MEASUREMENT OF ULTRASONIC VELOCITIES IN AQUEOUS SOLUTIONS OF SEVERAL SALTS

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by

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INTRODUCTION

Ultrasonic (or supersonic) waves are sound waves whose frequency is above the audible range. The human ear can hear sounds of frequencies up to about 20 kilocycles and ultrasonic frequencies extend from there upwards, 500,000 kilocycles being the highest frequency that it is now possible to produce. The wave-length range of ultrasonic sound waves in air is from 1.5 to 0.00006 cm. while the wave-length of an audible sound whose frequency is, say, 256 vibrations per second (middle C on the musical scale) is more than 100 cm. As sound velocity is usually obtained from wave-length measurements, this shortness of ultrasonic waves greatly simplifies measurement of sound velocities.

There is a great concentration of energy in ultrasonic waves as compared to audible waves, an intensity of 10 watts per $cm.^2$ being not uncommon in ultrasonic waves as contrasted with intensities in the order of 10^{-10} watts per $cm.^2$ in audible waves.

Rao[7] states that a dispersion of sound velocity with frequency has been definitely established in gases but that such a dispersion in liquids, if it exists, is only 1 or 2 meters per second and thus within the range of experimental error. Thus, in general, ultrasonic velocit-

ies are the same as audible sound velocities.

Fortunately, the laws of sound which are valid for the audible range also hold for the ultrasonic range, although some phenomena appear in the latter which are not observed in the former. Use of ultrasonics for velocity measurements in liquids has three outstanding advantages because of the shortness of the waves. These are: (1) it is possible to make measurements in a small space thus eliminating complicated and cumbersome equipment otherwise necessary; (2) the influence of the walls of the containing vessel, which is so difficult to correct for with audible sound waves, is negligible with the short waves; (3) it is possible to make velocity measurements with small amounts of the medium. Because of these advantages it has been possible, for example, to make measurements in liquid oxygen and heavy water.

THE PURPOSE OF THIS RESEARCH

Ultrasonic velocity measurements are chiefly important in that they yield values for the adiabatic compressibility of the medium. Given this, and the isothermal compressibility derived from static measurements, it is then possible to calculate the ratio of the specific heats of a liquid. There is also a good possibility that when enough data has been accumulated it will be possible to explain completely the changes of volume and compress-

ibility which occur when salts are dissolved in water. Velocity measurements have been made in most of the common organic liquids and the compressibilities computed but very little work has been done with aqueous solutions of salts. For this reason the author decided to work in the latter field.

A series of velocity measurements in various concentrations of potassium and sodium halides have been made by Freyer[3]. Only a few other investigators have made measurements in electrolytic solutions and none of them has dealt with a specific series of salts as did Freyer. In choosing a series of salts for investigation it seemed best to choose a series other than those studied by Freyer in order that there might be a greater range of data from which to make conclusions. A series of nitrates seemed the best one to choose because they are easily obtained, the nitrates of practically all metallic ions exist, and especially because of their very high solubility. The three lowest mono-valent nitrates (potassium, sodium, and lithium) and two di-valent nitrates of high solubility (magnesium and zinc) were the ones chosen for the investigation. Both mono-valent and di-valent nitrates were chosen because the change of compressibility with concentration was expected to differ in the two types.

METHOD AND APPARATUS

Many different methods have been used for determining the wave-length of ultrasonic waves in liquids and one of the simplest and, strangely enough, least used methods was chosen. It is an optical method suggested by Bergmann[2] in which light from a slit source is allowed to diverge through the liquid containing stationary ultrasonic waves and fall on a screen on the other side. The standing acoustic waves also have associated with them, due to standing density waves, standing waves in the optical index of refraction of the medium. This means that there is periodically set up in the medium a row of "lenses" more or less of the cylindrical type. These "lenses" appear and disappear with a frequency twice that of the ultrasonic wave and are spaced at intervals of one-half the acoustic wave. There appears then on the screen a pattern of parallel bright and dark lines of approximately equal width. If each dark line arises from a nodal point in the liquid then the distance between the dark lines is one-half of the wave-length of the sound wave. Now if the stationary wave pattern be moved parallel to the screen and perpendicular to the light beam by moving the trough, the lines on the screen will move along the screen. If a point is chosen on the screen, at the center of the light beam in order to eliminate all distortion, and the trough moved until one dark line has passed this point, then the

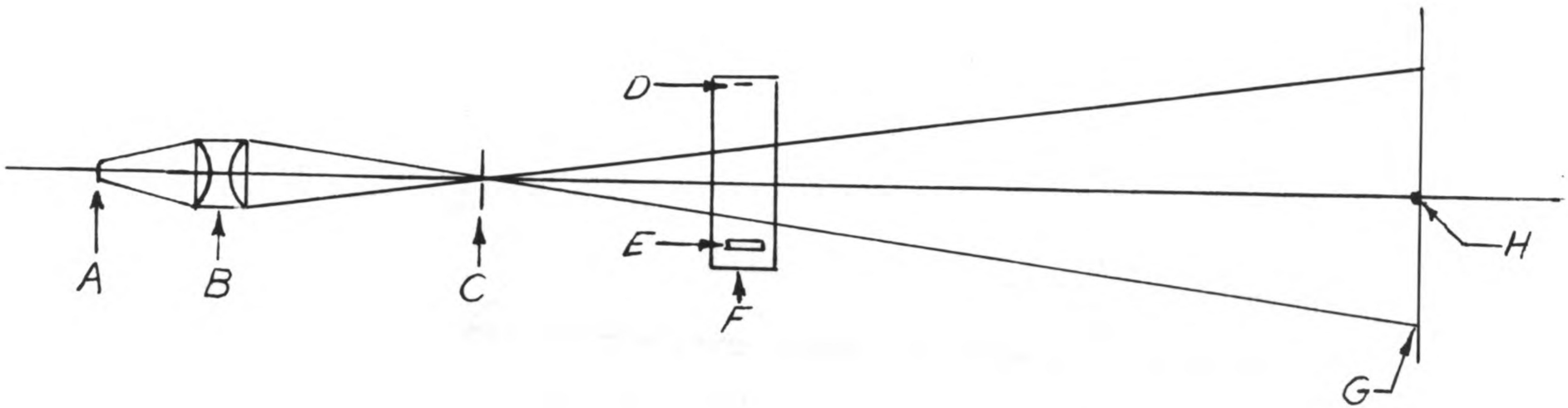
distance through which the trough has moved must be one-half of the wave-length of the ultrasonic waves in the liquid. Because of the shortness of the ultrasonic waves it is possible to cause a large number of lines to pass the point on the screen by moving the trough a few centimeters and the wave-length may then be found by dividing the distance moved by the trough by one-half the number of dark lines passing the chosen point on the screen. If the frequency is known then the velocity is found by taking the product of frequency and wave-length.

