

Equation of State of Water and Sea Water¹

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The P - V - T data on water by Amagat and Kennedy et al. and on sea water by Newton and Kennedy, the compressibility data on water by Diaz Peña and McGlashan, the bulk compression data on water and sea water by Ekman, and the sound velocity data on water and sea water by Del Grosso and Wilson have been analyzed using the Tait and the Tait-Gibson equations. The P - V - T relationship for water can be well represented by the Tait equation, $V_0^{(P)} = V_0^{(0)} - C \times \log [(B + P)/(B + 1)]$, and for sea water by the Tait-Gibson equation, $V^{(P)} = V^{(0)} - (1 - S \times 10^{-3}) \times C \log [(B^* + P)/(B^* + 1)]$ where $C = 0.315 \times V_0^{(0)}$ and $B = 2668.0 + 19.867t - 0.311t^2 + 1.778 \times 10^{-3}t^3$, for Amagat data in the range of $0 \leq t \leq 45^\circ\text{C}$ and $1 \leq P \leq 1000$ bars and $B^* = (2670.8 + 6.89656 \times S) + (19.39 - 0.0703178 \times S)t - 0.223t^2$ for Ekman's sea water data in the range of $0 \leq t \leq 20^\circ\text{C}$, $1 \leq P \leq 1000$ bars, and $30 \leq S \leq 40\%$.

INTRODUCTION

Tait [1888] first discovered a simple P - V relationship for water that can be written as

$$\beta_0^{(P)} = \frac{-1}{V_0^{(P)}} \left(\frac{\partial V_0^{(P)}}{\partial P} \right)_T$$

$$= \frac{0.4343C}{B + P} \times \frac{1}{V_0^{(P)}} \quad (1)$$

or in integrated form

$$V_0^{(P)} = V_0^{(0)} - C \log \frac{B + P}{B + 1} \quad (2)$$

where

$\beta_0^{(P)}$ is compressibility of water at pressure (bar⁻¹).

V_0 is specific volume of water (ml/g).

C and B are empirical functions of temperature which are independent of pressure.

From the compression data of water through the temperature range 25° to 85°C , Gibson and Loeffler [1941] found that C in equation 1 is equal to $0.3150 \times V_0^{(0)}$, in other words, $C/V_0^{(0)} = 0.3150$ is independent of temperature. Also, B can be expressed by

$$B_{\text{bars}} = 2996.0 + 7.5554(t - 25)$$

$$- 0.17814(t - 25)^2$$

$$+ 608 \times 10^{-6}(t - 25)^3 \quad (3)$$

Gibson [1935] extended the Tait equation to solutions by introducing a single additional parameter called effective pressure, P_e , and assuming that the volume of 1-gram solution containing X_1 grams of solvent and X_2 grams of solute could be represented by

$$V^{(P)} = X_1\psi_1^{(P)} + X_2\psi_2^{(P)} \quad (4)$$

where

ψ_1 is apparent specific volume of the solvent in solution (ml/g).

ψ_2 is apparent specific volume of the solute.

X_1 and X_2 are weight fraction of solvent and solute, respectively.

Then, the P - V relationship for solution can be written [Harned and Owen, 1958, p. 382] as

$$V^{(P)} \times \beta^{(P)} = - \left(\frac{\partial V^{(P)}}{\partial P} \right)_T$$

$$= \frac{0.4343X_1C}{B + P_e + P} - X_2 \frac{\partial \psi_2^{(P)}}{\partial P} \quad (5a)$$

$$V^{(P)} \times \beta^{(P)} \approx \frac{0.4343X_1C}{B^* + P} \quad (5b)$$

or, in integrated form

¹ Lamont Geological Observatory Contribution 1039.

TABLE 1. B of Water Calculated from Amagat's Data in Units of Bars
 $C/V_0^{(1)} = 0.3150$.

P , atm	Temperature					
	0°C	5°C	10°C	15°C	20°C	30°C
100	2656.2	2761.2	2820.8	2877.7	2911.9	2965.0
200	2672.1	2769.8	2840.9	2906.8	2949.3	3015.6
300	2670.0	2781.3	2839.1	2906.9	2960.0	3027.5
400	2669.1	2776.6	2837.7	2904.1	2958.2	3032.5
500	2666.3	2763.3	2836.3	2901.2	2956.3	3029.5
600	2668.5	2760.4	2835.9	2900.2	2955.4	3033.7
700	2668.2	2757.9	2837.7	2902.2	2954.5	3031.5
800	2667.7	2758.0	2837.2	2902.0	2951.4	3032.7
900	2669.2	2761.2	2836.3	2901.8	2954.3	3027.5
1000	2667.6	2762.2	2833.9	2905.1	2956.5	3028.3
Average	2668.1	2762.8	2836.4	2902.4	2955.2	3030.8
$\pm\sigma$	1.0	6.1	1.4	1.5	2.1	2.3
	40°C	50°C	60°C	70°C	80°C	90°C
100	3035.9	3035.1	2996.1	2947.5	2890.6	2879.6
200	3065.2	3078.5	3040.5	2982.0	2921.8	2893.9
300	3082.5	3088.6	3064.8	2998.6	2933.4	2890.0
400	3085.2	3099.1	3074.7	3021.8	2945.1	2884.2
500	3084.4	3095.2	3083.0	3033.3	2955.7	2885.3
600	3082.5	3092.6	3084.7	3038.2	2960.6	2892.4
700	3080.6	3095.0	3080.6	3043.3	2967.3	2900.0
800	3077.1	3093.8	3082.8	3044.1	2971.9	2908.8
900	3078.7	3093.5	3083.2	3044.0	2981.9	2914.6
1000	3081.1	3094.2	3080.0	3042.1	2988.2	2923.7
Average	3081.4	3094.8	3081.3	3038.1	2967.2	2901.3
$\pm\sigma$	2.6	1.8	2.5	7.5	13.8	14.2

TABLE 2. B of Water Calculated from Amagat's Data in Units of Bars
 $C/V_0^{(1)} = 0.3150$.

