Lecture 2

Stratospheric Chemistry: The Ozone Layer

17 January 2013

- UV radiation and its impact
- Chemical reactions induced by light
- The Ozone Layer
- Review/Thermodynamics Principles



A cross section of our atmosphere -review



The atmosphere is divided vertically into four layers based on temperature: the **troposphere**, **stratosphere**, **mesosphere**, and **thermosphere**.

http://www.ucar.edu/learn

Stratosphere

-where UV light induced chemistry dominates



- It extends from the earth's surface to an average of 12 km (7 miles).
- The pressure ranges from 1000 to 200 millibars (29.92 in. to 5.92 in.).
- The temperature generally decreases with increasing height up to the tropopause (top of the troposphere); this is near 200 millibars or 36,000 ft.
- Winds increase with height up to the jet stream.
- The moisture concentration decreases with height up to the tropopause.
- The sun's heat that warms the earth's surface is transported upwards largely by convection and is mixed by updrafts and downdrafts.

http://www.ucar.edu/learn

Sunlight as the Source of Energy

Chemistry with Sunlightthe good





Chlorophyll in plant leaves are attached to the membranes of disc-like structures, called chloroplasts, inside the cells. In chloroplasts, the light absorbed by chlorophyll transforms carbon dioxide and water into oxygen and carbohydrates, which have a general formula of $C_x(H_2O)_y$.

 $x \operatorname{CO}_2 + y \operatorname{H}_2\operatorname{O} + \operatorname{light} \rightarrow x\operatorname{O}_2 + \operatorname{C}_x(\operatorname{H}_2\operatorname{O})_y$

The energy of the light absorbed by chlorophyll is converted into chemical energy stored in carbohydrates. This chemical energy drives the biochemical reactions that cause plants to grow, flower, and produce seed.

Vitamin D3 can be produced photochemically by the action of sunlight or ultraviolet light from the precursor sterol 7-dehydrocholesterol which is present in the epidermis or skin

http://www.emc.maricopa.edu/faculty/farabee/BIOBK/BioBookPS.html Zhu, G.-D and Okamura, W.H. Synthesis of vitamin D (calciferol). <u>Chem. Rev</u>. **95**:1877-1952 (1995).

Chemistry in Sunlight





...the bad

Overexposure to the sun's invisible rays - ultraviolet A (UVA) and ultraviolet B (UVB) - can cause skin damage.

Any tan is a sign of skin damage.

Tanning occurs when the skin produces additional pigment (coloring) to protect itself against sunburn from ultraviolet rays.

Indoor tanning devices also give off ultraviolet rays that can be as harmful as those from the sun.

The damage can be immediate and long-term, with effects ranging from sunburn, rashes, and cell and tissue damage to premature wrinkling and skin cancer.

Many skin changes that often are identified with aging actually result from damage by too much sun.

Most of the body's vitamin D supply, about 75% of it, is generated by the skin's exposure to UVB rays. Using a sunscreen drastically lowers the cutaneous production

Chemistry in Sunlight



Incidence of nonmelanoma skin cancer per 100000 males versus annual light intensity

...the ugly

UV Photons are energetic and can induce chemical reactions in biological and environmental systems.

Excess UV exposure of can influence plant growth and alter the ecological balance.

Solar Flux





Wavelength (nm)	Major range	Wavelength (nm) Subrange
<50	X-rays	
50		
	Ultraviolet	²⁰⁰ } UV-C
1		280 J
		320 UV-A
400		400 Violet
}	Visible	
750		750 Red
	Infrared	4,000 (4μm)
		Thermal IR
		100,000 (100 μm)

Light Energy and Wavelength

In 1905, Albert Einstein demonstrated the photoelectric effect to postulate the existence of photons, quanta of light energy with particulate qualities. Einstein explained this conundrum by postulating that the electrons were knocked free of the metal by incident photons, with each photon carrying an amount of energy E.

E is related to the frequency, *v* and wavelength, λ of the light by

E = hv or $E = hc/\lambda$ since $v = c/\lambda$

where *h* is Planck's constant (6.626 x 10^{-34} J seconds) c = speed of light (2.997925 x 10^8 m/s).

Only photons of a high-enough frequency, (above a certain *threshold* value) could knock an electron free. For example blue light, but not red light, had sufficient energy to free an electron from the metal.

Since hc = $(6.626 \times 10^{-34} \text{ J s}) \times (2.997925 \times 10^8 \text{ m/s})$ = 19.86 x10⁻²⁰ kJ nm or 119627 kJ nm/mole(N= 6.023×10^{23} photons)

Using this expression we can obtain the energy of a photon at a specific wavelength

 $\mathbf{E} = \mathbf{hc}/\lambda = 119627/\lambda$ (kJ/mole) λ is expressed as nm

Examples: What is the energy of 300 nm photon? $E = hc/\lambda = 119627/300 = 398.75 \text{ kJ/mole} \text{ or } 4.13 \text{ ev}$

96.486 kJ/mole =1 eV

What wavelength corresponds to 1 eV?

