

The Physical Chemistry of Compounds of Copper and Mercury and Their Interactions with Sea Water

For an adequate understanding of the mechanism of action of antifouling paints, a knowledge of the chemistry of paint ingredients and of their interactions with sea water is necessary. Both the toxic ingredients and the nontoxic matrix ingredients may react with sea water, but the toxics are naturally of primary interest.

Considerable biological evidence now exists, as described in Chapter 14, to show that toxics exert their antifouling action in the dissolved state, and that antifouling effectiveness is closely correlated with rate of solution of toxic. The most important problems in the chemistry of the toxic ingredients are, therefore, concerned with solubilities and processes of dissolution.

Nearly all of the antifouling toxics in current use are compounds of copper or mercury, and, among these, cuprous oxide and metallic copper are used most widely. The purpose of this chapter is, first, to summarize what is known of the reactions and solubilities in sea water of copper and mercury compounds; and, second, to examine in detail the processes involved in the dissolution of cuprous oxide. The data are taken in part from work at the Woods Hole Oceanographic Institution and in part from the previous literature. Details of thermodynamic calculations are given in an appendix.¹

COPPER COMPOUNDS

In summarizing the physical chemistry of copper, several compounds, as well as metallic copper, are treated in some detail. These are cuprous oxide, which is the most widely used antifouling toxic; cuprous chloride, also occasionally used as a toxic; cupric oxide; and basic cupric carbonate, a mixed salt which is a frequent end-product in the reactions of cuprous oxide or copper metal with sea water in the presence of air. Qualitative information on the solubilities of a number of other compounds is also included, and certain other equilibria involving copper ions are discussed.

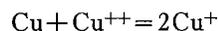
Solubilities, equilibrium constants, and free energy changes are calculated both indirectly from

¹ The calculated data differ somewhat from those given in the original Reports to the Bureau of Ships. The discrepancies are due to revisions in the evaluation of data from the literature, and do not alter the general description of these systems, nor any conclusions previously drawn.

data in the literature and from experimental measurements. All calculations are for a temperature of 25°C. Symbols in brackets [] refer to concentrations, and in parentheses () to thermodynamic activities, both in moles per liter.

Metallic Copper

When metallic copper is immersed in a solution containing cuprous ion, Cu^+ , and cupric ion, Cu^{++} , in the absence of oxygen, the following equilibrium is established at the surface of the metal:



The equilibrium constant of this reaction is

$$(\text{Cu}^+)^2/(\text{Cu}^{++}) = 0.84 \times 10^{-6}. \quad (1)$$

This means that for all concentrations greater than about 10^{-6} moles per liter (about 0.1 microgram copper per cc.)—*i.e.*, all except extremely dilute solutions—cupric copper ion will be in excess of cuprous copper ion when in equilibrium with copper metal.

In solutions containing chloride ion, however, as will be shown in the next section, the total dissolved cuprous copper may exceed the cupric, owing to complex formation. Furthermore, if oxygen or air is present, the cuprous copper will be oxidized to cupric, thereby displacing the equilibrium and permitting more metallic copper to dissolve.

In the absence of oxygen, metallic copper does not dissolve or corrode in sea water unless copper ions are already present. Corrosion once started in the presence of oxygen may continue in its absence by means of copper ion concentration cells, if conditions should favor the establishment of this mechanism.

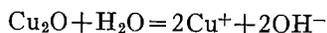
Cuprous Oxide

Equilibrium between cuprous oxide and sea water can be established only in the absence of oxygen, since otherwise the cuprous copper in solution is rapidly oxidized.

The solubility of cuprous oxide in oxygen-free sea water has been calculated from thermodynamic data in the literature, and has been measured under a variety of conditions (6, 7, 9, 14). The

agreement of these results is close and shows that the calculations are substantially correct.

According to the calculations, if cuprous oxide dissolves in water in the absence of air to form cuprous ion, as follows:



then the concentration of cuprous ion is proportional to the hydrogen ion activity, and is

$$\text{Cu}^+ = 0.18(\text{H}^+). \quad (2)$$

At the average pH of sea water, 8.1, the hydrogen ion activity is 8.0×10^{-9} moles per liter, and the maximum concentration of cuprous ion in equilibrium with cuprous oxide is 1.5×10^{-9} moles per liter.

The actual solubility of cuprous copper in sea water is far greater than this, however, because the cuprous ion associates with chloride ion to form the complexes CuCl_2^- and CuCl_3^{--} . At the chloride concentration of normal sea water,¹ 0.48 mole per liter, the ratio of chloride complexes to free cuprous ion is about 60,000, and the solubility is accordingly increased by this factor.

The total solubility of cuprous copper in sea water is, according to the calculation, proportional to the hydrogen ion activity, and is

$$[\text{Cu}^{\text{I}}] = 1.06 \times 10^4 (\text{H}^+). \quad (3)$$

At a pH of 8.1, the maximum concentration of cuprous copper in equilibrium with cuprous oxide is 0.84×10^{-4} moles per liter, or 5.4 μg . of copper per cc.

This calculated solubility of cuprous oxide in sea water may now be compared with experimental measurements.

In the Woods Hole investigations, the solubility in oxygen-free sea water has been studied under a variety of conditions:

(a) Preliminary experiments (9) without control of pH (in which the sea water became alkaline when carbon dioxide was removed along with oxygen).

(b) Experiments (14) in which the pH was adjusted in carbonate-free sea water by acid and alkali, and also in sea water with its normal carbonate buffer by controlling the partial pressure of carbon dioxide in the absence of oxygen.

(c) Experiments (6, 7) in which elaborate care was taken to exclude oxygen.

(d) Experiments (6, 7) in the presence of basic cupric carbonate and of rosin. (The cupric copper dissolved from the carbonate was of course subtracted from the analytical values.)

(e) Experiments (6, 7) in which a surface coated with an antifouling paint (Bakelite Corporation No. AF-6, containing rosin, Vinylite resin, and Celite) was employed as the saturating body.

The results of these experiments are all given in

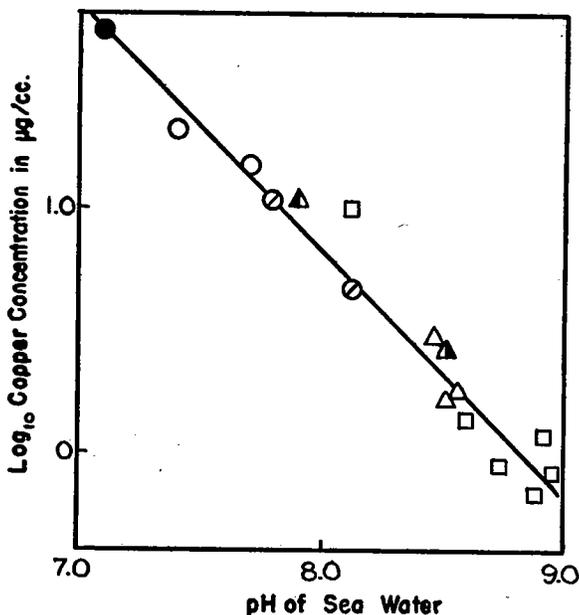


FIGURE 1. Solubility of cuprous oxide in oxygen-free sea water plotted against the pH (at 25° C.): □, series (a); ○, series (b), carbonates absent; ⊙, carbonates present; △, series (c); ▲, series (d), B.C.C.; ▲, series (d), rosin; ●, series (e).

