Regulation of O_2, N_2 and CO_2 in the atmosphere; thoughts of a laboratory chemist

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(Manuscript received October 14, 1965)

ABSTRACT

The real system (air + sea + sediments) is compared with an equilibrium model, an imaginary system containing the same components at equilibrium. In the model, the presence of five aluminosilicate phases (six, if Fe is included) SiO_2 and $CaCO_3$ will fix the concentrations of the major ions, pH, and $p(CO_2)$, if temperature and $[Cl^-]$ are given. It is suggested that the real system behaves similarly to the model. The T-dependence of $p(CO_2)$ may be a more important factor than industrial activity.

The behavior of the equilibrium model system on reduction is described; it may resemble earlier states of our real system. The present $p(O_2)$ is probably regulated by a steady state, even if some data might seem to indicate the equilibrium (3) to be nearly fulfilled.

Nitrogen exists as N_2 instead of the equilibrium form, NO_3^-. There is a nitrate sink close to the surface of the ocean, but the explanation still seems to be unknown.

Es irrt der Mensch, so lang er strebt.
(The Lord; Faust, 'Prologue in Heaven')

Wer immer strebend sich bemüht,
den können wir erlösen.
(Angel choir, ibid. II: 5)

According to the now prevalent "cold" theory of planet formation, the Earth and the other planets have been formed by agglomeration of cold particles. Whatever atoms we now have in the volatiles of ocean and atmosphere would thus, for the most part, have been brought to a young Earth in solid particles and later on set free by various processes, especially radioactive heating.

Geochemical balance

Various attempts have been made to make up a "geochemical balance", accounting for the formation of sea water and sediments. The first balance that made the two ends meet was, to my knowledge, that of V. M. GOLDSCHMIDT (1933). Among the more recent ones, that of M. K. HORN (1964) may be mentioned. Their balance may be summarized by the reaction formula:

$$\begin{aligned}&\text{Primary igneous rock (0.6–1.2 kg)}\\&+\text{volatile substances } (\approx 1\text{ kg})\\\rightarrow&\text{sea water (1 liter)} + \text{sediments (0.6–1.2 kg)}\\&+\text{air } (\approx 3\text{ liters}).\end{aligned} \qquad (1)$$

Table 1 gives the geochemical balance for the most abundant components, according to GOLDSCHMIDT/HORN. The amounts have been recalculated to the unit "moplis" = mol per liter sea water; the total volume of sea water is about $1.4 \cdot 10^{21}$ liters, and the estimated total amounts have been divided by that figure.

Both GOLDSCHMIDT and HORN seem to have thought of (1) as a one-way process: in the course of time, a certain amount of igneous rock (0.6 kg according to GOLDSCHMIDT, 1.2 kg according to HORN) has been torn down

TABLE 1. *Balance of materials for the formation of one liter of sea water, calculated from the estimates of* V. M. GOLDSCHMIDT/M. K. HORN.

Unit = moplis = mole per liter sea water

Component		From		Now in		
		Primary rock	Volatile	Air	1 l sea water	Sediments
H_2O			54.90		54.90	
Si	(SiO_2)	6.06/12.25				6.06/12.25
Al	($AlO_{1.5}$, $Al(OH)_3$)	1.85/3.55				1.85/3.55
Cl	(HCl)	0.01/0.02	0.54/0.94		0.55	−/0.40
Na	($NaO_{0.5}$, NaOH)	0.76/1.47			0.47	0.29/1.00
Ca	(CaO, $Ca(OH)_2$)	0.56/1.09			0.01	0.55/1.08
Mg	(MgO, $Mg(OH)_2$)	0.53/0.87			0.05	0.48/0.82
K	($KO_{0.5}$, KOH)	0.41/0.79			0.01	0.40/0.78
C*		0.02/0.03	0.60/2.06		0.002	0.62/2.09
	(CO_2)	0.02/0.03	0.53/1.05		0.002	0.55/1.08
	(C(s))		0.07/1.01			0.07/1.01
O_2^*			0.027/0.022	0.027/0.022		
Fe*		0.55/0.91				0.55/0.91
	(FeO, $Fe(OH)_2$)	0.32/0.53				0.18/0.32
	($FeO_{1.5}$, FeOOH)	0.23/0.38				0.37/0.59
Ti	(TiO_2)	0.06/0.12				0.06/0.12
S*		0.01/0.02	0.03/0.06		0.03	0.04/0.05
F	(HF)	0.03/0.05				0.03/0.05
P	($PO_{2.5}$, H_3PO_4)	0.02/0.04				0.02/0.04
Mn*	($MnO_{1\text{ to }2}$)	0.01/0.05				0.01/0.05
N_2^*			0.101/0.082	0.101/0.082		

