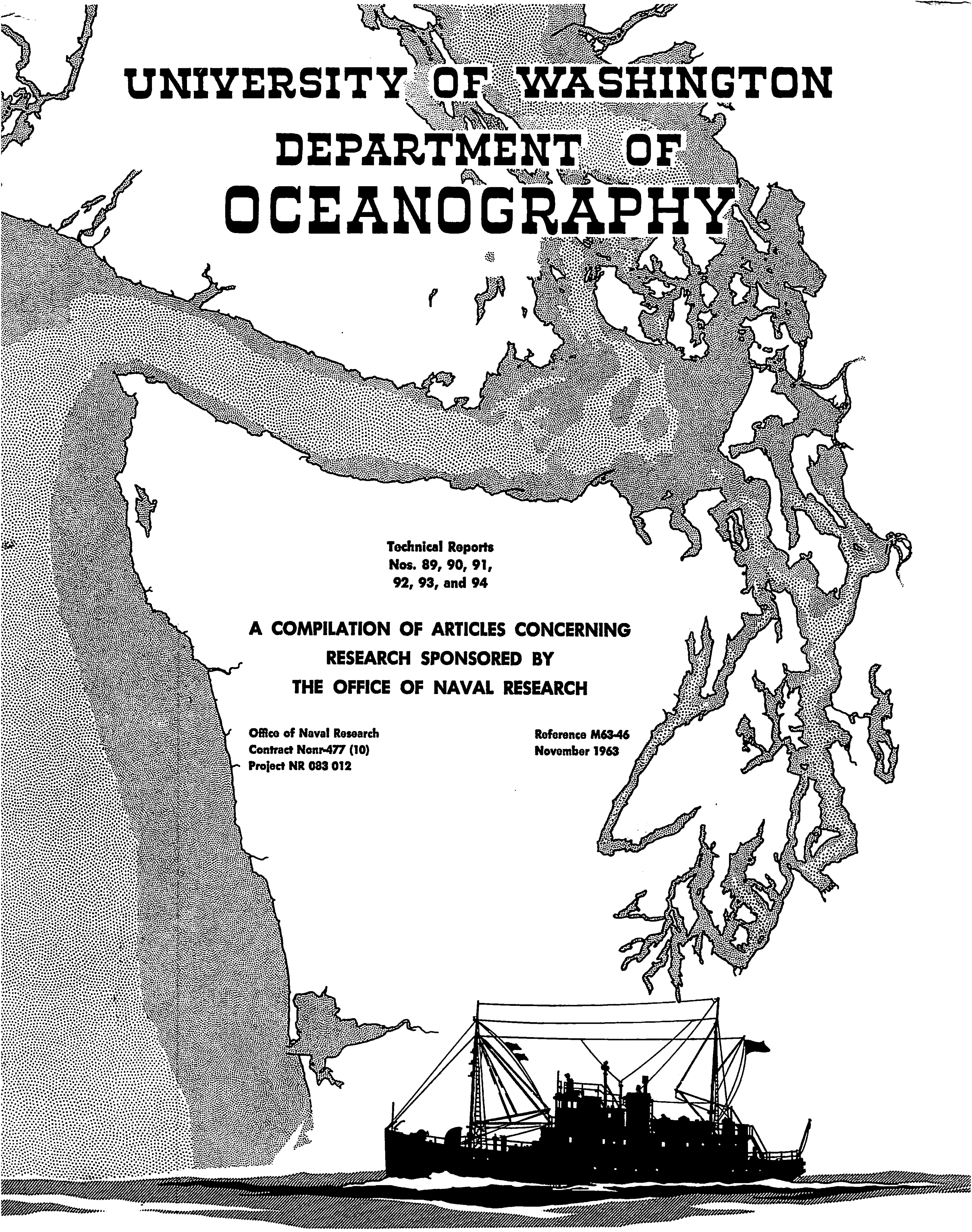
UNIVERSITY OF WASHINGTON
DEPARTMENT OF
OCEANOGRAPHY



Technical Reports
Nos. 89, 90, 91,
92, 93, and 94

A COMPILATION OF ARTICLES CONCERNING RESEARCH SPONSORED BY THE OFFICE OF NAVAL RESEARCH

Office of Naval Research
Contract Nonr-477 (10)
Project NR 083 012

Reference M63-46
November 1963

SEATTLE, WASHINGTON 98105

UNIVERSITY OF WASHINGTON
DEPARTMENT OF OCEANOGRAPHY
Seattle, Washington 98105

Articles Concerning Research Sponsored by the Office of Naval Research:

Technical Report No. 89

ELECTRONIC DATA PROCESSING IN SEDIMENTARY SIZE ANALYSES, by Joe S. Creager, Dean A. McManus and Eugene E. Collias. Journal of Sedimentary Petrology, 32(4):833-839, December 1962.

Technical Report No. 90

DISTRIBUTION OF LIVING PLANKTONIC FORAMINIFERA IN THE NORTHEASTERN PACIFIC, by A. Barrett Smith. Contributions, Cushman Foundation, 14(1):1-15, January 1963.

Technical Report No. 91

A NEW HYPOTHESIS FOR ORIGIN OF GUYOTS AND SEAMOUNT TERRACES, by Y. Rammohanroy Nayudu. Crust of the Pacific Basin, Geophysical Monograph No. 6, pp. 171-180, December 1962.

Technical Report No. 92

PHYSICAL AND SEDIMENTARY ENVIRONMENTS ON A LARGE SPITLIKE SHOAL, by Dean A. McManus and Joe S. Creager. Journal of Geology, 71(4):498-512, July 1963.

Technical Report No. 93

GRAVITY AND THE PROPERTIES OF SEA WATER, by Ricardo M. Pytkowicz. Limnology and Oceanography, 8(2):286-287, April 1963.

Technical Report No. 94

POSTGLACIAL SEDIMENTS IN UNION BAY, LAKE WASHINGTON, SEATTLE, WASHINGTON, by Dean A. McManus. Northwest Science, 37(2):61-73, May 1963.

Office of Naval Research
Contracts Nonr-477(10)
Project Nr 083 012

Reference M63-46
November 1963

RHFleming

RICHARD H. FLEMING
Chairman

Made in United States of America
Reprinted from Limnology and Oceanography
Vol. 8, No. 2, April, 1963
pp. 286–287

GRAVITY AND THE PROPERTIES OF SEA WATER[1]

In general, the concentrations of salts in the oceans are not at equilibrium with respect to gravity because molecular diffusion, the mechanism for equilibration, is slow compared to advection and eddy diffusion (Pytkowicz 1962). At equilibrium the concentration of sodium chloride would increase 18% per kilometer of depth and the contribution of gravity to the activity would be constant with depth.

In actual systems, equilibrium is not achieved and the activity of solutes, equilibrium constants, and the colligative properties change with depth. Such effects were observed in the experiments of Des Coudres (reviewed by MacInnes 1939), who showed that the EMF generated between identical electrodes, placed at different heights, is accounted for by the gravity effect.

Pressure has an effect similar to gravity. Klotz (1961) has shown that gases dissolved in a deep water column are not at equilibrium with respect to the hydrostatic pressure gradient. This non-equilibrium should provide an additional term to the direct effect of the pressure gradient on equilibrium constants.

The slowness of molecular diffusion is demonstrated by the following considerations:

The usual form of Fink's law does not apply to a uniform distribution, for which it would predict no diffusion. A general form of the law, based on the chemical potential gradient as the driving force for molecular diffusion, is required.

The flow J is proportional to the gradient of the chemical potential

$$J = -K \nabla \mu . \tag{1}$$

For an ideal solution

$$\mu = \mu^0 + RT \ln m , \tag{2}$$

where μ^0 refers to a standard state and m is the molarity of the solution.

