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EQUATION OF STATE OF PURE WATER AND SEA WATER

F.H. Fisher and O.E. Dial, Jr.

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temperature. For pure water $S=0$ and for sea water V_{∞}^* and P_0 are the pure water values. For pure water we have obtained an analytic function which fits the data of Kell and Whalley to ~ 8 ppm from $0-100^\circ$ and ~ 15 ppm from $100-150^\circ$ up to 1000 bars. The calculated density maximum is at 4.00° . The form of the equation appears to be useful not only for representing the properties of sea water but for deriving partial molal properties of solutions at low concentrations from high concentration data.

* V_{∞} , γ and $P_{sub 0}$

xx approx.

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PREFACE

This work on the equation of state was done initially in 1967. It has led to an equation of state for pure water based on the work of Kell and Whalley. Subsequent work by Millero,[†] including corrections in the data of Kell and Whalley based on his results have yielded a more complex equation of state for pure water and sea water. The results in this report are useful not only in developing an easily differentiated equation of state of sea water suitable for a number of purposes requiring less accuracy than Millero's equation but providing a basis for the representation of the PVT properties of other solvents and solutions containing water such as for dioxane-water mixtures.

F.H. Fisher, October 16, 1975

[†]F.J. Millero, R.A. Fine and D.P. Wang "The Equation of State of Seawater," J. Mar. Res., 32, pp. 433-456, (1974).

EQUATION OF STATE OF PURE WATER AND SEA WATER

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ABSTRACT

For representing the PVT properties of pure water and solutions, sea water in particular, we have selected the Tumlirz equation

$$V = V_{\infty} - K_1 S + \frac{\lambda}{P_0 + K_2 S + P.}$$

where V is the specific volume as a function of pressure P , Salinity S and temperature. For pure water $S = 0$ and for sea water V_{∞} , λ and P_0 are the pure water values. For pure water we have obtained an analytic function which fits the data of Kell and Whalley to ~ 8 ppm from $0 - 100^{\circ}$ and 15 ppm from $100 - 150^{\circ}$ up to 1000 bars. The calculated density maximum is at 4.00° . The form of the equation appears to be useful not only for representing the properties of sea water but for deriving partial molal properties of solutions at low concentrations from high concentration data.

INTRODUCTION

The goal of an equation of state of a liquid is to represent PVT data in a simple form and provide insight into the physical properties of the liquid. In particular, an equation of state for a solution such as seawater should reduce to that of the pure solvent as the solute concentration goes to zero. In order to understand the effects of adding solute, the equation of state for the solvent should be established as accurately as possible. In this paper we consider two equations which have been used before to represent electrolyte solution and sea water as well as pure water.

Since Eckart's^{1/} review on the equation of state for pure water and sea water, further measurements have been made on both pure water^{2/} and sea water^{3,4,5/}. The high precision specific volume data Kell and Whalley obtained for pure water as a function of temperature and pressure have been particularly useful.

Two equations have been used for fitting specific volume data as a function of pressure, the original Tait equation^{6/}

$$\frac{\Delta V}{V_1 \Delta P} = \frac{A}{\pi + P} \quad (1)$$

and the usual Tait equation (UTE) as McDonald^{7/} denotes it in his recent review on equations of state,

$$V_p = V_1 + C \log \frac{B+1}{B+P} \quad (2)$$

The original Tait equation is equivalent to the Tumlirz equation^{8/}

$$V_p = V_\infty + \frac{\lambda}{P_0 + P} \quad (3)$$

that Eckart used in his analysis. Non-linear fitting techniques for this equation were developed (see Appendix I) to avoid errors inherent in less direct methods.

We find that Kell and Whalley data can be described to their stated precision by using the Tumlirz equation at low temperatures (0-90°) and the UTE at high temperatures (50-150°). Older pure water data were not sufficiently accurate to select one equation in preference to the other. Since the Tumlirz equation describes the Kell and Whalley data within its stated accuracy over the entire temperature range, we have chosen it as the basis for representing P-V-T properties of pure water and sea water. The V_∞ , λ , and P_0 parameters can be described by simple polynomials of temperature, completing the equation of state for pure water.

The Tumlirz equation was fit to isotherms of Wilson and Bradley and Newton and Kennedy seawater data at constant salinity. While the equation described the data to its precision, the parameters of the equation, V_∞ , λ , and P_0 varied erratically with salinity and temperature. We found that by constraining λ to the same value as for pure water at that temperature, V_∞ and P_0 become linear functions of salinity. This procedure yields an equation to describe the P-V-T-S properties of seawater, which differs in form from that used by Eckart and Wilson and Bradley.

CALCULATIONS

A. Pure Water

For their measurements, Kell and Whalley (20 temperatures up to 150° and 26 pressures from 5 to 1000 bars) claim accuracies which vary from 5 ppm at low temperatures (0-50°) and pressures to 40 ppm at high temperatures and pressures. Although Kell and Whalley^{2/} published both their experimental and smoothed data, we use their experimental data to avoid any systematic errors introduced by their smoothing procedure.