chemically by the action of volatile substances, especially H_2O, HCl and CO_2 that came from the interior of the earth and perhaps from the original atmosphere (if any).

There are, however, reasons to believe that (1) is a two-way process, and that the reversal may happen when sediments and sea water (or evaporites) are buried and transformed at increased temperatures and pressures. According to some present views on continental drift, ocean floor is continually being pressed down below the continents, to depths of the order of magnitude 700 kilometers. In such case, there must be a gradual exchange of material with the mantle, and in an attempt at a material balance one must consider a system many hundred times larger than that first assumed. It is then by no means necessary that the both sides of of a "geochemical balance", such as that in Table 1, can be made to agree and if they do, this may indicate that our system has reached a steady state.

At any rate, in the following we may concentrate our attention to the right hand side of (1), since reactions between sea water, sediments and air may be expected to be much more rapid than those between igneous rock and sea water, or air.

Let us first ask what it is that determines the composition of sea water (0.470 M Na^+, 0.054 M Mg^{2+}, 0.548 M Cl^- etc.), and especially its pH ($\approx$8.1). One might perhaps start by guessing that [Cl^-] is determined by the ratio HCl/H_2O in the mixture delivered from the interior of the Earth: both Cl^- and H_2O have mainly accumulated in the ocean.

The equilibrium model and the phase rule

To search for an answer one may consider an imaginary model, "the equilibrium model". This model system would contain exactly the same amounts of the various components in Table 1 as does the real system; one liter of sea water and the corresponding amounts of sediments and air. The difference is that the model will be kept at constant temperature and pres-

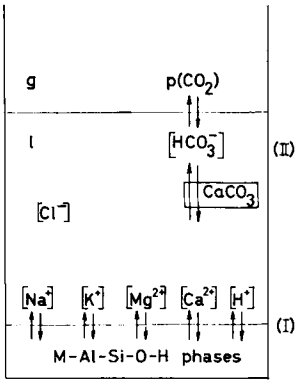

FIG. 1. Schematic picture of regulation of $p(CO_2)$ in equilibrium model. (I) Equilibria between solution and solid phases, especially aluminosilicates, determining major ionic concentrations, and $[H^+]$. (II) Equilibria between $CaCO_3(s)$ and a solution, with the values for $[Ca^{2+}]$ and $[H^+]$ given by (I), determine $[HCO_3^-]$ and $p(CO)_2$.

sure, and allowed to reach true equilibrium. One would like to know the composition of the various phases of the equilibrium model, and to compare them with the real system.

The equilibrium model for the system sea water + air + sediments was first suggested in 1959 (SILLÉN, 1959) and was explained in a perhaps more pedagogic way in a later paper (SILLÉN, 1963; see especially the section "A simple pH-stat model"). The conclusion is that if one mixes the most abundant components, H_2O, SiO_2, AlOOH, HCl, NaOH, KOH, MgO and CaO (and sets enough CaO aside to bind the CO_2 as $CaCO_3$),[1] then *in the model* the ionic concentrations of the major cations, and the pH, will be uniquely determined by equilibria between the solution and the various solid phases, especially alumino-silicates. If then $CaCO_3$(s) is added, this will not perceptibly change $[Ca^{2+}]$ and pH. However, small concentrations of HCO_3^- and other carbonate species in the solution, and a well-defined $p(CO_2)$ in the gas phase will be set up as a result of new equilibria with $CaCO_3$(s). Thus, *in the model*, the carbonate system would not determine the pH but rather act as an indicator of the pH and $[Ca^{2+}]$ already determined by the aluminosilicate equilibria (see Fig. 1).

