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THE CARBON DIOXIDE OF THE OCEAN AND ITS RELATIONS TO THE CARBON DIOXIDE OF THE ATMOSPHERE.¹

OUTLINE.

1. Introduction.
2. Laws of dilute solutions
 - 1. Mass action.
 - 2. Dissociation.
 - 3. Heterogeneous equilibrium and the change in the solubility of one salt due to the presence of others.
 - 4. Hydrolitic dissociation.
3. Solution of gases in pure water.
 - 1. Class I.
 - 2. Class II. } Physical solubility.
 - 3. Carbonic acid. } Chemical solubility.
 - 4. Amount of gases dissolved.
4. Solution of gases in salt solutions.
 - 1. Class I. Oxygen, Nitrogen, etc.
 - 2. Carbonic acid.
5. The ocean salts.
 - 1. Amounts.
 - 2. Degree of dissociation.
6. The ocean gases.
 - 1. Oxygen, nitrogen and argon.
 - 2. Carbon dioxide.
 1. Simple Solution.
 2. As $H_2 CO_3$.
 3. Modified by the ocean salts.
 4. Maximum amount held thus in the ocean under the laws of gas absorption.
 5. Ditto. As second equivalent of bicarbonate.
7. Relation of the atmospheric and oceanic CO_2 .
 1. CO_2 of the bicarbonates.
 2. Dissociation of the bicarbonates.
 3. Degree of dissociation as a function of temperature and pressure.

¹ Especial thanks are due to Dr. Chamberlin, Dr. Stieglitz and Dr. Lengfeld, of the University of Chicago, for careful revision of this article and many valuable suggestions.

4. Effect of variation of pressure and temperature postulated by Dr. Arrhenius. (a) Upon bicarbonate in the waters of the temperate zone. (b) Upon bicarbonates in equatorial waters. (c) Upon bicarbonates in colder waters.
5. Changes in volume of the belts due to cold water advancing southward.
6. Conclusions.

THIS subject has come to have special importance on account of the investigations of Professor Arrhenius¹ and Dr. Chamberlin,² on the effects of the atmospheric CO₂ upon the climate of the earth. Some of the earlier important contributions on the subject are as follows:

Tyndall calculated from his experiments that the absorption of radiant heat by atmospheric CO₂ is eighty times that of the oxygen or nitrogen, and that water vapor has an absorbing capacity of ninety-two times that of oxygen or nitrogen.³

By repeating and extending Tyndall's experiments, Dr. Lecher and his colleague, Pretner, concluded that carbon dioxide is the only agent in absorbing the sun's heat, and maintaining the earth's temperature above that of space.⁴

Mr. J. S. Keeler criticised the above and stated that the heat is absorbed by carbon dioxide and some other agent; either water vapor or matter in suspension.⁵

Professor Röntgen showed that water vapor has a marked absorption band in the ultra red and, therefore, plays an important part in maintaining the present surface temperature of the earth.⁶

Paschen demonstrated that both these gases play important parts in the atmosphere's heat absorption, and that sometimes one, and sometimes the other is the predominant factor.⁷

¹ Phil. Mag., Vol. XLI, pp. 237-279.

² JOUR. GEOL., Vol. V, 1897, pp. 663-683. Also this No., pp. 545-584.

³ Introduction of Chemical and Geological Essays, T. S. HUNT.

⁴ Sitzungsberichte des Akad. der Wissenschaften d. Wien (2) Vol. LXXXII, p. 851 (2) Vol. LXXXVI, p. 52.

⁵ Am. Jour. Sci. (3) Vol. XXVIII, p. 190.

⁶ Poggendorf's Annalen (2) Vol. XXIII, p. 1259.

⁷ Phil Mag., S. 5, Vol. XLI, No. 251, April 1896, p. 239.

The discovery that this constituent of the atmosphere is an important dynamic factor among geological agencies has led us to investigate the eighteen potential atmospheres of carbon dioxide in the ocean. This at once leads us to a consideration of the chemistry of the ocean, and here we find that the indefiniteness of our notions upon this subject is not so much due to lack of data, for that has been collected by individuals and by well equipped expeditions, as to erroneous conceptions of the relations and reactions that obtain between the several constituents of a mixed solution. Important investigations involving large outlays of time and money have been rendered nearly valueless, because they were based upon assumptions which were accepted without proof, and which are now known to be false. The importance of the first principles which govern solution and precipitation in such a solvent as water (and which have but recently been formulated) justify a review of some of them as an aid to the interpretation of the reactions taking place in that great laboratory the ocean.¹

*Mass action.*²—It will be remembered that Berthollet in 1803 was the first to conceive of chemical reactions as governed by equilibrium, dependent both on the mass and the affinity of the constituents. The value of his discovery was not realized because he unfortunately did not believe chemical compounds to have definite compositions.

In 1864 Goldberg and Waage re-stated the law of mass action, which may be developed as follows. Let us consider any two substances, A and B uniting to form two other substances C and D.³

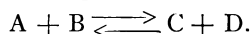
All simple reactions that have been carefully studied have been shown to be reversible, therefore, as soon as any of C and

¹ Complete discussion of the laws of dilute solution, etc., may be found in any of the up-to-date text-books on physical chemistry.

² W. NERNST: *Theo. Chem.*, pp. 353-455, etc., 117-150. OSTWALD'S *Outlines of Chemistry*.

³ GOLDBERG and WAAGE: *Videnskabernes Selskabs Forhandling*, 1864.

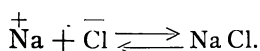
D is formed there will be a union of C and D to form A and B. This reversible reaction is expressed thus:¹



Let the degrees of concentration of the active masses, *i. e.*, the masses in units volume of A, B, C and D be respectively p, q, p' and q' . The unit measure of concentration is the gr. equiv. per liter. Let K be the rate of combination of unit masses of A and B, and K' that of C and D. Now the magnitude of the reaction of A upon B is evidently $K p q$ (for the number of impacts of A upon B depends directly on their concentration) and that of C and D is $K' p' q'$. Now when equilibrium is established, the reaction of A upon B = the reaction of C upon D or $K p q = K' p' q'$ (the law of mass action).

Dissociation.—From the study of electrolysis² of salts, Clausius was compelled to assume that at least a small portion of the salt was dissociated into its positive and negative ions, Na Cl, for instance, into the positive ion ($\overset{+}{\text{Na}}$) and the negative ion ($\overline{\text{Cl}}$).

Arrhenius³ found that the osmotic pressure of a dilute solution of a salt in water, is that which it should have if a large proportion of the molecules of the salt are split into two smaller molecules (Na Cl for instance, into Na and Cl) and also that this change in osmotic pressure is a function of the electric conductivity. He was therefore compelled to conclude that practically all of the salt may be dissociated in very dilute solutions, but, in more concentrated solutions the proportion dissociated becomes smaller. It then became evident that this action is reversible and is expressed



¹ A simple illustration of a reversible reaction is the evaporation of water in an enclosed dish. Particles of water leave the liquid to form the superincumbent layer of water gas. As soon as any of the gas is formed it in turn gives back water particles to the liquid. Equilibrium is established and there is apparently no farther evaporation when the number of particles given off by the liquid equals the number of particles returned by the gas.

² Ges. Abh. (sep. papers) II, 135, 1867.

³ ZEITS: Phys. Chem., Vol. I, pp. 631 ff.

