LECTURE 5

The Atmosphere

Evolution of the Atmosphere

The atmosphere which surrounds our planet is the product of billions of years of biological activity. The modern opinion is that the primordial atmosphere was composed largely of carbon dioxide (CO₂). Formerly it was thought to have consisted of a mixture of water vapour (H₂O) methane (CH₄) and ammonia (NH₃) together with proportions of carbon dioxide and free nitrogen which were increasing over time. (See for example F.H.T. Rhodes (1962), The Evolution of Life). In a famous experiment of the 1953, Miller subjected a mixture of such gasses to electrical discharges. The experiment produced numerous complex organic molecules, including a whole series of amino acids which are the structural units of proteins; and it suggested a way in which life might have emerged.

It is estimated that Earth was formed 4.6×10^9 years ago. About 3.5×10^9 years ago, the photosynthetic bacteria (cyanobacteria) made their first appearance. These early life forms, and the phytoplankton, or grey-green algae, which evolved from them, caused a fundamental change in the earth's atmosphere by absorbing carbon dioxide and generating free oxygen via the process know as photosynthesis. The phytoplankton drew the carbon dioxide from the sea water in which it has a tendency to dissolve.

The process of photosynthesis, which is powered by the energy of sunlight, depends chlorophyll, which is the green pigment found in almost all plants except in fungi and bacteria and a few flowering plants.

Table 1. The present-day composition of the earth's atmosphere compared with what it might have been before life evolved:

Gas	Present day Earth $\%$	Early Earth $\%$	
oxygen	21	0	
carbon dioxide	0.03	98	
nitrogen	79	1.9	

Evidence of the emergence of the grey-green algae is provided by the stromatolites, which are the fossilised remains of the layer upon layer of the algae. Early evidence of the accumulation of oxygen in the earth's atmosphere is provided by geological strata from the Precambrian period. In the strata of an earlier period, there are banded ironstones. In the later Precambrian strata, these are replaced by so-called red beds which contain oxidised compounds of iron and other minerals.

Eventually plants and animals emerged which could take advantage of the free atmospheric oxygen which they were able to use in the process of respiration whereby carbohydrates are converted into other chemicals which serve as a store of energy. Respiration, which generates CO_2 and H_2O , is, in effect, the reverse of photosynthesis. Green plants avail themselves of both photosynthesis and of respiration. However, animals derive their energy entirely by respiration; and therefore they depend ultimately upon plants for their sustenance.

For the free oxygen to accumulate in the atmosphere, the carbon incorporated in the dead phytoplankton had to be locked away. This happened when their remains sank to the bottom of the ocean. The process has continued unabated to the present. Carbon derived from ancient photosynthesis was removed in other ways as well. Coal, which dates from late Paleozoic times is simply the remains of ancient land forests which were preserved in an anaerobic environment. Petrochemicals are thought to have a similar origin in the main.

Another way in which carbon was locked away was by its incorporation in limestones which consist largely of calcium carbonate, $CaCO_3$. The agents in this process were a type of marine phytoplankton know as coccoliths which form shells by combining the dissolved carbon dioxide with the calcium ions which are also present in sea water. The calcium which is present in sea water originates in the rocks which have been leached by the acid rain. The acidity of the rain in primordial times was due largely to the carbonic acid formed when carbon dioxide dissolved into the rain.

2. Greenhouse Gasses and the Energy Budget

The earth is subject to a fundamental physical law concerning the conservation of energy. This is the first law of thermodynamics. Short of the destruction and creation of matter via nuclear processes, energy can be neither created nor destroyed. If the earth is in a state of thermal equilibrium, with its temperature neither rising nor falling, then all of the incoming solar energy must return to space as heat. This is achieved partly by the direct reflection of the radiation and partly by its absorption into the earth and its re-emission from it.

The rate at which a body emits radiation is directly proportional to its surface area and to its surface temperature. Since the sun is very hot, the incident radiation is of a high frequency. The earth, which has a much cooler Table 2. The energy budget of the solar radiation received by the earth

- 100 Incoming solar radiation
 - **31** Reflected short-wave radiation
 - 11 Directly reflected by the thermosphere
 - 15 Reflected from the clouds
 - 5 Reflected from the earth's surface
 - 69 Absorbed and re-emitted as long-wave radiation
 - 20 Atmospheric warming by the sun
 - 5 Warming of the atmosphere by the earth
 - 26 Warming of the atmosphere by evaporated water
 - 19 Greenhouse cycle: convection within the atmosphere

surface, emits the radiation at a lower frequency.

