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band at this position in a sample of polymerized ketene may easily be a case of coincidence of bands. In view of these considerations, the authors are inclined to assign  $\sim 925$  and  $731\text{ cm}^{-1}$  as the two  $\text{CH}_2$  wagging fundamentals, as was done in the present paper, and to seek some other explanation of the  $1967\text{ cm}^{-1}$  band.

As Halverson and Williams have implied, it is not possible to explain the  $1967\text{ cm}^{-1}$  band as an overtone, combination, or difference band (other than in the manner criticized above). Also it does not seem possible to explain it as the  $\text{C}=\text{C}=\text{O}$  stretching vibration (fundamental:  $2155\text{ cm}^{-1}$ ) shifted by interaction with an excited low frequency, i.e. a band of the type  $(\nu_{\text{C}=\text{C}=\text{O}} + \nu_{\text{low}}) - \nu_{\text{low}}$ . Judging from  $\text{CO}_2$  and  $\text{N}_2\text{O}$ ,

the shift to be expected for this reason is only a few  $\text{cm}^{-1}$ . The most plausible, but not wholly satisfactory, explanation of the  $1967\text{ cm}^{-1}$  band is that it is the isotopic analog for the  $\text{C}^{12}=\text{C}^{13}=\text{O}^{16}$  molecule of the  $2155\text{ cm}^{-1}$  band. The intensity ratio is close to 100:1, exactly as is necessary. However, force-constant calculations based on either the simplified linear-triatomic molecule approximation used in this paper, or on the more extended treatment given by Halverson and Williams, predict an isotopic shift in the neighborhood of 50–100  $\text{cm}^{-1}$  instead of the required 200  $\text{cm}^{-1}$  shift.

It is clear that further work toward resolving the bands from 700 to  $1050\text{ cm}^{-1}$  is needed before an unequivocal assignment can be made.

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## Hydrodynamic Properties of Sea Water at the Front of a Shock Wave\*

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The Rankine-Hugoniot relations have been applied to appropriate equation-of-state data in order to calculate the propagation velocity, particle velocity, enthalpy increment, Riemann function, etc. at shock fronts of various amplitudes in sea water. One set of tables provides values over a wide pressure range (up to about 80 kilobars) and is principally intended for use in conjunction with theories of propagation of shock waves originated by underwater explosions. A second set of tables contains values which are closely spaced up to pressures of 14 kilobars. These are calculated with somewhat greater precision and are intended for use in connection with experimental measurements of particle and propagation velocities, etc.

### I. INTRODUCTION

IT has long been recognized that the velocity of propagation of sound waves of finite amplitude in a fluid medium is a function of the pressure in the wave. Lamb<sup>1</sup> ascribes the early

development of the theory to independent investigations of Earnshaw and Riemann. Qualitatively this work indicated that, since the higher pressure portions of a wave travel with greater velocity, an arbitrarily-shaped pressure pulse of finite amplitude must, during propagation, alter its shape in such a manner as to build up into a shock front. By applying the laws of conservation of mass, energy, and momentum to the transfer of matter across the shock front, Rankine and Hugoniot obtained a set of three relations among the five variables: pressure, density, particle velocity ( $u$ ), shock front

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<sup>1</sup> H. Lamb, *Hydrodynamics* (Cambridge University Press, London, 1932) 6th Ed., p. 481.

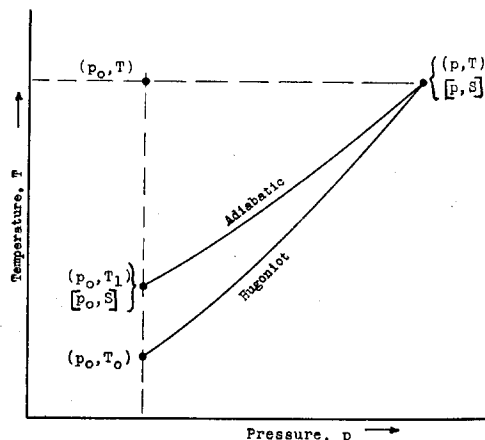


FIG. 1. Adiabatic and Hugoniot contours in  $p$ - $T$  plane.

velocity ( $U$ ), and enthalpy increment ( $\Delta H$ ). These relations, when applied to data on the equation-of-state and specific heat, make it possible to calculate  $u$ ,  $U$ , and  $\Delta H$  and to evaluate certain other functions applicable to the theory of the formation and propagation of shock waves originated by explosions.<sup>2</sup>

Precise knowledge of  $u$  and  $U$  also makes it possible to calculate shock wave pressures in cases where the particle velocity or propagation velocity can be measured. The purpose of the calculations described below was to apply the Hugoniot relations to appropriate equation-of-state data for sea water in order to provide (a) tables of the desired functions up to very high pressures (ca. 80 kilobars) for use in the theory of propagation of underwater explosion waves,<sup>2</sup> and (b) tables of particle and propagation velocity at fairly close pressure intervals in a lower pressure region (up to ca. 14 kilobars).

## II. OUTLINE OF THE THEORY AND COMPUTATIONAL PROCEDURES

In this section we give an account of the hydrodynamical and thermodynamical relations, and the computational procedures leading to the numerical results tabulated in Sections III and IV. For the convenience of the reader a glossary of symbols is presented in Appendix III.

When a shock wave advances with velocity  $U$  into a stationary fluid of unperturbed pressure

<sup>2</sup> J. G. Kirkwood and H. Bethe, *The Pressure Wave Produced by an Underwater Explosion* (Dept. of Commerce Bibliography No. PB 32182), OSRD Report No. 588, Part I.

$p_0$  and specific volume  $v_0$ , the pressure  $p$ , specific volume  $v$ , and particle velocity  $u$  of the fluid behind the shock front are determined by the Rankine<sup>3</sup>-Hugoniot<sup>4</sup> conditions, which express the conservation of mass, momentum, and energy of an element of fluid passing through the front. For the purposes of this paper, these conditions may conveniently be written

$$u = [(p - p_0)(v_0 - v)]^{\frac{1}{2}}, \quad (2.1)$$

$$U = v_0[(p - p_0)/(v_0 - v)]^{\frac{1}{2}}, \quad (2.2)$$

$$\Delta H = (1/2)(p - p_0)(v + v_0). \quad (2.3)$$

In the last equation,  $\Delta H$  is the specific enthalpy increment of an element of fluid when it passes through the front. The specific enthalpy is defined as the sum of the internal energy per gram and the pressure-volume product,  $pv$ .

