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New Tables for Oxygen Saturation of Seawater

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ABSTRACT

This paper presents new tables and a nomogram for the calculation of oxygen saturation values of pure water and of seawater. The tables are based on recent careful determinations of the Bunsen absorption coefficient for oxygen and on accepted values of the vapor pressure of water.

Introduction. Currently accepted tables for the calculation of oxygen saturation values of seawater, widely used in oceanography, limnology, as well as in health and sanitation studies, are based on two independent sets of measurements: those by Fox (1909) and those by Truesdale et al. (1955). Between these measurements there exist serious discrepancies of about 4%. From the gasometric determinations of the Bunsen absorption coefficient for the solubility of oxygen in distilled water by Klots and Benson (1963) it became evident that none of the tables existing at that time was reliable over the full range of temperature. The "nonchemical" determinations by Klots and Benson were confirmed in the titrimetric measurements by Worthington and by Grasshoff with different types of equilibrators.

Montgomery et al. (1964) examined the methods used for the determination of the solubility of oxygen in water and made new determinations for both pure water and seawater. Their values for pure water also showed excellent agreement with those by Klots and Benson, but Montgomery et al. presumed that it was unnecessary to verify the assumption made by previous workers regarding a linear solubility dependence upon salinity. Potential errors in the Winkler titration method have recently been exhaustively discussed by Carpenter (1965) and by Carritt and Carpenter (1966). A new set of solubility tables for oxygen in seawater, based on determinations made with a very precise modification of the Winkler method, has recently been presented by Carpenter (1966). These data can now be compared directly with the measurements by Green (1965),

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for the tables presented herein are for a water-saturated atmosphere, as are those by Carpenter (1966). It has been observed that, for temperatures above 10°C, Carpenter's tables agree with the tables presented here to within the accuracy claimed for the data. At very low temperatures, however, Carpenter's solubility tabulations are about 1% lower than ours. It is not clear why these two sets of careful measurements diverge at temperatures below 10°C, and it is therefore difficult to establish which values are more accurate. Unfortunately, a great many important oceanographic measurements fall into the temperature range below 10°C.

Carpenter (1966) has pointed out that Green's (1965) determinations may be biased toward slightly higher values due to the absence of a correction for oxygen that is added with reagent solutions. However, Carpenter's (1965) own estimate of the magnitude of this correction (0.018 ml/l) shows that it is unlikely to be greater than 0.2% below 10°C. Moreover, the manometric determinations by Klots and Benson, although restricted to pure water, also diverge at low temperatures from Carpenter's in the same direction and to about the same magnitude. The excellent correspondence between the manometric determinations by Klots and Benson and the titrimetric determinations by Green (1965) for oxygen solubility in distilled water leads us to suggest that the new tables for oxygen saturation presented in this paper are the most accurate of any yet presented over the entire temperature range of interest.

Redetermination of Oxygen Solubility. The redeterminations of the solubility coefficient for oxygen in seawater from 0°C to 35°C and from 0‰ to 30‰ chlorinity were made by Green with a "Jacobsen-Worthington" equilibrators and a titration method very similar to that described by Carpenter (1965). The data clearly demonstrate the nonlinear dependence of the oxygen solubility upon the salt content of the water (Green and Carritt). Carpenter (1966) used a smoothing function that was quadratic in the chlorinity, although Green had earlier shown that the data were well represented by a one-parameter exponential relation that had, in addition to simplicity, a thermodynamic basis. The difference in choice of smoothing functions probably lies in the fact that Carpenter was smoothing solubilities from a water-saturated atmosphere (that is, at a nonconstant partial pressure of oxygen) and Green was smoothing Bunsen coefficients, which may be expected to have a simpler functional representation. Green's data were represented as an integrated form of the Van't Hoff equation:

$$\alpha \cdot 10^3 = \exp \left\{ (-7.424 + \frac{4417}{T} - 2.927 \log_e T + 0.04238 T) - \right. \\ \left. - \text{Cl}(-0.1288 + \frac{53.44}{T} - 0.04442 \log_e T + 7.145 \cdot 10^{-4} T) \right\},$$

where α is the Bunsen coefficient, T is the absolute temperature, and Cl is the chlorinity in parts per thousand.

