Human Impacts on the Atmosphere Review Questions

Review Questions A: Composition and Stratification of the Atmosphere

A1. Which three gases constitute most of the earth's atmosphere?

The major constituent gases of the atmosphere are molecular nitrogen N_2 (78%), molecular oxygen O_2 (21%), and argon (1%)

A2. What range of altitudes constitute the troposphere? the stratosphere?

The troposphere is the lowest level of the atmosphere, and extends from Earth's surface up to anywhere from about 7-8km at the poles, to around 18-20km near the equator. The stratosphere is the layer above the troposphere, so extends from the top of the troposphere up to a height of 50km.

A3. Describe the stratification of the atmosphere. Consider the basis on which stratification is achieved, and the names, features, and predominant chemical species and chemical process which occur in each of the strata.

The atmosphere consists of four main layers: from ground level up they are the troposphere, stratosphere, mesophere, and thermosphere. Stratification is defined by the pattern of temperature and pressure variations with increasing altitude. The trophosphere extends upwards for roughly the first 10km above the Earth's surface, and is the portion of the atmosphere where essentially all weather phenomena take place. At the top of the troposphere is the tropopause, a region where the temperature (which decreased with altitude throughout the troposphere) first stabilises and then begins the increase, with temperature continuing to increase with altitude throughout the stratosphere. This warming in the stratosphere is caused by absorption of ultraviolet radiation by the ozone layer, a region of significantly higher concentration of the UV absorbing molecule ozone O_3, and is located at an altitude of around 20-30km. The stratopause marks the boundary between the stratosphere and the mesosphere, the third layer of the atmosphere where temperatures once again decline with altitude, as distance from the relatively warm ozone layer diminishes, and also owing to the fact that the mesophere lacks significant concentrations of radiation-absorbing species. The mesosphere extends from 50 to 85km, its upper boundary marked by the mesopause, where temperatures once again begin to increase with altitude. The upper layer of the atmosphere, extending above 85km in altitude, is called the thermosphere, and here the temperature once again increases with altitude owing to the absorption of high energy ultraviolet radiation.

The troposphere is comprised mostly of molecular nitrogen, molecular oxygen, argon gas and carbon dioxide. It also contains smaller amounts of methane, ammonia, carbon monoxide, nitrous oxides, and other noble gases, in addition to particulate matter such as dust, soot, salt, and organic particles, products of both natural processes such as volcanoes and wind, as well as anthropogenic pollutants. Radical species are rare in most of the troposphere owing to the presence of so many other species with which they readily react. In the stratosphere the most important species is ozone O_3, which absorbs UV radiation to produce molecular oxygen, thereby protecting the surface of the earth from radiation that would otherwise be harmful to terrestrial life if it reached the earth's surface. The composition of the mesophere is relatively poorly understood, though it is known that

O_2^+ and NO^+ radicals predominate. The thermosphere has a similar composition to the stratosphere, though it lacks the concentrations of ozone found in the stratospheric ozone layer. Important chemical species in this layer include O_2^+, O^+, and NO^+ ions, which are formed when respectively O_2 and N_2 absorb UV radiation or interact with cosmic rays.

A4. What phenomenon is responsible for the temperature maximum at the boundary of the stratosphere and the mesosphere?

The temperature maximum which occurs at the stratopause is the result of the distribution of UV-absorbing species within the atmosphere. Specifically, there are relatively high concentrations of ozone (which absorbs UV very readily) in the mid stratosphere, and very few such UV-absorbing species in the thermosphere. By the nature of the diffusion of heat in gases, there will be some point of maximum temperature where the heating effect of the UV-warmed ozone layer is exactly counterbalanced by the cooling effect of the mostly UV-transparent mesosphere. The altitude where this equilibrium occurs will correspond to a temperature maximum, and is referred to as the stratopause.

Review Questions B: Energy and Mass Transfer in the Atmosphere

B1. Outline how the interactive effects of the circulation of air masses, the evaporation and condensation of water, and the redistribution of solar energy results in the weather pattern of a particular area.

Weather refers to variations in such properties as temperature, pressure, wind, humidity, cloud cover, and precipitation in a particular location over relatively short periods of time. The ultimate source of essentially all weather phenomena is differential heating of the Earth's surface by the sun, and consequent redistribution of this energy about the Earth, notably through changes in air pressure and evaporation and condensation of water.

