The Carbon Dioxide Theory of Climatic Change

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Abstract

The most recent calculations of the infra-red flux in the region of the 15 micron CO_2 band show that the average surface temperature of the earth increases 3.6° C if the CO_2 concentration in the atmosphere is doubled and decreases 3.8° C if the CO_2 amount is halved, provided that no other factors change which influence the radiation balance. Variations in CO_2 amount of this magnitude must have occurred during geological history; the resulting temperature changes were sufficiently large to influence the climate. The CO_2 balance is discussed. The CO_2 equilibrium between atmosphere and oceans is calculated with and without $CaCO_3$ equilibrium, assuming that the average temperature changes with the CO_2 concentration by the amount predicted by the CO_2 theory. When the total CO_2 is reduced below a critical value, it is found that the climate continuously oscillates between a glacial and an inter-glacial stage with a period of tens of thousands of years; there is no possible stable state for the climate. Simple explanations are provided by the CO_2 theory for the increased precipitation at the onset of a glacial period, the time lag of millions of years between periods of mountain building and the ensuing glaciation, and the severe glaciation at the end of the Carboniferous. The extra CO_2 released into the atmosphere by industrial processes and other human activities may have caused the temperature rise during the present century. In contrast with other theories of climate, the CO_2 theory predicts that this warming trend will continue, at least for several centuries.

1. Introduction

In 1861, TYNDALL wrote that "if, as the above experiments indicated, the chief influence be exercised by the aqueous vapour, every variation of this constituent must produce a change of climate. Similar remarks would apply to the carbonic acid diffused through the air ... It is not, therefore, necessary to assume alterations in the density and height of the atmosphere to account for different amounts of heat being preserved to the earth at different times; a slight change in its variable constituents would suffice for this. Such changes in fact

may have produced all the mutations of climate which the researches of geologists reveal. However this may be, the facts above cited remain: they constitute true causes, the *extent* alone of the operation remaining doubtful." A century of scientific work has been necessary in order to calculate with any certainty the extent of the influence of carbon dioxide.

Although Tyndall was the first to attempt a calculation of the infrared flux in the atmosphere, FOURIER (1827) had compared the influence of the atmosphere to the heating of a closed space beneath a pane of glass. The calculation by ARRHENIUS (1896) of the influence of carbon dioxide on the temperature was the most extensive made during the nineteenth century. In a series of articles

CHAMBERLIN (1897, 1898, 1899) presented in detail the geological implications of the carbon dioxide theory. As a result of these early articles, during that period the carbon dioxide theory was probably the most widely held explanation of climatic change.

In recent years the carbon dioxide theory has had relatively few adherents. Most authors have dismissed this theory with a remark similar to the following quotation from C. E. P. BROOKS (1951): the carbon dioxide theory was "abandoned when it was found that all the long-wave radiation absorbed by CO_2 is also absorbed by water vapour." This often quoted conclusion is based on early, approximate calculations of the radiation flux in the atmosphere. The results of more accurate calculations of the radiation flux have recently become available. Thus it seems worthwhile to reappraise the CO_2 theory of climatic change. A preliminary report of these results has been given by PLASS (1953).

Many authors believe that most of the world-wide climatic changes are caused primarily by variations of a single factor. In this article simple explanations are given in terms of the carbon dioxide content of the atmosphere for many of the known facts about climatic change. Although it seems significant that so many facts can be explained by the carbon dioxide theory, the possibility remains that variations in solar energy, volcanic dust in the atmosphere and the heights of the continents may have had an important influence on the climate at particular places and periods in the earth's history.

2. Calculation of the radiation flux

An extensive calculation of the radiation flux in the region of the 15 micron CO_2 band has recently been made by PLASS (1956 b). Recent accurate laboratory measurements of the absorption in the CO_2 band by CLOUD (1952) were used to calculate the radiation flux in the atmosphere with the aid of the MIDAC high speed digital computor. None of the many approximations were used that had necessarily been made in earlier attempts to solve this complex problem. Accurate laboratory absorption data, recent theoretical work and the availability of an electronic computer made it possible to obtain an accurate solution of this problem.

The method of calculation took into account the many properties of the line spectrum. In particular it was valid for: (1) any arbitrary variation from one spectral line to another of the spacing between lines and of the line intensity; (2) any degree of overlapping of the spectral lines; (3) the actual variation in the atmosphere of the half-width of the spectral lines with pressure. At the highest altitudes a correction for the Doppler line shape was introduced. Another correction took account of the variation of the line intensity and half-width with temperature. The reduction from beam to hemisphere radiation was made by a new, more accurate method. Certain restrictions on the path-length for this method of calculation were checked against the experimental data.

The accuracy of the results were checked at each stage of the calculation. The upward and downward flux in the atmosphere could be computed with the same accuracy as the original laboratory measurements. It is estimated that the calculated upward and downward atmospheric radiation flux is accurate to within 4 per cent; this figure includes an allowance for the additional corrections that must be introduced into the atmospheric calculation. Further details are given by PLASS (1956 b).

3. Temperature variations caused by changes in CO_2 concentration

The upward and downward radiation flux was calculated by PLASS (1956 b) for intervals of 1 km from the surface of the earth to 75 km and for three different CO_2 concentrations. From these results the change in temperature at any level can be calculated for a given change in the CO_2 concentration. It is assumed that nothing else changes that affects the radiation balance when the CO_2 amount varies. In order to obtain the temperature change it was assumed that an additional amount of heat energy equal to 0.0033 cal/cm^2 min would be radiated to space from the surface of the earth, if the average temperature increased by 1° C. Unfortunately this number cannot be calculated accurately until a detailed study of the H_2O spectrum has been made. When a more accurate value for this number is obtained in the future, all the temperature

changes given here should be multiplied by the ratio of the new to the old values.

With this assumption, PLASS (1956 b) finds that, in order to restore equilibrium, the surface temperature must rise 3.6° C if the CO_2 concentration is doubled and the surface temperature must fall 3.8° C if the CO_2 concentration is halved. It is also assumed here that no other factors change at the same time which can influence the radiation balance.

