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Corrosion Rate Trajectories of Concreted Iron and Steel Shipwrecks and Structures in Seawater—The Weins Number

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ABSTRACT

The Weins number (Wn) concept is proposed to predict the long-term corrosion rate of wrought iron and steel in seawater for variable marine environments. Plotted as a function of reciprocal absolute temperature, Weins numbers generate a linear plot from which the corrosion rates are calculated when temperature, oxygen concentration, and concretion thickness are known. Application of the theory of absolute reaction rates is described.

KEY WORDS: corrosion rate, marine archaeology, seawater, steel, Weins number, wrought iron

INTRODUCTION

A survey of National Oceanic and Atmospheric Administration's (NOAA) automated shipwreck and information system has identified more than 12,000 sites in U.S. coastal waters.¹ More than 3,800 ships sunk in the Pacific theater during World War II (WWII) have been mapped; an estimated 170 are believed to be oil tankers.² Worldwide, more than 8,500 potentially polluting shipwrecks containing perhaps as much as

20 million tons of oil have been identified; more than 6,000 of these vessels were lost during WWII.³ Along with site identification, it is also necessary to know the structural state of these wrecks and their potential for environmental, human, and economic risk.⁴

Assessment of hull deterioration typically occurs after oil release has taken place, "continuing a reactive strategy to oil spill response."¹ A "preventive" approach, allowing for mitigation or salvage of oil prior to release, results in an "active" response strategy. A typical example of a "preventive" response strategy is the USS *Arizona* Preservation Project conducted by the National Park Service (NPS) Submerged Resources Center ([SRC] Lakewood, Colorado). Using corrosion and other site data, finite element modeling on the USS *Arizona* predicts a substantial time interval for contingency planning in the event of a major fuel oil release in the confined waters of Pearl Harbor.⁵ Environmental concerns go back to the Japanese attack at Pearl Harbor on December 7, 1941. Just prior to December 7, 1941, the USS *Arizona* was topped to near capacity of just over 6,000 tons (5.0×10^6 kg), including emergency fuel oil. Although a significant amount of fuel oil was released into the harbor from the USS *Arizona* during the attack, an estimated 2,500 to 3,000 tons of fuel oil (2.3 to 2.7×10^6 kg) remains in bunkers or trapped in compartment overheads. A principal research domain of the USS *Arizona* Preservation Project was developing methods that could be applied to other legacy steel vessels containing hydrocarbons that potentially would affect the environment.

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The Weins number draws upon the principle of the dimensionless ratio utilized in engineering design of fluid flow and thermal systems. By reference to a temperature-dependent Weins number profile, the corrosion rate is estimated knowing concretion thickness, temperature, and percent dissolved oxygen. Significance of the ratio in marine corrosion of concreted Fe and steel was first revealed by comparison of the directly measured in situ corrosion rate on the USS *Arizona* submerged in shallow seawater and the Japanese Midget Submarine sunk by the USS *Ward* on December 7, 1941, submerged in 1,300 ft (400 m) of water.⁶⁻⁷ Corrosion rate calculations were based upon in situ measurements and concretion analysis comparable to the *Arizona*. The ratio of the *Arizona* corrosion rate, when divided by a theoretical rate calculated from oxygen available at the metal surface, was nearly 20 times greater than the corresponding ratio of the midget submarine. While this difference is an "indirect" response to site water depth, it is in "direct" response to site environmental parameters including temperature, O₂ concentration, O₂ solubility, viscosity, salinity, and O₂ diffusivity, and to the thickness of the overlying concretion. This paper presents the derivation of the Weins number and illustrates how it is applied to estimate corrosion rate and time-to-failure.

DEFINITIONS AND DERIVATION

The Weins number (Wn) is defined by the dimensionless ratio:

$$Wn = i_{\text{corr}} / i_{\text{aoer}} \quad (1)$$

where i_{corr} is measured (actual) corrosion rate and i_{aoer} is apparent oxygen-driven corrosion rate calculated from the rate of molecular O₂ diffusion through the water phase retained in concretion voids.