Then, according to the law of mass action—

$$K_1 ab = K_2 c$$

where a and b are the concentrations of the ions (Na^+ and Cl^-) and c of the dissociated salt.¹

$$\frac{ab}{c} = \frac{K_2}{K_1} = K \quad (2)$$

This K is called the ionization or dissociation constant, and is a constant under constant temperature and pressure, but is different for each different salt.

Salts, strong acids and bases (hydrochloric acid, sodic hydrate, etc.) are the substances most dissociated, while the weaker acids and bases (acetic acid, ferric or ammonium hydrate, etc.) are dissociated to a less degree, *i. e.*, the constant K is smaller.

It follows directly from equation (2) that the more diluted the solution the more complete is the dissociation. If the strength of the solution is such that concentration a and b are each represented by 2 and c by 4; and then the concentration of all be decreased so that a and b become 1, we find by substitution in the equation (2) that c also must become 1, and the ratio of dissociated to undissociated or *molecular* salt, is 1:1 instead of 1:2.

Heterogeneous equilibrium.—We may have some undissolved substance (C) in contact with a saturated *molecular* solution (C_1) of the same substance which is dissociated, more or less, into its ions (A and B). The concentrations are a and b for the ions, c for the undissolved (solid) salt, and c_1 for the undissociated dissolved part of C . Equilibrium being established between the solid C and the molecular solution of the solid ($C \rightleftharpoons C_1$), the equation is

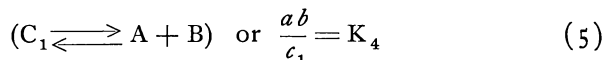
$$\frac{c}{c_1} = K_1 \quad (3)$$

But the concentration of a solid at given temperatures and pressures is a constant (its specific gravity) ($c = K_2$), therefore

¹ This simple formula is not strictly accurate in the case of electrolytic dissociation but is correct enough for our purpose.

$$c_1 = \frac{K_2}{K_1} = K_3. \quad (4)$$

Now the dissolved undissociated part of the salt dissociates into its ions



but substituting from (4)

$$ab = K_3 K_4 = K. \quad (6)$$

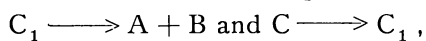
This K is called the constant of solubility, or the ion product. This is the law governing precipitation of electrolytes, and under it there are three cases.

- (a) $ab > K$.
- (b) $ab = K$.
- (c) $ab < K$.

(a) If ab is greater than K the action goes $A + B \longrightarrow C_1$, and again $C_1 \longrightarrow C$, therefore we have precipitation.

(b) If $ab = K$, we have equilibrium, and neither precipitation nor solution takes place.

(c) If ab is less than K the action goes



that is solution takes place.

Now, if we mix solutions of two or more salts, besides the undissociated salts which were present in the separate solutions in equilibrium with their respective dissociated ions, we will have in the mixture also the salts that can be formed by the union of the positive ion of each salt with the negative ion of each of the other salts. From the foregoing the following propositions are derived:

Proposition 1.—Mixed solutions of two or more salts will contain all the salts that can be made by the combination of the ions of the original salts together with the free ions.

Proposition 2.—Of all these salts that one will be precipitated first whose product of ionic concentration first exceeds its constant of solubility or ion product.

If a salt be added to a mixture of salts in solution, there is added not only the salt itself but its ions also. If one of the

salts of the original mixture have an ion in common with the new salt (as for instance Cl in Na Cl and KCl), then the product of the ionic concentration of each salt is increased. Now if, before mixing, this product for either salt nearly equaled its constant of solubility, the increase may be enough to bring about precipitation. If, for instance, to a solution of lead chloride, which is not altogether insoluble in water, is added a sufficiency of K Cl, this addition causes a precipitate of lead chloride, since the addition of the Cl ions of the potassium chloride causes the product $Pb \times Cl^2$ to be larger than K where Pb = concentration of lead ions, and Cl = concentration of chlorine ions.

If, however, the salt added has no ion in common with ions of the other salts, it will take away from the ions of all the salts to form some of all the undissociated salts that result from the combination of the two new ions with all the ions of the original salts, therefore the product of ionic concentration for all the salts is decreased, or, in other words, the solubilities of all the salts are increased. Hence,

Proposition 3.—In a mixture of salts those with a common ion increase the ionic concentration of each, aiding precipitation, and those without a common ion decrease ionic concentration of each, and retard precipitation, each increasing the solubility of the other.

Hydrolytic dissociation.—Water, which is one of the weakest of acids, is itself dissociated into hydrogen and hydroxyl ions ($H_2O \rightleftharpoons H + OH$); but this takes place to a very slight extent only. Kohlrausch found that at 18° C. for water distilled in a vacuum there is less than one gram of hydrogen ions in two million liters of water,¹ and Ostwald, Arrhenius, and Weis, and Kohlrausch² in later experiments (see reference below), found about one-sixth of this dissociation by other methods. Of course these free ions will react with ions of the salts in

¹ W. NERNST: Theo. Chem., pp. 658–662.

² F. KOHLRAUSCH and AD. KEYDWEILLER, Zeits. f. Phys. Chem., XIV, pp. 317–330.

solution to form some undissociated acid and base ($\text{Na Cl} + \text{HOH} \rightleftharpoons \text{NaOH} + \text{H Cl}$). But since there is such a very small amount of free dissociated ions of water and the dissociation constants of sodic and hydrochloric acid are large, this action is very slight. However, the salts of the weakest acids and bases are affected more by the same amount of dissociated water than those of the stronger ones, because, as shown by equation (2), K is smaller, therefore a larger amount of the undissociated acid, or base, exists in proportion to the ions.

Water when heated becomes more dissociated, and therefore a stronger acid, and this fact is sometimes made use of in the analytical laboratory, and is an important factor determining the composition of minerals deposited from hot solutions.

Solutions of gases in pure water.—If a gas dissolves in a substance with which it is perfectly neutral, that is, if no chemical reaction takes place between the gas and the solvent, then the amount of the gas dissolved in the liquid at a given temperature varies directly with the gaseous pressure, or partial pressure, if there be more than one gas.

Now, if any gas were absolutely neutral to the solvent, and if on solution its molecule suffered no change in constitution, we should get the same amount of heat absorbed or given off in the solution that would be absorbed or radiated by the same amount of gas brought to the density of the dissolved gas.

But upon solution in water it is found that some gases suffer a larger heat change than can be explained by any mere physical change in volume, while others have the same or nearly the same change in temperature, as that calculated upon the assumption of simple physical absorption. It has been shown that the gases with this large heat change upon solution undergo besides physical diffusion, a chemical change, more or less extensive. Therefore, gases may be arranged in two classes. The first class is composed of those gases which have but a slight reaction with water, and are sparingly soluble in that menstruum, and the other, of those which have large coefficients of solubility and which react with water to form definite compounds.

Of the former, those found in the ocean are nitrogen, oxygen, argon, etc., and of the latter, none are found in appreciable quantities, but we may take ammonia as a good example. This last unites with water to form NH_4OH which compound is known to exist as such.¹ The behavior of carbon dioxide towards water places it between these two classes. It unites with water to form H_2CO_3 . This acid has never been separated as such, but doubtless exists.² This action does not give such a large coefficient of solubility as is characteristic of the gases of the second class.

The solution, then, of oxygen, hydrogen and argon, etc., is simple diffusion due to the attraction between the molecules of the solvent and those of the gas, while the solution of CO_2 in pure water includes (1) a diffusion of the gas molecules between water molecules and (2) a chemical reaction between the gas and water molecules to form carbonic acid.