If the earth were devoid of atmosphere, then it would absorb and emit the sun's radiation with only a small rise in its surface temperature. It is calculated that, without an atmosphere and with the same reflectivity as the moon, the earth's surface would have an average temperature of -18° C. The ability of the earth to absorb and emit radiation in this manner is diminished by the presence of the atmosphere; and to achieve the thermal equilibrium, the temperature is raised by some 33°C to an average of 15°C.

The effect of raising and stabilising the temperatures at the earth's surface is achieved by the so-called greenhouse gasses which comprise carbon dioxide, methane, water vapour, ozone and nitrous oxide. These gasses allow most of the incident high-frequency radiation, including most of the light in the visible spectrum, to reach the surface. However, they tend to absorb the low-frequency radiation which is re-emitted by the earth.

The thermal energy of the molecules of the greenhouse gasses is raised directly by their absorption of the infrared radiation of certain wavelengths; and the resulting heat is carried into the rest of the atmosphere and back to the earth's surface by processes of convection and conduction. Each gas has a characteristic absorption spectrum which may have peaks at several different frequencies. The superposition of the individual spectra, weighted by the relative quantities of the gasses, gives the overall absorption spectrum of the atmosphere; and this covers a wide band of the infrared radiation.

The greatest contribution by far to the atmosphere's absorptivity in the infrared part of the spectrum, which is where the earth's radiant heat lies,

is that of water vapour. The second greatest contribution is that of carbon dioxide. Oxygen and ozone also absorb low-frequency radiation and can also be described as greenhouse gasses. However, ozone has, in addition, the important property of absorbing a band of high-frequency ultra-violet radiation which, if it were admitted by the atmosphere, would prove seriously harmful to terrestrial life. The remaining natural greenhouse gasses are methane and nitrous oxide. Whilst these have a lesser concentration in the atmosphere than carbon dioxide and water vapour, they nevertheless play a significant role. Their importance is enhanced by the fact that, in common with carbon dioxide, their concentrations in the atmosphere are affected by human activities. Volume for volume, methane is twenty times more effective than carbon dioxide in absorbing infrared radiation.

A detailed account can be given of how the radiant energy of the sun which is incident on the earth is returned to space by reflection and emission. By an analogy with economics, this account, which is presented in Table 2, can be described as the Energy Budget.

The Global Thermostat

Over the last million years, the surface temperature of the earth, averaged over the globe, has varied over a range of only a few degrees centigrade. The temperature has risen steadily from a low point reached at the time of the last glacial maximum; but it has taken 20,000 years to achieve an increase of less than 3° C.

The stability of the temperature is evidence of the existence of equilibrating mechanisms acting within the atmosphere, the land and the oceans. In their absence, the temperature might have fluctuated widely under the impact of small disturbances, or it might have rise or fallen to the life-threatening extremes which are found on neighbouring planets.

On Venus, which is closer to the sun than earth, and where there is no mechanism for removing carbon dioxide from the atmosphere, the greenhouse effect has led to a runaway escalation of temperature. The average temperature of the surface of the planet is estimated at 460°C. This is higher than the melting point of lead; and it is enough to disassociate molecules of water vapour into the constituent hydrogen and oxygen molecules which have been lost to space.

At another extreme is the planet Mars from which the atmosphere, which may have originally resembled that of the primordial Earth, has been lost to space because the planet's gravitational force has not been sufficient to retain it.

The equilibrating mechanisms which preserve the equable nature of the earth's climate are not yet fully understood. Nor is it clear whether the equilibrium is a tenuous one or a stable one. However, it is widely recognised nowa-

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days that the present equilibrium is the product of the interaction of biological and geological processes. Thus geologists and others talk of the co-evolution of the geochemical and biochemical components of our environment.

Some of the equilibrating mechanisms which have been described operate over very large time scales. The most important of these processes is entailed in the carbonate-silicate cycle which operates on a scale of millions of years.

In any cyclical process, the selection of a staring point is arbitrary. In describing this cycle, we may start with the process by which the atmospheric CO_2 is dissolved in rain to form carbonic acid. The acid rainwater washes down onto rocks containing calcium silicate materials from which it leaches these minerals. The water containing the calcium and carbonate ions is carried by rivers into the oceans. There, various organisms combine the calcium and carbonate ions to form chalk shells. When the organisms die, the shells sink to the bottom of the ocean where they accumulate as beds of limestone or calcium carbonate, $CaCO_3$.

