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Physicochemical Investigations

by

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APPLICATION OF ULTRASONIC METHODS TO THE PRACTICE OF PHYSICO-
CHEMICAL RESEARCH

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Until comparatively recently, acoustics was considered a completely investigated field of physics. It seemed that work in the field of acoustics could develop only in the direction of making more precise what is already known.

It was difficult to visualize the possibility of new fundamental discoveries in this seemingly well investigated field. And yet, acoustics underwent a renaissance, literally before our eyes.

Discoveries, which expanded immensely the field of acoustical research followed one after another. This brought about a situation where papers on acoustics, which up to then had appeared only rarely in specialized physical journals, began to appear extensively in physico-chemical, chemical, biochemical, technological, biological, and medical journals. The revival of interest in acoustics is due, first of all, to the discovery of new sources of acoustic vibrations, which made it possible to obtain vibrations of frequencies and strength entirely different from what was possible earlier. Strong acoustic vibrations of high frequency are called ultrasonic: these possess characteristics which are distinct from those of ordinary sound. It was established that ultrasonics are capable of producing chemical transformations, possess a strong dispersing and coagulating action, affect living substances and seeds of plants, produce specific sound-luminescence, etc.⁽¹⁾ It is precisely these characteristics of ultrasonics which attracted the attention of investigators whose interest lay in the fields of natural science contiguous to physics. The investigation of ultrasonics brought about the development of experimental methods

for their study. In addition, the methods developed for making ultrasonic measurements are characterized by experimental simplicity and high accuracy of results. Quite naturally, an attempt was made to utilize ultrasonic measurements as a means of physico-chemical inquiry into the different properties of materials. At the present time, ultrasonic measurements are firmly rooted in the practice of various research laboratories.

It would be desirable to give a brief review of the possibilities which are introduced by ultrasonic measurements into the practice of physico-chemical research. The solution of this problem is the purpose of this paper.

At the present time, piezoelectric and magnetoconstriction transducers are used to produce ultrasonics.

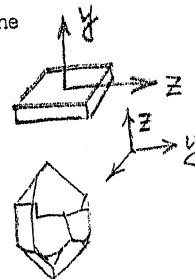
Of the various piezoelectric materials (quartz, tourmaline, Rochelle salt) used in acoustics, quartz is used almost exclusively for the preparation of transducers.

Quartz is the crystalline modification of SiO_2 ; it crystallizes in hexagonal syngony. Quartz crystals possess piezoelectric characteristics, i.e., they are capable of being charged by deformation and deformed by charging. The sign of the charge which occurs on the surface of the quartz is of one kind under compression and of the opposite kind under tension.

In order to obtain ultrasonic vibrations from quartz, it is cut into blanks of different shapes and dimensions, which have a definite orientation with regard to the crystallographic axes (Figure 1). The emissive surface is covered with a layer of metal (usually

silver). The quartz blank is positioned on a polished metal base which serves, at the same time, as the electrode for feeding the charge to the rear surface of the blank.

Figure 1. Quartz crystal and quartz blank cut out perpendicular to the electrical axis



In investigating the propagation of ultrasonics in gases and dielectrics, the quartz blank is placed directly in a vessel filled with the test substance (2). In working with substances which conduct electricity, the quartz is separated from the substance under investigation with the aid of a thin membrane. In the latter case, the emissive surface of the quartz need not be covered with metal; instead, a membrane can be used as the electrode for feeding an alternating potential to this surface of the quartz.

Contact with metal covered surface of the quartz blank is accomplished with the aid of a compression spring, although, in general, this practical and very important problem is solved by different methods, depending on the special features of the work.

The electrodes which feed the alternating potential to the quartz blank are connected to the electromagnetic oscillator as shown in Figure 2.

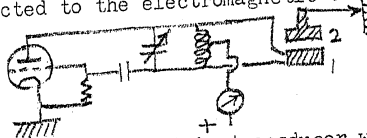


Figure 2. Diagram of piezoelectric transducer with an interferometer: 1 - quartz blank; 2 - reflector of the interferometer

In investigating the propagation of ultrasonics in gases, the

oscillator is adjusted to a frequency corresponding to the basic frequency of the natural vibrations of the quartz blank; in working with liquids, the quartz can be excited also at the highest harmonic frequencies.

In order to obtain the very strong ultrasonic vibrations necessary for investigating the dispersing action of ultrasonics, the quartz is mounted in a separate vessel filled with a liquid which has insulating properties, while the substance under investigation is placed in a thin-walled vessel, which is placed in the insulating liquid, above the oscillating quartz.

In acoustic practice, magnetostriction transducers are used in addition to piezoelectric transducers. The magnetostriction effect consists of varying the dimensions of ferromagnetic bodies during magnetization and demagnetization. By subjecting a ferromagnetic rod to the action of an alternating electromagnetic field, we can compel it to change its dimensions with a frequency which is equal to double the frequency of the superimposed field. Besides, resilient vibrations will occur in the substance adjacent to the rod. Pure iron is of little use for making magnetostriction transducers because of its very small magnetostriction effect. Nickel and various alloys of nickel with iron and chromium possess a large magnetostriction effect; these are used for making transducers.

The diagram of a magnetostriction transducer is shown in Figure 3⁽³⁾. The magnetostriction oscillator L is placed in the coil M, which is connected to the electromagnetic oscillator; the rod L protrudes directly into a vessel filled with the substance which serves for the study of the propagation of ultrasonics.