Bunsen³ has determined the solubility of the carbon dioxide for different temperatures as follows :

Solubility of CO_2 in H_2O , 1 vol. H_2O at t degrees and 760 mm. pressure dissolves V vols. CO_2 gas reduced to 0°C . and 760^{mm} pressure.

$t^\circ\text{C}$.	V.	$t^\circ\text{C}$.	V.	$t^\circ\text{C}$.	V.
0	1.7967	7	1.3339	14	1.0321
1	1.7207	8	1.2809	15	1.0020
2	1.6481	9	1.2311	16	0.9753
3	1.5787	10	1.1847	17	0.9519
4	1.5126	11	1.1416	18	0.9318
5	1.4497	12	1.1018	19	0.9150
6	1.3901	13	1.0653	20	0.9014

In the above table the solubility is determined for pure CO_2 unmixed with other gases under 760^{mm} pressure. For low pressures the solution of the gas is proportional to the pressure or the partial pressure of the CO_2 .

¹ PROFESSOR MALLET, Am. Chem. Jour., Vol. XIX, pp. 804-809.

² DAMMER, Anorg. Chem. II, I, p. 871.

BUNSEN'S Gasometry, pp. 287, 128, 152.

The atmosphere, of course, is not pure CO_2 , but a mixture of gases in the following proportions: Oxygen, 20.9 vol.; nitrogen, 79.1 vol., of which 01.18 per cent. belongs to that group of gases called argon,¹ CO_2 .03 vol.

At any given temperature the amount of the atmospheric gas dissolved in pure water is the product of the amount dissolved under 760^{mm} pressure of the pure gas by the partial pressure of gas in the air. This holds for the carbon dioxide in spite of the chemical reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$. This may be seen as follows:

Let a , b , and c be the concentrations respectively of CO_2 , H_2O , and H_2CO_3 , therefore

$$\frac{ab}{c} = K_1,$$

but the water is so greatly in excess that its concentration, b , can be considered as a constant (K_2) or

$$\frac{a}{c} = \frac{K_1}{K_2} = K.$$

Therefore the amount H_2CO_3 [c] varies directly with the amount CO_2 [a] dissolved, and this is proportional to the partial pressure of the gas. Making the calculations from Dittmar's tables, we find that one liter of pure water at 15° C. dissolved from the atmosphere .32^{cc} of CO_2 , 7.2^{cc} of oxygen, and 13.2^{cc} of argon and nitrogen.²

The absorption of gases in salt solutions.—The researches of J. Setchenow³ show us that a gas dissolved in salt solution obeys the same laws as if the salt were not present, if there is no chemical reaction between the gas, the salt, and the solvent. In this case, however, the attractive power between the molecules of the solvent and the gas is partially satisfied by the salt mole-

¹ Chem. News, 72 p. 308. Comptes Rendus de l'Academie des Sciences, CXXI, p. 605.

² Challenger Reports, Vol. I, pp. 167-168.

³ Ann. de Chemie: pp. 226-270.

cules. From some of his tables we find that for a solution of the strength of the oceanic brine the diminution of the solubility for gases of this class is somewhere near 20 per cent. (*loc. cit.* pp. 245-259).

If, however, there is a chemical reaction between the gas and the salt, the solubility is increased by so much. Oxygen, nitrogen, and argon do not react with the salts of the ocean, but CO_2 does. The carbonic acid dissociates into its ions, and these ions react with the ions of the salts to form small quantities of undissociated compounds. This reaction has an appreciable effect only where the original salt is formed from weak acids and bases. From Mr. Setchenow's tables¹ for Na Cl solution of the strength of the sea water we gather that this increase for CO_2 would not be over 20 per cent. of that dissolved by pure water (.3^{cc} per liter, a quantity wholly negligible).

*The ocean salts.*²—The average temperature of the surface of the ocean is about 15° C.

The proportion of the different salts in the ocean, Professor Dittmar finds to be wonderfully constant for all parts of the sea water. He gives the following analysis for the salt :

Cl	-	-	-	-	-	-	-	55.292%
Br	-	-	-	-	-	-	-	.1884
SO ₃	-	-	-	-	-	-	-	6.410
CO ₂	-	-	-	-	-	-	-	.152
CaO	-	-	-	-	-	-	-	1.676
MgO	-	-	-	-	-	-	-	6.200
K ₂ O	-	-	-	-	-	-	-	1.332
Na ₂ O	-	-	-	-	-	-	-	41.234
Basic O (equivalent to Hologen)								—12.493

100

This table we have recalculated for the percentages of the ions according to modern usage, and in order to facilitate subsequent discussion, as follows :

¹ *Loc. cit.*, p. 246.

² *Phys. Chem. Chall. Exp.*, Vol. I. Narrative of the Cruise of H. M. S. Challenger, 1885; *Ency. Brit.* XXI, pp. 611 to 614.

(Cl)	-	-	-	-	55.292%
(Br)	-	-	-	-	.188
(SO ₄)	-	-	-	-	7.692
(CO ₃)	-	-	-	-	.207
(Na)	-	-	-	-	30.593
(K)	-	-	-	-	1.105
(Mg)	-	-	-	-	3.725
(Ca)	-	-	-	-	1.197
					99.999

While the average constitution of the salts remains a constant, the salinity of the ocean is variable. Averaging 327 analyses, it is found that the average amount of salt is 34.7 grams per kilogram sea water, or taking the average specific gravity of the ocean as 1.026, about 35.6 grams per liter.

Applying this to the second table, we find that the total number of grams of the different ions per liter is as follows:

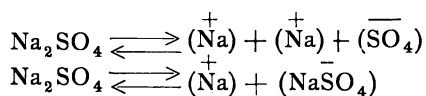
(Cl)	-	-	-	-	19.68
(Br)	-	-	-	-	0.07
(SO ₄)	-	-	-	-	2.74
(CO ₃)	-	-	-	-	0.08
(Na)	-	-	-	-	10.89
(K)	-	-	-	-	0.4
(Mg)	-	-	-	-	1.33
(Ca)	-	-	-	-	0.43
					35.69

Dividing by the equivalent weights, we find the relative strength of the ions per liter to be as follows, where the normal solution (one which contains as many grams per liter as the equivalent weight of the substance) is taken as unity.

Dividing the relative strength of the bivalent ions by 2, we find the relative number of ions.

Relative strength per liter				Relative No. of ions			
(Cl)	-	-	0.55 N. sol.	(Cl)	-	-	5500
(Br)	-	-	0.0009 "	(Br)	-	-	9
(SO ₄)	-	-	0.057 "	(SO ₄)	-	-	285
(CO ₃)	-	-	0.0027 "	(CO ₃)	-	-	13
(Na)	-	-	0.47 "	(Na)	-	-	4700
(K)	-	-	0.01 "	(K)	-	-	100
(Mg)	-	-	0.112 "	(Mg)	-	-	560
(Ca)	-	-	0.022 "	(Ca)	-	-	110

In the light of the previous discussion, we see that there must be sixteen different salts and eight different ions in the solution, under the supposition that the salts with bivalent ions dissociate completely into their metal and acid ions, and always neglecting the subordinate elements, such as strontium, iodine, gold, etc. Since, however, in a solution as strong as the sea water, there are two reactions in the dissociation of the salts having one bivalent ion, viz.:



there are also these extra ions, viz., (Na SO_4) , of the bivalent acids and bases. Also instead of simply the salt of the radical CO_3 (normal carbonate) we have both the bicarbonate of the acid radical (H CO_3) and the acid radical itself.

