

proposed (1,1), (1,2), (2,2), (3,3), and (4,4), to see whether a better fit could be obtained by assuming other complexes than those proposed earlier from this laboratory.

We used three combinations of data: (1) all data (78 points) of Ref.³, $B \approx 0.001$ to 0.049 M. (2) 122 points selected at random from Ref.⁴, $B \approx 0.040$ to 1.0. (3) Data as in 1 + 2, except for 42 points from the two highest B values and two points from Ref.³ which had very high deviations, thus 156 points with $B \approx 0.001$ to 0.318 M.

The results are given in Table 1; the limits given are the standard deviations $\sigma(\beta)$. "Minus" β_{pq} -values were set = 0 in calculating the final set.⁵

These calculations thus confirm the existence of the three main complexes suggested by earlier work from this laboratory; the (4,4) and (2,2) complexes are not supported by the present data, even as minor products.

Obviously "data 1" (low B) are less sensitive to (4,4), and "data 2" (high B) to (2,1) and (1,1). Using "data 3" and giving, as usual, 3σ , and logarithms,⁶ we obtained the results given in Table 2.

From the 3σ limits we estimate as a maximum value, $\log \beta_{11} < -6.1$.

Again, we find that our earlier graphical methods gave practically the same result as the computer refinement by LETAGROP.

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Processes Regulating the Oxidation State of the System (Air + Sea + Sediments) in Past and Present

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From present theories of planet formation it seems likely that there was little or no oxygen in the original atmosphere of the Earth. Oxygen is formed by biological photosynthesis and by photochemical splitting of H_2O ; it is consumed by biological oxidation, and by some inorganic processes such as weathering of sulfides and oxidation of Fe(II). As estimated by Goldschmidt,¹ the free O_2 (0.027 mole) and the O_2 buried in Fe(III) (0.030 to 0.065 mole) are roughly equivalent to the carbon (0.06 to 0.08 mole) that has been buried and thus withdrawn from circulation. Goldschmidt's figures have been recalculated here to the unit mole per liter of sea water.

One may ask whether $p(O_2)$ is still increasing slowly, or whether it is fixed around 0.21 atm (its present value) by some equilibrium or steady-state mechanism. For instance, Redfield² has suggested a regulating biological mechanism involving the oxidation of organic matter with SO_4^{2-} in regions deficient in O_2 on the ocean floor.

From Goldschmidt's figures¹ one may calculate that (1 l seawater + 0.6 kg sediments + 3 l H_2O) have been formed by the reaction of (0.6 kg primary rock and \approx 1 kg volatiles), containing 54.90 mole H_2O , 16.06 SiO_2 , 1.85 $Al(OH)_3$, 0.55 HCl, 0.47 NaOH, 0.56 $Ca(OH)_2$, 0.53 Mg $(OH)_2$, 0.41 KOH, 0.55 CO_2 , 0.03 O_2 , 0.55 Fe, 0.06 Ti, 0.07 S, 0.03 F, 0.02 P, 0.01 Mn and 0.10 N_2 .

Some time ago, the author^{3,4} made an attempt to compare the system (sea + sediments + air) with a model in which the components were allowed to reach equilibrium. In this way, the pH (\approx 8.1) and the concentrations of the major ions in seawater may be explained as a result of equilibria with various aluminosilicates and SiO_2 .

The small amounts of carbonate in seawater, and of CO_2 in air roughly correspond to equilibrium with solid $CaCO_3$ at around 5°C.

It may be interesting to calculate what happens to this model mixture if pE^* (and thus the oxidizing power) is decreased from its present value ≈ 12.5 . This might correspond to going back in time to a more reduced state, returning to the system C and hydrocarbons that have been buried, and H_2 that has been lost to outer space. In the calculations, for simplicity, complete equilibrium at $25^\circ C$ was assumed. The inorganic, pE -independent equilibria were assumed to fix pH , $p(CO_2)$, and the concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , borate and carbonate species.

