rightarrow 0$ and we approach the steady state.
- If $\frac{R}{kV} + [c_o]$ are zero the equation reduces to:

  $$[c_i(t)] = [c_i(0)]e^{-kt}$$

  which is the equation for first order kinetics.

Lifetimes

- The lifetime or residence time is defined as:

  $$\tau = \frac{\text{Amount in Reservoir}}{\text{Source or Sink Term}}$$

  - In terms of sinks, the lifetime of the indoor air contaminant becomes:

    $$\frac{[c_i t]}{[kc_i(t)]} = \frac{1}{k} = \tau$$

- The half life is defined as the time required for the concentraion of the substance to drop to one half of the initial value.
    - For a first order reaction, the half life is:

$$\tau_{1/2} = \frac{\ln(2)}{k} = 0.693\tau$$

Example Calculation

- Indoor Formaldehyde
- Building materials have a typical emission rate of 10^{-6} g HCHO per g building materials per day.
- Assume 200 kg building materials in room.
- Preferred time units will be taken as hours.
- Determination of R, the indoor emission rate.

$$\frac{10^{-6}\text{g HCHO}}{\text{g material day}} \times 200 \text{ kg material} \times \frac{10^{-3}\text{g}}{1 \text{ kg}}$$

$$\times \frac{1 \text{ day}}{24 \text{ h}} = 8.3 \times 10^{-3} \text{ g h}^{-1}$$

- One air change per hour gives $k = 1$ h^{-1}.

- A typical room dimension is 14 feet by 20 feet by 8 feet.

$$V = 14 \text{ ft} \times 20 \text{ ft} \times 8 \text{ ft}$$

$$= 4.27 \text{ m} \times 6.10 \text{ m} \times 2.44 \text{ m}$$

$$= 63.43 \text{ m}^3$$

- The outdoor concentration of formaldehyde $[c_o]$ depends on the surroundings.
    - Clean air has 2 - 10 ppb.
    - Urban air has 10 - 20 ppb.
    - Polluted air has 20 -75 ppb.
    - We will assume urban outdoor air at 20 ppb.
- The desirable indoor level $[c_i]$ will be assessed with respect to:
    - Olfactory threshold of 100 - 200 ppb.
    - The TLV of 1.5 mg m^{-3}.
- Select units of $[c_i]$
    - For this example use ppb.

- Carry out necessary unit conversion prior to evalulating:

$$[c_i] = [c_o] + \frac{R}{kV}$$

  - In units given so far:

$$\frac{R}{kV} = \frac{8.3 \times 10^{-3}\ \mathrm{g\ h^{-1}}}{1\ \mathrm{h^{-1}} \cdot 63.43\ \mathrm{m^3}} = 1.31 \times 10^{-4}\ \mathrm{g\ m^{-3}}$$

  - To determine ppb, need to assume a temperature and pressure, therefore assume:

$$P_{tot} = 1\ \mathrm{atm} = 101.325\ \mathrm{kPa} = 1.01325 \times 10^5\ \mathrm{Pa}$$

$$T = 293\ \mathrm{K}$$

  - Molar mass of HCHO is 30 g $\mathrm{mol^{-1}}$

$$P_{HCHO} = \frac{n}{V}RT = \frac{1.31 \times 10^{-4}\ \mathrm{g}}{\mathrm{m^3}} \cdot \frac{1\ \mathrm{mol}}{30\ \mathrm{g}}$$

$$\cdot 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}} \cdot 293\ \mathrm{K} = 1.07 \times 10^{-2}\ \mathrm{Pa}$$

$$\frac{P_{HCHO}}{P_{tot}} = \frac{1.07 \times 10^{-2}\ \mathrm{Pa}}{1.01325 \times 10^5\ \mathrm{Pa}} = 1.05 \times 10^{-7}$$

$$1.05 \times 10^{-7} \cdot \frac{10^9\ \mathrm{ppb}}{1} = 105\ \mathrm{ppb\ HCHO}$$

- Under these assumptions, evaluate $[c_i]$

$$[c_i] = 20\ \text{ppb} + 105\ \text{ppb} = 125\ \text{ppb}$$

- Is the TLV (1.5 mg m^{-3}) exceeded?
  - Need to get $[c_i]$ and TLV into the same units, so convert $[c_i]$:

$$125\ \text{ppb} \cdot \frac{10^{-9}}{1\ \text{ppb}} \cdot 1.01325 \times 10^{5}\ \text{Pa} = 1.27 \times 10^{-2}\ \text{Pa}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.27 \times 10^{-2}}{8.31441\ \text{J mol}^{-1}\ \text{K}^{-1} \cdot 293\ \text{K}}$$

$$= 5.20 \times 10^{-6}\ \text{mol m}^{-3}$$

$$5.20 \times 10^{-6}\ \text{mol m}^{-3} \cdot \frac{30\ \text{g}}{1\ \text{mol}} \cdot \frac{10^{3}\ \text{mg}}{1\ \text{g}} = 0.16\ \text{mg m}^{-3}$$

- The lower limit of the olfactory threshold (100 - 200 ppb) is exceeded, so some people may be able to smell it.
  - Therefore it is desirable to increase ventilation.
  - Suppose the air change rate is doubled. How long will it take for $[c_i]$ to drop to 80 ppb?