A computer routine was written to fit equations (2) and (3) to an isotherm of water data. The routine calculated parameter values so as to minimize the quantity,

$$\sigma = \left[\sum_P (V_p - V_p')^2 / n \right]^{1/2} \quad (4)$$

where V_p' is the volume predicted by the given equation at pressure P and the indicated summation is at each pressure along a single isotherm; this quantity is the standard deviation of observed data points about the fitted curve, sometimes called the standard error of estimate. The details of how these calculations were carried out may be found in Appendix I. Tables I, II, and III show the results of calculations fitting these equations to the data of Amagat^{9/} and Kell and Whalley^{2/} and the much higher pressure data of Vedam and Holton^{10/}. Figure 1 shows the temperature dependence of the various parameters for the Tumlirz equation as determined from the Kell and Whalley data. Figure 2 shows the temperature dependence of the parameters for the UTE also fit to the Kell and Whalley data.

TABLE I
Fits of Tumlirz and Usual Tait
Equations to Amagat Data.

Temp., degrees	Tumlirz Equation			
	P_0 (bars)	λ bar cc/gm $\times 10^{-3}$	V_∞ cc/gm	σ cc/gm $\times 10^6$
0	5812.6	1.7228	0.70379	11
5	6421.1	2.0164	0.6860	27
10	6228.4	1.8584	0.70193	15
15	6322.9	1.8742	0.70449	19
20	6569.9	1.9833	0.69989	23
30	6851.0	2.1026	0.69741	30
40	6888.2	2.1027	0.70244	27
50	6787.1	2.0447	0.71069	25
60	6704.8	2.0126	0.71670	39
70	6189.5	1.7609	0.73802	51
80	5493.9	1.4483	0.76529	19
90	5467.4	1.4262	0.77006	21
100	5357.9	1.4694	0.76901	28
198	3328.4	1.0941	0.82994	91
	Usual Tait Equation			
	B (bars)	C bar cc/gm	V_1 cc/gm	σ cc/gm $\times 10^6$
0	2697.7	0.3180	1.00014	13
5	3002.2	0.3392	1.00000	29
10	2893.1	0.3204	1.00026	15
15	2930.6	0.3176	1.00086	22
20	3052.3	0.3242	1.00174	24
30	3185.1	0.3298	1.00428	27
40	3205.5	0.3283	1.00767	26
50	3155.1	0.3237	1.01192	23
60	3109.8	0.3219	1.01684	34
70	2850.8	0.3032	1.02249	44
80	2509.5	0.2789	1.02889	14
90	2453.1	0.2812	1.03574	27
100	2449.8	0.2904	1.04322	36
198	1425.3	0.3298	1.15868	82

TABLE II

Fit of Tumlrz and Usual Tait Equations to Kell and Whalley Data.

Temp., degrees	Tumlrz Equation				Usual Tait Equation			
	P_0 (bars)	λ bar cc/gm $\times 10^{-3}$	V_∞ cc/gm	$\sigma \times 10^6$ cc/gm	B bars	C bars cc/gm	V_1 cc/gm	$\sigma \times 10^6$ cc/gm
Kell and Whalley								
0.000	5825.80	1.73619	0.702201	4.5	2685.04	0.31773	1.000101	11.9
10.002	6323.46	1.92008	0.696711	6.2	2932.58	0.32553	1.000315	11.9
19.997	6644.11	2.03391	0.695724	4.6	3091.72	0.32919	1.001808	9.0
24.998	6722.75	2.05508	0.697320	6.1	3131.12	0.32899	1.002973	10.3
24.998	6723.00	2.05585	0.697262	5.1	3131.51	0.32904	1.002971	9.0
25.005	6729.02	2.05889	0.697041	5.1	3134.15	0.32931	1.002974	9.5
30.112	6773.51	2.06654	0.699357	3.5	3155.79	0.32845	1.004410	6.5
39.999	6783.43	2.05450	0.705013	4.3	3160.30	0.32605	1.007847	5.3
50.007	6772.43	2.04980	0.709488	4.9	3155.27	0.32584	1.012119	7.8
60.001	6591.20	1.96582	0.718884	5.0	3064.46	0.32048	1.017097	5.2
70.003	6433.54	1.90833	0.726164	4.8	2986.09	0.31825	1.022749	5.3
80.003	6189.63	1.81601	0.735672	6.0	2864.41	0.31395	1.029029	4.1
90.007	5924.39	1.72028	0.745605	5.8	2732.84	0.30982	1.035939	5.6
100.005	5683.60	1.64577	0.753932	7.8	2612.81	0.30803	1.043459	4.7
110.005	5370.53	1.54927	0.764236	9.1	2467.31	0.30455	1.051602	6.3
110.003	5410.85	1.56000	0.763330	8.5	2477.33	0.30559	1.051600	4.6
120.007	5104.37	1.46075	0.774234	11.9	2324.93	0.30195	1.060370	5.4
130.010	4810.89	1.37208	0.784642	12.5	2179.43	0.29950	1.069803	4.2
140.009	4544.00	1.29984	0.793891	15.9	2047.01	0.29895	1.079907	5.4
150.016	4249.49	1.21429	0.805041	19.3	1901.13	0.29686	1.090750	4.7

TABLE III

Fit of Tumlrz and Usual Tait Equations to Vedam and Holton Data.

