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OF AQUEOUS SOLUTIONS OF NaCl AND KCl AT 25°C

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*A FREQUENCY-MODULATED ULTRASONIC INTERFEROMETER:
ADIABATIC COMPRESSIBILITY OF AQUEOUS SOLUTIONS
OF $NaCl$ AND KCl AT $25^{\circ}C$ **

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As part of a systematic study of thermodynamic properties of solutions we have developed a new type of ultrasonic interferometer for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, the electrical reaction of the cell upon the oscillator is used to fix standing-wave positions at a standard frequency, and their locations are determined with a suitable cathetometer.

The Interferometer.—As shown in Figure 1, the interferometer cell containing the solution was a vertical fused-quartz cylinder, M , M , closed at the bottom by a fused-quartz transmission plate, N , 40 mm in diameter and 3 half-wavelengths (2.14 mm) thick, polished flat to 1.3μ . The transmission plate was adequately rigid, and its thickness of an integral number of half-wavelengths ensured maximum energy transmission.¹

The cell was surrounded by a cylindrical stainless steel jacket, K , with a long sleeve, C , at the top, which carried two bearings, F , F , to support the reflector shaft. Type 67 Graphitar² was used for the bearings because the essential equality of its coefficients of static and dynamic friction allows smooth motion without sticking or chatter. Both ends of the quartz tube were made flat and parallel within about 1μ , as was a collar, J , at the bottom of the stainless steel sleeve, C , supporting the Graphitar bearings. The quartz tube was clamped between this collar and the shoulder, W , supporting the transmission plate. This arrangement aligned the reflector face parallel to the transmission plate. A rubber O -ring, O , formed an oil-tight seal between the transmission plate and the shoulder. A thin film of sealing compound³ prevented leaks between the quartz tube and the transmission plate. The cell was filled and emptied through the holes, H , using a 50-ml syringe connected to a length of small-bore polyethylene tubing. The syringe could be clamped in place and operated through a gear train connected to the drive screw for the reflector, so that solution was added to the cell as the reflector was raised, and withdrawn from the cell as the reflector was lowered, to compensate for the liquid displaced by the reflector shaft.

A rod of Carpenter Type-310 stainless steel was machined to form a rigid vertical shaft, G , 19 mm in diameter, drilled and threaded internally at the top and supporting a plane horizontal reflector, L , 32 mm in diameter, worked flat to 1μ . The reflector was immersed in the solution and could be raised or lowered without rotation by means of a lead screw, B . An adjustable thrust bearing, A , was used to reduce backlash in the lead screw drive. Motion was transmitted to the shaft through a bronze bushing, d (see detail inset in Fig. 1), screwed down into the top of the shaft and threaded internally to fit the lead screw. The bronze bushing was held in place on the shaft with an external lock nut, e . A stiff spring, c , was compressed between the bronze bushing and a second nut, a , which was screwed down

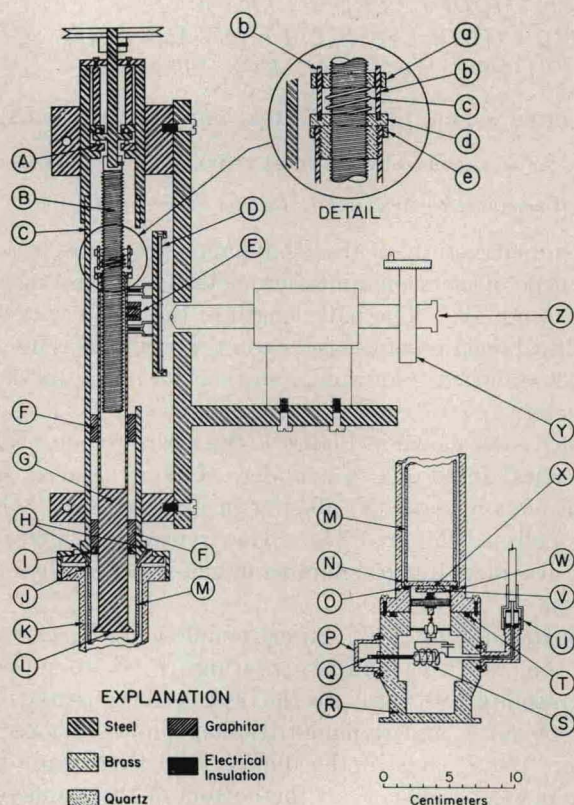


FIG. 1.—Ultrasonic interferometer cell assembly.

