

1. The flames of rich mixtures of Pittsburgh natural gas,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , are extinguished when the upstream electrode is negatively charged; the flames of lean mixtures of these gases cannot be extinguished with this direction of the field.

2. The flames of lean mixtures of  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , iso- $\text{C}_4\text{H}_{10}$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_4\text{H}_8$  are extinguished when the upstream electrode is negatively charged; the flames of rich mixtures of these gases cannot be extinguished with this direction of the field.

3. The flames of rich or lean mixtures of all the above hydrocarbon gases and in addition lean mixtures of  $\text{C}_2\text{H}_2$  and  $\text{CO}$  are extinguished when the downstream electrode is negatively charged.

4. Certain effects with a tranverse field are cleared up.

A brief discussion of the results is given. It is concluded that the positive ion plays an important role in the maintenance of flames.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

## SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS. II. THE VELOCITY OF SOUND IN SOLUTIONS OF CERTAIN ALKALI HALIDES AND THEIR COMPRESSIBILITIES

BY EGBERT B. FREYER<sup>1</sup>

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In a previous paper<sup>2</sup> the velocities of sound in a number of organic liquids were reported. The measurements were made according to the method of Hubbard and Loomis,<sup>3</sup> and from the data so obtained, with the aid of other data, the adiabatic compressibilities, and in some cases also the isothermal compressibilities, were calculated. For the details of the method reference must be made to the earlier papers. It shall suffice here to mention that the high frequency or supersonic waves were generated by the piezo action of a quartz disk. For producing the high frequency alternating field a common type of vacuum tube oscillator was employed, and the positions and separation of nodes were indicated by abrupt changes of frequency. A secondary quartz controlled oscillator served to fix the frequency at resonance, and using a double heterodyne method the position of nodes as read from a micrometer screw could be determined to within

<sup>1</sup> From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

<sup>2</sup> Freyer, Hubbard and Andrews, *THIS JOURNAL*, 51, 759 (1929).

<sup>3</sup> Hubbard and Loomis, *Phil. Mag.*, [7] 5, 1177 (1928).

0.002 mm. The following equation relates the velocity of sound  $V$  in a liquid to its adiabatic compressibility  $\beta_\phi$ , and density  $\rho$

$$\beta_\phi = \frac{1}{V^2 \rho}$$

The isothermal compressibility  $\beta_\tau$  may be calculated from  $\beta_\phi$  by means of the thermodynamic relation

$$\beta_\tau = \beta_\phi + \frac{\alpha^2 T}{J C_p \rho}$$

where  $\alpha$  is the coefficient of thermal expansion,  $C_p$  the specific heat at constant pressure at absolute temperature  $T$ , and  $J$  is the mechanical equivalent of heat. These equations were used to calculate the data presented in this paper.

### Solutions of Alkali Halides

Since Hubbard and Loomis<sup>8</sup> had observed an apparently anomalous behavior of sodium iodide solutions (compared to those of potassium chloride and sodium chloride) in respect to the course of their curves of velocity of sound against temperature, it was considered desirable to study rather closely the velocity of sound in the chlorides, iodides and bromides of sodium and potassium.

The samples of the salts used were of the "Baker's c. p. Analyzed" grade, the purity of these being sufficiently high for the precision of this investigation. Considering, for example, that the most likely impurity in a given halide of potassium would be the same halide of sodium, it is evident from Fig. 2 that a trace of one salt in the other would have only a very slight effect on the velocity of sound. As much as a tenth of a per cent. of potassium chloride in sodium chloride would lower the velocity of sound in a solution only 0.05 m./sec., and the effect diminishes in the order Cl > Br > I. A precision greater than 1.0 m./sec. is not claimed for these measurements.

### Results

In Table I are recorded the same quantities calculated from the velocity of sound as were reported for the organic liquids, except that here the compressibilities, etc., are given as a function of the weight per cent. of salt in solution. The data are for 20°. The density values are from the "International Critical Tables." The coefficients of expansion were calculated from density tables. The specific heat data were taken from the Landolt-Börnstein "Tabellen."

