

taking that of air from standard tables, lead capacitances were eliminated giving a vacuum capacitance  $C_0 = 4.356$  pF. (b) The cell was filled with a dilute solution of tetra-ethyl ammonium iodide in ethanol, and the resistance  $R$  of this solution was measured at 25° with a Leeds and Northrup Jones-Dike conductance bridge. The conductance  $\kappa$  of the solution was also measured in normal calibrated conductance cells. The cell-constant  $J$  of the capacitance-cell was then calculated as  $J = R\kappa$ . Since the electric field distribution is the same whether the cell is used for conductance or capacitance, the corresponding cell constants are related by

$$JC_0 = 8.854 \times 10^{-16} \text{ farad m}^{-1}.$$

This method also yielded  $C_0 = 4.356$  pF. For other temperatures and pressures, values of  $C_0 = 4.356$  pF. For other temperatures and pressures, values of  $C_0$  were calculated from the thermal expansion coefficients and compressibilities of platinum and Pyrex and the geometry of the cell.

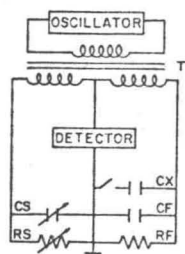


FIG. 2.—Transformer bridge.

#### TRANSFORMER BRIDGE

A balanced, screened equal-arm transformer  $T$  (fig. 2) was specially built for bridge use. It was energized by an oscillator providing several volts at 10-520 kHz. The out-of-balance signal from the bridge was displayed on an oscilloscope. The standard arm of the bridge consisted of a calibrated General Radio 722 D precision capacitor  $CS$ , in parallel with a resistance-balance element  $RS$  which was specially designed to show a negligible capacitance-change with change of resistance setting.  $CF$  and  $RF$  were fixed capacitance and resistance elements used to bring the standard arm readings to a suitable point on the scale.  $CX$  represents the dielectric cell, which could be switched in or out by unplugging a coaxial cable. An alternative substitution mode of the bridge was also available and was used for some of the measurements; the extrapolated capacitances in this mode agreed with the direct-reading ones within the reading uncertainty. A parallel  $R-C$  network with set values can match the impedance of the capacitance-cell at all frequencies only if the equivalent circuit of the cell is also a parallel  $R-C$  network. This is an oversimplification for any real cell containing a conducting liquid, because of the unusual frequency dependence of the Warburg impedance  $W$  of the solution-electrode interface (fig. 3). However, the coating

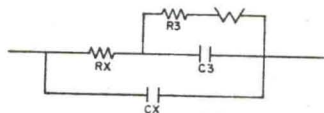


FIG. 3.—Network electrically equivalent to capacitance cell.

of the electrodes with platinum black has the effect of shunting this awkward component of the impedance by a large simple capacitance  $C3$ , greatly reducing its influence on the apparent values of  $CX$  and  $RX$ . Graphs of the capacitance in the substitution network against  $f^{-1}$  ( $f$  = frequency) were linear within 0.02% over the range 10-520 kHz and the total change in capacitance over this range was only 0.15%. Values extrapolated to infinite frequency on such graphs (fig. 4) were used in calculating all permittivities reported here.

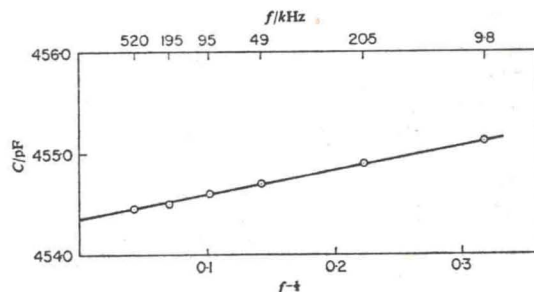


FIG. 4.—Frequency dependence of capacitance; formamide at 45°C, 1 bar.

Since there is no dispersion in the frequency-range used, the permittivities so obtained are static values. The validity of the extrapolations is indicated by the fact that for most of the samples used the resistive component  $RX$  of the cell impedance decreased with time (owing to ionic contamination) without affecting the constancy of the extrapolated capacitance. In tests with water, the same results were obtained for highly purified water of conductance  $8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ , and a relatively contaminated sample of conductance  $\sim 1 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of the cell contents could drop to a few hundred ohms without affecting the extrapolated capacitance readings.

TABLE 2.—DIELECTRIC CONSTANTS OF WATER AT 1 BAR IN THE TEMPERATURE RANGE 5-65°C

$t/^\circ\text{C}$	$\epsilon$	$\delta\epsilon$	$-10^4 (\partial \ln \epsilon / \partial t)_p = 1 \text{ bar}$
5	85.75 <sub>2</sub>	0.005	4.54 <sub>2</sub>
10	83.82 <sub>2</sub>	0.003	4.54 <sub>2</sub>
15	81.97 <sub>2</sub>	-0.025	4.54 <sub>7</sub>
20	80.10 <sub>0</sub>	0.005	4.54 <sub>8</sub>
25	78.30 <sub>0</sub> *	0.000	4.54 <sub>8</sub>
30	76.54 <sub>1</sub>	0.003	4.54 <sub>8</sub>
35	74.81 <sub>0</sub>	0.005	4.54 <sub>6</sub>
40	73.15 <sub>0</sub>	-0.008	4.54 <sub>4</sub>
45	71.50 <sub>3</sub>	-0.004	4.54 <sub>1</sub>
50	69.89 <sub>3</sub>	0.002	4.53 <sub>7</sub>
55	68.33 <sub>6</sub>	-0.008	4.53 <sub>2</sub>
60	66.80 <sub>2</sub>	-0.004	4.52 <sub>0</sub>
65	65.30 <sub>3</sub>	0.002	4.51 <sub>0</sub>

$\epsilon$  (1 bar) =  $87.727 - 0.398 t + 8.699 \times 10^{-4} t^2 - 7.948 \times 10^{-7} t^3$  (1).  $\delta\epsilon = \epsilon$  (eqn (1)) -  $\epsilon$ .

\* calibration point.