

P_{CO_2} AS A MASTER VARIABLE IN GEOSCIENCES*

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ABSTRACT

Some new properties of the master variable P_{CO_2} , the partial pressure of Carbon dioxide in the atmosphere, will be discussed during equilibrium models for the atmosphere-hydrosphere-lithosphere carbon species.

INTRODUCTION

THE OCCURRENCE of carbon dioxide in the atmosphere, hydrosphere, lithosphere and biosphere is well known. In the atmosphere elemental carbon occurs as $CO_2(g)$, the major species, and in the hydrosphere as $CO_2(aq)$, H_2CO_3 , HCO_3^- , and CO_3^{2-} . In aqueous media a small fraction of the bicarbonate and carbonate ions is reported to be present as the metal carbonate complexes both in fresh water and sea water (Krishnamurty *et al.*, 1970). The lithosphere, however, consists of carbonates of calcium and magnesium mostly, although other metal ions exist either as natural carbonate deposits and as solid solutions with the abundant carbonates. The biosphere apparently makes full use of all forms of carbon-containing species that occur in the geospheres. The facility with which CO_2 traverses the various geospheres and the biosphere constitutes what is commonly known as the CO_2 cycle in nature.

The various physico-chemical problems associated with the geospheres can be studied in terms of a few master variables (Silten, 1967), of which the partial pressure of carbon dioxide in the atmosphere P_{CO_2} , is the most important one and is related to other master variables such as pH, PO_2 , $mCa(II)$ and $mMg(II)$ and temperature in some way. In this paper the P_{CO_2} -pH relationship is studied in detail.

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DESCRIPTION OF GEOSPHERES

The description of CO₂ in the various geospheres is shown in Table 1.

TABLE 1. Occurrence of carbon-containing species in nature

Major sphere	Range and description	Chemical species
Stratosphere	from 10 upto 25 miles above earth	CO ₂ (g)
Troposphere	5 to 11 miles above earth ; clouds	CO ₂ (g)
Biosphere	~400 ft. max. overland and ends at snowline, limit of Alpine vegetation. Upper 500 ft. of ocean and underground to depth of tree roots	CO ₂ (g), CO ₂ (aq) HCO ₃ ⁻² (aq), CO ₃ ²⁻ (aq) Metal carbonate complexes
Hydrosphere	fresh water and sea water	same as in biosphere
Lithosphere	crust, upper mantle 3959 miles down to earth center	carbonate rocks

Properties of carbon dioxide

Carbon dioxide is a colourless, odourless gas with a density 1.9769 g/l at 0°C and 760 mm Hg. It is soluble in water and its solubility presents an interesting chemistry unlike the other gases of the atmosphere, for example, oxygen, nitrogen and argon. Its solubility not only depends upon temperature and pressure but also on other factors like dissolved solids, pH as well as the structure of the natural system whether open or closed. Some physical properties are, however, influenced to a degree because of the special nature of the CO₂ molecule. In general chemically it is very stable. It is not combustible by itself nor a supporter of combustion. Its thermal decomposition temperature is >1300°C and for all purposes it is chemically a permanent gas. It is unique in its distribution between air (10^{-3.5} atm) and water (0.034 M) almost equally around room temperature.

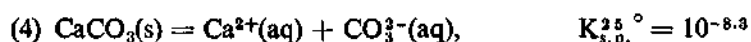
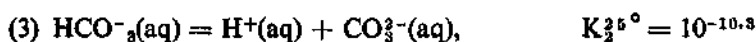
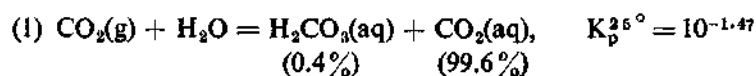
Origin and abundance of carbon dioxide in the atmosphere

The amount of carbon dioxide present in the atmosphere is determined by the carbon dioxide budget between the hydrosphere, lithosphere and biosphere. The estimated value of 2.3 × 10¹³ tons of CO₂ in the earth's atmosphere for the present time is around 0.03% of its total mass (Rubey, 1964). Slight fluctuations are believed to be responsible for variations in the world climate during the geologic time according to the so called 'carbon dioxide theory' (Plass, 1959). Volcanic activity, respiration and 'the decay of organisms' constitute the net gain of CO₂ whereas weathering of rocks and photosynthesis by plants consume CO₂ from the atmosphere. These natural processes seem to balance each other to account for a more or less constant partial pressure of CO₂ in the atmosphere allowing only for small variations at a given time.

