OXIDATION-REDUCTION POTENTIAL IN SEA WATER

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In bacteriological studies much attention is now given to oxidation-reduction potentials. The systems studied have usually potentials at least 0·4 V. below that of the reversible oxygen electrode, are reasonably well poised and obey laws thermodynamically deduced. Owing to the irreversibility of the oxygen electrode and to difficulties of measurement no such attention has been given to oxidation-reduction potentials in sea water or other aerated natural waters. Nevertheless, such waters can exert a potential which may be of considerable biological, geological and industrial importance.

One record only of the oxidation-reduction potential of sea water was found in the literature, 0·25 V. recorded incidentally by Reiss & Vellinger (1929) in the course of a study of sea-urchin eggs. Of the 2 mg./l. of organic carbon which Keys, Cristensen & Krogh (1935) have found in sea water, practically nothing is known beyond the fact that it is somewhat inert, how inert we do not know. Since the oxidation-reduction system based on dissolved oxygen appears to be much the most likely to be that giving poise to the water, a theoretical examination of the system was made. Certain thermodynamic properties of sea water, a knowledge of which is required for other investigations, are also treated at some length.

The reaction at an oxygen electrode is:

$$O_2 + 2H_2O + 4\epsilon = 4OH^-.$$

If this reaction can take place reversibly, in the thermodynamic sense, the oxidation-reduction potential of any oxygen electrode, E^h, will be given by

$$E^h = E^\circ - \frac{RT}{4F} \ln \frac{a_{OH^-}{}^4}{a_{O_2}}. \qquad \ldots\ldots(1)^*$$

E° is the potential, relative to the normal hydrogen electrode, which should be realized at an inert metal electrode saturated with oxygen at 1 atm. pressure acting in an electrolyte containing hydroxyl-ion at unit activity (nearly equi-

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* On modern chemical theory a uni-univalent strong electrolyte, dissolved in water, dissociates practically completely into ions each having concentration, m_x. Owing to electrostatic forces between the ions, not all at any instant are able to participate actively in chemical reactions. That part which can do so is termed the activity, a_x, and is related to the concentra tion by the activity coefficient, γ_x:

$$a_x = \gamma_x m_x.$$

Activity and concentration are measured in the same units. The activity coefficient is a number without dimensions. The activity concept is used wherever it applies so that, for instance, K_w is defined in terms of activities and not, as in most of the earlier work, in terms of concentrations. The system of notation here followed is that of Lewis & Randall (1923).

valent to a normal solution of sodium hydroxide). For reasons which will be made clear below, this standard potential of the oxygen electrode is not realizable in practice.

Equation (1) may be rewritten

$$\mathrm{E^h} = \mathrm{E}^\circ - \frac{\mathrm{RT}}{\mathrm{F}} \ln \frac{a_{\mathrm{OH^-}}}{\sqrt[4]{p_0}}, \qquad \text{......(2)}$$

so that to evaluate $\mathrm{E^h}$ we need to know E°, p_0 and $a_{\mathrm{OH^-}}$. These quantities will be examined in turn.

The Standard Oxygen Electrode Potential, E°

At 25° C. E° has been calculated to be 0·3976 V. (Lewis & Randall, 1923, p. 487). For other temperatures E° has been computed from the free energies of formation, and of ionization, of water. We may write three thermodynamic equations, where ΔF°_T represents the increase in free energy of the system concerned with reference to the standard states of the components at the temperature T° abs.:

$$\Delta F^\circ_T$$

H_2O (liquid) $= H^+ + OH^-$ ... ... x ......(3)

H_2 (gas) $+ \frac{1}{2}O_2$ (gas) $= H_2O$ (liquid) ... ... y ......(4)

$2H^+ = H_2$ (gas) ... ... 0 ......(5)

Multiplying (3) by 2, adding (4) and (5) and then dividing by 2 we get

$\frac{1}{4}O_2$ (gas) $+ \frac{1}{2}H_2O$ (liquid) $= OH^-$ ... ... $x + \frac{y}{2}$ ......(6)