Temp., degrees	Tumlrz Equation				Usual Tait Equation			
	P_0 bars	$\lambda \times 10^{-3}$ bars cc/gm	V_∞ cc/gm	$\sigma \times 10^6$ cc/gm	B bars	C bars cc/gm	V_1 cc/gm	$\sigma \times 10^6$ cc/gm
Vedam and Holton								
30	8024	2.7583	0.6600	334	2730	0.2927	1.0046	178.0
40	8934	3.2767	0.6398	597	2824	0.2995	1.0082	161.0
50	8956	3.2931	0.6431	599	2833	0.3004	1.0124	156.0
60	9004	3.3443	0.6443	618	2853	0.3037	1.0173	137.0
70	8936	3.3353	0.6480	657	2822	0.3046	1.0228	109.0
80	8760	3.2747	0.6535	718	2742	0.3036	1.0290	81.5

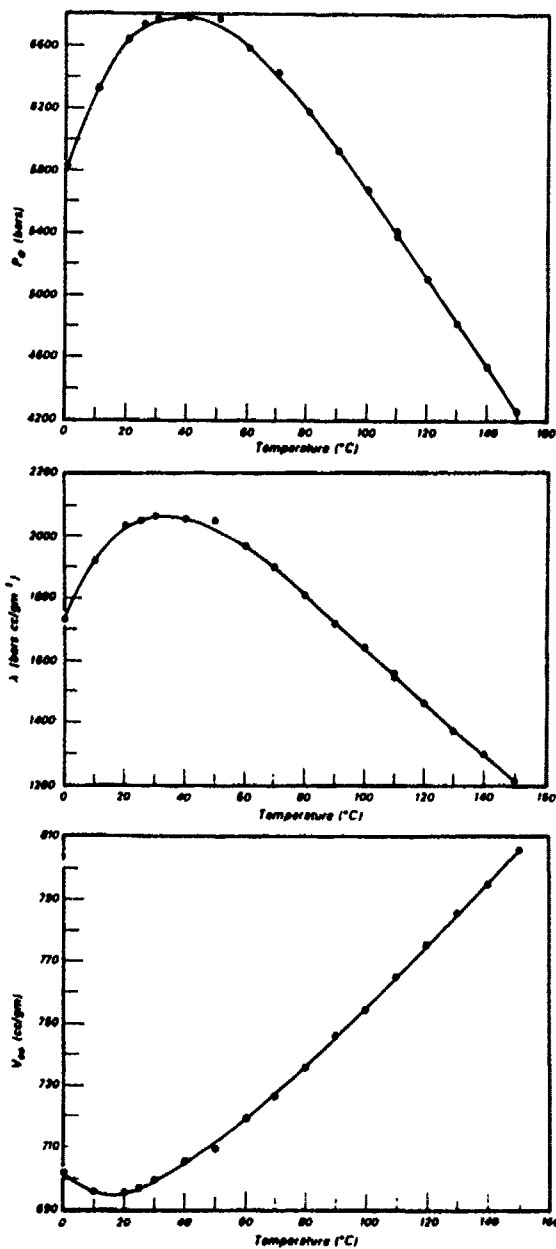


Fig. 1 Temperature dependence for pure water of the parameters P_0 , λ and V_∞ for the Tumlirz equation.

From Table I the goodness of fit, σ , for the Amagat data shows a rather good uniform fit. The standard error is about the same as the quality of the data. The two equations fit about equally well so that a superiority of one equation over the other is not demonstrated. These fits do not seem to display any inherent limitations in the applicability of either the Tumlirz or UTE to pure water data.

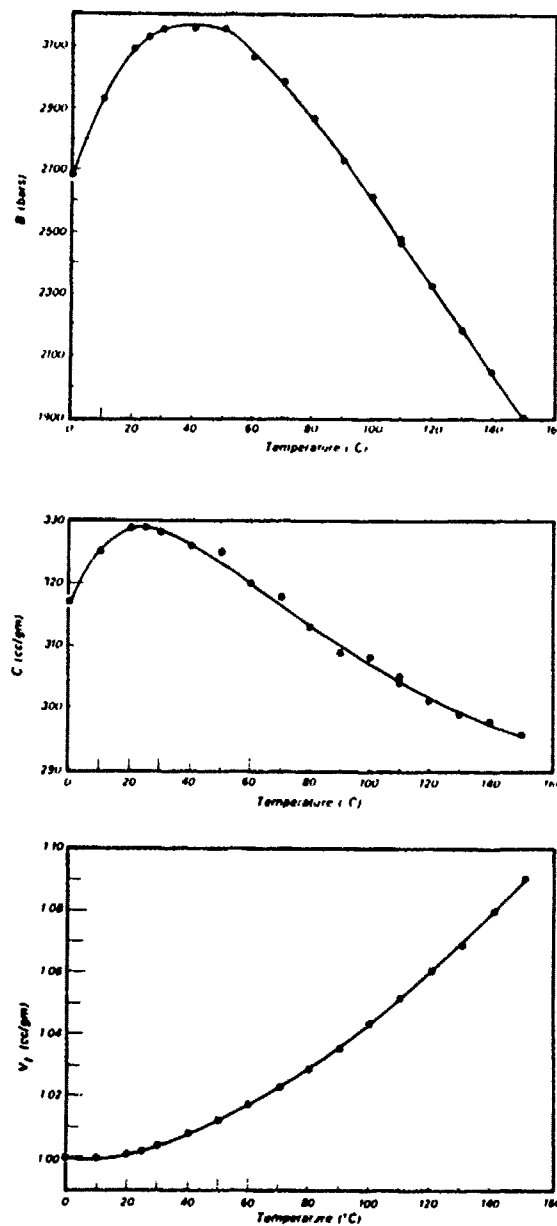


Fig. 2 Temperature dependence for pure water of the parameters B , C and V_1 for the Usual Tait Equation.

