Temperature Rule for the Speed of Sound in Water: A Chemical Kinetics Model

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Abstract: Water forms three-dimensional polymeric structures due to the influence of hydrogen bonds and is fundamentally different from other substances. One of the simplest ways to analyze the structure of water in any system, such as hydration, is to measure the degree of compressibility, which can be determined from the speed of sound, by making use of the physical laws established by Newton and later perfected by Laplace. Although the speed of sound is strongly dependent on the temperature of a liquid, Laplace's equation does not refer to temperature in any of its terms. It is necessary, therefore, to determine the degree of temperature dependency. However, only approximate expressions of a fifth-order polynomial have been reported so far in the literature. In this paper, a universal method for describing the speed of sound from the perspective of physicochemical reaction kinetics is presented. It is shown that the speed of sound U [$\mathrm{ms^{-1}}$] changes with temperature T [K] according to a thermodynamically-derived formula given as $U = \exp(-A/T - B\ln T + C)$ and that the motion and propagation phenomena of sound energy can also be regarded as chemical reactions.

Keywords: analytical methods · kinetics · speed of sound · temperature function · water

Introduction

Water exhibits certain remarkable characteristics due to its structure, and it plays a crucial role in biological processes, particularly in its cooperative interactions with proteins. Information on the structure of materials containing water can be obtained by measuring various physical properties, such as nuclear magnetic resonance, dielectric constants, and compressibility.[1] The degree of compressibility is the simplest to measure because it can be determined from the speed of sound propagating through a substance.[2] The original theoretical derivation of the speed of sound U by Newton was based on the equation of continuity and the equation of motion with respect to pressure P and density ρ, expressed as $U = (P/\rho)^{1/2}$, with $P/\rho = \text{constant}$ and $T/\rho = \text{constant}$, for an isothermal process in an ideal gas. However, the calculated U has been found to be about 1/6 smaller than the actual measured value.

Laplace later pointed out that the speed of compression or expansion due to sound waves was very rapid, and he interpreted this to mean that there was insufficient time for heat exchange to occur from a compressed region to a rarefied region. Assuming that pressure and temperature change adiabatically, that is, both P/ρ^{γ} and $T/\rho^{\gamma-1}$ are constants, Laplace expressed the speed of sound $U = 1/(\kappa\rho)^{1/2}$ in terms of adiabatic compressibility (κ) and density (ρ). (Here, γ is the ratio of heat capacity under a constant pressure and in a constant volume, C_p/C_v.)

In an ideal gas, Laplace's equation can be approximated by Tailor's series, as a function of temperature, but this relation does not hold in the case of a liquid. In other words, the equation of state is not applicable to an aqueous solution per se.[3] Incidentally, in the case of water at room temperature, for example, a change of only 1 K is equivalent to a significant difference of about 2 $\mathrm{ms^{-1}}$ for speed, and naturally the temperature must therefore be held constant in order to make meaningful comparisons of speed. However, it is very difficult to maintain the temperature exactly at a set value for every measurement. Consequently, the interpolation of the intended temperatures out of multiple points has become the only practical way to do it. For this reason, a theoretical formulation of the speed of sound in a liquid as a function of temperature and pressure would be desirable, but at present, it is necessary to rely on an approximation formula with a fifth-order polynomial for analysis.[4]

Laplace's equation is a theoretically derived formula and indicates that the speed of sound is a purely thermodynamic quantity, but the given equation can not be used directly as a temperature function. Can there be any alternative to Laplace's equation? Here, Laplace's correct deduction is explained as follows: The heat transmission and small adsorption of sound energy can be regarded as being negligible

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because the wave length of sound is long compared with the mean free path (the average distance a molecule travels before colliding with another molecule), that is, the sound wave is propagated under isentropic conditions. However, it is an undeniable fact that the increasing tendency of the entropy has also been expressed as a principle of the degradation of energy, by which it becomes less available for useful work. Therefore, it should be taken into account that the wavefront of sound passing through media is perturbed as the duration of the time interval for observation becomes infinitesimally small. As a result, we can no longer disregard the viewpoint of change in entropy and it becomes necessary to consider another interpretation. Is it possible to describe the speed of sound by some other means, for example, in terms of chemical reactions? In other words, is it possible to regard the speed of sound in terms of the chemical kinetics of energy propagation from an exiting molecule with sufficient potential energy to the nearest molecule (in its neighborhood) with lower potential energy? The answers to these questions are yes.