P , atm	Temperature							
	0°C	4.35°C	10.10°C	14.25°C	20.40°C	29.45°C	40.45°C	48.85°C
100	2666.9	2682.8	2839.0	2852.6	2861.9	2984.4	2929.9	3117.9
200	2672.1	2737.3	2834.7	2874.0	2896.6	3015.1	3044.2	3113.4
300	2670.0	2754.6	2854.2	2904.3	2932.6	3017.3	3078.0	3091.9
400	2675.1	2755.9	2857.8	2905.5	2945.9	3013.2	3081.9	3085.7
500	2672.4	2764.5	2848.7	2916.6	2950.7	3022.8	3073.9	3087.1
600	2671.6	2761.5	2851.3	2915.8	2958.1	3034.5	3080.3	3086.7
700	2672.9	2752.0	2846.1	2908.3	2957.0	3036.7	3084.7	3085.9
800	2667.7	2742.9	2845.7	2901.7	2950.6	3038.5	3093.8	3090.8
900	2666.1	2746.6	2844.8	2896.1	2954.6	3040.3	3102.0	3095.5
1000	2667.6	2749.4	2844.2	2895.7	2958.4	3038.3	3110.0	3100.5
1500	2696.5	2767.6	2857.8	2906.5	2967.6	3030.7	3108.5	3119.0
2000	1835.3	1874.7	1925.8	1956.8	1995.8	2038.4	2069.9	2081.8
2500	2728.0	2798.5	2873.0	2928.1	2984.3	3057.9	3100.2	3120.2
3000	4068.4	4176.4	4305.7	4371.5	4457.5	4567.4	4643.7	4678.2
Average	2670.5	2753.3	2848.4	2905.7	2952.6	3032.0	3089.5	3090.3
$\pm\sigma$	3.2	7.0	4.5	5.7	4.3	9.4	12.0	5.0

$$V^{(P)} = V^{(1)} - X_1 C \log \frac{B + P_* + P}{B + P_* + 1} - X_2 [\psi_2^{(P)} - \psi_2^{(1)}] \quad (6a)$$

$$V^{(P)} \approx V^{(1)} - X_1 C \log \frac{B^* + P}{B^* + 1} \quad (6b)$$

where $B^* = B + P_*$. Since at moderate pressure and concentration $[\psi_2^{(P)} - \psi_2^{(1)}]$ and X_2 are both small, the last terms in equations 5a and 6a are negligible.

The physical meanings of the Tait and Tait-Gibson equations have been discussed elsewhere by Gibson and Kincaid [1938], Ginell [1961],

Simha and Madden [1956], and Nanda and Simha [1966]. Throughout this paper, whole calculations have been aimed at discovering B of water and B^* of sea water by applying equations 1, 2, 5b, and 6b to different sources of data. Gibson's $C/V_0^{(1)} = 0.3150$ has been adapted as the basis of comparison among the different data. All different pressure units have been converted to bar units before calculations.

CALCULATIONS AND RESULTS

Pure Water

P-V-T data of Amagat, Newton and Ken-

TABLE 3. B of Water Calculated from Kennedy's Data in Units of Bars
 $C/V_0^{(1)} = 0.3150$.

P , bars	Temperature					
	0°C	10°C	20°C	30°C	40°C	50°C
100	2605.6	2832.2	2899.2	2972.3	3051.7	3065.0
200	2652.8	2860.5	2930.8	2972.5	3018.2	3031.5
300	2654.0	2838.5	2932.9	2987.7	3022.8	3036.3
400	2647.3	2837.2	2928.4	3009.4	3039.4	3053.2
500	2649.5	2832.1	2922.1	3005.0	3047.5	3045.8
600	2647.0	2825.7	2928.0	3000.4	3038.4	3052.6
700	2651.6	2829.6	2920.3	2984.7	3031.1	3045.4
800	2645.1	2822.4	2913.8	2982.6	3025.5	3040.0
900	2646.3	2816.1	2917.5	2990.5	3031.0	3045.7
1000	2646.6	2810.9	2912.8	2989.4	3036.6	3051.5
1100	2646.7	2806.9	2909.6	3141.7	3034.5	3049.5
1200	2646.9	2810.9	2915.2	2991.0	3034.1	3049.3
1300	2647.6	2808.9	2914.5	2993.8	3035.4	3050.8
1400	2648.8	2808.3	2915.4	2991.3	3031.5	3047.0
Average	2647.6	2824.9	2920.4	2994.5	3035.6	3047.7
$\pm\sigma$	2.0	8.5	5.3	9.6	6.8	4.6
	60°C	70°C	80°C	90°C	100°C	
100	3080.3	3027.6	2979.3	2872.5	2775.9	
200	3047.0	3028.8	2978.9	2900.6	2799.1	
300	3052.0	3020.9	2969.6	2900.3	2815.8	
400	3050.2	3011.8	2959.1	2893.6	2817.2	
500	3046.3	3018.1	2963.4	2898.9	2813.2	
600	3042.2	3020.9	2964.3	2900.0	2807.0	
700	3038.6	3010.8	2952.7	2888.7	2809.8	
800	3035.7	3002.6	2952.9	2888.2	2801.8	
900	3033.9	3005.5	2953.1	2887.4	2802.6	
1000	3033.3	3000.1	2945.3	2886.9	2802.9	
1100	3033.9	2996.5	2947.1	2886.9	2803.2	
1200	3035.9	3002.1	2949.7	2887.6	2810.5	
1300	3039.3	3001.4	2946.5	2889.3	2811.5	
1400	3037.2	3002.4	2944.9	2885.7	2813.2	
Average	3040.0	3010.0	2955.8	2892.0	2807.8	
$\pm\sigma$	5.8	6.9	6.2	4.3	5.3	

TABLE 4. B of Water Calculated from Newton and Kennedy's Data in Units of Bars
 $C/V_0^{(1)} = 0.3150$.

P , bars	Temperature					
	0°C	5°C	10°C	15°C	20°C	25°C
100	2658.7	2771.3	2832.2	2896.6	2899.2	2968.1
200	2678.8	2736.4	2828.7	2894.8	2930.8	2968.2
300	2673.3	2732.6	2816.9	2884.5	2932.9	2983.3
400	2677.2	2738.6	2820.4	2873.1	2928.4	2967.9
500	2674.1	2750.4	2818.3	2876.0	2922.1	2970.1
600	2668.1	2744.3	2814.0	2875.6	2928.0	2969.8
700	2670.3	2747.3	2819.2	2873.9	2931.4	2968.7
800	2670.4	2748.4	2813.1	2871.8	2923.7	2967.6
900	2669.3	2748.5	2816.1	2878.8	2926.6	2967.1
1000	2667.9	2748.5	2810.9	2876.9	2921.2	2967.3
1100	2666.6	2748.6	2814.2	2875.9	2925.2	2976.6
1200	2665.6	2749.2	2810.9	2876.0	2922.5	2978.5
1300	2671.3	2750.5	2815.4	2877.2	2928.4	2981.7
Average	2671.1	2746.6	2816.0	2875.1	2925.9	2968.4
$\pm\sigma$	3.1	4.8	2.8	2.1	3.4	1.2

ned, Kennedy et al. Rearranging equation 2 yields

$$B = \frac{P-1}{\{\exp[(1-V_0^{(P)}/V_0^{(1)})/0.1368]-1\}} - 1 \quad (8)$$

B 's calculated for different pressure should be independent of pressure, if the Tait equation is valid. The results, as given in Tables 1, 2, 3, and 4 and summarized in Figure 1, show that this is the case, except that B 's at pressures less than 300 bars tend to have a greater scatter. In averaging B , only the values between 400 and 1000 bars have been taken into account. This selection is justified and will be explained in the summary of this section.