Temperature Dependence

As an electrochemical reaction, corrosion is a thermally activated process; hence, the rate is temperature-dependent. The Weins number, though constant at constant temperature, incorporates selected variables to compensate for environmental conditions at each site and is expressed in a semi-logarithmic profile according to the absolute reaction rate theory:⁸⁻⁹

$$\ln[Wn] = \ln[Wn(o)] - \Delta H^\ddagger / RT \quad (2)$$

where Wn(o) is frequency factor, $\Delta H^\ddagger$ is activation enthalpy (cal/mole or J/mole), T is absolute temperature (K), and R is the gas constant (cal or J/mole/K).

Corrosion Rate

Corrosion research on the USS *Arizona* led to the pioneering development of the minimum impact meth-

odology, concretion equivalent corrosion rate (CECR), to determine the corrosion rate of the steel wreck at positions on the hull other than the midship area where metal coupon samples were taken.¹⁰⁻¹² Equation (3) expresses the corrosion rate in terms of CECR:

$$i_{\text{corr}} = i_{\text{CECR}} = K\rho d (w/o \text{ Fe}) / t \quad (\text{mmpy or mpy}) \quad (3)$$

where ρ is concretion density (g/cm³), d is concretion thickness (cm), w/o Fe is total Fe in weight percent, t is time submerged (y), K = 0.02 (mmpy) (K incorporates reciprocal iron density and a correction factor of 1.6), and K = 0.80 (mpy or [in/1,000]) per year.

Because steel does not passivate in seawater, corrosion is relatively uniform over the surface, and irregularities are gradual and not sharply penetrating as would be expected if pitting were to occur. Long-term corrosion rate, determined from the difference between archival plate thickness and laboratory measured coupon thickness, was the basis for the correction factor incorporated into Equation (3). For deep sites where submersibles use robotic arms to perform tasks, CECR was the primary experimental technique utilized to determine the corrosion rate. Determination of corrosion rate from concretion analysis obviates the necessity of conducting very expensive and difficult coupon collection from hulls potentially containing hydrocarbons. Concretions can be collected remotely with the equivalent of an underwater hole saw that captures the analytical sample.

Available Oxygen Corrosion

Assuming available O₂ at the metal/concretion interface is sourced only from molecular O₂ diffusion through the water phase trapped in the concretion, each gram-mole of O₂ available at the metal/concretion interface oxidizes two gram-atoms of iron. Oxygen availability as a result of charge transfer is assumed to be negligible compared to diffusion transport in the water phase. i_{aoer} is calculated from the electrical equivalent of Fick's first law:

$$i_{\text{aoer}} = nFD(O_2)(\Delta C(O_2) / d) \quad (\text{mmpy}) \quad (4)$$

where n = 2, the number of electron charges transferred [Fe⁺²], F is Faraday's constant (96,500 amp s/equivalent wt), C(O₂) is the concentration of molecular oxygen in water at the concretion/water interface (mg/L), $\Delta C(O_2)/d$ is the oxygen concentration gradient across concretion (mg/L)/cm, D(O₂) is diffusivity of molecular oxygen in water trapped in concretion voids (cm²/s), and d is concretion thickness (cm) (d assumed $\approx$ diffusion thickness).

Collecting constants in Equation (4):

$$i_{\text{aoer}} = 141C(O_2)D(O_2) / d \quad (\text{mmpy}) \quad (5)$$

where $C(O_2) \approx 0$ at d = 0 (metal/concretion interface).

By definition:

$$\%DO = [C(O_2) / S(O_2)] \cdot 100 \quad (6)$$

where $S(O_2)$ (mg/L) is O_2 solubility and %DO is percent dissolved oxygen.

Rearranging Equation (6) and substituting into Equation (5):

$$i_{aocr} = 141[(\%DO)S(O_2)D(O_2)] / 100d \quad (7)$$

Defining O_2 permeability by:

$$P = S(O_2)D(O_2)(\text{mg} / \text{L})(\text{cm}^2 / \text{s}) \text{ or } \text{mg} / (\text{cm} \cdot \text{s}) \quad (8)$$