until the tension in the spring sufficed to remove backlash between the lead screw and the bronze bushing. This second nut was then fixed in position relative to the bushing with six steel pins, of which only two, *b, b*, are shown. An *O*-ring, *I*, prevented the shaft from carrying solution to the bearings, *F, F*. The first reflector shaft, constructed from Carpenter Type-317 stainless steel, became pitted in concentrated alkali halide solutions and had to be replaced; Type-310 showed no sign of attack.

The position of the reflector was read from a 100-mm scale, *D*, precision-ruled by the Bausch and Lomb Optical Company at 0.1-mm intervals. It was supported in a holder rigidly attached to the reflector shaft by two posts which rode in a vertical slot in the sleeve, *C*, without touching the sides. A rectangular block of Graphitar, *E*, somewhat wider than these posts, was screwed tight to the reflector shaft and fitted snugly in the slot to prevent the shaft from turning. The scale was viewed through a rigidly mounted microscope, *Z*, with a 10 \times objective and a filar micrometer eyepiece, *Y*, adequate to determine the position of the reflector to about 1 μ .

The brass base, *R*, of the interferometer was attached to the main body of the instrument by Allen bolts, with a rubber *O*-ring, *T*, to form an oil-tight seal. The bottom of the transmission plate, *N*, was covered with a thin sputtered coating of gold for electrical grounding to the case and for contact with a concentric circular

4-Mc X-cut quartz crystal transducer, X , 15 mm in diameter. A drop of oil on the upper surface of the transducer assured mechanical coupling to the transmission plate. The transducer was supported by an adjustable brass holder, V , through which it was connected to the electronic apparatus via a slug-tuned coil, S , and a length of coaxial cable attached to the base at U . The impedance of the coil was adjusted by varying the position of the slug attached to the screw, Q . A removable cap, P , was screwed down on a gasket (not shown) and prevented leakage of oil into the base of the interferometer.

The interferometer was immersed in an oil bath which was thermostated at $25.000 \pm 0.005^\circ\text{C}$, using the electronic proportional regulator developed by Ransom.⁴ The oil bath was surrounded by an insulated wooden box which also enclosed the upper part of the interferometer and the microscope (except for the micrometer eyepiece), thereby increasing the temperature stability of the system.

Electronic Circuits.—Our previous interferometer⁵ followed the familiar method of using a microammeter to determine the change in reactance of the cell with motion of the reflector. Unfortunately, the maximum galvanometer deflection, corresponding to a standing-wave position, could only be discerned after it had been passed, and the lead screw had enough residual backlash to prevent determination of the exact position by moving the reflector back and forth. A better method of determining standing-wave positions was needed, in which the off-balance is visible at all times and can be reduced to zero by moving the reflector continuously in one

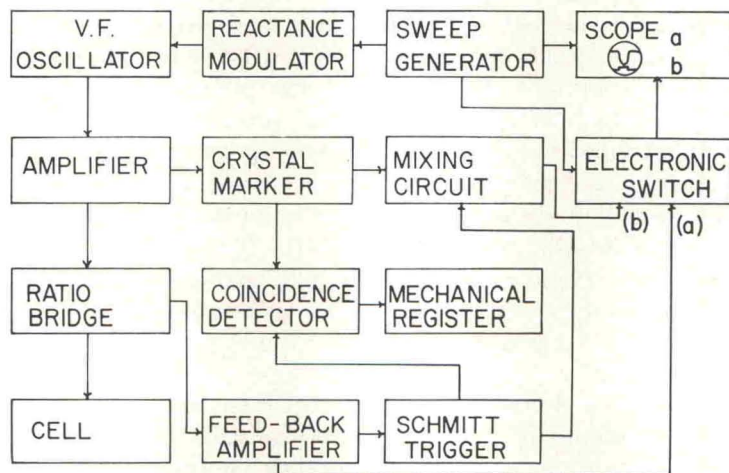


FIG. 2.—Block diagram of FM-interferometer circuits.

