Self-balancing high-precision ac Wheatstone bridge for observing diffusion processes in electrolyte solutions

H. J. Kiggen and H. Laumen

Institut für physikalische Chemie, Abteilung Biopolymere, RWTH Aachen, Wüllnerstr. 1, D-51 Aachen, West Germany

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To observe long-time diffusion experiments in electrolyte solutions a self-balancing ac Wheatstone bridge has been built up. The bridge has six decimal places of controllable R and C decades; a resolution of 10^{-6} is achieved. The balancing of the bridge is done by a microcomputer system.

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INTRODUCTION

The electrical conductivity is often used as a characteristic and easily accessible quantity for monitoring physico-chemical processes.

To measure conductivities, manually balanced ac bridges with a resolution of 10^{-6} are available. Conductivities depending on time are usually measured by self-balancing bridges. The bridges have an accuracy of only 10^{-4}. For high precision measurements, however, this accuracy is not sufficient. This paper describes a self-balancing ac Wheatstone bridge of high precision.

The bridge and the peripheral units are controlled by an ordinary microcomputer system. The results of the measurements are given to a printer or paper tape punch. The self-balancing bridge was designed to observe diffusion experiments in electrolyte solutions. The changes in concentration depending on time are measured through the ohmic part of the impedance.

I. DESCRIPTION OF THE SELF-BALANCING BRIDGE

The Wheatstone bridge consists of two reference resistors, resistor and capacitor decades (R_d, C_d), the impedance to be measured (Z_x), an oscillator, a bandpass amplifier, and a voltage measurement device (see Fig. 1).

The balancing of the bridge is done by varying the R and C decades so that the balancing voltage V_b reaches the minimum. In this case, the impedance to be measured and the R and C decades have the same ratio as the reference resistors.

In our self-balancing bridge the variation of the decades is done by a microcomputer system.

The conductivity cells for electrolyte solutions usually have a resistivity between 1000 and 8000 Ω. To measure these resistivities with a resolution up to 10^{-6}, R decades with six decimal places from 0.01 Ω to 1 kΩ are necessary. The elements of the decades are switched by reed relays. The reed relays have a transition resistivity of 50 mΩ (±10%), which is in the range of the lowest decimal place. To transfer the transition resistivity below the range of the decades, we chose decade resistor values from 0.1 Ω up to 10 kΩ.

To measure resistivities in the requested range of 0.01 Ω–10 kΩ, a ratio of 1:10 for the reference resistors is necessary.

It is observable that with any combination of decade values, the decade array has an additional resistance