A reasonable lower limit corresponding to the first ocean is $pE \approx -5.5$, where solid C would exist at equilibrium. At this point, Fe and S exist mainly as $Fe_3O_4(s)$ and $FeS_2(s)$, and N mostly as NH_4^+ in the solution or in solid aluminosilicates, although some gaseous N_2 may be left. We would have $p(CH_4) \approx 0.03$ atm; in the aqueous solution the equilibrium concentrations of organic compounds at $25^\circ C$ would be very low, and the solution would in no way correspond to the "thick soup" which is sometimes claimed. Admittedly, photochemical reactions and concentration by evaporation may have changed the picture in limited regions.

If we again increase pE to ≈ -3.8 , FeS_2 disappears at equilibrium, and also most of the CH_4 and NH_4^+ . The predominant forms of our major redox elements will then be $Fe_3O_4(s)$, SO_4^{2-} , N_2 , $CaCO_3$ (CO_2 etc.)

If pE is further increased, toward the present value of ≈ 12.5 , the next important buffering reactions are (neglecting the Mn) the formation of appreciable amounts of (1) O_2 (at $pE \approx +12$), (2) $FeOOH(s)$ and (3) NO_3^- (around $pE \approx 11$, however, see below).

Let us consider the reaction, and its equilibrium constant: $12 FeOOH(s) \rightleftharpoons 4 Fe_3O_4(s) + 6 H_2O(l) + O_2(g)$, $K = p(O_2)$ (1)

If O_2 is added to the system at a steady rate, by photosynthesis and withdrawal of C, $p(O_2)$ will at first increase. Finally, there will be a steady state where the backward reaction (1) consumes the O_2 added. We may ask if $p(O_2) = 0.21$ atm corresponds to this steady state, and if so, how far this is from the equilibrium value for (1). The present data on $FeOOH(s)$ are uncertain; in thermodynamic tables the substance is usually not even recognized, but the non-

existent $Fe(OH)_3(s)$ is quoted instead. Using the ΔG° values accepted in the NBS tables and many other standard texts, and writing the reaction as " $12 Fe(OH)_3(s) \rightleftharpoons 4 Fe_3O_4(s) + 18 H_2O + O_2(g)$ " one would calculate $\log p(O_2) \approx -1.5$ which could easily, within the errors of uncertainty, be equal to the present $\log p(O_2) \approx -0.7$. If this were so, the present $p(O_2)$ might be close to the equilibrium pressure of reaction (1). On the other hand, by other combinations of literature data, one may make equally defensible estimates of the order of $\log p(O_2) \approx -5.0$.

It is consequently hard to decide whether reaction (1) has fixed the $p(O_2)$ of our atmosphere in a steady state more or less close to equilibrium, or whether it acts at present only as a brake slowing down the steady increase of $p(O_2)$. At any rate, this reaction seems so important for understanding the oxygen balance of our planet that it would be worthwhile to make a more precise study of its thermodynamics, under conditions comparable to those in the system (air + sea + sediments). At equilibrium with sea water $Fe_3O_4(s)$ may well be a solid solution, with some O^{2-} replaced by OH^- , cation vacancies etc., quite different from the Fe_3O_4 studied in solid-gas reactions; if so, its composition will also vary with pE . If one uses the solubility product K_s of $FeOOH$, and the equilibrium constants for redox equilibria (Fe^{3+} , Fe^{2+} , Fe) one must remember that they appear with high coefficients: $\log K_s$ for instance is multiplied by 12; since at present $\log K_s$ is uncertain by several units, the wide range in $\log p(O_2)$ for (1) is easily understood. If the thermodynamic values for Fe_3O_4 and $FeOOH$ are revised, this will affect the pE for this disappearance of FeS_2 , and may also give more importance to $FeCO_3(s)$.

Variations of the average temperature of the system (air + sea + sediments) will influence rate and equilibrium of reaction (1) and in the long run, $p(O_2)$ on the planet.