If the CO_2 amount is doubled, ARRHENIUS (1896) calculated that the temperature increased about 6° C, while CALLENDAR (1938) obtained a 2° C increase. The values quoted here are larger than other recent calculated values primarily because: (1) the weaker lines far from the band center have an important influence and the entire frequency interval from 12 to 18 microns was included in the calculation; (2) the pressure broadening of the spectral lines was taken into account, which results in the radiation varying approximately as the square root of the CO_2 concentration (PLASS and FIVEL, 1955 a) over a considerable portion of the frequency interval.

The actual temperature change due to CO_2 variations is slightly smaller than the results given above for clear sky conditions. When clouds are present, the CO_2 is less effective in changing the net amount of radiation from the surface. In order to estimate the magnitude of this effect, PLASS (1956 b) also calculated the temperature change at the earth's surface for variations in the CO_2 amount when the lower cloud surfaces are at 4 and 9 km. When these values are averaged over a reasonable average cloud distribution for the earth, the result is obtained that the average surface temperature must increase by 2.5° C or decrease by 2.7° C when the CO_2 amount in the atmosphere is doubled or halved.

The usual objection to the CO_2 theory of climatic change has been that, since the H_2O absorbs so strongly in the same spectral region as CO_2, the CO_2 can have little influence on the infrared flux. Until a more detailed study is made of the H_2O spectrum and its influence on the atmosphere, it is not possible to investigate this matter quantitatively. However, several considerations suggest that H_2O has a much smaller effect than has generally been believed in recent years. In the first place, the mixing ratio of H_2O decreases very rapidly with height whereas the mixing ratio of CO_2 is nearly constant with height. Even if the H_2O absorption were greater than that of CO_2 near the surface of the earth in certain frequency intervals, the H_2O absorption would decrease with height very much more rapidly than the CO_2 absorption. Calculations by PLASS and FIVEL (1955 b, Figs. 1 and 2) have shown the magnitude of this effect. Thus, even a relatively short distance above the earth's surface, the CO_2 controls the radiative flux in the frequency interval from 12 to 18 microns.

In the second place, it is important to take account of the structure of the individual spectral lines. The various lines in the spectrum of H_2O and CO_2 occur at random with respect to each other. When this happens there are theoretical calculations and experimental measurements which indicate that the combined transmission is nearly the product of the individual transmissions of the two gases. Thus, changes in the CO_2 amount still cause appreciable changes in the transmission of the atmosphere. In order to obtain a more accurate estimate of this effect, a numerical calculation was made with the average line strength for H_2O given by ELSASSER (1942, Fig. 19) and with the assumption that the H_2O lines occur at random with respect to the CO_2 lines. The results of this calculation show that the temperature changes at the surface of the earth already given would not be decreased by more than 20 per cent because of absorption by H_2O. Since the temperature change due to CO_2 variations would be further increased by 10 to 20 per cent from the additional spectral lines outside the 12 to 18 micron region included in Plass' calculation, this factor would at least partly cancel the H_2O effect just discussed. Thus the values for the temperature change already given are probably as accurate as can be calculated at the present time and take into account all known effects of the structure of the spectral lines.

The radiation calculations predict a definite temperature change for every variation in CO_2 amount in the atmosphere. These temperature changes are sufficiently large to have an appreciable influence on the climate. A relatively small change in the average temperature can have a large effect on the climate;

Table 1. Major factors in the CO_2 balance at the
present time

	tons/year	
Photosynthesis	$- 60 \quad \times 10^9$	organic world
Decay, respiration	$+ 60 \quad \times 10^9$	
Formation of new coal beds and other organic deposits	$- 0.01 \times 10^9$	
Weathering of igneous rocks	$- 0.1 \quad \times 10^9$	inorganic world
Released from interior of earth by hot springs, volcanoes, etc........	$+ 0.1 \quad \times 10^9$	
Combustion of fossil fuels; clearance of forests; cultivation of land	$+ 6.0 \quad \times 10^9$	man's activities

some geologists estimate that another period of glaciation would result from a drop of 3 or 4° C in the average temperature. In order to explain climatic changes, it is necessary to understand the role of the various factors that control the CO_2 content of the atmosphere. In the next sections these factors are investigated together with the CO_2 equilibrium between the atmosphere and the oceans.

4. The CO_2 balance

Many authors have discussed the CO_2 balance in recent years. The fascinating book about climatic changes edited by SHAPLEY (1953) gives many of their results together with numerous references to the literature. RUBEY (1951) has made one of the most extensive studies of the CO_2 equilibrium. UREY (1952) and KUIPER (1952) have given a discussion of the many factors that influence the amounts of various gases in the atmosphere.

Estimates of the magnitude of some of the principal factors that influence the atmospheric CO_2 concentration at the present time are given in Table I. Most of these figures are known only to an order of magnitude; naturally, the estimates of different authors vary widely. An attempt has been made to average some of the more careful estimates for each factor.

Estimates made by reliable scientists of the amount of CO_2 used in photosynthesis vary from 7 to 200 × 10⁹ tons per year. Regardless of the exact value, in a steady state precisely the same amount of CO_2 must be returned to the atmosphere each year by all the processes

of respiration and decay of plants and animals, provided none of this CO_2 is permanently lost in forming new coal, oil and other organic deposits. At the present time, at least, the amount lost in this manner is very small compared to the CO_2 used in photosynthesis and can be neglected in a discussion of the balance of factors from the organic world. Let us suppose that the steady state absorption and emission of CO_2 by the organic world is disturbed, for example, by a sudden increase in the amount of CO_2 in the atmosphere. The amount of CO_2 used in photosynthesis would increase, but in a very short time interval the processes of decay and respiration would also have increased. Since an average carbon atom that has been used in photosynthesis returns to the atmosphere from the biosphere in about 10 years and virtually all the carbon atoms return in 250 years, it follows that the factors from the organic world would again be in balance in a relatively few years following a change in the CO_2 concentration in the atmosphere.