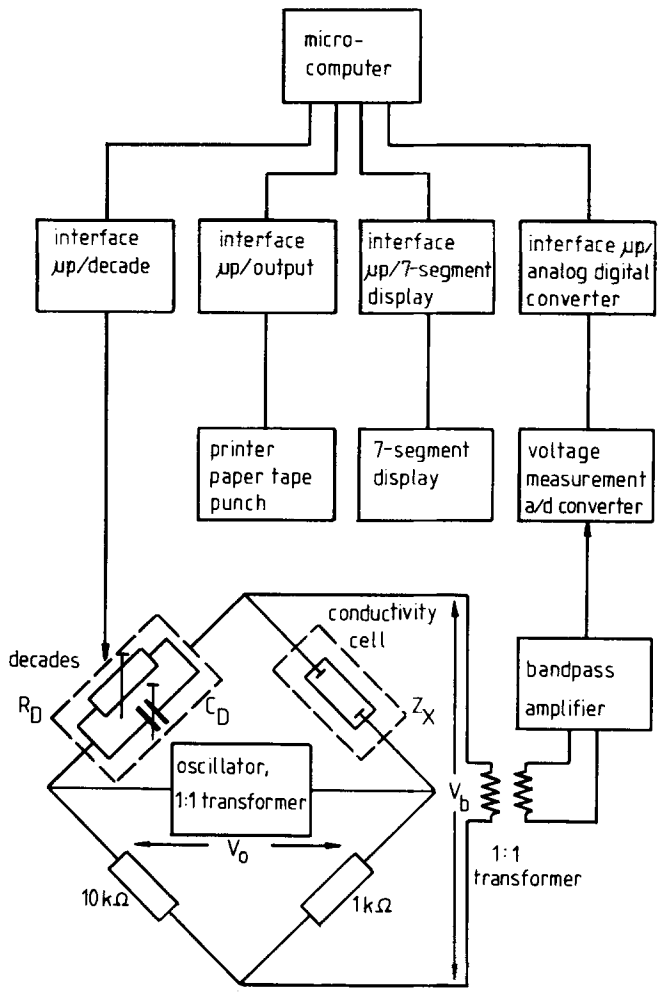

FIG. 1. Block diagram of the self-balancing bridge. The balancing voltage V_b of the Wheatstone bridge is filtered, measured, and then registered by the microprocessor. The values of the R_D and the C_D decades are changed by the microprocessor in order to minimize V_b. When the minimum of V_b is reached, the result of the balancing (R_D) is output by the microprocessor.

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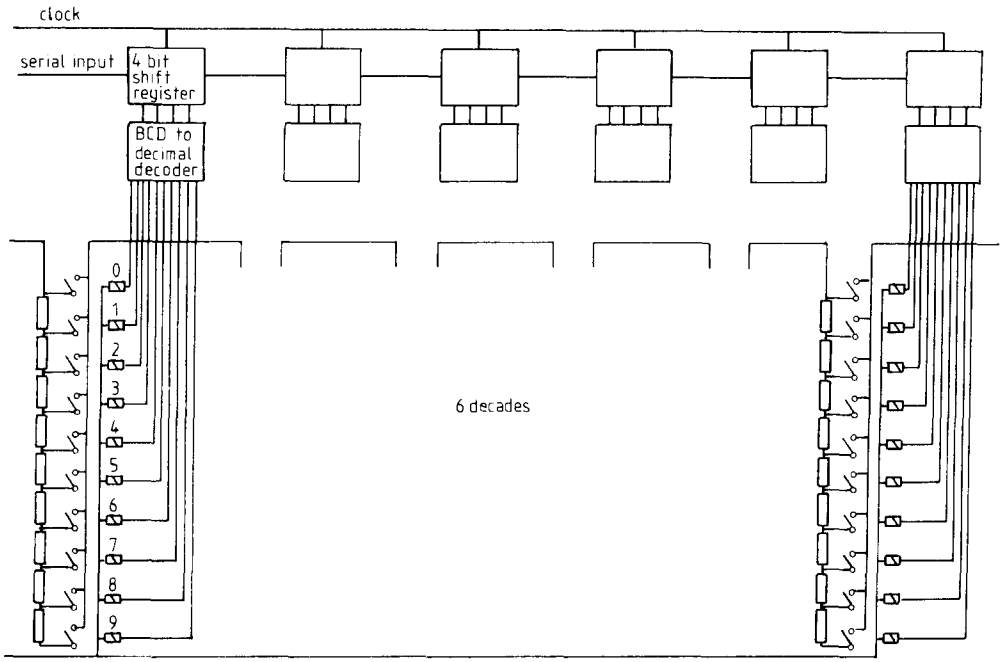


FIG. 2. Schematic of the R decades and the interface. The serial output of the microprocessor is converted into parallel data by the six 4-bit shift registers (6 IC 7495). The resistors of the decades are switched by reed relays. The relays are driven by BCD to decimal decoders (6 IC 7442).