From the propositions of the theory of dilute solutions it is possible to develop equations whose solutions will give the proportions of the various undissociated salts and of the free ions, but these computations would be of little value because of their complexity, and because the ocean water is too strong a solution for a numerical application of the equations developed for dilute solutions.

However, assuming that the constant K is of the same order of value for all the salts, and that the concentration of the free ions may be expressed by the relative number of ions calculated under the assumption that the salt is completely dissociated (see table p. 596), and neglecting the presence of the bicarbonate ion, we see that the relative amount of the undissociated salts will be expressed roughly by the products of the concentration of their respective radicals, and, therefore (from table p. 597) 1) Na Cl , 2) Mg Cl_2 , 3) Na SO_4 exist in molecular form in greatest quantity, the rest following in about the order:

water are nitrogen, oxygen, argon, and carbon dioxide. The nitrogen, argon, and oxygen are absorbed into the ocean directly from the air. Since the ocean is very generally agitated into waves, we may suppose that the gases dissolved in the outer portion of the surface water are in direct equilibrium with those of the air. The surface waters are being saturated with gas at temperatures varying with the daily and seasonal changes. Therefore, if there is no depletion or increase of these gases due to chemical or organic agencies we may assume roughly that the ocean, on the average, contains these gases in a proportion which may be calculated from the coefficients of absorption for the average temperature of the surface of the sea, which we assume to be 15° C. Therefore, to find the average amount of nitrogen, argon, and oxygen dissolved in the ocean we must determine their respective coefficients of absorption for sea water. From the remarks on the effect of salts on the solution of gases we should expect that the salt water would dissolve a little less of the above-mentioned gases than fresh water, because (1) salts in solution decrease the solubility of gases, and (2) because none of the gases react chemically with the ocean salts.

The following table, which is taken from a larger table of Dittmar, shows that these theoretical conclusions are correct :

° AIR DISSOLVED PER LITER.¹

	Pure water	Sea water
- 5°	27.27
0°	29.54	23.78
5°	26.09	21.08
10°	23.37	18.92
15°	21.16	17.17
20°	19.33	15.72
25°	17.80	14.44
30°	16.49	13.44
35°	15.36	12.53
40°	14.37
45°	13.50
50°	12.73

¹ Loc. cit., pp. 172 and 175.

Taking, therefore, the coefficient of absorption for sea water as given by Dittmar¹, we find that at 15° C. the sea water dissolves 5.83^{cc} of oxygen and 11.34^{cc} of nitrogen and argon, which is less than shown by the figures given on page 594 for the absorption of pure water. We find on comparing these figures with the average of the gases as found in the Challenger analyses that the amount of the nitrogen and argon is near the amount calculated for the temperature of the water at the time it was collected, as we might expect in view of the mixing, etc., it undergoes. The oxygen, however, is always low, as it is used up in the oxidation of the organic matter in the ocean. It is almost up to the calculated amount in the surface water but a very large deficit in the deeper water. We may suppose, then, that the above figure for nitrogen and argon is approximately correct, but that the oxygen figure is considerably too high.

It is evident that we have a very different case to deal with in the solution of the CO₂ in the ocean. We have already found three ways in which the gas is held in solution. (1) Simple physical absorption; (2) united with the water to form (H₂CO₃); (3) held by equilibrium reactions with the salt ions. The total that can be held in these three ways at atmospheric partial pressure of the gas and at the average temperature of 15° is about 0.3^{cc} of CO₂ per liter of sea water.

Now, under the assumption that the partial pressure of the CO₂ increases with the depth of the ocean; and that the rate of this increase obeys the same laws as the increase of atmospheric pressure with the depth of the atmosphere, and, taking the average depth of the ocean at the large figure of three miles, we find a formula developed by Professor Woodward² that the pressure at that depth is 4.4 that at sea level. Also assuming that *all* the ocean is at a temperature of 0° C. (instead of only the portion at great depths) we find as a maximum estimate the ocean cannot hold over 2.4^{cc} CO₂ per liter dissolved as a gas,

¹ Loc. cit., p. 139.

² Communicated in a letter to Dr. Chamberlin.

according to the laws of gas absorption; this it is to be noted, under the unrealizable conditions of a uniform temperature of 0° C. and an average depth of three miles. But Mr. Buchanan found that on boiling, sea water gives an average 45^{mg} or 23^{cc} CO_2 per liter, or ten times the greatest amount the ocean could hold as a gas under more favorable conditions than those of the present time. Mr. Jacobson found 90^{mg} upon distilling the water to dryness. Mr. Buchanan thought that this great excess of CO_2 over that which could remain in solution under atmospheric pressure of CO_2 must be held in some sort of loose combination with one of the salts, and he decided upon the sulphates as the retaining agent. Such a misinterpretation, of course, might be expected at that time from the imperfect knowledge of the nature of the solutions. Before determining the free CO_2 , therefore, he precipitated the sulphate with barium chloride, and unfortunately he must have obtained a mixture of Ba SO_4 and Ba CO_3 , so that his numerous determinations are all probably somewhat too small.

But in spite of this his analyses show that the ocean contains about eighteen times the CO_2 of the atmosphere. Now, bearing in mind Professor Arrhenius' statement, "that to lower the temperature of the temperate region 5° , and bring on glaciation, the CO_2 of the atmosphere needs to be diminished to from 62 per cent. to 55 per cent. of its present value,"¹ the following questions suggest themselves:

1. How is the excess of the CO_2 found in the ocean at the present time held in solution?
2. Is it in equilibrium with that of the air?
3. If so, what proportion of the ocean gas will be brought out into the air by a diminution of the partial pressure of the CO_2 to an amount from 62 per cent. to 55 per cent. of its present value?
4. How much will the consequent fall of temperature increase the ocean's capacity for CO_2 ?
5. What is the relation between these two?

¹ Loc. cit., pp. 237-279.

In its immediate action, the ocean certainly has a moderating effect upon the temperature of the land. The great amount of heat necessary to raise the temperature of the water one degree, together with its vast evaporating surface, distributes the warmth received during the day over the night, much of the excess of the heat of summer throughout the winter, and the great downpour of radiant energy upon the tropics over the temperate and frigid zones. The question then arises: In the greater cycles of the variation of the earth's climate (whether dependent directly or only in part upon the fluctuations of the carbon dioxide content of the atmosphere) does the ocean still play the beneficent rôle of protector against the advances of the greater winters, furnishing the atmosphere some of its enormous supply of CO_2 as a blanket against the cold? Or, does the increasing cold cause the ocean, like a selfish monster, to keep a more grasping hold on the precious gas as the need of it becomes more imperative?

1. Besides the CO_2 which may be absorbed by the ocean from the air, it receives the gas (1) from the respiration of aquatic animals (2) from the decomposition of organic matter (3) from the interior of the earth through springs, etc., and (4) from the bicarbonates brought in by the rivers.

We find from analyses of the water of the principal rivers¹ of Europe, that about 60 per cent. of the entire mineral content of the river water is calcium carbonate dissolved as calcium bicarbonate. This calcium bicarbonate then is the great source of the extra carbon dioxide of the ocean. When this bicarbonate mixes with the ocean it is no longer strictly speaking, calcium bicarbonate, but mostly bicarbonate ions in equilibrium with small amounts of sodium, magnesium, calcium and potassium bicarbonates.

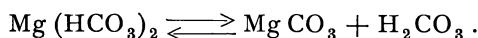
2. The various bicarbonates have been subject to numerous investigations since the researches of H. Rose² in 1835. These contributions show that sodium, potassium, ammonium, and

¹ BISCHOF, *Chemical and Physical Geology*, Vol. I, pp. 76, 77.