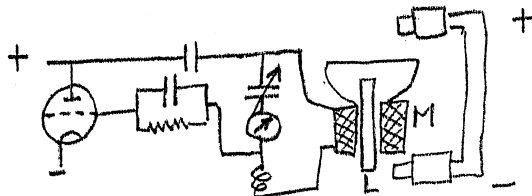


Figure 3. Magnetostriction transducer: M - coil; L - oscillating rod

One of the advantages of magnetostriction transducers is that it permits use of rods of any desired diameter, which is often of importance from the point of view of design. A disadvantage of the magnetostriction transducer is the rapid heating-up of the oscillating rod, which causes a change in the dimensions of the rod and, consequently, a change in its natural frequency, resulting in non-coincidence of the vibrations in the transducer.

In investigating the properties of a substance with the aid of acoustic measurements, it is possible to determine either the speed or the damping of the ultrasonics in the given substance under given conditions.

The experimental determination of the speed of propagation of ultrasonics is considerably simpler than the determination of damping and can, as a rule, be accomplished with much greater accuracy.

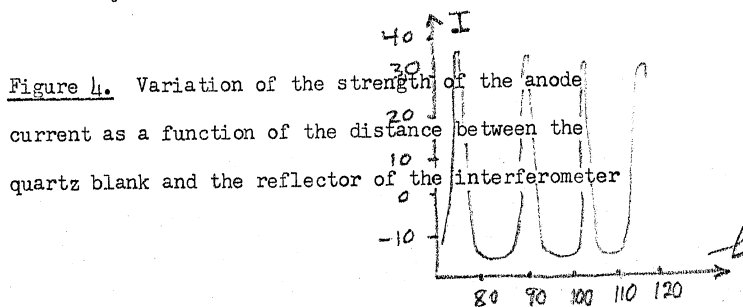
In considering the possibility of applying acoustic measurements to the practice of physico-chemical research, we shall limit ourselves to those problems in which the experimental phase consists of the determination of the speed of ultrasonics.

The speed of ultrasonics in gases, liquids, and solids can be determined by different methods.

The speeds of ultrasonics in gases are determined almost exclusively with the aid of an acoustic interferometer. In the acoustic interferometer, a polished metal reflector, capable of being displaced in a direction perpendicular to the surface of the quartz, is positioned parallel to the emissive surface of the quartz blank.

The ultrasonic wave, which is emitted by the quartz, reaches the reflector, is reflected from it, and again strikes the surface of the quartz. Upon striking the surface of the quartz, the reflected wave affects the operating conditions of the quartz. The magnitude of this influence can be evaluated in different ways (4). The simplest method of registering the action of the reflected wave on the quartz is to record the magnitude of the component constant of the anode current in the oscillating circuit connected with the quartz. Variations in strength of anode current are measured with a sensitive galvanometer which is connected so as to give a compensating circuit.

During the smooth displacement of the reflector, the magnitude of the reaction changes periodically, reaching a maximum when a whole number of half waves is fitted in the distance between the quartz and the reflector. In Figure 4, the distance l between the quartz and the reflector is plotted along the abscissa and the strength of anode current I in the circuit is plotted along the ordinate. Having determined the distance between two adjacent maxima or minima and knowing the frequency of the vibrations of the transducer, it is possible to determine the speed of the sound in the substance under investigation. Ordinarily, determination is made of the distance which contains several tens of maxima, which increases considerably the accuracy of the method. The error in determining the speed of sound by this method is usually of the order of tenths of one percent.



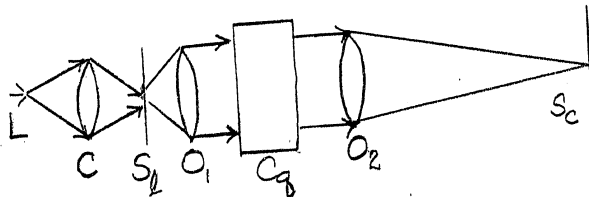
Recently, optical methods have come into wide use for determining the speed of sound in liquids. The diffraction of light in an ultrasonic grating is used mostly for this purpose.

During the propagation of an ultrasonic wave in a liquid, alternating compressions and rarefactions take place. Due to the relationship between the coefficient of refraction of the liquid and its density, periodic changes in the density of the liquid are accompanied by periodic changes in the coefficient of refraction. This holds true for both standing and passing waves.

Thus, if an acoustic wave is produced in a liquid contained in a transparent, plane-parallel cell, the cell will act as a quasi-diffraction grating with respect to the light ray. Besides, the length of the sound wave λ will act as the constant of this grating.

In determining the speed of sound by this method, a system, such as that shown in Figure 5, is assembled. Light from the source L (usually a mercury lamp) is focused by the condenser C on the narrow slit S. The divergent beam coming from the slot is made parallel by the objective O_1 . A cell C_q filled with the test liquid and containing a quartz blank, is placed in the path of the beam of parallel rays. The long focal objective O_2 focuses the rays on the screen S_c . If the quartz is not excited, an ordinary image of the slit will be seen on the screen. If the quartz oscillates, then, in addition to the basic image of the slit, easily visible patterns of the 1st, 2nd, 3rd, and sometimes higher order are also seen on the screen. When making actual measurements, the diffraction pattern is usually photographed.

Figure 5. Arrangement of system for observing the diffraction of light in ultrasonic waves: L - Lamp; C - condenser; S_l - slit; O_1 and O_2 - objectives; C_q - cell with quartz; S_c - screen



Having determined the distance between the diffraction images of the slit and knowing the geometric dimensions of the system, it is possible to calculate the constant of the acoustic diffraction grating. Since the constant of the diffraction grating, in this case, corresponds to the wavelength of the sound λ , then, knowing the frequency of oscillations of the quartz, we can determine the speed of the sound from $v = \lambda\nu$. The error in determining the speed of sound by this method is usually of the order of tenths of one percent.