[1] First, since dolomite equilibria are controversial, enough MgO, CaO and CO_2 was set aside to join the present amount of dolomite.

This is simply a consequence of Gibbs' phase rule. Let us consider a system with nine components: the eight mentioned above, plus CO_2. Assume now that we have nine phases present at equilibrium: a gas phase (containing CO_2 and H_2O), an aqueous solution, SiO_2, $CaCO_3$ and five more phases, presumably aluminosilicates. (Some of the latter we could probably search in the group kaolinite, illite, phillipsite, glauconite, chlorite and montmorillonite.) The system would then have two degrees of freedom, which means that we can set the values for two internal variables as we please (within certain limits). For convenience in regulation we let them be the temperature, T, and the concentration $[Cl^-]$ (which corresponds to the original ratio HCl/H_2O).

If T and $[Cl^-]$ are given, all the ionic concentrations in the aqueous solution, including pH, are fixed. They will not change on addition of reasonable amounts of the various components, whereas of course the relative amounts of the solid phases may change. Large additions may change the setup of phases so that some phase disappears and some other appears which will fix the ionic concentrations at some other set of values.

Addition of a new component will bring with it either a new phase (Fe_2O_3 brings FeOOH(*s*), FeO may bring a sixth aluminosilicate) or a new free concentration variable (N brings $p(N_2)$, HBr brings $[Br^-]$). If we take away the component CO_2, the phase $CaCO_3(s)$ disappears, but otherwise there is little change in the system.

It seems hard to dispute that *the model* will work in this way, since this follows from the equilibrium laws and especially from Gibbs' phase rule. In the 1959 paper, it was suggested that *the real system* may resemble the model so that even in sea water, pH and the concentrations of the major ions are determined by the silicate equilibria, whereas $p(CO_2)$ and $[HCO_3^-]$ are determined second-hand by equilibria with $CaCO_3$. In 1959, few laboratory data were available on silicate equilibria, and these ideas were considered as eccentric. The general feeling was that the pH of sea water is determined by carbonate equilibria, and that the silicates chiefly act as container walls.

In the meantime, more laboratory data on silicate equilibria have become available, notably through work of J. J. HEMLEY, and

this year, two earth scientists of the stature of ROBERT GARRELS (1965) and HEINRICH HOLLAND (1965) have begun to take the equilibrium model (or, if you prefer, the silicate theory) seriously as a useful first approximation; so it may now be considered as half-way respectable.

CO_2 in real system

If one assumes that $[Ca^{2+}]$ and pH are both determined by alumino-silicate equilibria, then one may compare the actual $p(CO_2)$ and $[HCO_3^-]$ with those calculated for equilibrium with solid $CaCO_3$ at the prevalent $[Ca^{2+}]$ and pH. Equilibrium constants and activities may always be disputed, but a survey calculation (SILLÉN, 1959) indicated that the real values are not far from those to be expected for equilibrium at 5°C, which is again not far from the average temperature of sea water.

Now, if I say that $p(CO_2)$ is regulated by the equilibria in Fig. 1, you must understand this in the same way as a statement that $p(H_2O)$ in the atmosphere is regulated by equilibria with solid and liquid water. Surely, the equilibrium value for $p(H_2O)$ varies with temperature, and temperature varies within the real system. You may find air in which $p(H_2O)$ corresponds to equilibrium with sea water, at the temperature of the air; you will find air that has been heated and is undersaturated, and you will find air that is supersaturated (but not very much, and not for a long time).

Analogously, fluctuations and local variations of temperature and pressure will influence the equilibrium values for $[HCO_3^-]$ and $p(CO_2)$, and may cause transport of large amounts of CO_2 and $CaCO_3$. By the way, it would be much easier to map these transports if ocean chemists would determine precisely the pressure-temperature independent quantities total carbonate and alkalinity, instead of measuring only pH (DYRSSEN & SILLÉN, 1966).