- Will use:

$$t = -\frac{1}{k} \ln \left[\frac{\frac{R}{kV} + [c_o] - [c_i(t)]}{\frac{R}{kV} + [c_o] - [c_i(0)]} \right]$$

- The starting condition is the "old" steady state concentration

$$[c_i(0)] = 125 \text{ ppb}$$

- Since we have doubled k, the $\frac{R}{kV}$ has half of its old value:

$$\frac{R}{kV} = \frac{105}{2} \text{ ppb} = 52.5 \text{ ppb}$$

- Now solve for t

$$t = -\frac{1}{2 \text{ h}^{-1}} \ln \frac{(52.5 + 20 - 80) \text{ ppb}}{(52.5 + 20 - 125) \text{ ppb}}$$

$$= -\frac{1}{2 \text{ h}^{-1}} \ln \frac{-7.5}{-52.5} = -\frac{1}{2 \text{ h}^{-1}} \ln .143$$

$$= -\frac{1}{2 \text{ h}^{-1}} \cdot -1.946 = .973 \text{ h}$$

- What would have been the concentration after 15 minutes?
  - Use equation for $[c_i(t)]$ in the form:

$$[c_i(t)] = [c_i(0)]e^{-kt} + \left(\frac{R}{kV} + [c_o]\right)\left(1 - e^{-kt}\right)$$

  - 15 minutes is 0.25 h, therefore $kt = 0.5$

$$[c_i] = 125 \text{ ppb } \cdot e^{-0.5} + 72.5 \text{ ppb } \cdot \left(1 - e^{-0.5}\right)$$
$$[c_i] = 104.57 \text{ ppb}$$

- Possible to construct a curve of concentration against time.

Time(h)	**Concentration (ppb) Formaldehyde**
0.	125
0.25	104.34
0.5	91.81
0.75	84.21
1.0	79.60
1.5	75.11
2.0	73.46
3.0	72.63
4.0	72.51

- How do we interpret this with respect to a lifetime?

$$[c_i(t)] = [c_i(0)]e^{-kt} + \left(\frac{R}{kV} + [c_o]\right)\left(1 - e^{-kt}\right)$$

  - Define lifetime with respect to sink term:

$$\tau = \frac{1}{k}$$

t	e^{-kt}	$1 - e^{-kt}$
τ	0.368	0.632
2τ	0.135	0.865
3τ	0.050	0.950

  - After one lifetime, the ambient level $[c_i]$ is 0.368 of the original value plus 0.632 of the steady state value.
  - After two lifetimes, the ambient level $[c_i]$ is 0.135 of the original value plus 0.865 of the steady state value.
  - After three lifetimes, the ambient level $[c_i]$ is 0.05 of the original value plus 0.950 of the steady state value.

Particulates and Indoor Air Quality (Size Matters!)

- The size of a particle determines how far it can penetrate into the lungs.
- Example: Asbestos
- One form of asbestos is chrysotile has serpentine fibres and was once widely used as spray-on insulation for pipes.
  - A chrysotile fibre is about 10 μm and can be trapped in the upper airways.
- Another form of asbestos is crocidolite or blue asbestos
  - This form has rod-like particles that are approximately 1 μm $\times$ 5 μm.
  - A particle this size can penetrate deep into the lungs, into the gas-exchange region and into the pleural cavity.
- Exposure to crocidolite is associated with mesothelioma, a form of cancer.
  - Latency period $\approx$ 20 years.
  - Caused by the mechanical properties of crocidolite.

  - Removal of asbestos from existing buildings is problematic in that the process of removal may lead to more exposure than if the asbestos were left undisturbed.
  - Current practice is to remove asbestos only if a building is being renovated or demolished.
  - The use of asbestos-containing building materials has been phased out since 1970.
  - Worker's compensation organizations in most jurisdictions recognize mesothelioma as an occupational disease.
  - Many companies have filed for bankruptcy protection to limit legal liability for claims. Some of these companies are: Johns Manville, Babcock & Wilcox, Pittsburgh Corning, Owens-Corning Fibreglas, Armstrong World Industries, Kaiser Aluminum.
- Other hazardous industrial particulates include:
  - Coal dust (Black lung)
  - Grain dust (Emphysema)
  - Silica dust (Silicosis)
  - Cement dust (which is alkaline)

Smoke, Ash, and Exhaust

- Impact is connected with particle size:
    - $> 10\ \mu m$ can be trapped by nose hairs and mucous.
    - $< 10\ \mu m$ can reach upper lungs and causes an inflammatory response.
    - $< 2.5\ \mu m$ can reach the alveolar region and is implicated in the onset of asthma.
- Like other particulates, smoke, ash, and exhaust can have both chemical and mechanical effects.
    - The smaller the particle, the less likely it is to settle and the further it will be transported.
- The chemical composition of the smoke depends on its origin and history.
- Smoke from woodstoves and cigarettes contain benzopyrene (BAP) and other polycylic aromatic hydrocarbons (PAH), both of which are regarded as carcinogenic.
    - PAH are also components of soot.
    - Production of PAHs are associated with inefficient combustion.