The exchange of oxygen across the air-sea interface takes place as a molecular process in a very thin layer in and above the water surface. In the boundary layer, this exchange is governed by the laws of molecular diffusion and is therefore dependent upon the partial-pressure gradient of the oxygen in the diffusion layer as well as upon any temperature and total-pressure gradients that may exist. The water vapor follows the same laws in the boundary film, and therefore the air is very near to saturation with water vapor in the layer immediately at the water surface (Kanwisher 1963).

Computed Oxygen Solubilities. Based on Green's equation above, new tables for the oxygen saturation have been prepared by machine computation. The vapor pressure of seawater has been computed by combining the Goff-Gratch (1946) formulation for the vapor pressure of pure water with a relationship for the vapor-pressure lowering by sea salt derived from the data of Arons and Kientzler (1954); this procedure yielded:

$$P_{\text{vap}} = \left\{ (1 - 9.701 \cdot 10^{-4} Cl) \right\} \exp \left\{ 18.1973 \left(1 - \frac{373.16}{T} \right) + \right. \\ \left. + 3.1813 \cdot 10^{-7} \left(1 - \exp \left[26.1205 \left(1 - \frac{T}{373.16} \right) \right] \right) - \right. \\ \left. - 1.8726 \cdot 10^{-2} \left(1 - \exp \left[8.03945 \left(1 - \frac{373.16}{T} \right) \right] \right) \right\} + \\ \left. + 5.02802 \log_e \left(\frac{373.16}{T} \right) \right\}.$$

The vapor pressure so derived was combined with the Bunsen coefficient to calculate the saturated solubility in milliliters of oxygen per liter of seawater, S , as a function of temperature and chlorinity:

$$S = 0.2094 (10^{-3} \alpha) (1 - P_{\text{vap}}),$$

where P_{vap} is in atmospheres. These data are presented in Table I. Table II presents the same data converted (by the factor $89.23 \mu\text{g-at/ml}$) to units of microgram-atoms of oxygen per liter, which units, though less widely used, have been recommended by the International Association of Physical Oceanographers (Helland-Hansen et al. 1948). Tabular data in terms of parts per million or milligrams of oxygen per liter have not been given here, although these units are in use, particularly in water-pollution studies. Conversion to these units may be made by multiplying the values in Table I by the factor 1.428 mg/ml . Table III, in which the same data are tabulated for closely

Table I. Oxygen solubility (ml/l) in seawater from a water-saturated atmosphere of which oxygen is 0.2094 mole fraction, excluding water vapor.