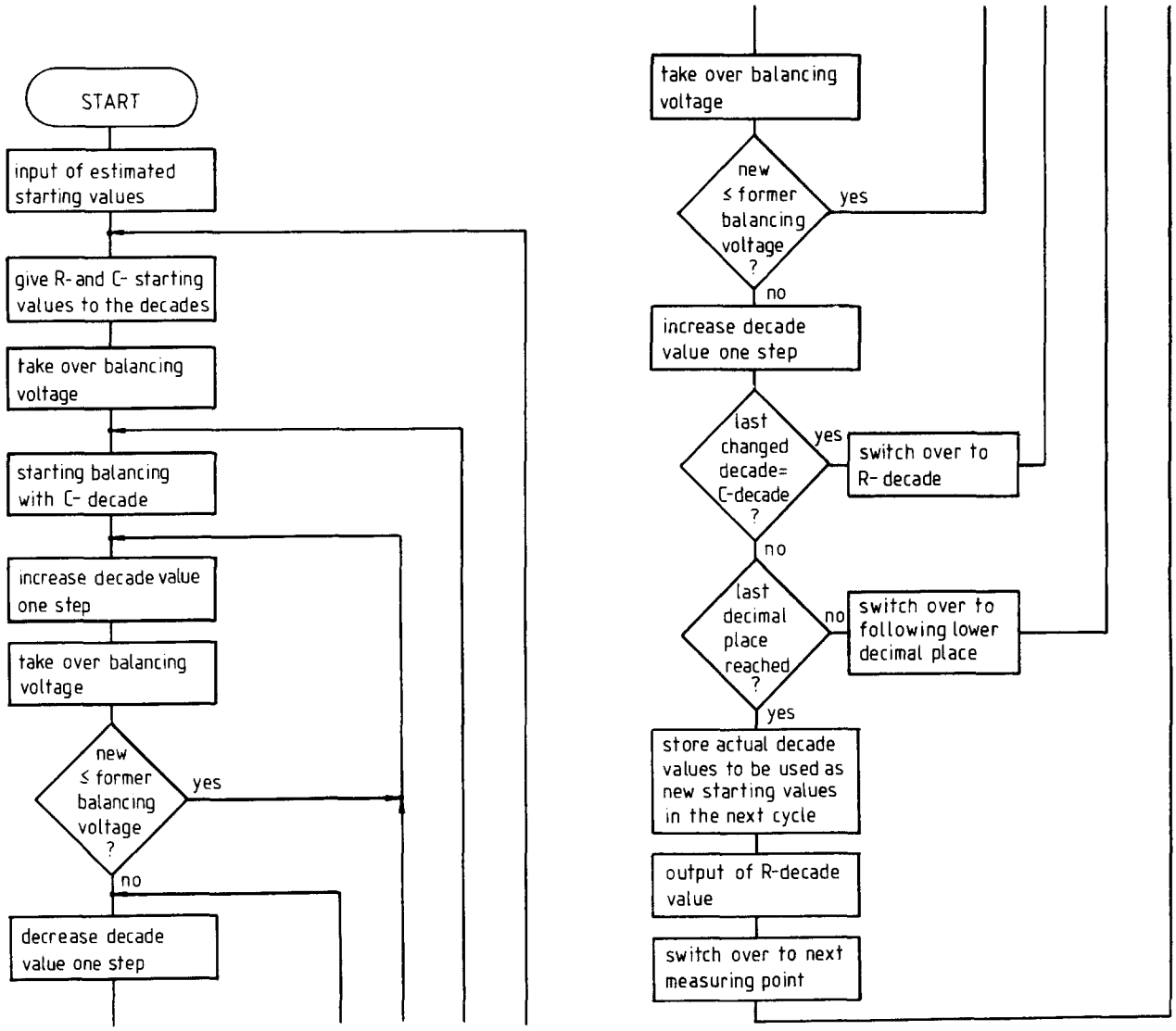


FIG. 3. Flow diagram of the balancing procedure.