Since water has such a high specific heat capacity, a significant amount of solar energy is consumed in the process of evaporating water from oceans and lakes, which naturally occurs in regions of relatively high insolation (e.g. the tropics). Parcels of air warmed by their proximity to the heated water experience decrease in density (as warm as is less dense than cool air), and so tend to rise. As the air rises, it expands (as it moves into regions of lower atmospheric pressure) and therefore cools, and as such its capacity to hold water vapour diminishes. Water vapour thus condenses, releasing the energy gained during evaporation, forming clouds or potentially falling to Earth as precipitation. Heat is also lost by diffusion and radiation to cooler upper parts of the troposphere. The now cool, dry parcel of air becomes denser and therefore subsides (moves toward ground level), producing regions of high pressure. Air tends to be pushed from these regions of high pressure towards regions of low pressure (often areas where air is experiencing heating and therefore rising as explained above), thereby generating horizontal movements of air called wind. These generic weather phenomena are often modified by details of local terrain, vegetation, elevation, proximity to the ocean, and other such factors, thereby yielding the unique weather patterns that characterise different regions of the globe.

B2. Discuss the causes and effects of the El-Nino Southern Oscillation (ENSO).

In the region of the south-central Pacific Ocean, near the equator, the usual trade winds typically blow from east to west, a product of the coriolis force produced by the earth's rotation. These winds move relatively warm water near the ocean surface along with them, which are replaced by upwelling of cold waters along the South American coast. This results in what is called a thermocline forming, that is a band of equal oceanic temperatures which gradually slopes upward (meaning that the same temperature occurs at a shallower depth) from west to east across the Pacific. As warm air reaches the western end of the pacific, it rises and thereby loses its ability to hold moisture, causing heavy rains in the areas of northern Australia, South-east Asia, and India.

Every two to seven years, this normal pattern is disrupted in what is called an El Nino event. During an El Nino year, for reasons still not fully understood, the trade winds are diminished or even reverse direction entirely, causing upwelling of air and hence heavy rain in the mid Pacific region, and leading to corresponding draughts in Australia and South-East Asia. The oceanic thermocline is also disrupted, halting the upwelling of cold water from the ocean bottom which typically occurs along the South American coast, thereby reducing nutrient availability for fishing stocks in the area and hence causing severe disruption to local fisheries. The ENSO phenomenon has a particularly strong effect on Eastern Australia, and has been responsible for many severe droughts and accompanying bushfires.

Review Questions C: Carbon Dioxide and Global Climate

C1. Explain in terms of the mechanism involved what is meant by the greenhouse effect.

The greenhouse effect is a physical process by which certain gases called greenhouse gases absorb infrared radiation as it is emitted by the Earth, re-radiating some of it towards the Earth, and thus causing a warming of the Earth's surface. The greenhouse effect is a natural phenomenon which raises Earth's surface temperatures by roughly 30 degrees Celsius, making the Earth habitable for life.

Greenhouse gases such as methane, water, and carbon dioxide are present in the troposphere. They are mostly transparent to the visible and ultraviolent light the earth receives from the sun, but are able to absorb significant amount of infrared light which is re-emitted by lower portions of the troposphere (it is sometimes said the Earth's surface radiates infrared, but most such light is actually emitted from the atmosphere, not the surface itself - the atmosphere is warmed by the surface mostly by the effects of heat convection and conduction rather than radiation). The light is re-emitted in all directions, including down towards the surface of the Earth. The effect of this is essentially to trap in some portion of the energy, thereby raising the surface temperature of the Earth.

C2. Is water vapor a greenhouse gas? If so, why is it not usually present on lists of such substances?

Water vapor is a greenhouse gas, and indeed is responsible for a large fraction (possibly even a majority) of the warming effect of the Earth's surface cause by absorption of infrared radiation. The reason water vapour is often excluded from lists of greenhouse gases is that it does not act as a forcing mechanism for increased global temperatures, but rather is a positive feedback mechanism. This is because water vapour has a very short residence time in the atmosphere, and so its atmospheric concentration is mostly a consequence of prevailing global temperatures (as more water vapour will be held in the atmosphere at higher temperatures) rather than a direct initial cause of such higher temperatures itself.

C3. What is meant by the term "window" as applied to the emission of IR from the Earth's surface? What is the range of wavelengths of this window?

Infrared radiation is emitted by the Earth across a range of wavelengths, each corresponding to a slightly different energy. Different greenhouse gas molecules have different vibrational energies, and thus are capable of absorbing different wavelengths of radiation. Those bands of wavelengths where little absorption occurs, because few or no chemical species exist in the atmosphere which can absorb these wavelengths, are known as 'windows', since they are relatively transparent to infrared radiation.

