Solar energy and photochemical reactions

- Photochemical reactions are caused or accelerated by light
- Sunlight can supply the energy to drive chemical reactions that would otherwise be unfavourable energetically
- Absorption of light raises the substrate to an "excited" state
- Photochemical reactions require prior absorption of photons: 1 photon absorbed per atom or molecule

\[ E_{\text{photon}} = \frac{hc}{\lambda} \]

\[ h = \text{Plank's constant} = 6.626 \times 10^{-34} \text{ J s} \]
\[ c = \text{the speed of light} = 2.998 \times 10^8 \text{ m s}^{-1} \]

- \( E \) is inversely proportional to \( \lambda \)
- multiply by Avogadro's number to get the energy per mole:
  \[ E (\text{kJ mol}^{-1}) = \frac{(1.19 \times 10^5)}{\lambda} \quad (\lambda \text{ in nm}) \]

- \( M \) in gas phase reactions is a “third body” which is any gas phase atom or molecule which carries away excess energy from the collision of the reactants. For problems, \( P(M) = P_T \)
Example

Calculate the energy of
(i) one photon of wavelength 530 nm;
(ii) a mole of photons of wavelength 530 nm.

i) \[ E = \frac{hc}{\lambda} \]
\[ = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{8} \text{ m s}^{-1})}{(530 \times 10^{-9} \text{m})} \]
\[ = 3.75 \times 10^{-19} \text{ J} \]

ii) \[ E = \frac{(1.19 \times 10^{5})}{\lambda} \]
\[ = \frac{(1.19 \times 10^{5})}{530} \]
\[ = 224 \text{ kJ/mol} \]
Primitive Earth

• primarily H$_2$O, CO$_2$ and N$_2$
• some NH$_3$ and CH$_3$
• without O$_2$ and O$_3$, shorter wavelengths of light would reach the earth's surface
• hostile environment for "life"
• the following reactions would be possible:

$$H_2O \rightarrow H + OH \ (\lambda< 240 \text{ nm})$$

$$CO_2 \rightarrow CO + O \ (\lambda< 240 \text{ nm})$$

• H and O would ultimately be cycled back to water, releasing energy in earth's atmosphere as heat
• Some H escapes Earth's atmosphere, creating an imbalance
• this and evolution of photosynthetic bacteria (under water) results in accumulation of O$_2$

$$O + O_2 \rightarrow O_3$$

• O$_2$ and O$_3$ filter out some shorter $\lambda$ → further evolution of life on earth
Ranges of radiation
(and presence in atmosphere of modern-day earth)

- visible 400 (blue) to 700 (red) nm
- UV-A 400 - 325 nm
- UV-B 325 - 295 nm (limit of λ reaching earth's surface)
- UV-C <295 nm (present in upper atmosphere)
### Energy vs. Wavelength of UV and visible radiation

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>170</td>
</tr>
<tr>
<td>500</td>
<td>240</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

### Some common bond strengths (kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O=O</td>
<td>495</td>
</tr>
<tr>
<td>C=O</td>
<td><strong>620</strong></td>
</tr>
<tr>
<td>O-H water</td>
<td><strong>490</strong></td>
</tr>
<tr>
<td>C-Cl</td>
<td><strong>330</strong></td>
</tr>
<tr>
<td>C-H (typical)</td>
<td><strong>414</strong> (range ~380-460)</td>
</tr>
<tr>
<td>N≡N</td>
<td><strong>946</strong></td>
</tr>
<tr>
<td>C-C</td>
<td><strong>350</strong></td>
</tr>
<tr>
<td>O-H (typical)</td>
<td><strong>464</strong></td>
</tr>
<tr>
<td>Cl-Cl</td>
<td><strong>243</strong></td>
</tr>
</tbody>
</table>
Example

The C-Cl bond has bond dissociation energy 330 kJmol\(^{-1}\), while CFCl\(_3\) absorbs radiation having \(\lambda < 220\) nm. Will CFCl\(_3\) undergo bond cleavage in the lower atmosphere?