Figure 1, in which the logarithm of the solubility of copper (in μg . per cc.) is plotted against the pH. The resulting straight line coincides very closely with the calculated solubility, equation (3), which cannot be distinguished from the experimental line on the scale shown. In view of the roundabout derivation of the calculated values (see Appendix), and the uncertainty in estimating the activity coefficients, the closeness of this agreement must be considered fortuitous, but it shows, certainly, that the dissolved cuprous copper does exist largely as chloride complexes. The experimental values may be taken as the most reliable figures now available, and may be expressed by the equation

$$[\text{Cu}^{\text{I}}] = 1.08 \times 10^4 (\text{H}^+)$$

or

$$\log_{10} [\text{Cu}^{\text{I}}] = 4.03 - \text{pH}. \quad (4)$$

The solubility of cuprous oxide in air-free sea

¹ The concentration of chloride ion in sea water varies; the figure of 0.48 M is based on a recommendation by A. C. Redfield to the Bureau of Ships, U. S. Navy Department, of a standard concentration for studies of the behavior of antifouling paints.

water at pH 8.1 is 0.86×10^{-4} moles per liter, or 5.4 $\mu\text{g.}$ of copper per cc.

The following additional conclusions may be drawn from these data:

1. The solubility is proportional to the hydrogen ion concentration, as predicted by equation (3).
2. The solubility is the same whether the carbonate-bicarbonate buffer components of sea water are present or absent. However, the carbonates do influence the solubility of cupric copper, as will be shown below.
3. The solubility is not affected by presence of rosin or basic cupric carbonate.
4. The solubility is the same for cuprous oxide compounded in a paint as in the pure state.¹

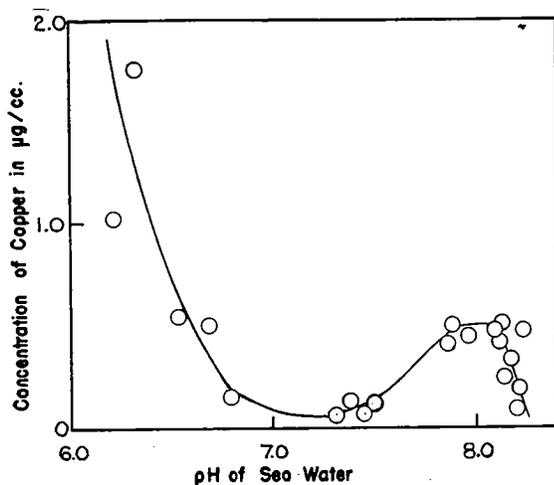


FIGURE 2. Solubility of B.C.C., plotted against the pH at which the precipitate was formed and equilibrated.

Cuprous Chloride

The solubility of cuprous chloride in oxygen-free sea water can be readily calculated from the thermodynamic data referred to in the previous section, and is found to be 0.051 mole per liter, or 3,100 $\mu\text{g.}$ copper per cc. There are as yet no reliable experimental measurements with which this figure may be compared. However, it is clear that the solubility of cuprous chloride should be several hundred times that of cuprous oxide (13).

Cupric Oxide and Hydroxide

The solubility of cupric oxide and hydroxide in sea water at pH 8.1 can be calculated from thermodynamic data to be 1.4×10^{-7} and 2.1×10^{-7} moles per liter, respectively. These values corre-

spond to concentrations of 0.0009 and 0.013 $\mu\text{g.}$ copper per cc., which are below the limit of detection by ordinary analytical methods. The Woods Hole investigations have shown no measurable solubility of cupric oxide in sea water (13).

Basic Cupric Carbonate

The solubility of cupric carbonate in sea water can be calculated from thermodynamic data to be 3.9×10^{-4} moles per liter, or 25 $\mu\text{g.}$ copper per cc. The solubility of the basic cupric carbonate which is actually formed in sea water is much lower than this.

When either cuprous oxide or metallic copper dissolves in sea water, in the presence of an adequate supply of oxygen, the end-product of the reaction is a bluish-green precipitate consisting of cupric carbonate, hydroxide, and chloride in somewhat variable proportions. The analyses of several investigators who have studied this type of product are summarized in Table 1.

TABLE 1. Analyses of the End-Product of the Reaction of Copper (or Cuprous Oxide) with Sea Water

Source	Cu, %	CO ₂ , %	Cl, %	Investigators
Copper	67	11	4	Sexton (37)
Copper	50-55	7-12	3-6	Bengough and May (1)
Copper	51-58	11	3	Woods Hole (42)
Cuprous Oxide	51	—	2	Woods Hole (42)

Bengough and May (1) considered their products to be mixtures of basic cupric carbonate and atacamite (cupric oxychloride, $\text{Cu}_4(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}$). On this basis, their analyses and those from Woods Hole indicate that the proportion of oxychloride is small (less than 20 per cent). "Basic cupric carbonate" is an approximate description of the composition, and the initials "B.C.C." have been used to describe the characteristic product which is formed in normal sea water.

Just as the composition of this precipitate shows variations, so also does its solubility in sea water. A large number of experimental determinations at Woods Hole has given values lying between 0.3 and 0.7 $\mu\text{g.}$ copper per cc. (9, 13). Harvey (17) quotes a value of 0.18 $\mu\text{g./cc.}$

Both the composition and the solubility refer only to normal sea water, whose pH is near 8.1. The solubilities of corrosion products of copper formed under other conditions of pH, and equilibrated with sea water at the corresponding pH values, are plotted against the pH in Figure 2. This complicated function indicates that different solid phases are precipitated under different conditions. Since there is practically no carbonate ion in sea

¹ A high ratio of paint area to solution volume is necessary to achieve saturation; cf. Chapter 16.

water (30) acid to pH 7.5, the portion of the curve at lower pH values probably does not represent the solubility of a carbonate at all. It agrees approximately with the calculated solubility of cupric oxide. No data for the compositions of products formed under these conditions have been reported.

The fact that cupric copper attains a concentration of about 0.5 μg . per cc. in normal sea water, whereas a cupric ion activity of one-thirtieth this value should result in precipitation of hydroxide, calls for some comment. Cupric copper may exist as a complex ion; calculations rule out ammonia complexes, but chloride complexes may be possible, even though their effect in increasing solubility be far less than in the case of cuprous copper. Certain other solubility products involving divalent ions in sea water are also considerably larger than values estimated on the basis of activity coefficients measured in simple systems (40).

On the other hand, sea water equilibrated with B.C.C. may be supersaturated with respect to hydroxide. The solubility of B.C.C. decreases after aging under sea water. One sample aged for a year was found to have a solubility of less than 0.1 μg . copper per cc. It contained 58 per cent of Cu and 14 per cent of Cl—close to the values for atacamite (57 per cent Cu and 16 per cent Cl). This suggests a slow conversion to a less soluble precipitate which may be the oxychloride. Rooksby and Chirnside (35) have identified atacamite by X-ray spectroscopy in the corrosion products of copper after three weeks' immersion in sea water.

Solubilities of Other Compounds

The solubilities of several other copper compounds in sea water have been roughly estimated (5). Expressed as μg . per cc., they are as follows: cuprous iodide, 15; cuprous sulfide, 4; cupric phosphide, 117; cupric derivative of acetyl acetone, 31; cupric derivative of n-caproic acid, 300.