Substituting Equation (8) into Equation (7):

$$i_{aocr} = 141[(\%DO)P] / 100d \quad (9)$$

Substituting P in Equation (21), Appendix A, into Equation (9):

$$i_{aocr} = 0.023[(\%DO)] / 100d \text{ (mmpy)} \quad (10)$$

UNDERWATER SITES AND SAMPLE ACQUISITION

Five sites are presently incorporated into the Weins number profile. In addition to USS *Arizona*, these include the Japanese Midget Submarine (JMS), located in deep water 3 miles offshore from Pearl Harbor; Submarine *Explorer*,¹³⁻¹⁴ located in the tidal zone, St. Elmo's Island, Bay of Panama; a recently examined 5th Japanese Midget Submarine (JMS #5) also located offshore from Pearl Harbor;¹⁵ and a Civil War Ironclad, USS *Monitor*,¹⁶ located off the coast of North Carolina. Historical background, time line, and data acquisition are discussed below. Concretion samples and corrosion products are sent to the University of Nebraska-Lincoln (UNL) for iron and calcium analysis and density and thickness measurements. Metallogical analysis is conducted at South Dakota School of Mines and Technology (SDSMT, Rapid City, South Dakota) and Engineering Scientific Investigations ([ESI] Omaha, Nebraska). Additional selected samples are delivered to University of Florida, Graduate Engineering and Research Center, Shalimar, Florida, for x-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM) analysis.¹⁷

USS Arizona

Launched in 1915, the USS *Arizona*, Figures 1(a) and (b), was the first U.S. Navy vessel to be fueled by oil rather than coal. Older coal-burning ships served in Europe during WWI because coal was more plentiful in Europe. During modernization between 1929 and 1931, several structural changes were made.

(a)

(b)

FIGURE 1. (a) USS *Arizona*, concretion drilling and probe insertion and (b) USS *Arizona*, positioning for corrosion potential probe measurements. Images courtesy of National Park Service Submerged Resources Center, Sun City West, Arizona.

Among the changes, fuel capacity was increased from 2,332 tons (2.115×10^6 kg) to 4,630 tons (4.200×10^6 kg) with emergency capacity at 6,180 tons (5.606×10^6 kg) or 1.48 million U.S. gallons ($5,600 \text{ m}^3$). Torpedo blisters were added port and starboard for protection against torpedo attack. While the original purpose of the torpedo blisters was to mitigate damage from torpedo attack, the blisters have provided significant corrosion protection to the intact inner hull.

The ship was anchored along battleship row in Pearl Harbor on December 7, 1941. During the Japanese attack, a 1,760 lb (800 kg) bomb penetrated the deck adjacent to gun turret no. 2 and sympathetically detonated forward magazines, destroying the forward part of the ship and killing 1,177 crew members. Multidisciplinary research including geological analysis, microbiology, oil analysis, structural monitoring, and corrosion studies were initiated by the NPS SRC in 1999 following underwater surveys and arti-

FIGURE 2. Japanese midget submarine sunk offshore Pearl Harbor by USS Ward, December 7, 1941. Image courtesy of Hawaii Undersea Research Laboratory (HURL), University of Hawaii at Mānoa, Honolulu, Hawaii.

fact inventory in the 1980s.¹⁰ Research was designed to input finite element modeling developed at the National Institute of Standards and Technology ([NIST] Gaithersburg, Maryland).⁵ Corrosion studies focused on four areas:

- corrosion potential
- metal coupon sampling
- environmental parameter measurements
- concretion analysis

Japanese Midget Submarine

One of five midget submarines launched from Class I fleet submarines in the early morning of

December 6, 1941, Figure 2, was observed attempting to enter Pearl Harbor an hour before air attack began. The vessel, 78 ft (24 m) long with a 6.0 ft (1.8 m) beam, carried a crew of two and was armed with two torpedoes. According to reports, the USS Ward sank the submarine 3 miles (5,000 m) outside the harbor in more than 1,300 ft (400 m) of water. Kerby, at the Hawaiian Undersea Research Laboratory ([HURL] Honolulu, Hawaii), discovered the intact vessel during operations of HURL's Pisces Submersible in August 2002. Concretion samples were recovered robotically in a subsequent dive.⁷