The author has been investigating the effects of inhalation anesthetics on hydration in an electrolyte solution by determining the speed of sound using the sing-around method. (There are several theories on the mechanism of anesthesia with regard to water structure.)[5–8] The results of such investigations have shown that there is a strongly negative correlation between the frequency and thermistor resistance (of a negative characteristic type); and the author has attempted to analyze the temperature rule for the speed of sound by associating such a relation between frequency and thermistor resistance with the chemical-reaction hypothesis mentioned previously.

Relationship between frequency and thermistor resistance as determined by the sing-around method: The diagram of the apparatus used in the experiment is shown in Figure 1. In the sing-around method, quartz oscillators are placed at both ends of a cylinder-type hard glass cell with a bore of about 2 cm. Voltage is supplied to one of the oscillators by a pulse generator (Nihon-Denki-Sanei, Tokyo, Japan), whose vibration waveform is received from the other element, converted to a voltage and then amplified. Then the next voltage pulse starts the cycle all over again. Thus, the speed of sound U in a solution can be expressed with respect to a repeating frequency F (Universal Counter, Takeda Riken, Tokyo, Japan), as shown in Equation (1).

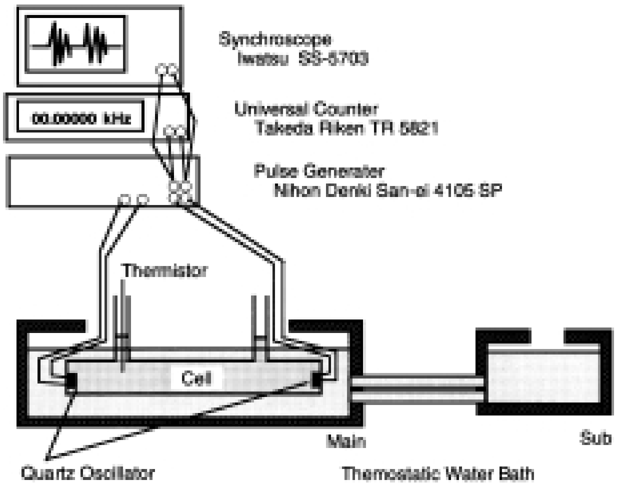

Figure 1. Diagram of measuring apparatus.

$$\frac{1}{F}=\frac{L}{U}+t_{\mathrm{d}} \tag{1}$$

Here, L and t_{d} are the distance between oscillators and the time delay of the electric circuit.

Two thermistors were used in this experiment. At the beginning and end of each measurement, one of the thermistors was used to verify that the other (used for actual measurement) was free from changes such as heat hysteresis. The constant R_{c} [Ω] at T_{c} [K] and the temperature coefficient R_{f} of the thermistor in Equation (2) were determined by repeated measurements of resistance R at various temperatures T while simultaneously being checked against a platinum resistance thermometer.

$$R=R_{\mathrm{c}}\exp\left(R_{\mathrm{f}}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{c}}}\right)\right) \tag{2}$$

The oscillators used on both the reception and transmission sides were 5 MHz types. The unit of measurement for resistance was 1 Ω, and for frequency 0.01 Hz in an average of 10 s. Since the temperature registered in a thermostatic water bath is affected by ripple changes in the operation of the heater, two thermostatic water baths were used in order to obtain a stable time scale and to maximize the accuracy of the measurements. The cell length and electrical delay time of the apparatus were calculated by referring to published data.[4a] All these constant values were determined by the least-squares method using measurements at multiple points.

One set of thermistor constants was 15.70 kΩ (R_{c}), 298.160 K (T_{c}), and 3465.0 K (R_{f}); the other was 15.80 kΩ ($\mathrm{R_c}$), 298.145 K (T_{c}), and 3475.0 K ($\mathrm{R_f}$). The temperature was controlled within 0.002 to 0.007 K (that is, about 1 to 2 Ω in resistance). The cell length and standard deviations were 10.8399 ± 0.0010 cm (cell A) and 12.3979 ± 0.0011 cm (cell B) when converted to 298.16 K. The coefficient of linear expansion of the hard glass cell calculated at the same time was within the reported range of values for this material. The delay constant of the electric circuit was 1.715 ± 0.001 µs.