The optical system is shown is figure I. The light source was a 100 watt ribbon filament lamp which was focused on the slit by a strong condensing lens. The trough was mounted on a traveling microscope base so that it could be moved perpendicularly to the optical path. The base was firmly fastened to an optical bench about 30 cm. from the slit. The position of the screen was not critical as the lines could be seen at any distance within several meters of the trough. However, it was not desirable to have the screen closer than 50 cm. because the lines were too close together to be counted easily and, since it was necessary to turn the microscope and count the lines at the same time, the screen was usually placed at about 80 cm. from the trough.

It should be noted that no lenses were necessary between the slit and the screen. A convergent lens may be placed

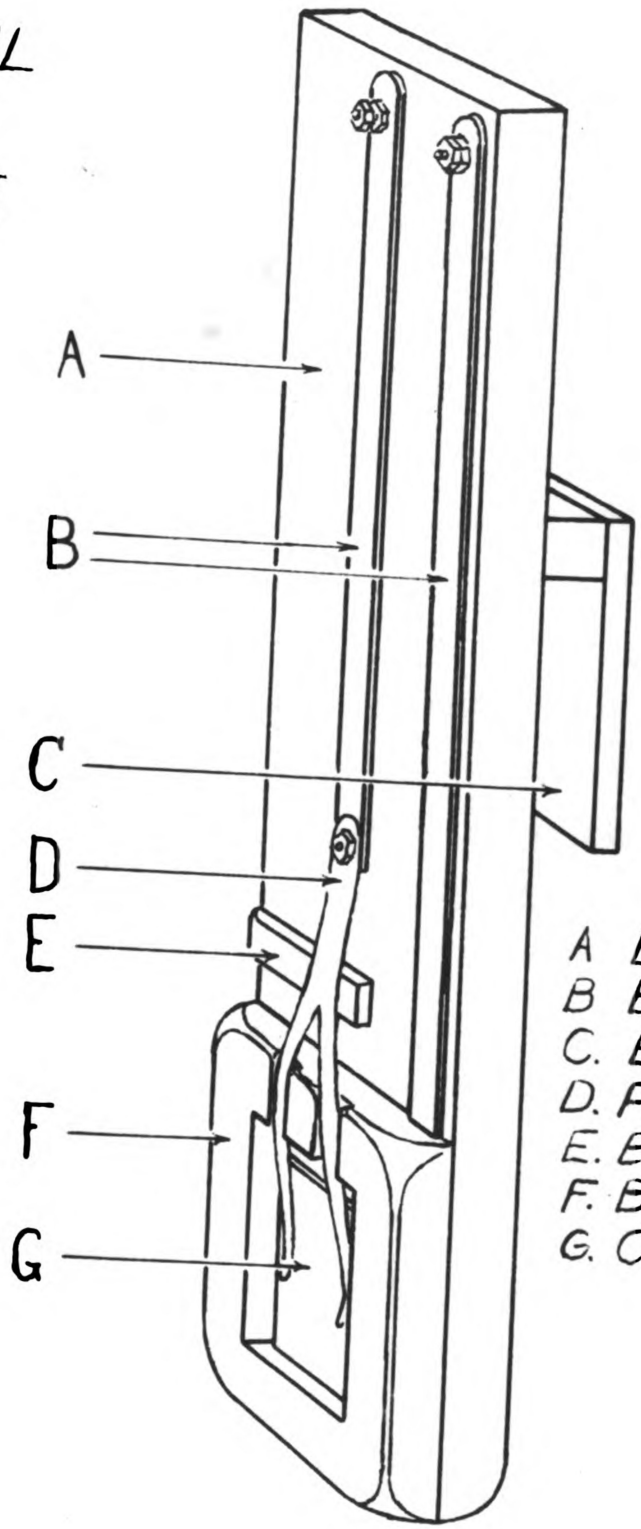
OPTICAL SYSTEM

Figure I



A. Ribbon Filament Source
B. Condensing Lens
C Slit
D Quartz Crystal
E. Reflector
F. Glass Trough
G. Screen
H. Fiducial Point

CRYSTAL
HOLDER
Figure II



A Bakelite
B Brass Leads
C. Brass Clip
D. Phosphar Bronze
E. Bakelite Element
F. Bakelite Element
G. Crystal

between the slit and the trough to send parallel light through the trough but the advantage of getting more distinct lines is counterbalanced by the disadvantage of bringing the lines closer together so that the lens was left out entirely.

The fiducial line on the screen was chosen exactly in the center of the optical beam so that the light reaching it would be passing perpendicularly through the trough and liquid and the distortion would be at a minimum. It should be noted here that the entire optical system was fixed and that the standing wave pattern was moved perpendicularly to the light beam.