During geological history the amount of CO_2 lost from the atmosphere by the formation of new coal beds and other organic deposits and by the weathering of igneous rocks and deposition of carbonates has varied widely, as has the CO_2 added to the atmosphere by such factors as the evolution of CO_2 from hot springs, volcanic vents, gas wells, and other sources. Since the variations in these factors occur independently of each other, the net gain or loss of CO_2 by the atmosphere from these factors must have changed frequently on a geological time scale. Although it is not always easy to deduce the net result of these many independent variations for a given epoch, the mere knowledge that these factors have changed many times in the past has important implications for studies of the climate.

In recent years industrial and other activities of man are adding considerably more CO_2 to the atmosphere than any of the above factors from the inorganic world (Table I). The combustion of fossil fuels is adding 6 × 10⁹ tons per year of CO_2 to the atmosphere at the present time. In addition such activities as the clearance of forests, the drainage and cultivation of lands, and industrial processes such as lime burning and fermentation release addi-

tional amounts of CO_2 that are not included in the above estimate. This is a large enough contribution to upset the carbon dioxide balance and to increase the amount in the atmosphere appreciably. Some of this additional CO_2 is used in photosynthesis, but as already discussed, very little of the extra CO_2 is permanently lost to the atmosphere since there is a corresponding increase in the rates of decay and respiration. Another part of this additional CO_2 is absorbed by the oceans; this factor is discussed in detail in the following sections. However, it seems probable that these losses are small at the present time. If this is true, then a major portion of the extra CO_2 from man's activities will remain in the atmosphere and the CO_2 concentration will increase for at least several centuries to come. If this extra CO_2 is remaining in the atmosphere, the concentration is increasing from this source at the rate of 30 per cent a century.

5. CO_2 exchange between oceans and atmosphere

Recent radiocarbon determinations (KULP, 1952) have shown that deep ocean water at the latitude of Newfoundland was at the surface about 1700 years ago. Kulp states in SHAPLEY (1953) that "if this sample water started near the surface in the Arctic, then the rate of turnover of the oceans must be on a scale of at least 10,000 years." Thus, the amount of CO_2 in the ocean and atmosphere must come to equilibrium after a change in the CO_2 balance in a period of time of this order of magnitude.

Several excellent studies have been made in recent years of the equilibrium between the oceans and the atmosphere (SVERDRUP, JOHNSON and FLEMING, 1942; RUBEY, 1951; DINGLE, 1954). We have recalculated this equilibrium with the additional assumption that the average temperature of the oceans is determined by the CO_2 concentration in the atmosphere. The average temperature of the oceans at the present time was taken as 8° C; for half the present amount of atmospheric CO_2, it was assumed that the average temperature of the oceans was lowered to 4.2° C. This is the same change in average temperature that a similar CO_2 variation causes on land. Similar changes in the ocean temperatures were assumed for other CO_2 concentrations.

The following equations were used to calculate the equilibrium between the gaseous CO_2 and the carbonates in the sea water:

$$[A] = [HCO_3^-] + 2[CO_3^=] + [H_2BO_3^-] + \\ + [OH^-] - [H^+], \tag{1}$$

$$[A_{CO_2}] = [A] - \frac{2.2(10)^{-5} Cl^0/_{00} K_B'}{[H^+] + K_B'} + [H^+] - \\ - [OH^-] \tag{2}$$

$$[H_2CO_3] = \frac{[A_{CO_2}]}{1 + \dfrac{2K_2'}{[H^+]}} \cdot \frac{[H^+]}{K_1'} \tag{3}$$

$$[HCO_3^-] = \frac{[A_{CO_2}]}{1 + \dfrac{2K_2'}{[H^+]}} \tag{4}$$

$$[CO_3^=] = \frac{[A_{CO_2}]}{1 + \dfrac{2K_2'}{[H^+]}} \cdot \frac{K_2'}{[H^+]} \tag{5}$$

$$P_{CO_2} = \frac{[A_{CO_2}]}{K_1' \alpha_0 a_{H_2O} \left(1 + \dfrac{2K_2'}{[H^+]}\right)} \cdot [H^+] \tag{6}$$

where $[A]$ is the excess base, $[A_{CO_2}]$ is the carbonate alkalinity, K_B' is the apparent first dissociation constant of boric acid in sea water, K_1' and K_2' are the first and second apparent dissociation constants of H_2CO_3, a_{H_2O} is the activity of water in sea water, and P_{CO_2} is the atmospheric CO_2 pressure. The remaining symbols have their usual meaning. The values of the constants were taken from the tables in HARVEY (1945).

It was assumed that the average ocean temperature is 8° C, the pH is 8.17 and the chlorinity is 19.5 ‰ at the present time. With $K_1' = 0.76 \times 10^{-6}$, $K_2' = 0.73 \times 10^{-9}$, $a_{H_2O} = 0.981$, $\alpha_0 = 0.0576$ moles/l, it follows from (1—6) that $P_{CO_2} = 3.0 \times 10^{-4}$ atm. Since this value for P_{CO_2} agrees with the average carbon dioxide concentration that was measured in the atmosphere at the end of the nineteenth century, the usual values for the above constants lead to the conclusion that the atmosphere-ocean system is nearly in equilibrium today. From (1—6) it also follows that at the
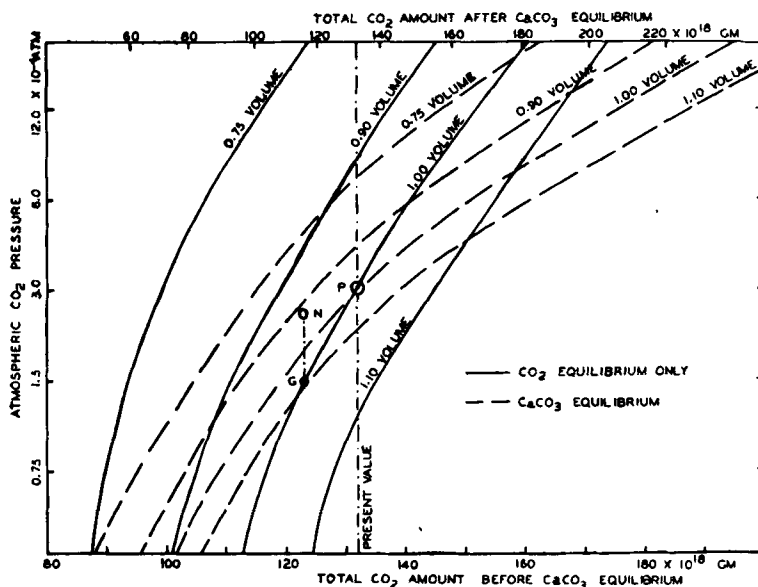
Fig. 1. Equilibrium amounts of CO_2 for the atmosphere-ocean system. The ordinate is the logarithm of the CO_2 pressure in the atmosphere; the abscissa is the corresponding total CO_2 amount present in both the oceans and atmosphere at equilibrium. The solid curves are for the CO_2 equilibrium only; the dashed curves assume in addition that $CaCO_3$ equilibrium has been established in the oceans. Each set of curves is given when the oceans have a volume equal to 0.75, 0.90, 1.00 and 1.10 times their present volume. For the curves that assume $CaCO_3$ equilibrium, the abscissa marked in the lower and upper margins give the total CO_2 amount before and after $CaCO_3$ equilibrium respectively. The CO_2 pressure today is marked by the point "P". The points "G" and "N" represent possible conditions when glaciers are forming and melting respectively. The dashed line between "G" and "N" represents the typical oscillations in the climate during a glacial epoch.