Sound propagation phenomena and chemical reactions: As can be seen from Equation (1), the frequency and speed of sound become proportional as the delay constant approaches an infinitesimal limit. Also, the relations for observed repetitive frequency (equivalent to speed) and resistance value (equivalent to temperature) were judged to be linear, as shown in Figure (2). Therefore, based on this linear relationship between resistance and temperature in Equation (2), which conforms to an Arrhenius plot, it was assumed that the speed was related to temperature by a thermodynamically exponential function. Therefore, chemical kinetics can also be applied here to determine the nature of sound propagation, since sound propagation phenomena can be interpreted as

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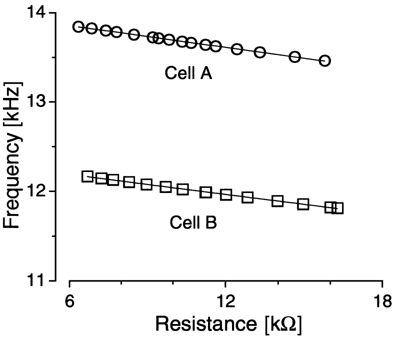

Figure 2. Relationship between frequency and thermistor resistance measured at 15 to 16 temperature points using high purity distilled water for HPLC (WAKO PURE CHEMICAL, Osaka, Japan) by the sing-around method. As shown in the diagram, a nearly linear relationship between frequency and resistance was confirmed in the two hard glass cells. The temperature was about 305.16 K at 12 kΩ and about 323.16 K at 6 kΩ.

rate processes, as long as their speed is kept constant under any arbitrary condition.

Thus, with a few assumptions, we can formulate the following chemical equation that represents the transition state of energy attenuation due to the energy exchange in collisions between activated molecules and neighboring molecules in the direction of propagation:

$$X_1^* + X_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (X_1 \cdot X_2)^* \xrightarrow{k} X_1 + X_2^* \quad (3)$$

In Equation (3), X* indicates activated molecules; **k** is the reaction rate constant determined from the coefficient of transmission (r_{tr}) through the potential energy barrier; and k_1 and k_2 are the molecular rate constants for activation and for deactivation.

Assumptions

1) Although a chemical reactions are generally understood to accompany a change in the composition or structure of molecules, the term chemical reaction as used here refers to the collision phenomenon by which only the propagation energies (signals) of sound are transferred. Therefore, in the given reaction formula, an activated molecule (X*) collides with an advancing molecule (X) and the sound energy of molecule X* is transmitted to molecule X. The transmission coefficient is defined as the rate of reactions that occur in the path of advancing molecules.

   According to this logic, collisions between different molecules not only in a homogeneous phase but also in a heterogeneous phase can be regarded as reactions. Furthermore, in the case of an association molecule such as water that may be considered "polymorphic", its reaction can be treated statistically in these reactions as a uniform reaction in terms of molecular weight (cluster size) and structure.

2) We assume that molecules are rigid spheres that are capable of elastic collision. We also assume that the intensity of sound, expressed in decibels [dB], corresponds to the concentration of X*.

   For convenience, the validity of the logic is explained for the case of gas. There are gaps between molecules, and collisions occur due to the movement of molecules. Thus, for any single collision, the molecules can propagate in any direction depending on the difference between the velocity energies of the two molecules and the angle of collision. However, a nitrogen molecule, for example, has an average velocity of about 450 ms^{-1} at 273.16 K, and the distance one molecule travels within a certain time interval is much greater than the distance between molecules in nitrogen gas; thus, the number of collisions per unit time for each nitrogen molecule is assumed to be very high. The sound signals that are transmitted due to collisions between molecules are, according to the definition of elastic collision, transmitted successively to the molecules that have been hit. It is assumed that the sound signals propagate (radiate) uniformly in all directions. However, it seems reasonable to consider the collision in one direction only, because collisions occur very rapidly and evenly (Pascal's principle). For any given direction, most signals will instantaneously reach the opposite site of the molecule that has been hit (according to the definition of a rigid sphere). The signals are continuously propagated forward due to repetition of the reaction (collision) and the number of reactions occurring within a unit time interval can be taken as an indication of the mean propagation distance. Therefore, the reaction speed and propagation speed can be treated as equivalent.

   In addition, the transmission coefficient, defined in this scheme as the rate of reaction in the forward direction for solid, liquid, and gaseous states, is thought to be on the order of solid > liquid > gas.

   Moreover, the propagation distance increases as the concentration of X* increases. (When the sound signal does not propagate uniformly in various directions under certain limiting concentration, in this case, the collision reaction converges.)