 $E = hc/\lambda \quad \text{ or } \lambda = hc/E = 119627 \text{ (kJ nm mole}^{-1} \text{)/96.486 (kJ mol}^{-1})$ = 1240 nm

1 eV of photon energy corresponds to 1240 nm. By remembering this number we can determine the energy of photon at any given wavelength.

Energy of a photon at given wavelength

 $E=1240/\lambda$

 $620 \text{ nm} \rightarrow 2 \text{ ev} \quad 413.3 \rightarrow 3 \text{ ev} \text{ and } 310 \text{ nm} \rightarrow 4 \text{ eV}$

Expressions to remember

E (kJ/mole) = $hc/\lambda = 119627/\lambda$ λ is expressed as nm

 $\mathbf{E} (\mathbf{eV}) = \mathbf{1240}/\lambda$

h = $6.626 \times 10^{-34} \text{ J s}$ C = $2.997925 \times 10^8 \text{ m/s}$ N= $6.023 \times 10^{23} \text{ photons}$ 96.486 kJ/mole =1 eV





Sunscreens



Chapter 1 Opener Environmental Chemistry, Third Edition © 2005 W. H. Freeman and Company

SPF is a rating for sunscreens and stands for Sun Protection Factor. A SPF of 30 means you can stay in the sun 30 times as long as you could without the sunscreen or sunblock with the same degree of sunburn.

http://www.fda.gov/fdac/

THERE ARE TWO basic types of active ingredients: inorganic and organic. Both afford protection against UV-B rays in the 280- to 320-nm range, the primary culprits in sunburn. They work primarily by absorbing UV light and dissipating it as heat.

Some offer additional protection from UV-A rays in the 320- to 400-nm range, which can penetrate more deeply into the skin and do greater long-term damage.

Inorganic sunscreens use titanium dioxide and zinc oxide. They work primarily by reflecting and scattering UV light.

The organics include widely used ingredients such as octyl methoxycinnamate (OMC), 4methylbenzylidene camphor (4-MBC), avobenzone, oxybenzone, and homosalate.

People who have lived in the desert intuitively know something we sun worshipers never learned: It may not be a bad idea at all to wrap yourself in white, light-reflecting robes



Ozone effectively absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage



Above stratosphere most of the oxygen absorbs UV-C and exists as O atoms

 $O_2 + hv \rightarrow 2O$

Because of the high concentration of O_2 in stratosphere, any O atom present gets converted to O_3

 $O_2 + O \rightarrow O_3$

$O_2 + O + M \rightarrow O_3$



Ozone is constantly being formed in the earth's atmosphere by the action of the sun's ultraviolet radiation on oxygen molecules. Ultraviolet light splits the molecules apart by breaking the bonds between the atoms. A highly reactive free oxygen atom then collides with another oxygen molecule to form an ozone molecule. Because ozone is unstable, ultraviolet light quickly breaks it up, and the process begins again.



Example:

For dissociation of O₂ $\Delta H^0 = 495 \text{ kJ/mole}$

What is the longest wavelength of photons that is capable of dissociating O_2 ?

 $O_2 + h\nu \rightarrow 2O$

Hint: Determine the wavelength of light that corresponds to the dissociation energy.

 $\lambda = hc/E = 119627$ (kJ nm mole⁻¹)//495 (kJ mole⁻¹)= 241.67 nm

UV-light with photons of wavelength <241 nm can dissociate O_2

Decomposition of O_3 What is the longest wavelength of photons that is capable of dissociating O_2 ?

$$O_3 \rightarrow O_2 + O$$
 $\Delta H^0 = 105 \text{ kJ/mole}$

$$\lambda = hc/E = 119627$$
 (kJ nm mole⁻¹)/105 (kJ mole⁻¹) = 1139 nm

Although the energy of the infrared light (λ < 1139 nm) is sufficient to decompose O₃, there is no absorption of the photons. However O₃ absorbs only in the UV ! (Hence most of the O₃ generated in the stratosphere is constantly destroyed) **Creation of Ozone in the Stratosphere**



 O_3 in the stratosphere is constantly being formed, decomposed and reformed during daylight hours by a series of reactions. Rates of these reactions differ depending upon altitude

O₃ is not formed below stratosphere. Why?

Ozone in the Atmosphere

- In the stratosphere, we find the "good" ozone that protects life on earth from the harmful effects of the sun's ultraviolet rays.
- Ozone molecules are transported in stratosphere much as water clouds are transported in the troposhere.
- In the troposphere, the ground-level or "bad" ozone is an air pollutant
- It is a key ingredient of urban smog.