- Typical levels:
    - Indoor “clean” air 20-60 μg m^{-3}.
    - Smoking area 100-700 μg m^{-3} of “second hand smoke”. (1 cigarette produces about 5 $\times 10^{12}$ particles and can double the particulate in indoor air.)

Radon

- Radon is a noble gas with atomic number 86.
- Commonly found isotope is $^{222}_{86}$Rn.
    - Formed from the radioactive decay of radium, $^{226}_{88}$Ra.
    - Radon is radioactive with a half-life of 3.8 days.
- Since Rn is a noble gas, it is chemically nonreactive and can penetrate deep into the lungs.
    - If the Rn atom undergoes radioactive decay while it is in the lungs, then tissue damage may result.
- Radon is heavier than air, so it settles to the basement of a building.

  - Average molar mass of air is ≈ 29 g mol^{-1}.
  - Average molar mass of Rn is 222 g mol^{-1}.
- Density of air can be found from the ideal gas law.

$$\frac{n}{V} = \frac{P}{RT} = \frac{101325 \ \ \text{Pa}}{8.31441 \text{ J mol}^{-1} \text{ K}^{-1} \ \ \cdot 293 \text{ K}}$$

$$= 41.6 \text{ mol m}^{-3} = 0.0416 \text{ mol L}$$

$$0.0416 \text{ mol L} \cdot 29 \text{ g mol}^{-1} = 1.20 \text{ g L}^{-1}$$

- The density of radon is:

$$\frac{222}{29} \cdot 1.20 \text{ g L}^{-1} = 9.2 \text{ g L}^{-1}$$

therefore radon will sink in air.

Radioactive Decay Sequence

- A radioactive event changes the number of nucleons in a nucleus by giving off a particle.
  - An α particle is a He^{2+} and its nucleons are two protons and two neutrons.
  - A β particle is an electron

Reaction	Energy (MeV)	Half-life
${}^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + \alpha$	4.8	1600 yr
${}^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + \alpha$	5.6	3.8 d
${}^{218}_{84}\mathrm{Po} \rightarrow {}^{214}_{82}\mathrm{Pb} + \alpha$	6.1	3.1 d
${}^{214}_{82}\mathrm{Pb} \rightarrow {}^{214}_{83}\mathrm{Bi} + \beta$	1.0	27 min
${}^{214}_{83}\mathrm{Bi} \rightarrow {}^{214}_{84}\mathrm{Po} + \beta$	3.3	20 min
${}^{214}_{84}\mathrm{Po} \rightarrow {}^{210}_{82}\mathrm{Pb} + \alpha$	7.8	0.0002 s
${}^{214}_{83}\mathrm{Bi} \rightarrow {}^{210}_{81}\mathrm{Tl} + \alpha$	5.6	20 min
${}^{210}_{81}\mathrm{Tl} \rightarrow {}^{210}_{82}\mathrm{Pb} + \beta$	5.5	1.3 min

- ${}^{210}_{82}\mathrm{Pb}$ has a half-life of 21 years, which is longer than the residence time of indoor air.
- The decay products of ${}^{222}_{86}\mathrm{Rn}$ are metallic elements and are known as radon daughters.
- If there is a local source of ${}^{226}_{88}\mathrm{Ra}$, ${}^{222}_{86}\mathrm{Rn}$ is formed.

- $^{222}_{86}$Rn can decay, releasing $^{218}_{84}$Po:
    - which is produced as a metal ion
    - which promptly forms the corresponding oxide,
    - which in turn is scavenged by the bronchial tissue.
- $^{218}_{84}$Po, now sequestered in bronchial tissue, undergoes further decay, each step of which gives off highly energetic α and β particles.
- The decay sequence from $^{222}_{86}$Rn to $^{210}_{82}$Pb releases:
    - Three α particles
    - Two β particles
    - 23.8 Mev of energy
- An α particle is a bare He nucleus. It will ionize biomolecules within 60 μ m, which may include stem cells.
- A β particle is an electron.
- Radon has become an indoor air quality issue due to energy conservation matters.

- In the 1930's radon was implicated in death of miners due to cancer.
- In the late 1940's there was rapid postwar expansion of urban areas into suburbs.
  - Construction took place on "brown" land reclaimed from industrial sites.
  - Mine tailings were used as fill.
- In the 1950's, the role of radon daughters was recognized.
- In the 1960's, the baby boom crests.
  - Recreation rooms become fashionable.
  - Basements are renovated into living space.
- In the 1970's the Energy Crisis hit.
  - Ventilation rates reduced
  - Homes retrofitted for energy efficiency.
- In the 1980's, mortgage rates are as high as 19%.
  - Basement suites increase.
- In Prince George, Harwin School had a radon problem which was resolved by increased ventilation.

- The TLV for radon is 0.
    - There is no level at which radon is regarded as safe.
- Various jurisdictions have “action levels” above which mitigation must be implemented.