Submarine Explorer

Construction of Submarine Explorer, Figures 3(a) and (b), was completed in November 1865, and is only one of five submarines from the period known to have survived either in museums or as in situ archaeological sites around the world. Kroehl designed and built a "submarine" for U.S. Navy use that included a pressurized air storage chamber to equalize ambient pressure during diving operations. It became one of the first successful uses of a "lock out" capability. Because the Civil War was ending, the U.S. Navy declined Kroehl's offer to build a second submarine. Kroehl dismantled the submarine and sent it to Panama to be used to recover oyster shells and pearls from the Bay of Panama. Following reassembly and testing in 1867, the craft was used briefly to harvest pearls but was soon abandoned because Kroehl and his crew died or became incapacitated as a result of decompression sickness. In 2001, Delgado was directed by local residents to the site of the craft in the tide zone of St. Elmo's Island. Research revealed that the craft was the Civil War era Sub-

(a)

(b)

FIGURE 3. (a) Submarine Explorer, St. Elmo's Island, Bay of Panama. Image courtesy of James D. Delgado, Director, Maritime Heritage Program, National Oceanic and Atmospheric Administration, Office of National Marine Sanctuaries, Silver Spring, Maryland. (b) Submarine Explorer, damage as of February 2008. Drawings courtesy of John McKay, Fort Langley, B.C., Canada.

(a)

(b)

(c)

FIGURE 4. (a) Mid section, 5th JMS, discovered offshore Pearl Harbor, 1992. Image courtesy of Hawaii Undersea Research Laboratory (HURL), University of Hawaii at Mānoa, Honolulu, Hawaii. (b) and (c) 5th JMS, robotic concretion removal at flange joint with calibrated sampling tube, before, left; after, right. Image courtesy of Hawaii Undersea Research Laboratory (HURL), University of Hawaii at Mānoa, Honolulu, Hawaii.

marine *Explorer*. Following an initial survey in 2004, Murphy and Johnson joined a team of specialists for a second field operation in February 2006 to analyze the hull. In situ hull thickness and corrosion potential measurements were documented and metal/concretion samples were recovered.¹³⁻¹⁴

Japanese Midget Submarine

On March 22 and 23, 2009, the HURL laboratory conducted dives to the last identified Japanese Midget submarine offshore from Pearl Harbor. The site was discovered in 1992 and recognized in 2001 as the probable fifth midget submarine involved in the Pearl Harbor attack. The hull is separated into three sec-

tions, the stern, mid section, and bow; how and why it was disassembled is unknown. Conjecture is that it was salvaged from the West Lock basin inside Pearl Harbor following recovery operations in the area after an explosion. Corrosion product samples and dimensional imaging data were obtained during the 2009 dive (Figures 4[a] through [c]).¹⁵

USS Monitor

Built in 1862, the *USS Monitor* (Figures 5[a] and [b]) was the first ironclad warship to be constructed during the Civil War. The vessel, 173 ft (52.7 m) long and 41 ft (12 m) wide with a flat deck of 1.0 in (2.5 cm) wrought iron, had waterline armor composed of five

(a)

(b)

FIGURE 5. (a) Officers, USS Monitor. Image courtesy of The Mariners' Museum, Newport News, Virginia. (b) Conservators cleaning an XI-inch Dahlgren shell gun recovered from the Civil War Ironclad USS Monitor. Image courtesy The Mariners' Museum, Newport News, Virginia.

layers of 1.0 in (2.5 cm) wrought iron plate. The cylindrical gun turret was constructed of eight layers, also of 1 in (2.5 cm) wrought iron plate. Four concretion samples from outer plates of the gun turret were provided for CECR analysis. The results obtained from CECR were found to be in reasonable agreement with rates obtained from ultrasound measurements.¹⁶

RESULTS—SITE WEINS NUMBERS

Corrosion rate, i_{corr} , is determined from site data referenced at the bottom of Table 1.^{6,13-16,18-20} Available O_2 corrosion rate, i_{aocr} , is calculated from %DO and d . If $\text{C}(\text{O}_2)$ is obtained in mg/L, then %DO is determined from Equation (6) knowing temperature and salinity.²¹ The Weins number is calculated from Equation (1).

The Weins number profile of the data in Table 1 is shown in Figure 6.