In addition to the above described method, there are many other optical methods for measuring the speed of sound. Some of these are very accurate. Descriptions of different methods can be found in monographs on ultrasonics (5).

Measurement of the speed of sound in solids can be accomplished by the following method (6). The test specimen is cemented to a properly cut quartz cylinder which is provided with electrodes. The resulting composite transducer is connected to the electric circuit shown in Figure 6. The quartz is connected in series with an ohmic resistance and with an electromagnetic oscillator of constant ampli-

tude and variable frequency 2. The current flowing through the quartz is measured with a lamp voltmeter 3, connected in parallel with an ohmic resistance. The current strength characterizes the amplitude of the mechanical vibrations of the quartz. The frequency of vibrations is measured very accurately by the method of beats; also, a second source of vibrations is the transducer 4 having a quartz-stabilized frequency and connected in series with the two multi-oscillators 5 and 6. By utilizing this system, it is possible to measure changes in current and, consequently, amplitudes of vibrations of the complete transducer with changes in frequency. With these measurements, it is possible to determine the frequency of natural vibrations of the composite transducer. Knowing the frequency of natural vibrations of the individual quartz, it is not difficult to calculate the frequency of natural vibrations of the test specimen 9 and its modulus of elasticity. On the basis of the theory of vibrations, it is possible to calculate the speed of sound in a material if its modulus of elasticity is known. By this method, it is possible to measure the speed of sound in solids with an accuracy of up to 0.01 percent.



Figure 6. Arrangement of system for determining the speed of ultrasonic waves in solids: 1- quartz rod; 2 - variable frequency oscillator; 3 - lamp voltmeter; 4 - quartz-stabilized transducer of 100 kilohertz; 5 - multioscillator of 10 kilohertz; 6 - multioscillator of 1 kilohertz; 7 - detector and amplifier; 8 - loud speaker; 9 - test specimen

In presenting an exposition of the possible ways of utilizing ultrasonic measurements for purposes of physico-chemical research, it is natural to start with their earliest application for the study of the elementary processes of the exchange of energy during the collisions

of gaseous molecules. This became possible in connection with the study of the dispersion of ultrasonics in gases. As is well known, the speed of ultrasonics in polyatomic gases depends on its frequency. At the present time, dispersion is usually explained on the basis of the so-called relaxation theory. On the basis of the hydrodynamics of compressible liquids, the speed of sound v is expressed by the equation

$$v = \sqrt{\frac{p}{\rho} \cdot \gamma} \quad (1)$$

where p is the pressure, ρ is the density, and γ is the ratio of the heat capacities c_p/c_v . In its turn, c_v is the partial derivative of the internal energy with respect to the temperature. The internal energy of a gas is distributed equally among the different degrees of freedom which the molecules of a gas possess.

In a polyatomic gas, a portion of the internal energy goes into translational and rotational movement of the molecules and another portion goes into vibrational degrees of freedom. Ordinarily, the heat capacity c_v of a gas is divided into the external heat capacity c_a , which depends on the external degrees of freedom, and into the internal heat capacity c_i , which depends on the internal degrees of freedom. During the alternation of compressions and rarefactions which take place in a sound wave, the additional acoustic energy which is supplied to the molecules is at first stored by the external degrees of freedom and only after this does it partly change into vibrational energy.

The fact that the establishment of an equilibrium distribution of energy between the external and internal degrees of freedom requires a finite time interval for completion is of fundamental significance for the theory of relaxation. By increasing the frequency of sound, a

frequency region is sooner or later reached, in which the process of establishing an energy equilibrium is not in phase with the process of varying the pressure. A phase difference takes place between the pressure phase and the internal energy phase and the equilibrium distribution of energy is disrupted.

At a sufficiently high frequency, all acoustic energy is in the form of kinetic energy of translational and rotational movement of the molecules. This is equivalent to a decrease of the heat capacity of the gas to a limiting value c_a . At a sufficiently low frequency, the heat capacity of the gas will have the second limiting value c_v . Between the two extreme values of frequency there is a region in which the heat capacity of the gas depends on the frequency of sound. Obviously, this region is, at the same time, also the dispersive region of sound.

Actually, if we plot the experimentally determined values of the speed of sound in a polyatomic gas as a function of the frequency, we obtain a characteristic dispersion curve.

Figure 7 shows a similar curve for CO_2 ; the logarithm of the frequency is plotted along the abscissa and the speed of sound along the ordinate.

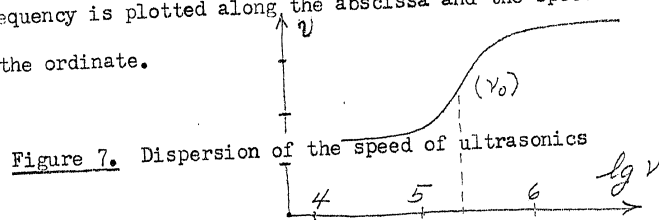


Figure 7. Dispersion of the speed of ultrasonics

On the basis of theoretical considerations, the frequency ν_0 , which corresponds to the point of inflection and determines the dispersive region, can be expressed by the equation

$$v_0 = \frac{1}{2\pi\beta} \cdot \frac{c_v}{c_a} \quad (2)$$

where β is the average life of the excited quantum. By proper development of the theory, it is possible to take into account the presence of two or more vibrational levels (7,8).