The very accurate data of Kell and Whalley is more revealing. Excellent fits are to the isotherms obtained below 90° with the Tumlirz equation and above 40° with the UTE. In either event, the standard error is about 5 ppm. Figure 3 shows a plot of the standard error at each temperature for the fit of both the proposed equations to Kell and Whalley data.

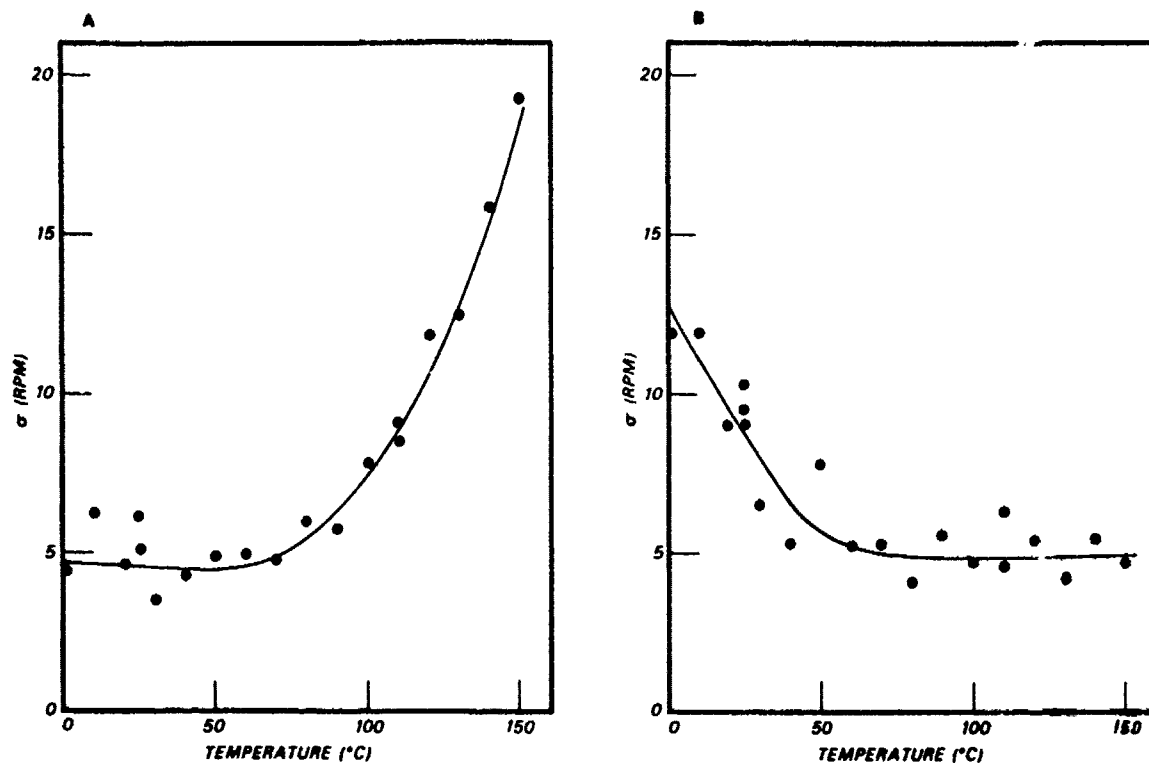


Fig. 3 Comparison of the standard deviations σ of fits of the Tumlrz equation (left) and the Usual Tait Equation (right) to the Kell and Whalley data.

TABLE IV
Fit of Tumlrz Equation to Pure Water Data at 10°.

Data	P_0 (bars)	λ bar cc/gm	V_∞ cc/gm	$\sigma \times 10^6$ cc/gm
Amagat (1893) I	6228	1858	0.7019	15
Amagat (1893) II	6570	2038	0.6907	82
Newton & Kennedy	6279	1902	0.6974	22
Kell & Whalley	6323	1920	0.6967	6
Vedam & Holton (low pressure)	6271	1882	0.7002	26
Wilson & Bradley	6215	1853	0.7022	24

As fits were made to data from different investigators, it became apparent that there were large differences in optimum parameter values at the same temperature as illustrated in Table IV with the Tumlrz equation for pure water at 10° . Examination of the Tumlrz equation shows that even small changes in any one parameter would greatly affect the predicted volumes and hence the quality of fit. However, as Tait noted, large changes in one parameter may be made provided compensating changes are made in the other parameters; for example, increasing λ and P_0 while decreasing V_{∞} would have little effect upon the resulting curve. This is illustrated in Figure 4a (λ vs. P_0) and Figure 4b (P_0 vs. V_{∞}) where the sloping line is derived from analysis of Kell and Whalley data. The derivation of these compensating relationships is explained in Appendix II.

In comparing the fits to the Kell and Whalley data with equations (2), UTE, and (3), Tumlrz, we see that even though UTE parameter B (Figure 2a) displays a rather smooth behavior, C (Figure 2b) shows an erratic temperature dependence at the higher temperatures. This contrasts with the smooth behavior of the Tumlrz parameters (Figure 1) over the whole temperature region except at 50° . Upon re-examining the σ vs. T dependence for the two equations in Figure 3, we should also note that the precision of fits of the Tumlrz equation vary in accord with the errors in accuracy estimated by Kell

and Whalley as a function of temperature. On this basis we select the Tumlrz equation to represent the PVT properties of pure water. In our final calculations we have included Kell's¹¹ data for pure water at atmospheric pressure.