Given equation of state and specific heat data for the fluid, any three of the variables  $p$ ,  $v$ ,  $U$  and  $u$  may be determined as functions of the fourth. Here we shall regard  $p$  as the independent variable. For certain hydrodynamic applications we must have, in addition to  $v$ ,  $U$ , and  $u$  as functions of  $p$ , the sound velocity

$$c = (\partial p / \partial \rho)^{\frac{1}{2}}_S; \quad \rho = 1/v, \quad (2.4)$$

the Riemann  $\sigma$ -function<sup>†</sup>

$$\sigma = \int_{p_0}^p [v[p', S]/c[p', S]] dp', \quad (2.5)$$

and the undissipated enthalpy

$$\omega = \int_{p_0}^p v[p', S] dp', \quad (2.6)$$

where  $S$  is the entropy.

In practice, one must resort to successive approximations to effect a reduction of the Hugoniot conditions, combined with equation-of-state and specific heat data, to a set of relations expressing  $u$ ,  $U$ , and  $v$  as functions of  $p$ . To this

<sup>3</sup> W. J. M. Rankine, Trans. Roy. Soc. London, A160, 277 (1870).

<sup>4</sup> H. Hugoniot, J. de l'ecole polyt. 51, 3 (1887); 58, 1 (1888).

<sup>†</sup> The Riemann  $\sigma$ -function occurs in Riemann's form of the hydrodynamical equations, which, for the case of spherical symmetry, may be written (see reference 1):

$$\begin{aligned} [(\partial/\partial t) + (c+u)(\partial/\partial r)](\sigma+u) &= -2cu/r, \\ [(\partial/\partial t) - (c-u)(\partial/\partial r)](\sigma-u) &= 0, \end{aligned}$$

where  $t$  is the time and  $r$  is the radial coordinate. The other quantities have already been defined.

end, it is expedient first to consider certain quantities as functions of pressure and temperature,  $p$  and  $T$ , or pressure and entropy,  $p$  and  $S$ . Before proceeding to a more detailed discussion of the calculations it may perhaps help to orient the reader if we consider, qualitatively, contours of some pertinent quantities in the  $p$ - $T$  plane. In Fig. 1, the possible states of a given fluid just behind the shock front lie along a single curve, which we have labeled "Hugoniot." An element of fluid initially in the state  $(p_0, T_0)$  which has attained a state  $(p, T)$  just behind the shock front finally returns to a state  $(p_0, T_1)$  along the adiabetic, so labeled in the figure. Also included are the designations of a few points on a  $p$ - $S$  basis using square brackets according to the convention introduced in Part b of this section. In general,  $T_1$  is larger than  $T_0$  because of the dissipation occurring at the front. The central part of our problem is the determination of the Hugoniot curve.

We shall consider in Part a the calculations due to Arons and Halverson<sup>5</sup> which are intended to be accurate in the range of relatively low pressure (ca. 0 to 20 kilobars). These results as stated in the introduction are intended for the determination of the peak pressure of a shock wave from measured values of the shock front velocity  $U$  or particle velocity  $u$ . In Part b, we shall consider the calculations of Kirkwood and Richardson,<sup>6</sup> the results of which were originally intended for the applications of the shock wave propagation theory of Kirkwood and Bethe<sup>2</sup> which required data over a higher range of pressures (ca. 20 to 50 kilobars).

### a. Calculations of Arons and Halverson

Here we outline the calculations<sup>7</sup> suitable for the relatively low pressure range (ca. 0 to 20 kilobars) based upon the equation-of-state and specific heat data discussed in detail in Appendix I. For the range 0 to 1.5 kilobars, the Ekman equation-of-state was used; in the range 0 to 25

kilobars, the Tait equation-of-state,

$$v(0, T) - v(p, T)/v(0, T) = (1/n) \log[1 + p/B(t)], \\ t = (T - 273.16)^\circ\text{C}. \quad (2.7)$$

In the first case, the initial temperature was  $t_0 = 15^\circ\text{C}$ ; in the second,  $t_0 = 25^\circ\text{C}$ . In both cases, the initial pressure  $p_0 = 0$ . Neither of the two equations-of-state are complete in the sense that  $v_0 = v(0, T)$  must be determined by auxiliary thermal expansion data (also discussed in Appendix I).

We express the enthalpy and volume increments

$$\Delta H = H(p, T) - H(0, T_0), \\ \Delta v = v(p, T) - v(0, T_0), \quad (2.8)$$

in terms of line integrals, first along an isobar from  $(0, T_0)$  to  $(0, T)$  and, secondly, along an isotherm from  $(0, T)$  to  $(p, T)$  (see Fig. 1). For the enthalpy increment we obtain

$$\Delta H = \Delta_p H + \Delta_T H, \\ \Delta_p H = \int_{T_0}^T c_p(0, T') dT' = \bar{c}_p \Delta T, \\ \Delta_T H = \int_0^p \left[ v(p', T) - T \frac{\partial v(p', T)}{\partial T} \right] dp', \\ \Delta T = T - T_0, \quad (2.9)$$

where  $c_p(0, T)$  is the specific heat extrapolated to zero pressure and  $\bar{c}_p$  is the mean of  $c_p$  over the temperature range  $\Delta T$ .

For the volume increment we obtain

$$\Delta v = \Delta_p v + \Delta_T v, \\ \Delta_p v = v(0, T) - v(0, T_0) = \bar{\beta}_0 \Delta T, \\ \Delta_T v = v(p, T) - v(0, T), \quad (2.10)$$

where  $\bar{\beta}_0$  is the mean thermal expansion at zero pressure over the temperature range  $\Delta T$ .