present time $[CO_2] = 1.41 \times 10^{-5}$ moles/l; $[HCO_3^-] = 1.89 \times 10^{-3}$ moles/l; and $[CO_3^-] = 0.204 \times 10^{-3}$ moles/l.

From the known volume of the oceans and the atmosphere it is found that there are 130×10^{18} gm of CO_2 (in the form of carbonates and dissolved gas) in the oceans and 2.33×10^{18} gm of CO_2 in the atmosphere or a total of 132×10^{18} gm of CO_2 in the atmosphere-ocean system. In Fig. 1 the present value for the atmospheric CO_2 pressure and the total CO_2 amount is marked "P".

Next, the equilibrium value of P_{CO_2} was calculated for a number of different values of the total CO_2 amount. It was assumed in agreement with the carbon dioxide theory of climatic change that the average temperature of the oceans was 15.0°C when $P_{CO_2} = 12 \times 10^{-4}$ atm; 11.6° C when $P_{CO_2} = 6 \times 10^{-4}$; 8.0° C when $P_{CO_2} = 3 \times 10^{-4}$; 4.2° C when $P_{CO_2} =$

$= 1.5 \times 10^{-4}$; 0.5° C when $P_{CO_2} = 0.75 \times 10^{-4}$. Although the constants in (1—6) are functions of the temperature, the curves shown in Fig. 1 are insensitive to the particular assumption that is made about their temperature variation. The equilibrium values of P_{CO_2} for various total CO_2 amounts in the atmosphere-ocean are shown in Fig. 1 as the solid curve marked "1.00 Vol."

These same calculations were repeated assuming that the oceans had 0.75, 0.90 and 1.10 times their present volumes. The other solid curves in Fig. 1 show the results for these cases.

RUBEY (1951) has emphasized that the oceans must reach equilibrium with $CaCO_3$ after a sufficient period of time following a change in the total amount of CO_2 in the atmosphere-ocean system. If there is an excess amount of $CaCO_3$, it precipitates; if there is

too little $CaCO_3$, it dissolves and at the same time accumulates from the rivers that flow into the oceans until the solubility product is reached. The equilibrium CO_2 pressure can be obtained when there is $CaCO_3$ equilibrium by solving equations (1—6) with the additional requirement that

$$[Ca^{++}] \; [CO_3^-] = K'_{CaCO_3} \qquad (7)$$

The results of this calculation are shown as the dashed lines in Fig. 1 for oceans with 0.75, 0.90, 1.00 and 1.10 times the present volume. The curves in Fig. 1 for the $CaCO_3$ equilibrium have abscissa marked at the bottom of the figure for the total amount of CO_2 in the atmosphere-ocean system before the $CaCO_3$ dissolves or precipitates to bring about equilibrium; the corresponding final amounts of CO_2 in the atmosphere-ocean system are marked on the top margin of Fig. 1. The following values were used for K'_{CaCO_3}: 1.3×10^{-6} at $30°$ C; 1.8×10^{-6} at $20°$ C; 2.1×10^{-6} at $10°$ C; 2.3×10^{-6} at $0°$ C. These values agree with the measurements of SMITH (1940) when they are corrected for temperature dependence. With these values of the constants, (1—7) show that the oceans are very nearly in equilibrium at the present time with $CaCO_3$ for an average temperature of $8°$ C and $P_{CO_2} = 3 \times 10^{-4}$ atm. Apparently the $CaCO_3$ dissociation constant is not known accurately. A change in its value would move the curves in Fig. 1 to the right or left, but would not change their qualitative features.

Curves are given in Fig. 1 for different volumes of the oceans, since the ocean volume decreases during a period of glaciation and would increase still further, if all the glacial ice present today should melt. Estimates show that water having a volume from 5 to 10 per cent of that of the oceans was frozen in the glaciers at the period of the last advance of the ice sheets (FLINT, 1947; SHAPLEY, 1953). This number may have been even larger during earlier great epochs of glaciation. Further, the volume of the oceans has probably changed during the recorded geological history of the earth by the addition of juvenile water from the interior of the earth.

The pH of the oceans does not change by more than one-half a unit as P_{CO_2} varies from one-fourth to four times its present value. For example, the pH range is 7.67 to 8.62 for this range of values of P_{CO_2} without $CaCO_3$ equilibrium and is 7.81 to 8.51 with $CaCO_3$ equilibrium. With $CaCO_3$ equilibrium, P_{CO_2} can vary from 0.38×10^{-4} to 20×10^{-4} atm without the pH changing by more than one-half unit. It is interesting to note that higher marine animals (herring, for example) can not tolerate pH changes of more than $\pm$ 0.5 and that lower marine animals are less sensitive, but many species (sea urchins, diatoms, algae) can not tolerate pH changes of more than ± 1.0 (RUBEY, 1951). This suggests that during the geological periods in which these animals have lived that the pH of the sea has either stayed constant within these limits or at most has changed very slowly so that the animals had a chance to adapt to their new environment. Thus the amount of CO_2 in the atmosphere can change relatively rapidly by a factor of fifty-three without influencing marine life appreciably and even more over long periods of time. Such variations in CO_2 amount are more than enough to cause appreciable climatic changes.