Jurisdiction	Level
EPA (USA)	4 picocuries L^{-1}
Canada	20 picocuries L^{-1}
UK	400 Bq m^{-3}

    - 1 Becquerel (Bq) is one disintegration per second.
    - 1 curie(Ci) = 3.7×10^{10} Bq
    - 1 picocurie = 10^{-12} curie.
- The extent of danger due to radon exposure is a matter of some controversy.
- The lung cancer risk due to exposure for 70 years for 75% of the time at
    - 4 pCi L^{-1} is equivalent to 200 chest xrays per year.
    - 20 pCi L^{-1} is equivalent to 2 packs of cigarettes a day.

- Epidemiological studies suggest that exposure to 1000 Bq m^{-3} for a lifetime increases the risk of lung cancer by 5%.
    - There is an issue of separating the effects of radon from those of exposure to dust and cigarette smoke.
    - Also an issue of determining actual exposure in a domestic setting.
- Sources of radon are gas infiltration from soil surrounding foundations and from ground water.
- Two methods are often used for monitoring radon over time.
    - Activated charcoal traps radon daughters. After a fixed time the filter is analyzed for the presence of ${}^{210}_{82}$Pb.

$$\text{Time} \times \text{Efficiency} \times \text{number of } {}^{210}_{82}\text{Pb atoms}$$

$$= \text{number of decays}$$

- Track etch monitors records the tracks of α particles on a film. The number of tracks after a certain time (several months) can be related to the number of decay events.

Mitigation Strategies for Radon Exposure

- The only solution is increased ventilation.
    - In retrofits of older buildings, increased ventilation can increase energy costs unless heat exchangers are used.
    - In new construction, a vent is laid under the foundation. This vents to the surroundings the radon coming from the soil before it has a chance to penetrate the foundation.
- Sealants are not effective.
- If the residential area is built on soil with a high ${}^{226}_{88}\mathrm{Ra}$ content, soil may have to be removed.
    - McClure Crescent is in a Scarborough Ontario subdivision built on the site of a second World War aircraft instrumentation manufacturing plant.
    - Radium paint used on gauges and dials leading to extremely high Rn exposure.
    - Resolution eventually took the form of soil replacement and buyouts.

Structure of the Atmosphere

- The structure of the atmosphere is a function of
  - Gravity
  - Composition
  - Radiation
- The density of the atmosphere decreases approximately exponentially.
- The composition of the atmosphere is influenced by gravitational fractionation.
  - The heavier gases sink.
  - The lighter gases can be lost to outer space.
- If there are no sources or sinks of chemical species (i.e. no reactions or emissions), the composition of the atmosphere is controlled by diffusion and mixing due to fluid motions (i.e. meteorology).
- If equilibrium were to be attained, the atmosphere would become stratified by composition.

THE ATMOSPHERE IS NOT AT EQUILIBRIUM!

- The atmosphere is not at equilibrium from a thermodynamic perspective because
  - It is an open system and mass and energy are transferred.
- Mass transfer takes the form of:
  - Terrestial emissions.
  - Loss to the interplanetary medium.
  - Chemical reactions in the atmosphere.
  - Deposition
- Sources of energy:
  - The Sun (approximately a blackbody at 5780 K).
  - Geothermal (approximately a blackbody at 255 K).
- Sinks of energy:
  - Radiative loss to the interplanetary medium.
- The stratification of the atmosphere is the result of the interaction between radiative energy and composition.

Radiation

- Light is quantized.
    - A quantum of light is a photon.
- The energy of a photon may be related to
    - ν, the frequency of light:

$$E = h\nu$$

    - λ, the wavelength of light:

$$E = \frac{hc}{\lambda}$$

- Many natural sources of radiation may be characterized as blackbody radiators which emit photons that have a distribution over wavelength (or frequency) that is characteristic of the temperature of the blackbody.
- In terms of wavelength the distribution function, ρ, the energy density per wavelength is:

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

- In terms of frequency the distribution function, ρ, the energy density per frequency is:

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

- For chemical reactions, the number density of the photons is more important than the energy density.
  - To transform the energy density distribution function into a photon density distribution function, divide the energy density function by the energy of a photon.

$$\rho_\phi(\lambda, T) = \frac{\rho(\lambda, T)}{hc/\lambda} = \frac{8\pi}{\lambda^4} \frac{1}{e^{hc/\lambda kT} - 1}$$

$$\rho_\phi(\nu, T) = \frac{\rho(\nu, T)}{h\nu} = \frac{8\pi\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

- From the number density distribution function for photons, the number of photons with energy in a particular energy range may be determined.
  - This is essential to the determination of rates of photochemical reactions.
- How photons can interact with a chemical entity such as an atom, a molecule, an ion or a radical is determined by the quantization of the energy levels for
  - Electronic energy
  - Vibrational energy
  - Rotational energy

- If a photon's energy matches an energy gap between quantized energy levels (and certain symmetry conditions required by quantum mechanics) then there is a probability that the photon will be able to be absorbed by that molecule.
    - The result is an excited chemical species that must do something with the extra energy.
- The fate of a photon's energy can:
    - cause a molecule to fall apart or photodissociate.
    - cause a chemical species to eject an electron or photoionize.
    - cause a molecule to rearrange or photoisomerize.
    - cause a chemical species to redistribute the energy internally. (Sunscreens do this).
    - cause a chemical species to transfer energy to other molecules. (This is how microwave ovens work. In the atmosphere, this is part of the greenhouse effect.)
    - cause a chemical species to emit a photon of the same or lower energy (fluorescence

and phosphorescence). This is also part of the greenhouse effect.