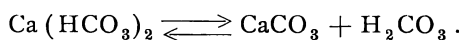
² *Journal für Praktische Chemie, Neue Folge* 10, 1879, pp. 417-444. *Zeits. für Anorg. Chemie.*, Vol. XVII, pp. 170-204.

magnesium bicarbonates, partially dissociate at ordinary temperatures into the normal carbonate, giving out CO_2 . Treadwell and Reuter have shown in the latest and most complete research on the subject (see reference above) that when calcium carbonate is dissolved under different partial pressures of CO_2 , that the proportion of calcium to carbon dioxide, indicates that practically a pure bicarbonate, and not a mixture of bicarbonate and carbonate, is present in the solution.

The difference between the sodium, magnesium, etc., bicarbonates on the one hand, and the calcium bicarbonate on the other is seen from the following: (1) For the dissociation of magnesium bicarbonate we have in a saturated solution,



We have seen that the H_2CO_3 is directly in equilibrium with the CO_2 in the air; therefore at a given temperature, the degree of dissociation depends upon the partial pressure of the CO_2 in air. With variations of temperature, the colder the water, the larger is the portion of bicarbonate present, and therefore, the larger is the proportion of carbon dioxide in the ocean to that in the air. (2) For calcium bicarbonate we have:



But CaCO_3 is very slightly soluble, and therefore practically a constant for a *saturated* solution. Therefore, we do not have a mixture of bicarbonate and appreciable quantities of the carbonate, but the salt in solution is nearly all bicarbonate, and by lessening the partial pressure of the CO_2 , CaCO_3 is precipitated from the saturated solution and the bicarbonate decreases. However, this difference between $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ which Treadwell has emphasized, only holds for saturated solutions. It is evident that for an under-saturated solution of $\text{Ca}(\text{HCO}_3)_2$ we may have a larger proportion of normal carbonate than in the saturated solution and still no precipitation. Also, in ocean water (see p. 591), the numerous different salts tend to increase the solubility of the normal

carbonate, and allow perhaps a somewhat greater dissociation of the bicarbonate into carbonate. The bicarbonate in the ocean is, as shown above, not calcium bicarbonate, but bicarbonate of all the bases in solution, so that Treadwell and Reuter's investigations upon *pure* calcium bicarbonate in *saturated solution* cannot be taken to prove that the bicarbonates of the unsaturated sea water cannot be dissociated.

As direct evidence that the ocean is not saturated with calcium acid carbonate, we find (1) of the many hundred bottles of the Challenger's samples of sea water, from all depths and collected at all temperatures, kept several years, only one or two showed deposit of lime.¹ (2) Seashells from the bottom of the Pacific show corrosion and resolution.² Pteropod shells and foraminifera tests are slowly dissolved as they sink. The Pteropod shells are not found below fifteen hundred fathoms, and two thousand eight hundred fathoms is the limit for the globigerina ooze.³ (3) Thoulet found by actual experiment that sea water will dissolve calcium carbonate from shells, corals, etc.⁴ (4) Usiglio, studying the evaporation of the Mediterranean water at Cette, found that no precipitate was formed until the specific gravity of the sea water increased from 1.02, the specific gravity of the unevaporated water, to 1.0503 when the first precipitation begins, composed largely of calcium carbonate with ferric oxide.⁵

DEGREE OF BICARBONATE DISSOCIATION.

From twenty-seven analyses by Jacobson, we find an average of 91.4^{mg} per liter of free CO₂, and 120^{mg} CO₂ in the normal carbonate, or the bicarbonate is so dissociated that 25 per cent. of its second equivalent of CO₂ is lacking.⁶

¹ Loc. cit., p. 221.

² JOUR. GEOL., Vol. I, p. 504.

³ Loc. cit., p. 221.

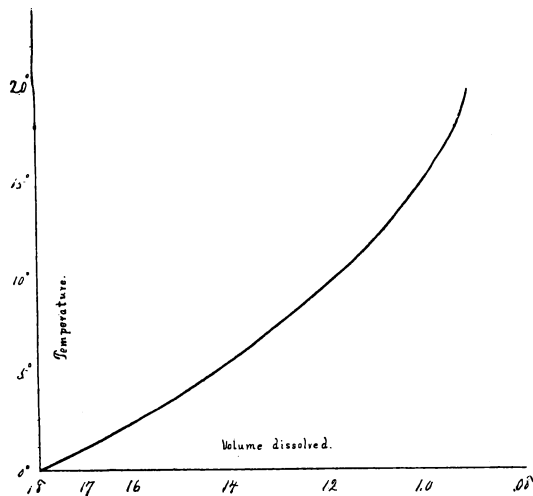
⁴ Comptes Rendus, Vol. CVIII, p. 753.

⁵ Encyl. Brit., Vol. XXI, p. 229.

⁶ Über die Luft des Meerwassers Ann. der Chemie und Pharm., Vol. CLXVII (1873), pp. 1-38.

From several hundred determinations of Buchanan, we strike an average of 45^{mg} free CO_2 per liter, to 53.4^{mg} CO_2 per liter of the *first* equivalent, *i. e.*, only 84 per cent. of the second equivalent is found in the ocean. Mr. Jacobson's analyses show a larger per cent. of the carbonates than were found in the Challenger's samples, which might be expected, as Jacobson's were collected only from the North Sea into which flow the great lime-bearing rivers of northwestern Europe.

To prove positively that the ocean bicarbonate dissociates into carbonate and free CO_2 , Professor Ditmar shook in the air



FIGS. 1 and 2 represent respectively the effect of temperature on the solubility of CO_2 in pure water, and upon the dissociation of Na H CO_3 .

FIG. 1 is taken from table on page 593 and under 760 mm pressure CO_2 . The temperature is recorded on the ordinate, and on the abscissa are the volumes of CO_2 absorbed, compared with the volume of water in which it is dissolved.

a sample of sea water, that had an excess of CO_2 , and found that CO_2 was given off, and that the ratio of the two equivalents was 100:84 at 13°C ., exactly the same, it happens, as we found from averaging Buchanan's analysis. Therefore we may consider it as certain that the largest part of free CO_2 in the

ocean is held as the second equivalent of bicarbonate, and that this is held in equilibrium with the gas in the air.

We know then from the above that the dissociation of the bicarbonate is a function of the temperature, and also of the partial pressure of the superincumbent CO_2 . The solubility of CO_2 as a gas not attached to form bicarbonate, is also a function of temperature and pressure, but that these functions are not the same, may be seen from an inspection of the