direction, thus avoiding backlash. It occurred to us that this might be accomplished by a slight modulation of the oscillator. The signal formerly read on the microammeter could then be applied to the vertical plates of an oscilloscope, while a uniform sweep proportional to the frequency was applied to the horizontal plates. This would give a trace with a peak at the frequency corresponding to a standing-wave system. As the reflector was moved steadily (e.g., away from the transmission plate), the maximum of the trace would move uniformly (in this case,

toward a lower frequency) until it coincided with a calibrated 4-Mc frequency marker signal. Such an arrangement not only would display the off-balance position at every instant, but also the wave form in the vicinity of a standing-wave position. This idea was discussed with Mr. George F. Siddons, Director of the Indiana University Electronics Department, who designed and supervised the construction of the frequency-modulated interferometer circuits shown in the accompanying block diagram (Fig. 2).

The variable-frequency (VF) oscillator employs a Clapp (series-tuned Colpitts) circuit, with a center frequency adjustable over the range 3.9–4.1 Mc and stable to ± 100 cps. Its frequency is varied by a reactance modulator with a band width adjustable from 0 to 24 kc. The modulator is triggered by a sweep generator operated at 60 sweeps per second to give a saw-toothed time-frequency curve.

The oscillator is connected through an amplifier (comprising two buffer stages and a power stage) to a ratio bridge consisting of three 52-ohm resistors with the cell as the fourth arm. The a-c component of the bridge output is passed through a three-stage 50-db feed-back-stabilized amplifier. The amplified signal is divided. One part passes through the electronic switch and a vertical amplifier (not shown) to appear as the upper, *a*, trace on the oscilloscope. Another part of the amplified bridge signal goes through a clipping circuit (not shown), which removes all but the highest peaks and drives a Schmitt trigger circuit which converts the input pulse to a square wave. The output from the Schmitt trigger circuit also is divided, part going to the mixing circuit and part to the coincidence detector.

A crystal marker connected to the amplifier is used to indicate a frequency of 4 Mc. This frequency is calibrated against WWV with a General Radio Type 1213-C Time/Frequency Calibrator and adjusted to 4 Mc (± 20 cps) by means of a piston-type trimmer capacitor. When the VF oscillator sweeps through 4 Mc, a crystal in the marker circuit tuned to exactly this frequency presents a low impedance path to a diode rectifier and clipper (not shown) which emits a sharp output pulse.

The output from the crystal marker circuit is divided and part is fed into the mixing circuit, part into the coincidence detector. The combined signals from the Schmitt trigger and crystal marker go from the mixing circuit to the electronic switch and appear as the lower, *b*, trace on the oscilloscope. The electronic switch is operated by the sweep generator, connected through a fly-back amplifier and a "flip-flop" circuit (neither shown). Alternate pulses of the sweep generator reverse the connections of the electronic switch and successively present to the vertical plates of the oscilloscope: (*a*) the amplified bridge signal forming the upper trace and (*b*) the output from the mixing circuit forming the lower trace.

The sweep generator consists of a gas-type discharge tube connected in a relaxation oscillator, with a frequency of 60 or 120 sweeps per second. This is coupled through an amplifier (not shown) to the horizontal plates of the oscilloscope, and also directly to the reactance modulator. Thus the sweep generator controls the electronic switch, the horizontal sweep of the oscilloscope, and the frequency modulation of the oscillator.