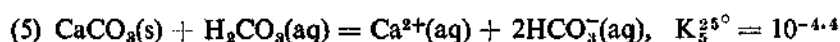
[2]

Carbon dioxide in the hydrosphere

The following equilibria are considered for deriving a relationship between P_{CO₂} and pH.



The solubility of CaCO₃(s) in water containing dissolved CO₂ can be represented by the following equilibrium



Although the equilibrium constant $K_5 = 10^{-4.4}$, in actual practice by saturating with CO₂ any suspended CaCO₃(s) can be brought in solution. This reaction suggests also a stoichiometric relation for the Ca²⁺ ion concentration in terms of the bicarbonate ion concentration

$$(6) (\text{Ca}^{2+}) = \frac{(\text{HCO}_3^-)}{2}$$

Representing the equilibrium constant K_p in terms of the partial pressure of CO₂ and (H₂CO₃) we have

$$(7) P_{\text{CO}_2} = \frac{(\text{H}_2\text{CO}_3)}{K_p}$$

Substituting for (H₂CO₃) from $K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)}$

$$(8) P_{\text{CO}_2} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{K_p K_1}$$

Further substitution of (HCO₃⁻) from $K_2 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)}$

$$(9) P_{\text{CO}_2} = \frac{(\text{H}^+)^2 (\text{CO}_3^{2-})}{K_p K_1 K_2}$$

Since $K_{s,p} = (\text{Ca}^{2+})(\text{CO}_3^{2-})$ and $(\text{Ca}^{2+}) = \frac{(\text{HCO}_3^-)}{2} =$

$$\frac{(\text{H}^+)(\text{CO}_3^{2-})}{2 K_2} \text{ the } (\text{CO}_3^{2-}) \text{ can be expressed as}$$

$$(10) \text{ (CO}_3^{2-}\text{)} = \sqrt{\frac{2K_2K_{s.p.}}{(\text{H}^+)}}$$

On substitution of (10) in equation (9) it can be shown

$$(11) P_{\text{CO}_2} = \frac{1}{K_p K_1} \left(\frac{2K_2 K_{s.p.}}{K_2} \right)^{\frac{1}{2}} (\text{H}^+)^{\frac{3}{2}}$$

This suggests, for a small change in pH large changes in P_{CO_2} would result. Conversely, increased P_{CO_2} in air would only alter the hydrospheric pH slightly.

The present atmospheric CO_2 levels are $P_{\text{CO}_2} = 10^{-3.5}$ atm. and 0.032% by volume. Increased activities imposed by civilization such as burning of fossil fuels, making cement from calcination of limestone, land clearing and other disturbing process (Peterson, 1969) would not very much effect the pH of sea water on a long time scale. If we consider sea water pH as 8.3 we can calculate P_{CO_2} using equation (11) and it works out to be $10^{-3.4}$ which is close to the present atmospheric CO_2 level.

It can also be shown that NaHCO_3 solutions have constant pH for moderate dilutions. Since sea water can be regarded as $\sim 2 \times 10^{-3}$ M HCO_3^- in close approximation a pH $\approx \frac{1}{2} (\text{p}K_1 + \text{p}K_2)$ can be predicted theoretically. The following mass balance and charge balance equations for a C, molar NaHCO_3 solution yield the expected relationship between pH and $\text{p}K_1$ and $\text{p}K_2$.

$$(12) \text{ mass balance : } (\text{Na}^+) = (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{H}_2\text{CO}_3)$$

$$(13) \text{ charge balance :}$$

$$(\text{Na}^+) + (\text{H}^+) = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-)$$

Substituting for (Na^+) in equation (13) we have

$$(14) (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{H}_2\text{CO}_3) + (\text{H}^+) = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-)$$

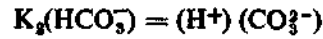
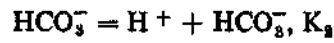
Dividing equation (14) throughout by (H^+)

$$(15) \frac{(\text{H}_2\text{CO}_3)}{(\text{H}^+)} + 1 = \frac{(\text{CO}_3^{2-})}{(\text{H}^+)} + \frac{(\text{OH}^-)}{(\text{H}^+)}$$

Each concentration term in equation (15) can be independently processed in terms of $(\text{HCO}_3^-) = C$, K_1 , K_2 and K_w (the ionic product of water).