The Tumlrz equation and the temperature dependence of its parameters are shown in Table V. Comparisons of fits obtained with our equation and that observed by Kell and Whalley are shown in Table VI. It is quite reassuring to note that the density maximum at atmospheric pressure according to our results occurs at 4.00° .

Although McDonald does not consider the Tumlrz equation as a best choice for representing the properties of pure water we believe it provides a good base for an analytic function to represent specific volumes on an absolute basis. In their representations for the PV isotherm data both McDonald and Kell and Whalley normalize their equations to the atmospheric pressure specific volumes. This, of course, makes it easier to include later and more accurate atmospheric pressure data. It also makes calculation of thermodynamic properties, particularly the thermal expansion coefficient, more involved.

The Tumlrz equation for pure water also provides a good basis for representing the properties of sea water as we shall see next.

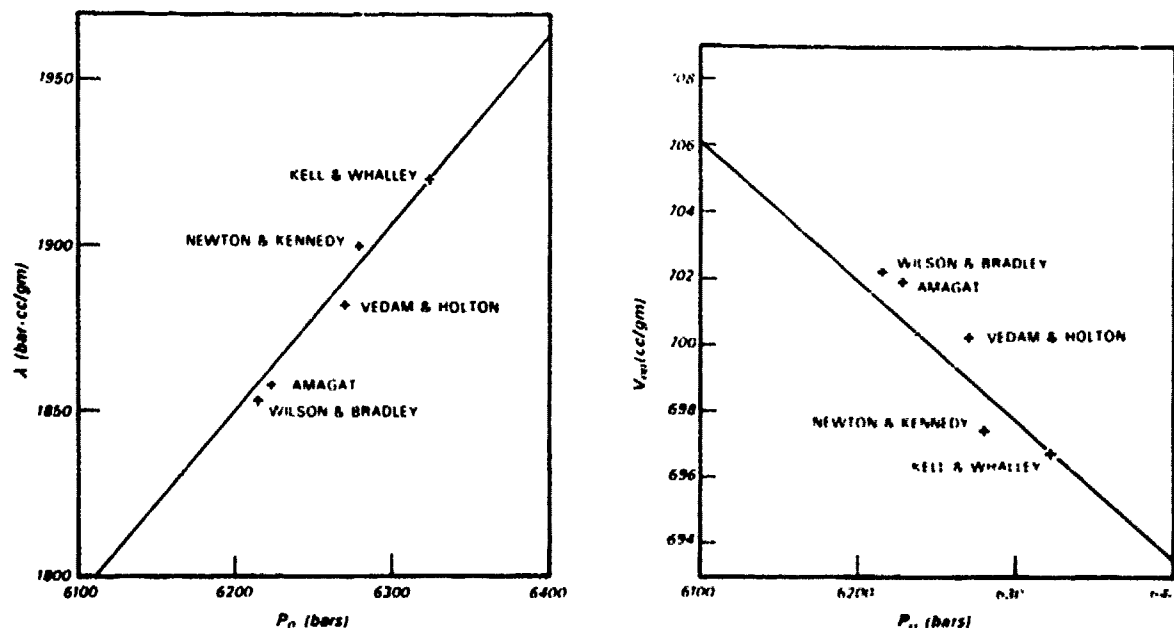


Fig. 4 Plot of λ and V_{∞} vs. P_0 values obtained at optimum fits of Tumlrz equation to pure water at about 10° from various sources. The straight line is the compensating relationship derived from Kell and Whalley data.

Table V

(a) Pure Water, 0 - 100°, 8 ppm and 100 - 150°, 15 ppm fits to Kell and Whalley data (λ in bars cc/gm) P , P_0 in bars and V_∞ , V in cc/gm.

$$\lambda = 1,788.316 + 21.55053 T - 0.4695911 T^2 + 3.096363 \times 10^{-3} T^3 - .7341182 \times 10^{-5} T^4$$

$$P_0 = 5918.499 + 58.05267 T - 1.1253317 T^2 + 6.6123869 \times 10^{-3} T^3 - 1.4661625 \times 10^{-5} T^4$$

$$V_\infty = .6980547 - .7435626 \times 10^{-3} T + .3704258 \times 10^{-4} T^2 - .6315724 \times 10^{-6} T^3 + .9829576 \times 10^{-8} T^4$$

$$T^4 - .1197269 \times 10^{-9} T^5 + .1005461 \times 10^{-11} T^6 - .5437898 \times 10^{-14} T^7 + .169946 \times 10^{-16} T^8$$

$$T^8 - .2295063 \times 10^{-19} T^9$$

B. Sea Water

The most extensive sea water measurements have been made by Wilson and Bradley^{3,4/} and Newton and Kennedy^{5/}.

The Wilson and Bradley data is published in two forms: the original experimental data and the smoothed data; the isotherm precision to be ± 20 ppm in density. With a 22 term parameter equation they obtained a fit with a standard deviation of 80 ppm and with the 10 parameter Tumlriz equation, which they finally chose, they obtained a standard deviation of 130 ppm. Because a Tumlriz equation was used as a part of the smoothing procedure, the smoothed data cannot be used to test the applicability of the

Tumlriz equation. The original data occurs at irregular temperature intervals, complicating comparison at different salinities. Consequently we have used polynomial interpolation to provide data at even 5° intervals; it is this interpolated data that will be referred to as the Wilson and Bradley data.