It is expected that the excitation of the vibrational state of the molecule during collision occurs only in case one of the colliding molecules possesses an increased reserve of energy or, in other words, there is a certain activation energy of the excitation process of the vibrational state. In this case, a detailed study of the relationship between the speed of sound and the temperature makes it possible to undertake the experimental determination of the activation energy of the vibrational process (9).

Thus, while investigating the dispersion of sound in pure gases and in gas mixtures, it is possible to determine the following characteristics of the elementary processes in the gases:

1. Probability of excitation of the vibrational state during collisions of the gas molecules.
2. Effectiveness (in the sense of the excitation of the vibrational state) of collisions between different molecules (10,11). Hence, it is possible to attempt to explain the observed considerable difference in the effectiveness of the impacts of different molecules.
3. Ascertain the presence of one or several vibrational levels of the molecule (7,8).
4. Determine the activation energy of the excitation process of the vibrational state of the molecule.

5. Calculate the average life of the vibrational quantum (12).

As an example, the probabilities of energy transfer from the impact of the internal energy of the CO₂ molecule to molecules of other gases, as determined by the acoustic method, are listed in Table 1 (10).

TABLE 1

<u>Mixture</u>	<u>Average probability of energy transfer</u>	<u>Possible reaction</u>
CO ₂ - CO ₂	2×10^{-5}	$\text{CO}_2 + \text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$
CO ₂ - N ₂	3×10^{-5}	$\text{CO}_2 + \text{N}_2 \rightarrow \text{CO} + \text{N}_2\text{O}$
CO ₂ - He	8×10^{-4}	
CO ₂ - H ₂	2×10^{-3}	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
CO ₂ - H ₂ O	1.5×10^{-2}	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$

On the basis of the data in Table 1, it can be concluded that the probability of the loss of a vibrational quantum by the CO₂ molecule depends greatly on the characteristics of the molecule with which it collides.

It is clear, from what has been said, that the investigation of the propagation of ultrasonics in different gases and gas mixtures is a valuable method of studying the elementary processes of the redistribution of energy during collisions of gas molecules.

However, another entirely different use of acoustic measurements for studying elementary processes in gases is possible.

If it is assumed that gas represents an aggregate of molecules moving independently of one another and that the reaction among them

is limited only by the collision time of the molecules, then the speed of propagation of the acoustic impulse in such a mechanical system should, of necessity, coincide with the average speed of movement of the molecules.

The experimentally observed difference between the speed of molecular movement and the speed of sound can be explained by the penetration of the molecules into one another for some time instead of rebounding instantaneously during collision, i.e., the existence of a finite collision time is considered probable. With such an interpretation of the propagation of sound in gases, it is possible to utilize acoustic measurements for determining the collision time of molecules of different gases (13). It is quite natural to consider effective collisions, which cause vibration of molecules, as particularly protracted. In this instance, the dispersion of sound is associated with the non-coincidence of effective collisions. The measurement of collision time is of interest from the point of view of chemical kinetics since it furnishes information for calculating the number of triple collisions.

One of the first applications of acoustic measurements for the investigation of the properties of liquids was in the study of the contraction of different liquids and mixtures of liquids. Considering that the speed of sound and the contraction of the medium are related by the equation

$$v = \sqrt{\frac{1}{\beta \rho}} \quad (3)$$

where ρ is the density of the liquid and β is the coefficient of the adiabatic contraction, it is possible to determine the latter by de-

termining experimentally the speed of sound v . Measurements obtained with binary mixtures revealed anomalous contractions in a number of cases. Thus, V. V. Tarasov and his coworkers (14) who investigated the contraction of mixtures of ethyl alcohol and water, discovered the anomalous contraction of the mixture containing approximately 25 percent alcohol. The results of these experiments are shown in Figure 8, in which the contraction of the mixture is plotted along the ordinate and the percent alcohol in the mixture along the abscissa.

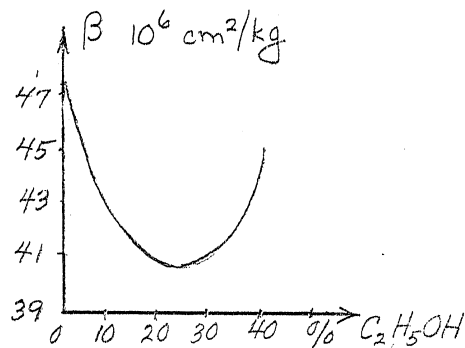


Figure 8. Contraction of a mixture of water and ethyl alcohol

The study of similar anomalies makes it possible to conclude that, in mixtures of liquids, compounds are formed between the components of the mixture. In this manner, I. G. Mikhaylov, who investigated the speed of sound in mixtures of formic acid and water (15), came to the conclusion that there are two compounds of the acid with the water. In one compound, the water and formic acid are in equimolecular amounts, but in the other compound, there are two molecules of water for each molecule of acid. Similar investigations came into considerable use (16) because they supplement the study of the melting and boiling curves of binary liquid mixtures.

In the case of solutions of electrolytes, the electrostatic field of the ions changes considerably the contraction of the water in the immediate vicinity of the ion. In practice, the variation of contraction is limited to several layers of water near the ion. By measuring the contraction of solutions of electrolytes, it is possible to characterize quantitatively the layers of solvent near the ion, which have strongly changed properties. Considering that the contraction of water in the immediate vicinity of the ion is extremely small and that the inner pressure caused by the field of force of the ion is great, it may be assumed that the ion is surrounded by a certain "non-contracting" volume of solvent. If the "non-contracting" volume is identified with the solvate sphere, then it becomes possible, on the basis of acoustic measurements, to determine the solvation of different ions (17).