6. Explanation of climatic change in terms of the CO_2 theory

According to Bell (SHAPLEY, 1953), Willett believes "that the similarity in the change of the circulation pattern, whether the change in climate be of the order of hundreds or thousands or tens of thousands of years constitutes a powerful argument in favor of a single variable factor underlying all changes". From this point of view, it seems significant that the CO_2 theory can provide simple, straight-forward explanations for many of the known facts about climatic change. These explanations are discussed in this and the following section.

a. Periodic oscillations from glacial to interglacial climate

Recent analysis of the sediments of the deep ocean floor by WISEMAN (1954) show 10 distinct temperature minima within the last 620,000 years. Four distinct periods of advance and retreat of the ice sheets have long been recognized by geologists. These fluctuations in the climate, which seem to be a characteristic of a glacial period, can be explained by the CO_2 theory. If the total amount of CO_2 in the atmosphere-ocean system is reduced by a small amount from its present value, the CO_2

theory predicts that the climate must fluctuate between periods with large ice sheets and warmer periods that have relatively small or no ice sheets; there is no possible stable state of the climate when the total CO_2 is slightly less than its present value.

In order to understand this phenomenon more clearly, let us assume some particular numbers that may represent conditions at the onset of a typical glacial period; none of the conclusions reached depends on the particular values chosen. First we assume that if the average temperature of the earth should fall 3.8° C (various authorities give values from 2° C to 8° C) that great ice sheets would again begin to cover sizeable portions of the continents. Further let us assume that the average period of circulation for the deep waters of the ocean is of the order of ten thousand years. It must take several of these periods for the atmosphere-ocean system to come to equilibrium after a change in the CO_2 amount; the time to return to equilibrium might perhaps be estimated as of the order of 50,000 years, although this time may actually be ten times longer or shorter than this.

Let us suppose that at the beginning of a glacial period for some reason the total amount of CO_2 in the atmosphere-ocean system is reduced 7 per cent from its present value of 132×10^{18} gm to 123×10^{18} gm and *remains fixed* at the latter value throughout the glacial epoch of some million years duration. After the atmosphere and ocean have returned to equilibrium (point G in Fig. 1), the CO_2 pressure in the atmosphere is 1.5×10^{-4} atm, just one-half of its former value. The average temperature at the surface of the earth is then 3.8° C less than its former value. This is a sufficient reduction in the temperature to bring on glaciation according to our hypothesis. Let us assume that after some thousands of years the large ice sheets that have formed reduce the volume of the oceans by 5 per cent. Since the ice sheet can permanently hold only a very small amount of carbonates compared to the same volume of ocean water, the remaining water in the oceans releases CO_2 to the atmosphere in order to return to equilibrium.

After a further period of tens of thousands of years the atmosphere and oceans are in equilibrium at the point N in Fig. 1 corre-

sponding to an ocean volume of 95 per cent of its present value and the constant total CO_2 amount of 123×10^{18} gm. The CO_2 pressure is then 2.5×10^{-4} atm and the surface temperature rises to practically its present value. The ice sheets then melt and the oceans return to their original volume. But then the atmosphere and ocean are no longer in equilibrium. After some ten thousand years, all the ocean waters have been able to circulate to the surface and the CO_2 equilibrium is restored again at point G in Fig. 1. The smaller CO_2 pressure in the atmosphere reduces the surface temperature 3.8° C and another ice sheet starts to form. These oscillations of climate would continue with a period roughly of the order of 50,000 years as long as the total CO_2 amount in the atmosphere-ocean system is 123×10^{18} gm. There is no possible stable state of the climate for this total CO_2 amount. The long period of alternation between glacial and interglacial climates ends when some factor in the CO_2 balance finally increases the total CO_2 amount in the atmosphere-ocean system above 123×10^{18} gm.

Under the assumptions made above, it is easily seen that these continuous fluctuations from a glacial to an interglacial climate and back again would occur for any total CO_2 amount from 117 to 123×10^{18} gm. If the total CO_2 amount should fall below 117×10^{18} gm, then a permanent glacial climate would result (assuming only 5 per cent of the oceans froze) until the total CO_2 amount increased; on the other hand, it would still be possible to have fluctuations from a glacial to an interglacial climate, if the colder temperatures froze an amount of water equivalent to more than 5 per cent of the volume of the oceans.

The time required for the oceans to reach equilibrium with $CaCO_3$ is not known. In the above numerical example it was assumed that this time is long compared to 10,000 years. If this is not true, the dashed curves in Fig. 1 referring to $CaCO_3$ equilibrium should have been used instead of the solid ones. It is easily seen that this would make no essential difference in the argument, although a slightly greater decrease in the total CO_2 amount would have had to be assumed.

The conclusions reached above do not depend on the particular numerical values assumed in the above example. The calculations

have been repeated for a large number of different sets of values for the assumed parameters. In each case there always exists a range of values for the total CO_2 amount in the atmosphere-ocean system, such that the climate continually oscillates between a glacial and an interglacial stage when the total CO_2 amount is fixed at some particular value in this range. For various values of the parameters these oscillations occur when the total CO_2 amount is reduced from 3 to 50 per cent below its present value. If the total CO_2 amount is reduced to 50 per cent or less of its present value, then a permanent period of glaciation results until the total CO_2 amount again increases.

b. *Increase in precipitation at onset of an ice age*

It has been emphasized by many authors that, in addition to lower temperatures, increased precipitation is necessary for the accumulation of extensive ice sheets. In the variable sun theory, a decrease in solar radiation would be expected to decrease the intensity of the general circulation and also to decrease the amount of precipitation. This difficulty led to the ingenious modification of this theory where it is assumed that increased solar radiation causes glaciation by increasing the amount of precipitation, in spite of the warmer average temperature that results.