The UTE and Tumlriz equation were used to fit the seawater isotherm data at each salinity. The fits were on the order of 30 ppm for both the UTE and Tumlriz equation; therefore, the Tumlriz equation was selected for further study because the quality of fit does not restrict the selection and provides a better fit to pure water.

Figure 5 shows λ , P_0 and V_∞ vs. salinity at 10° from the fits of the Tumlriz equation to Wilson and Bradley, and Newton and Kennedy data. The parameters do not appear to vary in any consistent way with salinity because random parameter variations resulting from imperfect data obscure the systematic variations with salinity.

Table VI

Comparison of Standard Deviations of Fits to Kell and Whalley Data of the Equations of State Kell and Whalley used and the one we use.

Temp	Standard Deviation $\times 10^6$ (cc/gm)	
	Fisher & Dial	Kell & Whalley
0.000	9.6	4.4
10.002	8.0	10.0
19.997	7.4	7.9
24.998	7.0	4.9
24.998	5.8	4.6
25.005	5.5	4.3
30.112	6.9	11.1
39.999	8.3	13.8
50.007	6.7	6.0
60.001	5.6	4.3
70.003	11.2	13.6
80.003	8.4	4.2
90.007	6.7	4.6
100.005	10.2	5.8
110.005	11.8	10.3
120.007	13.2	9.6
130.010	14.3	5.8
140.009	18.5	9.1
150.016	22.8	9.0

The sea water data was normalized to pure water by constraining λ to be equal to the value for pure water at the same temperature. The λ values for Kell and Whalley data were polynomial interpolated to the temperatures of the sea water data and least-square fits were made for V_∞ and P_0 at each temperature and salinity. Figure 6 shows the results at 10° from which a linear salinity dependence is now evident. A linear variation of P_0 with salinity is in accordance with Tammann's hypothesis^{12/} which states that internal pressure, the usual interpretation for P_0 , should increase linearly with salinity. Also, V_∞ is seen to vary linearly with salinity. Using the linear variations suggested by Figure 6 we may write^{13/}:

$$V_P = V_\infty - K_1 S + \frac{\lambda}{P_0 + K_2 S + P} \quad (5)$$

Equation (5) was fit to the Wilson and Bradley data by setting V_∞ , λ and P_0 equal to the pure water values calculated for the temperatures at which the data was taken; attempts to determine the temperature dependence of K_1 and K_2 were not entirely satisfactory partly because the data were

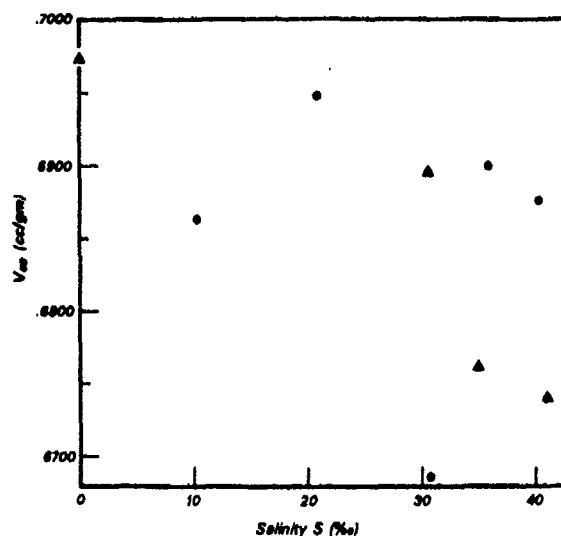
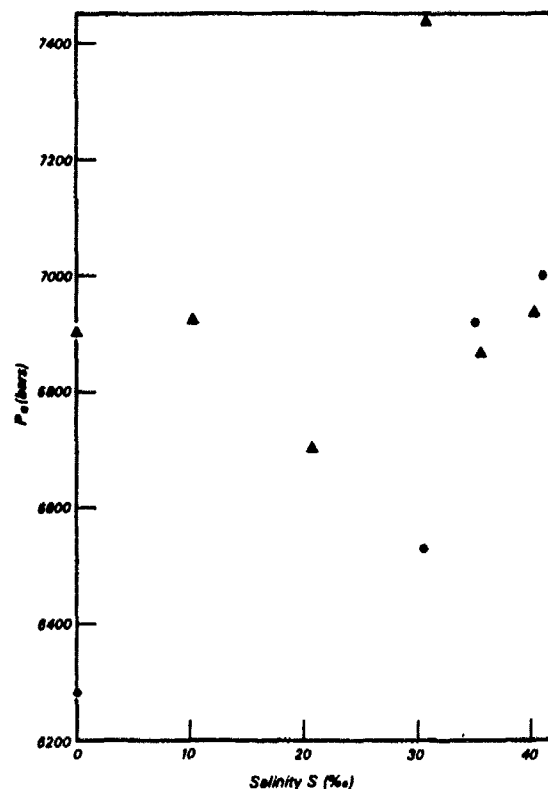
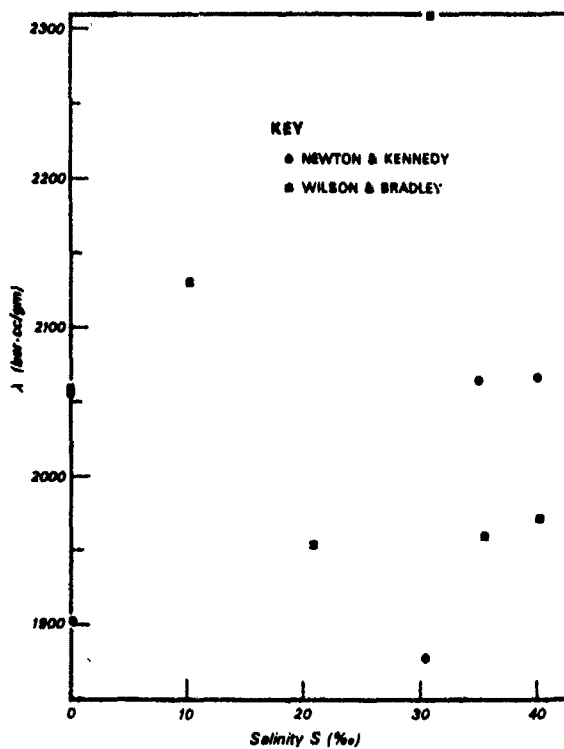