For the values of B between 400 and 1000 bars, Amagat's [Dorsey, 1940, Table 95-I] first table shows uniformly small deviations (less than 0.1%) up to 60°C temperature. For temperatures greater than 60°C, the deviations in B increase systematically with increasing temperature.

Amagat's second table shows greater deviation of B 's (about 0.3%) except at 0°C, but B 's still follow closely the pattern of the first table. B 's at pressure greater than 1500 bars are quite random.

B value at 0°C in Table 4 by Newton and Kennedy [1965] agree very well with that of

Amagat [Dorsey, 1940]. Other B values of Kennedy et al. [1958] (Tables 3 and 4) are systematically lower than values of Amagat, though they are internally consistent. The standard deviation of B 's in Table 3 is less than 0.3%; in Table 4, better than 0.2%.

Ekman's apparent bulk compression data. The bulk compression K_0 , by definition equal to $1 - V_0^{(P)}/V_0^{(1)}$, of water was obtained from apparent compression K_0' data by the relation

$$K_0 = K_0'(1 - K_g) + K_g \quad (9)$$

where K_g is compression of the glass in which the water is contained. $K_g = (P - 1)\nu$, where the average compressibility of glass $\nu = 0.225 \times 10^{-6} \text{ bar}^{-1}$ was used in calculation. Then, by means of equation 8, B 's have been determined and are listed in Table 5. The table shows that Ekman's [1908, Table 10] data are extremely internally consistent. The standard deviation of B 's is less than 0.03%. B values tend to be slightly higher than the value in Amagat's first table. It is fortunate that Ekman used Amagat's zero degree temperature data for pressure calibration, since both Amagat's zero degree temperature data are internally very consistent with respect to the Tait equation. In a footnote of Ekman's [1908, p. 36] paper, he suggested the revised value of average compressibility of glass $\nu = 0.215 \times 10^{-6} \text{ bar}^{-1}$, but this revised ν

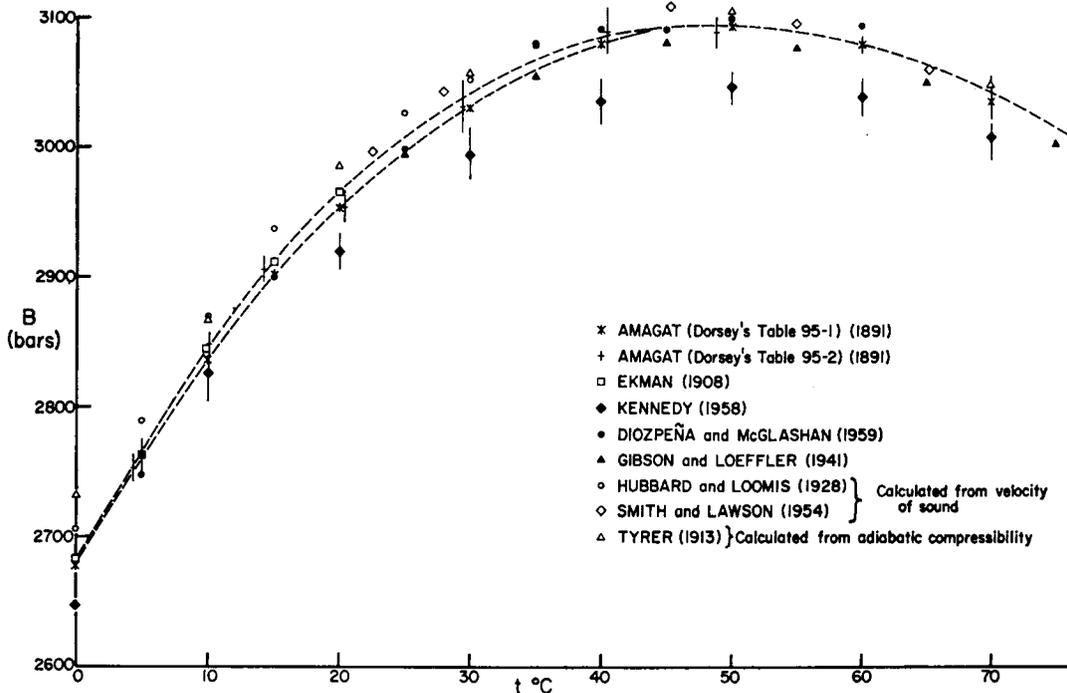


Fig. 1. B of water as a function of temperature.

value increases the B values only about 1 bar, which is still within experimental uncertainty. Ekman's data has been reviewed by Eckart [1958], but unfortunately Eckart made a mistake in pressure conversion and in so doing reached a pessimistic conclusion about Ekman's data.

Compressibility data of Diaz Peña and Mc-

TABLE 5. B of Water Calculated from Ekman's Data in Units of Bars
 $C/V_0^{(1)} = 0.3150$.

P , bars	Temperature				
	0°	4.97°	9.97°	14.96°	19.96°
201.08	2671.4	2763.2	2844.7	2911.7	2964.6
	2671.4	2763.5	2843.8	2909.8	2965.0
403.56	2670.8	2762.9	2843.3	2908.9	2964.1
	2670.8	2761.8	2843.3	2908.9	2965.2
599.44	2671.9	2763.2	2843.4	2909.7	2964.8
	2671.9	2763.2	2843.2	2909.3	2965.1
Average	2671.4	2763.0	2843.6	2909.7	2964.8
$\pm\sigma$	0.3	0.6	0.5	0.9	0.4

Glashan. The isothermal compressibility of water at one atmosphere $\beta_0^{(1)}$ was determined from data related to compression of water at pressures up to 30 atm and at temperatures up to 60°C.