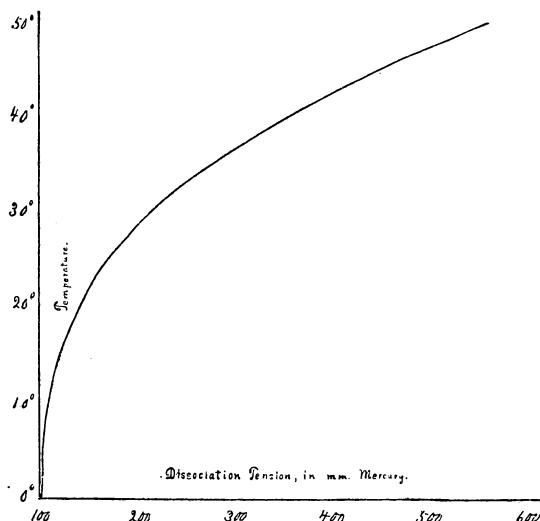


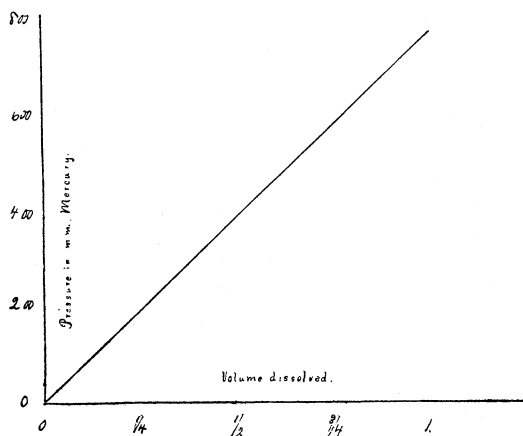
FIG. 2 is plotted from Dr. Dibbett's tables.² On the ordinate are the temperatures and on the abscissa the increase of the dissociation of the Na H CO_3 in mm of mercury which represents the loss of the second equivalent of CO_2 from the solution.

accompanying curves. Professor Ditmar has experimented upon the effect of changes of partial pressure and temperature upon the CO_2 in the ocean. This includes both the effect upon the portion simply dissolved and that as second equivalent of bicarbonate. We shall discuss these results under Professor Arrhenius' hypothesis of lowering the surface temperature to

² Ueber die Löslichkeit und die Dissociation des sauren kohlens Kaliumes, Natriums und Ammoniums, *Journal für praktische Chemie, neue Folge* 10, 1879, pp. 417-444.

an average of 10° C., and the diminution of the partial pressure he has postulated as sufficient to cause this drop in temperature.

We find from Professor Ditmar's investigation (see tables and figures, pp. 609 and 610) that as the waters of the ocean become warmer, the effect of a change in the partial pressure of atmospheric CO_2 upon the bicarbonate dissociation becomes greater, while near zero a change in partial pressure has no effect on the dissociation of the bicarbonates of the ocean. On the



FIGS. 3 and 4 show the relation between the partial pressure of CO_2 and its solubility in pure water on the one hand and the solubility of $\text{Ca H}_2 (\text{CO}_3)_2$ on the other.

FIG. 3 represents the simple law of gas absorption that the amount dissolved is directly proportional to the partial pressure. The pressure is plotted on the ordinates in mm of mercury and the volume of gas absorbed on the abscissa.

other hand, the effect of any postulated fall in temperature, causing the bicarbonates to take up CO_2 , is the greatest at the temperature just above 0° , and becomes less for higher temperatures. So that a fall in temperature of the colder waters of the ocean is correlated with the greatest absorption of CO_2 , and without the counteracting effect of decreasing partial pressure. In equatorial waters, however, the fall in temperature does not

produce so great an increase in the absorption of the CO_2 , and the effect of decreasing tension of atmospheric CO_2 approaches a maximum.

These facts, therefore, naturally divide the discussion into three parts. Under Professor Arrhenius' postulates as to change in temperature and pressure, we shall discuss the relative effect of these two opposing factors in the temperate waters whose temperature is the average surface temperature of the ocean, viz., 15°C . (2) Ditto for the tropical waters whose temperature is above 15°C . (3) Ditto for the polar waters whose temperature is below this.

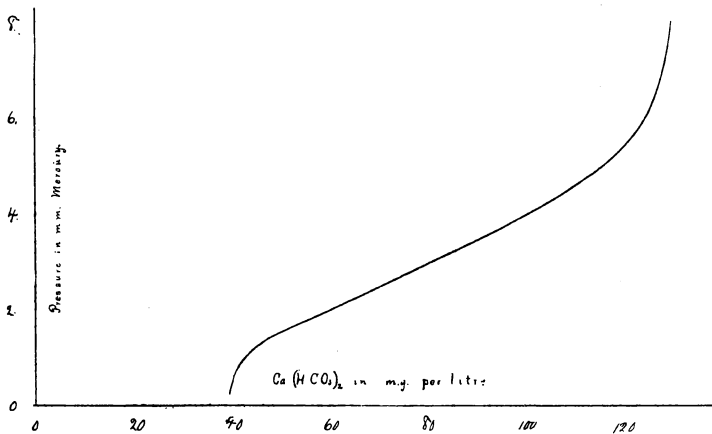


FIG. 4 is from Treadwell's and Reuter's dissertation (see reference, p. 603). The partial pressure is represented on the ordinate in mm of mercury and the amount of calcium bicarbonate dissolved in m. g. in the abscissa. At atmospheric pressure 15°C . the amount dissolved in pure water at saturation is 38.5 m. g. per liter, which is much less than the amount of bicarbonate in the sea, as we might expect from the previous discussion.

The only experiments which have been made upon sea water (and so under the actual conditions of the problem) are represented in Fig. 5. Professor Ditmar took a special sample of deep ocean water which was so charged with CO_2 as to have its bicarbonate fully saturated with CO_2 . This he shook violently in a bottle constantly renewing the air until there was no more

loss of CO_2 from the water and no more gain in the air above the water. The carbon dioxide remaining in the water was thus determined, and the degree of the bicarbonate dissociation calculated. This was repeated for various temperatures.

The table is as follows :¹

t	N	Pure Air (n_0)	Ordinary Air (n_1)
2	200	1.90	
2	200	2.04	
2	52		2.06
10	200	1.70	
13	50		1.84
15	100	1.63	
15	200	1.50	
20	200	1.42	
25	53	1.53	
32	52	1.33	
32	52		1.89
32	150		1.82

t=equals temperature. N=number of times air was renewed until loss of CO_2 from water ceased. n_0 =ratio of first to the second equivalent of CO_2 in bicarbonate when shaken in air free from CO_2 , where 2.00 represents fully saturated bicarbonate and 1.00 simply the normal carbonate. n_1 =the same for ordinary air.

These experimental data do not permit the drawing of any very accurate conclusions. Professor Ditmar states that these are only preliminary, and has promised us a completion of this work, which we await with impatience. However, we must needs use what we have, and referring to curve 5, we see that at 15° the ocean will contain about 83 per cent. of the total second equivalent of CO_2 , and at 10° , about 88 per cent. of it, or an increase of 5 per cent. of the second equivalent which is represented by the line *a-b* in figure. For pure air artificially freed of CO_2 at 10° the dissociation goes through 70 per cent. but Professor Arrhenius does not postulate a complete removal

¹ Encyc. Brit., Vol. XXI, p. 612.

of CO_2 from the air, but a diminution of from 62 per cent. to 55 per cent. of the present partial pressure of the gas, and this decrease in dissociation caused by the decrease of the partial

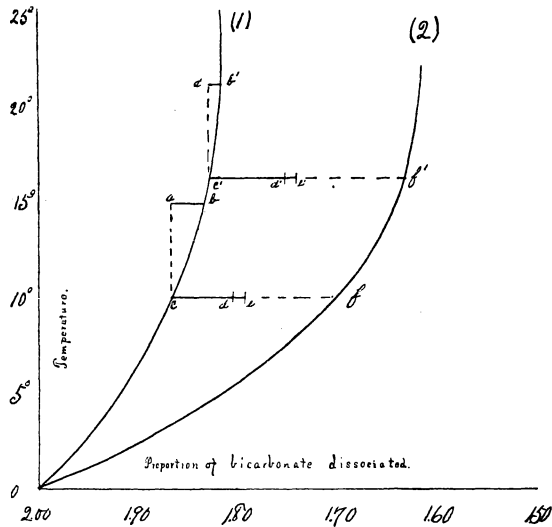


FIG. 5 is plotted from Professor Ditmar's table on page 609. The figures in the table are not very constant, but we have taken those that seem to correspond best with each other. On the ordinate are the temperatures, and on the abscissa the dissociation of the ocean bicarbonate, 2.00 representing fully saturated bicarbonate and 1.00 normal carbonate, the partial pressure of CO_2 in the curve (1) is that of the atmosphere as it is at the present time and for curve (2) there is 0 pressure of that gas. The two curves have been plotted arbitrarily to cut a 0° , but Professor Ditmar shows that there is probably no dissociation at 2° to 3° above zero.