DISCUSSION

At $\text{Wn} \approx 1.0$, O_2 reduction alone supports corrosion. For $\text{Wn} \geq 1.0$, O_2 permeation through the concretion is not sufficient to support corrosion. Hydrogen (H_2) discharge as a result of decreased pH at the concretion/metal interface becomes the dominant cathodic reaction as the Wn increases from 1 to 10. The hydrolysis reaction, $\text{Fe}^{+2} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$, is apparently responsible for the pH decrease observed at the metal/concretion interface on the USS *Arizona* hull.⁶ Hydrogen discharge, hydrolysis, and replacement of Ca^{+2} ions in the concretion with Fe^{+2} are the basis for assuming $n = 2$ in Equation (4). It is recognized that n may increase somewhat depending

upon environmental variations, though this would have little or no effect on the relative dimensionless Wn ratio. For $\text{Wn} \leq 1.0$, oxygen permeation is increasingly sufficient to support corrosion as the Wn decreases from 1.0 to ≈ 0.2 . Corrosion product formation may slow the rate,⁷ though sulfate-reducing bacteria would have the opposite effect of accelerating the rate.²²⁻²³

The activation enthalpy (Equation [2]) is a composite that incorporates the difference in activation enthalpies between i_{corr} and i_{aocr} . From the profile in Figure 1, $\Delta H^\ddagger = 22,500$ cal/mole (94,100 J/mole) and the frequency factor $W(0) = 2.01 \times 10^{17}$. From Appendix B and Equation (26), the corresponding potential $E^\ddagger$ vs. standard hydrogen electrode (SHE) = -0.360 mV at pH = 6.1. This pH is consistent with pH measurements taken at the concretion/metal interface on USS *Arizona*.¹⁸ A communication analyzing these results is in preparation.

Several factors may contribute to error. The most significant is the dependence of the Weins number on the square of the thickness as illustrated in Equation (11). Inserting Equation (3) ($K = 0.02$) and Equation (10) into Equation (1):

$$\text{Wn} = 87\rho(\% \text{Fe})d^2 / [\% \text{DO}(t)] \quad (11)$$

Other factors include fluctuations in daily and seasonal temperatures and oxygen concentration, presence of organic matter, microbial activity, water velocity, salinity, and pH. Variations in macrostructural features of the concretion, such as void volume and tortuosity of path for diffusion and counter diffusion of ions, are additional factors.

TABLE 1
Site Data and Calculated Parameters

Vessel	Water Depth (m)	i_{corr} (mmpy)	%DO	d (cm)	i_{aocr} (mmpy)	Wn	Temperature (T)		
							°C±	K	$1/(K) \times 10^3$
USS <i>Arizona</i> ^(A)	1	0.069	75	2.5	0.0069	10.00	28.9±0.5	301.9	3.312
USS <i>Arizona</i> ^(A)	10	0.033	38	1.1	0.0079	4.19	27.9±0.5	300.9	3.323
JMS ^(B)	365	0.015	47	0.4	0.0269	0.57	8.8±1.9	281.9	3.549
Sub Marine ^(C) <i>Explorer</i>	Tidal zone	0.051	106	1.4	0.0178	2.86	20.5±1.7	293.5	3.407
JMS #5 ^(D)	345	0.015	45	0.6	0.0173	0.99	10.2±1.3	283.2	3.531
USS <i>Monitor</i> ^(E)	73	0.028	≈68	1.7	0.0092	3.04	18.5±6.0	291.5	3.430

(A) Thickness change^{6,18}

(B) CECR⁷

(C) CECR and thickness change¹³⁻¹⁴

(D) CECR¹⁵

(E) Ultrasound, site temperature^{16,19-20}

APPLICATION OF THE WEINS NUMBER

Rearranging Equation (1) and solving for i_{corr} :

$$i_{\text{corr}} = Wn \times i_{\text{aocr}} \quad (12)$$

Substituting Equation (10) into Equation (12):

$$i_{\text{corr}} = 0.023 Wn[(\%DO) / 100] / d \text{ (mmpy)} \quad (13)$$

Example: Given that $C(O_2) = 4.7 \text{ mg/L}$, $T = 290 \text{ K}$ (17°C), salinity 33 PSU (practical salinity units), and $d = 0.78 \text{ cm}$.