From the last Hugoniot condition, Eq. (2.3), and Eq. (2.9) we obtain

$$\Delta T = \frac{[v(0, T_0) + (1/2)(\Delta_T v)]p - \Delta_T H}{\bar{c}_p - (1/2)(\bar{\beta}_0 p)}, \quad (2.11)$$

where  $\Delta_T H$  is to be calculated by means of the third of Eq. (2.9) and the appropriate equation-of-state, and where  $\Delta_T v$  is to be obtained from compressibility data. The right-hand side of Eq. (2.11) depends, of course, on the temperature  $T$ . The determination of  $\Delta T$  is accomplished by the method of successive approximations. A trial

<sup>5</sup> A. B. Arons and R. R. Halverson, *Hugoniot Calculations for Sea Water at the Shock Front*, OSRD Report No. 6577, NDRC No. A-469.

<sup>6</sup> J. G. Kirkwood and J. M. Richardson, *The Pressure Wave Produced by an Underwater Explosion, Part III*, OSRD Report No. 813 (Dept. of Commerce Bibliography No. PB 32184).

<sup>7</sup> J. G. Kirkwood and E. Montroll, *Pressure Wave Produced by an Underwater Explosion, II*, OSRD Report No. 676 (Dept. of Commerce Bibliography PB-32183).

TABLE I.  $U - c_0/c_0$ ,  $u$ , and  $\Delta H$  in low pressure region (based on Ekman equation-of-state). Sea water: Initial temperature 15°C; salinity 32 parts per thousand (3.79 wt. percent NaCl);  $c_0 = 4922.8$  ft/sec = 1500.5 m/sec.

A				B			
$p - p_0$ (kbar)	$U - c_0$ $c_0$ (%)	$u$ (m/ sec)	$\Delta H$ (cal/ gm)	$p - p_0$ (lb/in <sup>2</sup> )	$U - c_0$ $c_0$ (%)	$u$ (ft/ sec)	$\Delta H$ (cal/ gm)
0.00	0.00	0.0	0.0	0	0.00	0.0	0.0
.25	2.07	15.1	5.8	2,000	1.14	29.1	3.2
.50	4.03	31.2	11.5	4,000	2.27	57.6	6.4
.75	5.93	46.2	17.2	6,000	3.35	85.5	9.6
1.00	7.81	60.5	23.0	8,000	4.43	112.9	12.7
1.25	9.65	74.4	28.5	10,000	5.48	139.7	15.9
1.50	11.44	87.7	34.1	12,000	6.53	166.0	19.0
				14,000	7.56	191.8	22.1
				16,000	8.58	217.1	25.2
				18,000	9.59	242.0	28.3
				20,000	10.57	266.5	31.4
				22,000	11.55	290.6	34.5

TABLE II.  $U - c_0/c_0$ ,  $u$ , and  $\Delta H$  in intermediate pressure region (1.5 to 25 kilobars) (based on Tait equation-of-state;  $n = 7.800$ ,  $B = 3.012$ ). Sea water: Initial temperature 25°C; salinity 32 parts per thousand (3.79 wt. percent NaCl);  $c_0 = 5014.7$  ft/sec = 1528.5 m/sec.

A				B			
$p - p_0$ (kbar)	$U - c_0$ $c_0$ (%)	$u$ (m/ sec)	$\Delta H$ (cal/ gm)	$p - p_0$ (lb/in <sup>2</sup> )	$U - c_0$ $c_0$ (%)	$u$ (ft/ sec)	$\Delta H$ (cal/ gm)
0.0	0.00	0.0	0.0	0	0.0	0	0.0
1.0	8.18	59.2	23.0	20,000	11.0	258	31.3
1.5	11.88	85.5	34.2	30,000	15.8	375	46.6
2.0	15.39	110.1	45.3	40,000	20.5	483	62.0
2.5	18.71	135.0	56.3	50,000	24.7	584	77.0
3.0	21.88	157.8	67.2	60,000	28.7	676	92.0
4.0	27.84	200.5	88.8	70,000	32.5	767	107.0
5.0	33.39	240.2	110.1	80,000	36.0	853	121.0
6.0	38.59	277.5	131.2	90,000	39.4	937	135.0
8.0	48.13	346.1	172.9	100,000	42.8	1014	150.0
10.0	56.73	408.9	214.0	120,000	49.2	1168	178.0
12.0	64.70	466.9	254.8	140,000	55.2	1312	207.0
14.0	72.25	510.9	295.2	160,000	60.8	1445	235.0
25.0	108.40	769.1	514.4	180,000	66.3	1564	263.0
				200,000	71.5	1662	291.0

value of  $\Delta T$  is used in evaluating the right-hand side giving a more accurate value of  $\Delta T$  on the left-hand side, and the process is repeated until the results of two successive steps differ by a sufficiently small amount. One or two steps generally suffice.

We have thus obtained  $T$  as a function of  $p$  along the Hugoniot curve (see Fig. 1). It is now possible to calculate immediately the particle velocity  $u$ , the propagation velocity  $U$ , and the specific volume  $v$  as functions of  $p$  behind the shock front. The results using the Ekman equation-of-state and the Tait equation-of-state are tabulated in Tables I and II, respectively, of Section III.

## b. The Calculations of Richardson and Kirkwood

Here we outline the calculations<sup>6</sup> intended for the applications of the shock wave propagation

theory of Kirkwood and Bethe.<sup>2</sup> These are based upon the equation-of-state and specific heat data discussed in detail in Appendix II. We use a modified Tait equation-of-state connecting  $v(p, T)$  and  $v(0, T)$  to be discussed below. In most respects, the data is made to fit the properties of an aqueous 0.7 molal NaCl solution assumed to be roughly equivalent to sea water of salinity  $s = 32$  parts per thousand (see Section 1 of Appendix I).

In these calculations the initial pressure  $p_0$  is taken to be zero, and several different initial temperatures  $T_0$  are used: 0°C, 20°C, and 40°C.

Before indicating the precise nature of the modification of the Tait equation, it is desirable to mention that in this part two different pairs of independent variables will be used: pressure and temperature ( $p, T$ ), and pressure and entropy [ $p, S$ ]. Consequently, in order to indicate which pair are used in a function, we will use parenthesis to indicate the first pair and square brackets to indicate the second, i.e.  $v(p, T)$  and  $v[p, S]$ .