Eventually some of the limestone is subducted under the earth's crust by the process of tectonic drift whereby adjacent plates of the earth's crust are forced together so that one of them rides up whilst the other is pushed down. Usually, this occurs at the margin of a land mass. At the high temperatures and pressures which exist under the earth's mantle, the calcium carbonate reacts with silicon to form new silicate rocks. In the process of this rock formation, carbon dioxide is released which seeps thought faults in the earth's crust and which is spewed forth by volcanic eruptions situated along the geological fault lines where the processes of subduction are occurring.

With this cycle in view, it is not difficult to imagine a slow-acting feedback mechanism. Imagine that the sun's radiation which is incident on the earth is somewhat reduced, as it might be at the beginning of an ice age. In that case, there would be less evaporation of water from the oceans and therefore less rainfall. With less rainfall, less carbon dioxide would be washed out of the atmosphere and fewer calcium ions would be carried into the oceans. Also, with a reduction of incident sunlight, the rate of photosynthesis of marine organisms would be reduced and hence less calcium carbonate would be precipitated onto the floors of the oceans. However, the tectonic subduction of chalks and limestones would continue unchanged as would the escape of carbon dioxide from the earth and its output from volcanoes. The consequence would be an increasing concentration of carbon dioxide in the atmosphere with would lead to an increase in atmospheric temperature via an enhanced greenhouse effect.

The sequence of reactions which we have outlined begins with a reduction in atmospheric temperature and ends with a compensating increase. Therefore it amounts to what is described as a negative feedback mechanism. Such mechanisms lend stability to an equilibrium. It is also possible to describe plausible mechanisms of positive feedback which, once set in motion, could work within

Reservoir	Carbon: 10^9 tonnes
Atmosphere	700
Oceans	
dissolved carbon dioxide	37,000
dissolved residues from dead organisms	980
living marine organisms	3
marine sediments	
calcium carbonate	50,000,000
other residues from dead organisms	10,000,000
On the land surface	
living land organisms	600
soil humus	3,000
Fossil Fuels	5,000

Table 3. The quantity of carbon in the major reservoirs of the earth's surface:

the earth's atmosphere to drive the temperature away from a position of equilibrium. When a variety of positive and negative mechanisms co-exist, it can be difficult to evaluate their net effect in any given circumstance.

Some scientists have espoused a theory which depicts the biosphere as a self-regulating entity which has operated over billions of years in a manner which has ensured the survival of life and which can be depended upon to do so in future. In this view, the biosphere is seen as a super organism with a capacity for maintaining its equilibrium and of recovering from damage which is comparable to that of individual organisms.

One of the principal proponents of such views is James Lovelock who talks mystically of the goddess Gaia who protects life through the agency of natural feedback mechanisms. However, there is no evident reason why the goddess of nature should be peculiarly protective of human lives and human welfare. Many scientists believe that mankind's survival is threatened by his own activities which, unless they are regulated, are bound to result in a very rapid warming of the global atmosphere, amongst other perils.

The Evidence of Warming

The world is warming, climatic zones are shifting, glaciers are melting and the sea level is rising. These are not hypothetical events based on scientific extrapolations but actual occurrences. Many, if not most, informed observers expect these changes to accelerate over the next few decades as the amounts of carbon dioxide, methane and other greenhouse gasses accumulate in the atmosphere as a result of human activities.



Figure 1. Global annual temperature anomalies 1880–1990 plotted as deviations from the mean for 1940 to 1960, compiled by Hansen et al. of the Goddard Institute for Space Studies.

What remains unclear is how far and how fast these climatic changes will proceed and what the consequences for the environment and for human welfare are likely to be.

The reasons for the uncertainties are twofold. In the first place, the geophysical mechanisms which are involved are not well understood. Such is their complexity and their interdependence that much of the uncertainty is bound to remain in spite of the most active scientific investigations. We shall only learn the consequences of the increasing burden of greenhouse gasses as they unfold. The second reason for the uncertainties is the difficulty in predicting the human response to the crisis of global warming in its various phases. The crisis which is presently threatened will become imminent at some stage and then, in a short time, it will become actual. The nature of the response depends, to some extent, on the duration of these phases.

The greatest potential for increases in the emissions of greenhouse gasses now lies with the third world. The rapid economic development amongst the poorer nations would add far more to their levels than would the continued economic growth of the industrial countries who are largely responsible for their present level. China and India might greatly increase their emissions of carbon dioxide by burning coal as might the countries of the erstwhile Soviet Union.