C4. Why are CFCs such as CF_2Cl_2 and $CFCl_3$ such effective greenhouse gases?

Chlorofluorocarbons (CFCs) are a particularly effective greenhouse gas because of their long lifetime in the atmosphere (thousands of years for some varieties), and also the fact that they absorb infrared radiation from what would otherwise be an atmospheric 'window'.

C5. What are the four important trace gases that contribute to the greenhouse effect?

Four key trace gases which are also greenhouse gases are carbon dioxide, methane, nitrous oxide, and ozone.

C6. What characteristic molecular properties of H_2O and CO_2 cause their absorption of IR radiation?

Water and carbon dioxide are both able to absorb IR radiation because they are what is called 'IR active'. This means that they possess a dipoles which can be altered by absorption of an infrared photon, thereby inducing a new vibrational motion. Simple symmetrical molecules such as O_2 and N_2 are not IR active because they lack additional vibrational states to which they can be excited, and thus they are unable to absorb infrared photons.

C7. Describe the two opposing effects on climate resulting from combustion of coal with high sulfur content.

Coal combustion releases significant quantities of carbon dioxide, which being a greenhouse gas tends to increase global temperatures. On the other hand, the burning of sulphur rich coal will also tend to release significant quantities of particulate matter into the atmosphere, which will reflect incoming solar radiation and hence contribute a cooling effect.

C8. The amount of CH_4 emitted annually is estimated to be 25 to 50 times greater than the amount of N_2O emitted annually, yet the atmospheric concentration of CH_4 is estimated to be only 6 times higher. Explain.

The greater rate of methane emissions compared to nitrous oxide emissions over the industrial period has increased the relative concentration of methane in the atmosphere: in the preindustrial period the concentration of methane was only about three times higher than nitrous oxide, whilst today it is some six times higher. The reason the relative increase has not been greater, despite the much larger amount of methane released every year, is that the atmospheric lifetime for methane is only about ten years compared to 150 for nitrous oxide. This means that the rate at which methane is being removed from the atmosphere is greater than the rate at which nitrous oxide is being removed, thus explaining the apparent discrepancy.

Review Questions D: Chemical and Photochemical Reactions in the Atmosphere

D1. The enthalpy change for the decomposition of ozone into O_2 and atomic oxygen is +105 kJ/mol. What is the longest wavelength of light that could dissociate ozone in this manner? Calculate the longest wavelength of light that decomposes ozone to O_2 and O, given that the excited state of atomic oxygen lies 190 kJ/mol above the ground state?*

For the decomposition of ozone:

$$E = hv$$
$$\frac{105 \times 10^3 Jmol^{-1}}{6.022 \times 10^{23} mol^{-1}} = 6.626 \times 10^{-34} Js \times 3.00 \times 10^8 \times ms^{-1} \times \frac{1}{\lambda}$$
$$\frac{105 \times 10^3}{6.022 \times 10^{23}} = 19.878 \times 10^{-26} m \times \frac{1}{\lambda}$$
$$17.44 \times 10^{-20} \lambda = 19.878 \times 10^{-26} m$$
$$\lambda = 1.139 \times 10^{-6}\ m$$
$$\lambda = 1.14\ \mu m$$

For the decomposition of O_2 to O^*:

$$E = hv$$
$$\frac{190 \times 10^3 Jmol^{-1}}{6.022 \times 10^{23} mol^{-1}} = 6.626 \times 10^{-34} Js \times 3.00 \times 10^8 \times ms^{-1} \times \frac{1}{\lambda}$$
$$\frac{190 \times 10^3}{6.022 \times 10^{23}} = 19.878 \times 10^{-26} m \times \frac{1}{\lambda}$$
$$31.55 \times 10^{-20} \lambda = 19.878 \times 10^{-26} m$$
$$\lambda = 1.587 \times 10^{-6}\ m$$
$$\lambda = 1.58\ \mu m$$

D2. What is (a) an excited state (b) a quanta of light (c) a Dobson unit (d) a free radical (e) steady state concentration (f) a tropospheric sink?