From the rearranged form of equation 1

$$B = 0.1368/\beta_0^{(1)} - 1 \quad (10)$$

B 's were calculated. The results, as shown in Table 6 and Figure 1, agree very well with Amagat's first table in spite of the extremely different pressure range; i.e., B 's are independent of pressure.

Sound velocity data in water by Wilson. The isothermal compressibility of water $\beta_0^{(1)}$ at atmospheric pressure was calculated by the following relations:

$$\beta_s^{(P)} = 10^6 \times V^{(P)}/\mu_{(P)}^2 \quad (11)$$

$$\beta^{(P)} = \beta_s^{(P)} + 0.1T\alpha_{(P)}^2 V^{(P)}/C_P^{(P)} \quad (12)$$

where

μ = velocity of sound (cm/sec).

V = specific volume (cm³/g).

TABLE 6. B of Water Calculated from Diaz Peña and McGlashan's Data
 $C/V_0^{(1)} = 0.3150$.

$t, ^\circ\text{C}$	5	15	25	35	40	45	50	60
$\beta_0^{(1)} \times 10^6, \text{amt}^{-1}$	50.45	47.78	46.22	45.01	44.84	44.70	44.70	44.78
B, bars	2746.7	2900.3	2998.2	3078.8	3090.5	3090.5	3100.2	3094.7

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

C_P = specific heat (joules/deg gram).

T = absolute temperature ($^\circ\text{K}$).

β_s = adiabatic compressibility (bar^{-1}).

β = isothermal compressibility (bar^{-1}).

The atmospheric data of μ are given by *Wilson* [1959], V and α are given by *Chappins'* equation [*Dorsey*, 1940], and C_P is given by *Cox and Smith* [1959]. Then, by equation 10, B 's were determined.

B 's can be represented by the equation

$$B = 2689.81 + 20.233t - 0.3081t^2 + 1.38 \times 10^{-3}t^3 \quad (13)$$

in the temperature range $0^\circ \leq t \leq 30^\circ\text{C}$.

$\beta_0^{(w)}$ calculated from measurements of adiabatic compressibility and the sound velocity in water by other authors are summarized in Figure 5 of *Diaz Peña and McGlashan* [1959, p. 2023]. For comparison, some of the B 's calculated from those $\beta_0^{(w)}$ data are also plotted in Figure 1 along with that of *Wilson*. Agreement among the values are very good, but B 's are always higher than the values of *Amagat*, *Ekman*, and *Diaz Peña and McGlashan* at temperatures less than 30°C .

Once B values are known, $V_0^{(p)}$, $\alpha^{(p)}$, $C_P^{(p)}$, and $\beta_0^{(p)}$ at pressure P can be calculated by the *Tait* [1888] equation, so that the sound velocity at higher pressure can be predicted by equations 11 and 12. The pressure dependence of sound velocity in water at 0°C was calculated by using *Ekman's* and *Wilson's* B values (2670.8 and 2689.8, respectively, at 0°C). Since the second term in equation 12 is only a small fraction of β at 0°C (about 0.1%), calculation at 0°C minimizes the uncertainty involved in the second term of equation 12. The results are shown in Table 7. As noticed by *Del Grosso* [1952] and *Wilson* [1959, 1960], the sound velocity at atmospheric pressure predicted by *Ekman's*

data are systematically lower than sound velocity from direct measurements. In the pressure range between 100 and 800 bars, however, the predicted and the directly measured values agree within 2 m/sec in the present calculation. The results are essentially the same as *Mathews'* calculation [*Wilson*, 1959]. On the other hand, by using *Wilson's* B value, the predicted values are all higher than the measured values. For the difference of B calculated by *Ekman's* data and by *Wilson's* atmospheric sound velocity in water, there are two possible explanations:

1. The quantity B may be pressure dependent at lower pressure, though this explanation can hardly be reconciled with the results of *Diaz Peña and McGlashan* [1959].
2. As *Crease* [1962] noted, since sound velocity measurements have been made with high-frequency pulses, it is possible that the water does not remain in equilibrium at lower pressure, though *Del Grosso* [1952] has estimated that this effect is likely to be small.

In summary, it is interesting to note that the most internally consistent P - V - T data of water are the values of *Amagat* [1893] and of *Ekman* [1908], which are more than half a century old.

 TABLE 7. Sound Velocity in Water at 0°C (m/sec)

Pressure, psia	Pressure, bars	Measured by Wilson	Predicted (Ekman) $B = 2670.8$	Predicted (Wilson) $B = 2689.8$
14.7	1	1403.01	1398.3	1403.01
2000	137.89	1424.49	1423.5	1428.1
4000	275.79	1447.24	1448.4	1453.0
6000	413.68	1470.93	1473.1	1477.5
8000	551.58	1495.36	1497.3	1501.6
10000	689.47	1520.36	1521.2	1525.5
12000	827.36	1545.72	1544.9	1549.1
14000	965.26	1571.28	1568.3	1572.4

B values of Amagat's first table can be represented by the equation

$$B = 2668.0 + 10.867t - 0.3111t^2 + 1.778 \times 10^{-3}t^3 \quad (14)$$

in the range between 0° and 45°C .

$$B = 3009.4 + 7.555(t - 25) - 0.1781(t - 25)^2 + 0.608 \times 10^{-3}(t - 25)^3 \quad (15)$$

for $t \geq 45^\circ\text{C}$.

For Ekman's B values

$$B = 2670.8 + 19.90t - 0.260t^2 \quad (16)$$

in the range 0° to 20°C .

For Newton and Kennedy's B values

$$B = 2672.9 + 15.97t - 0.166t^2 \quad (17)$$

for $0^\circ \leq t \leq 25^\circ\text{C}$.

$$B = 2968.4 + 7.555(t - 25) - 0.1781(t - 25)^2 + 0.608 \times 10^{-3}(t - 25)^3 \quad (18)$$

for $t \geq 25^\circ\text{C}$.

The curvatures of B , as a function of temperature, by both Ekman and Wilson agree very well with each other. At higher temperatures ($t > 30^\circ\text{C}$), the curvatures of B by Amagat and Kennedy et al. agree with that by Gibson and Loeffler, as is apparent from Figure 1.