The sound trough was made of high optical quality plate glass and the edges were sealed together with paraffin. The dimensions of the trough were 6 cm. x 7 cm. x 20 cm. The glass was supported by a brass framework which removed tension from the paraffin joints. Care was taken to make the sides of the trough through which the light passed exactly parallel to each other to prevent distortion of the light beam. At first a trough with a brass base was used but chemical action on the brass by the electrolytes made it necessary to construct the trough entirely of glass. The traveling microscope base had a fine screw reading to 0.001 cm. It was possible to estimate one more decimal place.

In order to get stationary waves it ~~is~~ necessary to use

a plane reflector which can easily be adjusted to be parallel to the crystal. The reflector was constructed by fastening a flat piece of glass to a block of bakelite by means of paraffin. These materials were used because no metal could be used inside the trough. The reflector was moved in the plane of the crystal by rotating the whole block and perpendicular to the plane of the crystal by means of a plastic screw in the back of the bakelite block. This screw could be turned against the bottom of the trough and thus tilt the reflector.

The best way to produce ultrasonic waves is by use of quartz crystals. When a potential difference is applied to the faces of a slab of quartz, the quartz will either expand or contract in a direction normal to the faces. When the potential difference is reversed the effect is opposite to the first. Thus, when an alternating potential is applied to the faces of the quartz, the crystal will vibrate and produce sound waves. The change in thickness of the crystal, and consequently the particle displacement in the sound waves, is proportional to the potential difference applied. A piece of quartz has a natural frequency of vibration dependent on its dimensions. When the impressed frequency is equal to the natural frequency of the quartz the amplitude of vibration will be a maximum. The crystal used was an X cut crystal with dimensions 2.5 x 2.5 x .11 cm. and a rated frequency of

1802 kilocycles per second. A thin layer of gold was evaporated on both sides of the crystal in order to make a good electrical contact without adding appreciably to the mass of the crystal.

When velocity measurements are made on organic liquids the crystal may be in direct contact with the liquid, but this is not possible in the case of electrolytes for they conduct electricity and will not permit the crystal to oscillate. Therefore it was necessary to isolate the crystal from the solution. There is an additional advantage in the isolation of the crystal from the medium for undesirable heating effects and disturbing striations will be minimized. The methods tried for the solution of this problem are worthy of note here.

Maximum sound transmission occurs from one medium to a third medium when exactly an integral number of half-wave-lengths of sound occur in the intermediate medium, for certain specific acoustic resistivity relations. A piece of aluminum was ground until it was exactly one-half-wave-length thick and was then placed in the end of the trough with the crystal pressing against it from the outside. Satisfactory transmissions were not obtained in this way. Then a very thin piece of copper foil was placed between the crystal and the liquid across the end of the trough with the idea that the foil would vibrate as a diaphragm. But again transmission of the ultrasonic waves was unsat-

isfactory. Finally, a thin rubber diaphragm was placed around the crystal and crystal holder (figure II) and when this was filled with ethyl alcohol good sound transmission was obtained.[6]

The crystal holder is a slab of bakelite with two brass leads to the crystal on one side and a clip to fasten it to the end of the sound trough on the other. One lead goes to a brass plate against which the crystal rests and the other goes to a phosphor bronze spring which presses the crystal lightly against the plate as well as acting as a lead. The crystal is thus held vertically in the trough so that the wave fronts move horizontally across the light beam.

It is essential that the front surface of the rubber balloon be exactly parallel to the crystal face in order that all portions of it will vibrate in phase. The bakelite element F (figure II) was designed for this purpose and also to keep the rubber from touching the spring or crystal face. The element E prevents the rubber from forcing the spring too hard against the crystal face.

The space within the rubber enclosure must be filled with a non-conducting liquid to give the best acoustic transmission through the rubber. Ethyl alcohol was found to work well for this purpose. The level of the alcohol inside the diaphragm was found to be quite critical for if the pressure inside is even slightly different from

that outside at crystal level there will be a slight curvature of the diaphragm and it will be unable to vibrate as a unit. Thus the greater the density of the liquid being measured, the greater must be the height of the alcohol. The alcohol must be very pure in order to work at all. If it becomes contaminated with a few drops of water or a tiny drop of solution, the crystal ceases to vibrate at once. The alcohol must be changed about every half-hour for best results, either due to a reaction between alcohol and rubber or due to absorption of water from the air. This method of crystal isolation has these advantages: the unit is simple in design, the location and orientation of the crystal is only slightly limited, mechanical binding is kept at a minimum, and there is very adequate ultrasonic intensity transmission into the electrolyte.

There was a considerable heating effect near the crystal due to some of the energy of the ultrasonic waves being absorbed. Because of the fact that the velocity changed with temperature in most liquids, there was therefore a very slight shift of the standing wave pattern while a reading was being taken. This was practically eliminated, however, by carefully stiring the solution before each reading was taken. If unstirred, the temperature gradient directly in the path of the sound beam may be as much as three degrees in two centimeters close

to the crystal, but due to the large volume, when the liquid was carefully stirred the temperature rarely increased more than 0.3 degree during one trial.

In adjusting the reflector it was possible to get a good standing wave when the top was one or two wave-lengths ahead or behind the base. When this condition existed there was usually a discontinuity somewhere in the pattern which could be seen to right itself when the reflector was tilted slightly. In order to eliminate error due to the possible lack of parallelism between the crystal and reflector it was necessary to always very carefully set the relfector where there was a pattern of maximum intensity.

The acoustic crystal was driven by a crystal-controlled pentode oscillator. The control crystal was rated at 1806 ± 0.03% kilocycles per second. The oscillator tube was an RK-20A and was operated with a direct current potential of 1000 volts on the plate, 300 volts on the screen grid, and 45 volts on the suppressor grid, all of these being positive. The power was supplied by a full wave rectifier circuit with two 866 mercury vapor diodes.. Radio frequency power was transmitted from the oscillator to the acoustic crystal circuit by means of a link coupling. The coupled circuits were made as nearly alike as possible so that their impedances would be equal.[1] The acoustic crystal circuit was composed of the crystal in parallel with a coil and a tuning condenser and

in series with a thermo-ammeter which indicated a radio frequency current of about .15 amperes when the crystal was ocillating properly.