°C	Chlorinity ‰															
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
0	10.30	10.04	9.79	9.54	9.30	9.06	8.83	8.61	8.39	8.18	7.97	7.77	7.58	7.38	7.20	7.02
1	10.02	9.77	9.53	9.29	9.06	8.83	8.61	8.39	8.18	7.98	7.78	7.59	7.40	7.21	7.03	6.86
2	9.75	9.51	9.28	9.05	8.82	8.61	8.39	8.19	7.98	7.79	7.60	7.41	7.23	7.05	6.87	6.70
3	9.49	9.26	9.03	8.81	8.60	8.39	8.19	7.99	7.79	7.60	7.42	7.24	7.06	6.89	6.72	6.56
4	9.24	9.02	8.80	8.59	8.38	8.18	7.99	7.79	7.61	7.42	7.24	7.07	6.90	6.73	6.57	6.41
5	9.01	8.79	8.58	8.38	8.18	7.98	7.79	7.61	7.43	7.25	7.08	6.91	6.74	6.58	6.43	6.27
6	8.78	8.57	8.37	8.17	7.98	7.79	7.61	7.43	7.25	7.08	6.92	6.75	6.59	6.44	6.29	6.14
7	8.56	8.36	8.17	7.97	7.79	7.61	7.43	7.26	7.09	6.92	6.76	6.60	6.45	6.30	6.15	6.01
8	8.35	8.16	7.97	7.78	7.61	7.43	7.26	7.09	6.93	6.77	6.61	6.46	6.31	6.16	6.02	5.88
9	8.15	7.96	7.78	7.60	7.43	7.26	7.09	6.93	6.77	6.62	6.47	6.32	6.18	6.03	5.90	5.76
10	7.95	7.77	7.60	7.43	7.26	7.09	6.93	6.78	6.62	6.47	6.33	6.18	6.04	5.91	5.77	5.64
11	7.77	7.59	7.42	7.26	7.09	6.94	6.78	6.63	6.48	6.33	6.19	6.05	5.92	5.79	5.66	5.53
12	7.59	7.42	7.26	7.09	6.94	6.78	6.63	6.49	6.34	6.20	6.06	5.93	5.80	5.67	5.54	5.42
13	7.42	7.25	7.09	6.94	6.78	6.64	6.49	6.35	6.21	6.07	5.94	5.81	5.68	5.55	5.43	5.31
14	7.25	7.09	6.94	6.79	6.64	6.49	6.35	6.21	6.08	5.94	5.81	5.69	5.56	5.44	5.32	5.21
15	7.09	6.94	6.79	6.64	6.50	6.36	6.22	6.08	5.95	5.82	5.70	5.57	5.45	5.33	5.22	5.11
16	6.94	6.79	6.64	6.50	6.36	6.22	6.09	5.96	5.83	5.70	5.58	5.46	5.34	5.23	5.12	5.01
17	6.79	6.65	6.50	6.36	6.23	6.10	5.97	5.84	5.71	5.59	5.47	5.35	5.24	5.13	5.02	4.91
18	6.65	6.51	6.37	6.23	6.10	5.97	5.84	5.72	5.60	5.48	5.36	5.25	5.14	5.03	4.92	4.82
19	6.51	6.37	6.24	6.11	5.98	5.85	5.73	5.61	5.49	5.37	5.26	5.15	5.04	4.93	4.83	4.73
20	6.38	6.24	6.11	5.98	5.86	5.74	5.62	5.50	5.38	5.27	5.16	5.05	4.95	4.84	4.74	4.64
21	6.25	6.12	5.99	5.87	5.74	5.62	5.51	5.39	5.28	5.17	5.06	4.96	4.85	4.75	4.65	4.56
22	6.12	6.00	5.87	5.75	5.63	5.52	5.40	5.29	5.18	5.07	4.97	4.86	4.76	4.66	4.57	4.47
23	6.01	5.88	5.76	5.64	5.52	5.41	5.30	5.19	5.08	4.98	4.87	4.77	4.68	4.58	4.48	4.39
24	5.89	5.77	5.65	5.53	5.42	5.31	5.20	5.09	4.99	4.89	4.78	4.69	4.59	4.50	4.40	4.31
25	5.78	5.66	5.54	5.43	5.32	5.21	5.10	5.00	4.90	4.80	4.70	4.60	4.51	4.41	4.32	4.24
26	5.67	5.55	5.44	5.33	5.22	5.11	5.01	4.91	4.81	4.71	4.61	4.52	4.43	4.34	4.25	4.16
27	5.56	5.45	5.34	5.23	5.13	5.02	4.92	4.82	4.72	4.62	4.53	4.44	4.35	4.26	4.17	4.09
28	5.46	5.35	5.24	5.14	5.03	4.93	4.83	4.73	4.64	4.54	4.45	4.36	4.27	4.18	4.10	4.02
29	5.36	5.26	5.15	5.05	4.94	4.84	4.74	4.65	4.55	4.46	4.37	4.28	4.20	4.11	4.03	3.95
30	5.27	5.16	5.06	4.96	4.86	4.76	4.66	4.57	4.47	4.38	4.30	4.21	4.12	4.04	3.96	3.88
31	5.18	5.07	4.97	4.87	4.77	4.67	4.58	4.49	4.40	4.31	4.22	4.14	4.05	3.97	3.89	3.81
32	5.09	4.98	4.88	4.78	4.69	4.59	4.50	4.41	4.32	4.23	4.15	4.06	3.98	3.90	3.82	3.75
33	5.00	4.90	4.80	4.70	4.61	4.52	4.42	4.33	4.25	4.16	4.08	4.00	3.92	3.84	3.76	3.68
34	4.91	4.82	4.72	4.62	4.53	4.44	4.35	4.26	4.18	4.09	4.01	3.93	3.85	3.77	3.70	3.62
35	4.83	4.73	4.64	4.55	4.45	4.36	4.28	4.19	4.10	4.02	3.94	3.86	3.78	3.71	3.63	3.56