a) Atoms, molecules, and many other physical systems have multiple quantised energy states. The most stable, lowest energy of these is called the ground state, and any higher energy levels, which are generally less stable, are called excited states. A system in its ground energy state can reach an excited state by absorption of energy, often from a photon.
b) A quanta of light refers to a single discrete unit of electromagnetic radiation, commonly called a photon.
c) A Dobson unit is a unit of measurement applicable in describing the quantity of trace gases in the atmosphere. A single Dobson unit describes the height, at sea level, of all the gas of a certain type of chemical species contained in a column of atmosphere extending upwards from a given area. Thus, for instance, if all the ozone in a column of atmosphere were brought to sea level, it would form a column roughly 3mm tall. Since one Dobson unit is defined as a column of $10 \mu m$ in height, it is said that the atmospheric concentration of ozone is about 300 Dobson units.
d) A free radical is a chemical species with an unbonded electron. They are highly reactive
e) Many chemical reactions can occur in both directions, or in other instances a species may be created by one reaction and then consumed in a second reaction occurring concurrently. In either case, either all of the species (or the reactants which combine to form it) will be used

up and the reactions will quickly cease, or else an equilibrium will be established wherein the rate at which the species is produced in one reaction is equal to the rate it is consumed in another reaction. The concentration of the species that prevails under such conditions is called the steady state equilibrium concentration.

f) A tropospheric sink is any process which acts to remove a particular species from the troposphere. An example is the removal of the hydroxy radical by its reaction with methane:

$$CH_4 + HO \cdot \rightarrow H_3C \cdot + H_2O$$

D3. What is the two-step mechanism by which the hydroxyl free radical is produced in clean air?

The hydroxy radical $HO \cdot$ can be produced by photodecomposition of ozone:

$$O_3 + hv \rightarrow O^* + O_2$$
$$O^* + H_2O \rightarrow 2HO \cdot$$

D4. What two chemical species are most generally responsible for the removal of hydroxyl radical from the unpolluted troposphere?

The hydroxy radical can be removed by reaction with either carbon dioxide or methane:

$$CH_4 + HO \cdot \rightarrow H_3C \cdot + H_2O$$
$$CO + HO \cdot \rightarrow CO_2 + H$$

D5. By what mechanism is formaldehyde, H_2CO, decomposed in air?

Formaldehyde is decomposed by photodecomposition, which in a two stage process forms the formyl radical:

$$HCHO + hv \rightarrow H + \cdot CHO$$
$$\cdot CHO + O_2 \rightarrow HOO \cdot + CO$$

D6. What function does a third body play in an atmospheric chemical reaction?

A third body, often denoted M, is generally an inert molecule such as O_2 or N_2, which collides with a reactive intermediate, absorbing its excess energy which it then later dissipates as heat, thereby helping to stabalise the product of a reaction. For example an excited oxygen molecule could react with a third body as follows:

$$O_2^* + M \rightarrow O_2 + M^*$$
$$M^* \rightarrow M + heat$$

D7. Discuss, in general terms, the reactivity and stability of free radicals and electronically excited species in the upper atmosphere.

Free radicals and electronically excited states are both quite reactive, however their stability in the upper atmosphere differs. Electronically excited states are inherently unstable, and generally decay into their ground state counterparts quite rapidly, emitting photons containing the excess energy. This process occurs independently of surrounding chemical species, and so occurs readily in the upper atmosphere. Thus, electronically excited states do not persist any longer in the upper atmosphere than elsewhere, but require continual re-creation by reaction with high energy photons.

By contrast, free radicals are much longer lived in the upper atmosphere. This is possible because, although their unpaired electron makes them very reactive in the presence of other chemical species, the very low density of the upper atmosphere means that collisions with other molecule are rare, and hence free radicals can be fairly stable in the upper atmosphere, in spite of their high reactivity.

Review Questions E: Stratospheric Ozone

E1. Which atmospheric gas is primarily responsible for filtering sunlight in the 120-220 nm region? Which gas absorbs most of the sun's rays in the 220-320 region?

Molecular oxygen O_2 is primarily responsible for absorbing sunlight of wavelength 120-220nm, while ozone O_3 absorbs wavelengths around 220-320nm.

E2. Write the equation for the chemical reaction by which ozone is formed in the stratosphere. What are the sources of the different forms of oxygen used here as reactants?

Ozone is formed by the reaction:

$$O + O_2 + M \rightarrow O_3 + M$$

Where M is an inert third body which absorbs excess energy. Atomic oxygen is formed by the photodissociation of molecular oxygen:

$$O_2 + hv \rightarrow O + O$$

Molecule oxygen is released into the atmosphere by plants and bacteria performing photosynthesis.

E3. Write the two reactions that, aside from the catalysed reactions, contribute most significantly to ozone destruction in the stratosphere.

Ozone is destroyed by absorption of a high energy photon:

$$O_3 + hv \rightarrow O_2 + O$$

And also by reaction with atomic oxygen:

$$O + O_3 \rightarrow 2O_2$$

E4. Explain why the density of ozone peaks at 25 - 30 km altitude, yet the maximum temperature occurs at about 50 km.