At equilibrium the molarity m_{tz}, which is a function of time and depth, will reach an equilibrium distribution $m_{\infty z}$ such that

$$\nabla \mu_{\infty z} = \nabla \mu^0 + \frac{RT}{m_{\infty z}} \nabla m_{\infty z} = 0 . \tag{3}$$

This equation defines a convenient standard state. Differentiating equation (2), replacing the value of $\nabla \mu^0$ from equation (3) into it, and introducing the result into equation (1),

$$J_{tz} = J_{0z} - D \nabla m_{tz} , \tag{4}$$

where $J_{0z} = D \nabla m_{\infty z}$ is the initial flow and $D = KRT/m$ is the molecular diffusion coefficient. This equation represents the time change in flux as the gradient decreases, and reduces to the conventional form

$$J_{tz} = -D \nabla m_{tz} \tag{5}$$

in the absence of an external field, that is, if the equilibrium concentration is uniform.

The change in concentration with time is given by

$$\frac{\mathrm{d}m_{tz}}{\mathrm{d}t} = D \left(\frac{\mathrm{d}^2 m_{\infty z}}{\mathrm{d}z^2} - \frac{\mathrm{d}^2 m_{tz}}{\mathrm{d}z^2} \right) , \tag{6}$$

and a minimum time for half-equilibration can be estimated by assuming that the maximum initial rate is followed throughout the diffusion. D is of the order of 10^{-5} cm^2 sec^{-1} and $\mathrm{d}^2 m_{\infty z}/\mathrm{d}z^2$ is about 10^{-2}; thus $\mathrm{d}m_{tz}/\mathrm{d}z = 10^{-17}$ moles/sec or 3×10^{-10} moles/year. A 9% change in the molarity would take 18×10^6 years.

The change in activity of salt with depth will be determined for a uniform sodium chloride distribution. The gradient of the chemical potential is given by Pytkowicz (1962) as

$$\nabla \mu = -(M - \bar{v}_1 \rho) g , \tag{7}$$

---

[1] Contribution No. 280 from the Department of Oceanography, University of Washington. This work supported in part by the Office of Naval Research Contract Nonr-477(10), Project NR 083 012 and N.S.F. grant G-12343. The author thanks Professor Francis A. Richards, University of Washington, for helpful advice and suggestions.

and by definition is

$$\nabla\mu = \frac{RT}{a_2}\nabla a_2, \qquad (8)$$

where a_2 is the mean activity of the salt and μ^0 is now considered constant with depth. Equating (7) and (8) and integrating,

$$a_2 = Ke^{-U/RT}, \qquad (9)$$

where the potential energy $U(M - \bar{v}_1\rho)gz$ and RT is the thermal energy. $K = I$ because when U is zero the activity is unity. At a 1 km depth $a_2 = 0.83$. Thus, for a uniform concentration the ratio of surface activity to the activity at 1 km is $a_2^{(0)}/a_2^{(1)} = 1.21$.

The change in activity of the water is obtainable from the Gibbs–Dunheim equation

$$d \ln a_1 = -\frac{n_2}{n_1} d \ln a_2. \qquad (10)$$

Integrating equation (10) for water of salinity 35‰ and remembering that n_2/n_1 is constant, the ratio $a_1^{(0)}/a_1^{(1)}$ is 0.998.

The extent and rate of reactions that result in non-conservative concentrations, and many of the thermodynamic properties such as vapor-pressure, osmotic pressure, conductivity, and compressibility can only be measured in laboratories or at the surface of water masses. Our results suggest that activity correction factors should be applied before extending surface data to great depths, because of non-equilibrium with respect to the gravitational field.

REFERENCES

KLOTS, C. E. 1961. Effect of hydrostatic pressure upon the solubility of gases. Limnol. Oceanogr., **6**: 365–366.

MACINNES, D. A. 1939. The principles of electrochemistry. New York, Reinhold publishing Corp., pp. 174–180.

PYTKOWICZ, R. M. 1962. Effect of gravity on the distribution of salts. Limnol. Oceanogr., **7**: 434–435.

RICARDO MARCOS PYTKOWICZ

Department of Oceanography,
University of Washington.