On the other hand, the CO_2 theory suggests that a higher level of precipitation may occur at the same time as lower average surface temperatures. Although the physical processes that cause precipitation from a cloud are not completely understood, the radiation loss from the upper surface of a cloud is known to be one of the relevant parameters. If the upper surface of the cloud can lose more heat by radiation, the lapse rate in the cloud increases. This increases the convection in the cloud, which in turn hastens the onset of precipitation. The lapse rate would be expected to be greater at night than during the day and more precipitation is observed at night (HEWSON, 1937). It appears that the radiation loss from the upper surface of the cloud is an important factor in the development of nocturnal thunderstorms; in other situations the relative importance of this factor is not known.

During the period when glaciers are forming

there is a smaller than normal amount of CO_2 in the atmosphere. More radiation from the upper surface of a cloud is able to escape to space, thus cooling the upper surface more effectively. Calculations by PLASS (1956 b) show that the average temperature is lowered 2.2° C and 1.3° C for the upper surface of a cloud at 4 km and 9 km respectively, if the amount of CO_2 in the atmosphere is halved. This temperature change should increase the lapse rate in the cloud sufficiently to increase the average precipitation significantly. Further it should be noted that the increased cloud cover further reduces the surface temperature below the value calculated from the CO_2 theory alone. Both the decreased average temperature and the increased precipitation caused by the reduction in the atmospheric CO_2 content effectively promote the growth of ice sheets. Cold and wet climates should occur together when the CO_2 concentration in the atmosphere is reduced.

c. *Time lag between periods of mountain building and glaciation*

There is considerable geological evidence that there were extensive periods of mountain building some millions of years before the last two major glacial epochs. Tremendous quantities of igneous rock are exposed to weathering by mountain building. By far the most active zone for the disintegration of rock is the zone between the surface and the level of the permanent underground water. In mountainous country this level is farther below the surface than in flat country and there is a considerably larger volume in which the active weathering of the rocks takes place. In the weathering of igneous rocks carbonates are formed, thus removing CO_2 from the atmosphere.

After a period of mountain building, more CO_2 is being taken from the atmosphere in the weathering of rock than before. This could easily change the CO_2 balance sufficiently so that after a period of the order of a million years, the atmospheric CO_2 would be reduced sufficiently to start a period of glaciation.

During the period of mountain building it might be expected that the CO_2 escaping from the interior of the earth to the atmosphere through volcanic vents, hot springs, etc. would increase. If this happens to an appreci-

able degree, the extra CO_2 that is added to the atmosphere counteracts the CO_2 used up in weathering and the onset of glaciation is postponed. In fact, some major periods of mountain building have not been followed by extensive ice sheets. A possible explanation would be that more CO_2 had been added to the atmosphere from the interior of the earth than could later be removed by rock weathering. In any case, when a glacial epoch does follow a period of mountain building, the CO_2 theory clearly predicts an appreciable time delay between the two events.

d. Influence of man's activities on climate

At the present time the burning of fossil fuels is adding more than 6×10^9 tons per year of CO_2 to the atmosphere. Other activities of man such as the clearance of forests and the drainage and cultivation of land add additional amounts of CO_2 to the atmosphere each year. The total amount added each year from these sources is several orders of magnitude larger than any factor that contributes to the CO_2 balance from the inorganic world at the present time (see Table I). Therefore, this additional factor has greatly disturbed the CO_2 balance. If all this additional CO_2 remains in the atmosphere, there will be 30 per cent more CO_2 in the atmosphere at the end of the twentieth century than at the beginning. If no other factors change, man's activities are increasing the average temperature by $1.1°$ C per century. This argument was first presented by CALLENDAR (1938, 1949).

There appear to be only two ways in which the excess CO_2 could be removed from the atmosphere. More CO_2 is used in photosynthesis when the CO_2 concentration increases. However, as already discussed, in a relatively short period of time increased rates of respiration and decay bring the factors from the organic world into balance once again. Except for a small initial loss, no appreciable part of the extra CO_2 can be used up in this manner.

Some of the extra CO_2 will also be absorbed by the oceans. Because of the slow circulation of the oceans it would probably take at least 10,000 years for the atmosphere-ocean system to come to equilibrium after a change in the atmospheric CO_2 amount. The surface layers of the ocean start absorbing some of the extra

CO_2 from the atmosphere as soon as the P_{CO_2} is greater than the equilibrium amount. The rate at which this absorption takes place is not known accurately, but it is probably true that the surface layers can absorb only a small fraction of the extra CO_2 in a period of several hundred years. Thus it appears that most of the additional CO_2 that is released into the atmosphere will stay there for at least several centuries. Even if the oceans absorb CO_2 much more rapidly than has been assumed here, the accumulation of CO_2 in the atmosphere will become an increasingly important problem through the centuries.

The known reserves of coal and oil amount to about 13×10^{18} gm. After making allowance for the growth of industrial activity it is expected that this amount of fuel will be used up in less than one thousand years. If this occurs, nearly 40×10^{18} gm of CO_2 will have been added to the atmosphere. This is seventeen times the present amount of CO_2 in the atmosphere. Even if it is assumed that the atmosphere-ocean system will be near equilibrium at the end of this period, the total CO_2 amount will increase from 132×10^{18} gm to 172×10^{18} gm. From an extension of Fig. 1 the equilibrium value of P_{CO_2} is found to be 30×10^{-4} atm corresponding to a temperature rise of $12.2°$ C. Even if there were sufficient time for $CaCO_3$ equilibrium to set in, Fig. 1 shows that P_{CO_2} is 11×10^{-4} atm (nearly four times the present value) and the corresponding temperature rise is $7.0°$ C. Since complete equilibrium between the atmosphere and oceans cannot be maintained when the atmospheric CO_2 amount is constantly increasing, the actual temperature rise will be considerably greater than $7°$ C.