Fig. 5 Plots of λ , P_0 and V_∞ obtained from optimum fits of Tumlrz equation to sea water data at about 10° .

DISCUSSION A. Pure Water

Our calculations have led us to use the Tumlrz equation to represent the properties of pure water. It is rather interesting to note that the value of V_∞ is very close to the specific volume calculated for the close packed form of water in most theories which treat water in terms of a two state model^{15/}. Along another line of thought we note that David and Litovitz^{16/} calculate the temperature dependence of the relaxing and non-relaxing compressibilities for water and find a cross over point in the temperature region near the compressibility minimum at 45° and sound velocity maximum at 72° . In this paper we have seen that a crossover in the precision of fits of the Tumlrz and UTE equations also occurs near the same temperature.

Since the open packed structure (ice-like) predominates at lower temperatures, it is tempting to associate its properties with the Tumlrz equation and the close packed structure with the UTE. We have seen that the UTE equation provides a more precise fit to Kell and Whalley's data at higher temperatures and we also note that the very high pres-

obtained at varying temperatures. In addition it was found that thermal expansion coefficients calculated from our parameters for equation 5 did not agree with the recent work of Bradshaw and Schleicher^{14/}.

While we are able to obtain with our equation fits to the Wilson and Bradley data with standard deviations of about 10^{-4} cc/gm which is comparable to the Fit Wilson and Bradley obtained with their equation (1.3×10^{-4}) we feel that it is possible to obtain a better equation of state by using sound velocity data to determine K_2 and thermal expansion data to determine K_1 . This has been done in another paper^{15/}.

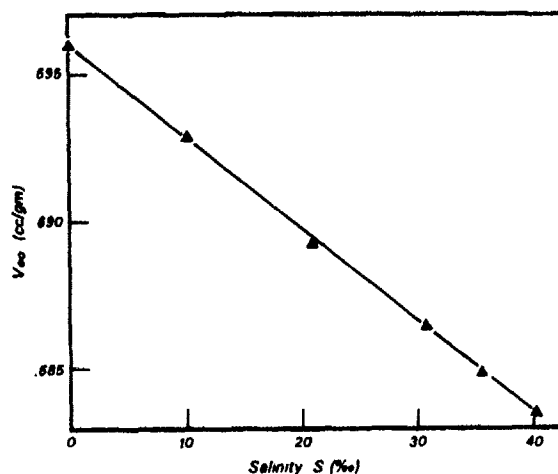
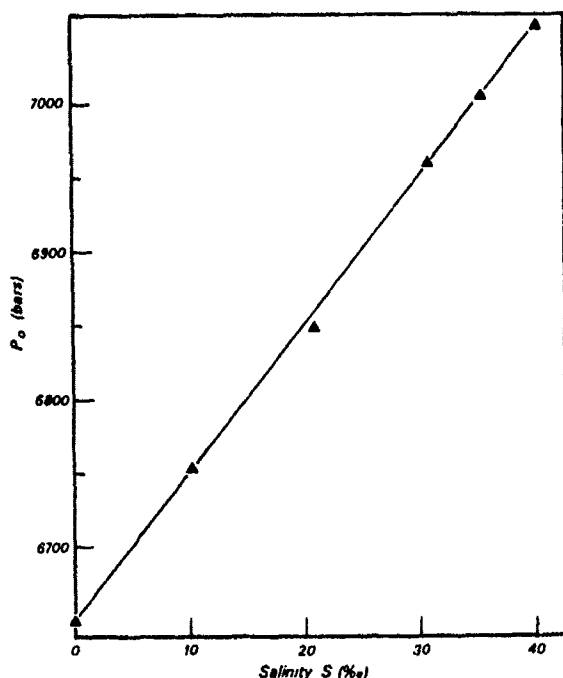


Fig. 6 Plots of P_0 and V_∞ obtained from optimum fits of Tumlrz equation to sea water data of Wilson and Bradley at 10° when λ is constrained to be the value for pure water.

sure data of Vedam and Holton^{10/} at lower temperatures shows a lower standard deviation when the UTE is used for fitting.

Although the accuracy of the data at higher temperatures and very high pressures is not as good as that of the low temperature Kell and Whalley data, the fact that the UTE provides better fit at the high temperature and pressures may be significant. Both increasing temperature and pressure

produce a breakdown of the open structure of water. In this sense, the transition from the Tumlrz to the UTE equation appears to be consistent. Using the results of Davis and Litovitz for the fractions of open and closed structure we attempted to fit the Kell and Whalley data with a linear combination of the Tumlrz equation and the UTE. The results so far are inconclusive and we hope to pursue the matter later, based in part on the work of Frank and Quist.^{17/}

The parameter B in the UTE and P_0 in the Tumlrz equation have been referred to as an internal pressure. Since no experimental data as yet exists on the ultimate tensile strength of water, we cannot ascribe an intermolecular significance to the internal pressure.^{18/} Going back to the two-state model we note that the lower internal pressure values of B would be attributed to the disordered close packed state and the much higher P_0 values to open-packed state. Again this seems to be reasonable from a qualitative viewpoint.