Equilibria with Citrate

In the presence of citrate ion, the solubility of cupric copper in sea water is enormously increased, owing to the formation of a very stable complex ion. Sodium cupric citrate (a crystalline salt whose copper content corresponds to the formula $\text{NaCuC}_6\text{H}_5\text{O}_7$) has a solubility in sea water of at least 176,000 μg . copper per cc. (7, 13). It is a convenient material for biological studies which may require copper concentrations exceeding the solubility of B.C.C.

Equilibria with Mercury, Zinc, and Iron

In the use of copper or cuprous oxide as an anti-fouling toxic, the question may arise as to whether certain reactions occur with other metals or compounds present in the system. These include mercuric oxide, often used as an additional toxic; metallic zinc, used as a pigment in some paints; and metallic iron, as the substrate. Thermodynamic calculations predict that certain reactions will tend spontaneously to take place, as follows:

1. Cuprous oxide will tend to react with mercuric oxide to form metallic mercury and cupric oxide. Thus, both toxics are converted to less soluble forms (see below for solubilities of mercury compounds¹).

2. Zinc will tend to react with cuprous oxide, with cupric ion in equilibrium with B.C.C., and even with cupric oxide, to form zinc hydroxide and metallic copper.

3. Iron will tend to react with cuprous oxide, with cupric ion in equilibrium with B.C.C., and even with cupric oxide, to form ferrous or ferric hydroxide and metallic copper.

Equilibria with Bacterial Slimes

Antifouling paints, like many other surfaces, often develop slimy coatings when immersed in sea water. This slime results from bacterial action and contains, among other things, salts of polyuronic acids.

Sodium alginate (a polymannuronic acid), which has been investigated as a simplified model of the more complex bacterial slime, forms compounds of copper which are sufficiently stable so that cupric ions are taken up even from quite dilute solutions. For example, a sodium alginate solution, equilibrated with a saturated solution of B.C.C. (enclosed in a cellophane bag to avoid mixing the viscous alginate with B.C.C. precipitate), combined with about 2 mg. copper per gram of alginate. Under similar conditions, bacterial slimes grown in sea water were able to combine with nearly 100 mg. copper per gram of organic matter in the slime (10). Other experiments which demonstrate the combination of copper with organic matter in sea water are quoted by Harvey (17).

Slime films formed on surfaces of antifouling paints also contain large amounts of copper, in agreement with the above result. It is difficult, however, to distinguish between copper combined

¹ In the preparation of certain hot plastic paints, containing both cuprous oxide and mercuric oxide, the formation of metallic mercury at elevated temperatures has been observed (20).

with the organic matter and copper present as occluded B.C.C. precipitate or even particles of eroded paint. In any case, it seems likely that any combined copper will have a far lower solubility than B.C.C., and that the amounts bound will be small compared with the total dissolved from the paint during the period of film growth. Hence the film should play a minor role in the dissolution process, provided that it offers no resistance to the diffusion of reactants to and reaction products away from the toxic surface.

Discussion and Summary

The solubilities of the most important compounds of copper, in sea water of normal chlorinity (17.0 parts per thousand, or 0.48 M) and normal

TABLE 2. Solubilities of Copper Compounds in Sea Water at pH 8.1

Compound	Solubility		Source
	Moles per l.	$\mu\text{g. Cu per ml.}$	
Cupric citrate		>176,000	Experimental
Cuprous chloride ^a	0.051	3,100	Calculated
Cuprous oxide ^a	8.6×10^{-6}	5.4	Experimental
B.C.C.	8×10^{-6}	0.5	Experimental
Aged B.C.C. ^b	$< 10^{-6}$	<0.1	Experimental
Compounds with slimes		low	Experimental
Cupric hydroxide	2.1×10^{-7}	0.013	Calculated
Cupric oxide	1.4×10^{-8}	0.0009	Calculated

^a In oxygen-free sea water.

^b Aged in sea water for one year.

pH (8.1) are given in Table 2. They cover a very wide range.

It is of interest that both cuprous oxide and B.C.C. have solubilities in the range where dissolved copper is toxic to adult barnacles within a reasonable time (2, 33), though that of B.C.C. is only barely above the toxic threshold (cf. Chapter 14). The extremely low solubilities of cupric oxide and hydroxide may be correlated with their ineffectiveness as antifouling toxics, whereas the high solubilities of cupric citrate and cuprous chloride suggest that either of these compounds might be an effective toxic but might dissolve so rapidly as to be wasted unless the rate is suitably controlled by the structure and composition of the paint in which it is compounded. The problems involved in such control are discussed in Chapter 16.

MERCURY COMPOUNDS

Certain compounds of mercury have found wide use as antifouling toxics. Among these are mer-

curous chloride, mercuric oxide, mercuric chloride, and mercurous sulfide. Less is known of the chemistry of their interactions with sea water than in the case of the more common copper compounds, but the following information has been reported.

Mercurous Chloride (13, 14)

Mercurous chloride is decomposed in the presence of other chlorides, and therefore presumably in sea water, with the formation of mercuric chloride and metallic mercury. The concentration of mercuric mercury in equilibrium with sea water is calculated to be 0.3 $\mu\text{g. mercury per cc.}$ The amounts dissolved as determined experimentally are of this order of magnitude, but depend upon the amount of solid phase present in a complicated manner which requires further study. Mercurous chloride has a measurable solubility in toluene (about 0.2 $\mu\text{g. mercury per cc.}$), and hence probably in many paint vehicles.

Mercuric Oxide (13, 14)

The solubility of mercuric oxide has been measured only at a pH considerably alkaline to that of normal sea water. At pH 9.7 it is about 400 $\mu\text{g. mercury per cc.}$ The solubility at pH 8.1 has been calculated from thermodynamic data as 78,000 $\mu\text{g. mercury per cc.}$ This enormous solubility is associated with the formation of the weak salt HgCl_2 .

Mercuric Chloride (13, 14)

The solubility of mercuric chloride in sea water is also enormous, being approximately 200,000 $\mu\text{g. mercury per cc.}$ Because of its nonpolar character, it also dissolves readily in organic solvents, including paint diluents. Its solubility in toluene is about 3,200 $\mu\text{g. mercury per cc.}$

Mercurous Sulfide (34)

The solubility of mercurous sulfide has been estimated as 1 $\mu\text{g. mercury per cc.}$

Discussion

Mercurous chloride and sulfide have solubilities of the same magnitude as cuprous oxide; the saturated solutions are toxic but do not greatly exceed the toxic threshold (2, 33). Mercuric oxide and chloride are so highly soluble that, in order to use them economically as antifouling toxics, their solution rates would have to be carefully controlled by proper specifications of the composition of the paint.

PROCESSES OF DISSOLUTION AND OXIDATION OF COPPER AND CUPROUS OXIDE

The previous sections have dealt with equilibrium solubilities of various toxic compounds. These data are not sufficient, however, for interpreting antifouling action of paints compounded with these materials. It is the *rate of solution* of toxic which is correlated with antifouling effectiveness, and the chemical problems involved are concerned with kinetics rather than with equilibria.

It will facilitate interpretation of the more complicated behavior of paint mixtures, which is described in Chapter 16, to discuss the two most widely used toxics, copper metal and cuprous oxide, and to describe the sequence of reactions which occur when these substances react with sea water, and kinetic studies of the factors which influence reaction rates.