Analysis of sound propagation according to theory of absolute rate: To evaluate a thermodynamic equation of state, it is necessary to know the variation of V with P. In the case of a liquid, there is no simple PV function available; hence, it is impossible to apply the general thermodynamic law. The key to the solution to this problem, however, lies in Eyring's theory of "absolute rate", which is normally applied to the field of physical chemistry when considering viscosity. However, several conditions must be met before Eyring's theory can be applied. First, it must be confirmed that the collision reaction is irreversible, since the propagation signal is no longer available in the reaction field as a result of having moved immediately to the opposite edge after a collision ($\Delta S \neq 0$). However, it is probably justifiable to assume that the reaction is organized with a small difference in the entropy of activation because the activated complex is similar in structure to the initial state ($\Delta S \cong 0$). In addition, if it can be assumed that the structure of water can be replaced by an equivalent mixture system composed of monomers and tetrahedrally-coordinated pentamers, such as a flickering cluster (represented by X··X),[9, 10] Equation (3) can be replaced by Equation (4) as in the case when the reaction corresponds to a triple collision (three-body reaction) in gas.[11a]

$$X^* + X{\cdot\cdot}X \leftrightarrow (X{\cdot}X{\cdot\cdot}X)^* \xrightarrow{k} X{\cdot\cdot}X + X^* \quad (4)$$

According to Eyring's theory of absolute rate, the reaction rate constant $\boldsymbol{k}$ can now be expressed as in Equation (5).[11b]

$$\boldsymbol{k} = r_{\text{tf}} \frac{k_B T}{h} \frac{Q_M^{\neq}}{Q_X {\cdot} Q_{X{\cdot\cdot}X}} \exp\left(-\frac{E_0^{\neq}}{RT}\right) \quad (5)$$

Here, h is the Planck constant, k_B the Boltzmann constant, R the gas constant, and Q_M, Q_X, $Q_{X{\cdot\cdot}X}$ are the partition functions per unit volume of the activated complex $(X{\cdot}X{\cdot\cdot}X)^{\neq}$ and reactants X and $X{\cdot\cdot}X$, respectively. The superscript ($\neq$) here indicates that the parameter is related to the state of the activated complex, and the subscript (0) indicates the energy state at 0 K.

Although the partition functions for molecular translational motion, molecular rotational motion, and molecular vibrational motion are all dependent on temperature, these partition functions are not known because it is difficult to define exactly the nature of the structure (i.e., the number of particles in the mixture system). These functions are therefore determined by parameterization. When the temperature terms can be factored out in the partition functions, that is, when the power coefficient m and k_{PF} can be settled as the temperature-dependent part and the others in the partition functions, the numerical formula can then be rewritten as $k_{PF} k_B T^m h^{-1}$.

Consequently, we obtain the following reaction rate constant $\boldsymbol{k}$ as a function of temperature and pressure in Equation (6).[11c]

$$\boldsymbol{k} = r_{\text{tf}} k_{PF} \frac{k_B}{h} T^m \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-E_a + RT - \Delta(PV)^{\neq}}{RT}\right) \quad (6)$$

where E_a and S are the experimental activation energy and the entropy of activation.

In the theory of absolute rate, the rate of reaction is the number per second of activated complexes passing over the summit of the potential-energy barrier, and this can be replaced by the transmission distance per unit time (that is, the speed of sound U).

Moreover, in the case of the propagation reaction of sound in water, the transmission coefficient (r_{tr}) can be approximated to be 1[12] because the relaxation time of water estimated from ultrasonic absorption is on the order of picoseconds and is much shorter than the propagation reaction of sound.[13, 14] Therefore, the reaction rate constant $\boldsymbol{k}$ can now be expression in terms of the propagation speed of sound U, as in Equation (7).

$$U = \exp\left[\frac{-E_a - \Delta(PV)^{\neq}}{RT} + m \ln T + \left(\frac{\Delta S}{R} + 1 + \ln\left(r_{\text{tr}} k_{PF} \frac{k_B}{h}\right)\right)\right] \quad (7)$$

Equation (7) can be further simplified to Equation (8) by $A = (E_a + \Delta(PV)^{\neq})/R$, $B = -m$, and $C = \Delta S/R + 1 + \ln(r_{\text{tr}} k_{PF} k_B h^{-1})$ at constant pressure.