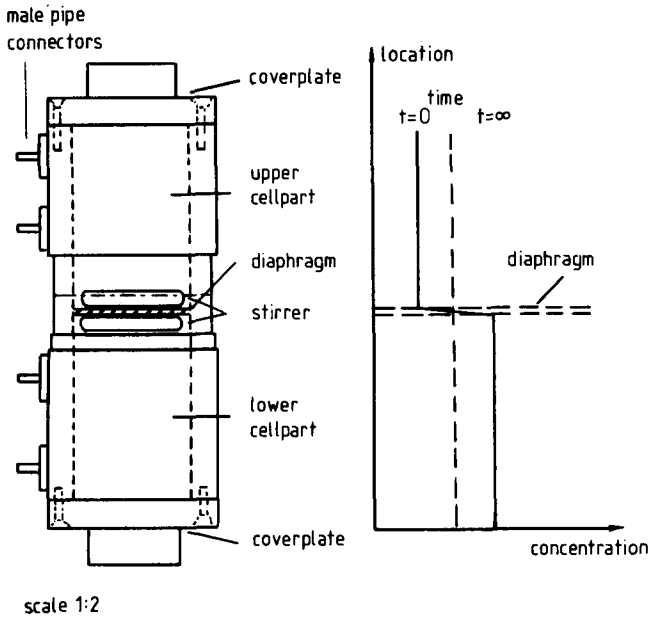


FIG. 4. Schematic of the diaphragm cell; concentration profiles for time $t = 0$ and $t = \infty$. The cell is divided into two equal parts by a diaphragm. The solutions in each cell part are stirred. The experiment starts with a concentration gradient between the two cell parts. The gradient decreases exponentially with time. To determine the concentrations the conductivities are measured. Therefore the solutions are pumped from the diaphragm cell to the conductivity cells.

of 0.3 Ω caused by six reed relays; therefore, the resistivity found for the impedance to be measured must always be corrected by 0.03 Ω.

For our bridge we used precision resistors with a tolerance of ±0.02% in the kΩ range. The tolerances for the lower ranges were ±0.1% and ±0.05%.

The resistors for the two upper decimal places were selected to keep the tolerance range smaller.

The temperature coefficient was $1 \cdot 10^{-5}$/°C for all resistors; therefore, the ambient temperature of the bridge should not vary more than 1 °C.

The impedance of an electrolyte solution has an ohmic and a capacitive part. Thus the balancing of both parts must be done.

For calculation of the concentration, only the ohmic part is of interest; therefore, the tolerance ranges of capacitors need not be as small as those of the resistors (selected capacitors: 1 pF . . . 0, 1 μF, tolerance: up to 15%).

The bridge is fed by a sine wave generator with a frequency of 2 kHz and an amplitude of 5 V.

The bandpass amplifier has the following data:

middle frequency:	2 kHz
bandwidth:	100 Hz, 6 dB
amplification:	80 dB.

The amplified balancing voltage is input into an analog to digital converter (kontron DMM 3003, basic accuracy ±0.06%, rise time 3 s).

To separate the bridge from ground potential, two 1 : 1 transformers are used. The bridge is controlled by a KIM I microcomputer system. KIM I:

processor:	MCS 6502 (MOS), 8bit
memory:	1 kbyte RAM 2 kbyte ROM

The balancing program is stored in a 2-kbyte EPROM. Interfaces are necessary to adapt the bridge to the microcomputer.

The interface between KIM I and the R and C decades is a 24-bit serial to parallel converter with a BCD to decimal decoder (see Fig. 2). The reed relays are directly driven by the BCD to decimal decoder. The interface between KIM I and the A/D converter is a 16-bit parallel to serial converter (IC's: 4 × SN 74LS95). The result of the balancing procedure (the resistivity of the conductivity cell) is given to a printer via an interface consisting of a 24-bit serial to parallel converter as described before.

II. DESCRIPTION OF THE BALANCING PROCEDURE

The microcomputer begins the balancing procedure with roughly estimated values for the decades. According to these values the microcomputer selects the relays of the decades and registers the resulting balancing voltage. Now the microcomputer increases the highest decimal place of the R decade by one step.

If the resulting balancing voltage is lower than before, the microcomputer continues changing the R decade in this direction. If the balancing voltage is higher than before, the direction of change was wrong and the microcomputer has to decrease the R decade by one step.

If the minimum for the first decimal place of the R decade is found, the same procedure begins for the first decimal place of the C decade, then for the second decimal of the R decade, and so on.

The absolute minimum of the balancing voltage is found when the lowest decimal places are balanced. The values of the R and C decades by which the minimum was reached are stored by the microcomputer and the ohmic part is printed out.

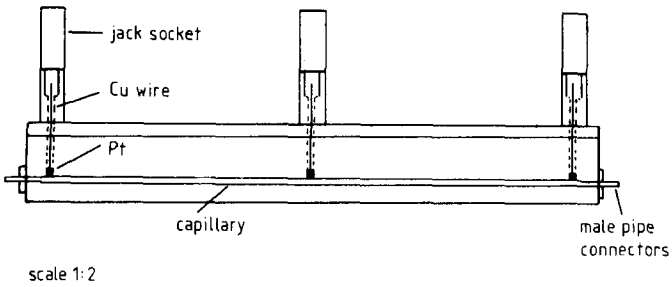
The microcomputer then starts the balancing for the next measuring point.