Thermodynamic Calculations

It is possible to predict from thermodynamics that certain reactions involving copper compounds and sea water should tend to take place and go very far toward completion. The following conclusions may be reached:

(1) The oxidation of cuprous ion to cupric ion by atmospheric oxygen should be very nearly complete. In aerated sea water, if this reaction were reversible, the equilibrium ratio of cupric to cuprous ion would be 10^{10} . The ratio of cupric to cuprous copper in solution would be somewhat smaller, because of cuprous chloride complex formation, but would be at least 10^5 .

(2) Copper metal should tend to react in sea water with cupric ion at the concentration corresponding to the solubility of B.C.C. to form solid cuprous oxide (provided there is insufficient oxygen for further oxidation).

(3) Cuprous oxide should tend to react in sea water with oxygen to form solid B.C.C.

(4) Copper metal should tend to react in sea water with oxygen to form solid B.C.C.

The details of the calculations are given in the Appendix.

The Sequence of Reactions

Experiments have shown that all the above reactions do take place. As a result, when either copper metal or cuprous oxide reacts with sea water in the presence of oxygen, the product is B.C.C. The sequence of reactions is shown in Figure 3, which represents the course of dissolution of both of these toxics.

The dissolution of copper metal in chloride solutions is an electrolytic reaction which is considered to involve the acceptance of electrons by oxygen molecules at cathodic areas on the surface (15). The details of the complicated process, which is influenced by the accumulation of cuprous oxide, cuprous chloride, and/or cupric salts on the surface of the metal, are not understood.

The dissolution of cuprous oxide, as shown in the next section, involves the reaction of both hydrogen and chloride ions with the solid surface.

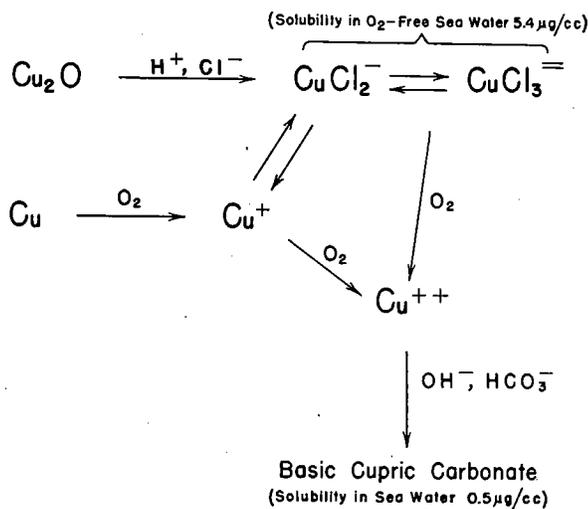


FIGURE 3. Sequence of Reactions in the Dissolution of Copper and Cuprous Oxide.

In each case, the solid toxic dissolves and is then partly reprecipitated as B.C.C. When the reaction proceeds in a limited volume, the precipitated B.C.C. accumulates. When the reaction proceeds in a large volume, as, for example, at the surface of a paint in the open sea, B.C.C. is or is not formed, depending presumably on whether its solubility is exceeded in the neighborhood of the surface. Under certain conditions the reprecipitation occurs on the surface itself, resulting in the formation of a green deposit, as described in Chapter 16.

Kinetics of Dissolution of Cuprous Oxide

For studying the rate of a heterogeneous reaction occurring at the surface of a solid, it is necessary to work with a surface of known, or at least constant, area. For cuprous oxide, this is most conveniently achieved by coating a panel with a mixture of the finely divided oxide and a small amount of a binder which is both inert and strong. It may be assumed that the rate of solution of copper from such a surface is proportional to the total

area of exposed cuprous oxide surface represented by particles projecting from the binder.

In the experiments described here (6, 11, 12, 14), a mixture of 90 per cent cuprous oxide and 10 per cent Vinylite, applied in a volatile solvent, was used. The strength and insolubility of this matrix permit high rates of agitation without erosion, and the large area of exposed toxic enables

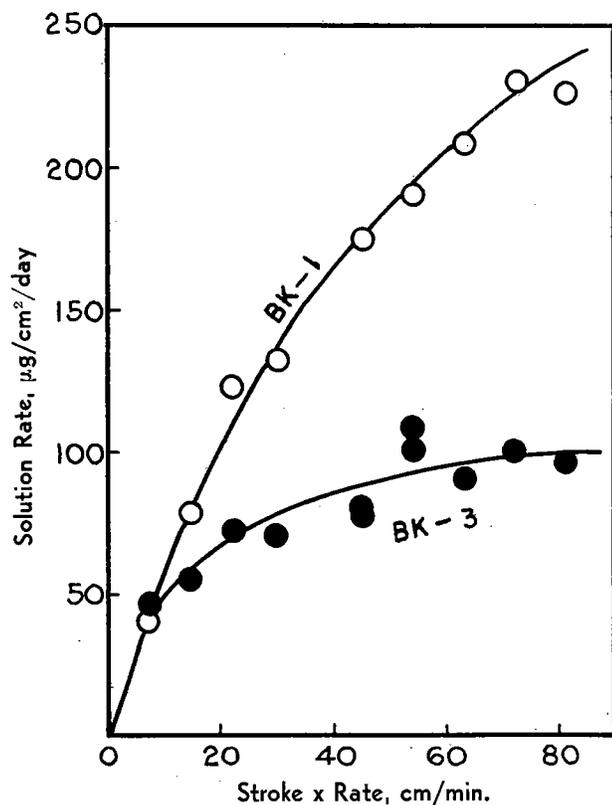
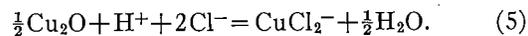


FIGURE 4. Effect of agitation on the rate of solution of cuprous oxide.

several successive experiments to be performed and compared without sensible change of the area through dissolving away of the particles. No attempt was made to estimate absolute areas. All measurements of solution rates are relative, referred to the rate in sea water under standard conditions, and are expressed as μg . copper per sq. cm. per day, the units adopted for the leaching rate.

The leaching rate of this paint, whose surface is nearly covered with cuprous oxide particles (8), and is therefore presumably qualitatively similar to a hypothetical surface of pure cuprous oxide, is about $250 \mu\text{g}$. per sq. cm. per day in sea water under standard conditions—twenty-five times the minimum effective leaching rate as given in Chapter 14.

The over-all reaction of the dissolution of cuprous oxide to form the complex CuCl_2^- (see Fig. 3) may be written



For elucidating the mechanism of this reaction, studies of the effects of hydrogen and chloride ions on the reaction rate are clearly of importance. Such studies have been carried out in synthetic buffer solutions rather than in sea water, which is a complicated mixture of electrolytes. However, the effects of agitation and temperature on the rate of reaction have been studied in natural sea water.