The modified form of Tait equation introduced by Kirkwood<sup>2, 6</sup> is

$$\log(v_1/v) = (1/n) \log(1 + p/A[S]), \quad (2.12)$$

where

$$v = v[p, S] = v(p, T[p, S]), \quad v_1 = v[0, S],$$

(see Fig. 1)  $n$  is an empirical constant, and the function  $A[S]$  is related to the function  $B(t)$  in the original isothermal form of the Tait equation, Eq. (2.7), as follows,

$$A[S] = B(t[0, S]), \quad t = (T - 273.16)^\circ\text{C}. \quad (2.13)$$

The reasons for introducing this modification of the Tait equation are at least twofold: (1) the anomaly of a vanishing specific volume  $v(p, T)$  at a finite pressure along a given adiabat (which does not differ markedly from the Hugoniot curve in the case of water) is removed to a higher pressure by replacing  $[v(0, T) - v(p, T)]/[v(0, T)]$

TABLE III. Values of  $U - c_0/c_0$  for different temperatures and salinities at a shock wave peak pressure of 1.00 kilobar.

Salinity (parts per 1000)	Temperature (°C)	$U - c_0/c_0$ (%)
32	15	7.81
32	25	7.81
35	15	7.76

by  $\log(v[0, S]/v[p, S])$ , and (2) the calculation of quantities defined by line integrals along adiabatics is greatly simplified by taking  $S$  instead of  $T$  as one of the independent variables.

The function  $A[S]$  is related simply to  $c_1$ , the sound velocity at zero pressure and entropy  $S$  according to Eq. (2.4) as follows

$$A[S] = c_1^2/nv_1; \quad c_1 = c[0, S]. \quad (2.14)$$

On the basis of Bridgman's  $p$ - $v$ - $T$  data for pure water, an average value of  $n$  equal to 7.15 has been selected for the present calculations. In Section 2 of Appendix II, it is shown that  $n$  deviates from this value by less than 4 percent in a large pressure-temperature field bounded by adiabatics starting at zero pressure and temperatures of 20°C and 60°C, respectively, and extending to pressures of 25,000 kg/cm<sup>2</sup>. We assume that  $n$  has the same value for an aqueous 0.7 molal NaCl solution as for pure water, and we obtain by interpolation the required values of  $B(t)$  from R. E. Gibson's values of  $B(t)$  for dilute aqueous NaCl solutions (see Appendix II, Section 1). The appropriate heat capacity and thermal expansion data are discussed in Section 1 of Appendix II.

We now proceed to the calculation of the quantities  $u$ ,  $U$ ,  $c$ ,  $\sigma$ , and  $\omega$ . We first express these quantities with use of Eq. (2.12) in terms of  $p$ ,

$$v = v(p, T) = v[p, S], \quad v_0 = v(0, T_0),$$

$v_1 = v(0, T_1) = v[0, S]$ , and  $c_1 = c(0, T_1) = c[0, S]$  (see Eqs. (2.1)–(2.6), also Fig. 1) as follows:

$$u = [p(v_0 - v)]^{1/2}, \quad (2.15)$$

$$U = pv_0/u, \quad (2.16)$$

$$c = c_1(v_1/v)^{(n-1)/2}, \quad (2.17)$$

$$\sigma = \frac{2c_1}{n-1} [(v_1/v)^{(n-1)/2} - 1], \quad (2.18)$$

$$\omega = \frac{c_1^2}{n-1} [(v_1/v)^{n-1} - 1], \quad (2.19)$$

Once the temperature  $T_1$ , to which an element of fluid returns along the adiabatic intersecting the Hugoniot curve at  $(p, T)$ , is determined, all of the above quantities may be determined as functions of  $p$ . To accomplish this, the enthalpy increment,  $\Delta H$ , occurring in the third Hugoniot condition, Eq. (2.3), is written as the sum of two line integrals, the first along an isobar from

$(0, T_0) = [0, S_0]$  to  $(0, T_1) = [0, S]$  and the second along an adiabatic from  $(0, T_1) = [0, S]$  to  $(p, T) = [p, S]$  (see Fig. 1), giving:

$$\Delta H = \omega + h,$$

$$\omega = \int_0^p v[p', S] dp', \quad (2.20)$$

$$h = \int_{S_0}^S T[0, S'] dS' = \int_{T_0}^{T_1} c_p(0, T') dT',$$

where  $\omega$  is the undissipated enthalpy already defined by Eq. (2.6) with  $p_0 = 0$  and given explicitly in terms of  $c_1$ ,  $v_1$ , and  $v$  in Eq. (2.19). The dissipated enthalpy  $h$  can be determined as an explicit function of  $T_0$  and  $T_1$  from specific heat data (Appendix II, Section 1). Combining the third Hugoniot condition, Eq. (2.3), with Eqs. (2.19) and (2.20) we obtain the relation

$$\frac{h}{c_1^2} = \frac{1}{2n} \left[ y - \frac{n+1}{n-1} (y^{(1-1/n)} - 1) - y^{-1/n} \right] - \frac{v_1 - v_0}{2nv_1} (y - 1), \quad (2.21)$$

TABLE IV. Properties of sea water at a shock front. (Initial temperature 0°C; salinity 0.7 m NaCl;  $C_0 = 1443$  m/sec.)

$p$ (kilo- bar)	$u$ (m/ sec)	$U$ (m/ sec)	$c$ (m/ sec)	$\sigma$ (m/ sec)	$\omega \times 10^{-8}$ (m/ sec) <sup>2</sup>	$h$ (joule/ gm)	$v$ (cm <sup>3</sup> / gm)
0	0	—	—	0	0	0	0.9915
5	257.0	1930	2190	253.5	0.4565	6.740	.8593
10	433.0	2290	2720	420.5	0.8720	25.80	.8040
15	575.0	2585	3145	552.0	1.270	54.40	.7710
20	697.5	2845	3510	664.0	1.655	86.55	.7483
25	805.5	3075	3835	763.5	2.030	122.5	.7319
30	905.0	3285	4125	855.5	2.405	160.5	.7186
35	997.0	3480	4395	940.5	2.770	201.5	.7075
40	1080	3665	4640	1020	3.140	244.0	.6989
50	1240	4000	5095	1175	3.860	331.0	.6842
60	1385	4300	5495	1315	4.575	419.0	.6728
70	1515	4585	5870	1455	5.285	509.0	.6641
80	1635	4855	6225	1585	6.000	595.5	.6579
90	1740	5120	6570	1705	6.730	676.0	.6542

TABLE V. Properties of sea water at a shock front. (Initial temperature 20°C; salinity 0.7 m NaCl;  $C_0 = 1517$  m/sec.)