Though the density of ozone peaks around 25-30km in altitude, ozone is still present at higher altitudes in the stratosphere, and even in the lower regions of the mesosphere. This uppermost ozone will be exposed to full intensity of UV from the sun, as very little will as yet have been absorbed or scattered by any gases. The lower one progresses in altitude, the more of the UV radiation has already been absorbed by the overlying ozone molecules. This means that it is the upper regions of the ozone layer which do most of the absorption of UV radiation (and hence are at the highest temperatures), not the area with the highest concentration of ozone, as much UV light has already been absorbed by the time light reaches that altitude.

E5. What are the two steps and the overall reaction by which species X such as $Cl^{\cdot}$ catalytically destroy ozone in the middle and upper stratosphere?

The catalytic reaction is given by:

$$O_3 + X \rightarrow O_2 + XO$$
$$XO + O \rightarrow O_2 + X$$

Note that X acts as a catalyst since it is a reactant that is regenerated as a product.

E6. What is the current estimate of the loss in stratospheric ozone per decade?

Since the Montreal Protocol of 1987, substantial reductions in emissions of CFCs have led to the stabilisation of global stratospheric ozone levels. It is currently estimated that, absent further major changes, they will return to pre-industrial levels roughly by the end of the century.

E7. What is the principal four step mechanism by which chlorine destroys ozone in the spring over Antarctica?

The mechanism involves a liberated chlorine radical reacting with ozone:

$$2Cl\cdot + 2O_3 \rightarrow 2ClO\cdot + 2O_2$$
$$2ClO\cdot \rightarrow ClOOCl$$
$$ClOOCl + hv \rightarrow ClOO\cdot + Cl\cdot$$
$$ClOO\cdot \rightarrow O_2 + Cl\cdot$$

Yielding an overall conversion of $2O_3$ to $3O_2$, and regenerating the chlorine radical.

E8. Describe the process by which chlorine becomes activated in the Antarctic ozone-hole phenomenon.

Beginning in the form $ClONO_2$, chlorine is first released by reaction with water ice:

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$$
$$HOCl + hv \rightarrow HO\cdot + Cl\cdot$$

Alternatively, the activation can occur by reaction with hydrochloric acid:

$$ClONO_2 + Hcl \rightarrow Cl_2 + HNO_3$$
$$Cl_2 + hv \rightarrow 2Cl\cdot$$

In both cases, absorption of a photon is necessary in order to yield the activated chlorine radical.

E9. Explain why ozone holes have not yet been observed over the Arctic.

Throughout most of the atmosphere, nitrogen dioxide reacts with chlorine monoxide to produce $ClONO_2$, thereby suppressing the catalytic activity of chlorine. During the Antarctic winter period, temperatures get so cold that nitrogen dioxide freezes out of the atmosphere, thereby significantly increasing the amounts of catalytically active chlorine present in the circumpolar atmosphere, and hence resulting in much more severe ozone loss. This does not occur to nearly the same extent in the Arctic because it does not get as cool as the Antarctic.

E10. Explain why ozone destruction via the reaction of O_3 with atomic oxygen does not occur to a significant extent in the lower atmosphere.

Ozone is not broken down by reaction with atomic oxygen in the lower atmosphere predominantly because atomic oxygen is extremely reactive, and so is largely absent in the lower atmosphere, where due to denser concentrations of other chemical species it would quickly react and be converted to an alternative form.

E11. Deduce the formulae for the compounds with the following code numbers: (a) 12 (b)113 (c)123 (d) 134.

a) 12+90=102, so formula is CF_2Cl_2
b) 113+90=203, so formula is $C_2F_3Cl_3$
c) 123+90=213, so formula is $C_2HF_3Cl_2$
d) 134+90=224, so formula is $C_2H_2F_4$

E12. Deduce the code numbers for each of the following compounds: (a) CH_3CCl_3 (b) CCl_4 (c) CH_3CFCl_2

a) $CH_3CCl_3 = C_2H_3Cl_3$ has the number 230-90=140
b) CCl_4 has the number 100-90=10
c) CH_3CFCl_2

E13. What are the effects to human health that scientists believe will result from ozone depletion?

Since ozone absorbs ultraviolet light, ozone depletion will cause more UV radiation to reach the surface of the Earth, causing an increase in cataracts and skin cancer, both of which can be caused by such radiation. It is also thought that UV radiation could potentially have negative effects on the immune system.