Assuming temperature and pressure have been calibrated quite accurately by different authors, the uncertainty in specific volume measurements of water, ΔV , can be related to the deviation of B value, ΔB , by

$$\pm \Delta V = C \times \log \left[\frac{B + P}{B + 1} \cdot \frac{B + 1 \pm \Delta B}{B + P \pm \Delta B} \right] \quad (19)$$

The P - ΔV - ΔB relationships at 0°C are shown in Figure 2. At different temperatures, the picture is essentially the same. It can be seen from Figure 2 that, for the same uncertainty in ΔV , ΔB must be greater at lower pressure than at higher pressure. For instance, $\Delta V = 3 \times 10^{-5}$

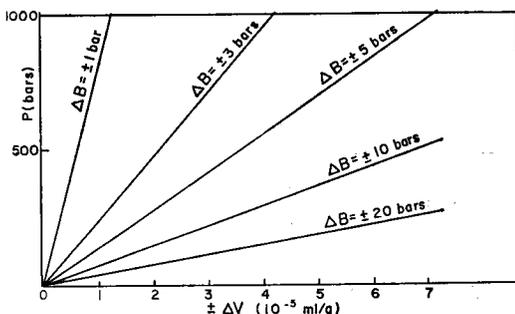


Fig. 2. P - ΔV - ΔB relations at 0°C .

ml/g causes 20-bar deviation of B at 100-bar pressure, but at 1000 bars ΔB is only 2 bars. This explains the greater scatter of B values at pressures less than 300 bars and justifies averaging only the B values between 400 and 1000 bars.

Ekman's standard deviation of B is better than ± 1 bar, which corresponds to about 1×10^{-5} ml/g deviation in specific volume of water.

For Amagat's first table, the standard deviation of B is about ± 2 bars at temperatures less than 60°C , i.e., ΔV about $\pm 2 \times 10^{-5}$ ml/g. For the rest of the data, ΔV is apparently better than $\pm 10 \times 10^{-5}$ ml/g.

The fact that Newton and Kennedy's B values, except at 0°C , are systematically far lower than the values of Amagat, Ekman, Diaz Peña and McGlashan, and Gibson may imply a systematic difference in volume measurement and/or in pressure scale calibration. A careful check on this matter is needed.

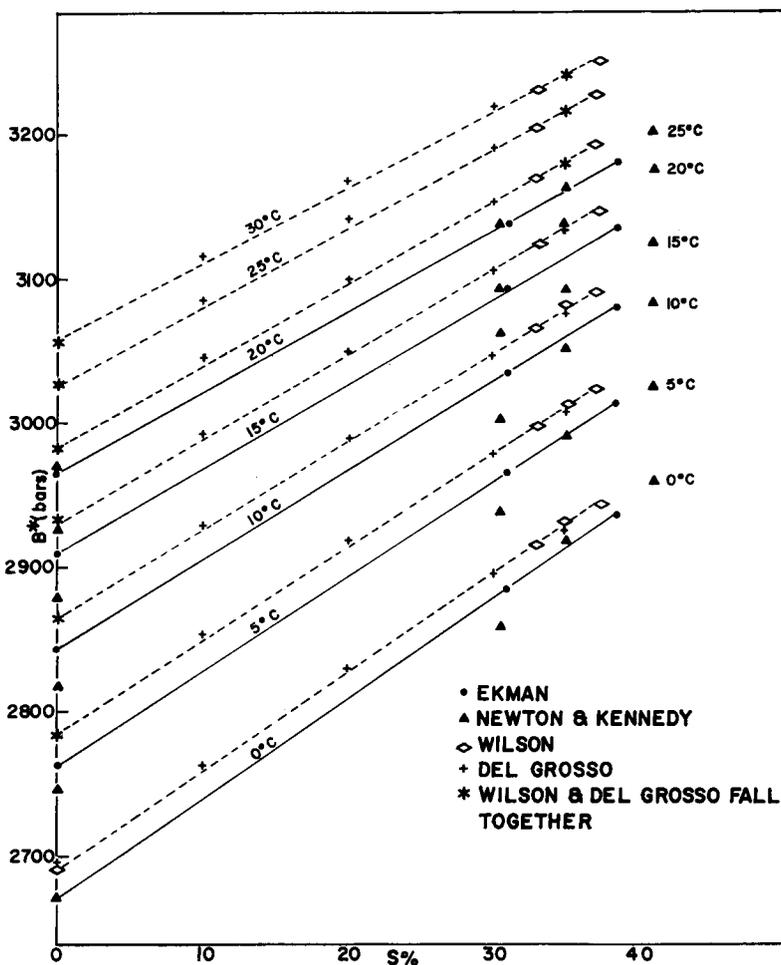
Sea Water

General. The P - V - T data of sea water used widely in dynamical oceanographic calculations are primarily based on Ekman's [1908] compression determination on two different salinity sea waters and Knudsen's [1901] V - T data on different chlorinity sea waters under atmospheric pressure. Tables summarizing Ekman's and Knudsen's data are given in Dorsey's Table 109-A and Table 108, respectively [Dorsey, 1940, p. 248].

Applying Dorsey's Table 109-A to equation 6b, B^* values were determined as shown in Table 8 and Figure 3. Again B^* 's are independent of pressure. The standard deviation of B^* is better than 0.05%.

TABLE 8. B^* of Sea Water Calculated from Ekman's Data

P , bars	Temperature				
	0°C	4.97°C	9.97°C	14.96°C	19.96°C
	$B_N^* = 31.13; C/V_0^{(1)} = 0.3150$				
201	2885.7	2968.2	3038.0	3096.6	3138.4
401	2886.1	2966.5	3034.7	3092.7	3139.1
601	2884.8	2964.8	3033.5	3091.9	3137.1
Average	2885.5 ± 0.5	2966.5 ± 1.4	3035.4 ± 1.2	3093.8 ± 1.8	3138.2 ± 0.8
	$B_N^* = 38.525; C/V_0^{(1)} = 0.3150$				
201	2938.1	3013.2	3080.3	3138.5	3181.7
401	2937.2	3015.1	3082.0	3135.8	3181.4
601	2936.4	3014.2	3079.9	3134.5	3179.6
Average	2937.3 ± 0.7	3014.2 ± 0.8	3080.7 ± 0.9	3136.2 ± 1.7	3180.9 ± 0.9

Fig. 3. B^* as a function of salinity.