$p$ (kilo- bar)	$u$ (m/ sec)	$U$ (m/ sec)	$c$ (m/ sec)	$\sigma$ (m/ sec)	$\omega \times 10^{-8}$ (m/ sec) <sup>2</sup>	$h$ (joule/ gm)	$v$ (cm <sup>3</sup> / gm)
0	0	—	—	0	0	0	0.9929
5	251.0	1975	2230	248.5	0.4595	5.570	.8668
10	425.5	2335	2755	415.5	0.8790	23.45	.8120
15	567.0	2630	3175	549.0	1.280	49.35	.7787
20	689.0	2880	3535	663.0	1.670	80.05	.7555
25	798.0	3110	3855	765.0	2.050	115.0	.7381
30	897.5	3320	4140	859.0	2.425	152.5	.7243
35	990.0	3510	4405	946.5	2.795	192.0	.7130
40	1075	3690	4650	1030	3.160	233.0	.7034
50	1235	4020	5100	1185	3.885	317.5	.6880
60	1380	4325	5505	1330	4.605	404.5	.6765
70	1510	4610	5880	1465	5.320	489.5	.6679
80	1625	4885	6240	1600	6.050	573.5	.6626

TABLE VI. Properties of sea water at a shock front. (Initial temperature 40°C; salinity 0.7 m NaCl.)

$p$ (kilo- bar)	$u$ (m/ sec)	$U$ (m/ sec)	$c$ (m/ sec)	$\sigma$ (m/ sec)	$\omega \times 10^{-6}$ (m/ sec) <sup>2</sup>	$h$ (joule/ gm)	$g$ (cm <sup>3</sup> / gm)
0	0	—	—	0	0	0	0.9993
5	249.5	2005	2255	247.0	0.4630	5.59	.8749
10	423.5	2360	2775	415.0	0.8870	22.75	.8198
51	566.5	2645	3195	550.0	1.290	48.30	.7859
20	689.0	2900	3550	666.5	1.685	78.70	.7621
25	798.5	3130	3865	770.5	2.065	113.5	.7441
30	899.0	3335	4150	866.0	2.445	151.0	.7298
35	992.0	3525	4415	955.5	2.815	189.5	.7179
40	1080	3705	4660	1040	3.185	230.5	.7080
50	1240	4035	5110	1200	3.915	315.0	.6926
60	1380	4340	5515	1345	4.640	400.5	.6813
70	1510	4635	5900	1485	5.370	483.0	.6737

where  $y = (v_1/v)^n$ . With the aid of tables of  $n/c_1^2$  and  $v_1$  as functions of  $T_1$  and  $T_0$ , Eq. (2.21) may be solved by successive approximations giving  $T_1$  as a function of the parameter  $y$ . Since the equation of state, Eq. (2.12), may be expressed simply as  $p = B(T_1 - 273.16)[y - 1]$ , the temperature  $T_1$  may be determined as a function of the pressure  $p$  by a tabular elimination of  $y$ . By graphical interpolation,  $T_1$  is finally determined for the desired integral values of  $p$  (in kilobars), and the functions  $u$ ,  $U$ ,  $c$ ,  $\sigma$ , and  $\omega$  are then computed as functions of  $p$  by means of Eqs. (2.15)–(2.19).

### III. NUMERICAL RESULTS OF ARONS AND HALVERSON

In fundamental shock wave studies, it is frequently necessary to know values of  $U - c_0/c_0$  and  $u$  at given pressure levels to the highest possible degree of accuracy. With this object in view, the calculation methods described in Section 2A were applied to the best available equation-to-state data. The numerical results are given in Tables I and II. A critical discussion of the equation-of-state data will be found in Appendix I together with references to the sources from which they were obtained.

Table I gives results for the "low pressure" region, covering shock wave peak pressures of from 0 to 1.50 kilobars (*ca.* 22,000 p.s.i.). The calculations in this table were based upon the Ekman equation-of-state for sea water (see Appendix I) which is used in the calculation of sound velocity for echo-ranging tables.

Since the Ekman equation deviates appreciably from experimental compressibility data at pressures exceeding 2 kilobars, this equation was abandoned in the "intermediate pressure" region.

The results in Table II are applicable principally to the region between 1.5 and 14 kilobars (*ca.* 200,000 p.s.i.) and are based on a careful fit of the Tait equation to Adams's experimental compressibility data (see Appendix I).

Tables I and II were computed for certain specific values of temperature and sea water salinity (equivalent to 0.675 molal NaCl), and it is shown in Table III that the value of  $U - c_0/c_0$  is not very sensitive to changes in these variables.

### IV. NUMERICAL RESULTS OF KIRKWOOD AND RICHARDSON

In Tables IV to VI, the particle velocity  $u$ , the shock front velocity  $U$ , the sound velocity  $c$ , the Riemann  $\sigma$ -function, the undissipated enthalpy  $\omega$ , the dissipated enthalpy  $h$ , and the specific volume  $v$  of sea water (0.7 molal NaCl solution) are presented as functions of pressure  $p$  along three Hugoniot curves, starting at zero pressure and the temperatures 0°C, 20°C and 40°C, respectively. These results have been calculated by the procedures of Part b of Section 2 and the data of Appendix II. The results above 30 kilobars represent extrapolations beyond the range of experimental data; consequently the validity of the results above, say, 50 kilobars, is questionable.

In closing this discussion of the calculations, the authors wish to acknowledge their gratitude and appreciation to Professor J. G. Kirkwood of Cornell University for his contributions in initiating the work and in supplying valuable guidance and advice.

### APPENDIX I††

#### 1. Salinity and Temperature Conditions

All calculations were made for sea water having a salinity of 32 parts per thousand (the average salinity of sea water at Woods Hole, Massachusetts). Salinity is defined in terms of directly measured chlorinity as:

$$s = 0.030 + 1.8050 \text{ Cl}$$

where  $s$  and Cl are expressed in parts per thousand.