Review Questions F: Particulates in the Atmosphere

F1. Suppose a cubic particle with sides of length 3k is split up into 27 particles with sides of length k. Calculate the relative increase in surface area.

Original surface area:

$$TSA_0 = 6 \times (3k)^2$$
$$= 6(9k^2)$$
$$TSA_0 = 54k^2$$

New surface area:

$$TSA_1 = 27 \times 6 \times k^2$$
$$TSA_1 = 162k^2$$

Which is a threefold increase in surface area.

F2. Per unit mass, why are smaller particles more effective catalysts for atmospheric chemical reactions?

Particulate matter can have catalytic effects generally as a result of chemical species adsorbing to or otherwise interacting with their surface. Reducing the size of particles whilst retaining the same mass increases the total surface area, thereby increasing the degree to which they can serve as catalysts.

F3. Define the term "aerosol" and differentiate between "coarse" and "fine" particulates. What are the usual origins of these types of atmospheric particles. Why are coarse particles usually of less danger to human health than fine particles?

An aerosol is a substance which consists of particles of either liquid or solid matter evenly dispersed throughout a medium of gas (often air). Dispersed particles that have a diameter greater than $5\mu m$ are described as coarse, while fine particles have a diameter less then $0.5\mu m$. Fine particles are of most concern to human health because they are sufficiently small to be able to become lodged deep in the lungs, causing various respiratory problems.

F4. What would the designation PM25 mean?

PM25 refers to particular matter the constituent particles of which are less than $25\mu m$ in diameter.

F5. Why are aerosols in the 0.1 to 1 μm size range especially effective in scattering light?

The 0.1 to 1 μm range corresponds to 100-1000nm, which covers the full range of wavelengths of visible light (roughly 380-750 nm). Particles this size will have the maximum surface area for a given mass of material, without being so small that they are too small to scatter the photons of visible wavelength. Thus they are particularly effective at scattering visible light.

F6. Name and define two types of particulates found in the atmosphere, and indicate the sort of physical or chemical processes from which they may be formed.

Polycyclic aromatic hydrocarbons are solid particles consisting of joined rings of carbon atoms. They are formed from incomplete combustion of fossil fuels, and typically found adsorbed to soot particles. Lead halides are another type of particle which consist of solid particles of most lead chloride, lead bromide, and lead chlorobromide, which are released from combustion engines burning petrol to which has been added tetraethyllead.

F7. What are some of the environmental effects of atmospheric particulates?

Atmospheric particles, especially fine particles, scatter visible light, and so can reduce visibility. Particles can also serve as nucleation bodies for condensation of water, thereby altering rainfall patterns. By increasing cloud formation through this nucleation effect, particulates also increase the albedo of the Earth, thereby causing an overall cooling effect, though this is also offset by the effect of clouds trapping infrared radiation and thus causing a greenhouse-like effect. Overall the effect of albedo is thought to be greater and particulates thus cause net cooling, though much uncertainty remains, however in either case it is clear that particulates have important effects on global temperatures.

F8. Discuss the control of particulate emissions.

A variety of methods exist for control of particulate emissions. Fine filters can remove even very small particles, allowing only gas to pass through. Wet scrubbers are another type of device which works by passing exhaust gases through a liquid solution, causing the solution to trap some proportion of the particulate matter from the exhaust, and thus reducing emissions to the environment. A cyclone is yet another device used for cleaning air, which works by rotating an air stream inside a cylinder at speeds fast enough such that the inertia of the more massive particulates is too great for them to follow the curved path of the air. Instead the particles (above a certain size) crash into the sides of the cylinder, falling to the bottom where they can be collected. A fourth method involves the use of electrostatic precipitators, which cause particles to acquire a charge by passing them through a high voltage, and then attract the particles to the sides of the container by electrostatic forces, allowing the cleaned air to pass through.

Review Questions G: Acid rain

G1. Calculate the pH of rain water in equilibrium with SO_2 in a polluted air mass where sulfur dioxide concentration is 1 ppm (ie., 1 x 10^{-6} atm), given that K_H = 1 M atm^{-1} and $K_a(H_2SO_3)$ = 1.7 x 10^{-2} M.