In the calculation of compressibility it is necessary that the density be known. Rather than determining the density experimentally, the density of the electrolytes to be measured for several different concentrations were taken from the International Critical Tables[4]. Those % concentrations were chosen such that the molar concentrations would be about 0.1, 0.5, 1.0, 2.0, and 4.0. Densities were taken for 25 degrees Centigrade. The product of desired percent concentration and density gave the amount of solvent necessary to make one ml. of solution of that concentration, and the difference between the density and weight of solvent was the amount of water necessary. These were multiplied by 500 as half a liter of solution was needed. Molar strengths were computed by dividing the amount of solvent per liter by the molecular weight of the solvent. The salts were weighed on a fine chemical balance which could weigh to 0.0001 gram. The water was weighed on mechanical balances which weighed to 0.01 grams.

The salts used were Baker's C.P. The water was doubly distilled and airfree, as any impurities were found to change the velocity of ultrasonics in it.

SPECIFIC PROCEDURE

The trough w s filled with solution to a level slightly above the top of the crystal. It is took about 450 ml. of solution. Ethyl alcohol was pipetted inside the diaphragm until it reached a level slightly higher than that of the liquid outside. The crystal in the control circuit was made to oscillate by tuning the variable condenser until the ammeter in the plate circuit showed a minimum va ue and then the condenser in the acoustic circuit was carefully tuned until the ammeter in series with the crystal showed a deflection. Both circuits were very sensitive to a small change in the condensers and had to be tuned very carefully. With the light beam from the slit passing directly through the center of the trough and the acoustic crystal oscillating, the reflector was carefully adjusted until bright and dark line could be clearly seen over a large portion of the screen. The liquid was carefully stirred and the temperature taken with a Centigrade thermometer reading to 0.05 degree. A dark line in the pattern was then carefully set on the line on the screen at the center of the light beam and the scale reading at the base of the trough recorded. The same line was then adjusted to the fiducial line three more times and then the trough moved until 119 lines had passed the fiducial line. After stirring and recording temperature, several readings were

taken on line number 120. About six readings were taken for each solution. As mentioned previously, the fiducial line should be at the center of the light beam. This line was easily found by moving the screen and observing that lines on both sides of the center move toward the center as the screen was moved towards the source.

To check the crystal frequency, a variable frequency oscillator was calibrated with a standard frequency oscillator. The standard was frequently checked with a radio station of known frequency. Then, mixing the output of the variable oscillator with the output of the acoustic control oscillator by means of an electronic mixer, the variable oscillator was adjusted to zero beat in the earphones and the frequency read from the calibrated scale. It was possible to read this scale to 10 kilocycles per second and to estimate to 1 kilocycle per second.

EQUATIONS INVOLVED

Sound waves whose wave-length is greater than 10^{-8} cm. travel adiabatically and so the adiabatic compressibility may be computed from the equation:[7]

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

where v is the velocity of the sound waves and ρ is the density of the medium. The following relationships also

exist: $$V = \sqrt{\frac{k}{\beta_{is.}\rho}} = \sqrt{\frac{1}{\beta_{ad.}\rho}}$$

$$\beta_{is.} = \beta_{ad.} + \frac{\alpha^2 T}{C_p J \rho}$$

where $\beta_{is.}$ is the isothermal compressibility, k is the ratio between the specific heat at constant pressure and the specific heat at a constant volume, α is the coefficient of thermal expansion, C_p is the specific heat at constant pressure and absolute temperature T, and J is the mechanical equivalent of heat.

Since the densities were obtainable in the International Critical Tables[4] and the velocities were measured, all of the adiabatic compres ibilities were computed.* Since neither $\beta_{is.}$ nor k were known in the second equation for most of the solutions it was impossible to compute either. The third equation is given mainly for interest as no atte pt was made to calculate $\beta_{is.}$. If C_p and α were known it would be possiole to compute $\beta_{is.}$ and hence k from equation 2. Approximate values for these can be found in the International Critical Tables[4] and Landolt-Bornstein Physikalisch-Chemische Tabellen[5].

* All compressibilities were computed except those for zinc nitrate. These could not be accurately determined because the d nsity was known only at 18° C. and all the data was taken at 25° C. The density for zinc nitrate listed in table I is for 18° C.

TABLE I

AVERAGE DATA AND RESULTS

Salt	% Conc. by wt.	Molar Conc.	Density g/cm^3	Temp. C°	Wave length incm.	Vel. in m/ sec.	Ad. Comp. x10^{-12} cm^2/ dyne
KNO_3	1.0	0.0992	1.00324	25.1	.08293	1497.9	44.425
"	6.0	0.6131	1.03479	24.9	.08458	1511.7	42.218
"	10.4	1.0980	1.06093	25.0	.08615	1527.7	40.387
"	18.0	1.987	1.11595	24.9	.08758	1556.1	37.007
"	24.0	2.753	1.15988	25.1	.08300	1581.9	34.452
$NaNO_3$	1.00	0.1181	1.0049	25.2	.08386	1499.2	44.274
"	4.0	0.4825	1.0254	25.0	.08508	1514.8	42.502
"	8.0	0.9912	1.0532	25.3	.08764	1556.7	40.208
"	16.0	2.093	1.1118	24.9	.08911	1582.9	35.898
"	22.0	3.000	1.1589	25.2	.08991	1623.9	32.722
"	35.0	5.216	1.2668	24.8	.09497	1715.4	26.827
$LiNO_3$	1.0	0.145	1.00287	25.0	.08304	1499.9	44.330
"	4.0	0.594	1.02054	25.2	.08410	1519.0	42.666
"	8.0	1.212	1.04477	25.2	.08523	1539.4	40.391
"	14.0	2.198	1.08276	25.2	.08734	1577.5	37.113
"	24.0	4.007	1.15128	25.3	.08120	1647.6	31.992
$Mg(NO_3)_2$	2.0	0.136	1.0119	25.0	.08334	1505.3	43.618
"	8.0	0.571	1.0584	25.3	.08540	1542.5	39.709
"	14.0	1.046	1.1079	24.9	.08746	1579.7	36.169
"	20.0	1.565	1.1607	25.1	.08985	1622.8	32.715
"	24.0	1.938	1.1977	25.5	.09174	1657.1	30.400
$ZN(NO_3)_2$	2.0	0.11	1.0154	24.9	.08308	1500.7	---
"	10.0	0.57	1.0559	24.9	.08449	1523.7	---
"	16.0	0.97	1.1445	25.2	.08600	1553.4	---
"	30.0	2.06	1.3029	25.2	.09009	1627.2	---