Notwithstanding the imponderable aspects of the crisis, there are no grounds for doubting the evidence which underlies the current anxieties. The most direct evidence of global warming is provided by temperature records from around the world. By collating a wide variety of records, Hansen et al. of the Goddard Institute of NASA have constructed a series which goes back to 1860. Their analysis suggests that the average global temperature has increased by between 0.5 and 0.7 degrees Celsius since that year. However, the greatest change has taken place in the last decade.

The observed rise in temperature has not been uniform though time or across the globe; and its the graph reflects influences other than those of the greenhouse gasses. Thus for example, there was a decline in mean global temperature between 1940 and 1950 in spite the rising concentration the heattrapping gasses. However, in retrospect, this decline now looks like any of the other local variations which beset the remorselessly rising trend. In fact, from the beginning of the century, to 1989, the six warmest years on record, listed in order of warmth, have been 1988, 1987, 1983, 1981, 1980 and 1986.

There are other sure signs of warming. Comparisons of photographs and lithographs show the retreat of glaciers in Alaska, in the French Alps and elsewhere. Further evidence is provided by the moraines or spoil heaps which lie exposed at the foot of the retreating ice. The depth of the soil which must be penetrated before reaching the level of the permafrost in the Alaskan and Canadian Arctic is reported to have increased in recent decades. Finally, data collected over an 80-year period from 1900 indicate a change in the global mean sea level of about 10cm. This correlates reasonably well with the record of the average surface temperature of the oceans which is also increasing, and it is almost certainly attributable in large measure to the thermal expansion of sea water.

The next body of evidence to be cited concerns the rising concentrations of the greenhouse gases. The longest series of direct observations on carbon dioxide and methane are those of the Mauna Loa observatory in Hawaii which has been taking regular measurements since 1958. The record shows a steady increase over a 30-year period. In 1958, a concentration of CO_2 of 315 parts per million (ppm) was recorded. In 1988, the concentration was 350 ppm which represents an increase of 11%. Apart from the regular annual cycle, this increase has been monotonic. A similar increase has been observed for methane.

To determine the significance of these increases, one needs to know how they compare with the variations which have occurred during the history and prehistory of mankind. We are remarkably fortunate in having accurate evidence on this account. The evidence is provided by tiny samples of air trapped in glacial ice. The atmospheric composition over the past 160,000 years has been assessed by analysing an ice core drilled to a depth of 2,200 metres by a joint Franco-Soviet team at the Antarctic Vostok research station.



Figure 2. The concentration, in parts per million by volume, of carbon dioxide measured at the Mauna Loa observatory. Annual oscillations arise from seasonal variations in photosynthesis and in other biological activities.

The evidence reaches back to the last but one glacial maximum, and thus it comprises one-and-a-half glacial cycles. The record show that, at the ends of the two most recent glacial periods, the concentrations of carbon dioxide increased rapidly from around 190 ppm to about 290 ppm with a probable upper bound of 300 ppm. Thus the concentrations recorded a Mauna Loa are beyond the range of the natural variation even at the start of the series.

Further data on the concentration of atmospheric CO_2 has been provided by another Antarctic ice core from the Siple station. This gives a detailed picture of the build-up over the last 250 years since 1740 when the level was 275 ppm; and thus it spans the period of the industrial revolution. Towards the end of its period, this ice-core data correlates closely with the direct observations from Mauna Loa in a way which tends to confirm the validity of the ice-core measurements.

The final body of evidence is that which serves to reaffirm the connection between increasing concentrations of the greenhouse gasses and the process of global warming. In this respect, it might be enough to point to the propensity of the gasses to absorb low-frequency radiation which is manifest in their individual absorption spectra. However, the data available from the ice cores provides further confirmation.

It is well-established that the ratio of two common isotopes of oxygen

Table 4. Annual fluxes of carbon to and from the earth's surface in units of 10^9 tonnes. The annual increment of carbon in the atmosphere is estimated at 3×10^9 tonnes:

Emissions

- 100 Physico-chemical diffusion from the sea
 - 50 Soil respiration
 - 50 Respiration by plants
 - 5 Burning of fossil fuels
 - 2 Deforestation

Absorption

- 104 Physico-chemical diffusion to the sea
- 100 Photosynthesis by plants

¹⁸O and ¹⁶O in cores of marine sediments reflects past temperature changes; and this ratio provides a good index of temperature in the ice core as well. Another index of temperature is the concentration in ice of deuterium, or heavy water. The Vostok data shows clear correlations between the concentration of atmospheric carbon dioxide and the indices of temperature. The carbon dioxide concentration appears to follow temperature closely during periods of deglaciation, whereas it seems to lag behind during periods of cooling. Even if the changes in carbon-dioxide concentration do not initiate the glacial cycles, they certainly serve to increase their amplitudes via a mechanism of positive feedback.