There is still no good explanation of the fact that nitrogen exists mainly as $N_2(g)$ whereas at equilibrium with H_2O at $pE = 12.5$ and $pH = 8.1$, it should have been converted to NO_3^- in the ocean. There must be some mechanism, at present overlooked, that destroys excessive nitrate in the ocean. The simplest explanation would be an organism living in the surface layers of the sea which consumes nitrate ions (as an oxidant, or for synthesis) at a greater rate,

* $pE = -\log \{e^-\}$

the lower the phosphate concentration is in the surroundings, even in the presence of O_2 . If such an organism exists, and can be found, it would solve what now seems to be riddle No. 1 in the regulation of the present composition of air and seawater.

Detailed calculations, and discussion will be published elsewhere.

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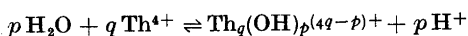
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Studies on the Hydrolysis of Metal Ions. 53. Preliminary Note on the Hydrolysis of Thorium(IV)

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The hydrolysis of thorium has been studied by many authors, with varying results. (For detailed references see the IUPAC tables of Stability Constants).¹ We shall write, as usual, β_{pq} , for the equilibrium constant of



and denote the complex as the (p,q) complex. Schaal, Faucherre and Souchay² deduced that (8,4) is the predominating complex from freezing-point and glass electrode data. Hietanen³ suggested, as an approximation, a series with $(3n, n+1)$. In solutions with 0.5 and 0.7 M Th^{4+} self-medium Hietanen and Sillén found evidence for (1,2) and (2,2). Kraus and Holmberg⁵ from glass electrode data concluded that the mononuclear (1,1) and (2,1), the binuclear (2,2), and in addition other,

undesignated complexes exist. Lefevbre,⁶ from the same data, calculated the equilibrium constants for (2,1), (2,2) and (12,5) and found evidence for a heptanuclear complex (18–21,7).

The generalized least squares program LETAGROP has recently been improved by Ingri and Sillén,⁷ and provided with procedure, MIKO for elimination of negative formation constants.

In the last few years, we have collected data on thorium hydrolysis, using the improved techniques (for instance coulometry for the lowest Th concentrations) which have been developed in this laboratory especially by Georg Biedermann. The medium has been 3 M NaCl and the temperature 25°C. Preliminary LETAGROP calculations have been made on these new data, which cover a range of total concentration B of Th from 0.0001 M to 0.100 M. The calculations are not yet completed, but we think some preliminary results may be of interest. We found the following equilibrium constants, with the standard deviations σ :

$$\begin{aligned} 10^{10}\beta_{21} &= 8.9 \pm 2.9; 10^3\beta_{12} = 2.24 \pm 0.81; 10^5\beta_{22} = 1.98 \pm 0.07; \\ 10^9\beta_{32} &= 1.47 \pm 0.22; 10^{37}\beta_{14,6} = 2.96 \pm 0.39; 10^{41}\beta_{15,6} = 4.28 \pm 0.69. \end{aligned}$$

The computer has rejected the following complexes, which thus do not lead to any improvement in the interpretation of the present data: (1,1), (6,3), (8,4), (9,4), (11,5), (12,5), (16,6), (17,7) and (20,8). If we transform to logarithms and give 3 σ we get the following preliminary values:

$$\begin{aligned} \log \beta_{21} &\approx -9.1 (< -8.7); \log \beta_{12} \approx -2.65 (< -2.33); \log \beta_{22} = -4.70 \pm 0.05; \\ \log \beta_{32} &= -8.83 \pm 0.21; \log \beta_{14,6} = -36.53 \pm 0.19; \log \beta_{15,6} = -40.37 \pm 0.23. \end{aligned}$$

As far as the calculations have now proceeded the data seem to indicate, besides the mononuclear $Th(OH)_2^{2+}$, three binuclear complexes (1,2), (2,2) and (3,2), and two hexanuclear complexes, (14,6) and (15,6). Thus a group of six Th atoms seems to be stable, just like groups of 7 Mo, or 6 Nb, or 10 V, which have all proved to exist in several states of protonation. Georg Lundgren⁸ has found octahedral "(12,6)" complexes $Ce_6O_4(OH)_4^{12+}$ and $U_6O_4(OH)_4^{12+}$ in the crystal structures of sulfates. It seems likely that the Th atoms form similar octahedra, and one need not be surprised if the state of protonation is different in the sulfate crystals from that in our solutions.