The line cf connects the two curves at 10° (the temperature of the temperate regions Dr. Arrhenius postulates to develop a glacial period) and the points d and e show the bicarbonate dissociation at a partial pressure of CO_2 reduced respectively to 62 and 55 per cent. of its present value. ab represents the decrease of the dissociation of the bicarbonates due to fall of temperature from 15° to 10°) and cd and ce the increase of the dissociation due to a decrease of 62 per cent. and of 55 per cent. of the present value of the partial pressure of CO_2 in the air. $a'b'$ and $c'd'$ and $c'e'$ represent the same factors for a decrease of temperature from 21° to 16° and the same decrease as postulated above in the partial pressure of the CO_2 .

pressure of the gas is represented by lines $c-d$ and $c-e$; so that the dissociation will be between the two, that is, viz., from 76 per cent. to 81 per cent., *i. e.*, these data show that the falling

temperature counteracts within 2 per cent. to 4 per cent. of the total CO_2 as second equivalent, the effect of the decrease in the partial pressure.

These estimates are of course founded on too small an experimental basis, and the data themselves show too great disagreements to conclude that the decrease of the dissociation due to the falling temperature, counteracts exactly within 2 per cent. to 4 per cent. of the second equivalent of CO_2 , the increase due to the diminishing partial pressure ; but we may conclude *that they are probably of the same order of magnitude*, or that *a-b* is comparable in length with *c-d* or *c-e*.

All this however, is under the proposition of Professor Arrhenius, that a 5° lowering of the average climate of the *temperate* regions will bring on glaciation. We have still to consider the effect of the waters of the equatorial region on the one hand, and those of the higher latitudes on the other.

The average temperatures of the ocean waters at the surf line between 45° north and south latitudes, are as follows :¹

For the belt between 15° north latitude, and 15° south latitude, 26 degrees centigrade.

For the belts between 15° - 30° north latitude, and 15° - 30° south latitude, 21 degrees centigrade.

For the belts between 30° - 45° north latitude, and 30° - 45° south latitude, 17 degrees centigrade.

The average temperature between 45° north latitude and 45° south latitude, at the depth of 1500 fathoms is between 2° - 3° centigrade.

Professor Ditmar has found that at temperatures between 18° - 21° C. that the dissociation tension of the bicarbonates of the sea water is five ten-thousandths of an atmosphere. On the other hand, at temperatures near zero, the dissociation does not take place, and the tension of course becomes nil. (See table above.)

The partial pressure of the CO_2 in the atmosphere at the present time is about three ten-thousandths. Therefore, he con-

¹Compiled from tables Challenger's Rep., Vol. I, Table VI, at end of volume.

cludes that the warmer portions of the ocean are constantly supplying CO_2 to the atmosphere, and the colder portions are always removing it.¹

The falling temperature which causes the glacial period must affect the temperature of the surface of the equatorial water, especially after an ice advance is inaugurated, but how much we cannot estimate. Taking the average surface temperature of these waters as 21° , and postulating the same fall of temperature as for the temperate waters, we see that the line $a' b'$ representing the decreasing dissociation due to the falling temperature, is much shorter than the line $c' d'$ or $c' e'$, representing the increase in the dissociation caused by the decreasing partial pressure of CO_2 . However, the data upon which this part of the curve is based are much more conflicting and less satisfactory than those represented by the curve at 10° . But we may conclude that in the equatorial region the diminishing partial pressure has a greater effect than the postulated fall of temperature. But, with the increasing cold, the heated areas which can give off carbonic acid to the air are greatly diminished, especially after the glaciation has commenced, and this acts directly counter to the diminishing partial pressure.

In the northern seas whose surface temperature is near zero, each molecule of carbonate has the power to take up carbonic acid until it becomes a fully saturated bicarbonate. Just how much increase this area will undergo on an approach of a glacial period we cannot well estimate, but perhaps we can get a fair idea of it by comparing the area of the ocean contained within the circle of latitude which bounds the northernmost point of Greenland glaciation with that contained within the circle bounding the southern limit of Pleistocene glaciation. The ratio between these two areas is 2 : 5. These figures may not even approximately represent the real increase of the cold waters during glacial times, but they emphasize the fact of an actual and great increase in the amount of these waters.

The table on p. 609, as stated before, shows that at low tem-

¹Chal. Rep., Vol. I, pp. 212, 213.

peratures the decrease in the partial pressure of the atmospheric CO_2 has practically no dissociating effect upon the bicarbonates of the ocean, and therefore that the large increase in the capacity for absorbing CO_2 is not affected by the diminishing partial pressure.

To sum up then: (1) the increase in the ocean's capacity for CO_2 at low temperatures, and (2) the invasions of the polar waters toward the equator, both tend directly to rob the atmosphere of CO_2 , unaffected by any diminishing partial pressure of that gas. In the temperate waters the effects of increasing cold and decreasing partial pressure seem to be fairly evenly balanced, with a possible advantage for the diminishing partial pressure, against which must be reckoned a decrease in the amount of these waters. In the equatorial waters the effect of the decreasing partial pressure exceeds that of falling temperature, counterbalanced by a large decrease in the amount of these waters.

This division of the ocean with three belts shows us clearly the factors in the problem, but does not give us means by which to find the relative values of these factors—that is, to show us whether or not the intensifying factors, such as falling temperature and increasing areas of polar waters and decreasing areas of equatorial waters, more than counteract the effect of the diminishing partial pressure of the CO_2 over the temperate and equatorial waters.

In order to get some rough comparative value of these factors without pretending to get any accurate quantitative estimate of their actual value, we have tried to estimate the volume of the ocean water, whose temperature is reduced from 7° to 2° , from 12° to 7° and from temperatures above 12° , etc., and to calculate the amount of CO_2 these volumes of the waters can absorb on account of their lower temperature on the one hand and to estimate the greatest amount of CO_2 that might be freed from the tropical waters compatible with their restricted volumes on the other hand.

As shown in Fig. 6, we have assumed that the polar waters

(viz. those with temperature of 2° – 3° C.) will advance southward at least as far as the southernmost limit of the ice-sheet. Therefore, we have started the line $a b$ at 60° N. and S. latitude (the latitude of the southern Greenland glaciation) and the line $e h$ at 37° (the latitude of the southernmost Pleistocene glaciation in North America). With this postulated southern advance of the cold waters, there must also have been a rise of these cold waters toward the surface. The amount of this rise is undeterminable at present. But since we have used Dr. Arrhenius' estimate of a drop of 5° in the temperature of the surface waters, we may assume the same fall of temperature for the body of the ocean. A given fall in temperature of the surface water must

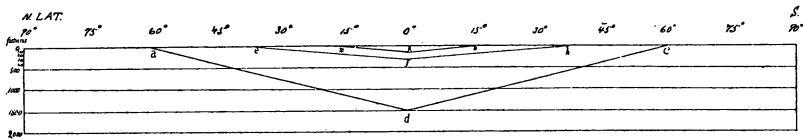


FIG. 6.—Section of ocean from north to south pole. Ocean taken at average depth of 2000 fathoms. Portion below 1500 fathoms has temperature below 2° to 3° C.