From equation (6) E°_T may be calculated by means of (7):

$$\mathrm{E}^\circ_T = -\frac{\Delta F^\circ_T}{\mathrm{F}}. \qquad \text{......(7)}$$

According to *International Critical Tables*, Vol. VII, p. 232, the free energy of ionization, x, at any temperature, T° abs., may be calculated from the relation

$$x = 29210 + 53 \ln T - 335{\cdot}86\, T. \qquad \text{......(8)}$$

Similarly, the free energy of formation

$$y = -70650 - 8{\cdot}0 \ln T + 92{\cdot}84\, T. \qquad \text{......(9)}$$

From these data the free energy changes and electrode potentials relevant to equation (6) have been calculated at temperatures between 0° and 25° C. (Table I). Thus the value of E° decreases linearly by 0·0016 V./degree.

Table I

			Oxygen system, equation (6)	
t° C.	x cal.	$y/2$ cal.	$\Delta F^\circ = x + y/2$ cal.	E°
0	+18684	−28775	−10091	+0·4373
5	+18760	−28676	− 9916	+0·4298
10	+18843	−28576	− 9733	+0·4218
15	+18926	−28476	− 9550	+0·4139
20	+19013	−28379	− 9366	+0·4059
25	+19105	−28280	− 9175	+0·3976

OXYGEN ACTIVITY OR PARTIAL PRESSURE, p_0

Due to the presence of water vapour the partial pressure of oxygen in saturated air varies slightly, but for our present purpose it is sufficient to take a round figure, 0·206 atm., for the partial pressure of oxygen over the sea. The partial pressure of oxygen in sea water at 100 % saturation must be identical with this and measures the oxygen activity. Sea water at various degrees of oxygen saturation will therefore have the following values of p_0 and $\sqrt[4]{p_0}$:

% saturation	p_0	$\sqrt[4]{p_0}$
100	0·206	0·674
50	0·103	0·567
10	0·0206	0·379
1	0·0021	0·213

THE THERMODYNAMIC IONIC PRODUCT, K_w, AND HYDROXYL-ION ACTIVITY, a_{OH^-}

The thermodynamic ionic product, $K_w = \frac{a_{H^+}\, a_{OH^-}}{a_{H_2O}}$, is independent of the presence of solutes, and in consequence in sea water the product of the activities of hydrogen and hydroxyl ions is the same as in pure water except in so far as the presence of salts alters the activity of the undissociated water. However, in moderately concentrated solutions of strong electrolytes, the product of the activity coefficients, $\gamma_{H^+}\, \gamma_{OH^-}$, decreases so that in a solution of sodium chloride, having the same ionic strength as sea water, $\gamma_{H^+}\, \gamma_{OH^-} = 0{\cdot}51$. Therefore

$$m_{H^+}\, m_{OH^-} = \frac{K_w\, a_{H_2O}}{\gamma_{H^+}\, \gamma_{OH^-}} = \frac{K_w\, a_{H_2O}}{0{\cdot}51},$$

that is, if we assume for the moment that the activity of the water a_{H_2O} is unity, the stoichiometric or molal ionic product will be about twice that in pure water. However, *p*H (so called) determined either electrometrically or with indicators is a measure of activity rather than of concentration of hydrogen ions and is more precisely denoted by pa_H (Sørensen & Linderstrøm-Lang; cf. Clark, 1928, p. 479). Again the majority of physico-chemical computations in aqueous media involve activities of hydrogen and hydroxyl ions and not molal concentrations. Since the uncertainty as to the value of the thermodynamic ionic product, $K_w = \frac{a_{H^+}\, a_{OH^-}}{a_{H_2O}}$, has been removed by the highly accurate and consistent work of Harned and his collaborators, this may be applied as it stands to our sea-water problems.