Just as with $p(H_2O)$, the approach to equilibrium sets certain limits to the possible range of $p(CO_2)$. If the average temperature of the sea has not been very different from what it is now, I would guess that $p(CO_2)$ has never been very far from the present values $\approx 10^{-3.5}$ atm (which are not far from the equilibrium value for ≈ 5°C). A CO_2 pressure, say, 10 times higher than now would require a considerable increase (perhaps 20–30°) of the average temperature. On the other hand, the much lower equilibrium pressures, down to 10^{-6} atm, that have sometimes been suggested (see e.g. MILLER & UREY, 1959) do not seem realistic since they have been calculated for equilibria with $CaSiO_3(s)$ and other solid silicates which could not exist at equilibrium with sea water; however slow one may think that the reactions are between sea water and solids in contact with it, the reactions between $CO_2(g)$ and igneous rock are much less likely to approach equilibrium.

In later years, there has been considerable interest in the present slow increase in $p(CO_2)$ in the atmosphere, which may correspond to roughly 10% ($\Delta \log p(CO_2) = 0.04$) in the last 50 years, and which has been related to industrial activity.

The kinetic aspects are of course important. The approach to equilibrium may be described as follows: Excess CO_2 that has been set free by the increasing combustion of fossil fuel is dissolved into the sea water, some more $CaCO_3(s)$ is formed, some aluminosilicates rich in Ca^{2+} are dissolved, whereas others are formed instead. (If these reactions spread out all over the ocean floor the effect will hardly be noticeable in the sediments.) If these reactions are slow, there may be a temporary excess of CO_2 in the atmosphere.

However, one should perhaps give attention also to the temperature dependence of the equilibria indicated in Fig. 1. One knows fairly well how the equilibrium(II), $CaCO_3(s) + 2H^+ \rightleftharpoons Ca^{2+} + CO_2(g) + H_2O$ is affected by temperature, and $p(CO_2)$ would even decrease by a few percent per degree, provided $[Ca^{2+}]$ and pH were kept constant. However, the silicate equilibria (I) would also be T-dependent, and from HEMLEY's data one may conclude that the equilibrium solution will be more acidic with increasing temperature, which would tend to increase $p(CO_2)$. By the crudest of estimates (using data from SILLÉN, 1965, p. 448) one finds that the net result of a temperature rise of 1°C might be an increase of $p(CO_2)$ by 10%. So, variations in climate, e.g. in the sun's radiation, might influence $p(CO_2)$ quite independent of industry.

The increase of the equilibrium $p(CO_2)$ with T may bring with it a process control with some interesting possibilities. A rise in T, for one reason or another, would be followed by an increase in the equilibrium $p(CO_2)$, which

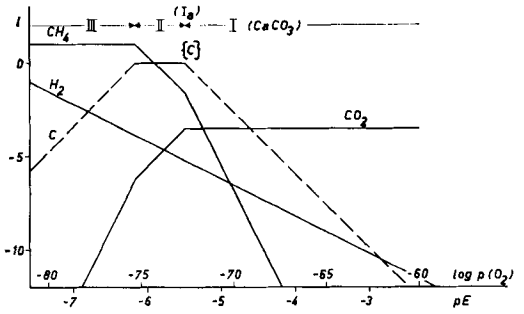

FIG. 2. Logarithms of activities of CO_2, C, H_2 and CH_4 in equilibrium model in reduced range (from SILLÉN, 1965, *Arkiv Kemi*, by permission).

would increase T again, by the green-house effect. There must be mechanisms that work in the other direction and eventually take over. For instance high evaporation gives rise to more clouds that deflect an increasing fraction of the sun's radiation. The result may be an oscillating system rather than a steady state.