The coincidence detector passes a pulse whenever the square wave from the Schmitt trigger coincides with a pulse from the crystal marker circuit. The output passes through a pulse stretcher and amplifier (neither shown) to a mechanical register. A count is registered when the pulse from the Schmitt trigger coincides

with the 4-Mc crystal marker signal. The circuit is so arranged that the next count cannot occur until after the Schmitt trigger pulse has gone out of coincidence with that from the crystal marker circuit, so that each standing-wave position is counted but once.

These FM interferometer circuits have proved sensitive and reliable. In making measurements with a modulation band width of 5 kc, a 1- μ motion of the reflector 6 cm from the transmission plate shifts the oscilloscope pattern 0.83 mm, while the same motion 16 cm from the transmission plate shifts the pattern 0.36 mm. Thus the reflector is easily brought within a micron of a standing-wave position.

Experimental Methods.—The water was distilled, passed through a deionization column, and degassed by boiling to prevent formation of air bubbles in the pycnometers and on the interferometer transducer or reflector. Its specific conductance was 1.8×10^{-6} mho. The salts, with a quoted purity of 99.9 per cent, were analyzed spectrometrically and found to have <0.1 per cent metallic impurities. They were dried by prolonged heating and final fusion in a platinum crucible. Solutions were prepared by weighing dried salt and dissolving it in a weighed amount of water. All weights were calibrated, weighings were by substitution, and vacuum corrections were applied. The atomic weights were taken from the report of the International Commission of Atomic Weights (1961).⁶

The density of each solution was determined as the mean of three measurements with 30-ml Ostwald-type quartz pycnometers. These were filled carefully to avoid trapping air bubbles, equilibrated for 20 min in a water thermostat at 25.000- (± 0.005)°C, capped, washed, dried, and equilibrated at room temperature to constant weight. Their volumes were determined by the weight of water they held at 25.000°C, and its density, d_1 (see tables).^{7, 8}

Two measurements of the wavelength of sound were made in each instance, moving the reflector away from the transmission plate in one and toward it in the other, through 411 standing wave maxima, none nearer than 6 cm from the plate. The positions of the first and last 11 maxima were measured, with about every hundredth between as a check. The wavelength was then determined in one of two ways. The first involved a least-squares solution of the equation:

$$x_n = x_0 + n(\lambda/2), \quad (1)$$

where n is the ordinal number of the maximum, x_n is its position, x_0 is that of the original maximum, and the wavelength, λ , is twice the slope of the curve. The least-squares solution, utilizing all points, was programmed for our IBM 709 electronic computer. A second, almost identical method was to calculate the average positions of the first and last 11 standing wave maxima and divide the difference by 200. The velocity, u , of sound in the liquid was determined from the wavelength, λ , and frequency, f , (4 Mc) by the equation

$$u = f\lambda. \quad (2)$$

Reversal of the direction of motion of the reflector shifted the positions of the maxima about 5 μ ; but this offset made much less change in the half-wavelength distances. The two values of the sound velocity agreed to within about 0.05 m sec⁻¹, with no observable systematic difference between them.

TABLE 1
SUMMARY OF RESULTS FOR NaCl ($M_2 = 55.442$)

$c^{1/2}$	d (gm cc ⁻¹)	$10^5 \Delta d$ obs. - calc.	ΦV_2 (cc mole ⁻¹)	u (m sec ⁻¹)	$10^6 \beta$ (bar ⁻¹)	$10^8 \Delta \beta$ obs. - calc.
0.00000	0.99704 ₆	...	(16.36)	1496.5 ₅	44.780 ₈	...
0.40568	1.00345	+1, -3, -4	17.38	1507.0	43.862	+0.9
0.54589	1.00924	-2, -1, -3	17.56	1515.2	43.156	+1.6
0.72262	1.01823	-3, -3, -3	17.92	1528.9	42.011	+1.2
0.99860	1.03699	+1, +1, +1	18.44	1557.6	39.750	-0.4
1.23398	1.05731	+5, +4, +3	18.92	1588.6	37.479	-1.3
1.40198	1.07409	+4, +1, +2	19.30	1614.3	35.727	-1.3
1.69325	1.10757	0, 0, 0	19.95	1665.2	32.560	+0.1
1.81497	1.12309	-8, -4, -5	20.24	1688.5	31.229	+1.2
1.93134	1.13884	-3, -2, -3	20.49	1711.9	29.961	+1.2
2.04248	1.15469	+5, +6, +5	20.71	1735.1	28.766	+1.1
2.12947	1.16746	0, 0, -2	20.92	1753.6	27.855	-1.0
deviations		$\sigma = 4$				$\sigma = 1.1$