It is tempting to give an explanation of the recent rise in average temperature over the entire globe in terms of the increased CO_2 amount in the atmosphere (CALLENDAR, 1938, 1949). A great deal more data in the form of accurate CO_2 measurements over a period of time and temperature records for the remainder of the century will be needed to prove or disprove this explanation. Many local variations, such as the extremely rapid rise in temperature in Scandinavia cannot be explained by the CO_2 theory and are probably due to changes in the general circulation. However, it is entirely possible that the general

temperature rise over the entire earth is due to the CO_2 effect. Furthermore, the influence of the extra CO_2 on the climate will become increasingly important in the near future as continuously greater amounts of CO_2 are released into the atmosphere by man's activities.

e. *Carboniferous period; glaciation in phase in both hemispheres*

A change in any of the other factors that influence the CO_2 balance can also influence the climate according to the CO_2 theory. Unfortunately it is often difficult to estimate the relative importance of the various factors at specific times in the past. Nevertheless it is certain that all of these factors have changed by large amounts during the earth's history.

The amount of organic material being trapped in new coal and oil deposits and other sediments may have been much greater at certain periods of the earth's history than it is today. This was presumably the case during the Carboniferous period when the relatively level land and many marshes created the proper conditions for the formation of large amounts of organic sediments. After a long period of time this had the effect of reducing the amount of CO_2 in the atmosphere-ocean system. It is perhaps significant that the glaciation at the end of the Carboniferous appears to have been the most severe in the earth's history.

Any large scale climatic variations due to changes in the CO_2 amount in the atmosphere must occur simultaneously (on a geological time scale) in both hemispheres. Presumably a few centuries or less would be sufficient time to equalize the atmospheric CO_2 amount in both hemispheres following a disturbance in one. An exception might occur if one hemisphere were considerably more mountainous than the other. The temperature drop would be the same in both hemispheres following a decrease in the CO_2 amount. Nevertheless the mountainous land of one hemisphere could provide a favorable source for the glaciers, whereas they would be unable to form on the relatively flat land of the other hemisphere.

7. Unsolved problems for the CO_2 theory

In this section various problems are discussed for which either more study is required in order to understand the various factors that

are involved or more time is needed to accumulate additional data. The answers to these questions can only be suggested at this time.

The temperature trend during the remainder of this century should provide a definitive test of the relative importance of such factors as CO_2, variations in the solar energy and volcanic dust in determining the climate at the present time. The predictions based on these theories are entirely different. The CO_2 theory states that the average temperature of the earth will continue to increase for many centuries, as the atmospheric CO_2 content increases due to the burning of fossil fuels and other activities of man. The solar theory predicts that the average temperature will decrease for some decades to come. The maximum of the eighty year period in the sunspot cycle probably occurred in 1947. The average energy that the earth receives from the sun including the ultraviolet should decrease for a number of years, thus causing the average temperature to decrease. A continual temperature rise could not be explained by the solar theory unless measurements at the same time should show an appreciable increase in the solar constant. The volcanic dust theory predicts a lower average temperature for several years after a major volcanic explosion that sends large amounts of dust into the atmosphere. There has been no such explosion since 1912 when Katmai erupted in the Aleutian Islands. Further attempts at verification of this theory must await new volcanic action.

There have not been sufficient measurements of the CO_2 content of the atmosphere in recent years to establish beyond doubt that the CO_2 amount has actually risen since 1900. In view of the importance of the problem, further measurements over a period of years should be undertaken. The predicted rise of 3 per cent in 10 years could be detected with measurements of moderate accuracy. At the same time more data could be accumulated on the variation in CO_2 amount with different types of air masses. Simultaneous measurements in both hemispheres could obtain in addition information on the rate of exchange of gases between the hemispheres. The level of industrial activity is so much less in the Southern Hemisphere than in the Northern at the present time that most of the increase for the Southern Hemisphere would be due

to CO_2 originally released in the Northern Hemisphere.

Is the atmosphere-ocean CO_2 system nearly in equilibrium today? Is the ocean in equilibrium with $CaCO_3$ today? Since the CO_2 amount should have been appreciably less at the time of the last glaciation ten thousand years ago, one would not expect that the CO_2 equilibrium could have been restored in such a relatively short time interval. Nevertheless the currently accepted values for the chemical constants of sea water indicate that the oceans are nearly in equilibrium today. However, this conclusion depends on the values of several equilibrium constants which are known only approximately. More accurate measurements of these constants would indicate whether or not the atmosphere-ocean system is in equilibrium today. If it should be found that equilibrium does not exist today, then the curves in Fig. 1 would be shifted somewhat from the positions given. However, their qualitative shape would not be changed and none of the previous conclusions that were based on this figure would be changed.

If the theory presented here of CO_2 variations in the atmosphere is correct, then the reduced CO_2 amount at the time of the last glaciation means that the radiocarbon dates for events *before* the recession of the glaciers are in question. A constant CO_2 amount in the atmosphere has been assumed in all the calculations to determine radiocarbon dates. Clearly some direct evidence is needed for the actual CO_2 amount in past epochs. It is possible that this may be calculated in the future from experimental determinations of the past temperature of the oceans and the rate of carbonate deposition.

Besides CO_2, both H_2O and O_3 have an important influence on the infra-red radiation from the surface of the earth. A variation in concentration of any of these gases can change the surface temperature. Estimates of the effect of O_3 on the surface temperature have been given by PLASS (1956 a). When the maximum of the ozone distribution is at a lower altitude, the surface temperature tends to rise because there is then a larger downward radiation flux from the lower, warmer layers near the O_3 maximum. Similar effects exist for H_2O. An estimate made by Wexler (SHAPLEY, 1953) shows that the temperature

would fall 6° C if the relative humidity changed from 100 to 50 per cent throughout a typical mass of polar maritime air. An accurate analysis of the effect of H_2O on atmospheric radiation has not been made as yet because of the complexity of this spectrum and the difficulty of making experimental measurements beyond 20 microns. Considerable further work needs to be done on the effect of H_2O. The influence of the greatly reduced amounts of H_2O in the atmosphere in the colder regions where glaciers form needs to be evaluated together with the influence of changes in the albedo due to greater precipitation.