The activity of the water itself, a_{H_2O}, which has still to be considered, may be evaluated from the depression of the freezing-point of sea water below pure water, Δt°, by means of the Lewis & Randall equation (1923, p. 284):

$$\log_{10} a_{H_2O} = -0{\cdot}004211\, \Delta t - 0{\cdot}0000022\, \Delta t^2. \qquad \ldots\ldots(10)$$

The necessary freezing-point data were determined by Matthews (1923, p. 667). For a range of chlorinities the values of a_{H_2O} calculated from equation (10), are given in Table II.

Table II. THE ACTIVITY OF WATER, a_{H_2O}, IN SEA WATER

Cl ‰	Δt °C.	a_{H_2O}
0	0·000	1·0000
5	−0·483	0·9953
10	−0·969	0·9906
15	−1·466	0·9858
18	−1·769	0·9830
19	−1·872	0·9820
20	−1·974	0·9810

The product of the ionic activities, $a_{H^+}\,a_{OH^-}$, is equal to K_w only when a_{H_2O} is unity as in pure water. In any aqueous solution the product

$$K'_w = a_{H^+}\,a_{OH^-} = K_w\,a_{H_2O}; \qquad \ldots\ldots(11)$$

$$\therefore\ pK'_w = pK_w - \log_{10} a_{H_2O}. \qquad \ldots\ldots(12)$$

In Table III are given values of pK_w calculated from Harned & Hamer's data (1933) and values of pK'_w for sea water of 35 °/₀₀ salinity and a range of temperatures calculated from equation (12). It will be seen that the difference between pK_w and pK'_w is of importance only for work of the very highest accuracy. Since from equation (11)

Table III. pK_w FOR PURE WATER AND pK'_w AND SOME VALUES OF pa_{OH} IN SEA WATER OF 35 °/₀₀ SALINITY AT A RANGE OF TEMPERATURES

		Sea water at 35 °/₀₀ salinity		
			pa_{OH} at	
t° C.	Pure water pK_w	pK'_w	$pa_H = 8·000$	$pa_H = 8·300$
0	14·939	14·947	6·947	6·647
5	14·731	14·739	6·739	6·439
10	14·533	14·541	6·541	6·241
15	14·345	14·353	6·353	6·053
20	14·167	14·175	6·175	5·875
25	13·997	14·005	6·005	5·705
30	13·832	13·840	5·840	5·540

$$pa_{OH} = pK'_w - pa_H,$$

the value of pa_{OH} for a given sample of sea water can now be found with an accuracy equal to that of the measurement of pa_H, providing that the salinity is known approximately and that the temperature is known to within 0·1° C. Values of pK_w for intermediate temperatures may be found either by graphical interpolation or with great precision from Harned & Hamer's equation (1933):

$$pK_w = \frac{4787\cdot3}{T} + 7\cdot1321 \log_{10} T + 0\cdot010365\,T - 22\cdot801. \qquad \ldots\ldots(13)$$

THE THEORETICAL OXIDATION-REDUCTION POTENTIAL

Using these values for E°, p_0 and a_{OH^-}, the following theoretical values for the oxidation-reduction potential of the oxygen system have been calculated by equation (2) (Table IV):

Table IV. THEORETICAL OXIDATION-REDUCTION POTENTIAL OF THE OXYGEN SYSTEM IN VOLTS

	$O_2 = 100\%$ saturation		$O_2 = 10\%$ saturation	
t° C.	*p*H 8·00	*p*H 8·30	*p*H 8·00	*p*H 8·30
0	0·804	0·788	0·790	0·774
15	0·767	0·750	0·753	0·735
25	0·742	0·724	0·727	0·710

Thus, decreasing the percentage saturation of oxygen from 100 to 10% or raising the *p*H by 0·30 unit will each lower the potential by 0·02 V. only. Similarly, raising the temperature by 10° C. will lower the potential by 0·025 V. Thus variations in oxygen concentration, *p*H and temperature within the limits usually found cannot affect the potential by more than about 0·10 V. at most.