- This provides a context from which the thermal structure of the atmosphere may be examined.
- Each layer of the atmosphere is separated by a thermal inversion.
- The thermosphere is regarded as that above 85 km with a pressure of less than 10−8 atm.
    - Exposed to the sun's full radiative flux of 1370 W m^{-2}, including wavelengths less than 200 nm.
    - A photon of 200 nm wavelength has an energy of:

$$E(\lambda = 200 \ \ \mathrm{nm}) = \frac{hc}{\lambda} =$$

$$\frac{6.626 \times 10^{-34} \ \mathrm{J \ s} \cdot 2.998 \times 10^{8} \ \mathrm{m \ s}^{-1}}{200 \times 10^{-9} \ \mathrm{m}} =$$

$$9.9324 \times 10^{-19} \ \mathrm{J \ photon}^{-1}$$

    - This could dissociate a molecule with a bond energy of:

$$9.9324 \times 10^{-19}\ \text{J molec}^{-1} \cdot 6.022 \times 10^{23}\ \text{molec mol}^{-1}$$

$$= 5.98 \times 10^{5}\ \text{J mol}^{-1} = 598\ \text{kJ mol}^{-1}$$

which includes most chemical bonds.

- Shorter wavelengths can dissociate or ionize chemical species:

$$N_2\ +\ h\nu\ \rightarrow 2N \quad \Delta H = 946\ \text{kJ mol}^{-1}$$

$$N\ \rightarrow\ N^{+}\ +\ e^{-} \quad \Delta H = 1400\ \text{kJ mol}^{-1}$$

$$O_2\ \rightarrow\ O_2^{+}\ e^{-} \quad \Delta H = 1160\ \text{kJ mol}^{-1}$$

  - Therefore the thermosphere is mostly atoms and ions.

- The top of the thermosphere is hot, because collisions are rare and energy transfer for excited chemical species is inefficient.

- As the altitude decreases, the thermosphere gets colder because fewer high energy photons are able to penetrate this far.

- At the mesopause (85 km altitude), the density of gas has increased to the point that collisional energy transfer can be effective in the redistribution energy of absorbed photons.

- In the mesophere (50-85 km altitude), the density continues to increase as altitude decreases.
  - Collisional energy transfer increases in efficiency as density increases.
  - Less energy is lost as photons.
  - More of the sun's energy is transferred to kinetic energy of the chemical species.
  - Ozone can play an important role in this.

	Δ H (kJ mol^{-1})
$O_2 + h\nu(\lambda < 240nm) \rightarrow 2O$	495 -E_{photon_1}
$O + O_2 + M \rightarrow O_3 + M$	-105
$O + O_3 \rightarrow O_2 + O_2$	-389
$O_3 + h\nu(\lambda < 325nm) \rightarrow O_2 + O$	105 - E_{photon_2}

- This is the Chapman cycle and gives the net reaction:

$$2O_3 + 3O + 3O_2 \rightarrow 2O_3 + 3O + 3O_2 - E_{photon_1} - E_{photon_2}$$

which has the net effect of converting photon energy to thermal energy.

- The mass of the mesophere is about two orders of magnitude greater than the mass of the thermosphere.
    - With sufficient density for efficient energy transfer, warm air will rise, cold air will sink and there will be efficient mixing.
- At the stratopause ($\sim$ 50 km) there is a temperature inversion.
    - Absorbable photons have been depleted by the stratoshere and energy transfer stops being efficient.
- The stratosphere is very stratified.
    - Not well mixed.
    - Temperature at the top of the stratosphere is $\sim$ 273 K.
    - Temperature at the bottom of the stratosphere is $\sim$ 213 K and the density is $\sim$ 0.4 atm, which is sufficient for three body collisions to become significant.
- Chapman cycle is important.
    - With significant O_3 formation, absorption between 200 and 290 nm is efficient as is

transfer of radiative energy to collisional energy.

- Other molecules are present since there are not enough high energy photons to destroy them, such as NO, NO_2, CFC's, Cl_2, and H_2O.
- At the tropospause ($\sim$ 18 km), virtually all radiation with wavelength shorter than 290 nm is screened out.
- The troposphere has two energy sources.
  - Solar radiation ($\lambda > 290$ nm).
  - Geothermal radiation (infrared).
- The troposphere absorbs geothermal radiation more efficiently near the earth's surface.
- The troposphere cools as altitude increases.
  - Because of its thermal structure, the troposphere is well mixed.
  - Fewer molecules are available to absorb radiation and fewer infrared photons are available to be absorbed.
  - The absorption of long wavelength radiation by the troposphere is known as the greenhouse effect.

