

## How does Environmental Chemistry Differ from Laboratory Chemistry?

### Environmental

- open
- Dynamic T, P , V, n
- Multiphase
- Observable, monitoring
- Dynamic
- Missing information
- Mismatched information

### Laboratory

- open, closed, or isolated
- Controlled T, P , V, n
- Few reactions
- Reproducible experiments
- Often equilibrated

## 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 solvent
  - Normality - equivalents/L solution (context determines “equivalents”)
  - Mole fraction
  - ppm - parts per million or mg/L
- Gas Phase
  - moles/L
  - moles/cm<sup>3</sup>
  - molecules/cm<sup>3</sup>
  - 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:

$$PV = nRT$$

$$P_i V = n_i R T$$

$$P_{tot} V = n_{tot} R T$$

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:

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

- Consider 0.1 M NH<sub>3</sub>:

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

- 5 ppm  $\text{ClO}_2$  solution:

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

$$\begin{aligned} \frac{5 \times 10^{-3} \text{ g } \text{ClO}_2}{\text{L}} &\times \frac{1 \text{ mol } \text{ClO}_2}{67.5 \text{ g}} \\ &= 7.4 \times 10^{-5} \text{ M } \text{ClO}_2 \end{aligned}$$

- Gas phase examples:
  - $\text{H}_2\text{S}$  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:

$$P_{tot} = 100.10 \text{ kPa}; \quad T = 0.1^\circ\text{C} = 273.15 \text{ K}$$

Therefore:

$$\begin{aligned} P(\text{H}_2\text{S}) &= 10^{-9} \times 100.10 \text{ kPa} \\ &= 1.001 \times 10^{-7} \text{ kPa} = 1.001 \times 10^{-4} \text{ Pa} \end{aligned}$$

$$\begin{aligned}
\frac{n}{V} &= \frac{P}{RT} = \frac{1.001 \times 10^{-4} \text{ Pa}}{8.31441 \text{ J mol}^{-1} \text{ K}^{-1} \times 273.25 \text{ K}} \\
&= 4.41 \times 10^{-11} \text{ mol m}^{-3} \\
&= 2.65 \times 10^{13} \text{ molec m}^{-3} \\
&= 2.65 \times 10^7 \text{ molec cm}^{-3}
\end{aligned}$$

Note that:

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

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

- $\text{O}_3$  at  $0.2 \text{ mg m}^{-3}$

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

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

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

$$= 10.15 \text{ Pa}$$

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

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

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



## 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:

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

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

- 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 it 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:
  - variability 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.

$$\frac{\sum \text{time}_i c_i}{\sum \text{time}_i}$$

- 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  $\times$  exposure time).
  - Usually tracked with a badge monitor.

## **Modes of Toxicity**

- Irritants
- Carcinogens
- Asphyxiants (Displace O<sub>2</sub>)
- 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<sub>2</sub> groups)
  - O<sub>3</sub> (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.

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

then sum

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

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:

$$\text{TLV}(\text{mixture}) = \frac{1}{\sum \frac{f_i}{\text{TLV}_i}}$$



## **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 chemotherapy 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:

- $\text{Fe}^{2+}$  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<sup>3</sup>.

- 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  $\text{mg h}^{-1}$ .
  - Mixing Volume (usually room size) in units such as  $\text{m}^3$ .
  - These are combined to give a source term of the form:

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

- The air change rate,  $k$ , is usually given as air changes per hour or ach.
  - $k$  has units such as  $\text{h}^{-1}$ .
  - 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:

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

- The half life is defined as the time required for the concentration 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.

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


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$$1 \text{ kg}$$

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

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

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

$$\begin{aligned} V &= 14 \text{ ft} \times 20 \text{ ft} \times 8 \text{ ft} \\ &= 4.27 \text{ m} \times 6.10 \text{ m} \times 2.44 \text{ m} \\ &= 63.43 \text{ m}^3 \end{aligned}$$

- 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  $1.5 \text{ mg m}^{-3}$ .
- Select units of [ $c_i$ ]
  - For this example use ppb.

- Carry out necessary unit conversion prior to evaluating:

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

- In units given so far:

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

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

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

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

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

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

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

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

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

- Under these assumptions, evaluate  $[c_i]$

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

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

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

$$\begin{aligned} \frac{n}{V} &= \frac{P}{RT} = \frac{1.27 \times 10^{-2} \text{ Pa}}{8.31441 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 293 \text{ K}} \\ &= 5.20 \times 10^{-6} \text{ mol m}^{-3} \end{aligned}$$

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

- 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  $t$

$$\begin{aligned} t &= -\frac{1}{2 \text{ h}^{-1}} \ln \frac{(52.5 + 20 - 80) \text{ ppb}}{(52.5 + 20 - 125) \text{ ppb}} \\ &= -\frac{1}{2 \text{ h}^{-1}} \ln \frac{-7.5}{-52.5} = -\frac{1}{2 \text{ h}^{-1}} \ln .143 \\ &= -\frac{1}{2 \text{ h}^{-1}} \cdot -1.946 = .973 \text{ h} \end{aligned}$$



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

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

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

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

$$[c_i] = 104.57 \text{ ppb}$$

- Possible to construct a curve of concentration against time.

<b>Time(h)</b>	<b>Concentration (ppb) Formaldehyde</b>
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?