TABLE II

COMPRESSIBILITY ANALYSIS

Salt	Slope-k*	Log	
KNO_3	-.0419	.6518-11	44.85×10^{-12}
$LiNo_3$	-.03632	.6500-11	44.65×10^{-12}
$NaNO_3$	-.0454	.6508-11	44.75×10^{-12}
$Mg(NO_3)_2$	-.0879	.6516-11	44.83×10^{-12}

β_{ad} for water = 44.79×10^{-12} average = 44.77×10^{-12}

EMPIRICAL FORMULAE

$$\beta_{ad} = \beta_o e^{-KC} \qquad V = V_o \sqrt{\frac{\rho_o}{\rho}}\, e^{\frac{1}{2}KC}$$

KNO_3 $\beta = (44.77 \times 10^{-12}) e^{-.0964C}$ $V = 1496.8 \sqrt{\frac{.9971}{\rho}}\, e^{.0482C}$

$NaNO_3$ $\beta = (44.77 \times 10^{-12}) e^{-.1045C}$ $V = 1496.8 \sqrt{\frac{.9971}{\rho}}\, e^{.0522C}$

$LiNO_3$ $\beta = (44.77 \times 10^{-12}) e^{-.0837C}$ $V = 1496.8 \sqrt{\frac{.9971}{\rho}}\, e^{.0418C}$

$Mg(NO_3)_2$ $\beta = (44.77 \times 10^{-12}) e^{-.2023C}$ $V = 1496.8 \sqrt{\frac{.9971}{\rho}}\, e^{.1011C}$

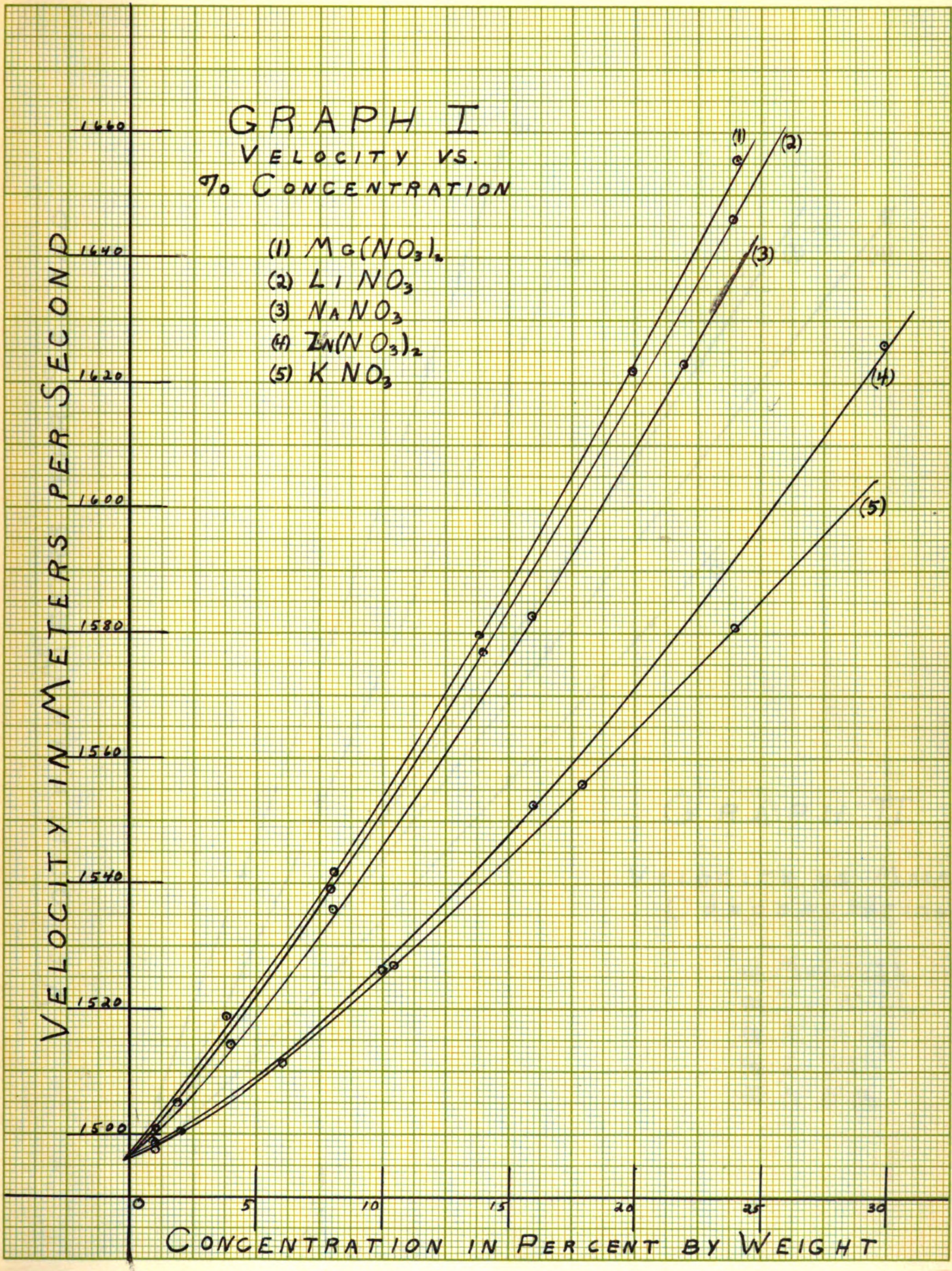
* The logarithms are to the base 10 so that it is necessary to multiply k by 2.303 in order to write it in the exponential form.