Agitation: The rate of dissolution of cuprous oxide in sea water increases with agitation (4). The behavior of two paints is shown in Figure 4. For paint BK-1, which has a high proportion of cuprous oxide and consequently a large surface area of exposed particles, the rate of dissolution has apparently not attained a maximum value under the most violent conditions of agitation employed although it appears to be approaching a

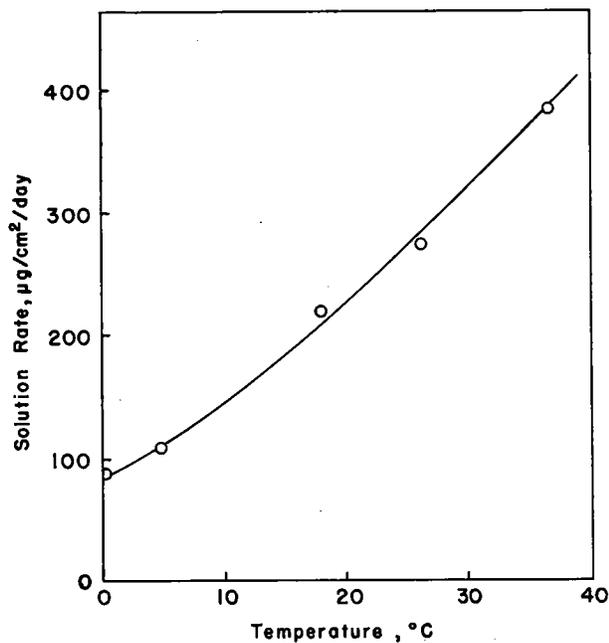


FIGURE 5. Effect of temperature on the rate of solution of cuprous oxide.

maximum. Paint BK-3, which has a smaller area of cuprous oxide exposed, has apparently attained a maximum rate. In terms of the simple Nernst theory of reactions at solid surfaces (41), this behavior means that at the maximum agitation employed, the rate of dissolution from BK-3 is entirely, and that of BK-1 largely determined by

reactions taking place at the surface; and that it is only secondarily dependent upon rates of diffusion of reactants toward or products away from the surface. The maximum agitation in these experiments was produced by a reciprocating motion, at a frequency of 120 cycles per minute, of a 3-inch by 4-inch panel through a stroke of 1.2 cm. in a direction perpendicular to its own plane, in 1,500 cc. of water.

Temperature: At high agitation, the solution rate increases by a factor of 4 between 0°C. and

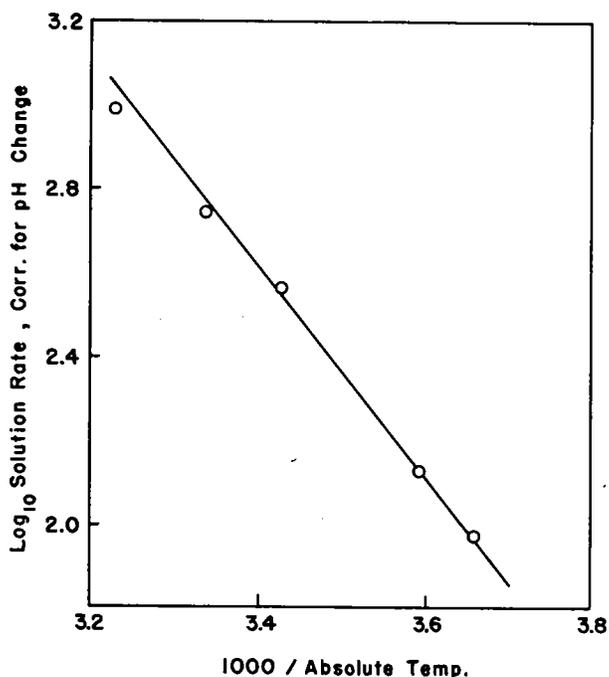


FIGURE 6. Logarithm of the rate of solution reduced to constant pH, plotted against the reciprocal absolute temperature.

36.5°C. (Fig. 5). Increasing the temperature of sea water in equilibrium with the atmosphere raises the pH, however, by expulsion of carbon dioxide, so that this does not represent the effect of temperature alone. When corrected to constant pH (assuming that the rate of solution is proportional to hydrogen ion concentration), the rates show an increase by a factor of 10 over the range studied. The logarithm of the solution rate, reduced to constant pH, is a linear function of the reciprocal absolute temperature (Fig. 6). From the slope, an activation energy of 12,000 calories per mole is calculated, representing the energy barrier of the rate-determining process in the dissolution of cuprous oxide.

Hydrogen Ion Concentration: The solution rates of cuprous oxide in borate buffers containing 0.1 molar boric acid and 0.48 molar sodium chloride

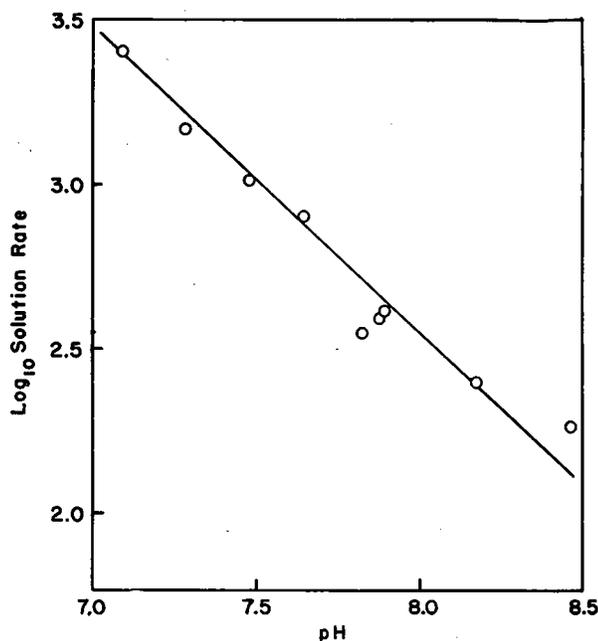


FIGURE 7. Effect of pH on the rate of solution of cuprous oxide.

(i.e., the same chloride concentration as sea water) are plotted logarithmically against the pH in Figure 7. The resulting straight line has a slope of -0.94 , which indicates that the rate of solution of cuprous oxide is proportional to the 0.94 power of the hydrogen ion concentration. This is probably not a significant deviation from an exponent of 1.0. Thus the rate is approximately proportional to the first power of the hydrogen ion concentra-

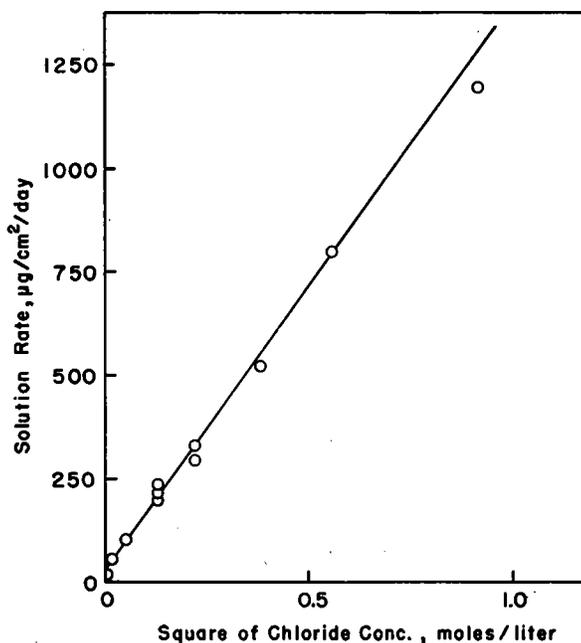


FIGURE 8. Effect of chloride concentration on the rate of solution of cuprous oxide.

tion, as would be expected if the rate-determining step involves attack by one hydrogen ion, equation (5).