Table II. Oxygen solubility ($\mu\text{g-at/l}$) in seawater from a water-saturated atmosphere of which oxygen is 0.2094 mole fraction, excluding water vapor.

°C	Chlorinity ‰															
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
0	919.	896.	873.	851.	830.	809.	788.	768.	749.	730.	712.	694.	676.	659.	642.	626.
1	894.	872.	850.	829.	808.	788.	768.	749.	730.	712.	694.	677.	660.	644.	628.	612.
2	870.	849.	828.	807.	787.	768.	749.	730.	712.	695.	678.	661.	645.	629.	613.	598.
3	847.	826.	806.	787.	767.	749.	730.	713.	695.	678.	662.	646.	630.	615.	600.	585.
4	825.	805.	786.	767.	748.	730.	713.	695.	679.	662.	646.	631.	616.	601.	586.	572.
5	804.	784.	766.	748.	730.	712.	695.	679.	663.	647.	631.	616.	602.	587.	573.	560.
6	783.	765.	747.	729.	712.	695.	679.	663.	647.	632.	617.	603.	588.	575.	561.	548.
7	764.	746.	729.	712.	695.	679.	663.	648.	632.	618.	603.	589.	576.	562.	549.	536.
8	745.	728.	711.	695.	679.	663.	648.	633.	618.	604.	590.	576.	563.	550.	537.	525.
9	727.	710.	694.	678.	663.	648.	633.	618.	604.	591.	577.	564.	551.	538.	526.	514.
10	710.	694.	678.	663.	648.	633.	619.	605.	591.	578.	565.	552.	539.	527.	515.	504.
11	693.	678.	662.	648.	633.	619.	605.	591.	578.	565.	553.	540.	528.	516.	505.	493.
12	677.	662.	647.	633.	619.	605.	592.	579.	566.	553.	541.	529.	517.	506.	494.	484.
13	662.	647.	633.	619.	605.	592.	579.	566.	554.	542.	530.	518.	507.	496.	485.	474.
14	647.	633.	619.	606.	592.	579.	567.	554.	542.	530.	519.	508.	496.	486.	475.	465.
15	633.	619.	606.	593.	580.	567.	555.	543.	531.	520.	508.	497.	487.	476.	466.	456.
16	619.	606.	593.	580.	568.	555.	543.	532.	520.	509.	498.	487.	477.	467.	457.	447.
17	606.	593.	580.	568.	556.	544.	532.	521.	510.	499.	488.	478.	468.	458.	448.	438.
18	593.	581.	568.	556.	544.	533.	522.	510.	500.	489.	479.	469.	459.	449.	439.	430.
19	581.	569.	557.	545.	533.	522.	511.	500.	490.	479.	469.	459.	450.	440.	431.	422.
20	569.	557.	545.	534.	523.	512.	501.	491.	480.	470.	460.	451.	441.	432.	423.	414.
21	558.	546.	535.	523.	513.	502.	491.	481.	471.	461.	452.	442.	433.	424.	415.	406.
22	547.	535.	524.	513.	503.	492.	482.	472.	462.	453.	443.	434.	425.	416.	408.	399.
23	536.	525.	514.	503.	493.	483.	473.	463.	453.	444.	435.	426.	417.	409.	400.	392.
24	526.	515.	504.	494.	484.	474.	464.	454.	445.	436.	427.	418.	410.	401.	393.	385.
25	516.	505.	495.	485.	475.	465.	455.	446.	437.	428.	419.	411.	402.	394.	386.	378.
26	506.	496.	485.	476.	466.	456.	447.	438.	429.	420.	412.	403.	395.	387.	379.	371.
27	497.	486.	477.	467.	457.	448.	439.	430.	421.	413.	404.	396.	388.	380.	372.	365.
28	487.	478.	468.	458.	449.	440.	431.	422.	414.	405.	397.	389.	381.	373.	366.	358.
29	479.	469.	459.	450.	441.	432.	423.	415.	406.	398.	390.	382.	374.	367.	359.	352.
30	470.	461.	451.	442.	433.	425.	416.	408.	399.	391.	383.	376.	368.	361.	353.	346.
31	462.	453.	443.	434.	426.	417.	409.	400.	392.	384.	377.	369.	362.	354.	347.	340.
32	454.	445.	436.	427.	418.	410.	402.	394.	386.	378.	370.	363.	355.	348.	341.	334.
33	446.	437.	428.	420.	411.	403.	395.	387.	379.	371.	364.	357.	349.	342.	335.	329.
34	438.	430.	421.	413.	404.	396.	388.	380.	373.	365.	358.	350.	343.	336.	330.	323.
35	431.	422.	414.	406.	397.	389.	382.	374.	366.	359.	352.	345.	338.	331.	324.	318.