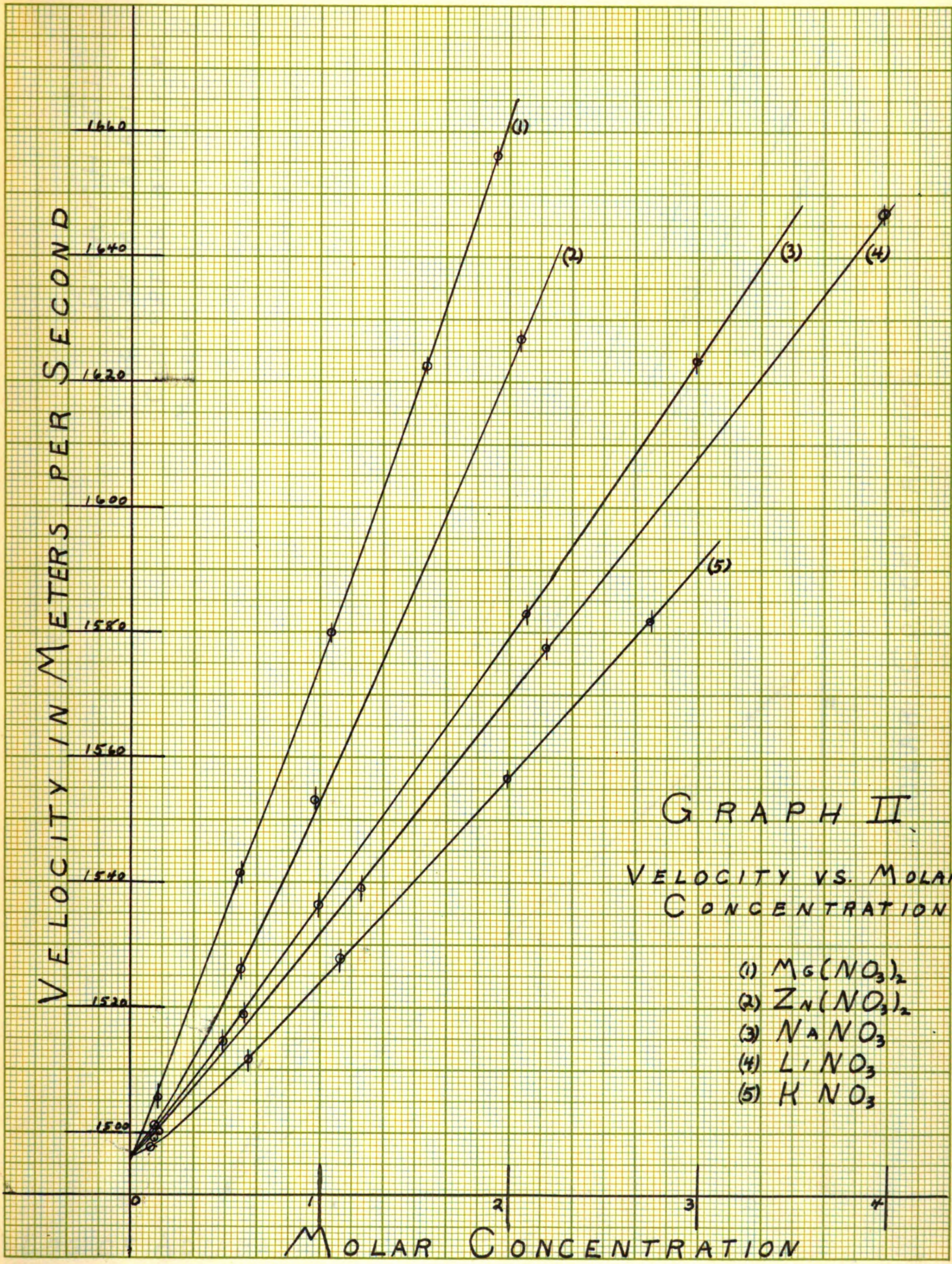
TABLE III

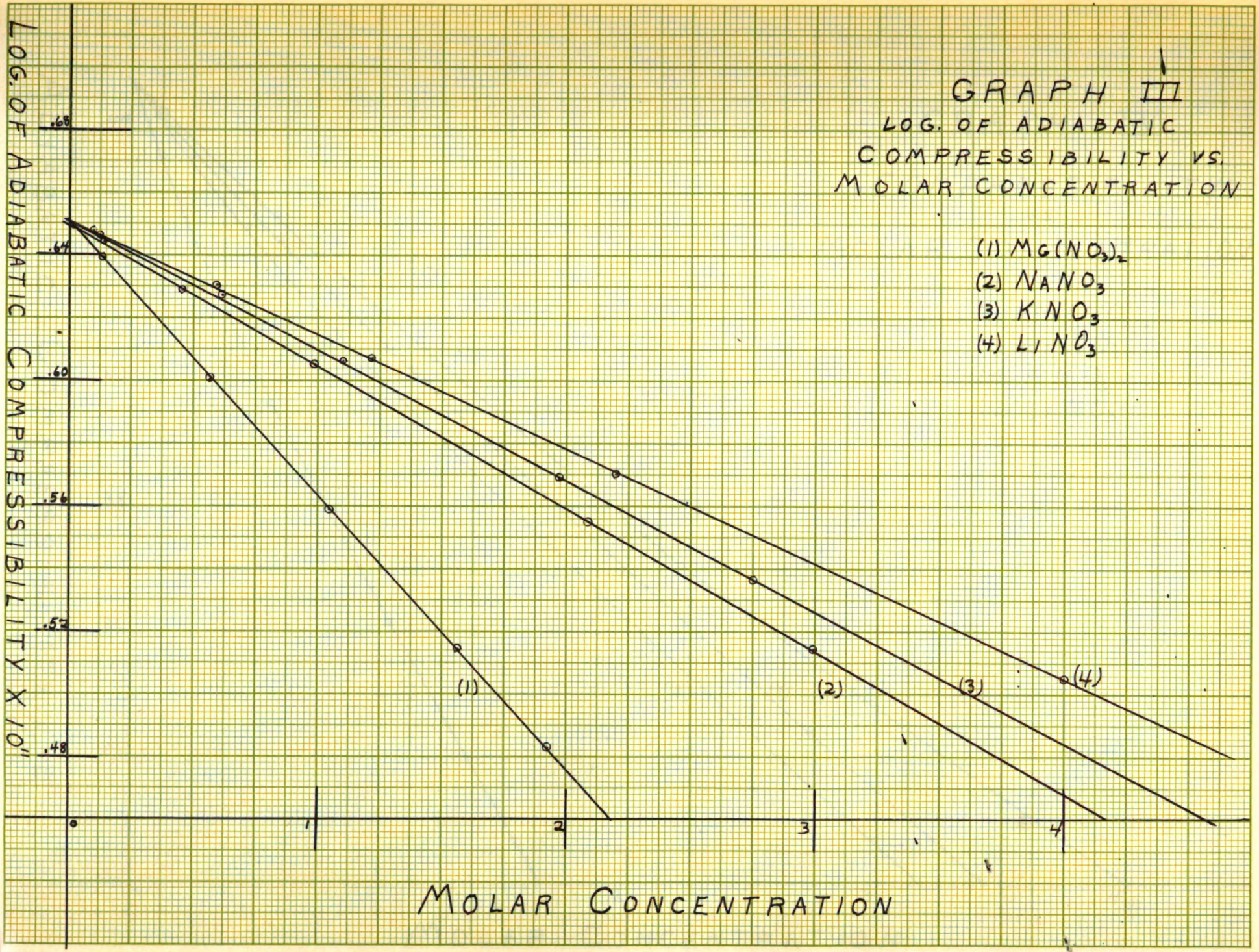
VELOCITY FORMULA CHECK

Solution	Molar Conc.	Computed Velocity	Measured Velocity	Deviation
KNO_3	.0992	1499	1498	+1
	.6131	1514	1512	+2
	1.0980	1531	1528	+3
	1.987	1557	1556	+1
	2.733	1584	1582	+2
$NaNO_3$	.1181	1500	1499	+1
	.4825	1513	1515	-2
	.9912	1534	1537	-3
	2.093	1581	1583	-2
	3.000	1625	1624	+1
	**5.216	1743	1715	+28
	.145	1501	1500	+1
$LiNO_3$	.593	1516	1519	-3
	1.212	1538	1539	-1
	2.194	1574	1577	-3
	4.007	1648	1648	0
$Mg(NO_3)_2$	.136	1507	1505	+2
	.571	1540	1542	-2
	1.046	1579	1580	-1
	1.565	1626	1623	+3
	1.938	1661	1657	+4

** This point for $NaNO_3$ does not appear on any of the curves because it was not convenient to make the scale large


GRAPH I
VELOCITY VS.
% CONCENTRATION
(1) $Mg(NO_3)_2$
(2) $LiNO_3$
(3) $NaNO_3$
(4) $Zn(NO_3)_2$
(5) KNO_3
VELOCITY IN METERS PER SECOND
1660
1640
1620
1600
1580
1560
1540
1520
1500
0
5
10
15
20
25
30
CONCENTRATION IN PERCENT BY WEIGHT


VELOCITY IN METERS PER SECOND
1660
1640
1620
1600
1580
1560
1540
1520
1500
0
1
2
3
4
MOLAR CONCENTRATION
(1)
(2)
(3)
(4)
(5)