In our diffusion experiments we have three measuring points: two conductivity cells and a thermocouple for temperature surveillance during the experiment.

When the microcomputer has reached the first measuring point again, it starts the new balancing with the stored values of the previous cycle.

With these new starting values the minimum is reached in a few steps since the concentration and resultant conductivity changes only slightly with time during our diffusion experiments.

The average time for one balancing procedure is two minutes. This is mainly limited by the rather slow A/D converter utilized. For our experiments this working speed is sufficient. If higher working speed is



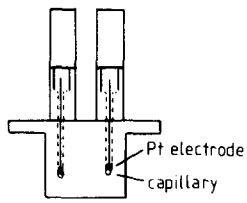


FIG. 5. Conductivity cell. The solution from one diffusion cell part flows through one capillary of the conductivity cell and passes three black platinized Pt electrodes.

required, a faster A/D converter should be used. The flow diagram (Fig. 3) shows the described balancing procedure in a simplified form.

III. REPRODUCIBILITY

The reproducibility of the bridge has been checked on a metal film resistor of about 2 kΩ. The ambient temperature of the bridge and the resistor was held constant at 25° ± 1 °C. The result of 20 measurements was 2007.34 Ω ± 0.02 Ω; therefore, the reproducibility of measurements on a pure ohmic resistor is about $1 \cdot 10^{-5}$.

IV. DIFFUSION EXPERIMENTS MONITORED BY THE SELF-BALANCING BRIDGE

Diffusion in electrolyte solutions is measured with the help of the well-known diaphragm cell,[1] which is shown in Fig. 4. Our diffusion cell is made of lucite and is divided into two equal parts by a porous diaphragm (Fig. 4). At the beginning of the experiment there is a concentration gradient between the two cell parts.

The concentration gradient decreases exponentially with time. With the usual cell dimensions this process of equalization takes several days. To determine the concentration with time, the electrical conductivity has been measured with the self-balancing bridge.

The conductivity is measured outside the diffusion cell in a specially designed conductivity cell (Fig. 5).

The conductivity cell is made of lucite. The Pt electrodes are black platinized.

The solution from one diffusion cell part is pumped through one capillary of the conductivity cell, passes three Pt electrodes, and flows back into the diffusion cell part.

The outer jack sockets are connected and therefore have the same electrical potential against the middle electrode. With this arrangement of electrodes, there is no electric current outside the conductivity cell (piping, diaphragm cell). The whole experimental setup (diffusion cell, conductivity cell, connecting pipes, pump) is placed in a water-filled bath at a constant temperature of 25 °C ∓ 0.005 °C.

The continuous flow avoids a warmup of the solution in the conductivity cell.

The resistance of the two parts of the conductivity cell in a 0.5 N KCl solution was:

$$R_1 = 1702.25\ \Omega \pm 0.05\ \Omega,$$

$$R_2 = 1732.81\ \Omega \pm 0.06\ \Omega.$$

These values were derived from 20 measurements, each made in a time frame of two hours. During that time the temperature stability was better than ±0.002 °C.

For the evaluation of binary diffusion experiments the logarithm of the difference between the conductivities of the solutions in the lower (χ_B) and in the upper (χ_T) cell part is plotted vs time.

The solutions in the two cell parts have rather equal temperature coefficients; therefore, by plotting the differences between the two conductivities, the influence of slight temperature variations are mainly eliminated.

The least square fit gives the slope of the straight line; the slope is directly proportional to the diffusion coefficient of the solution.[2,3]

The relative error of a single $\ln(\chi_B - \chi_T)$ value is 10^{-4}. One value of $\ln(\chi_B - \chi_T)$ includes errors of four resistivity measurements: the R_T and R_B measurements and the two resistivities measured for determination of the cell constants of the conductivity cells.

Therefore the accuracy of the bridge has to be 10^{-5}. With the self-balancing bridge and our special diaphragm cell, it is possible to measure diffusion coefficients with a reproducibility of 10^{-3}.[4]

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