— $T (17^\circ\text{C}) = (17 + 273) = 290 \text{ K}$, where $1/T (K^{-1}) \times 1,000 = 3.45$

—From Figure 6, locate 3.45 at the intersection point with the linear profile and read horizontally to locate $Wn \approx 1.9$ on the vertical axis.

—From Equation (20), $S(O_2) = 0.0296 \exp(3,220 / (1.987 \times 290)) = 7.91 \text{ mg/L}$

—From Equation (6), $\%DO = (4.7/7.91)100 = 59.4$

—From Equation (13), $i_{\text{corr}} = 0.023 \times 1.9 (59.4/100)/0.78 \approx 0.033 \text{ mmpy}$ (1.3 mpy). Since Wn is located in the O_2 -deficient region ($Wn \geq 1$), H_2 discharge is expected. (If site data is given directly in %DO, application of Equation [6] is unnecessary.)

CONCLUSIONS

❖ Results to date indicate the feasibility of the Weins number concept. Broadening of the database is needed and should incorporate the following on a site by site basis:

- Independent value of i_{corr} —from CECR, direct coupon, or other sources
- Environmental parameters—temperature, oxygen concentration, and salinity, preferably over extended time periods
- Concretion thickness—where direct acquisition of concretion is impractical, in situ visual and laser thickness imaging should be refined

FIGURE 6. Semi log profile of Wn as a function of reciprocal absolute temperature. Trendline $R^2 = 0.914$; temperature range 5°C to 34°C . Graphics courtesy of Dr. Jon E. Johnson, Research Specialist, Dow Water and Process Solutions R&D, Edina, Minneapolis.

❖ Galvanic effects caused by potential difference such as rivet/plate, weld metal/plate, heat treatment, and chemistry are the subject of an on-going study in metallurgy laboratories at the South Dakota School of Mines and Technology.²⁴ Preliminary results show significant differences in corrosion rate between rivet head, shaft, and base metal, differences not reflected in hull plate corrosion data obtained on site. The age and source of raw materials used to manufacture structural materials used in construction are also important because steel chemistry resulting from Fe ore mined in the United States may be significantly different from ore mined in other parts of the world. The reason for the difference is the geochemistry of the ore from which the Fe was extracted and the differences in refining processes. For example, steel used in construction of HMS *Titanic* was obtained from acid open-hearth steelmaking practice in Europe; whereas, steel used in construction of USS *Arizona* was obtained from basic open-hearth steelmaking practice in the United States that resulted

in lower phosphorous and sulfur content in USS Arizona steel.²⁵

❖ Environmental parameters are incorporated into the determination of the corrosion rate as a function of the transport properties of the concretion, i_{aoc} . Hence, a primary element of the Weins number is the role of concretion/corrosion product in the corrosion process. As will be noted from examination of data in Table 1, calculated i_{aoc} decreases as the temperature increases because the ratio (%DO)/d decreases. Multiple readings are required to ensure maximum accuracy of d. Areas where shell or debris are dominant should be avoided. In general, O₂ drives corrosion in the sense that its availability determines whether H₂ discharge, O₂ consumption, or a combination of both is the controlling cathodic reaction(s).

❖ Standardized techniques to obtain physical and chemical properties of concretion are presently in place through partnerships among the UNL, SDSMT, ESI, University of Florida Graduate Engineering and Research Center, and NPS SRC.

❖ Fundamental issues related to concretion are under further investigation. Among these issues is a better understanding of oxygen and Fe ion transport within the concretion. For example, void volume in terms of water retention can be determined. However, the shape and continuity of water-containing voids is unknown.

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APPENDIX A—PERMEATION

Oxygen Diffusivity in Seawater

D(O₂) in water at 25°C is 2.45 × 10⁻⁵ cm²/s. At 8.8°C, D(O₂) is given by:²⁶

$$D(\text{O}_2)^{8.8^\circ\text{C}} = D(\text{O}_2)^{25^\circ\text{C}} \times T / T^{25^\circ\text{C}} \times \mu^{25^\circ\text{C}} / \mu$$

$$= 1.72 \times 10^{-5} \text{ cm}^2 / \text{s} \quad (14)$$

where T (K) is absolute temperature and μ is the viscosity of water.