We see, therefore, that if the oxidation-reduction potential of sea water is due to a reversible oxygen system, then the potential will lie between 0·7 and 0·8 V. This theoretical discussion has served to clear the ground by giving us values for the reversible potential, E^h, which we can now discuss further in the light of certain peculiar properties possessed by the oxygen electrode.

THE IRREVERSIBLE OXIDATION-REDUCTION POTENTIAL OF SEA WATER

Of prime importance is the practical difficulty involved in measuring the potential at an oxygen electrode. Oxygen electrodes tend to be irreversible, do not obey the thermodynamic relationship between electrode potential and partial pressure of oxygen, and are readily polarized even by minute currents. From a careful examination Hoar (1933) concluded that the platinum used in the electrode forms an oxide film, but that the irreversibility results not so much from the presence of this film but, due to crack formation, to its permeability to the electrolyte which results in self-polarization.

Due to this irreversibility, determinations of the potential by different workers vary considerably. Hoar (1933) has found the potentials of a saturated oxygen electrode against a hydrogen electrode in the same solution, E_β, which should be typical of results obtained with a bright platinum electrode under good working conditions. The difference between the reversible and irreversible potentials of an oxygen electrode will be the same, no matter what half-cell is used as reference electrode so that

Reversible potential against hydrogen in same solution, E_α, *minus* Irreversible potential against hydrogen in same solution, E_β; *equals* Reversible potential against normal hydrogen electrode, E_γ, *minus* Irreversible potential against normal hydrogen electrode, E_δ.

$$\therefore\ E_\delta = E_\gamma - E_\alpha + E_\beta.$$

In Table V Hoar's observed values of E_β are given in column 3 together with the calculated theoretical values of E_γ. Since $E_\alpha = 1{\cdot}2256$ V. (Lewis & Randall, 1923, pp. 408 and 487), E_δ can be readily computed. The *p*H values in $N/10\ H_2SO_4$ and $N/10$ NaOH have been calculated from the activity coefficients given by Harned & Hamer (1935) and Harned & Hecker (1933).

Table V

1 Solution	2 *p*H (calc.)	3 Irreversible potential against hydrogen electrode in same solution (Hoar; obs.) E_β	4 Reversible potential against hydrogen electrode in same solution (theoretical) E_γ	5 Irreversible potential against normal hydrogen electrode (calc. from cols. 3 and 4) E_δ
$N/10\ H_2SO_4$	1·47	0·828	1·168	0·770
$M/15$ phosphate buffer	7·0	0·936	0·813	0·523
$N/10$ NaOH	12·88	0·981	0·457	0·212

Dr W. R. G. Atkins has very kindly undertaken determinations of the oxidation-reduction potential of sea water, E^h, using bright platinum electrodes which had barely cooled, after having been heated to redness right in a methylated spirit flame. The potentials were measured against a calomel ($N/10$ KCl) half-cell which has a potential against the normal hydrogen electrode of 0·338 V. He found that the potential of sea water lies in the neighbourhood of 0·43 V. Determinations were also made of the E^h and *p*H of sea water acidified with varying amounts of hydrochloric acid. Following the immersion of the electrodes the potential fell away rapidly so that the initial readings were taken as most nearly correct. After the apparatus had been improved enabling several seconds to be saved before making this initial reading, a second series was made which lay somewhat higher than the first. Values of E^h corresponding to the experimental *p*H values have also been read from a curve constructed from Hoar's data (Table V) and are included in Table VI for comparison with Atkins' results which have been rounded off to the nearest centivolt owing to the uncertainty inherent in the measurement. It will be seen that the agreement is considerably better than might have been expected. Furthermore, Heintze (1935) has collected all the evidence available on the E^h of soil solutions and has shown that at *p*H 8·0 most of the values fall between E^h 0·4 and 0·5 V., and that the potential of a standard buffer solution at *p*H 8 lay at about 0·45 V. Thus these measurements also were those of an irreversible oxygen electrode.