TABLE 2
SUMMARY OF RESULTS FOR KCl ($M_2 = 74.555$)

$c^{1/2}$	d (gm cc ⁻¹)	$10^5 \Delta d$ obs. - calc.	ΦV_2 (cc mole ⁻¹)	u (m sec ⁻¹)	$10^6 \beta$ (bar ⁻¹)	$10^8 \Delta \beta$ obs. - calc.
0.00000	0.99704 ₆	...	(26.84)	1496.5 ₅	44.780 ₈	...
0.51492	1.00947	+1, +3, +2	27.77	1510.9	43.393	-0.5
0.71405	1.02070	-2, -1, -2	28.24	1523.2	42.225	-1.8
0.99386	1.04239	+9, +9, +1	28.73	1547.0	40.082	+0.9
1.20506	1.06293	+1, +1, -1	29.27	1569.1	38.213	+0.1
1.37587	1.08225	+3, +6, +3	29.63	1589.3	36.580	0.0
1.65955	1.11917	+3, +2, +1	30.30	1627.0	33.755	-1.5
1.89158	1.15375	+7, +7, +6	30.85	1660.8	31.421	-1.1
deviations		$\sigma = 5$				$\sigma = 1.0$

The adiabatic compressibility, β_S , of the liquid was calculated from its density, d , and the sound velocity by the equation of Newton and Laplace:

$$\beta_S = -(\partial \ln V / \partial P)_S = 1/u^2 d. \quad (3)$$

Here V , P , and S , are volume, pressure, and entropy, respectively.

Results.—These are shown in Tables 1 and 2. Each molarity, c , is calculated from the weights of the components and the average of the measured densities (self-consistent to about 0.001%). The densities of the solutions are represented by cubic equations in $c^{1/2}$, fitted by the method of least squares:

$$d = d_1 + 4.2129 \times 10^{-2}c - 2.028 \times 10^{-3}c^{3/2} - 5.07 \times 10^{-5}c^2 \quad (\text{NaCl}), \quad (4)$$

$$d = d_1 + 4.7795 \times 10^{-2}c - 1.807 \times 10^{-3}c^{3/2} - 16.69 \times 10^{-5}c^2 \quad (\text{KCl}). \quad (5)$$

These give quadratic equations in $c^{1/2}$ for the apparent molar volume,

$$\Phi V_2 = v_1[M_2 - 10^3kc^{-1}(d - d_1)] \quad \text{cc mole}^{-1}, \quad (6)$$

when v_1 is the specific volume of solvent in gm cc^{-1} , M_2 the solute molecular weight, and $k = 1.000028 \text{ cc ml}^{-1}$. Our equations for d reproduce the classic results of Baxter and Wallace⁹ and later more precise work of Kruis,¹⁰ Geffken and Price,¹¹ and MacInnes and Dayhoff¹² as well as they do our own. Our values of ΦV_2° may be compared with those reported in the last three papers: 16.60 cc mole^{-1} for NaCl¹⁰ (corrected to current values of M_2 and d_1), and 26.81¹¹ and 26.50¹² cc mole^{-1} for KCl.