Oxygen

Previous speakers have already indicated the main reactions that are thought to affect the oxygen balance of our atmosphere. Oxygen is *formed* by photochemical reactions, especially by the dissociation of water vapor, and by biological photosynthesis. If there is to be a net excess of oxygen, one must get rid of the other reaction product: H_2 must be lost to outer space, and C must be buried as fossil carbon, or as hydrocarbons.

On the other hand, oxygen is *consumed* by biological oxidation, nowadays to some extent by industrial combustion, and by oxidation in the Earth's crust of Fe(II) to Fe(III), and of sulfides to sulfate. Oxygen is also consumed by the oxidation of volcanic gases, especially H_2. Volcanic H_2 is very likely to be equilibrated with H_2O, Fe(II), and Fe(III) somewhere on its way toward the surface, and if its origin is circulating H_2O, the reaction of O_2 with volcanic H_2 may be equivalent to indirect oxidation of Fe(II) in the crust or mantle.

We may now ask, if there is any chemical process that regulates the present $p(O_2)$ and makes it close to 0.21 atm.

Reduced states of the equilibrium model

In two recent publications (SILLÉN 1965, 1965*a*) I have tried to calculate what would happen to a model system consisting of the components in Table 1, if it is gradually reduced at 25°C, for instance by adding H_2 and establishing equilibrium after each addition (which is easier in imagination than in the laboratory). The successive states of the equilibrium model might, with good luck, resemble earlier states of the real system, sea water + sediments + air. Someone might object to the choice of 25°C, but it seems hard to tell whether the real temperature was higher or lower, and equilibrium data are readily available at 25°C. As a check, calculations were made also at 100°C, and the results gave much the same general picture.

The oxidation state of the model was expressed by means of the quantity

$$\mathrm{pE} = -\log \{e^-\} \qquad (2)$$

which is related to the reversible oxidation potential of the system. For the present purpose it suffices to say that pE is more positive in more oxidizing systems (it is around 12.5 in the present system), and more negative in reducing systems.

It was assumed that the concentrations of Cl^- and the major cations, and also pH = 8.1, are fixed by the pE-independent aluminosilicate equilibria, and moreover that $p(CO_2)$ is fixed at

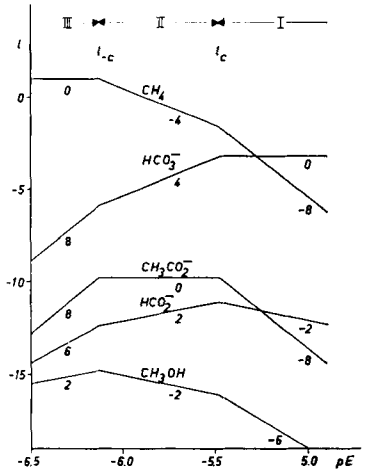

FIG. 3. Logarithms of equilibrium activities in solution of some molecules containing C as a function of pE (from SILLÉN, 1965, *Arkiv Kemi*, by permission).

$\approx 10^{-3.5}$ atm as long as $CaCO_3(s)$ is present. (Here is a little flaw since the present $p(CO_2)$ may correspond to equilibrium at $\approx 5°C$, and the equilibrium $p(CO_2)$ might be higher at 25°C. This difference, however, does not affect the main conclusions.)

Fig. 2 gives the logarithms of the activities for CO_2, H_2, C and CH_4 around $pE = -5$, thus in much more reducing states than the present $pE \approx 12.5$, which would be far to the right of the diagram. If the system is continuously reduced, pE will halt close to $pE = -5.5$, at which point $CaCO_3$(s) is reduced to C(s). After $CaCO_3$(s) has disappeared completely, pE can decrease further. C(s) will be present until, at equilibrium around $pE = -6.1$, all C(s) has been transformed to CH_4(g).

Fig. 3 gives log (activity) for a few species containing C. If one excepts CH_4 and C_2H_6, the highest equilibrium concentration for any organic species seems to be reached by $[CH_3CO_2^-]$, which is at most around 10^{-10}: the equilibrium concentrations of other organic species are still lower. This finding has some interest since it has been suggested by HALDANE (1929), OPARIN (1957) and others that the first ocean was a thick soup containing various organic substances in high concentrations (10% has been mentioned). I must admit that I find it hard to understand how this is possible.