$$U = \exp\left(-\frac{A}{T} - B \ln T + C\right) \quad (8)$$

Goodness of fit of chemical kinetics model: The chemical kinetics model expressed in Equation (8) was fitted against published data at 1 atmospheric pressure (i.e., $\Delta PV^{\neq} = 0$) by regression analysis and good results were obtained (see Figure 3).[4a, 4c, 4d] The results were 1145.3294 (A), 3.30479 (B), and 29.9811 (C) from the data of Del Grosso et al.,[4d] and 1177.0675 (A), 3.41448 (B), and 30.7133 (C) from the data of Greenspan et al.[4a] In the results for water, the numerical values obtained from calculation using the above formulas are naturally different, because the values between the two references differ by about 0.31 ms^{-1}, in the temperature range of 288.16 to 307.16 K. Although there is no reason to doubt the validity of the Equation, strictly speaking, this analysis requires further improvement in the entropy change dependence on temperature with respect to the partition functions. (The analysis is carried out by parameterization based on a simplified structural conception in which the molecular number constituting the cluster is not decided and the entropy is not affected by temperature. However, changes in entropy have in fact been observed; for example 63.63 J K^{-1} mol^{-1} at 273.16 K and 87.07 J K^{-1} mol^{-1} at 373.16 K.[10] Furthermore, in a monomer–pentamer model, the entropy of the cluster is largely dominated by the vibrational and rotational entropy of pentamers up to about 308.16 K, after which the degree of contribution by the translational and rotational entropy of monomers increases sharply with temperature.[10] Therefore, in order to analyze exactly Equation (5), we must include the number of particles in the partition function.)

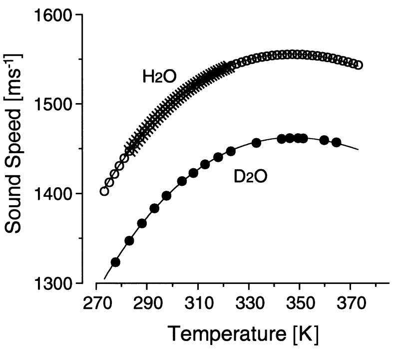

Figure 3. Fitting of chemical kinetics model to reference data. The figure shows the fitting of Equation (8) to the reference data calculated by the polynomial approximation by Greenspan et al. (×),[4a] and Del Grosso et al. (○).[4d] The figure also shows the regression curve for the data related to the speed of sound in heavy water by Wilson (●).[4c]

The negative value of the power index m is reasonable because this negative index indicates that if E_a is not excessively large or small, the reaction rate constant increases with increases in temperature up to a certain point and then declines with further increases in temperature. This phenomenon is compatible with the temperature dependence of the speed of sound in water. It thus appears that this thermodynamic analysis can be understood as a method for determining the essential characteristics of water.

Incidentally, a similar result was obtained by regression analysis of the speed of sound in heavy water using the data of Wilson,[4c] and the same correlations as those determined in water were obtained at various pressure levels in heavy water, as shown in Figure 4.

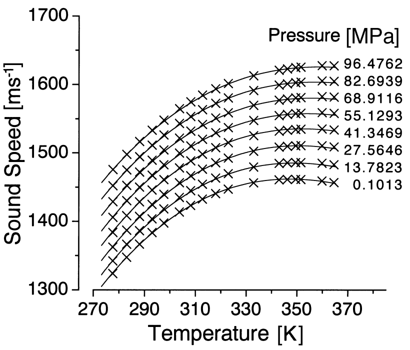

Figure 4. Goodness of fit to different pressures: Scatter plots of the speed of sound in heavy water in Wilson in the temperature range of about 277 K to 365 K and pressure range of about 0.1 MPa to 96.5 MPa and the regression lines adapted for matching these data by using Equation (8) at each pressure level.[4c]

Relation between speed of sound and pressure: If U_{st} is regarded as the speed of sound in a standard state ($\Delta PV = 0$) in Equation (7), the speed of sound at any given pressure (U_p) at a given constant temperature can be expressed as in Equation (9) as follows:

$$\ln\left(\frac{U_p}{U_{st}}\right) = -\frac{\Delta(PV)^{\neq}}{RT_{const}} \tag{9}$$

Figure 5 shows $\Delta V^{\ddagger}/R$ in the relation between $\ln(U_p/U_{st})$ and P/T at each temperature point obtained by direct calculation using Wilson's data.[4c] A definite linear correlation ($r^2 = 0.9986$ to 1) was observed at each temperature. As can be seen from the Figure, although $\Delta V^{\ddagger}$ is correlated with pressure at a constant temperature, it varies with temperature changes. That is, $\ln(U_p/U_{st})/(P/(RT))$ is not constant. It is difficult to find a linear relation between the speed of sound and pressure changes.