Table III. Oxygen solubility (ml/l) in seawater from a water-saturated atmosphere of which oxygen is 0.2094 mole fraction, excluding water vapor.

°C	Salinity ‰																
	33.00	33.25	33.50	33.75	34.00	34.25	34.50	34.75	35.00	35.25	35.50	35.75	36.00	36.25	36.50	36.75	37.00
0...	8.15	8.14	8.12	8.11	8.10	8.08	8.07	8.05	8.04	8.02	8.01	8.00	7.98	7.97	7.95	7.94	7.93
1...	7.95	7.94	7.93	7.91	7.90	7.88	7.87	7.86	7.84	7.83	7.82	7.80	7.79	7.77	7.76	7.75	7.73
2...	7.76	7.75	7.73	7.72	7.71	7.69	7.68	7.67	7.65	7.64	7.63	7.62	7.60	7.59	7.58	7.56	7.55
3...	7.58	7.56	7.55	7.54	7.52	7.51	7.50	7.49	7.47	7.46	7.45	7.44	7.42	7.41	7.40	7.38	7.37
4...	7.40	7.39	7.37	7.36	7.35	7.34	7.32	7.31	7.30	7.29	7.27	7.26	7.25	7.24	7.23	7.21	7.20
5...	7.23	7.21	7.20	7.19	7.18	7.17	7.15	7.14	7.13	7.12	7.11	7.09	7.08	7.07	7.06	7.05	7.04
6...	7.06	7.05	7.04	7.03	7.01	7.00	6.99	6.98	6.97	6.96	6.95	6.93	6.92	6.91	6.90	6.89	6.88
7...	6.90	6.89	6.88	6.87	6.86	6.84	6.83	6.82	6.81	6.80	6.79	6.78	6.77	6.76	6.75	6.73	6.72
8...	6.75	6.74	6.73	6.71	6.70	6.69	6.68	6.67	6.66	6.65	6.64	6.63	6.62	6.61	6.60	6.59	6.57
9...	6.60	6.59	6.58	6.57	6.56	6.55	6.54	6.52	6.51	6.50	5.49	6.48	6.47	6.46	6.45	6.44	6.43
10...	6.45	6.44	6.43	6.42	6.41	6.40	6.39	6.38	6.37	6.36	6.35	6.34	6.33	6.32	6.31	6.30	6.29
11...	6.32	6.31	6.30	6.29	6.28	6.27	6.26	6.25	6.24	6.23	6.22	6.21	6.20	6.19	6.18	6.17	6.16
12...	6.18	6.17	6.16	6.15	6.14	6.13	6.12	6.11	6.11	6.10	6.09	6.08	6.07	6.06	6.05	6.04	6.03
13...	6.05	6.04	6.03	6.02	6.02	6.01	6.00	5.99	5.98	5.97	5.96	5.95	5.94	5.93	5.92	5.91	5.90
14...	5.93	5.92	5.91	5.90	5.89	5.88	5.87	5.86	5.85	5.85	5.84	5.83	5.82	5.81	5.80	5.79	5.78
15...	5.81	5.80	5.79	5.78	5.77	5.76	5.75	5.74	5.74	5.73	5.72	5.71	5.70	5.69	5.68	5.68	5.67
16...	5.69	5.68	5.67	5.66	5.65	5.65	5.64	5.63	5.62	5.61	5.60	5.60	5.59	5.58	5.57	5.56	5.55