330 kJ mol\(^{-1}\) corresponds to \(\lambda = 360\) nm

CFCl\(_3\) absorbs \(\lambda < 220\) nm which would provide sufficient energy to break the C-Cl bond, but…

\(\lambda < 220\) nm does not penetrate to the lower atmosphere (cutoff is 295 nm)

so bond dissociation will not occur
Temperatures in the Atmosphere

- Thermosphere, mesosphere:
  - radiation <200 nm is absorbed
    \[ \text{N}_2 \rightarrow 2\text{N} \]
    and \( \text{N} \rightarrow \text{N}^+ + e^- \)
    followed by recombination

- Stratosphere:
  - radiation 200-300 nm is absorbed by \( \text{O}_2 \)
    \[ \text{O}_2 \rightarrow \rightarrow \text{O}_3 \]
    followed by \( \text{O}_3 \rightarrow \rightarrow \text{O}_2 \)

- These processes convert solar radiation (light) into heat
- Radiation >300 nm reaches the Earth's surface
- The lowest part of the troposphere is warm because the Earth radiates infrared radiation which is trapped by the atmosphere

**Greenhouse gases and climate change**
• Greenhouse effect = trapping of outgoing infrared radiation by "radiatively active gases"

Definition: *radiative forcing*

• Physical chemistry: infrared radiation always accompanied by a change of dipole moment in the lower and upper vibrational states
• Above rule means that the following do NOT absorb IR: N₂, O₂, Ar (all the major constituents of the troposphere)
• Conclusion: Trace gases are responsible for IR absorption in the troposphere (H₂O, CO₂, O₃, CH₄, N₂O, CFCs (chlorofluorocarbons))

• Without IR absorption, the average surface temperature of Earth would be ~ -30°C rather than ~ +15°C
• "Greenhouse effect" as commonly understood means increased IR trapping due to increases in the concentrations of CO₂, CH₄, N₂O, and CFCs leading to warming of the troposphere
• potential positive feedback from H₂O if temperature increase

Definition: *positive feedback*
<table>
<thead>
<tr>
<th></th>
<th>Atmospheric conc. (1998)</th>
<th>Atmospheric Lifetime(^1,2) (years)</th>
<th>Global Warming Potential(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>365 ppmv</td>
<td>50-200</td>
<td>1</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>1,745 ppbv</td>
<td>12</td>
<td>56</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>314 ppbv</td>
<td>114</td>
<td>280</td>
</tr>
<tr>
<td>CFCs</td>
<td>high pptv</td>
<td>60-150</td>
<td>&gt;3000</td>
</tr>
</tbody>
</table>

\(^1\) Intergovernmental Panel on Climate Change (IPCC) (2001)
\(^2\) Atmospheric lifetime and residence time are used interchangeably
\(^3\) IPCC (1996); 20 year GWP

**Definition: Global Warming Potential**

- a quantified measure of the globally averaged relative radiative forcing impacts of a particular greenhouse gas.
- the cumulative radiative forcing (both direct and indirect effects) integrated over a period of time from the emission of a unit mass of gas relative to some reference gas (IPCC 1996).
- CO\(_2\) was chosen as the reference gas
**CO₂: atmosphere and ocean**

\[
\text{CO}_2 (\text{g}) \leftrightarrow \text{CO}_2 (\text{aq}) \leftrightarrow \text{H}_2\text{CO}_3 (\text{aq}) \leftrightarrow \text{HCO}_3^- (\text{aq}) \leftrightarrow \text{CO}_3^{2-} (\text{aq}) \leftrightarrow \text{CaCO}_3 (\text{s})
\]

Issues:

- How fast will the oceans take up injections of CO₂ into the atmosphere?
  - \( t_{1/2} \) for uptake into surface water = 1.3 years
  - for exchange between surface and deep water \( t_{1/2} = 35 \) years

- What would be the effect of an increase in water temperature?
  \[
  \text{CO}_2 (\text{aq}) \rightarrow \text{CO}_2 (\text{g})
  \]
  - equilibrium constant \( K_H \) increases with T hence possibility of positive feedback
Global Warming

• Is global warming a fact?
• If so, is it due to increased concentrations of greenhouse gases?
• If so, are human activities to blame?
• **Historic Increases of CO$_2$, CH$_4$, and N$_2$O [IPCC Report]**
  • Data are from ice cores in Antarctica and Greenland,
  • supplemented in recent years by direct atmospheric analysis
The Kyoto Agreement?

- International agreement reached in 1990 for developed countries to cut back their $\text{CO}_2$ emissions by 6% from their 1990 levels
- The 2001 IPCC Report suggests that temperature increases of $>3^\circ\text{C}$ are likely before 2100; this would greatly change the climate in many regions
- Controversies: easier for some countries than others, depending on their "energy mix"
- Not all (but most!!) commentators agree that human activities are to blame
- Even if the cause is human activities, there is little point in only some countries meeting their targets
- Canada is a huge fossil fuel user per capita, but does not contribute a high percentage of the world's total $\text{CO}_2$ budget
- Canada, like most other countries, will not impose a carbon tax
- Canada is arguing for carbon credits for agriculture and reforestation
- Quebec is on a collision course with Alberta, because Alberta is a source of fossil fuels, whereas Quebec generates a lot of hydroelectricity
What should be done?