Table II shows (a) the velocity of sound and adiabatic compressibility as a function of temperature for concentrated solutions of the salts, and (b) the velocity of sound alone as a function of both temperature and concentration in the case of the iodides. All these data were taken from smooth curves drawn through the experimental points found by the author

TABLE I  
 DATA FOR SALT SOLUTIONS

Concn., %	Velocity of sound, m./sec.	$\rho$	$\beta\phi$	$\alpha$	$C_p$	$\beta_r$	$C_p/C_v$	$\beta\phi_0 - \beta\phi$
NaCl								
1	1497.0	1.0053	$45.00 \times 10^{-6}$	0.03223	0.986	$45.36 \times 10^{-6}$	1.008	1.10
6	1554.5	1.0413	40.28	283	.931	40.86	1.014	5.82
10	1600.5	1.0707	36.96	344	.892	37.84	1.024	9.14
16	1673.0	1.1162	32.45	396	.844	33.62	1.036	13.65
20	1722.5	1.1478	29.76	423	.818	31.11	1.045	16.34
24	1771.5	1.1804	27.36	449	.794	28.89	1.056	18.74
NaBr								
1	1487	1.0060	45.56	0.03218	.987	45.90	1.007	0.58
6	1503	1.0462	42.89	276	.932	43.45	1.013	3.21
10	1517	1.0803	40.77	320	.889	41.52	1.018	5.33
16	1541	1.1352	37.60	383	.827	38.70	1.029	8.50
20	1558	1.1745	35.55	421	.788	36.91	1.038	10.55
30	1605	1.2841	30.64	505	.697	32.67	1.066	15.46
NaI								
6	1483	1.0463	44.05	0.03269	.936	44.57	1.012	2.05
10	1483	1.0808	42.64	308	.894	43.33	1.016	3.46
20	1486.5	1.1769	38.97	400	.788	40.19	1.031	7.13
30	1494	1.2907	35.18	477	.688	36.99	1.051	10.92
40	1509	1.4271	31.21	537	.592	33.63	1.078	14.89
45	1524	1.5062	28.97	561	.550	31.66	1.093	17.13
KCl								
1	1492	1.0046	$45.32 \times 10^{-6}$	0.03215	.985	$45.65 \times 10^{-6}$	1.007	0.78
6	1530	1.0369	41.76	258	.923	42.25	1.012	4.34
10	1560	1.0633	39.17	287	.877	39.80	1.016	6.93
16	1604	1.1043	35.67	324	.818	36.50	1.023	10.43
20	1633	1.1328	33.55	345	.784	34.50	1.028	12.55
24	1662.5	1.1628	31.55	365	.753	32.63	1.034	14.55
KBr								
1	1486.5	1.0054	45.74	0.03215	.987	46.07	1.007	0.36
6	1495.0	1.0426	43.50	260	.927	44.00	1.011	2.60
10	1502.5	1.0740	41.80	292	.880	42.44	1.015	4.30
20	1521.5	1.1601	37.74	360	.767	38.77	1.027	8.36
30	1545.5	1.2593	33.70	408	.658	35.13	1.042	12.40
40	1573.0	1.3746	29.80	433	.553*	31.55	1.059	16.30
KI								
6	1480.5	1.0437	44.31	0.03257	.932	44.79	1.011	1.79
16	1475	1.1284	41.29	333	.819	42.14	1.021	4.81
30	1472	1.2712	36.80	441	.667	38.24	1.039	9.30
45	1477	1.4672	31.67	462	.512*	33.70	1.063	14.43

and by Hubbard and Loomis, plotted as shown in Figs. 1 and 2. From the first it is seen that increasing the concentration of salt increases the ve-

TABLE II  
EXPERIMENTAL DATA  
(a)