17...	5.57	5.57	5.56	5.55	5.54	5.53	5.53	5.52	5.51	5.50	5.49	5.48	5.48	5.47	5.46	5.45	5.44
18...	5.46	5.46	5.45	5.44	5.43	5.42	5.42	5.41	5.40	5.39	5.38	5.38	5.37	5.36	5.35	5.34	5.34
19...	5.36	5.35	5.34	5.33	5.33	5.32	5.31	5.30	5.30	5.29	5.28	5.27	5.26	5.26	5.25	5.24	5.23
20...	5.26	5.25	5.24	5.23	5.22	5.22	5.21	5.20	5.19	5.19	5.18	5.17	5.16	5.16	5.15	5.14	5.13
21...	5.15	5.15	5.14	5.13	5.12	5.12	5.11	5.10	5.10	5.09	5.08	5.07	5.07	5.06	5.05	5.04	5.04
22...	5.06	5.05	5.04	5.04	5.03	5.02	5.01	5.01	5.00	4.99	4.98	4.98	4.97	4.96	4.96	4.95	4.94
23...	4.96	4.96	4.95	4.94	4.93	4.93	4.92	4.91	4.91	4.90	4.89	4.89	4.88	4.87	4.86	4.86	4.85
24...	4.87	4.86	4.86	4.85	4.84	4.84	4.83	4.82	4.82	4.81	4.80	4.80	4.79	4.78	4.77	4.77	4.76
25...	4.78	4.78	4.77	4.76	4.76	4.75	4.74	4.73	4.73	4.72	4.71	4.71	4.70	4.69	4.69	4.68	4.67
26...	4.70	4.69	4.68	4.68	4.67	4.66	4.66	4.65	4.64	4.64	4.63	4.62	4.62	4.61	4.60	4.60	4.59
27...	4.61	4.61	4.60	4.59	4.59	4.58	4.57	4.57	4.56	4.55	4.55	4.54	4.53	4.53	4.52	4.51	4.51
28...	4.53	4.52	4.52	4.51	4.50	4.50	4.49	4.48	4.48	4.47	4.47	4.46	4.45	4.45	4.44	4.43	4.43
29...	4.45	4.44	4.44	4.43	4.42	4.42	4.41	4.41	4.40	4.39	4.39	4.38	4.37	4.37	4.36	4.36	4.35
30...	4.37	4.37	4.36	4.35	4.35	4.34	4.34	4.33	4.32	4.32	4.31	4.30	4.30	4.29	4.29	4.28	4.27
31...	4.30	4.29	4.28	4.28	4.27	4.27	4.26	4.25	4.25	4.24	4.24	4.23	4.22	4.22	4.21	4.21	4.20
32...	4.22	4.22	4.21	4.20	4.20	4.19	4.19	4.18	4.18	4.17	4.16	4.16	4.15	4.15	4.14	4.13	4.13
33...	4.15	4.14	4.14	4.13	4.13	4.12	4.12	4.11	4.10	4.10	4.09	4.09	4.08	4.08	4.07	4.06	4.06
34...	4.08	4.07	4.07	4.06	4.06	4.05	4.05	4.04	4.03	4.03	4.02	4.02	4.01	4.01	4.00	3.99	3.99
35...	4.01	4.01	4.00	3.99	3.99	3.98	3.98	3.97	3.97	3.96	3.96	3.95	3.94	3.94	3.93	3.93	3.92