The Greenhouse Effect

- The greenhouse effect results in the trapping of energy in the troposphere.
  - Infrared radiation is efficiently converted to thermal energy.
- In order to be able to absorb infrared radiation the molecule must have either
  - a transient dipole.
  - or a permanent dipole.
- A heteronuclear diatomic has a permanent dipole:
  - CO
  - NO
- Many nonlinear molecules also have permanent dipoles:
  - CH_2F_2
  - H_2O
  - O_3
- Non-symmetric linear molecules often have permanent dipoles:
  - NNO

- Symmetric molecules can have transient dipoles as the result of asymmetric stretching vibrations.
  - CO_2
  - CH_4
- Greenhouse gas levels are increasing.
- Methane (CH_4) 1.7 ppmv and increasing by 1 to 2% annually.
- Methane is a product of anaerobic decay.
  - 150×10^6 tonnes from natural sources such as marsh gas, wetlands, and ruminants.
  - 25×10^6 tonnes from oceans
  - 150×10^6 tonnes from natural gas
  - Anthropogenic sources include 95×10^6 tonnes from rice paddies and 120×10^6 tonnes from cattle.
- Carbon dioxide (CO_2) is at a level of about 350 ppm and is rising by about 0.5% per year.
  - Carbon dioxide is the result of fossil fuel combustion.

  - Speciates in water:

$$CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3(s)$$

    with about 60 times as much in the aqueous phase as in the gas phase.

- $\mathrm{CO_2}$ is also the product of atmospheric decomposition of $\mathrm{CH_4}$ and other hydrocarbons.

- The atmospheric decomposition of methane occurs as a sequence of reactions:

$$CH_4 \ + \ OH \ \rightarrow \ CH_3 \ + \ H_2O$$

$$CH_3 \ + \ O_2 \ + \ M \ \rightarrow \ CH_3OO \ + \ M$$

$$CH_3O_2 \ + \ NO \ \rightarrow \ CH_3ONO_2$$

$$CH_3O_2 \ + \ NO \ \rightarrow \ CH_3O \ + \ NO_2$$

$$CH_3O \ + \ O_2 \ \rightarrow \ CH_2O \ + \ HO_2$$

$$CH_2O \ + \ OH \ \rightarrow \ H_2O \ + \ HCO$$

$$CH_2O + h\nu \rightarrow H_2 + CO$$

$$CH_2O + h\nu \rightarrow H + HCO$$

$$HCO + O_2 \rightarrow CO + HO_2$$

$$OH + CO \rightarrow H + CO_2$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

- Other fates for HO_2:

  $$HO_2 + O_3 \rightarrow OH + 2O_2$$

- Other fates for NO_2:

  $$NO_2 + h\nu \rightarrow NO + O$$

- Atomic oxygen contributes to the formation of ground level ozone.

  $$O + O_2 \rightarrow O_3$$

- Decomposition of other hydrocarbons is initiated by the abstraction of an H atom by OH.

Nitrous Oxide

- N_2O (N=N=O) is present in the troposphere at $\cong$ 300 ppbv.
    - Asymmetric with a permanent dipole. Therefore it is a greenhouse gas.
- Sources include:
    - natural biological denitrification
    - anthropogenic biological denitrification as the result of the use of fertilizers.
    - industrial sources such as nylon manufacture.
    - combustion of fossil fuels.
- No tropospheric sinks.
    - This means that N_2O becomes globally distributed.
    - Transported to the stratosphere resulting in a tropospheric lifetime of about two years.
    - Stratospheric sink reactions include:

$$N_2O + h\nu \rightarrow N_2 + O^*$$

$$N_2O + O^* \rightarrow 2NO$$

Chlorofluorocarbons and Halons

- Chlorofluorocarbons or CFC's follow a nomenclature based on the rule of 90.
    - Consider CFC-11.
    - Add 90 to 11 to get 101.
    - The first digit indicates the number of carbon atoms present in the molecule.
    - The second digit indicates the number of hydrogen atoms present in the molecule.
    - The third digit indicates the number of fluorine atoms present in the molecule.
    - The remaining valence sites are occupied by chlorine.
    - Thus CFC-11 is $CFCl_3$.
    - HCFCs (hydrochlorofluorocarbons) also follow the rule of 90 (see page 19 of Bunce.)
- Halons are brominated analogs of CFC's with one or more bromine atoms in the structure.
- Halons are designated by a four digit number.
    - Consider Halon-1211

  - The first digit indicates the number of carbon atoms.
  - The second digit indicates the number of fluorine atoms.
  - The third digit indicates the number of chlorine atoms.
  - The fourth digit indicates the number of bromine atoms.
  - All remaining valence sites are occupied by hydrogen.
- CFCs, HCFCs and Halons are substituted hydrocarbons.
  - Therefore they are greenhouse gases.
  - Whether or not they have a tropospheric sink depends on whether an H atom is present in the structure.
  - In the absence of an H atom, they are sufficiently longlived to be transported to the stratosphere, where photodissociation can occur.