Beginning with the reaction for the formation of sulphuric acid from sulphur dioxide:

$$SO_2(g) + \frac{1}{2}O_2(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

We can calculate the equilibrium concentration of H_2SO_4:

$$\begin{aligned}[H_2SO_4] &= K_H \times p(SO_2) \\ &= 1\ M\ atm^{-1} \times 10^{-6}\ atm \\ [H_2SO_4] &= 1 \times 10^{-6}\ M\end{aligned}$$

Then using the reaction for the dissociation of sulphuric acid:

$$H_2SO_4(aq) \rightarrow HSO_4^-(aq) + H^+(aq)$$

We can calculate the concentration of hydrogen ions:

$$\begin{aligned}[H^+] &= \sqrt{K_a \times [H_2SO_4]} \\ &= \sqrt{1.7 \times 10^{-2}\ M \times 1 \times 10^{-6}\ M} \\ &= \sqrt{1.7 \times 10^{-8} M^2} \\ [H^+] &= 1.3 \times 10^{-4} M\end{aligned}$$

Using this we can calculate the pH of the water solution:

$$\begin{aligned}pH &= -\log_{10}[H^+] \\ &= -\log_{10}(1.3 \times 10^{-4}) \\ &= -\log_{10}(1.3) - \log_{10}(10^{-4}) \\ &= -0.1139 + 4 \\ pH &= 3.9\end{aligned}$$

G2. What are the names and main sources of the primary pollutants that produce acid rain?

The primary atmospheric pollutants responsible for the production of acid rain are sulphur dioxide and nitrogen dioxide. Emissions from power generation, heavy industry, and automobiles are the main source of these compounds.

G3. What is the rationale for classifying most acid rain as secondary pollution?

Secondary pollutants are substances that form in the atmosphere by reacting with primary pollutants, that is substances which themselves are directly produced by human activity. Acid rain is a secondary pollutant because the acids that cause it are mostly not directly emitted by humans, but form in the atmosphere by reactions involving primary pollutants that are directly emitted.

G4. Outline a general mechanism for the formation of acid rain.

Acid rain forms from the oxidation under moist conditions, and generally catalysed on the surface of particular matter, of primary pollutants such as sulphur dioxide and nitrogen dioxide (released as a result of fossil fuel combustion and other industrial processes) in the atmosphere, as per the reactions:

$$SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4(aq)$$
$$2NO_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2HNO_3(aq)$$

The aqueous products are highly soluble and strongly acidic, and thus significantly reduce the pH of precipitation in the region they form (or to where they are transported by air currents), thus causing acid rain.

G5. Describe the environmental effects of acid precipitation.

Acid rain can cause a variety of environmental problems. It can lead to the acidification of rivers and lakes, killing fish and disrupting habitats of various other species. Acid rain can directly damage plants, and hamper their growth by acidification of the soil, which can kill vital soil bacteria and disrupt plant uptake of nutrients. Acid rain can also damage plants by metal toxicity, as exchangeable ions such as Al^{3+} can be replaced by H^+ ions in soils with relatively low buffer capacities. Acid rain also leads to the erosion of exposed metal and stone surfaces, particularly monuments and statues.

G6. How may acid rain be controlled?

The primary control method for acid rain is to reduce sulphur emissions at the source, either by removing them from the fossil fuel prior to combustion, for example using the reaction:

$$2H_2S + SO_2 \rightarrow 3S + H_2O$$

Or by removing the sulphur dioxide from the flue gas emitted after combustion by reaction with calcium carbonate:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$$

Emissions of particulate matter to which sulphur dioxide commonly adheres can also be reduced by the use of filters, scrubbers, and cyclones, as described in F8 above. Finally, mitigation of the effects of acid rain can occur through environmental application of neutralising bases such as lime, which can be applied to acidified soils and lakes. This latter method, of course, will not undue damage that has already been done, nor will it prevent initial direct corrosive effects of acid rain on plants and monuments.

G7. What are the main anthropogenic sources of sulfur dioxide? Describe the strategies by which these emissions can be reduced, providing chemical equations where appropriate.

The main anthropogenic sources of sulphur dioxide are emissions produced by the combustion of fossil fuels, particular sulphur-rich coal. I believe I have outlined the emission reduction strategies adequately in G6.

G8. Using chemical equations, describe how acid rain can be neutralised by limestone.

Limestone is comprised mostly of calcium carbonate, which acts as a base to neutralise acidic rainwater, for example:

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + CO_2(g) + H_2O(l)$$
$$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

Review Questions H: Photochemical Smog

H1. What are the names and main sources of the primary pollutants that produce photochemical smog?

The primary sources of primary pollutants which are responsible for photochemical smog are nitrogen oxides and various hydrocarbons, both released from the imperfect combustion of fossil fuels by power stations, and particularly by automobiles during the morning hours of peak traffic.

H2. Outline a general mechanism for the formation of photochemical smog.