The solvation numbers of certain ions, as determined by the acoustic method, are listed in Table 2.

Recently, this method was used to determine the solvation of various high molecular compounds, e.g., gelatin in pure water and in solutions of different pH, nitrocellulose, acetylcellulose, and ethylcellulose in acetone, etc. (18) This investigation emphasizes the experimental advantages of the acoustic method of determining solvation; the only disadvantage noted is a certain arbitrariness of theoretical assumptions which form the basis of the calculations.

TABLE 2

<u>Ion</u>	<u>Solvation Number</u>
H	1 - 2
Li	5 - 6
Na	6 - 7
K	6 - 7
Mg	16
Ba	16
Be	8
Al	31
F	2
Cl	0 - 1
Br, I	0

In 1940, Rao (19) established the empirical rule, according to which the product of the molecular volume and the cube of the speed of sound is not dependent on the temperature

$$v^3 \frac{M}{\rho} = V. \quad (4)$$

In this expression, M is the molecular weight, ρ is the density, and V is a magnitude independent of temperature and is usually called the "molar speed of sound". This relationship was checked with a large number of experiments and V remained a perfect constant in practically all the cases under investigation. Sometimes, this rule does not strictly hold; in particular, deviations from this rule are observed in the cases of water, methyl alcohol, and acetone. There is a viewpoint, according to which the failure of V to remain constant in these

cases is explained by the molecular association of the corresponding substances in the liquid phase ⁽²⁰⁾; in this manner, the utilization of acoustic measurements for investigating the formation of molecular aggregates in liquids is made possible. By comparing the data of the association of liquids, obtained with the aid of Raman spectra, with the data obtained with the acoustic method at different frequencies of sound, one may attempt to determine the life of molecular aggregates which occur in liquids. It seems to us, however, that these conclusions are based on an insufficiently firm foundation.

As it turned out, the magnitude V is an additive function of the composition of the substance and, in individual homologous series, it can be represented by a linear function of the molecular weight (21). In Figure 9, the molecular weight M is plotted along the abscissa and the corresponding magnitude V along the ordinate. As is obvious from an examination of the curve, the linearity of the variation of the magnitude V with the molecular weight is perfect. The molar speed of sound V can also be represented as an additive function of the bonds which are present in the given compound (22). By introducing the increments of the bonds (C - H) - 95.2; (C - C) - 4.25; (C - O) - 34.5; (O - H) - 99.0; (C - Cl) - 230; (C = C) - 129; and (C = O) - 186, it is possible to calculate V for different organic compounds, in perfect agreement with experimental data. Thus, for example, in the case of paraffins, the following formula was obtained:

$$V = (n - 1)(C - C) + (2n + 2)(C - H). \quad (5)$$

By making use of the indicated property of the molar speed of sound, it is possible to utilize acoustic measurements for verifying proposed structures of organic compounds.

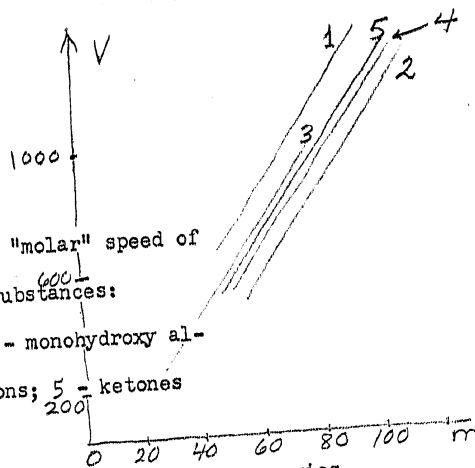


Figure 9. Relationship between "molar" speed of sound and molecular weight of substances:

1 - paraffins; 2 - acetates; 3 - monohydroxy alcohols; 4 - aromatic hydrocarbons; 5 - ketones

For different members of one and the same homologous series, the molar speed of sound is directly related to the parachor, molar refraction, constant b in the Van der Waal equation, molecular magnetic rotation, and critical volume (23).

In Figure 10, the molar speed V is plotted along the abscissa and the parachor P along the ordinate. There is a perfectly direct relationship between the parachor and V for individual homologous series. It was established empirically that the boiling point of a substance is a linear function of the logarithm of the molar speed:

$$T_b = A + B \log V \quad (6)$$

where A and B have the same value for different representatives of a definite homologous series. In this case too, deviations are noted for associated liquids. This is shown by Figure 11, in which the boiling point t_b of different organic compounds is expressed as a function of $\log V$. For homologous series consisting of non-associated liquids, the linear dependence holds true.