Chloride Ion Concentration: The chloride ion concentration may be varied at constant ionic strength by replacing sodium chloride, mole for mole, by sodium nitrate, the pH being held constant by borate buffer. The significance of the ionic strength is explained in the paragraph below. Under these conditions, the corrected solution rate of cuprous oxide is a linear function of the *square* of the chloride concentration (Fig. 8). This would be expected if the rate-determining step involves attack by two chloride ions, equation (5). The in-

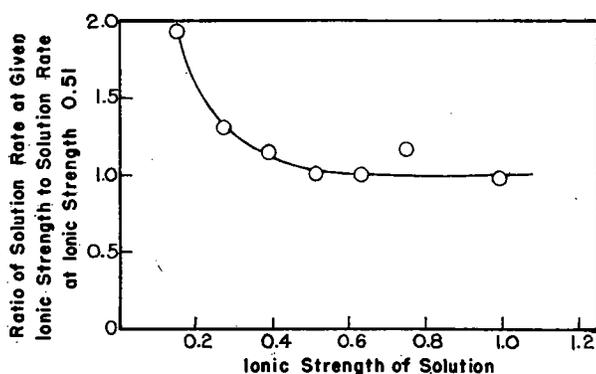


FIGURE 9. Influence of ionic strength on the rate of solution of cuprous oxide.

tercept at zero chloride corresponds to the slight dissolution which takes place in sodium nitrate-borate buffer solution in the absence of chloride.

Ionic Strength: The ionic strength of a solution of electrolytes is defined as half the sum of the concentrations of the individual ions, each multiplied by the square of its valence. Rates of ionic reactions show a marked dependence on the ionic strength; this is due to the interaction of electrical charges and not to any specific chemical factors. It is for this reason that the ionic strength was kept constant in determining the effect of chloride ion concentration.

The effect of varying the ionic strength is shown in Figure 9, where the ordinate is the ratio of the solution rate in a chloride-borate buffer of a given ionic strength to that in a solution with the same chloride concentration and an ionic strength of 0.51. The leaching rate at constant chloride concentration decreases with increasing ionic strength up to about 0.5, and thereafter changes relatively little. When sea water is diluted with distilled water, both the chloride concentration and the ionic strength are diminished, and the resultant effect is such that the rate of solution of

cuprous oxide is approximately proportional to the first power, instead of the square, of the chloride in the mixture (28).

The rate of solution in sea water, and in diluted sea water, is slightly less than in a synthetic chloride-borate-nitrate solution of the same chloride concentration and ionic strength; the ratio of the two values is about 0.8. This difference is small enough so that it may be concluded that the synthetic buffers represent an adequate system for investigating the effects of hydrogen and chloride ion concentrations and ionic strength, and that the results are applicable to sea water as well.

Mechanism of Dissolution of Cuprous Oxide: Since the rate of solution is proportional to the first power of the hydrogen ion concentration and the second power of the chloride ion concentration, it may be concluded that the process represented by equation (5) actually is the rate-determining step of the reaction. The influence of ionic strength is in agreement with this mechanism. The rate of a reaction which involves the combination of ions of opposite sign always decreases with increasing ionic strength, in dilute solutions (21, 36). It is impossible to make a quantitative comparison of the data of Figure 9 with the theories of ionic reactions, because no confident extrapolation to zero ionic strength can be made. Qualitatively, however, the results are entirely in agreement with equation (5).

Hence, the rate-determining step of the dissolution of cuprous oxide in sea water is concluded to be a simultaneous attack on the solid by one hydrogen and two chloride ions. It is possible that one hydrogen and one chloride ion approach, respectively, an oxygen and a copper atom adjacent on the cuprous oxide surface, and the collision of a second chloride ion results in detaching the complex.

The Pseudosaturation Effect: When dissolution of cuprous oxide takes place in a small volume of sea water, the sequence of reactions shown in Figure 3 does not continue indefinitely at the initial rate; the dissolution slows down to a much slower rate after the copper concentration has risen to a value between 1 and 2 $\mu\text{g. per cc.}$ The nature of this "pseudosaturation effect" is not yet understood. At pseudosaturation, the system is not truly saturated with respect to cuprous oxide (which has a solubility of 5.4 $\mu\text{g. per cc.}$ in the absence of air); nor is the concentration of any of the reactants in Figure 3 (chloride, hydrogen ion, oxygen, and carbonate) perceptibly di-

minated. Change in agitation appears to have no effect on it except to alter the time scale (Fig. 10). Furthermore, changing the proportion of the area of exposed surface to the volume of the sea water simply alters the time scale. In an experiment with many different combinations of areas and volumes (20), the concentrations of leached copper plotted against the quantity (area \times time)/volume all fell on the same curve (Fig. 11). The pseudosaturation effect is of no practical importance except that it must be avoided in leaching tests by selecting time intervals along the initial linear portion of the time-concentration curve.

The studies described in this chapter have given some information on the chemical reactions which take place between antifouling toxics and sea water, and on the solubilities and rates of solution in sea water of certain compounds of copper and mercury. This information is necessary, though not sufficient, for understanding the action of successful antifouling paints.

The various compounds of copper and mercury which have been used as toxics in antifouling paints cover an extremely wide range of solubilities in sea water. The most common successful toxic, cuprous oxide, has a solubility in the absence of oxygen of about 5 $\mu\text{g.}$ copper per cc., which is about ten times the minimum lethal concentration as given in Chapter 14. In the presence

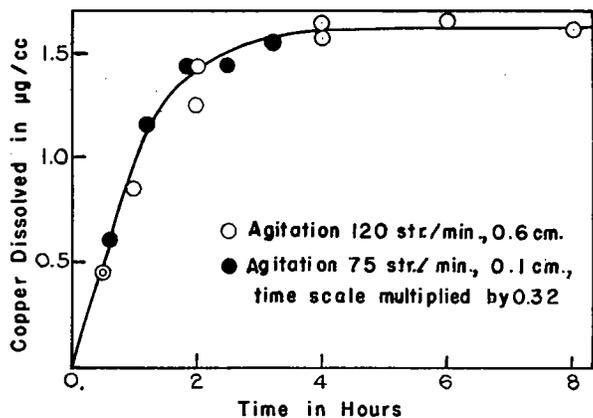


FIGURE 10. Influence of agitation on the pseudosaturation effect (Paint BK-5).

of oxygen, the dissolved copper is reprecipitated as a cupric salt whose solubility is just about at the minimum lethal level.

An effective copper toxic must have not only a solubility above the lethal minimum, but also a rate of solution above the value of 10 $\mu\text{g./cm.}^2/\text{day}$ which has been found minimal for antifouling action. The rate of solution of cuprous oxide is

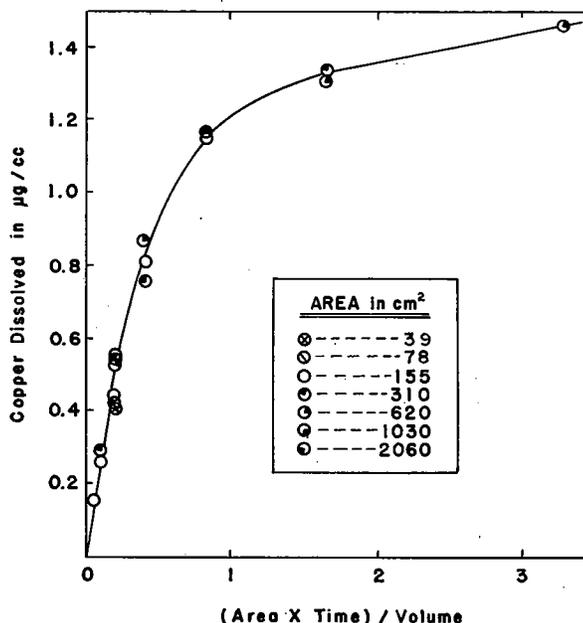


FIGURE 11. The pseudosaturation effect: concentration of leached copper as a function of (area \times time)/volume.

many times this value—of the order of several hundred $\mu\text{g./cm.}^2/\text{day}$. It is profoundly affected by alterations in temperature, salinity, and pH of the solvent, but in practice the effects of changes in these variables should lie within a reasonable factor of safety.