The ratio $\frac{(\text{H}_2\text{CO}_3)}{(\text{H}^+)}$ is equal to $\frac{(\text{HCO}_3^-)}{K_1}$ from the equilibrium constant expression for K_1 .

The ratio $\frac{(\text{CO}_3^{2-})}{(\text{H}^+)}$ can be shown to be equal to $\frac{K_2(\text{HCO}_3^-)}{(\text{H}^+)^2}$ as follows :



Dividing the above by $(\text{H}^+)^2$ both sides

$$\frac{K_2(\text{HCO}_3^-)}{(\text{H}^+)^2} = \frac{(\text{CO}_3^{2-})}{(\text{H}^+)}$$

The ratio $\frac{(\text{OH}^-)}{(\text{H}^+)}$ is equal to $\frac{K_w}{(\text{H}^+)^2}$ as can be shown by multiplying the numerator and denominator by (H^+) and identifying $(\text{H}^+) (\text{OH}^-) = K_w$

The equation (15) can now be written as

$$(16) \frac{(\text{HCO}_3^-)}{K_1} + 1 = \frac{K_2 (\text{HCO}_3^-)}{(\text{H}^+)^2} + \frac{K_w}{(\text{H}^+)^2}$$

Substituting $(\text{HCO}_3^-) = C$

$$(17) \frac{C}{K_1} + 1 = \frac{K_2 C}{(\text{H}^+)^2} + \frac{K_w}{(\text{H}^+)^2}$$

crossmultiplying and rearranging we have

$$(18) (\text{H}^+)^2 = \frac{K_1 (K_2 C + K_w)}{C + K_1}$$

and the (H^+) can be readily shown

$$(19) (\text{H}^+) = \sqrt{\frac{K_1 K_2 C + K_1 K_w}{C + K_1}}$$

with the approximations $C \gg K_1$ and K_w and $(C + K_1) \cong C$, and $K_1 K_w \ll C$ since both K_1 and K_w are small it can be shown

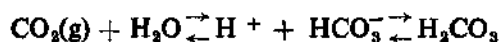
$$(20) (\text{H}^+) \cong \sqrt{K_1 K_2}$$

Thus $\text{pH} \cong \frac{1}{2} (\text{p}K_1 + \text{p}K_2)$ suggesting independence of C for moderate dilutions. This is in general agreement with the statement that increased (HCO_3^-) by absorption of excess CO_2 from the atmosphere by the ocean would not show any noticeable pH changes in the hydrosphere.

If the equilibrium model for CO_2 in the hydrosphere is thermodynamically simple, the kinetics of CO_2 hydration and dehydration are extremely complicated.

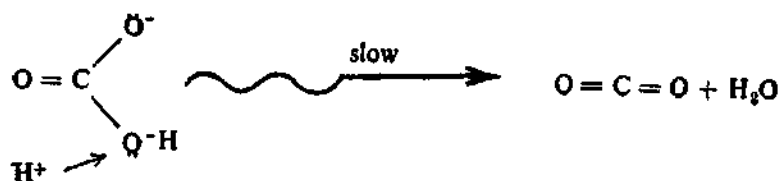
Kinetics of Hydration and dehydration

A variety of methods have been used to study the kinetics of CO_2 hydration and dehydration, for example, manometric and rapid mixing techniques, (Faurholt, 1924; Roughton and Booth, 1938; Pinsent and Roughton, 1951; Pinsent *et al.*, 1956) carbon-14 traces studies, (Himmelblau and Babb, 1958) oxygen-18 isotope fractionation studies, (Mills and Urey, 1940) nuclear magnetic resonance spectroscopy, (Patterson and Ettinger, 1960) hydration under conditions of enforced stationarity (Koefoed and Engel, 1961), chemical relaxation studies (Eigen *et al.*, 1961), enzyme catalysis (Chion Ho and Sturtevant, 1963; Gibbons and Edsall, 1963), and catalysis by inorganic ions (Sharma and Danckwerts, 1963; Denckwerts and Melkersson 1962; Dennard and Williams, 1966; Grønvald and Faurholt, 1960; Johansen and Faurholt, 1960). Some of these investigations clearly suggest that the HCO_3^- ion indeed is the intermediate in the dissolution of CO_2 in water :