B^* 's can be closely represented as a parabolic function of temperature by

$$B^*_{S=38.525} = 2936.5 + 16.68t - 0.223t^2 \quad (20a)$$

$$B^*_{S=31.15} = 2885.5 + 17.20t - 0.223t^2 \quad (20b)$$

in the temperature range 0° to 20°C .

Since for most electrolyses solutions of single salts at concentration less than 1 molarity B^* is a linear function of molarity (or ionic strength) [Gibson, 1935], equations 20a and 20b can be linearly extrapolated back to zero salinity; i.e.,

$$B^*_{S=0} = B = 2670.8 + 19.39t - 0.223t^2 \quad (20c)$$

The close agreement between equation 20c and B values obtained from Ekman's compression data on water, as shown in Figure 4, again indicates the excellent internal consistency of

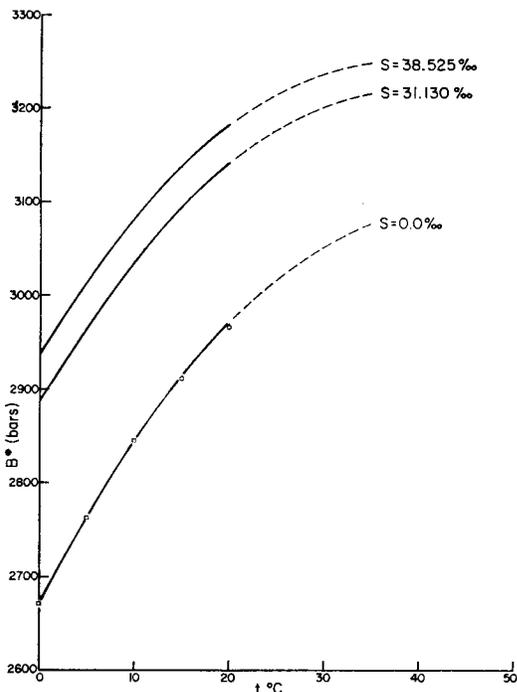


Fig. 4. B^* as a function of temperature and salinity.

TABLE 9

The difference of specific volume of sea water (with 35‰ salinity, at 0°C temperature, and at different pressures) calculated from Ekman's equation of state of sea water and the Tait-Gibson equation given in this paper [$(V_{35,0,P})_{\text{Ekman}} - (V_{35,0,P})_{\text{calcl}}$] $\times 10^6$ ml/g.

Pres- sure, bars	0	10	20	30	40	50	60	70	80	90
1	0	0	0	0	0	-1	0	0	-1	-1
101	-1	0	-1	0	-1	-1	-1	-1	-1	0
201	-1	0	0	0	0	0	-1	0	-1	0
301	0	0	0	0	0	0	-1	-1	-1	-1
401	-1	0	0	-1	0	0	-1	0	-1	-1
501	0	0	0	0	0	0	0	0	0	0
601	0	0	0	0	0	0	0	0	0	0
701	0	0	0	0	0	0	0	0	0	0
801	0	0	0	0	0	+1	+1	+1	+1	0
901	+1	+1	0	+1	+1	+1	0	0	+1	+1

Ekman's compression measurements both on water and on sea water.

In summary, the P - V - T relationship of sea water in the range of $0^\circ \leq t \leq 20^\circ\text{C}$, $1 \leq P \leq 1000$ bars, and $30 \leq S \leq 40\%$ can be well represented by

$$V^{(P)} = V^{(1)} - (1 - S \times 10^{-3}) \times C \log \frac{B^* + P}{B^* + 1} \quad (21a)$$

where $C = 0.3150 \times V_0^{(1)}$ and S is salinity (‰) and where

$$B^* = (2670.8 + 6.8966S) + (19.39 - 0.0703S)t - 0.223t^2 \quad (21b)$$

(Equation 21b can be used for $S = 0$, except at 20°C ; B is about 3 bars higher than the value given by Ekman's [1908] pure water data.)

To substantiate the validity of equation 21a the specific volume of sea water of salinity 35‰ at 0°C and at different pressures have been calculated by equation 21a and are compared with $V_{35,0,P}$ values given in Bjerknes and Sandström's [1910] table, which were based on Ekman's data using his equation of state of sea water [Bjerknes and Sandström, 1910, p. 31]. The results are shown in Table 9. The agreement between them is excellent; i.e., Ekman's

TABLE 10. B^* , ψ_1 , and ψ_2 for Sea Water

B^* 's of sea water are calculated from equation 21b. The most possible apparent specific volumes of solute in sea water ψ_2 are calculated from equation 24.

	S‰	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C
B^*_{calc}	38.525	2936.5	3014.32	3081.0	3136.52	3180.9	(3214.12)*	(3236.2)	(3247.1)
	31.130	2885.5	2965.92	3035.2	3093.32	3140.3	(3176.12)	(3202.8)	(3214.3)
	0.0	2670.8	2762.17	2842.4	2911.47	2969.4	(3016.17)	(3051.8)	(3076.2)
ψ_1	38.525	.98716	.98806	.98924	.99067	.99233			
	31.130	.98955	.99027	.99129	.99257	.99409			
ψ_2	38.525	.54066	.52987	.51906	.50824	.49718			
	31.130	.54119	.53010	.51932	.50803	.49697			
ψ_2 Most possible values		.54100	.53005	.51910	.50815	.49720	(.48625)	(.47530)	(.46435)

* Parentheses indicate extrapolated values.

very involved equation of state of sea water is equivalent to the much simpler expression given here.

Another check on the validity of the Tait-Gibson equation for sea water is as follows:

The apparent specific volume of water in sea water solution, $\psi_1^{(w)}$, can be calculated from equation 2 by assuming that $\psi_1^{(w)}$ is equal to the specific volume of pure water under the ex-

ternal pressure equal to the effective pressure, P_e , of the considered solution; i.e.,

$$\psi_1^{(1)} = V_0^{(P_e)} = V_0^{(1)} \left(1 - 0.315 \log \frac{B^*}{B + 1} \right) \quad (22)$$

where B^* and B can be obtained from equation 21b for any salinity at different temperatures.

TABLE 11

The difference of density of sea water between the values calculated from the Tait-Gibson equation and the values given by Knudsen $(\rho_{\text{calc}} - \rho_{\text{Knudsen}}) \times 10^{+5}$ g/ml.

