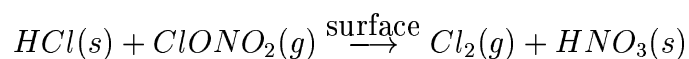


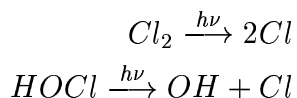
## Ozone Depletion: Part 2

**Antarctic Ozone Hole:** Each spring, the ozone layer thins over the poles.

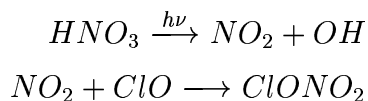
- Regional *and* seasonal
- No CFC production and very limited regional pollutants
- Special winter weather conditions:
  - Severe cold and isolated air flow: circumpolar vortex
  - North pole vortex breaks down before sunlight returns: smaller ozone hole
  - Formation of polar stratospheric clouds (PSC)
    - \* Crystals of  $HNO_3 \cdot 3H_2O$  and larger crystals form in cold
    - \* Reservoir gases formed outside polar regions drift in and undergo reaction on surface of crystal: surface catalysis



- \*  $HNO_3$  forms more crystals with  $H_2O$
- \* Released  $Cl_2$  builds up in polar night: Photolysed in arctic morning sunlight.
- \*  $HOCl$  also formed in surface catalysis reactions
- \* Photo-initiation reactions:



- \* Rapid destruction of ozone via catalytic cycle: Under cold conditions, dimers  $ClO - OCl$  form which are unstable in light.
- \* Once concentration of ozone drops, reservoir reactions dominate and  $HCl$  and  $ClONO_2$  reformed.
- \* In antarctic spring, rise in temperature melts PSCs, liberating  $HNO_3$



- \* Vortex breakdown replenishes ozone layer from outside: mixes air

# Effects of UV radiation

1. Photosynthetic plants: UV B rays make photosynthesis less efficient
  - Plants sensitive to spectrum: Less leaf, seeds and fruit
  - Photoplankton near surface of seas may be affected: Severe repercussions on marine food chain
2. Drop in populations of amphibians (like frogs): Effects of UV radiation on genetic material during development
3. Systematic immunosuppression in humans
  - Conformational change in compound in skin triggered by UV B absorption:  $\pi \rightarrow \pi^*$  electronic transition
    - Trans urocanic acid transforms to cis-urocanic acid under UV radiation
  - Cis-urocanic acid believed to hinder Langerhans cells' ability to recruit killer T-cells: weakens immune response
4. Cancer caused by mutations in genetic material
  - Amino acids tryptophan and tyrosine  $\pi \rightarrow \pi^*$  transitions: protein damage through production of reactive free radicals
  - Thymine and pyrimidine dimerisation in DNA: mutations and cancer
    - Distortions in DNA caused by linkages (dimerisation) between successive Thymine or pyrimidine bases
    - Natural repair mechanisms:
      - (a) DNA photolase: binds to pyrimidine dimer and gains UV absorption band; UV absorption cuts dimer link
        - \* UV light utilized to fix UV damage!
      - (b) UV r-ABC enzyme recognizes pyrimidine dimer and excises it; DNA polymerase builds complementary strand and DNA ligase attaches it
    - Repair not 100% efficient: mutations eventually result
    - Mutations to gene which regulate cell division can lead to cancers

## Skin Cancer and UV Radiation

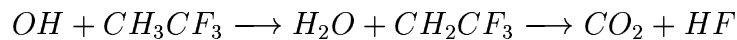
- Almost all skin cancers due to overexposure to UVB light (290 nm)
- 1% decrease in ozone layer  $\implies$  2% increase in ground UVB intensity
- Predict a 1 – 2% increase in cancer for 1% decrease in ozone layer
  - 1979-1992: 6.6% decrease in ozone level in southern Canada; expect a 15 – 20% increase in skin cancer in the long run
  - Australia: estimated that 75% of skin cancers due to exposure
    - \* Leading the CFC control movement
- Research indicates that sunscreens can *increase* rate of cancer
  - Sunscreens that filter out only UVB rays and not UVA rays (315 nm) can lead to false sense of security: longer exposure times and bad times of day

### Sunscreens and sunburns:

- Melanin in melanocytes absorbs UV radiation
  - Production of melanin stimulated by radiation
  - Stops UV damage to underlying tissue
  - People differ not in number of melanocytes but in amount of melanin produced per melanocyte
- Sunburn characterised by erythema-reddening of skin
  - Function of energy of photon and not total energy absorbed: UVC and UVB most energetic
- Melanin scatters UV light-Zinc oxide
- Some sunscreens absorb UV light but undergo no harmful photochemical reaction
  - Phototoxic: photochemical reactions which are toxic
  - Philosophy: Absorb UV radiation via an electronic excitation; either a harmless internal chemical reaction occurs or energy is transferred into vibrational excitations and heat
  - Examples: PABA and O-Hydroxybenzophenone

# CFCs and Controls

- Problem: Catalytic destruction of ozone by *Cl* and *Br* in stratosphere
- Source: CFCs like CFC-12 (refrigerant) and CFC-11 (blowing agent)
- Goal: Replace CFCs with environmentally safe alternatives
- Strategy: short-term use of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) in existing technology
  - Contain *C – H* bonds which can be attacked by *OH* radical in troposphere: converted into water soluble gases and rained out of atmosphere
  - Shorter lifetimes in atmosphere so don't diffuse into stratosphere
  - Example: HFC-134a (refrigerant, air-conditioners) has similar properties to CFC-12 but has 1/10 lifetime in atmosphere: not very short life since Fluorine atoms stabilize *C – H* bond



- Best idea: alternative technology or replacements for all CFCs, HCFCs, HFCs
  1. Aerosol propellants: isobutane or dimethyl ether
  2. Hydrocarbon blowing agents (in styrofoam production)
    - Old styrofoam has residual CFCs from blowing process that gradually leak into atmosphere
  3. Refrigerants: more challenging
    - Propane-butane mixture made in Germany: “Greenfreeze”
    - New mechanisms avoiding compressors
  4. Halons: used to smother fires
    - $CF_3Br$ ,  $CF_3I$  possible, but toxicity questions

# History of CFC Controls

- 1974: Sherwood Rowland and Mario Molina at U.C. Irvine demonstrate chlorine catalytic ozone destruction mechanism and predict depletion on ozone layer: no experimental evidence at time
- Late 70s: North America and some Scandinavian countries ban use of CFCs
- Early 80s: Increasing evidence and awareness of ozone depletion
- 1987: “Montreal Protocol”-international conference in Montreal: reach agreement to reduce and phase out CFC production and usage on a timetable
- 1990 London and 1992 Copenhagen conferences lead to amendments to
  1. Cease all CFC and Halon production by 1995
  2. Phase out all chlorinated compounds (HCFCs) by 2040
- Canada’s role in ozone depletion
  - Active in ozone research since 1930: part of studies of upper atmosphere and impact on weather forecasting
  - Published ozone level data under United Nations World Meteorological Organisation (UNWNO)
  - High arctic ozone observatory in Ellesmere Island in 1993 established by Canadian government
    - \* Designed two ozone measuring devices; sunphotometer and Brewer ozone spectrometer

**Outlook?** Not bad if controls observed

- Ozone hole may start to fill in by 2050 if 1992 Copenhagen revisions to Montreal protocol observed: Uncertainty due to global warming and climate modelling