Greenhouse Gases and Climate Change

- Increases in levels of greenhouse gases has been correlated with increases in tropospheric temperatures.
- The impact of a greenhouse gas may be considered in terms of its global warming potential.
  - Usually defined relative to the global warming potential of CO_2.
- Radiative forcing is represented by F_R and has units of watts m^{-2}.
  - It may be thought of as the amount of photon energy converted to thermal energy per unit area.
- Global warming potential is defined as:

$$GWP = \frac{\int_0^T \Delta F_{R,i}(t)dt}{\int_0^T \Delta F_{R,CO_2}(t)dt}$$

  - $\Delta F_{R,i}$ is the change in radiative forcing due to an instaneous release at $t = 0$ of 1 kg of gas i.
  - T is the time horizon of interest.

- This may be approximated by:

$$GWP = \frac{\int_0^T a_i n_i(t)dt}{\int_0^T a_{CO_2} n_{CO_2}(t)dt}$$

  where

  - a_i in W m^{-2} kg^{-1} is the radiative forcing due to the presence of trace gas i
  - $n_i(t)$ is the amount of gas i present at time t after release.

- If τ_i is the atmospheric lifetime of molecule i then

$$n_i(t) = n_i(0)e^{-t/\tau_i}$$

  - Since $n_i(0)$ is 1 kg, the global warming potential becomes:

$$GWP = \frac{a_i \int_0^T e^{-t/\tau_i} dt}{a_{CO_2} \int_0^T e^{-t/\tau_{CO_2}} dt}$$

$$\frac{a_i \tau_i \left(1 - e^{-T/\tau_i}\right)}{a_{CO_2} \tau_{CO_2} \left(1 - e^{-T/\tau_{CO_2}}\right)}$$

- The integration time T depends on the timescale for the phenomena of interest.

  - Maximum change in temperature or sea level ~ 100 years
  - Maximum rate of change in temperature or sea level ~ 50 years.
- Values for a_i and $\Delta F_{R,i}$ are determined from general circulation models (GCM).

Stratospheric Ozone

- O_3 absorbs photons with λ between 240 and 320 nm.
- The term "ozone layer" refers not to a physical layer, but rather the ozone distributed throughout the stratosphere at ~ 10 ppmv.
  - If all the stratospheric O_3 were compressed to into a layer at standard temperatue and pressure, the layer would be 3 mm thick.
  - The stratosphere is not well mixed and concentration of O_3 varies with altitude.
- Recall the Chapman cycle:

Δ H (kJ mol^{-1})

$O_2 + h\nu(\lambda < 240nm) \rightarrow 2O$ 495 -E_{photon_1}

O + O_2 + M → O_3 + M -105

O_3 + h$\nu(\lambda < 325\ nm)$ → O_2^* + O^*
383 -E_{photon_2}

or

O_3 + h$\nu(\lambda < 325\ nm)$ → O_2 + O 105 - E_{photon_2}

O + O_3 → O_2 + O_2 -389

  - The associated rate coefficients are k_1, k_2, k_3, $k_{3'}$, and k_4

- The Chapman cycle can reach a steady state:

$$\frac{d[O_2]}{dt} = 0 = -k_1[O_2] - k_2[O][O_2][M]$$
$$+(k_3 + k_{3'})[O_3] + 2k_4[O][O_3]$$
$$\frac{d[O]}{dt} = 0 = 2k_1[O_2] - k_2[O][O_2][M]$$
$$+(k_3 + k_{3'})[O_3] - k_4[O][O_3]$$
$$\frac{d[O_3]}{dt} = 0 = k_2[O][O_2][M] - (k_3 + k_{3'})[O_3]$$
$$-k_4[O][O_3]$$

- But this steady state is NOT an equilibrium because energy is processed from photons into kinetic energy.
    - k_1, k_3, and $k_{3'}$ depend on the photon supply.
- From the steady state equations, relative amounts of O, O_2 and O_3 may be predicted.
- Observed O, O_2 and O_3 levels do not match that predicted from steady state equations.
    - Observed O_3 levels are low.
    - Therefore there must be additional sinks for O_3.
- O_3 can be depleted catalytically by a species "X":

  $$X + O_3 \rightarrow XO + O_2$$

  $$XO + O \rightarrow X + O_2$$

  with the net reaction:

  $$O_3 + O \rightarrow 2O_2$$

- "X" is usually an odd electron species.
- Some X/XO pairs are:

- Cl/ClO

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

- Br/BrO

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + O \rightarrow Br + O_2$$

- NO/NO$_2$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

- OH/HO$_2$

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow OH + O_2$$

- H/OH

$$H + O_3 \rightarrow OH + O_2$$

$$OH + O \rightarrow H + O_2$$

- Cl and Br in the stratosphere are mostly anthropogenic and come from CFC's and Halons.
- NO, H and OH occur naturally.
- These act as catalysts, increasing the rate of reaction by decreasing the activation energy. (See Table 1 page 37.)
- Consider:

$$\text{Rate}_1 = k_1[X][O_3]$$

$$k_1 = A_1 e^{-E_1/RT}$$

$$\text{Rate}_2 = k_2[XO][O]$$

$$k_2 = A_2 e^{-E_2/RT}$$

  where

  - k's are the rate coefficients
  - A is the Arrhenius pre-exponential factor which represents the chance of two molecules hitting each other in an orientation favourable for reaction.
  - E is the Arrhenius activation energy and $e^{-E/RT}$ is the fraction of molecular collisions with at least this energy.