Temp., °C.	Velocity of sound, m./sec.	$\rho$	$\beta\phi$	Temp., °C.	Velocity of sound, m./sec.	$\rho$	$\beta\phi$
26% NaCl				20% KCl			
20	1796	1.1972	$26.25 \times 10^{-6}$	15	1623	1.1347	33.91
25	1799	1.1944	26.23	20	1633	1.1328	33.55
30	1801	1.1917	26.22	25	1641	1.1307	33.29
40	1802	1.1861	26.32	30	1649	1.1285	33.03
30% NaBr				40	1661	1.1240	32.68
15	1599	1.2870	30.80	50	1669	1.1192	32.51
20	1605	1.2841	30.64	30% KBr			
25	1609	1.2811	30.56	20	1545.5	1.2593	33.70
30	1612	1.2780	30.53	25	1554	1.2566	33.40
40	1615	1.2718	30.56	30	1561	1.2539	33.17
50	1616	1.2654	30.67	40	1571	1.2484	32.90
45% NaI				50	1576	1.2423	32.85
10	1525	1.5146	28.77	30% KI			
20	1524	1.5062	28.97	10	1457	1.2762	37.42
30	1525	1.4980	29.09	20	1472	1.2712	36.80
40	1525	1.4897	29.26	30	1483.5	1.2658	36.38
				40	1492	1.2600	36.14
				50	1498.5	1.2537	36.01
				60	1504	1.2472	35.93

(b)

Temp., °C.	KI				Pure water	NaI				
	5%	15%	30%	45%		15%	30.5%	40%	45%	46.8%
15	1465	1464	1465	1473	1467.5	1472	1488	1507	1525	1534
25	1495	1486	1478.5	1481	1498.1	1495	1500	1512	1525	1532
35	1516.5	1503	1488.5	1488	1520.6	1511.5	1508	1515	1525	1530
45	1530	1515	1495.5	1492						1528
55	1538	1522	1501							

locity of sound in solutions of sodium chloride, potassium chloride, sodium bromide and potassium bromide. In the case of potassium iodide the velocity decreases and passes through a minimum at about 37%, at 25, 35 and 45°, whereas at 15° the minimum occurs at 20% salt concentration. Considering sodium iodide, the minimum shifts to lower concentration as the temperature is lowered. An explanation of the general course of these curves will be given presently. In Fig. 2 is shown the change in the velocity of sound in solutions of varying concentration as the temperature changes. A characteristic of all the curves is the decrease in slope at a given temperature and a general flattening as the concentration increases. This tendency is least in the case of potassium chloride. The slope of the curve is zero for 45% sodium iodide and becomes negative at higher concentration. Figure 3 shows the lowering of the adiabatic com-

pressibility produced by adding the various salts to water as a function of the quantity of salt added.

### Discussion

Since the velocity of sound in a liquid is related to its density and adiabatic compressibility, we should be able to predict changes in the first

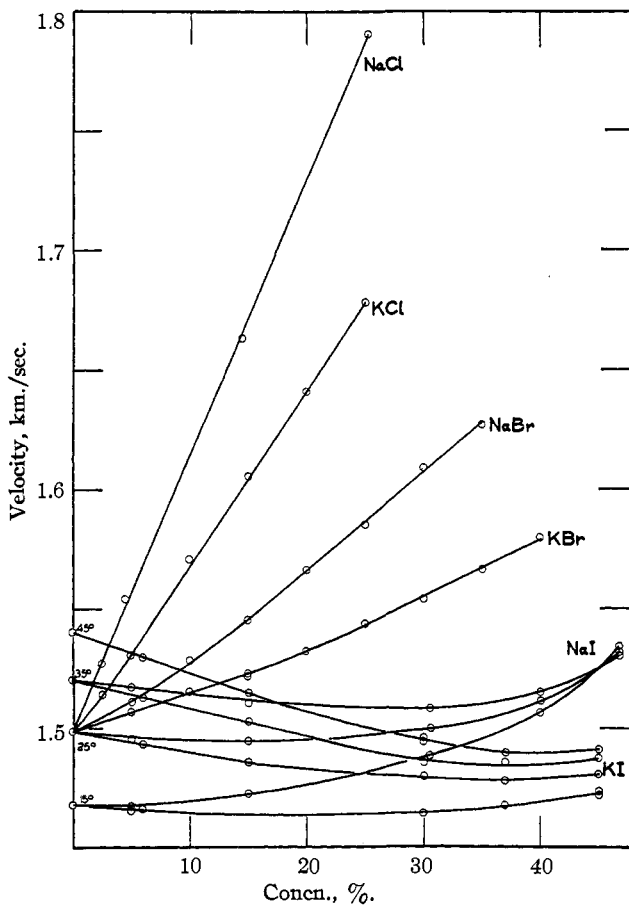


Fig. 1.