The leaching rate of a toxic from the surface of an antifouling paint will depend not only on the rate of solution of the pure toxic, but also on how it is compounded in the paint. The relation between leaching rate and paint composition is the subject of the following chapter.

APPENDIX: DETAILS OF CALCULATIONS Copper Compounds (3, 15, 22)

Metallic Copper. The equilibrium constant, equation (1), is quoted by MacInnes (26) from the measurements of Heinerth (18).

Cuprous Oxide. The solubility product ($\text{Cu}^+(\text{OH}^-)$) is given by Latimer (22) as 1.2×10^{-15} . Taking the ion product (22) ($\text{H}^+(\text{OH}^-)$) as 1.0×10^{-14} , we have ($\text{Cu}^+ = 0.12 (\text{H}^+)$).

The activity coefficient of cuprous ion in sea water can be estimated from the ionic strength, which is calculated from the analytical data for the various ions present. Lyman and Fleming (24) give the ionic strength of sea water corresponding to a chloride ion concentration¹ of 0.48 M. as 0.63. A reasonable value for the activity coefficient (23) of a univalent ion in this medium is 0.67. Accordingly² the concentration of cuprous ion is 0.18 (H^+), as stated in equation (2).

¹ See footnote on p. 265.

² Strictly speaking, the activity coefficient of a single ionic species has no physical meaning; this treatment implies certain conventions regarding the definition of pH, which are discussed in Reference 26, pp. 271 ff.

The enhanced solubility by chloride complex formation is now calculated from the association constants of the ions CuCl_2^- and CuCl_3^{--} . The solubility product $(\text{Cu}^+)(\text{Cl}^-)$ is quoted by Latimer as 1.85×10^{-7} . Noyes and Ming Chow (31) give the equilibrium constant for the reaction $\text{CuCl}(s) + \text{Cl}^- = \text{CuCl}_2^-$ as $(\text{CuCl}_2^-)/(\text{Cl}^-) = 0.066$. Combining this with the solubility product $(\text{Cu}^+)(\text{Cl}^-)$, we have $(\text{CuCl}_2^-)/(\text{Cu}^+)(\text{Cl}^-)^2 = 3.4 \times 10^5$. The corresponding equilibrium constant of the complex ion CuCl_3^{--} was determined (29) by v. Naray-Szabo and Szabo:

$$(\text{CuCl}_3^{--})/(\text{Cu}^+)(\text{Cl}^-)^3 = 6.9 \times 10^5.$$

In order to determine the saturation concentrations of the complexes in sea water, the activities must be replaced by concentrations and activity coefficients in these equations. Since the principal cation is sodium, this is equivalent to writing (27)

$$\frac{[\text{CuCl}_2^-] f^2_{\text{Na}(\text{CuCl}_2)}}{[\text{Cu}^+][\text{Cl}^-]^2 f^2_{\text{CuCl}} f^2_{\text{NaCl}}} = 3.5 \times 10^5$$

and

$$\frac{[\text{CuCl}_3^{--}] f^2_{\text{Na}_2(\text{CuCl}_3)}}{[\text{Cu}^+][\text{Cl}^-]^3 f^2_{\text{CuCl}} f^4_{\text{NaCl}}} = 6.9 \times 10^5$$

where the f 's are the mean activity coefficients of the electrolytes indicated. We shall assume $f = 0.67$ in all cases, as for cuprous ion (see above). Then, taking $[\text{Cl}^-] = 0.48$, we obtain

$$[\text{CuCl}_2^-]/[\text{Cu}^+] = 0.36 \times 10^5$$

$$[\text{CuCl}_3^{--}]/[\text{Cu}^+] = 0.23 \times 10^5$$

$$[\text{Cu}^I] = [\text{CuCl}_2^-] + [\text{CuCl}_3^{--}] = 0.59 \times 10^5 [\text{Cu}^+].$$

This value combined with equation (2) yields

$$[\text{Cu}^I] = 1.06 \times 10^4 (\text{H}^+), \text{ as stated in equation (3).}$$

It is worth noting here that the effect of ammonia complexes in enhancing of solubility of cuprous copper, although considerable, should be negligible in sea water compared with that of the chloride complexes.

The association constants for the complexes $\text{Cu}(\text{NH}_3)^+$ and $\text{Cu}(\text{NH}_3)_2^+$ were determined by Stackelberg and Freyhold (39).

$$(\text{Cu}(\text{NH}_3)^+)/(\text{Cu}^+)(\text{NH}_3) = 0.86 \times 10^6$$

$$(\text{Cu}(\text{NH}_3)_2^+)/(\text{Cu}^+)(\text{NH}_3)^2 = 0.74 \times 10^{11}.$$

In sea water, the concentration of ammonia is normally (32) well below 10^{-5} moles per liter. Taking this figure as a maximum, we have

$$(\text{Cu}(\text{NH}_3)^+)/(\text{Cu}^+) = 8.6$$

$$(\text{Cu}(\text{NH}_3)_2^+)/(\text{Cu}^+) = 7.4.$$

The existence of cuprous ammonia complexes in about ten times the concentration of cuprous ion is negligible compared with the existence of chloride complexes in about 10^5 times the concentration of cuprous ion.

Cuprous Chloride. The solubility product of cuprous chloride quoted, together with an assumed mean activity coefficient of 0.67 and a chloride concentration of 0.48 M,

yields for the concentration of Cu^+ in equilibrium with solid cuprous chloride in sea water the value 8.6×10^{-7} M. To obtain the total concentration of $[\text{Cu}^I]$, in the form of chloride complexes, we must multiply by the same factor of 0.59×10^5 used in the cuprous oxide equilibrium. The result is a concentration of 5.1×10^{-2} moles per liter.

Cupric Oxide and Hydroxide. The free energy of the reaction $\text{CuO} + \text{H}_2\text{O} = \text{Cu}(\text{OH})_2$ is given by Latimer (22) as 1,590 cal., and the solubility product $(\text{Cu}^{++})(\text{OH}^-)^2$ in equilibrium with cupric hydroxide is 5.6×10^{-20} . From these data, the solubility product $(\text{Cu}^{++})(\text{OH}^-)^2$ in equilibrium with CuO can be calculated to be 0.37×10^{-20} . Taking $(\text{H}^+)(\text{OH}^-)$ as 1.0×10^{-14} , we have $(\text{Cu}^{++}) = 5.6 \times 10^8 (\text{H}^+)^2$ for the solubility of the hydroxide, and $(\text{Cu}^{++}) = 0.37 \times 10^8 (\text{H}^+)^2$ for the solubility of the oxide. A reasonable value for the activity coefficient of a divalent ion in a medium of the ionic strength of sea water is 0.17. Using this value (23), we obtain for the concentration of cupric ion $[\text{Cu}^{++}] = 33 \times 10^8 (\text{H}^+)^2$ and $[\text{Cu}^{++}] = 2.2 \times 10^8 (\text{H}^+)^2$, respectively. At a pH of 8.1, this is 2.1×10^{-7} moles per liter for the hydroxide, and 1.4×10^{-8} moles per liter for the oxide.