It was calculated from the average composition

†† Equation-of-state data used in computation of Tables I and II:

of sea water that (on the basis of *ionic strength*) a salinity of 32 parts per thousand is equivalent to an NaCl solution having a molality of 0.675 or a weight percentage of 3.79 percent NaCl.

Table I was computed for an initial temperature of 15°C because this temperature is a rough average of conditions normally encountered in experimental work. Table II was computed for an initial temperature of 25°C because this was the temperature quoted for the available compressibility data.<sup>8</sup> Table III shows that the results are not sensitive to small variations in temperature and salinity.

## 2. Specific Volume and Coefficient and Thermal Expansion

The best sources of data seem to be the oceanographical tables of Knudsen.<sup>9</sup> Second power equations in  $t$  (°C) were fitted to the data tabulated for  $s = 32$ :

For Table I:

$$v(t) = 0.97709 + 2.05 \times 10^{-4}(t - 15) + 4 \times 10^{-6}(t - 15)^2.$$

For Table II:

$$v(t) = 0.97956 + 2.85 \times 10^{-4}(t - 25) + 4 \times 10^{-6}(t - 25)^2.$$

## 3. Heat Capacity

The heat capacity data used in computing Tables I and II are those quoted by S. Kuwahara.<sup>10</sup>

$$C_p = C_p' - 0.0004226t + 0.000006321t^2 \text{ cal./gm}^\circ\text{C},$$

TABLE VII. Comparison of experimentally measured sound velocity with calculations based on the Ekman Compressibility Equation. (Salinity = 31.7 parts per thousand.)

Temperature (°C)	Velocity of sound (ft/sec)		Deviation (%)
	Measured	Calculated	
10.9	4887.7	4875.6	0.26
11.6	4885.8	4883.8	0.04
11.6	4893.1	4883.8	0.19
11.5	4902.4	4882.5	0.41
11.1	4888.3	4878.5	0.20

<sup>8</sup> Adams, J. Am. Chem. Soc. **53**, 3769 (1931).

<sup>9</sup> *Oceanographical Tables*, Commissariat of Agriculture, USSR, Moscow, 1931. (A general compilation of oceanographic data by N. N. Zubov.)

<sup>10</sup> S. Kuwahara, *Velocity of Sound in Sea Water and Calculation of the Velocity for Use in Sonic Sounding* (Hydrographic Dept. I.J.N. Tokyo, 1938).

TABLE VIII. Comparison of Adams's experimental compressibilities and the empirical fit given by the Ekman and Tait equations.

P (kbar)	$(v_0 - v)/v_0$				
	Adams (experimental)		Ekman equation $S = 32$ (Table I)	Tait* equation	
	Pure H <sub>2</sub> O	3.79% NaCl		$n = 7.800$ $B = 3.012$ (Table II)	$n = 7.445$ $B = 3.156$
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	.0212	.0196	.0198	.0197	.0198
1.0	.0393	.0368	.0370	.0368	.0370
1.5	.0555	.0522	.0522	.0518	.0522
2.0	.0699	.0658	.0655	.0653	.0659
3.0	.0945	.0894	.0871	.0887	.0897
4.0	.1152	.1091	—	.1083	.1095
5.0	.1330	.1265	—	.1254	.1275
6.0	.1485	.1417	—	.1405	.1431
7.0	.1622	.1552	—	.1540	.1569
8.0	.1746	.1670	—	.1662	.1695
9.0	.1858	.1781	—	.1775	.1812
10.0	.1964	.1886	—	.1876	.1917
11.0	.2059	.1980	—	.1972	.2017

$$* (v_0 - v)/v_0 = (1/n) \log(1 + p/B).$$

where

$$C_p' = 1.005 - 0.004136s + 0.0001098s^2 - 0.000001324s^3.$$

In the above equations,  $t$  is temperature in °C and  $s$  is salinity in parts per 1000. These data are in good agreement with those used by Kirkwood and Richardson, quote in Appendix II.

## 4. Compressibility Data for Low Pressure Region (Table I)

The following equation was used in computing Table I:

$$10^5 \mu = \frac{4886}{1 + 0.183p} - [227 + 28.33t + 0.551t^2 + 0.004t^3] + p[105.5 + 9.50t - 0.158t^2] - 1.5p^2t - \left(\frac{\gamma - 28}{10}\right)[147.3 - 2.72t + 0.04t^2 - p(32.4 - 0.87t + 0.02t^2)] + \left(\frac{\gamma - 28}{10}\right)^2[4.5 - 0.1t - p(1.8 - 0.06t)],$$

where  $p$  is pressure in kilobars,  $t$  is temperature in degrees centigrade, and  $\mu$  is defined by:

$$v = v_0(1 - \mu p),$$

$\gamma$  is defined by:

$$\gamma = -0.069 + 1.4708 \text{ Cl} - 0.001570 \text{ Cl}^2 + 0.0000398 \text{ Cl}^3.$$



The above empirical equation for sea water compressibility is due to Ekman<sup>11</sup> and has been widely used for computation of sound velocity in sea water.<sup>10,12</sup> The validity of the Ekman equation for sound velocity calculations was verified experimentally as indicated in Table VII.

Experimental sound velocity measurements were made by recording with a rotating drum camera the signals applied to a cathode ray oscilloscope by two very small piezoelectric gauges placed a known distance apart. The sound source was a No. 8 detonator cap placed far enough away from the gauges so that the effect of finite pressure amplitude was less than 0.03 percent. An error of about 0.2 percent was inherent in the experimental work owing to slight errors in the alignment of the two recording gauges with the sound source. This accounts for the magnitude and systematic nature of the discrepancy apparent in Table VII.

Further verification of the applicability of Ekman's equation in the region up to 1.50 kilobars is given in Table VIII where values obtained from the equation are compared with the experimental values of Adams for NaCl solutions.