quantity if we know how the other two vary. The general trend of the velocity of sound-concentration curves is accounted for as follows: the decreasing compressibility tends to increase the velocity, while the increasing density tends to lower it. The predominating effect obviously determines whether addition of salt shall increase or decrease the velocity of sound in the solution. These relations are clearly illustrated by the figures of the first two columns of Table III, where the fractional changes

TABLE III  
DATA FOR 10% SALT SOLUTIONS

	(a) $\frac{\beta\phi_0 - \beta\phi}{\beta\phi_0}$	(b) $\frac{\rho - \rho_0}{0.01 \rho_0}$	(c) $\gamma$	(d) $\frac{(b)}{(c)}$	(e) Molecular weight
NaCl	0.198	7.07	0.64	11.1	58.5
KCl	.150	6.33	.58	10.9	74.6
NaBr	.116	8.03	.70	11.4	102.9
KBr	.093	7.39	.61	12.1	119.0
NaI	.075	8.09	.72	11.2	149.9
KI	.065	7.61	.67	11.4	166.0
LiCl		5.59	.93	6.0	
HCl		4.57	1.15	4.0	

in the compressibility and percentage density change due to adding 10% of each salt are recorded. In the case of sodium chloride the compressibility change greatly pre-

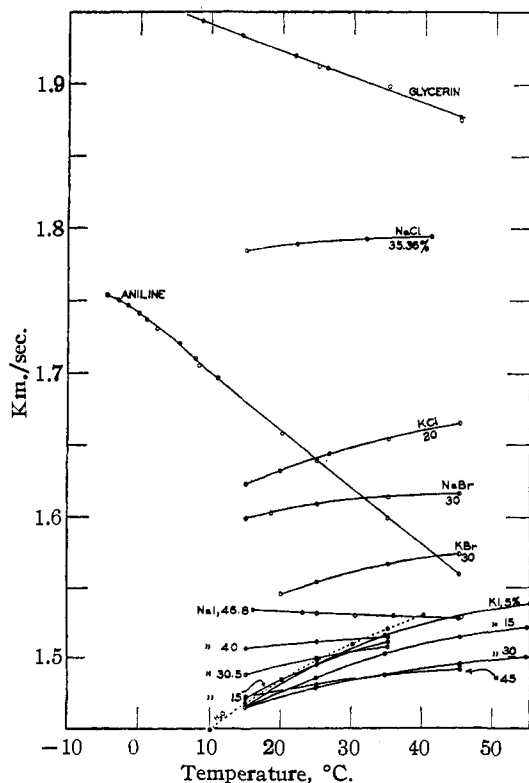


Fig. 2.

dominates and the velocity of sound increases relatively quite rapidly. This predominance decreases in the order  $\text{NaCl} > \text{KCl} > \text{NaBr} > \text{KBr}$ . The density change has the greater influence in the case of sodium iodide and potassium iodide, and the velocity of sound in solutions of these salts accordingly decreases with concentration. The same reasoning evidently applies also to the curves of Fig. 1, except that here the velocity of sound change is determined by the effect of temperature on the compressibility and density.

Figure 3 shows that a solution of each of the several salts has a lower compressibility than has the pure solvent, and that the lowering produced is greater the

larger the amount of salt added. It seemed of interest to examine rather closely the specific effect of each salt at one concentration.