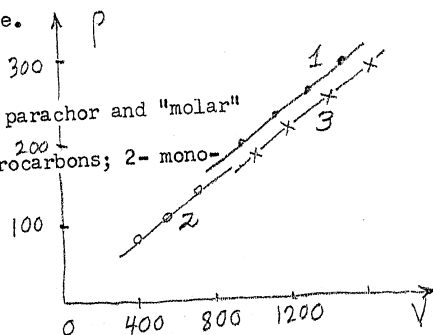


Figure 10. Relationship between parachor and "molar" speed of sound: 1- aromatic hydrocarbons; 2- monohydroxy alcohols; 3- paraffins

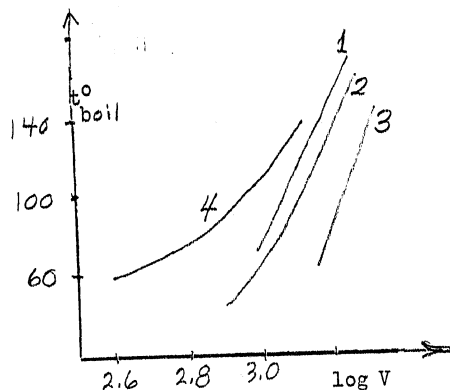


Figure 11. Relationship between boiling point and "molar" speed of sound: 1 - aromatic hydrocarbons; 2 - acetates; 3 - paraffins; 4 - monohydroxy alcohols

On the basis of the indicated relationships, a new method of determining the molecular weights of high polymer compounds was proposed; this method is based on the simultaneous determination of the molar refraction and the molar speed of sound. (24)

The experimental complexity, together with some uncertainty of the theoretical bases of this method, gives little hope that it will find wide use, although in individual special cases, its use is quite possible.

As was mentioned above, the speed of sound is related to the adiabatic contraction of a substance β by a single value; in its turn, β is related to the inner energy of a substance U by the following

$$\frac{1}{\beta} = v_0 \frac{\partial^2 U}{\partial v^2} \quad (7)$$

where v is the volume.

If we accept as a working hypothesis the determination of the liquid state, which was first proposed by Brillouin (25) and Born (26) and in accordance with which the liquid differs from the corresponding solid by the lack of a modulus of shear, then it is possible to obtain an expression of the speed of sound as a function of the density of the liquid and of magnitudes which determine the field of force of the molecules (27). If we assume that the inner energy of the liquid is essentially potential energy resulting from the interaction of the molecules and, also, if in calculating the potential energy, we limit the calculations to the reaction of the molecules with their nearest neighbors only and ignore the reaction with more distant molecules, then it is possible to obtain (27) the following equation for the speed of sound

$$v = \sqrt{\frac{\phi''(r)}{r \cdot \rho}} \quad (8)$$

where r is the distance between the molecules, $\phi(r)$ is the potential energy of the interaction of two molecules, expressed as a function of the distance between them, ρ is the density of the liquid, and $\phi''(r)$ is the second derivative of $\phi(r)$ with respect to r .

Quantum mechanics makes it possible to determine the potential energy of molecular interactions (28). However, the calculations are so complex that it is preferable to use the approximate equation of Lennard-Jones, which is a good approximation, if the distances between the molecules are not too great (29), and yields results which are practically not different from those obtained by a strict quantum mechanical solution.

According to Lennard-Jones, the potential energy of two atoms or molecules $\phi(r)$ can be expressed by the following:

$$\phi(r) = \lambda r^{-n} + \mu r^{-m} \quad (9)$$

where r is the distance between the atoms and $\lambda, \mu, n,$ and m are constants. Lennard-Jones calculated the values of λ and μ , using $n = 12$ and $m = 8$ for helium, argon, hydrogen, and nitrogen (30).

The possibility of calculating the speed of sound in liquids, on the basis of the numerical values of constants which determine the potential field of the molecules and of intermolecular distances, is of considerable interest. Therefore, it would be desirable to verify the agreement between the results obtained by equation (8) and those obtained by experiment. Such a comparison was first made for the speed of sound in liquid nitrogen, hydrogen, and helium; in calculating the intermolecular distances, it was assumed that the particles of simple liquids form a cubic face-centered lattice.

The speeds of sound in nitrogen, as calculated from equation (8) and observed experimentally, are listed in Table 3. The presence of two numbers in the column of the calculated speed of sound is due to differences between the densities of liquid nitrogen, as cited in the literature.

[See next page for representation of Table 3]

Considering the characteristics of such a comparison, the agreement between theory and experiment can be considered as quite satisfactory.

TABLE 3

Temperature, in degrees Kelvin	Calculated speed of sound, in meters/second	Experimentally determined speed of sound, in meters/second
76	841 - 826	869
74	878 - 861	889
72	910 - 894	909
70	952 - 929	929

For liquid hydrogen at 20.3 degrees Kelvin, the calculated value of v is 1006 meters per second, which is in close agreement with the experimentally observed value of 1127 meters per second.

The calculated and experimental values of v for liquid helium at 4 degrees Kelvin are 270 and 255 meters per second, respectively.

Recently, Jaffe calculated the values of the constants in the Lennard-Jones equation for various liquids; at the same time, he also calculated the average intermolecular distances in the corresponding liquids at their boiling points. With the aid of these data, the speeds of sound listed in Table 4 were calculated.

The agreement between theory and experiment can be considered as satisfactory, especially, if it is considered that the calculated lower speed values can be explained by the disregard of the kinetic energy in calculating the inner energy of the liquid.

It seems to us that, in the future, acoustic measurements will find use as a method of studying the fields of force of molecules.

In investigating a substance in the solid state, acoustic methods

TABLE 4

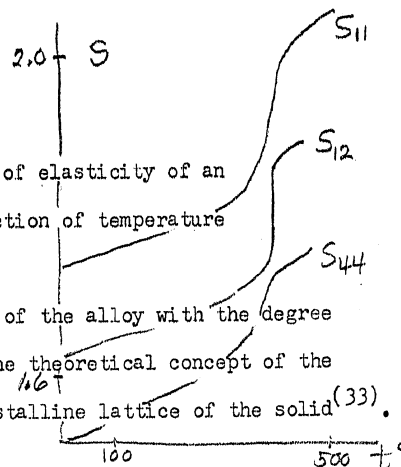
<u>Substance</u>	<u>Calculated speed of sound, in meters/second</u>	<u>Experimentally determined speed of sound, in meters per second</u>
Acetone	1009	1032
Carbon disulfide	961	1074
Chloroform	711	860
Carbon tetrachloride	616	750
Ethyl ether	869	934
Benzene	842	1030
Ethyl Alcohol	1030	1000
Water	1466	1550

make it possible to study the thermal characteristics of the solid, the variation of magnetic properties with the temperature, the plasticity, the phase changes in solids, etc.