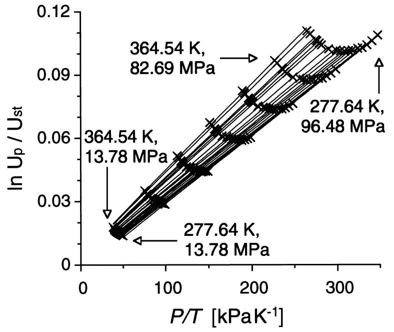

Figure 5. Changes in $\Delta V^{\ddagger}$ at various pressure and temperature levels: $\Delta V^{\ddagger}/R$ in the relationships between $\ln(U_p/U_{st})$ on the y axis and P/T on the x axis at each temperature point between about 277 K and 365 K. U_{st} and U_p are the speeds of sound calculated directly from Wilson's data in a standard state and under an arbitrary pressure level, respectively.[4c]

Regarding the relation between pressure and the parameters A, B, and C in Equation (8), if the potential energy surface does not change due to pressure, only parameter A should be affected by pressure change. However, contrary to expectation, the relations between each parameter value for A, B, and C and 4/3 power of the pressure [MPa] were linear (which was determined by the least-squares method to be 4/3 in each case), as shown in Figure 6. These relations for heavy water were $A = -6.66089 \times 10^{-1} P^{4/3} + 1269.58837$, $B = -2.10644 \times 10^{-3} P^{4/3} + 3.64241$, and $C = -1.40146 \times 10^{-2} P^{4/3} + 32.26319$.

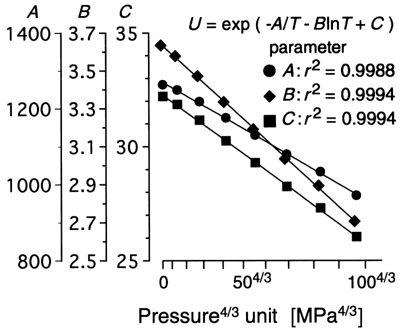

Figure 6. Relationship between pressure and parameters of chemical kinetics model: Linear relationship between the values of parameters A, B, and C (calculated using Equation (8) and Wilson's data[10] and the 4/3 power of pressure.

Since the absolute rate theory can explain viscosity, it is reasonable to assume that it is also applicable, in the same manner, to the sound-propagation reaction, which does not involve any change in chemical structure. Therefore, given the results of the linear relationships between the thermodynamic parameters A, B, C and the 4/3 power of pressure (The power index of water calculated from the data by Smith et al.[15] was about 0.5, although it was not exact because there were only four data points.), it is possible that there are some unique effects of pressure other than compressibility change, especially in the case of an association molecule such as water. Therefore, it is reasonable to assume that in an association molecule, there is a pressure-dependent conformational change in structure, which is manifested as changes in the thermodynamic parameters. Furthermore, it is thought that the restriction of molecular motion and the shift of the potential energy surface caused by pressure has the effect of changing the temperature factor of the partition function, the activation energy, and the entropy. The pressure effects on the thermodynamic parameters in heavy water should be greater than those in light water, and we therefore speculate, based on the differences in the strength of hydrogen bonds, that there is a difference in the size of association molecules in heavy water and light water.

Although it can not be theoretically determined whether such a discrepancy regarding pressure is due to the structure of water or not (pressure influences all thermodynamic parameters), the speed of sound can still be well represented by Equation (8) even when pressure changes occur. It is also theoretically possible that such a pressure-temperature function can be applied to gases as well.

Conclusion

The rate of any chemical reaction can be theoretically formulated according to activated complex theory and/or collision theory. However, it can be argued that theoretical analysis is extremely difficult given the fact that there does not exist an unequivocal method for calculating the equation of state in a liquid solution. Given this, the use of ultrasonic sound waves seems to be a very promising and useful means of investigating the state of water.[16] For example, the ultrasonic absorption method can be used as an effective means of obtaining directly measurable physical parameters in the composition fluctuation theory of Kirkwood–Buff,[17] and Andreae[12] has made use of ultrasonic absorption to explain the chemical reaction in a two-component solution. As the results presented in this paper have shown, the sound speed method is useful in *PVT* data analysis for calculating collision-theoretic parameters, etc., in turn.

In conclusion, the results of this study confirmed that the speed of sound can be described as a reaction rate in chemical kinetics; thus, the speed of sound obeys the theory of rate processes.

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