From diffusivity values at 25°C and 8.8°C , the diffusion coefficient is given as a function of temperature:

$$D(\text{O}_2) = 0.0114 \exp(-3,640 / RT) (\text{cm}^2 / \text{s}) \quad (15)$$

Oxygen Solubility in Seawater

$S(\text{O}_2)$ is determined from the reaction:

The Gibbs energy for the reaction at equilibrium is $\Delta G^s = -RT \ln S(\text{O}_2) = (\Delta H^s) - T\Delta S^s$, where ΔG^s , ΔH^s , and ΔS^s are Gibbs energy, enthalpy, and entropy of solution, respectively. Dividing the Gibbs energy expression through by RT and solving for $S(\text{O}_2)$:

$$S(\text{O}_2) = \exp[(-\Delta H^s) / RT + \Delta S^s / R] \quad (17)$$

where ΔH^s and $\Delta S^s/R$ are assumed constant.

Rearranging:

$$S(\text{O}_2) = (B) \exp(-\Delta H^s) / RT \quad (18)$$

where B is the preexponential constant incorporating $\Delta S^s/R$.

Converting to logarithmic form:

$$\ln(S(\text{O}_2)) = \ln(B) - \Delta H^s / RT \quad (19)$$

Taken from the solubility data at 33 PSU,²¹ $S(\text{O}_2) = 10.03 \text{ mg/L}$ at 5°C and $S(\text{O}_2) = 6.20 \text{ mg/L}$ at 30°C . An expression for solubility as a function of temperature is given by:

$$S(\text{O}_2)(\text{mg} / \text{L}) = 0.0296 \exp(3,220 / RT) \quad (20)$$

Inserting Equation (15) and Equation (20) into Equation (8):

$$P = S(\text{O}_2)D(\text{O}_2) =$$

$$3.37 \times 10^{-4} \exp(-420 / RT) \approx 1.63 \times 10^{-4} \quad (21)$$

where P is approximately constant for $5^\circ\text{C} \leq T \leq 35^\circ\text{C}$.

Since $S(\text{O}_2)$ increases and $D(\text{O}_2)$ increases with temperature, the two cancel with minor error.

APPENDIX B—ABSOLUTE REACTION RATE THEORY

In nonlogarithmic form, Equation (2) is given by:

$$(Wn) = Wn(o) \exp(-\Delta H^\dagger / RT) \quad (22)$$

where $[Wn(o)] = (RT/Nh) \exp(\Delta S^\dagger/R)$ and $\Delta H^\dagger$ is activation enthalpy, R is the gas constant, $T = T$ (K), N is Avogadro's number, h is Plank's constant, $\Delta S^\dagger$ is entropy of activation, and $\Delta H^\dagger$ is enthalpy of activation.

From Figure 6 and Reference 9:

$$W(o) = (RT / Nh) \exp(\Delta S^\dagger / R) = 2.01 \times 10^{17}$$

$$[10^{11}(291) / 4.8] \exp(\Delta S^\dagger / R) = 2.01 \times 10^{17} \quad (23)$$

$$\Delta S^\dagger = 20.7 \text{ cal} / \text{mole} / \text{K} (86.6 \text{ J} / \text{mole} / \text{K})$$

Assuming $\Delta H^\dagger$ and $\Delta S^\dagger$ are constants and independent of temperature:

$$\Delta G^\dagger = \Delta H^\dagger - T\Delta S^\dagger = 22,500 - 291(20.7)$$

$$\approx 16,500 \text{ cal} / \text{mole} (69,100 \text{ J} / \text{mole}) \quad (24)$$

where $T = T_m = 291 \text{ K}$ is the approximate mean temperature.

From the Nernst equation:

$$\Delta E^\dagger = -\Delta G^\dagger / nF \quad (25)$$

where $\Delta E^\dagger$ is activation potential, n is valence of iron, and F is Faraday's constant.

Therefore:

$$\Delta E^\dagger = 16,500 / [2(23,062)] = -0.358 \text{ mV}_{\text{SHE}} \quad (26)$$

$$\text{pH} = 0.358 / 0.0592 = 6.05$$