In the case of ferromagnetic substances, the elastic and magnetic properties are interlocked because of the magnetostriction; for this reason, the composite piezoelectric transducer (32) was used for studying the variation of the elastic and absorbing characteristics of individual crystals and polycrystalline specimens of nickel as a function of the intensity of magnetization and temperature.

The alloy of copper and gold, Cu_3Au , upon being cooled gradually, forms crystals with a cubic lattice. Upon raising the temperature, the regularity disappears and, above 390 degrees the alloy changes into a solid solution. In Figure 12, the temperature is plotted along the abscissa and the three chief moduli of elasticity of the crystal with a cubic lattice are plotted along the ordinate.

Figure 12. Variation of the modulus of elasticity of an individual crystal of AuCu_3 as a function of temperature



From the variation of the elasticity of the alloy with the degree of regularity, it is possible to verify the theoretical concept of the nature of the forces which act in the crystalline lattice of the solid⁽³³⁾.

By observing the variation of the modulus of elasticity of the solid near its critical point, it is possible to study the kinetics of transformations in the solid phase⁽³⁴⁾.

An investigation was made of the variation of the modulus of shear in solids with rising temperatures, up to the melting points⁽³⁵⁾. The earlier investigations gave rise to the expectation that the modulus of shear will approach zero value gradually, as the melting point is approached. According to the theoretical concepts of Born and Fuert, the modulus of shear has a limiting value just below the melting point. In order to verify the correctness of these concepts, an investigation was made of the variation of the modulus of elasticity of crystalline NaCl in the immediate proximity of the melting point.

In this investigation, the specimen of rock salt was cemented directly to a rod of fused quartz and the latter to a piezoelectric transducer. Such an arrangement made it possible to place the specimen in the center of a tube furnace, in the region of uniform high temperature, while the vibrating quartz rod was in the cold section of the furnace. The latter condition was necessary since the quartz changes at 575 degrees from the α -modification into the β -modification which does not possess piezoelectric characteristics.

Figure 13 shows the variation of the modulus of elasticity of torsional vibrations of the NaCl specimen at a temperature close to the melting point. As can be concluded from an examination of the given curve, the modulus of elasticity has, in accord with the views of Born, a limiting value just near the melting point. The general nature of the curve is in qualitative agreement with the developed theory.

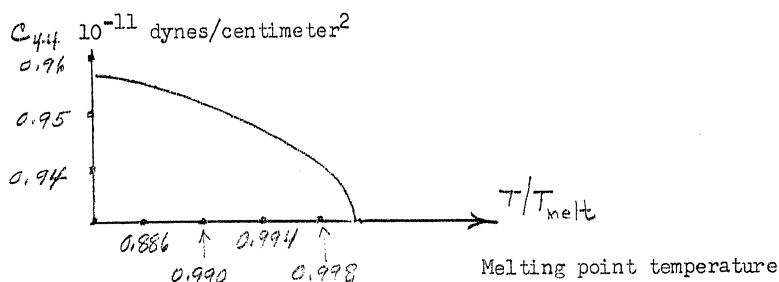


Figure 13. Variation of the modulus of elasticity of crystalline NaCl as a function of the temperature, near the melting point.

The few above-mentioned examples indicate that acoustic methods can be successfully utilized for expanding our knowledge of the nature of the solid state of matter.

Recently, ultrasonic methods have come into use in the investigation of high polymer compounds which are acquiring greater industrial importance (36,37).

If a concentrated solution of gelatin in water is subjected to the action of an ultrasonic field of medium intensity, then, after a short time, one can detect a considerable decrease in the viscosity of the solution. However, this change is reversible and, a certain time after the ultrasonic action has ceased, the original viscosity

of the solution is restored. The explanation of this phenomenon is that the anomalously large viscosity of the gelatin solution is caused by the mobile skeleton which is formed by the fantastic interlocking of the long, thread-like molecules of gelatin in which the solvent is retained as in a sponge. The indicated skeleton is held together by relatively small Van der Waal forces, the energy equivalent of which is between 2,000 and 8,000 calories per mol of the bonding groups.

Upon subjecting a solution to the action of ultrasonics, cavitations take place; the formation of these cavitations is facilitated by the air dissolved in the water. The cavitations which take place in the liquid under the action of the ultrasonic wave begin to pulsate and these pulsations are equivalent to microscopic jarring. It is precisely this microscopic jarring which destroys the skeleton that was formed by macromolecules. The effect of pressure on the dispersion of ultrasonics can be regarded as direct proof of this viewpoint. The formation of cavitations is considerably hindered under a pressure of 10 atmospheres and, at the same time, there is practically no effect of the ultrasonics on the viscosity of the solutions. In this manner, the reversible change in the viscosity of solutions of high molecular substances can be regarded as the result of temporary damage to the skeleton of macromolecules by the pulsation of the cavitations resulting from the action of ultrasonics. When the action of the ultrasonics ceases, the macromolecules, under the action of the Brownian movement, form a skeleton again and restore the original viscosity of the solution.