- Immediately reduce emissions of greenhouse gases?
- Adjust to changed climatic conditions?
- Stabilization of Atmospheric CO$_2$ Levels [IPCC Report]

Some solutions to greenhouse gas accumulation

Reduce emissions by vehicles:

- Improved fuel efficiency - Ontario "Drive Clean" program, California's greenhouse gas law
- New power sources for vehicles:
  - Ethanol fuel - Sunoco's ethanol-in-gasoline expected to reduce CO$_2$ emissions by 130,000 tonnes/yr (equiv. to taking over 23,000 cars off the road)
  - Ethanol sources = wood/cellulose, grains & oil crops eg. corn, wheat and barley
  - Economical and ecological impact ???
- Natural gas - "Phill"
- Hybrid electric vehicles (Toyota Prius; NYC buses)
- Hydrogen vehicles - USA, commercial hydrogen fueling station
- Bio-diesel - animal fats, vegetable oils from soybean, canola, corn, sunflower
Lower emissions standards for industry:
• global efforts are forcing more efficient processes and clean-up prior to discharge.

Alternative sources of electricity:
• Solar energy - Australian tower, fairly new technology, costly.
• Wind - fastest growing energy source, potential to provide 12% of global electricity by 2020? well established, cost?
• Tidal forces - Hammerfest, Norway; considerable potential, renewable, but costly, unknown problems re: maintenance, ecological impact
• Nuclear and hydroelectric - 75% of electricity produced by Ontario, minimal emissions

Find new sinks or uses for excess greenhouse gases
• Methane hydrates - USA; proposals to harness the released methane as a fuel source
• CO₂ storage - injection into deep ocean, deep saline aquifers (potential problems: leaks causing asphyxia, pH reductions (eg. Mammoth Mountain http://wrgis.wr.usgs.gov/fact-sheet/fs172-96/), displacement of brine into overlying aquifers?)
• Liquid CO₂ solvent - similar properties to pyridine, already replaced methylene chloride for coffee decafination, safer, cannot be oxidized, does not react to free radicals (Env. Sci. Technol. v36 Sept. 1/02)
Ozone formation and destruction in the stratosphere

- The composition of the stratosphere is similar to that of the troposphere
  - but \( T \sim 220 \text{ K} \)
  - and \( p(\text{total}) \sim 0.1 \text{ atm} \)
- The "ozone layer" is not really a layer

"Chapman Mechanism"

Ozone formation:

\[
\begin{align*}
  O_2 (g) + h\nu & \rightarrow 2 O (g) \\
  \lambda & < 240 \text{ nm (not in troposphere)}
\end{align*}
\]

\[
O (g) + O_2 (g) \rightarrow O_3 (g)
\]

Ozone destruction:

\[
\begin{align*}
  O_3 (g) + h\nu & \rightarrow O (g) + O_2 (g) \\
  \lambda & < 325 \text{ nm (stratosphere and troposphere)}
\end{align*}
\]

\[
O (g) + O_3 (g) \rightarrow 2 O_2 (g)
\]
• Steady state does not correspond to equilibrium (solar driven)
  • note energetics of these reactions
• Over 300,000 t of ozone are made and destroyed each day in the atmosphere
• Experimental concentration of ozone is less than the Chapman mechanism predicts
  • Other sinks for ozone loss

The other sinks are chain reactions involving radical species X, where X can be any of NO, Cl, Br, OH, H

\[
\begin{align*}
X (g) + O_3 (g) & \rightarrow XO (g) + O_2 (g) \\
XO (g) + O (g) & \rightarrow X (g) + O_2 (g)
\end{align*}
\]

Net reaction is:

\[
O (g) + O_3 (g) \rightarrow 2 O_2 (g)
\]

• X is a catalyst that is re-formed in each cycle
• The upper atmosphere contains small concentrations of these "X" substances, and these reactions proceed naturally
What is the significance of stratospheric ozone?

- the conversion of solar radiation into heat makes the stratosphere warmer than the upper troposphere

*Generalization:* the warm parts of the atmosphere all have energy deposited in them

- the absorption of solar radiation < 300 nm in the stratosphere prevents this damaging radiation from reaching the Earth's surface
- in the wavelength range 300-325 nm (UV-B) just a little radiation does leak through, and this is enough to dissociate tropospheric ozone