The experiments of McDowell and Johnston (25) on the solubility of cupric oxide in distilled water gave a considerably higher value, namely, 2.9×10^{-5} moles per liter. However, the pH of solution was not measured, and it may have been slightly acidic. A pH of 6.4 would have accounted for the observed solubility, according to the above equation.

Ammonia complexes should play an even smaller part in increasing the solubility in sea water of cupric copper, than of cuprous. Stackelberg and Freyhold (39) give for the association constants of the first two cupric complexes:

$$(\text{Cu}(\text{NH}_3)^+)/(\text{Cu}^{++})(\text{NH}_3) = 0.2 \times 10^5$$

$$(\text{Cu}(\text{NH}_3)_2^+)/(\text{Cu}^{++})(\text{NH}_3)^2 = 0.95 \times 10^8.$$

Taking the concentration of ammonia in sea water as 10^{-5} moles per liter, as before, we have

$$(\text{Cu}(\text{NH}_3)^+)/(\text{Cu}^{++}) = 0.2$$

$$(\text{Cu}(\text{NH}_3)_2^+)/(\text{Cu}^{++}) = 0.01.$$

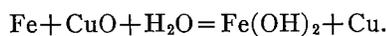
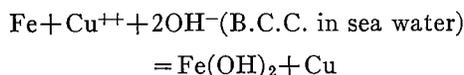
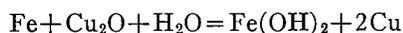
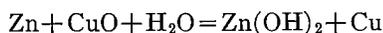
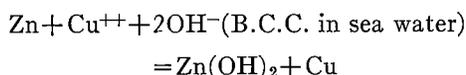
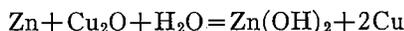
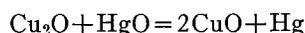
The ammonia complexes are thus capable of increasing the solubility of cupric copper in sea water only about 20 per cent. The effect of chloride complexes of cupric ion, if at all appreciable in sea water, is undoubtedly (39) far smaller than that observed for cuprous ion, with its associated 60,000-fold enhancement of solubility.

Cupric Carbonate. Kelley and Anderson (19) doubt if solubility measurements have been made on any material known definitely to have the composition of cupric carbonate, CuCO_3 , but assuming that the material used by Haehnel (16) had this composition, they have calculated the solubility product $(\text{Cu}^{++})(\text{CO}_3^{--}) = 2.36 \times 10^{-10}$. The concentration of carbonate ion in sea water at pH 8.2 is given by Moberg *et al.* (30) as 0.24×10^{-3} moles per liter, with the surprisingly low activity coefficient of 0.015, making the activity $(\text{CO}_3^{--}) = 0.36 \times 10^{-5}$. This figure, with the solubility product above, and the value of 0.17 for the activity coefficient of copper ion, as used before, gives for the concentration of copper in equilibrium with copper carbonate in sea water $[\text{Cu}^{++}] = 3.9 \times 10^{-4}$ moles per liter, or 25 μg . copper per cc. This does not, of course, apply to B.C.C.

Mercury, Zinc, and Iron. The free energies used in the calculations are taken from Latimer (22), as follows:

Cu ₂ O	- 35,150 cal.
CuO	- 30,400
HgO	- 13,940
Zn(OH) ₂	- 132,000
Fe(OH) ₂	- 115,700
Fe(OH) ₃	- 166,300.

From these values, together with the experimentally determined concentration of Cu⁺⁺ in equilibrium with B.C.C., and the normal pH of sea water, it is found that each of the following reactions is accompanied by a large decrease in free energy:



Accordingly these reactions will tend to take place spontaneously.

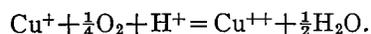
Mercury Compounds

Mercurous Chloride. The equilibrium constant for the reaction $\text{Hg} + \text{Hg}^{++} = \text{Hg}_2^{++}$ is given by Latimer as 81, and the solubility product of Hg_2Cl_2 , $(\text{Hg}_2^{++})(\text{Cl}^-)^2$, as 1.1×10^{-18} . The dissociation constant of the weak salt HgCl_2 is given by Sherill (38) as 10^{-14} . From these data, neglecting activity coefficients, the concentration of dissolved mercuric mercury in equilibrium with mercurous chloride and metallic mercury is calculated to be 1.4×10^{-6} moles per liter, or 0.3 μg . per cc.

Mercuric Oxide. The solubility product $(\text{Hg}^{++})(\text{OH}^-)^2$ in equilibrium with HgO is given by Latimer (22) as 2.7×10^{-26} . At pH 8.1, therefore, neglecting activity coefficients, the concentration of mercuric ion should be 1.7×10^{-14} . Taking the dissociation constant of HgCl_2 to be 10^{-14} , and the chloride concentration of sea water 0.48 M, we obtain for the concentration of dissolved mercury 0.39 mole per liter, or 78,000 μg . per cc.

Processes of Dissolution and Oxidation

The over-all reaction for the oxidation of cuprous copper by oxygen may be represented by the equation:



The oxidation-reduction potential Cu^+ , Cu^{++} is given by MacInnes as -0.159 volt. The potential of the oxygen electrode, corresponding to the reaction $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4e$, is given by Latimer as -0.401 volt. From these

data, taking the ionization constant of water as 10^{-14} , the following equilibrium constant is derived:

$$(\text{Cu}^{++})/(\text{Cu}^+)(\text{H}^+)(p_{\text{O}_2})^{1/4} = 10^{18.1}$$

where p_{O_2} is the partial pressure of oxygen in atmospheres. At a pH of 8.1, and at the atmospheric partial pressure of oxygen of 0.21, this yields for the equilibrium ratio of $\text{Cu}^{++}/\text{Cu}^+$ in aerated sea water the value 0.68×10^{10} .

The free energy of the reaction $\text{Cu} + \text{Cu}^{++}$ (B.C.C., in sea water) $+ 2\text{OH}^-$ (sea water) $= \text{Cu}_2\text{O} + \text{H}_2\text{O}$ is calculated from the data already quoted to be -9,000 cal.

The free energy of the reaction $\frac{1}{2}\text{Cu}_2\text{O} + \frac{1}{4}\text{O}_2(\text{atm.}) + 2\text{H}^+$ (sea water) $+ \text{carbonate}$ and hydroxide (sea water) $= \text{B.C.C.} + \text{H}_2\text{O}$ is calculated to be -8,600 cal.

The free energy of the reaction $\text{Cu} + \frac{1}{2}\text{O}_2(\text{atm.}) + 2\text{H}^+$ (sea water) $+ \text{carbonate}$ and hydroxide (sea water) $= \text{B.C.C.} + \text{H}_2\text{O}$ is calculated to be -26,000 cal.

Accordingly, these three reactions will tend to take place spontaneously.

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