Chapman theory describes how sunlight converts the various forms of oxygen from one to another, explains why the highest content of ozone occur in the layer between 15 and 50 km, termed the ozone layer

Read pages 42-46 (18-26)

The Steady State Analysis

Rate of change of a reaction = Rate of formation- rate of destruction

 $A \rightarrow B$ (1) $B \rightarrow C$ (2) Rate of change of $B = k_1[A] - k_2[C]$

At Steady State the rate of change is zero \therefore Rate of formation-Rate of destruction = 0 Or Rate of formation=Rate of destruction

In the above example,

 $k_1[A] = k_2[C]$ or $[A]/[C] = k_2/k_1$

Concentration Units and **Thermodynamics Principles**

Review of Fundamentals

Concentration Units. (see page 68 in the book)

Molecules per cubic centimeter

Partial Pressure of the gas expressed in the units of atmosphere or kilopascal or bar
According to ideal gas law
PV = nRT
Partial Pressure is proportional to the Molar concentration or n/V (at constant T)

Mole Fraction or Molecule fraction per million or billion Example: 100 ppm of CO_2 in air refers to 100 molecules of CO_2 per 10⁶ molecules of air

Mole Fraction Ratios are also referred as Mixing ratios

Henry's Law

The concentration of a solute gas in a solution is directly proportional to the partial pressure of that gas above the solution.

For example, the equilibrium between oxygen gas and dissolved oxygen in water is

 $O_2(g) \iff O_2(aq)$

The Henry's Law constant K_H is defined as

 $K_H = c(O_2)/p(O_2)$

$$Or \qquad c(O_2) = p(O_2) \times K_H$$

Henry's Law constant K_H equals to equilibrium molar concentration of the substance in the liquid phase at one atmosphere

Oxygen at one atmosphere has a molar solubility of 1.32 mmol/litre. Hence $K_{\rm H} = 1.32 \times 10^{-3}$ M/atm

The partial pressure of oxygen in air is 0.2095 atm. The concentration of O_2 in an air saturated water is 0.2095 atm x 1.32x10⁻³ M/atm

or 2.765 x 10⁻⁴ mol/litre or 0.2765 mmol/litre.

Thermodynamic Principles

First Law: Energy is neither destroyed nor created Or Sum of energy and mass is conserved

 $E=mC^2$

Second Law: Entropy always increases in a spontaneous process Entropy is a measure of disorder

One measure of Entropy is the heat energy q divided by the temperature s=q/T

q/T increases in a spontaneous process. Heat energy produces greater disorder for a cold sample (smaller T) than for a hot sample

Entropy and Energy

Chemical reactions are associated with changes of entropy and energy. Entropy limits the work that can be extracted

The amount of energy available for work is called the *Free Energy Change* or ΔG of the reaction

$\Delta G = \!\! \Delta H - T \Delta S$

 ΔH is the enthalpy change and ΔS is the entropy change of the reaction

	лЦ		
		$\Delta \Theta_0$	 Free energy trends parallel
O ₃	142.2	163.4	enthalpy trends
CO ₂	-393.4	-394.4	 -ve free energy trends show
CO	-110.5	-137.2	the formation of these
NO	90.4	86.7	compounds are favored.
NO_2	33.8	51.8	• O_3 , NO, NO ₂ have +ve ΔG .
SO_2	-296.8	-300.3	Hence they are readily
SO ₃	-395.1	-370.3	decomposed

Standard Enthalpy and Free Energies of Formation (kJ) at 298K

Free energy and Equilibrium Constant

$$A + B \xleftarrow{k_{f}} C + D$$
$$K=[C][D]/[A][B]$$

Rate(Forward) = k_f [A][B] and Rate (back) = k_b [C][D]

At equilibrium k_f [A][B] =k_b[C][D]

$K = k_f / k_b$

The thermodynamic relationship between the equilibrium constant and the free energy change is

$\Delta \mathbf{G} = -\mathbf{RTInK}$

R is a gas constant and has a value of 8.314 JK⁻¹ (or 0.082 L atm mol⁻¹K⁻¹)

 $\Delta G = -8.314xTx2.303xlogK = -19.57T(logK)$ joules = -5706 log K at 298 K Determine the equilibrium Concentration of NO in the atmosphere at sea level and 25 °C Known: For NO $\Delta G_0 = 86.7$ kJ

The concentration of N_2 and O_2 in terms of partial pressures at 1 atm $[N_2] = 0.78$ atm and $[O_2] 0.21$ atm $N_2 + O_2 \iff 2 \text{ NO}$ $K = [NO]^2 / [N_2] [O_2]$ $Or [NO] = (Kx[N_2][O_2])^{0.5}$