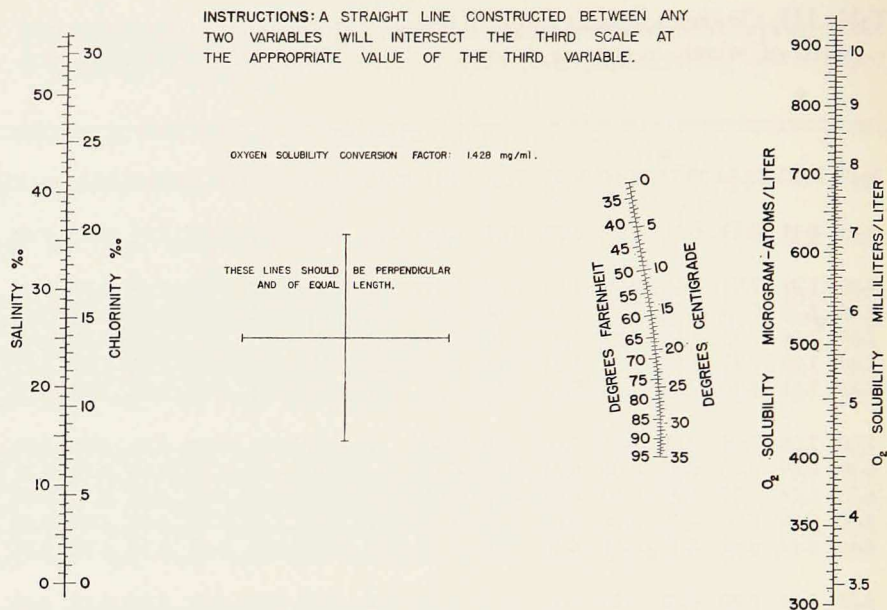


Figure 1. Nomogram for oxygen solubility in seawater at equilibrium with water-saturated air at one atmosphere total pressure and oxygen 0.2094 mole fraction excluding water vapor. Based on data of Green (1965).

spaced values of seawater salinity, will enable oceanographers to obtain saturation values by interpolation in one direction only (between listed temperatures). Salinity, in Table III, is the quantity defined by the Knudsen equation:

$$S = 1.805 Cl + 0.030,$$

where Cl is the chlorinity in parts per thousand. In addition to Tables I–III, a nomogram is presented in Fig. 1 for convenient use in the laboratory.³

The tables below give the saturation values for true thermodynamic equilibrium at a smooth surface. Under natural conditions of turbulence and bubble formation in breakers, two processes tend to increase gas pressure—surface tension and hydrostatic pressure. In addition to these physical sources for supersaturation, biological oxygen production will lead to an increase in oxygen tension above the compensation depth. It has been noted that establishment of equilibration at the surface is a relatively slow process, so that oxygen may be carried downward by eddy diffusion before gas exchange at the sea surface leads to an equilibrium state.

3. Larger nomograms are available from E. J. Green, Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 15213.

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