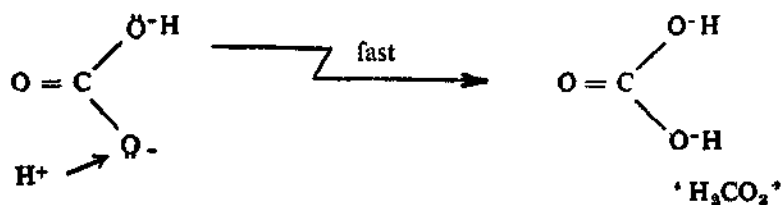


Although there is indirect evidence for the molecular species ' H_2CO_3 ' there is so far no independent detection method available. The unhydrated form, $\text{CO}_2(\text{aq})$ is the major species in aqueous solutions of carbon dioxide and it is almost 500 times more abundant than ' H_2CO_3 '.

The following mechanism explains the barrier for CO_2 hydration and the intrinsic slowness of the rate. In nature, however, the hydration as well as dehydration reactions are remarkably catalyzed by a zinc containing enzyme, *carbonic anhydrase* (Davies, 1961). It would seem this enzyme plays an important part in the overall carbondioxide-carbonate cycle in natural systems, particularly in the biosphere.



For hydration
as well as
dehydration
molecular
and electronic
redistribution
is involved



(Mechanism of bicarbonate protonation)

Recent study on the carbonic acid dehydration and its activation energy suggests even more complicated mechanism. (Sørensen and Jensen, 1970). The subject requires further study and until then a kinetic approach to the general problem of CO₂-hydration-dehydration must wait. With the available rate data one could examine the problem either for pH below 7 or for pH above 10, but in the intermediate pH range of 8-10 the rate law exhibits mixed order and has not been fully understood. This pH range, apparently, is the important one in most natural systems. To add further confusion to the system it is surmised if some metal carbonate complexes of the ion-pair type—CaCO₃⁰, MgCO₃⁰, ZnCO₃⁰ etc. have something to do with the hydration—dehydration mechanism both with the enzyme catalyzed and uncatalyzed reactions (Krishnamurty, 1969). Obviously these factors in the aqueous systems will have some degree of control on the P_{CO₂} in the atmosphere to account for short term fluctuations. It is not known if the time intervals involved are of the order of hundred or thousand years or more. It has been estimated (Plass, 1959) that nearly 200 billion tons of CO₂ are annually transported across the air-sea interface. This colossal hydration-dehydration reaction must also take into account the part played by several natural factors like winds, vertical mixing (Kanwisher, 1963), and the overall chemistry of CO₂ in the hydrosphere and biosphere (Berger and Libby, 1969 ; Peterson, 1969).

Relationship between P_{CO₂} and pH

Equation (11) describes the relationship between the two master variables P_{CO₂} and pH. The master variable P_{CO₂} is important for the following reasons : (a) P_{CO₂} and P⁰₂ in the photosynthetic apparatus at the present time and in the past and the observed spatial, temporal and diurnal variations, (b) P_{CO₂} in chemical weathering, (c) P_{CO₂} in the control of depositional processes in nature such as CaCO₃ (aragonite, calcite) and CaMg(CO₃)₂ (dolomite) and in general maintaining m_{Ca²⁺} + m_{Mg²⁺} + ratio in the marine hydrosphere, (d) P_{CO₂} in carbonate complexing—CaCO₃⁰, MgCO₃⁰, ZnCO₃⁰, CuCO₃⁰ etc., (e) P_{CO₂} in temperature regulation and the green house effect in climatology and (f) P_{CO₂} in carbonate solubility with changing m_{Cl⁻} or salinity.

Although some of these areas of research (Rubey, 1964 ; Ingerson, 1962) received attention no rigorous study has ever been made.