Carbon Fluxes and Global Warming

There are numerous factors which make it difficult to assess the potential for global warming. These factors may be assigned to two categories.

On the one hand, there is the vastly complex scientific problem of determining the nature of the processes which are involved in the evolution of the climate. If precise predictions are to be made, then a complex web of climatological, chemical and geophysical processes must be studied in detail so as to reveal the full extent of their interrelationships. These processes must also be parametrised in a way which makes them amenable to numerical modelling.

On the other hand, there are major difficulties in projecting the course of the economic developments which have posed the problem of global warming in the first place. It is even more difficult to predict the likely response of human societies in the face of a hazard which is, as yet, ill-defined.

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The anxieties of those who study the problem of global warming in detail are often accentuated by its very imponderability. There may be mechanisms of fast positive feedback, as yet undiscovered, which could severely exacerbate the problem and hasten its onset. On the other hand it is possible that some of equilibrating mechanisms which have been recognised are more effective than is commonly imagined; and there might even be some undiscovered benign mechanisms which could serve to avert the worst disasters which have be envisaged.

Much of the difficulty in predicting the future of global warming lies in the fact that the annual increment to atmospheric carbon dioxide is the small difference between two aggregate flows of considerable magnitude which go in opposite directions. Small percentage changes within the components of these flows can have large effects upon the net annual increment.

In table 4, a summary is given of the carbon flow or fluxes. In assessing the overall increment to atmospheric carbon dioxide, some account must be taken of the release of methane. Whilst methane is, in it own right, an most effective greenhouse gas, it is quite rapidly oxidised to produce carbon dioxide and water.

Although carbon dioxide and methane are by no means the only significant greenhouse gasses which need to be considered, it is helpful to illustrate some of the problems of assessing the potential for global warming by considering how their fluxes might develop.

The two natural processes which are most important in determining the size of the net addition of carbon dioxide are photosynthesis and respiration. As we have already indicated, the first of these serves to subtract carbon dioxide from the atmosphere whilst the second adds to it. Both processes are liable to be enhanced by an increase in temperature; but it is probable that the rate of respiration will increase faster than the rate of photosynthesis. In order to adjudicate the issues, it is necessary to assess the extent of the world's vegetation and the amount of phytoplankton in the seas. A major scientific effort aimed at measuring the global biomass is now underway.

There are other processes linked to the world's vegetation by which an increase in temperature might serve to increase the flux of carbon dioxide to the atmosphere. The most obvious of these is the tendency for the rate of the bacterial decay of organic matter to increase with temperature. Another likely eventuality, if temperature rises significantly, is the release of large quantities of methane which are currently trapped in the tundra of the sub-Arctic regions of the northern hemisphere.

The difficulties of reaching an overall assessment of the perils are indicated by the wide range of the estimates for the increase of temperature which would result from the doubling of the amount of atmospheric carbon dioxide relative to its preindustrial level. The doubling is an arbitrary benchmark; and some authorities predict that this level will be reached by the year 2040. In 1979, a

committee of the American National Academy of Sciences estimated that the doubling would produce a rise of 3° in average global temperature. However, they gave a range of 1.5° on either side of the estimate; and , in effect, they implied that all estimates within the range of 1.5° – 4.5° were equally plausible. It should also be emphasised that the available quantities of fossil fuels are enough to produce several doublings in the fullness of time.

There is an understandable tendency amongst economists to ignore matters of science and technology which lie outside the sphere of their own professional competence. They may listen to the opinions of the experts, but they are disinclined to accept their judgments unless they are voiced unanimously. Moreover, when experts disagree or fail to reach firm conclusions, economists are liable to disengage themselves from the issues at hand.

This effect is particularly striking in connection with the debate concerning the peril of global warming. The majority of economists appear to believe in the inherently self-regulating nature of the economies which they study. It is to be expected that many of them should imagine that the mechanism of the physical world are also self-regulating. This may well be the case, but these mechanisms are unlikely to be guided, as if by a hidden hand, in ways which are designed to promote the welfare of human societies.

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