It is clear, therefore, that in sea water, the oxidation-reduction potential is governed solely by this irreversible oxygen system. The conclusion is almost certainly of general applicability, so that it should be unnecessary to repeat the

Table VI. OXIDATION-REDUCTION POTENTIAL OF SEA WATER, E^h, IN VOLTS AT A RANGE OF *p*H VALUES

*p*H	E^h of oxygen electrode in water at 25° C. (derived from Hoar's results)	E^h of an air electrode in sea water at 15° C.	
		1st series	2nd series
1·09	0·79	0·78	—
2·05	0·75	0·75	0·80
2·14	0·75	0·70	0·76
2·58	0·73	0·69	0·76
3·09	0·71	0·66	0·73
3·55	0·69	0·67	0·72
6·87	0·53	0·57	0·47
7·14	0·52	0·45	0·45
8·15	0·46	0·42	0·44

The potential in water saturated with oxygen at 25° C. should lie close to the potential in water saturated with air at 15° C. If the reversible laws can be applied:

$$E^h \text{ (air, } 15° \text{ C.)} = E^h \text{ (} O_2 \text{, } 25° \text{ C.)} - 0{\cdot}021 + 0{\cdot}002\, pH.$$

work on sea water from other regions unless there is a strong suspicion that reducing substances able to impart poise to sea water are present.

Although the divergence of the experimental from the theoretical potential is due in the first place to the formation of an oxide film on the electrode, Hoar considers that even with a perfectly inert metal electrode, should such ever be found, the theoretical reversible potential could never be quite reached owing to the extreme sluggishness of the reaction: oxygen $\rightleftharpoons$ hydroxyl-ion. Much more work is required before this point of view, which is not in complete accord with present ideas of ionic reactions, may be taken as established.

Oxidation-reduction potentials lower than that of the irreversible oxygen electrode may well be found off the west African coast in 10° S. latitude, where Wattenberg (1933) found partial pressures of carbon dioxide more than four times that in the atmosphere and where extensive breakdown of organic material is taking place. If the irreversible oxygen potential should be found to prevail in that or similar regions, it may be expected to prevail throughout the open ocean. Since conditions of temperature, partial pressure of carbon dioxide (P_{CO_2}) and *p*H are as extreme at Meteor Station 188 as at any place that has as yet been fully investigated it is of interest to evaluate the *p*OH (strictly speaking, pa_{OH}) *in situ* and the reversible oxidation-reduction potential based on the oxygen system (Table VII). In spite of the great depletion of oxygen around 400 m. the temperature remains the dominant factor and the reversible potential increases steadily right through the stratum of stagnant water.

Reactions which depend on the activity of hydroxyl ion *in situ* (pOH_t) will be affected by the change in pK'_w as well as in pH_t. Thus although the values of pH_t at 25 and 1980 m. are similar the values of pOH_t differ by 0·75 unit. On account of this, ferric hydroxide, for example, would be more than 200 times as soluble at the greater depth and, in general, solubilities dependent on *p*OH will be much affected.

Table VII. STATION 188 OF THE METEOR EXPEDITION ON SEPTEMBER 5 1926 IN 8° 58·0′ S., 8° 57·7′ E. (Wattenberg, 1933, pp. 72 and 292). Columns marked with an asterisk contain Wattenberg's data; the remaining columns include data calculated from these

True depth m.*	Temp. °C.*	$P_{CO_2} \times 10^4$*	pH_t†*	$p'K_w$	pOH_t†	O_2 c.c./l.*	E° V.	E^h (reversible) V.
0	22·4	3·2	8·15	14·10	5·95	4·81	0·4017	0·740
25	21·0	3·7	8·09	14·14	6·05	4·52	0·4043	0·746
50	16·2	6·1	7·91	14·31	6·40	1·40	0·4120	0·761
100	14·3	6·9	7·86	14·38	6·52	1·40	0·4148	0·768
195	12·2	8·4	7·78	14·46	6·68	0·88	0·4183	0·775
395	8·5	12·2	7·62	14·60	6·98	0·45	0·4242	0·788
590	5·8	10·7	7·66	14·71	7·05	1·43	0·4285	0·800
785	4·5	8·2	7·76	14·76	7·00	2·72	0·4306	0·801
990	4·1	7·1	7·81	14·78	6·97	3·22	0·4312	0·801
1980	3·3	4·1	8·01	14·81	6·80	5·06	0·4325	0·793