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

- Define lifetime with respect to sink term:

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

<b>t</b>	$e^{-kt}$	$1 - e^{-kt}$
$\tau$	0.368	0.632
$2\tau$	0.135	0.865
$3\tau$	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  $10\ \mu\text{m}$  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  $1\ \mu\text{m} \times 5\ \mu\text{m}$ .
  - 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 polycyclic 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  $20\text{--}60\ \mu\text{g m}^{-3}$ .
  - Smoking area  $100\text{--}700\ \mu\text{g m}^{-3}$  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  $^{222}_{86}\text{Rn}$ .
  - Formed from the radioactive decay of radium,  $^{226}_{88}\text{Ra}$ .
  - 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  $\approx 29 \text{ g mol}^{-1}$ .
- Average molar mass of Rn is  $222 \text{ g mol}^{-1}$ .
- 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  $\alpha$  particle is a  $\text{He}^{2+}$  and its nucleons are two protons and two neutrons.
  - A  $\beta$  particle is an electron

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

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



- $^{222}_{86}\text{Rn}$  can decay, releasing  $^{218}_{84}\text{Po}$ :
  - which is produced as a metal ion
  - which promptly forms the corresponding oxide,
  - which in turn is scavenged by the bronchial tissue.
- $^{218}_{84}\text{Po}$ , now sequestered in bronchial tissue, undergoes further decay, each step of which gives off highly energetic  $\alpha$  and  $\beta$  particles.
- The decay sequence from  $^{222}_{86}\text{Rn}$  to  $^{210}_{82}\text{Pb}$  releases:
  - Three  $\alpha$  particles
  - Two  $\beta$  particles
  - 23.8 Mev of energy
- An  $\alpha$  particle is a bare He nucleus. It will ionize biomolecules within  $60\ \mu\text{m}$ , which may include stem cells.
- A  $\beta$  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 $\text{L}^{-1}$
Canada	20 picocuries $\text{L}^{-1}$
UK	400 $\text{Bq m}^{-3}$

- 1 Becquerel (Bq) is one disintegration per second.
  - 1 curie(Ci) =  $3.7 \times 10^{10}$  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  $\text{L}^{-1}$  is equivalent to 200 chest xrays per year.
  - 20 pCi  $\text{L}^{-1}$  is equivalent to 2 packs of cigarettes a day.

- Epidemiological studies suggest that exposure to  $1000 \text{ Bq m}^{-3}$  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  $^{210}_{82}\text{Pb}$ .

$$\begin{aligned} \text{Time} \times \text{Efficiency} \times \text{number of } ^{210}_{82}\text{Pb atoms} \\ = \text{number of decays} \end{aligned}$$

- Track etch monitors records the tracks of  $\alpha$  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  $^{226}_{88}\text{Ra}$  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:
  - Terrestrial 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
  - $\nu$ , the frequency of light:

$$E = h\nu$$

- $\lambda$ , 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,  $\rho$ , 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,  $\rho$ , 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  $1370 \text{ W m}^{-2}$ , including wavelengths less than 200 nm.
  - A photon of 200 nm wavelength has an energy of:

$$E(\lambda = 200 \text{ nm}) = \frac{hc}{\lambda} =$$
$$\frac{6.626 \times 10^{-34} \text{ J s} \cdot 2.998 \times 10^8 \text{ m s}^{-1}}{200 \times 10^{-9} \text{ m}} =$$
$$9.9324 \times 10^{-19} \text{ J photon}^{-1}$$

- 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.

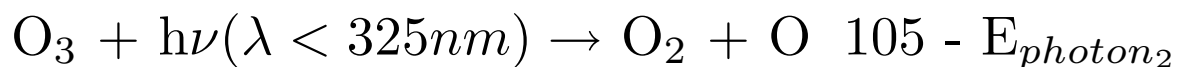
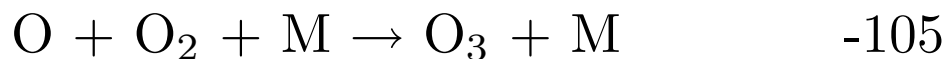
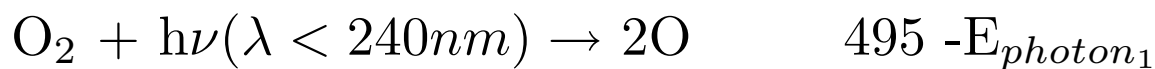
- Shorter wavelengths can dissociate or ionize chemical species:



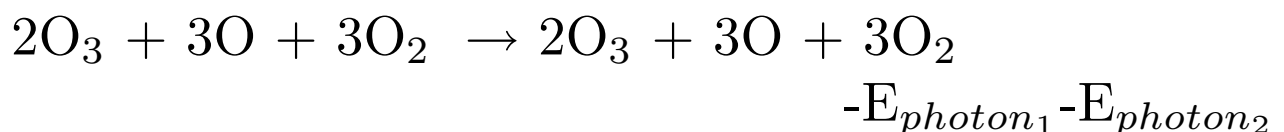
- Therefore the thermosphere is mostly atoms and ions.
- The top of the thermosphere is hot, because collisions are rare and energy transfer for excited chemical species is inefficient.
- As the altitude decreases, the thermosphere gets colder because fewer high energy photons are able to penetrate this 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 of energy of absorbed photons.

- In the mesosphere (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.

$$\Delta H \text{ (kJ mol}^{-1}\text{)}$$



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



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

- The mass of the mesosphere 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 mesosphere 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<sub>2</sub>, CFC's, Cl<sub>2</sub>, and H<sub>2</sub>O.
- At the tropopause ( $\sim 18$  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.