The concentration of N_2 and O_2 in terms of partial pressures at 1 atm

 $[N_2] = 0.78 \text{ atm and } [O_2] \ 0.21 \text{ atm}$ $\Delta G \text{ for } 2NO = 2 \text{ x } 86.7 \text{ kJ} = 173.4 \text{ kJ}$ $\Delta G = -RTInK \text{ or } InK = 2.303 \log K = (-\Delta G)/(RT)$

 $\log K = (-173.4 \times 10^3 \text{ J})/(8.314 \text{ J/K} \times 298 \text{ K} \times 2.303)$

 $\log K = -30.4 \text{ OR } K = 10^{-30.4}$

 $[NO] = (Kx[N_2][O_2])^{0.5} = (10^{-30.4}x0.78x0.21)^{0.5} = 1.6x10^{-15.7} \text{ atm}$

This is relatively small concentration compared to the polluted concentration of 10⁻⁴ ppm (or 10⁻¹⁰ atm) in urban areas!

Free Energy and Temperature

 $\Delta G = \Delta H - T \Delta S$ and $\Delta G = -RT \ln K$

$InK = -\Delta H/RT + \Delta S/R$

 $A + B \iff C + D$ K = [C][D]/[A][B]

Raising the temperature increases the difference between ΔH and ΔG

If ΔH is negative (exothermic) lnK is positive (unless overcome by ΔS)

- products are favored over reactants

- with increasing temperature K becomes less positive (or less products)

If ∆H is positive (endothermic) InK is negative (or products are not favored) - with increasing products InK becomes less negative and the equilibrium drives towards products

In either case the effect of raising temperature is to produce more even distribution of reactants and products

Nitrogen Oxides: Kinetics

$$N_2 + O_2 \iff 2 \text{ NO}$$

The reaction proceeds when the temperature is sufficiently high as in combustion. When the temperature decreases, it should drive the reaction to the left. In the atmosphere other reactions with $-ve \Delta G$ are favored.

> $2NO+O_2 \rightarrow 2NO_2 \quad \Delta G = -69.8 \text{ kJ}$ $NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \quad \Delta G = -239.6 \text{ kJ}$

Activation Energy

- Activation energy represents additional energy to drive a reaction in addition to the thermodynamic requirement
- Depends on the reaction mechanism
- Reaction proceeds with the lowest activation path
- In gas phase reactions are inherently slow because of high activation energies

Enthalpy Cycles & Hess's Law

According to **Hess's Law** the total enthalpy change for a reaction is independent of the route taken.

The enthalpy change of formation of methane cannot be determined directly by experiment. It is possible, however, to determine the enthalpy changes of combustion of carbon, hydrogen and methane. The key idea is that the total enthalpy change for one route is the same as the total enthalpy change for an alternative route.

C(s) + $2H_2(g)$ - AH -)≻CH₄(g ΔH_1 Enthalpy cycles $\Delta H_{\rm a}$ are useful because they enable a $CO_2(g)$ + 2H₂O(I) value for an enthalpy change to If we can measure ΔH_2 and ΔH , we can find ΔH_1 . Using Hess's Law: be determined for a reaction which $\Delta H + \Delta H_2 = \Delta H_1$ cannot be determined directly Hence: $\Delta H = \Delta H_1$ ΔH_2 from experiment.

Free Radicals

Free radicals are atoms or molecules having an unpaired electron

```
CH_4 \rightarrow {}^{\bullet}H + {}^{\bullet}CH_3
```

Since electron pairing is the basis of covalent bond in chemistry, a free radical gains energy by pairing its electron with an electron or atom

It can also induce chain reactions. For example, a mixture of H_2 and CI_2 is irradiated with UV-light, the reaction proceeds rapidly

 $Cl_{2} + hv \rightarrow 2Cl^{\bullet}$ $Cl^{\bullet} + H_{2} \rightarrow HCl + H^{\bullet}$ $H^{\bullet} + Cl_{2} \rightarrow HCl + Cl^{\bullet}$

 H_2 + $CI_2 \iff HCI$ ΔH =-184.6 kJ, the reaction mixture is exothermic but is stable at room temp.

Other important Radicals:

Oxygen Radicals $O_2 + hv \rightarrow 20^{\bullet}$

Organic Oxygen Radicals

 $RCH_2^{\bullet} \rightarrow RCH_2OO^{\bullet}$ (alkylperoxy radicals)

 $RCH_2OO^{\bullet} + X \rightarrow XO + RCH_2O^{\bullet}$

X can be NO and SO₂ or organic molecules

Hydroxyl Radical $O_3 + hv \rightarrow O_2 + O^*$ $O^* + H_2O \rightarrow 2OH^*$ $OH^* + RCH_3 \rightarrow RCH_2 + H_2O$ $OH^* + NO_2 \rightarrow HNO_3$ $OH^* + SO_2 \rightarrow HSO_3 \rightarrow O_2 + H_2O \rightarrow H_2SO_4 + HO_2^*$