Cl, ‰	x_1	x_2	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C
1	0.99816	0.00184	-4	-4	-4	-4	-4	-4	-4	-4
2	636	364	-5	-5	-5	-5	-6	-6	-5	-5
3	455	545	-4	-4	-5	-4	-6	-5	-5	-4
4	275	725	-4	-4	-5	-5	-6	-7	-6	-6
5	094	906	-4	-4	-5	-5	-6	-6	-7	-6
6	0.98914	0.01086	-4	-4	-4	-6	-6	-7	-8	-7
7	733	267	-3	-3	-4	-5	-5	-6	-7	-7
8	553	447	-3	-3	-3	-5	-6	-6	-8	-7
9	372	628	-2	-2	-2	-4	-5	-5	-6	-6
10	192	808	-2	-2	-2	-4	-4	-5	-6	-6
11	011	986	0	-1	-1	-3	-4	-4	-5	-5
12	0.97831	0.02169	0	-1	-1	-3	-3	-4	-5	-5
13	650	350	0	0	0	-1	-2	-4	-4	-4
14	470	530	0	+1	0	-1	-2	-4	-4	-4
15	289	711	+1	+1	+1	0	-2	-2	-4	-3
16	109	891	+1	+1	+1	0	-2	-3	-4	-3
17	0.96928	0.03072	+1	+1	+1	0	-1	-2	-4	-3
18	748	252	0	0	+1	+1	-1	-2	-3	-3
19	567	433	+1	+1	+2	+1	0	-2	-2	-3
20	387	613	-1	0	+1	+1	0	-2	-3	-4
21	206	794	0	0	+1	+1	+1	-1	-2	-3
22	026	974	-2	0	0	+1	0	-1	-3	-4
23	0.95845	0.04155	-3	-2	0	0	0	0	-2	-3

TABLE 12. B^* of Sea Water Calculated from Newton and Kennedy's Data (in units of bars)

P , bars	0°	5°	10°	15°	20°	25°
$S = 30.52\%$; $C/V_0^{(1)} = 0.3150$						
100	2804.4	2933.8	3004.1	3078.7	3081.5	3085.0
200	2866.3	2934.2	3006.5	3083.2	3086.1	3128.4
300	2856.4	2949.9	3025.2	3078.7	3108.0	3138.5
400	2880.7	2953.6	3011.7	3073.0	3096.2	3141.3
500	2849.0	2937.7	3001.0	3067.7	3087.3	3141.9
600	2849.3	2938.1	3005.9	3063.4	3094.9	3142.4
700	2859.3	2937.7	2997.4	3060.3	3101.0	3143.3
800	2856.8	2937.4	3001.7	3058.5	3095.4	3133.6
900	2854.9	2938.1	2996.3	3058.2	3092.0	3137.8
1000	2862.1	2929.9	2993.9	3050.0	3081.3	3123.6
1200	2869.1	2943.9	2999.5	3058.0	3094.3	3140.5
1300	2877.5	2955.7	3008.7	3072.1	3106.8	3151.0
Average	2858.9	2937.5	3002.0	3061.6	3092.6	3138.7
$\pm\sigma$	10.1	6.8	5.9	6.6	6.2	6.5
$S = 34.99\%$						
100	2920.4	2989.2	3062.4	3064.3	3143.1	3146.6
200	2920.5	2991.2	3066.6	3068.5	3149.6	3153.2
300	2935.0	3009.6	3061.9	3090.1	3147.0	3150.6
400	2920.8	3015.4	3056.0	3098.6	3143.2	3168.2
500	2923.4	3000.9	3050.5	3085.7	3139.9	3161.0
600	2923.6	2989.8	3046.0	3090.7	3137.6	3156.2
700	2923.0	2993.0	3054.1	3094.8	3136.5	3166.6
800	2912.2	2985.2	3051.8	3099.0	3136.9	3164.3
900	2913.1	2989.3	3050.2	3093.4	3128.1	3164.1
1000	2914.6	2984.9	3050.3	3090.4	3132.3	3165.9
1100	2909.0	2982.6	3043.4	3080.7	3128.9	3160.4
1200	2913.0	2982.2	3039.3	3082.6	3128.1	3166.6
1300	2918.1	2983.6	3045.4	3086.6	3129.8	3166.5
Average	2918.7	2994.1	3051.4	3093.2	3136.4	3163.8
$\pm\sigma$	5.1	10.0	2.3	4.4	4.6	3.8
$S = 41.03\%$						
100	2970.4	3042.0	3118.4	3120.3	3202.5	3206.0
200	2972.2	3045.9	3085.2	3126.4	3211.0	3214.7
300	2965.3	3040.9	3094.5	3123.5	3210.3	3214.0
400	2957.3	3034.7	3096.6	3119.4	3186.5	3212.2
500	2965.2	3029.0	3096.6	3133.0	3189.1	3210.9
600	2957.2	3024.2	3081.9	3127.9	3176.1	3195.2
700	2960.7	3032.9	3084.0	3124.7	3180.8	3198.1
800	2953.9	3029.4	3075.3	3123.3	3174.0	3202.1
900	2958.7	3027.5	3079.8	3123.9	3170.3	3196.2
1000	2954.8	3027.4	3075.6	3116.4	3159.2	3193.5
1100	2952.9	3020.2	3073.9	3121.1	3161.3	3193.6
1200	2952.7	3024.0	3074.5	3118.9	3165.6	3197.2
1300	2954.3	3021.6	3077.2	3119.4	3163.6	3192.7
Average	2958.1	3026.6	3084.3	3124.1	3176.6	3201.2
$\pm\sigma$	3.4	4.1	8.1	5.2	9.1	6.8

Once $\psi_1^{(w)}$ is known, $\psi_2^{(w)}$ can be calculated from equation 4; i.e.,

$$\psi_2^{(1)} = (V^{(1)} - X_1\psi_1^{(1)})/X_2 \quad (23)$$

Following above procedures, $\psi_1^{(w)}$ and $\psi_2^{(w)}$ for sea water with 38.525 and 31.13‰ salinity have been determined. The results, as given in Table 10, show that $\psi_2^{(w)}$'s are almost independent of salinity and may be represented by

$$\psi_2^{(1)} = 0.541 - 0.00219t \text{ ml/g} \quad (24)$$

So once temperature and salinity of sea water are known, the specific volume of sea water under atmospheric pressure can be calculated from

$$V^{(1)} = X_1\psi_1^{(1)} + X_2\psi_2^{(1)} = \frac{1}{\rho(1)} \quad (25)$$

where $\psi_1^{(w)}$ and $\psi_2^{(w)}$ can be obtained from equations 22 and 24, respectively.