### 5. Compressibility Data for Intermediate Pressure Region (Table II)

As indicated in Part 1 of this appendix, a sea water salinity of 32 parts per thousand corresponds to a 3.79 weight percent solution of NaCl. The compressibility of NaCl solution of this concentration was obtained by graphical interpolation of Adams's data.<sup>8</sup>

The Tait equation in the form:

$$v(0, T) - v(p, T)/v(0, T) = (1/n) \log[1 + p/B(t)], \\ t = (T - 273.16)^\circ\text{C}$$

was then fitted to Adams's data. In an effort to

TABLE IX. Values of  $n$  computed from  $p$ - $v$ - $T$  data (using  $n = 7.15$  in computation of  $\Delta T$ ).

$t^*$ ( $^\circ\text{C}$ )	5000	$p$ (kg/cm <sup>2</sup> ) 15,000	25,000
20	7.211	7.183	7.130
40	7.360	7.126	6.969
60	7.411	7.054	6.868

\*  $t_0$  = centigrade temperature through which the adiabat for  $S$  passes at zero pressure.

<sup>11</sup> V. W. Ekman, *Publications de Circonstance No. 43* (Conceil Permanent Internationale Pour L'Exploration de la Mer. November 1908).

<sup>12</sup> Matthews, *Tables of the Velocity of Sound in Pure Water and Sea Water for Use in Echo Sounding and Sound Ranging* (Hydrographic Dept., Admiralty, H.D. No. 282).

check the Tait equation against the Ekman equation used for computation of Table I, a fit was first made to the lower pressure region. Values of  $n$  and  $B(25^\circ\text{C})$  were so selected that the equation not only fitted the data of Adams with adequate precision but also yielded the correct velocity of sound in the limit of zero pressure. This additional restriction (that the equation give  $c_0 = 1528$  m/sec. at  $25^\circ\text{C}$  and  $s = 32$ ) required that  $nB(25^\circ\text{C}) = 23.497$ , the latter relation being obtained from the thermodynamic equations:

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{v_0^2}{c_0^2} - \frac{T}{c_p} \left(\frac{\partial v}{\partial T}\right)_p, \\ \left(\frac{\partial v}{\partial p}\right)_T = -\frac{v_0}{nB(t)} \text{ at } p = 0.$$

In this case  $n$  was taken as 7.445 and  $B(25^\circ\text{C})$  as 3.156 kilobars, and the resulting equation fits the data of Adams quite closely up to pressures of about 4 kilobars as shown in Table VIII. For purposes of further calculation, the temperature variation of  $B$  was assumed to be the same as that used by Kirkwood and Richardson on the basis of a private communication from Gibson (see Appendix II). Calculation of  $U - c_0/c_0$  at 1.00 kilobar yielded a value of 7.85 percent, in good agreement with the value of 7.81 percent obtained from the Ekman equation.

Having verified the accuracy of results obtained from the Tait equation when fitted as described above, the same technique was used to fit the equation to the intermediate pressure range (up to values for 11 kilobars quoted by Adams; it was assumed safe to extrapolate the resulting equation to pressures of 14 or 15 kilobars). It was found that the best fit of the data as well as a correct value for the velocity of sound were obtained by taking  $n = 7.800$  and  $B(25^\circ\text{C}) = 3.012$ , the temperature variation of  $B$  again being assumed to be that mentioned above. The Tait equation containing these parameters was then used for the computation of Table II. The fit of the equation to Adams's data is shown in Table VIII.

## APPENDIX II

### 1. Data Employed in the Computations of Part B of Section II

In the modified Tait equation, Eq. (2.12), the function  $A[S] = B(t)$ , where  $t = T[0, S] - 273.16$ ,

is determined from the empirical values of  $B(t)$ , fitting the original isothermal Tait equation, Eq. (2.7), to experimental data. R. E. Gibson<sup>13</sup> gives third-degree  $t$ -expansions of  $B(t)$  for various molalities of NaCl. By interpolating the coefficients (the constant term numerically and the other graphically) for a molality of 0.7, one obtains  $B(t) = 3.134 - 1.65 \times 10^{-3}(t - 55) - 1.181 \times 10^{-4}(t - 55)^2 + 5.32 \times 10^{-7}(t - 55)^3$  kilobars.

The specific heat  $c_p(0, T)$  for a 0.7 molal NaCl solution was obtained by interpolation from the values quoted in the *International Critical Tables* and *Physikalischchemische Tabellen*. The resulting set of values is fitted adequately by the expression

$$c_p(0, t + 273.16) = 3.9644 + 6.24 \times 10^{-4}t \text{ joule/gm. deg.}$$

From Gibson and Loeffler<sup>14</sup> a set of values of  $v(0, T)$  covering the range from 25°C to 95°C inclusive was obtained for a 0.7 molal NaCl solution by means of empirical equations giving  $v(0, T)$  as a function of concentration for each temperature. In extrapolating to higher temperatures, the relation,

$$v(0, t + 273.16) = 0.994150 + 2.929 \times 10^{-4}(t - 25) + 3.241 \times 10^{-6}(t - 25)^2 \text{ cm}^3/\text{gm.}$$

was used; for lower temperatures ( $t < 10^\circ\text{C}$ ),

$$v(0, t + 273.16) = 0.991442 + 6.025 \times 10^{-6}(t - 3.8)^2 \text{ cm}^3/\text{gm.}$$

## 2. Test of the Modified Tait Equation with Bridgman's Data for Pure Water. Determination of the Characteristic Constant $n$ .

The modified Tait equation-of-state, Eq. (2.12), may for our present purposes be written in the form

$$\log[v[0, S]/v[p, S]] = (1/n) \log(1 + p/A[S]) \quad (\text{II-1})$$

where  $A[S]$  is related to the  $B(t)$  in the original isothermal equation of state as follows,

$$\begin{aligned} A[S] &= B(t_0), \\ t_0 &= T_0 - 273.16, \\ T_0 &= T[0, S]. \end{aligned} \quad (\text{II-2})$$

According to the convention introduced in Part B of Section II, parentheses ( ) after a function denotes that the independent variables are  $p$  and  $T$ , whereas square brackets [ ] denote that they are  $p$  and  $S$ .

Now we wish to test Eq. (II-1) with Bridgman's<sup>15</sup>  $p$ - $v$ - $T$  data for pure water with the ultimate object of finding the best value for  $n$ . We assume implicitly that  $n$  does not vary rapidly with NaCl concentration. To make the comparison, we first must know the values of the temperature  $T$  corresponding to the various points  $[p, S]$ , the calculation of which we consider below.