B. Sea Water

Although we have not established the temperature dependence of the parameters K_1 and K_2 to our satisfaction in this paper, we have clearly demonstrated the linear salinity dependence of the corrections to V_∞ and P_0 as shown in equation 5. This promises to be a very useful equation in that atmospheric pressure data on the density, sound velocity, and heat capacity can be used to determine the high pressure properties of electrolyte solutions. Furthermore, it promises to be useful for determining partial molal properties of solutions at infinite dilution from data at high concentrations. Unfortunately, most data at atmospheric pressure and elevated pressures up to now on solution densities are not accurate or precise enough to do a definite study utilizing equation 5 in this matter.^{19/} Experiments are in progress at various laboratories which promise to yield data of the necessary accuracy. It may also be possible to calculate the properties of solutions with more than one solute by additions of their respective values of K_1 and K_2 .

The principal difference in the form of equation 5 from that used by Eckart and Wilson and Bradley is that λ is not a function of salinity. This may be an artificial constraint. More precise solution data will determine the utility of this equation. Yayanos^{18/} has used another equation

$$PV^4 = A - V/V_0 \quad (6)$$

to analyze his PV isotherms for water and NaCl. In further work we expect to test this equation also.

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This work was initiated partly in response to discussions of the equation of state of sea water^{20/} at the meeting of the Joint Panel on Oceanographic Tables and Standards in Berne, 1967. The authors are grateful for the interest and encouragement of C. Eckart, W. Wooster and R. Arthur in this work. We particularly wish to acknowledge the stimulating discussions with Dr. Eckart.

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APPENDIX I:

COMPUTATIONAL PROCEDURE FOR NONLINEAR, LEAST-SQUARE CURVE FITTING

Nonlinear least-square curve fitting requires the use of iterative approximation to calculate parameters of the curve. We use the fit of the UTE equation (2), to the Kell and Whalley data at 10.002° to illustrate the iteration.

We define σ , the standard error, by equation (4). Least square curve fitting implies the selection of parameters V_1 , C, and B to minimize σ . Of these, B is nonlinear.

If the value of B in equation (2) were known, we could use conventional, linear least-square fitting to determine V_1 and C and calculate the resulting σ . Table VII shows the results of these calculations for tabulated values of B. It is readily seen that σ smoothly comes to a minimum value near B = 2900 bars. The nonlinear, least-square fit is implemented by searching successively smaller

Table VII

Least-Square χ , V_0 , and σ from Fit of Tumlirz Equation to Kell and Whalley Data at 10°C.

P_0 (bar)	lambda(bar-cc/gm)	V_0 (cc/gm)	σ (ppm)
5600	1,530.894	0.727055	60.4
5800	1,634.105	0.718665	42.5
6000	1,740.662	0.710276	26.0
6200	1,850.564	0.701888	11.2
6323.46*	1,920.082	0.696711	6.2
6400	1,963.813	0.673502	8.4
6600	2,080.406	0.685117	20.7
6800	2,200.346	0.676733	33.7

*optimum value found after continued search

intervals about the optimum value found by the previous search. This search was coded into a computer routine which terminated when the optimum B was localized to $\pm .001$ bar.

The fitting procedure for the Tumlirz equation is quite similar. Values of V_0 , λ , and σ are calculated for selected values of P_0 . A search for the optimum is continued until P_0 is localized $\pm .001$ bar.

By computerizing nonlinear least-square calculations, we are able to obtain the optimum fits. In all cases the standard error is computed to provide a simple, uniform measure of the quality of fit; indeed, the minimization of this quantity is the essence of least-square fitting.

APPENDIX II:

CORRELATED PARAMETER ESTIMATES

Parameter estimates obtained from different sets of data show both random and systematic variations. Experience with the Tumlirz equation has shown that there are large variations in parameter estimates obtained from all but the most precise data. Figure 5 shows that random variations of parameters for seawater data are so large that they obscure any systematic variations with salinity.

By considering different sets of data, we have found that the estimates of the parameters are correlated as shown in Figure 4. Also, any one parameter can be changed without significantly degrading the quality of fit provided that compensating (i.e., the correlated) changes are made in the other parameters. Table V may be considered to tabulate the values of λ and V_∞ necessary to compensate for variations of P_0 . Indeed, when the λ vs. P_0 and V_∞ vs. P_0 columns from Table V are plotted in Figure 4 the previously obtained parameter estimates are seen to agree closely.

Similarly correlated parameter estimates occur with the UTE. These correlations explain the success of previous work which constrained the C parameter because B values could then be selected which largely compensated for the non-optimum C values chosen^{21/}.

The existence of the compensating relations also provides a rationalization for constraining a parameter of the seawater equation. We know such constraints won't degrade the fit and that the compensating relations will reduce the erratic variations of the remaining parameters. In particular, constraining the λ parameter to its value for pure water at the same temperature produced the linear variations of V_∞ and P_0 with salinity which Tamman had suggested.

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