GRAPH II
VELOCITY VS. MOLAR CONCENTRATION
(1) $Mg(NO_3)_2$
(2) $Zn(NO_3)_2$
(3) $NaNO_3$
(4) $LiNO_3$
(5) KNO_3


GRAPH III
LOG. OF ADIABATIC COMPRESSIBILITY VS. MOLAR CONCENTRATION
(1) $Mg(NO_3)_2$
(2) $NaNO_3$
(3) KNO_3
(4) $LiNO_3$
LOG. OF ADIABATIC COMPRESSIBILITY X 10"
.68
.64
.60
.56
.52
.48
0
1
2
3
4
(1)
(2)
(3)
(4)
MOLAR CONCENTRATION

enough to include it. It was plotted on separate paper and found to be considerably low so that the fact that it is so far off here is not due to an error in the equation but due to an experimental error.

ANALYSIS OF ERRORS

Errors occured in taking the initial and final readings of the position of the trough because of the difficulty in setting a line from the projected stationary wave pattern exactly on the fiducial line. The maximum value of this error was judged to be 0.0020 cm. and, since the trough was moved between five and six centimeters, the maximum percentage error in measuring the wave-length was ± 0.08%. This is for one measurement. Since averages of several measurements were obtained, the average wave-lengths have a considerably smaller maximum error.