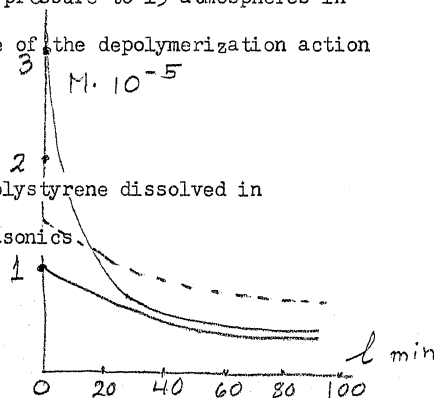
It is possible to observe also an irreversible change in the viscosity of solutions of high molecular substances subjected to the action of ultrasonics; such a change must naturally be related to the decrease

in the molecular weight of these substances.

It was shown that, under the influence of an ultrasonic field with a frequency of 300,000 hertz and a strength of approximately 10 watts per square centimeter, the viscosity of solutions of nitrocellulose, polyvinyl acetate, and polystyrene decreases considerably and irreversibly, thus indicating that a chemical depolymerization of these substances takes place.

Figure 14 shows the kinetics of depolymerization of three solutions of polystyrene in toluene at 70 degrees under the action of ultrasonics. At first, the molecular weight of the polymers, as determined from the viscosity of the solutions, was 100,000, 150,000, and 300,000, respectively. After a two-hour treatment with ultrasonics the original molecular weight decreased to 30,000, 70,000, and 40,000 respectively. It should be pointed out that the depolymerization is essentially completed in the first 20 minutes of ultrasonic action. Also, the polystyrene specimen with an original molecular weight of 150,000 was relatively more stable against the dispersing action of the ultrasonics. This circumstance can be regarded as confirmation of the existence of macromolecules of different configuration but of the same chemical composition. In the given case, we are dealing with the action of ultrasonics only, and not with the result of the pulsation of the cavitations, because by increasing the pressure to 15 atmospheres in this case, there is observed an increase of the depolymerization action under the influence of the ultrasonics.

Figure 14. Depolymerization of polystyrene dissolved in toluene, under the action of ultrasonics.



In order to determine the causes of the chemical depolymerization, it is necessary to know those forces which are required to rupture the chemical bonds in the given compounds.

The magnitudes of the forces necessary to rupture different chemical bonds are listed in Table 5⁽³⁸⁾.

TABLE 5

<u>Bond</u>	<u>Force, in dynes per bond (x 10⁵)</u>
C - C	4.5
C - O	5.77
C = O	9.77
C = N	12.06
C ≡ N	16.6
C ≡ C	17.2

The problem of the shape of the macromolecules is also of considerable importance. According to recent investigations, the shape is intermediate between that of a stretched chain and that of a chain coiled into a ball.

In the case of polystyrene with a molecular weight of 100,000 the stretched molecule has a length of 3,000 angstroms and a diameter of 6 angstroms. The ratio of the axes is equal to 500. In the case of molecules actually in existence in solutions, the length is approximately 1,500 angstroms and the diameter 15 angstroms, which corresponds to a ratio of the axes equal to 100. Such macromolecules perform irregular internal movements in the solution and, in addition, are also gradually displaced as a whole. The movement of such a mole-

cule, as a whole, is gradual, with an average speed of 0.5 to 1.0 per second. Under the influence of the sound wave, the molecules of the solvent acquire speed, the maximum value of which, under the indicated conditions, is approximately 40 meters per second.

If it is assumed that the macromolecules, under the influence of the large inertia, do not follow at all the movement of the liquid caused by the action of the ultrasonic wave, then friction will take place between the macromolecule and the solvent. The magnitude of the force of friction can be determined approximately. For the given case (assuming that the force of friction is 10^{-2} poises), the force of friction is of the order of $2 - 3 \times 10^{-4}$ dynes. By comparing this value with those listed in Table 5, we see that the force of friction exceeds considerably the strength of the C - C and C - O bonds. If the calculation of the forces of friction is correct, then the polymer should depolymerize completely as soon as it is subjected to the action of ultrasonics. Obviously, the assumption that the macromolecules cannot follow completely the movement of the solvent is incorrect. It is probable that in individual cases sufficient friction will occur to rupture the chemical bonds. This circumstance explains the prolonged time necessary for depolymerization and the small degree of depolymerization. Discontinuation of depolymerization with decreasing molecular weight of the polymer can probably be explained also by this circumstance.

In this manner, one can hope that the investigation of the action of ultrasonics on solutions of high molecular substances will make possible a better understanding of the nature and properties of this very important class of substances in the future.

In concluding the review of the methods of utilizing ultrasonics, it is necessary to point out the continually growing importance which ultrasonic dispersion is acquiring as a secondary operation in the practice of physico-chemical research (39,40).

The present review is not exhaustive. In order not to exceed the reasonable limits of the review, it was necessary to say nothing about the application of acoustic methods for the investigation of the kinetics of chemical reactions (41), the use of ultrasonics in research laboratories of the ceramic industry (42), the use of ultrasonics in the detection of defects in metals (43), the use of ultrasonics in colloid chemistry (44), acoustic miniature-scale operation with the aid of ultrasonics (45), etc.

However, it seems to us that the mentioned examples of the successful use of ultrasonics in research practice is quite sufficient to make clear the great importance of acoustic methods of physico-chemical research.

One should think that, in the near future, ultrasonic methods will come into routine use in physical chemical laboratories and will assist us in better understanding the properties in different states and the laws which govern the transformation of matter during physical and chemical processes.

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