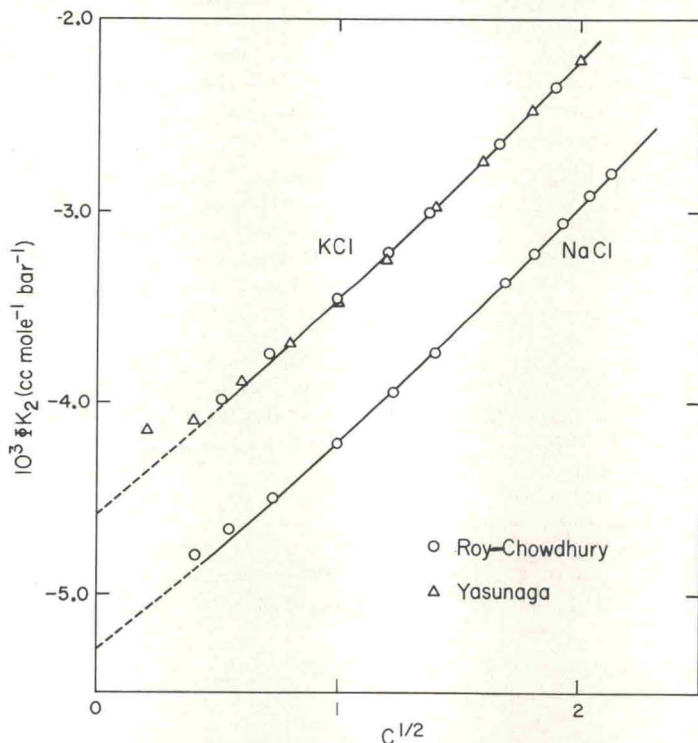


FIG. 3.—Apparent molar adiabatic compressibilities of NaCl and KCl.

The mean of our nine determinations of the velocity of sound in water at 25°C, $u_1 = 1496.55 \text{ m sec}^{-1}$ ($\sigma = 0.035 \text{ m sec}^{-1}$), agrees quite well with 1496.73 ($\sigma = 0.05$) m sec^{-1} found by Owen and Simons.¹³ The compressibilities of the solutions also are represented by cubic equations in $c^{1/2}$, fitted by the method of least squares.

$$\beta = \beta_1 - 6.0112 \times 10^{-6}c + 8.827 \times 10^{-7}c^{3/2} + 8.85 \times 10^{-8}c^2 \quad (\text{NaCl}), \quad (7)$$

$$\beta = \beta_1 - 5.7596 \times 10^{-6}c + 9.519 \times 10^{-7}c^{3/2} + 6.21 \times 10^{-8}c^2 \quad (\text{KCl}). \quad (8)$$

These yield quadratic equations for the apparent molar adiabatic compressibility,

$$\Phi K_2 = v_1[M_2\beta_1 - 10^3kc^{-1}(d\beta_1 - d_1\beta)] \quad \text{cc bar}^{-1} \text{ mole}^{-1}. \quad (9)$$

Plots of ΦK_2 for the two salts in Figure 3 include results for KCl obtained by Dr. Tatsuya Yasunaga of the University of Hiroshima with an earlier apparatus in our laboratory. He found $u_1 = 1496.92 \text{ m sec}^{-1}$, hence his values of u were multiplied by $(1496.55/1496.92)$ to put them on a common basis with our results. Since no systematic difference was found between the two series, his values of β and d were combined with ours to determine the coefficients of the empirical equations.

The Debye-Hückel limiting law predicts that ΦK_2 is a linear function of $c^{1/2}$ in very dilute solutions, with the same limiting slope for all salts of the same valence type. However, the theoretical slope depends upon pressure derivatives of the dielectric constant which are not known with sufficient accuracy, and we must rely upon extrapolation to zero concentration with empirical equations until the experimental limiting slope can be determined by more accurate measurements of sound velocities and densities now under way in our laboratory.

It is a pleasure to acknowledge our indebtedness to Mr. Maurice Williams for construction of most of the mechanical apparatus here described, to Mr. George Siddons and Mr. Gerald L. Stout for the electrical equipment, to Dr. Richard K. Leininger for the spectroscopic analyses, and to Dr. David Hill for help with the calculations and preparation of the paper.

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