Fig. 4 surveys the fates of the major elements in the course of the reduction or our model system. Log p is indicated by broken lines, log c with full-drawn lines, and at the lower end the solid phases are indicated. We see how C is transformed from mainly $CaCO_3(s)$ over C(s) to CH_4. Sulfur will be transformed around $pE \approx -3.8$, from SO_4^{2-} in the ocean to solid FeS_2. In the course of the reduction, Mn(IV) is transformed to Mn(II), and Fe(III) to Fe(II). We shall return to the dotted line for NO_3^-. Nitrogen is reduced from N_2 to ammonium ions, most of which will probably exist in solid aluminosilicates, where they can take the place of K^+.

Another way of representing the changes in the model is Fig. 5 (from SILLÉN, 1965a), a "titration curve" showing the number of oxidation equivalents that must be added to the model system at various stages of reduction in order to carry it back to the present $pE \approx 12.5$. At the lowest point in Fig. 5, the system would have started with all C as CH_4 and some excess

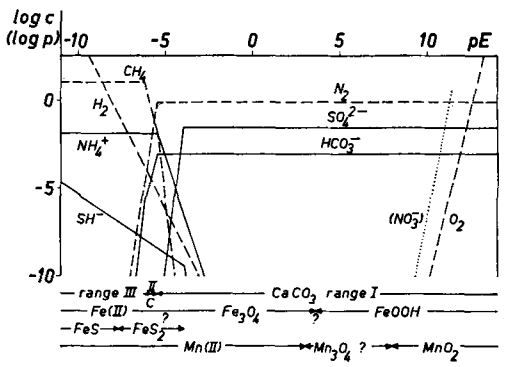

FIG. 4. Redox diagram, giving log c (or log p) for the major variable species as functions of pE. Solid phases indicated at bottom of figure (from SILLÉN, 1965a, *Arkiv Kemi*, by permission).

H_2. There are distinct steps for the oxidation of H_2 to H_2O, of CH_4 to C, of C to CO_2 (or rather $CaCO_3$), of NH_4^+ to N_2, of FeS_2 to SO_4^{2-}, and of Fe and Mn. The last step corresponds to the formation of O_2. The latter part of the curve is shown also on a tenfold scale.

Oxygen in real system

One might like to compare the behavior of the model with the real system. It is hard to say exactly in what oxidation state the real system started, if we count the starting point as the first time when the Earth had a coherent ocean of reasonably uniform composition. At any rate the number of oxidation equivalents needed to form our free O_2 is quite small compared to what is needed for many of the other processes indicated.

Let us look especially at the step for Fe. In Fig. 5, the amount of Fe(II) to be oxidized was calculated from the difference between the oxidation number of Fe in "igneous rock" and in sediments, using HORN's values from Table 1 which, even if they are larger than GOLDSCHMIDT's, still represent a fairly small system. Now, if there has been considerable exchange of material with the mantle, as indicated above, enormously larger amounts of Fe(II) may have been oxidized so that the Fe step may have been larger than any of the C steps.

Let us ask again, is $p(O_2)$ determined by some equilibrium, or are the reactions forming new O_2 struggling against other reactions consuming

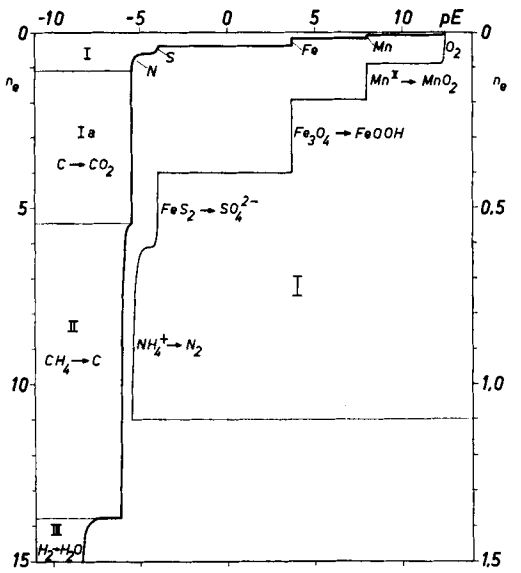

FIG. 5. "Titration curve" for equilibrium system showing number of oxidation equivalents necessary to carry system back to present pE ≈ 12.5 from various states of reduction (from SILLÉN, 1965*a*, *Arkiv Kemi*, by permission).