The salts were weighed on a fine chemical balance to 0.001 gm. and, as the minimum amount weighed was 5 grams, the maximum error here was ± 0.02%. Water was weighed accurately to 0.1 gm. and, the minimum weight of water used in one concentration being 300 grams, the maximum error here was ±0.03%. Hence the maximum error in concentration was at the most ± 0.05%. It is possible that there was an error due to evaporation of water from the solutions while the measurements were being taken but such an effect must have been very small and so it was judged to be a negligible source of error.

The frequency of the control crystal was rated at 1806 ± 0.03% vibrations per second. The method used for checking the frequency was estimated to be accurate within 2 kilocycles per second. Measurements gave 1806 ±0.11%. It seemed logical to assume that the rated control crystal frequency was the actual acoustical frequency within the rated value. The change of frequency when the circuit was being tuned was ~~not~~ noticeable as a beat note in the earphones connected to the electronic mixer but the variation was well below the 0.03%.

In all but the first few measurements (on KNO_3) the liquid was carefully stirred before every reading. This eliminated practically all the possible error due to the existence of a temperature gradient in the stationary sound beam between the crystal and the reflector. It cannot be assumed that the temperature is everywhere exactly the same, but, when the velocity change in pure water is only 2 meters per second per degree (less for concentrated solutions), the error due to temperature may be considered negligible.

The temperature always gradually increased while a series of measurements were being taken on a solution. The temperature of the solutions was therefore taken initially as 24° C. and the readings were taken as the temperature increased so that the average would be as nearly 25° C. as possible. The average value of the temperature in the several trials is the value recorded in Table I.

The total maximum error in velocity was therefore estimated to be ±0.11%. This amounts to a velocity range of ± 1.8 meters per second and a compressibility range of ±0.22% or ±0.09 x 10^{-12} cm^2 per dyne (assuming the densities correct).

For velocity of ultrasonic waves in water at 25° C. Freyer[3] gives the value 1498.1 meters per second. He states that his results are not accurate to less than one meter per second. Bergmann[2] gives the velocity as 1494 meters per second at 24° C. From Freyer's data it can be shown that the velocity of sound in water changes about 3 meters per second per degree at 24° C. and this correction would make Bergmann's value 1496 meters per second at 25° C. The value for ultrasonic velocity in water was found in this research to be 1496.8 ± 1.6 meters per second at 25° C.

DISCUSSION OF RESULTS and CONCLUSIONS

Freyer[3] is the only one who was found to have made a complete series of measurements on electrolytic solutions with the specific purpose of investigating the relationships existing between concentration, velocity, compressibility, and temperature. He measured ultrasonic velocities in in the sodium and potassium halides for several concentrations and temperatures and computed the adiabatic compressibilities and the ratio of the specific heats. He plotted compressibilities and velocity against per cent concentration but was

unable to find any empirical relationship between them. The results of this research check perfectly with all of his conclusions and in addition two empirical relationships have been determined. So far as the author has been able to find, no one has ever previously determined these two empirical formulas.

When the logarithm of the adiabatic compressibility was plotted against molar concentration the resulting curve was a straight line. This is the determining factor for an exponential relationship and it can be expressed as follows:

$$\beta = \beta_0 e^{-\kappa C} \qquad (1)$$

where β is the adiabatic compressibility of the solution whose molar concentration is C, β_0 is the compressibility at zero concentration or the compressibility of pure water at the same temperature, and k is the slope of the straight line formed when the logarithm of compressibility is plotted against the molar concentration. See Table II for empirical values. Since $\beta_{ad} = \sqrt{\frac{1}{V^2\rho}}$ it follows that the velocity is related to molar concentration in the following way:

$$V = V_0 \sqrt{\frac{\rho_0}{\rho}}\, e^{\frac{1}{2}\kappa C} \qquad (2)$$

where V is the velocity of the ultrasonic waves in a solution of molar concentration C and density ρ, V_0 is the velocity of sound in pure water and ρ_0 its density at the same temperature, ρ is the solution density, and k is the

same constant as that in the first equation. The relation between logarithm of velocity and molar concentration was found not linear. The cause is obviously the variable density factor. Thus it is possible to evaluate k directly only by use of the compressibility-concentration relation.

The values found for β_0 from Graph # 3 were so nearly equal for the different salts that the average value was taken. This average value was 44.77×10^{-12}, while that for pure water as calculated directly form the measured velocity and density was 44.79×10^{-12}. The value found from the graph for k in equation 1 was substituted into equation 2 along with the already known factors and the computed values found to check with the measured ones with-in experimental error. (Table III). This is considered to be an absolute check on the correctness of the two formulas.

Equation 1 shows that the compressibility decreases exponentially with the molar concentration. This means that for any certain increment, the addition of each increment of salt to the solution causes the same fractional decrease in compressibility. This is not true for velocity because the density is a function of the concentration. It is well known that when a soluble salt is dissolved in water the volume of the water decreases. Bergmann[2] (quoting Debye) suggests the following: when an ion, charged either positively or negatively, is placed in water the water molecules are pulled toward the ion because of their high dipole

moment. The electrostatic pressure around the ions is of the order of 10,000 atmospheres and causes the contraction of the water. This electrostatic pressure causes a decrease in compressibility in much the same way as does increasing the external pressure. It seems logical that this effect should decrease exponentially as the number of ions per unit volume of solution increases.

Bergmann shows that the compressibility for the monovalent salt solutions is greatest for sodium and potassium and slightly less for litnium. It is much greater for magnesium. The empirical results listed in Table II indicate that addition of mono-valent positive ions to a solution lowers the compressibility exponentially and that the power of e is practically the same for all such ions. Although calculations have been made on only one di-valent ion, from the results one may guess that, in general, di-valent ions lower the compressibility exponentially also but here the exponent of e is, twice as large. Thus it appears that the effect of increasing concentration on the compressibility depends mainly on the ion charge and not on the mass or size of the ion.

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