The densities of sea water under atmospheric pressure with the same salinity and temperature values given in *Dorsey* [1940, Table 108] have been calculated from equation 25 and are compared with *Dorsey's* Table 108. The agreement between them, as shown in Table 11, is again quite satisfactory. The minor disagreement at lower salinity may reiterate the statement that $\psi_2^{(w)}$ diminishes slightly with concentration [*Harned and Owen*, 1958, p. 385]. The disagreement above 25°C is as expected, since B^* and B above 25°C can no longer be closely represented as a parabolic function of temperature.

Data of Newton and Kennedy. From *Newton and Kennedy's* [1965] P - V - T - S data on sea water, the B^* for three different salinities

were determined by equation 6b and are shown in Table 12 and Figure 3. B^* values for salinities 34.99 and 44.03‰ in the temperature range between 0° and 10°C agree quite satisfactorily with *Ekman's* values, but other B^* points are all too low with respect to *Ekman's* values, as in the case of distilled water.

Sound velocity data in sea water by Del Grosso [1952] and *Wilson* [1960]. The isothermal compressibilities at atmospheric pressure were calculated from equations 11 and 12; then from equation 5b B^* was calculated. The results are plotted in Figure 3.

Wilson's B^* values can be well represented by the equation

$$B^* = B + S/37(252.59 - 2.883t + 4.365 \times 10^{-2}t^2 - 0.4017 \times 10^{-3}t^3) \quad (26)$$

where S = salinity (‰) and B = equation 13. B^* values are systematically higher than *Ekman's* [1908] values by about 20 bars. The B^* 's show a linear relation with salinity, however, and have almost the same slopes as *Ekman's* values. *Del Grosso's* B^* points show slight curvature and are concave downward as a function of salinity. As shown by *Wilson* [1960], the sound velocities predicted by *Kuwahara*, using *Ekman's* compression data, agree quite well with *Wilson's* direct measurements except at lower pressure, as already seen for the case of pure water.

Crease [1962] has also calculated the specific volume of sea water under pressure by using *Wilson's* sound velocity data under pressure and the new C_p data at atmospheric pressure by *Cox and Smith* [1959]. He has confirmed that *Ekman's* compression data between

TABLE 13. B of Water Calculated from Bridgeman's Data [*Dorsey*, 1940, Table 95-III]
 $C/V_0^{(w)} = 0.3150$.

P , atm	Temperature								
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C
500	2722	2856	3021	3061	3088	(3201)	(3252)	3121	3048
1000	2711	2897	3012	3092	3123	3147	3146	3120	3053
1500	2725	2895	3008	3091	3118	3134	3125	3105	3042
2000	2731	2903	3016	3081	3117	3134	2119	3104	3038
Average	2722	2888	3014	3081	3111	3139	3130	3115	3045
$\pm\sigma$	7	18	5	12	13	6	11	7	6

TABLE 14. B of Water Calculated from Bridgeman's Data
 $C/V_0^{(1)} = 0.3150$.

P , Kg/cm ²	Temperature					
	0°C	20°C	40°C	60°C	80°C	100°C
500	2659	3130	3151	2972	2876	2534
1000	2688	3010	3153	3072	2969	2698
1500	2714	3029	3143	3106	3006	2762
2000	2731	2994	3126	3115	3028	2807
Average	2698	3016	3143	3066	2970	2700
$\pm\sigma$	30	16	10	53	58	100

200 and 600 bars are in agreement with his calculation.

The disagreements of B^* values between Ekman and Wilson can be explained by the same argument used for pure water.

Murnaghan Equation of State

From analysis of Bridgeman's P - V - T data of water, McDonald [1966] suggested that Murnaghan's equation may be superior to the Tait equation. But, as shown in Tables 13 and 14, the B values of Bridgeman's data are far higher than other values in the range of interest. The parameter n in the Murnaghan equation

$$n = \frac{1}{(P-1)\beta_0} \left[\left(\frac{V_1}{V_P} \right)^n - 1 \right]$$

was calculated for Ekman's water data. The results are given in Tables 15 and 16. The compressibility of water at atmospheric pressure, β_0 , was taken from sound velocity data and from smoothed values of Diaz Peña and Mc-

TABLE 15. n Value of Murnaghan Equation for Ekman's P - V - T Data of Water
 β_0 from M. Diaz Peña and M. L. McGlashan.

P , bars	Temperature				
	0°C	5°C	10°C	15°C	20°C
201.08	5.38	5.34	5.55	5.67	5.59
201.08	...	5.36	5.48	5.52	5.62
403.56	5.74	5.73	5.80	5.80	5.85
403.56	...	5.69	5.80	5.80	5.89
599.44	5.89	5.86	5.90	5.92	5.95
599.44	...	5.86	5.90	5.91	5.96

TABLE 16. n Value of Murnaghan Equation for Ekman's P - V - T Data of Water
 β_0 from sound velocity data.

P , bars	Temperature				
	0°C	5°C	10°C	15°C	20°C
201.08	3.69	3.51	3.60	3.62	3.51
201.08	...	3.53	3.53	3.48	3.53
403.56	4.88	4.81	4.81	4.77	4.80
403.56	...	4.77	4.81	4.77	4.84
599.44	5.30	5.23	5.22	5.21	5.23
599.44	...	5.23	5.22	5.20	5.24

Glashan's data, which agree with Amagat's and Ekman's β_0 extrapolated from the Tait equation. As is clear from the table, n is both temperature and pressure dependent, though n usually is considered to be pressure independent.

It is interesting to note that the n values of water corresponding to Anderson's [1966] pressure derivative of bulk modulus B' also are near 4 and 5.3, as are n values of oxide compounds.

CONCLUSIONS

1. The most internally consistent P - V - T data on water with respect to the Tait equation are the values of Ekman and of Amagat.

2. For Ekman's data the standard deviations average less than 1×10^{-5} ml/g; for Amagat's first table, about 2×10^{-5} ml/g at temperature less than 60°C.

3. Ekman's compression measurements of water and sea water are internally very consistent with respect to the Tait and Tait-Gibson equations.

4. B and B^* values calculated by sound velocity at atmospheric pressure are systematically higher than Ekman's values by about 20 bars, but they all show the same linearity and slope with respect to salinity.

5. B and B^* values calculated by Newton and Kennedy's data are systematically lower than the values of others except at 0°C.

6. For Ekman's and Amagat's P - V - T data of water, the Tait equation fits better than the Murnaghan equation.

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