it? When I first thought over the problem, my attention was drawn to the possible equilibrium

$$12\mathrm{FeOOH}(s) \rightleftharpoons 4\mathrm{Fe_3O_4}(s) + 6\mathrm{H_2O}(l) + \mathrm{O_2}(g),\ K = p(\mathrm{O_2}). \qquad (3)$$

My first approach was to calculate $p(O_2)$ using the ΔG° values in Latimer (1952), and I was pleasantly surprised to find that the equilibrium $p(O_2)$ came out not far from the present value, 0.21 atm. So, for a couple of days I was playing with the idea that the equilibrium (3) really determines $p(O_2)$ in our atmosphere. Then, O_2 would first have accumulated until the equilibrium pressure was reached, but from that time on, excess O_2 would have been consumed by the reversal of (3). However, when I looked more closely into the data it came out that by giving more weight to one set of experimental data or another one could easily deduce equilibrium pressures anywhere between 0.2 and 10^{-117} atm. Hence, much better laboratory data on equilibrium (3) are needed, but my present feeling is that the equilibrium pressure for (3) is not 0.21 atm but considerably lower, as is also indicated in Fig. 5. The present $p(O_2)$ would then be determined by a steady state in the competition between O_2-forming and O_2-consuming reactions.

Nitrogen: bugs at work?

If N had been at true equilibrium at the present $p(O_2)$ and pH in the ocean, then one may show that practically all N would have been present as NO_3^- in the ocean, and not as $N_2(g)$. Many processes are known that transform N_2 to NO_3^-, the most important ones being perhaps the formation of NO_3^- by atmospheric processes such as lightning, and the action of nitrogen-assimilating bacteria in soil and sea. By the action of such processes, a steady stream of NO_3^- is being added to the sea by rivers and rain water, and one may ask why, in the course of time, all N has not accumulated in that form. ERIKSSON (1958) and EMERY *et al.* (1955) have tried to make up nitrogen budgets for various parts of the ocean but could not make the ends meet: it seems that some process is missing that transforms NO_3^- to N_2.

To discuss this problem we may have to pay attention to life processes in the sea. A good survey is given by REDFIELD, KETCHUM & RICHARDS (1963) in which they give summaries and recalculations of earlier work by REDFIELD, RICHARDS and VACCARO etc. It seems that the average composition of zooplankton in sea water is $PN_{16.5}C_{103}$, and of phytoplankton $PN_{15.5}C_{106}$; either figure applies not to any individual species, but to the mixture that can be caught. The figures are equal, within the limits of error, and we shall denote

$$\mathrm{P_{org}} = \mathrm{PN_{16}C_{106}}(+\mathrm{O\ and\ H}). \qquad (4)$$

Living matter is ultimately formed by photosynthesis, starting from inorganic material which we shall write as

$$\mathrm{P_{ox}} = \mathrm{HPO_4^{2-}} + 16\mathrm{NO_3^-} + 106\ \mathrm{HCO_3^-}. \qquad (5)$$

We may then write the photosynthesis briefly as

$$\mathrm{P_{ox}} + h\nu \rightarrow \mathrm{P_{org}} + 138\ \mathrm{O_2}. \qquad (6)$$

We have not balanced (6) with respect to H_2O, protons etc., and $h\nu$ stands for several quanta. The biological oxidation, which occurs in the bulk of the sea, may by and large be

written as the reversal of (6). (In some regions, especially in stagnant water and bottom layers, O_2 is deficient and NO_3^- and SO_4^{2-} are used instead as oxidants.)