To this end a number of properties of the salts and of their ions were sought in the literature, in the hope that a qualitative relation, at least, might be found between some of these properties and the effect of the ions on the compressibility of their solution. The following question presents itself: what factors may be operative when a salt is added to water that might produce a compressibility change? First, it is conceivable that the presence of ions may change the condition of aggregation of the solvent molecules, *i. e.*, may shift the trihydrol-dihydrol-monohydrol equilibria. Second, it is known that ions concentrate solvent molecules in their immediate vicinity, this hydration being, in effect, a compression, and related to a volume change observed when the components are mixed. It seems a fairly remote possibility that the compressibility of a salt as measured

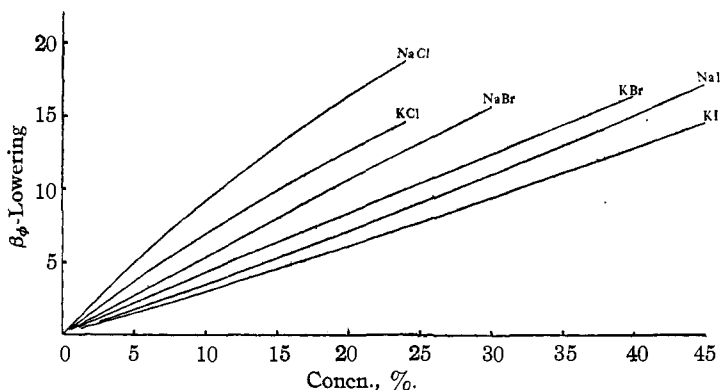


Fig. 3.

for the solid should have an appreciable effect on that of its solution. The first two possibilities become one when we consider that any effect of the ions on the equilibria between the various hydrols would actually be brought about as a result of hydration. Now the compressibility of a substance decreases with increasing pressure or, simply, the more a substance is compressed the less it can be compressed. It should accordingly be expected that for a given concentration those solutions will have the lower compressibility whose ions are most hydrated, or, expressed in another way, the lowering of the compressibility produced when different salts are added to water should vary in the same order as the relative degrees of hydration of their ions. Thus Webb<sup>4</sup> has calculated the contraction of the solvent produced by ions of various radii.

The figures in column two of Table IV represent the mean contraction produced by the two ions composing the salts which affect the fractional compressibility lowerings given in the first column. The assumption is made that this contraction effect is a measure of the relative mean degree

<sup>4</sup> Webb, *THIS JOURNAL*, **48**, 2598 (1926).

of hydration of the ions. The third column shows how nearly the compressibility change is proportional to the contraction. The mean ionic radii of the salts as calculated by Webb are given in the fourth column. It is to be noted that in the range considered, the contraction of the solvent is almost inversely proportional to the mean radii of the ions producing it. This is due to the greater intensity of the electric field about the ions of the low atomic number and small radii, resulting in a greater attraction of the water dipoles for the ions. This is the so-called electrostriction.

TABLE IV  
DATA FOR 3 MOLAL SALT SOLUTIONS

	(a) $\beta\phi_0 - \beta\phi$	(b) Mean relative contraction	(b) (a)	Mean $r$ , Å.
NaCl	0.129	10.7	83	1.87
NaBr	.124	10.2	83	1.95
NaI	.113	9.5	84	2.05
KCl	.116	9.5	82	2.05
KBr	.108	9.0	83	2.12
KI	.105	8.4	80	2.23

It would seem desirable, before concluding, to direct attention to one further observation. It is the approximate proportionality between the activity coefficients and percentage density changes due to equal weight percentages of the six salts in solution. This is shown in the last column of Table III. The data are for 10% solutions. The relation is seen to be not even approximate in the case of lithium chloride and hydrochloric acid. This is not surprising in view of the differences in properties usually observed between the elements of the first series of the periodic table and those of the other series. It was found also not to hold for salts of other valence types.

### Summary

The velocity of sound in solutions of iodides, chlorides and bromides of sodium and potassium has been measured, using high frequencies and a resonance method of detecting nodes. The data cover nearly the entire concentration range for the various salts, and the temperature range 15 to 45°.

The adiabatic and isothermal compressibilities have been calculated for various concentrations at 20°. The adiabatic compressibilities have been calculated as a function of temperature for certain concentrated solutions of the salts.

It is shown that addition of salt lowers the adiabatic compressibility of the solutions, the lowering being quite different for equal percentages of the different salts, and much more nearly equal for equal molalities. In the latter case, the lowering is shown to be related to the contraction of the solvents and hence, presumably, to the hydration produced by the ions.