

# Atmospheric Chemistry I

## Knowledge "explosion"

Space probes, remote sensing  
Growing awareness that Man can interfere  
    ozone hole, acid rain, smog formation  
CO<sub>2</sub> as greenhouse gas (return later to greenhouse effect)

## Nature of atmospheric chemistry

Atmospheric concentrations; sources, sinks  
    e.g. COW → CH<sub>4</sub> → [chemistry in atmosphere] → CO<sub>2</sub> + H<sub>2</sub>O  
            ↑                                    ⇐ photosynthesis      ⇐ deposition  
Laboratory studies of reaction paths and rates  
Models linking lab. and field data

## Need for CHEMISTS with understanding of problems

## Nature and structure of course

In pursuit of knowledge, good vehicle for illustration both of fundamental physico-chemical principles and of experimental studies

Overview and principles  
Atmospheric ozone in stratosphere; Man's influence on stratospheric ozone  
Troposphere; heterogeneous processes and droplet chemistry; pollution  
Mesosphere; airglow

Nature of course – limitations; handouts; books

## Variety of atmospheres

Mercury

Venus, Mars .. to .. Jupiter, Saturn .. Uranus, Neptune

The moons of Jupiter, Saturn, and Neptune: Callisto, Io, Titan, Triton

Earth: H<sub>2</sub>O liquid (temperature stability over geological time);

Major constituents: O<sub>2</sub>/N<sub>2</sub>; CO<sub>2</sub> in carbonate rocks

Other minor gases: CH<sub>4</sub>, CO, H<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>: "combustible mixture"

Biological processes have effected the disequilibrium: entropy reduction, driven by Solar energy

## Cycles

Almost closed, but some escape, and some input from outside

On Earth, importance of biota: biogeochemical cycles

Atmospheres as giant photochemical reactors

    Penetration of UV, and energetics of chemistry

        UV progressively filtered out by atmospheric constituents: by the ground, just about enough to give you a suntan.

## Origin of solar system, planets and atmospheres

Primordial (outer planets – solar abundances) and secondary (Venus, Earth, Mars) atmospheres

Big bang → H, He; Fusion → heavier elements; > Fe from supernova explosions that scatter C, H<sub>2</sub>O, silicates of Mg, Fe. Accretion, galaxies, formation of stars, etc.

## Composition of Earth's atmosphere

Major constituents: already presented in handout 1.1

Noble gases:

<sup>36</sup>Ar about 10<sup>6</sup> too low, <sup>20</sup>Ne 55 x 10<sup>6</sup> too low

Ar and He from radioactive decay

RMM of Ar means almost all is <sup>40</sup>Ar (<sup>36</sup>Ar/<sup>40</sup>Ar ≈ 1/300)

In natural gases, [Ar]/[He] roughly 1, but in atmosphere nearly 2000: evidence that He has escaped

Main point: all original (primordial) gas has escaped, that which remains has degassed from the interior of the planet

## Comparison of Venus, Mars, and Earth

Compositions of atmospheres: pie charts

Carbon dioxide on the three planets

The Greenhouse effect

$\lambda_{\text{peak}}$  for 5780K just less than 1 $\mu\text{m}$

$\lambda_{\text{peak}}$  for 256K just more than 10 $\mu\text{m}$

Runaway Greenhouse Effect

Venus - all CO<sub>2</sub> in atmosphere: no H<sub>2</sub>O

Mars - almost all CO<sub>2</sub> condensed

Life on Earth

CO<sub>2</sub> in rocks (biological and abiological weathering) and oceans. Liquid H<sub>2</sub>O; ? Temp control.

## EARTH

### Pressures

Hydrostatic Equation: effectively single mass 28.8 to 100km (reason)

P drops by factor of 10 in ca. 18km: 90% mass of atmosphere in first 17km.

Mean Free Paths: mixing, separation, and escape

### Temperatures

Division into regions: expect to drop with z, but note inversions (reasons soon): stability of inversion regions

adiabatic lapse rate (dry) ~ 6K km<sup>-1</sup>

### Chemosphere

Minor neutral constituents

Altitude profile: note O atom dominance at high z

O<sub>3</sub> in the atmosphere: rôle in stratosphere and troposphere

## Atmospheric Chemistry I : Slides

1. YG 60 Growth of carbon dioxide levels
2. B 50 Mercury mosaic
3. B 3 Clouds of Venus
4. YG 6 Mars and Phobos:  
n.b. Polar caps (N = water; S = carbon dioxide)
5. YG 7 Mars: Plume of water ice
6. YG 8 Mars: Clouds of water ice
7. B 75 Voyager trajectory
8. B 16 Jupiter: General view
9. B 61 Saturn: General view (Voyager 2; 21Mkm)
10. B 52 Jupiter with Io and Europa
11. B 14 Jupiter and moons (closer in)
12. B 55 Callisto
13. B 56 Io: General
14. B 58 Io: Volcanic activity
15. B 59 Io: Volcanic lava flow
16. B 65 Titan (Voyager 1)
17. B 73 Titan Haze (more detail)
18. B 76 Neptune (Voyager 2)
19. B 77 Neptune (methane enhanced)
20. B 78 Triton (geysers)
21. YG 9 Earthrise
22. YG 10 Earth (USA)
23. YG 4 Cyclic processes: Sources & sinks of atmospheric gases
24. YG 61 Cyclic processes with biota (from C of A)
25. YG 1 Origin of atmospheres: Nebula M42
26. BG 10B Noble Gases: Graph of abundances
27. YG 63 Volcano eruption
28. YG 11 Abundance of Gases: Pie chart for Venus
29. YG 12 Abundance of Gases: Pie chart for Mars
30. YG 13 Abundance of Gases: Pie chart for Earth
31. BG 50 Greenhouse effect
32. BG 16 Runaway greenhouse effect for Venus: phase diagram
33. R 1 Regions of Earth's atmosphere
34. R 2 Concentration of neutral species in Earth's atmosphere

## **Atmospheric Chemistry I : Viewgraphs**

1. Nature of atmospheric chemistry
2. Tropospheric gases
3. Methane from enteric fermentation
4. Cyclic processes of biogeochemistry (from C of A): see also slide 24
5. Pressure and mean free path as a function of altitude; hydrostatic equation
6. Regions of Earth's atmosphere: troposphere, stratosphere, mesosphere