Equation (11) can be written in the logarithmic form as follows :

$$(21) \log P_{CO_2} = -\log K_p - \log K_1 - \frac{1}{2} \log K_2 + \frac{1}{2} \log K_{s,p} + \frac{1}{2} \log 2 + \frac{3}{2} \log [H^+]$$

Representing the same as pH and pK's we have

$$(22) \log P_{CO_2} = pK_p + pK_1 + \frac{1}{2} pK_2 - \frac{1}{2} pK_{s,p} - \frac{3}{2} pH + \frac{1}{2} \log 2$$

$$(23) \log P_{CO_2} = (pK_T + 0.15) - 1.5 pH$$

where pK_T is pK_p + pK₁ + $\frac{1}{2}$ pK₂ - $\frac{1}{2}$ pK_{s,p}.

With the available thermodynamic data, pK_p = 1.47, pK₁ = 6.4, pK₂ = 10.3 and pK_{s,p} (CaCO₃) = 8.3 corresponding to the standard state pK_T is evaluated to be 8.87 and a plot of log P_{CO₂} vs. pH is shown in Fig. 1. Since pK_T is a sum

of several constants and since each constant depends on pressure, temperature and the ionic medium, pK_T is therefore the function of these variables. If data are available corresponding to a given natural system with different pK_T values one can present them as a family of straightlines in Fig. 1 parallel to each other having the same slope.

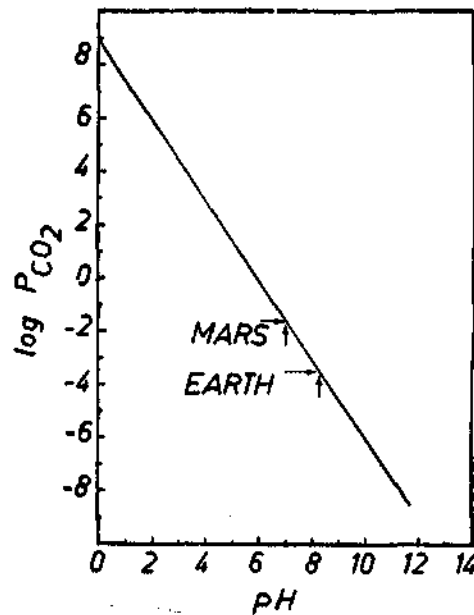


Fig. 1. P_{CO_2} -pH Relationship

Extension of P_{CO_2} -pH relation to Mars and other planets

There have been recent reports concerning the existence of CO_2 on Mars from Mariner experiments and interestingly, water also in bound state such as $CO_2 \cdot 6H_2O$ as a clathrate compound (Miller and Smythe, 1970), and even liquid water limited to concentrated solutions of strongly deliquescent salts (Ingersoll, 1970). If we assume a reasonable value for P_{CO_2} (MARS) = 25 mb = $10^{-1.6}$ atm. a value for $pH(MARS) = 7$ can be read out from the plot. It is tempting to suggest, assuming all equilibria to exist on Mars, the pH of Martan water is not after all hostile! Although CO_2 has been reported in large abundance on Venus no evidence of any water is available. The origin and evolution of the atmosphere and the hydrosphere will be fascinating areas of research in the future and it seems likely that P_{CO_2} is the starting point for such studies.

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DISCUSSION

- DR. K. R. SAHA : What would be a practical method of measuring P_{CO_2} and then deducing the value of (H^+) in the terrestrial as well as extra-terrestrial atmosphere ?
- DR. K. V. KRISHNAMURTY : Assuming an equilibrium model, as presented here, the (H^+) of the coexisting hydrosphere can be read out from plots of the type shown in Figure 1. However, in a natural system there might be several other factors that should be taken into account.
- DR. D. R. SIKKA : Are there any measurements on the carbon dioxide in the atmosphere over the Indian Ocean region ? If so, are there any seasonal variations observed ?
- DR. K. V. KRISHNAMURTY : I am sure there must be some measurements on P_{CO_2} made in the Indian Ocean during the various cruises of several oceanographic research vessels. Whether any correlation between the hydrospheric pH and the atmospheric P_{CO_2} has been made with special reference to the Indian Ocean I do not know.