Line $a d c$ incloses section of ocean whose temperature is now above 2° to 3° . Line $e f h$ limits the equatorial and upward migration of the polar waters during maximum Pleistocene glaciation, when the ice reached the latitude 37° N.

Line $m k n$ ditto for waters with Pleistocene temperature of 2° to 7° .

Above line $m k n$ ditto for water of higher temperature.

take a very long time to communicate itself throughout the body of the ocean, but the larger the period during which the surface waters maintain their low temperature the more completely does the body of the ocean lose its extra heat.

At 1500 fathoms the temperature of the temperate and equatorial waters is 2° – 3° C. above zero; therefore, the maximum depth which the line $a-c$ reaches is placed at d . At 300 fathoms the warm waters have a temperature of about 7° .[†] Therefore, we place here f on the line $e f h$, designating the maximum advance upwards of the polar waters.

Point k on $m-k-n$ is 150 fathoms below the surface and at that

[†] All temperatures calculated from tables of temperatures, given in Vol. I of the Challenger Reports.

depth the equatorial waters have average temperature of 12° . Therefore, this will be the limit of the waters of the belt that had temperatures of 2° to 7° during maximum glaciation. Above *K* are the waters which now have temperatures above 12° , and during glaciation temperatures above 7° .

To get a correct conception of this section of the ocean waters from pole to pole, we must multiply the length given here by 550.

The portion of the ocean below 1500 fathoms is already down to the limiting temperature; therefore, its carbon dioxide content is not subject to fluctuations. This leaves out of the 18 atmospheres of "free" CO_2 about 13 atmospheres above the 1500 fathom line.

The volume of these waters is divided as follows:

90° to 60° N. and S. latitudes,	-	-	-	11%
60° to 37° " " "	-	-	-	24
37° to 6° " " "	-	-	-	65

Now, the volume of water included between *adc* and *efh* is considerably over one half that above the 1500-fathom line, or it holds about seven atmospheres CO_2 , and a change of temperature from 7° to 2° represents a change in the dissociation of the bicarbonates from 1.9 to 2.00 (see Fig. 5, p. 610), or more than a 10 per cent. increase in the "free" CO_2 . Therefore, this advance of the cold waters upward and toward the equator represents an increased capacity of the ocean for CO_2 , equal to about seven tenths that of the present atmosphere.

The waters above *mkn* represent those which now have a temperature above 12° C. (we neglect the warm surface waters now spread far poleward by the warm currents), and it is in the warmer of these waters that the diminishing partial pressure of the CO_2 may cause a loss of CO_2 from the ocean.

Now this volume represented by *mkn* is considerably less than 2 per cent. of the volume above the 1500 fathoms line, so that for a limiting case if *all* the second equivalent were lost in these waters, instead of only at most a small portion of it, it would amount to less than one third that gained by the advance of the

cold waters, and in the actual case probably not more than one fortieth of the same.

Admitting all the inaccuracies of our assumption, still it seems to be clear that with falling temperature *the ocean will dissolve CO₂ from the air.*

The effect becomes more pronounced as the glaciers become more extensive and thus directly chill the ocean waters. We offer this as the most important accumulative factor causing the great extent of the glacial invasion, acting until overcome by a number of opposite agencies.

Dr. Chamberlin[†] has shown that the amount of CO₂ in the atmosphere at any one time, and therefore the climate of the earth at that time, depends upon the value of the ratio of the supply of the gas to its depletion. Besides the continuous supply that the atmosphere receives from the interior of the earth and from planetary space and the continuous depletion due to the formation of the carbonates in place of the igneous alkali earth silicates, there are variations in the ratio of supply to depletion dependent upon the attitude of the land and water.

A large exposure of land surface is correlated with a rapid solution of calcium and magnesium carbonates, and this solution is accompanied by a change from the normal carbonate to the bicarbonate form, and therefore represents a loss of CO₂ from the atmosphere.

On the other hand the formation of the normal carbonate by lime-secreting animals causes a direct liberation of the second equivalent of the bicarbonate. Therefore extensive oceans and abundant marine life are correlated with warm climate, and restricted seas and elevated land cause loss of CO₂ and colder climate.

Now, to investigate the rôle the ocean plays in this conflict :

1. The chief agencies in the *removal* of the carbon dioxide from the air are (a) the formation of the carbonates from the silicates; (b) the solution of the carbonates as bicarbonates. These are dependent upon the attitude of the land and water,

[†] See PROFESSOR T. C. CHAMBERLIN, *JOUR. GEOL.*, Vol. V, p. 682.

the elevated land being accompanied by rapid disintegration and erosion. The increasing cold only slightly affects this process (a') by the decrease in vegetation; (b') by the slight decrease in chemical activity of the CO_2 ; (c') by the freezing of the ground, preventing free percolation of the underground water, etc. But it aids disintegration by frost action, etc. (c) The polar seas constantly absorb CO_2 from the atmosphere. The increasing cold, with the increasing volume of cold waters, therefore *directly robs* the atmosphere of the CO_2 . This process is not so marked in the warmer waters, because of the counter-acting effect of the postulated diminishing partial pressure of CO_2 .

2. The *supply* of CO_2 , outside of that of plutonic and extra-terrestrial origin comes (a) from the dissociation of bicarbonates in equatorial waters. The decreasing partial pressure aids this and the restricted area of warm water counteracts it. (b) The second equivalent of bicarbonate freed by lime-producing animals. The fall of temperature directly affects this most important source of supply, as it is well known that a fall of a few degrees in the ocean water would wipe out whole genera of test-producing animals.

To sum up, then: Accepting Dr. Chamberlin's proposition that the advance of a cold period is primarily dependent upon the altitude of land and water, the effect of the ocean is both to remove the atmospheric carbonic acid gas by the southern and upward invasion of the cold waters, and to decrease the supply of CO_2 to the atmosphere by the destruction of the lime-secreting animals. Therefore we conclude that *the ocean very greatly intensifies the secular variation of the earth's temperature, although acting as a moderating agent in the minor cycles.*

It is interesting to note what a different state of affairs we would have if the CO_2 in the ocean were simply dissolved as a gas from the atmosphere according to the laws of gas absorption. A diminution of the partial pressure of the CO_2 in the atmosphere, as postulated, would bring out of the ocean 38 to 45 per cent. of its great store of CO_2 . A lowering of 5° in

temperature from 5° to 0° would only produce an increase in the solubility of the gas of 24 per cent., and from 20° to 15° of 14 per cent., and so, under such conditions, an excess of 14 to 31 per cent. of all the CO_2 in the ocean would have to be removed and consumed before a cold period could be inaugurated.

Although future investigations may cause a modification of Dr. Arrhenius' estimate, and such a change will affect some of these conclusions, the principles on which they are based will not be affected. If it be found that on account of certain intensifying agencies, or for other reasons, it is not necessary to postulate so large a decrease of the CO_2 of the atmosphere, or if this decrease is accompanied with a greater fall of temperature than 5° , then the depleting effect of the ocean will become more marked. If, however, the estimated decrease of the atmospheric CO_2 is too small, the intensive effects may be lessened, but probably not completely destroyed.

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