In general terms, the production of photochemical smog proceeds as follows:

1. Unburnt hydrocarbons react with hydroxyl radicals to form a $RHC \cdot CH(OH)R'$ radical
2. This radical reacts sequentially with oxygen gas and NO to form a $RHO \cdot CCH(OH)R'$ radical
3. The NO_2 so produced photodissociates to form $NO + O$, with the atomic oxygen reaction with O_2 to produce ozone, one key pollutant component of photochemical smog
4. Meanwhile, the $RHO \cdot CCH(OH)R'$ radical decomposes spontaneously to form an aldehyde and a $\cdot CH(OH)R'$ radical, the latter of which in turn reacts with O_2 to form a second aldehyde
5. After some hours of exposure to sunlight, most of these aldehydes photochemically decompose to form large numbers of $HCO \cdot$ and other radicals, which can react to produce a wide range of chemical species and also further radicals
6. Aldehydes can also react sequentially with hydroxyl radicals, oxygen, and NO_2 (passing though a number of intermediate radical species), to produce peroxyacyl nitrates, another crucial component species of photochemical smog

H3. What is the main species responsible for the oxidation of NO to NO_2 in a smoggy atmosphere?

The main species responsible for the oxidation of NO to NO_2 is a peroxy radical, with the general formula:

$$RH(OO \cdot)CCH(OH)R'$$

H4. Why does the production of high concentrations of NO_2 lead to an increase in ozone levels in air? Why does this not occur if much NO is present?

In the atmosphere NO_2 quickly absorbs a photon, dissociating to form NO and atomic oxygen. This atomic oxygen then reacts with molecular oxygen to form ozone: $O + O_2 \rightarrow O_3$. This reaction will not occur in the presence of appreciable concentrations of NO, as this species reacts directly to decompose ozone by the reaction: $NO + O_3 \rightarrow NO_2 + O_2$.

H5. What is the fate of NO_2 molecules that photodissociate? that react with $RC(O)OO^{\cdot}$ radicals?

NO_2 molecules that photodissociate are converted back to NO, which may either react again with a peroxy radical, or may instead react with a hydroxy radical (once the concentration of these has built up to sufficient levels), forming (unstable in daylight) nitrous acid $HONO$, or react with ozone to produce NO_2. In all cases NO_2 is the eventual end product once again.

NO_2 molecules that react with $RC(OO\cdot)O$ radicals to form peroxyacyl nitrates $RC(ONO_2)O$, which are a major component of photochemical smog.

H6. What may be said about the time and place of the occurrence of maximum ozone levels from smog in respect to the origin of the primary pollutants that result in smog formation?

In cities, ozone levels typically peak during the early-mid afternoon, after most of the NO compounds that react to decompose ozone have already been oxidised to NO_2, and also after most NO has already been emitted by traffic during the morning peak traffic period. As more NO is released during the evening peak hour period, ozone levels once against decline as the two species react to form NO_2 and O_2.

H7. What are the environmental effects of photochemical smog?

Photochemical smog causes eye irritation, reduces visibility, and can prudence pungent odours. Smog can cause respiratory diseases, and trigger or exacerbate conditions such as bronchitis and asthma. Chemicals in smog can also be toxic to plants, and reduce photosynthesis activity by blocking sunlight during the day. Certain constituents of smog such as polycyclic aromatic hydrocarbons and peroxyacyl nitrates, are known carcinogens, and have been associated with birth defects.

H8. How may photochemical smog be controlled?

Remedies for reducing photochemical smog mostly relate to various ways of reducing the emissions of NO, NO_2, and uncombusted hydrocarbons from automobiles and industrial factories. Factory pollution can be reduced by building higher chimney stacks (this will not reduce pollution but may allow pollutants to be emitted high enough above the city not to contribute much to smog formation), or by installing scrubbers, filters, or cyclones (as described in a previous question) to remove NO_x from the emitted gases. Automobile pollution can be reduced by the installation of catalytic convertors, which reduce NO to harmless nitrogen gas and promote the more complete combustion of hydrocarbons, thus reducing emissions of incompletely combusted materials. Greater reliance on public transportation options and/or reductions in automobile usage are also potential control strategies.

H9. Why are two catalytic reactors necessary to control all major automotive exhaust pollutants?

Two catalytic reactors are necessary because two different types of reactions need to take place: rhodium serves as a catalysing agent for the reduction of unburnt hydrocarbons and NO to hydrogen and nitrogen gases, while palladium or platinum serve as catalysts for oxidation of carbon monoxide to CO_2 and H_2 and unburnt hydrocarbons to CO_2 and water.