Letting  $T(0, S) = T_0$ ,  $T[p, S] = T$ , and  $T - T_0 = \Delta T$ , we have

$$\Delta T = \int_0^p \frac{\partial T[p, S]}{\partial p} dp = \int_0^p \frac{\partial v[p, S]}{\partial S} dp. \quad (\text{II-3})$$

Using Eq. (II-1), a simple calculation yields

$$\begin{aligned} \Delta T &= \frac{G}{(1 + p/A)^{1/n}} [(1 + D)(1 + p/A) \\ &\quad - (n + D)(1 + p/A)^{1/n} + n - 1], \end{aligned} \quad (\text{II-4})$$

where

$$\begin{aligned} A &= A[S] = B(t_0), \\ G &= \frac{A'[S]v[0, S]}{n - 1} = \frac{T_0 B'(t_0) \cdot v(0, T_0)}{(n - 1) \cdot c_p(0, T_0)}, \\ D &= \frac{nA[S] \frac{\partial v[0, S]}{\partial S}}{A'[S]v[0, S]} = \frac{nB(t_0)\beta_0}{B'(t_0)v(0, T_0)}, \\ \beta_0 &= \left( \frac{\partial v(0, T)}{\partial T} \right)_{T=T_0}. \end{aligned}$$

To calculate  $T$ , given a specified  $p$  and  $T_0 = T[0, S]$ , a tentative value of  $n = 7.15$  was chosen for use in Eq. (II-4). The corresponding value of  $v[p, S] = v(p, T)$  was obtained by interpolation from Bridgman's<sup>15</sup>  $p$ - $v$ - $T$  data. Inserting these values of  $v[p, S]$  in Eq. (II-1), and knowing the values of  $v[0, S] = v(0, T_0)$  and  $B(t_0)$  for pure water, a set of values of  $n$  was calculated for  $p = 5,000, 15,000, 25,000 \text{ kg/cm}^2$

<sup>13</sup> Private communication.

<sup>14</sup> Gibson and Loeffler, J. Am. Chem. Soc. **53**, 443 (1941).

<sup>15</sup> Bridgman, J. Chem. Phys. **3**, 597 (1935) and private communication.

and  $t_0 = T_0 - 273.16 = 20^\circ, 40^\circ, 60^\circ\text{C}$ , the results summarized in Table IX.

Additional data (for pure water) used in Eqs. (II-1) and (II-4) were

$$B(t) = 2.996 + 7.285 \times 10^{-3}(t - 25) - 1.790 \times 10^{-4}(t - 25)^2 + 6.13 \times 10^{-7}(t - 25)^3 \text{ kilobars},^{13}$$

and

$$\frac{1}{2.303} \frac{\partial \log v(0, 273.16 + t)}{\partial t} = \frac{2(t - 3.98)}{244,860 + 15,040(t - 3.98)^{0.62}} \frac{(0.62)(15,040)(t - 3.98)^{-0.62}}{[244,860 + 15,040(t - 3.98)^{0.62}]^2}$$

obtained from Ipatov's<sup>16</sup> empirical equation for  $v$  by differentiation.

The average value of  $n$  is 7.146. In the present calculations this value has been rounded off to 7.15.

The entries in Tables IV, V, and VI therefore contain more significant figures than the test justifies. On the basis of the test, the errors associated with the use of the modified Tait equation are of the order of several percent. In

<sup>16</sup> I. V. Ipatov, J. Phys. Chem. (U.S.S.R.) 5, 1230 (1934).

particular, the results obtained for low pressures will disagree with known data by several percent.

### APPENDIX III

#### Symbols

$A[S]$  = parameter in modified ("adiabatic") Tait equation-of-state.

$B(t)$  = parameter in isothermal Tait equation-of-state.

$c$  = local velocity of sound.

$c_0$  = velocity of sound at zero pressure.

$c_p$  = specific heat at constant pressure.

$h$  = dissipated enthalpy increment:  $\int_{T_0}^T c_p(0, T') dT'$ .

$\Delta H$  = enthalpy increment:  $\Delta H = \omega + h$ .

$n$  = characteristic constant in Tait equation-of-state.

$p_0$  = initial pressure ahead of shock front,  $p_0 = 0$ , in these calculations.

$p$  = pressure behind shock front.

$S$  = entropy.

$s$  = sea water salinity.

$t$  = temperature in  $^\circ\text{C}$ .

$T$  = absolute temperature.

$u$  = particle velocity behind shock front.

$U$  = shock front propagation velocity.

$v_0$  = specific volume of medium ahead of shock front.

$v$  = specific volume of medium behind shock front.

$\bar{\beta}_0$  = mean compressibility at zero pressure over temperature range  $\Delta T$ .

$\rho$  = density.

$\sigma$  = Riemann function:  $\int_{p_0}^p \frac{v[p', S]}{c[p', S]} dp'$ .

$\omega$  = undissipated enthalpy increment:  $\int_{p_0}^p v[p', S] dp'$ .

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## The Absorption Spectrum of Ozone in the Visible

### I. Examination for Fine Structure. II. The Effect of Temperature

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The absorption spectrum of ozone in the visible spectral region has been investigated for fine structure and for changes in absorption with temperature. No fine structure was observed in spectrograms taken in the second order of a 21-ft. grating spectrograph. The absorption coefficients remained constant within experimental error in going from room to dry-ice temperature.

#### INTRODUCTION

THE effect of temperature on the absorption of ozone in the visible region of the spectrum has been the subject of considerable study, the results of which have been conflicting. In

1880 Chappuis<sup>1</sup> discovered the visible absorption bands of ozone and two years later published observations on the change in this absorption when the ozone was cooled from room temperature to  $-50^\circ\text{C}$  by rapid evaporation of methyl

\* Contribution No. 1140 from the Gates and Crellin Laboratories of Chemistry.

<sup>1</sup> J. Chappuis, Comptes Rendus 91, 985 (1880); *ibid.* 94, 858 (1882); Ann. de l'école normale sup. 11, 137 (1882).