Why should the major glacial epochs of the earth recur at intervals of approximately 250,000,000 years? What is the factor that finally brings a glacial epoch to a close? These are some of the questions for which the CO_2 theory can only suggest answers at the present time. According to the CO_2 theory, the 250,000,000 year interval between glacial epochs is connected with a similar periodicity in the occurence of major periods of mountain building. Thus the fundamental question that must be answered is to explain why the major mountain chains appeared when they did. Also there are several possible factors in the CO_2 theory that can bring a glacial epoch to a close. We have discussed how the alternate advance and retreat of the glaciers can be explained if the total CO_2 amount in the atmosphere-ocean system stays at a constant level a few per cent below the present value. In order to bring the glacial cycle to a close, some factor must increase the atmospheric CO_2 amount. A reduced amount of rock weathering due to the increasing flatness of the land as the mountain ranges erode or to reduced weathering under the land covered by glaciers or an increase in the CO_2 released from the interior of the earth are all factors that would act to increase the total CO_2 amount.

Some interesting evidence about the CO_2 content of the atmosphere in the past can be deduced from the fact that plants grow more luxuriantly and rapidly in an atmosphere that has from five to ten times the normal CO_2 amount. Since plants are completely adapted in photosynthesis for the maximum utilization of the spectral range and intensity of the light

that reaches them from the sun, it seems strange that they are not better adapted to the present CO_2 concentration in the atmosphere. The simplest explanation of this fact is that the plants evolved at a time when the CO_2 concentration was considerably higher than it is today and that the CO_2 concentration has been at a higher level during the majority of the ensuing time. This higher CO_2 concentration would have caused higher temperatures than today during most of the earth's history. In fact, the geological evidence shows that the earth has had a warm climate for at least nine-tenths of the time since the Cambrian period.

8. Conclusions

The latest calculations of the influence of CO_2 on the infrared flux show that if the CO_2 concentration in the atmosphere doubles the average temperature rises 3.6° C and if it falls to half of its present value the average temperature falls 3.8° C. The pressure broadening and overlapping of the spectral lines is taken into account in this calculation. The shielding effect due to H_2O does not appear to be large. Thus reasonable changes in CO_2 amounts can cause appreciable climatic variations.

Many reasons for climatic change have been proposed, such as variations in the radiation from the sun that reaches the earth, the amount of volcanic dust in the air, the average elevation of the lands and changes in the general circulation. It is entirely possible that some of these factors may have had an appreciable influence on the climate at particular times and places in the earth's history. A recent summary of the evidence for and against these theories has been given by WILLETT (1949).

However, it does seem significant that there are many facts about world-wide variations in the climate that can be explained in a simple, straight-forward manner only by the CO_2 theory. Some of these are: (1) the cycles in which the glaciers alternately advance and retreat in a single glacial epoch; (2) the increase in precipitation as well as the decrease in temperature that occurs when glaciers form; (3) the time interval of several million years between the uplifting of major mountain ranges and the appearance of glaciation; (4)

the extremely severe period of glaciation that followed the Carboniferous period when extensive coal deposits were laid down; (5) the world-wide increase in temperature that has occurred since 1890 with a greater warming in the Northern than in the Southern Hemisphere; (6) the variations in climate have been in phase in both hemispheres.

Brief explanations of these changes in terms of the carbon dioxide theory are as follows: (1) If the total carbon dioxide amount in the atmosphere-ocean system is reduced slightly and held fixed at this new value, the atmospheric CO_2 amount is initially lowered. The temperature falls sufficiently to start a glacial epoch with the following cycle of oscillations that has an average period of tens of thousands of years because of the slow exchange of CO_2 between the atmosphere and the oceans: (a) the glaciers form decreasing the volume of the oceans by perhaps five per cent so that they slowly release additional CO_2 into the atmosphere; (b) eventually the CO_2 amount in the atmosphere is increased sufficiently to raise the temperature enough to melt the glaciers, thus increasing the volume of the oceans which now slowly begin to absorb more CO_2 from the atmosphere; (c) after a further period of time the decreased CO_2 in the atmosphere brings lower temperatures and the glaciers form again repeating the cycle. This cycle will continue as long as the total amount of CO_2 in the atmosphere-ocean system is unchanged. If the total CO_2 amount is reduced by a large amount, a permanent period of glaciation can occur without oscillations. (2) The probability of obtaining precipitation from a cloud depends on the rate of convection in the cloud. With a smaller CO_2 concentration the radiation from the upper layer of the cloud can escape more effectively to space. This increases the temperature difference between the top and bottom of the cloud. The lapse rate steepens and the intensity of the convection currents increases. This increases the probability of precipitation forming in the cloud. Therefore, increased precipitation is expected to occur when the CO_2 amount is small and conditions are favorable for glacial formation. (3) The weathering of igneous rock exposed by the new mountain ranges removes enough CO_2 from the atmosphere after millions of years

to bring on glaciation. This process may be delayed, at first, by additional quantities of CO_2 released from the interior of the earth when the mountain ranges are first formed. (4) The removal of large quantities of CO_2 from the atmosphere-ocean system in the formation of the coal deposits of the Carboniferous eventually reduced the CO_2 concentration to a very low value. (5) The addition of CO_2 to the atmosphere by industrial processes and other activities of man is increasing the CO_2 concentration of the atmosphere at the rate of nearly 30 per cent a century and causing the average temperature to rise $1.1°$ C per century. Due to the relatively slow exchange of air between the hemispheres, the CO_2 concentration may be increasing more rapidly in the Northern than in the Southern Hemisphere. (6) Over a time interval of several hundred years, the CO_2 concentration in the two hemispheres must be nearly the same. Therefore changes in climate that occur over longer time intervals must be in phase in both hemispheres.

Some of the problems that remain unsettled in connection with the CO_2 theory have been discussed in the previous section. However, the present evidence suggests that variations in the atmospheric CO_2 concentration are one of the important reasons for changes in the climate. From recent radiation studies it is possible to calculate with some confidence the temperature change that must result from any given variation in the CO_2 amount. The factors that influence the CO_2 balance are so complex that the CO_2 amount must have varied over a wide range through geological history. The problem is to be able to determine the atmospheric CO_2 concentration for past geological periods. We would then know one of the most important factors that determined the climate of that epoch.

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