Now, if one plots $[HCO_3^-]$ versus $[NO_3^-]$ for various water samples, it seems that the points lie within a band of the slope required by the ratio C/N in P_{org} (4) or P_{ox} (5). This is as one might expect, if N and C are withdrawn from, or added to, the sea water in a constant ratio.

If one plots total $[PO_4]$ versus $[NO_3^-]$ in sea water, one will likewise find that the points fall close to reasonably straight lines of the slope expected, assuming that ($\approx 16N + 1P$) are withdrawn from, or added to the water simultaneously. Reaction (6) and its reversal require a slope of around 16, but would be compatible with any position of the line. For instance, one might well imagine that there could be a considerable concentration of nitrate left when all phosphate was depleted, and that nitrate would be able to accumulate in the ocean until all $N_2(g)$ were used up. The phosphate concentration cannot very much exceed the limit given by the solubility of some calcium phosphate.

In diagrams, nitrate versus phosphate, it is striking not only that the slope is approximately the expected one, but also that the lines pass through the origin or close to it. This means that nitrate and phosphate are depleted simultaneously, and this occurs close to the ocean surface in periods of high biological activity, as was first shown by Harvey in the English Channel (1926, 1928; see also COOPER, 1933).

It seems that there is a sink for nitrate somewhere close to the ocean surface, and I find it very hard to think that processes close to the ocean floor could cause $[NO_3^-]$ to approach zero exactly at the surface.

I have tried to ask as many specialists as I could in the fields of marine biology and biochemistry but nobody has been able to indicate the cause of this sink. Perhaps nobody has been looking out for such a process. Of course, if there is an organism that can use nitrate as an oxidant, even in the presence of excess O_2, and transform NO_3^- to N_2, this might well remain secrete for a long time if nobody were looking specifically for it; surely the process would not smell.

The simplest mechanism for a sink would be a biological process in an organism that uses nitrate and transforms it to N_2, even in the presence of O_2, and at a higher rate the lower the concentration of phosphate. On the other hand, the explanation may well be a series of processes rather than a single process. At any rate, it seems likely that it is to the life sciences we should go to find the missing term in the nitrogen balance of our present system.

To sum up, if there is any resemblance between the real system and the model we have made, it seems that the composition of the present air is regulated as follows: $p(CO_2)$ is regulated by an approach to the equilibria indicated in Fig. 1. $p(O_2)$ is increasing, slowly but steadily, in a competition between opposing processes; whereas $p(O_2)$ is not fixed by any specific reaction, it is in the main at equilibrium with the bulk of the components of the system (air + sea water + sediments). Finally, N_2 is very far from the true equilibrium state (which would be NO_3^- in the ocean) and the approach to equilibrium is being hindered by one or more unknown processes, that give a nitrate sink in the top layers of the ocean.

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РЕГУЛИРОВАНИЕ O_2, N_2 и CO_2 В АТМОСФЕРЕ; РАЗМЫШЛЕНИЕ ЛАБОРАТОРНОГО ХИМИКА

Реальная система (воздух–море–осадочные породы) сравнивается с равновесной моделью, содержащей те же самые компоненты. Если температура и Cl^- заданы, то в модели присутствие пяти алюминосиликатных фаз SiO_2 и $CaCO_3$ (шести, если включить) будет фиксировано концентрацией главных ионов pH и $p(CO_2)$. Зависимость температуры от $p(CO_2)$ может быть более существенна, чем деятельность промышленности. Описывается поведение равновесной модели при восстановлении. Это, возможно, имеет сходство с более ранними состояниями нашей реальной системы. Современное значение $p(O_2)$, вероятно, определяется установившимся состоянием, даже если некоторые данные, может быть, указывают на то, что равновесие (3) осуществляется приближенно. Азот существует как N_2 вместо равновесной формы NO_3^-. Вблизи к поверхности океана наблюдается уменьшение азотнокислых солей, но причины этого пока неизвестны.