† These quantities would be more strictly written as pa_{H_t} and pa_{OH_t}.

BIOLOGICAL IMPLICATIONS

The implications of the irreversibility of the oxygen electrode system for a study of sea water as a biological environment must now be discussed. Two facts are clear: (i) under no circumstances will the oxygen system function strictly reversibly, but (ii) we are not concerned with a metal electrode which may form porous oxide films. From a system functioning irreversibly less free energy can be got than from the same system functioning reversibly. In consequence the effective oxidation potential will be lower, for this is merely another way of describing the free-energy state of the system, but it does not follow that the biologically effective potential need be as low as that found with a platinum electrode. The effective E^h may vary considerably with the system under investigation according to the greater or less degree of irreversibility of its reaction with oxygen.

The ferric-ferrous system, which is of importance for other investigations in progress here, is recognized as not being very sensitive to oxygen. It has been most studied in the *p*H range 0–2, where its oxidation-reduction potential is independent of *p*H and lies only just below that of the irreversible oxygen electrode. The driving force of the reaction of dissolved oxygen with ferrous-ion is therefore small. Moreover, the resulting ferric-ion collects in solution tending to reverse the direction of the reaction. In our problem we are concerned with iron in sea water at *p*H 8; at this *p*H the very low solubility of ferric hydroxide results in the removal of ferric-ion from solution as fast as it is formed. In consequence the tendency for ferrous-ion to be oxidized is enormously increased, and solutions of ferrous salts are very unstable and a state approaching equilibrium is rapidly attained. It appears reasonable to extend these conceptions to the very small amounts of iron present in sea water.

This paper has been developed for the particular case of sea water, but the treatment is general and may be extended to all aerated natural waters. In many cases where reducing substances are definitely known not to be present, it may well be sufficiently accurate to read off the irreversible potential from a curve constructed from Hoar's data and to calculate the theoretical reversible potential from equation (2). The potential for biological studies will lie somewhere between these limits; no electrometric measurements can give more information than this. Whilst there must always be some uncertainty in any work involving the oxidation-reduction potential of the oxygen system it is felt that, even so, knowledge of much importance on the behaviour of natural waters may be obtained. In many cases, such as those involving solubilities and the behaviour of multivalent metals, information may be obtained as to what conditions are and what are not possible. Such a case, the behaviour of iron in sea water, will be discussed in a subsequent paper.

SUMMARY

The activity of oxygen in sea water and standard oxygen electrode potentials at a range of temperatures have been computed.

Accurate values for the thermodynamic ionic product of water, K_w, found by Harned & Hamer, have been applied to the calculation of the activity of hydroxyl ion in sea water from *p*H measurements.

The activity of water in sea water has been computed from the lowering of the freezing-point.

From these data the theoretical reversible oxidation-reduction potential of sea water has been calculated.

Typical data for the irreversible potential in the *p*H range 1–8 have been derived from Hoar's results with which experimental determinations made by Dr Atkins agree. Thus the oxidation-reduction potential of sea water is controlled solely by the oxygen system.

The biological implications of the reversible and irreversible (at platinum electrode) potentials is discussed. Under no circumstances will the oxygen system function strictly reversibly, but on the other hand we are not necessarily concerned with metal electrodes which form porous oxide films. It is considered that in sea water the potential effective in systems of biological importance may lie anywhere between 0·43 and 0·75 V., the irreversible (Pt electrode) and reversible potentials.

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