- The uncatalyzed reaction

$$O + O_3 \rightarrow 2O_2$$

  has an activation energy of 18.4 kJ mol^{-1}

- The X/XO pairs provide a lower energy two step pathway.
    - Some activation energies in kJ mol^{-1}:

X	X+O_3	XO+O
Cl	2.1	1.1
NO	13.1	0
H	3.9	0
OH	7.8	0

- Exact rate of O_3 decomposition depends on altitude, [X], and [XO].
- At 30 km altitude:
    - Decomposition by NO/NO_2 dominates over uncatalyzed rate.
    - Decomposition by Cl/ClO is comparable to the uncatalyzed rate.
    - The second step of each pair of catalytic reactions is the rate limiting step because

  of the low concentration of XO, not the activation energy.

  - Both steps of the catalyic reaction are free radical propagation reactions.

- To complete a model of stratospheric ozone, it is necessary to consider other reactions involving ozone depleting species.

- These reactions can provide temporary reservoirs:

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

  - An active ozone depleting species NO_2 is converted to the inactive (from an ozone depleting perspective) HNO_3.

  - Photolysis can regenerate NO_2:

$$HNO_3 + h\nu \rightarrow HO + NO_2$$

- Consider the reactions:

$$Cl + CH_4 \rightarrow HCl + CH_3$$

$$HCl + OH \rightarrow Cl + H_2O$$

  - Again an ozone depleting species (Cl) is converted to a reservoir species (HCl), which in turn (this time by reaction with OH) can be converted back to an active ozone depleter.

- There are also null cycles which have the effect of converting photons to thermal energy.

$$NO_2 + h\nu(\lambda < 400 \text{ nm}) \rightarrow NO + O$$

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

$$O_3 + NO \rightarrow NO_2 + O_2$$

  which may be rewritten as a pseudoequilibrium:

$$NO_2 + O_2 \rightleftharpoons NO + O_3$$

  with the forward reaction driven by availability of photons.

  - This cycle can affect ratios of NO/$\mathrm{NO_2}$ and HO/$\mathrm{HO_2}$.

- Termination reactions permanently remove free radical species.

$$2ClO + M \rightarrow ClOOCl + M$$

$$2HO_2 \rightarrow H_2O_2 + O_2$$

$$NO_2 + Cl \rightarrow NO_2Cl$$

- Initiation reactions produce free radicals:

$$HNO_3 + h\nu \rightarrow HO + NO_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O_3 + h\nu \rightarrow O_2 + O$$

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl$$

$$O + H_2O \rightarrow 2OH$$

$$N_2O + O \rightarrow 2NO$$

- Ozone depleting potential (ODP) is the propensity of a substance (i.e. a source of X) to destroy O_3 over the life of the compound relative to the propensity of CFC-11 to lead to the destruction of O_3 over its lifetime.
  - Replacement compounds for CFC's need to have a lower ODP.
- CFC's were developed as working fluids for a heat engine working as a refrigerator.
- Heat engines are based on the Carnot Cycle with $T_H > T_L$.
  - T_H is the temperature of the surroundings.
  - T_L is the temperature of the refrigeration chamber.

- For an ideal Carnot Cycle:
    - The system starts at T_H and P_1, V_1.
    - The first stroke is an adiabatic expansion to P_2, V_2 accompanied by cooling to T_L.
    - The next stroke is isothermal at T_L and the fluid absorbs heat and expands to P_3, V_3.
    - The third stroke is an adiabatic compression that warms the fluid to T_H at P_4, V_4.
    - The fourth stroke compresses the gas isothermally at T_H to P_1, V_1, transferring heat to the surroundings.
- The choice of a working fluid, in this case a refrigerant, is selected on the basis of its ability to transfer heat.
    - Therefore a substance that can undergo a gas liquid phase transition between T_L and T_H with a large ΔH_{vap} is desirable.
- CFC's were chosen because:
    - Inexpensive
    - Easy to make
    - Nontoxic

  - Nonflammable
  - Odourless
- Candidate compounds for CFC's must have all these properties plus:
  - A short (< 2 years) tropospheric lifetime
  - Decomposition products that have short tropospheric lifetimes and do not get transported to the stratosphere.
  - Compatibility with existing technology.
- HFC's and HCFC's have shorter tropospheric lifetimes because an H atom can be abstracted leading to products that are scavenged in the troposphere.
  - More expensive than CFC's to produce.
  - Cost also affected by proprietary interests, which in turn can affect the availability in the developing world.
  - HCFC's have tropospheric lifetimes that are longer than two years, and thus they can produce stratospheric chlorine, so they are being phased out in favour of HFC's.