We have suggested a simpler device (see diagram) for this purpose, its advantage being that the number of parts to be made in the workshop is reduced to a minimum, the instrument being based on the commercial PPZ-10 rotary selector switch, size I.[2] Three of the seven insulators of the switch are removed and replaced by the starting mechanism *2* mounted on the bracket *1*. A laminated plastic ("Textolite") cam *4* is fitted tightly on the square spindle *3* of the switch, its shape being evident from the diagram. One of the vertices of the cam presses tightly against the push-rod *5*, the conical end *6* of which rests in the starting knob *7* of the stop-watch *8*. The push-rod moves along the guiding sleeve *9* and has both a return spring *10* and a damping spring *11*. A 1SO stop-watch, which has a stop knob at the side, was used.

The PPZ-10 switch is fitted with a mechanism for instantaneous switching[2]. When the knob of the switch is rotated, the cam is also rotated through 90° almost exactly at the same time as the current in the heater circuit is switched on; as the cam rotates, the knob of the stop-watch first leaves its original position, and then returns to it, thus starting the stop-watch. In order to disconnect the heater, a fresh rotation of the knob of the switch turns the cam again through 90°; thereby both the stop-watch and the supply of current to the heater circuit are stopped simultaneously.

The changeover switch has four terminals, the heater circuit being connected to one pair, and an auxiliary circuit of the same resistance to the other pair. This enables the heater to be replaced by another equal resistance when the former is switched off, so that the steady discharge of the accumulator is not disturbed.

In order to make better contact, it is advisable to silver both the movable and the fixed contacting parts of the switch.

Any of the available block switches may be used to make this device, with appropriate change in the arrangement of the movable contacts. Furthermore, the use of multipole switches enables several circuits to be closed or opened at the same time as the stop-watch is started.

The instrument was calibrated by means of a type 21P recording chronograph, the results of the test being set out in the Table. It can be seen that, when the measured time interval did not exceed 10 min, the difference between the stop-watch and the chronograph readings was < 0.1 sec. With greater time intervals this difference reached 0.2–0.3 sec, and even 0.8 sec (after 1 h). This increase in the discrepancy between the chronograph readings and those of the proposed device as the measured time interval becomes longer can be explained by the error in the functioning of our stop-watch, which was confirmed on checking the stop-watch against radio time signals.

Thus the proposed device enables time intervals to be measured within error of 0.1 sec for every 10 min, which is a quite adequate accuracy in many calorimetric measurements. In particular, this device has been used by us in a series of determinations of the heat capacity of liquids, and has proved to be quite satisfactory.

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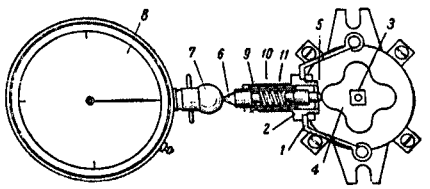

Diagram of device.

TABLE.

Measured time interval, sec		Difference, sec	Measured time interval, sec		Difference, sec
according to stop-watch of device	according to chronograph		according to stop-watch of device	according to chronograph	
600.1	600.180	0.08	1800.1	1800.309	0.21
600.3	600.380	0.08	1800.2	1800.441	0.22
600.1	600.192	0.09	1800.0	1800.248	0.25
1200.2	1200.354	0.15	3600.0	3600.841	0.84
1200.0	1200.208	0.21	3600.1	3600.848	0.75
1200.2	1200.338	0.14	3600.1	3600.792	0.69

USE OF AN OSCILLOGRAPHIC POLAROGRAPH TO DETERMINE ZERO-CHARGE POTENTIALS

B. B. Damaskin and O. A. Petrii

If a test electrode approaches an ideally polarisable electrode in properties[1], the equivalent circuit of the electrochemical cell can be represented by the capacity C of the double layer and the resistance R of the solution† connected in series (Fig. 1*a*). If a linearly varying voltage is then applied to the cell (Fig. 1*b*), a current I_C will flow through the circuit, the magnitude of which can be found from the equation

$$R\frac{dI_C}{dt} + \frac{I_C}{C} = v, \qquad (1)$$

where t is time and v the rate of change of the voltage. If the resistance R can be neglected, it follows directly from Eqn. (1) that the charging current observed by means of an oscillographic polarograph using a sawtooth or a triangular voltage will be proportional to the capacity of the double

† In work with a dropping electrode the quantity R includes also the resistance of the mercury in the capillary.

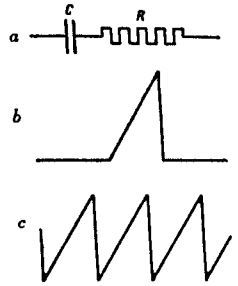

Fig. 1. *a*) Equivalent electrical circuit of a cell with an ideally polarisable electrode; *b*) and *c*) forms of sawtooth voltage.

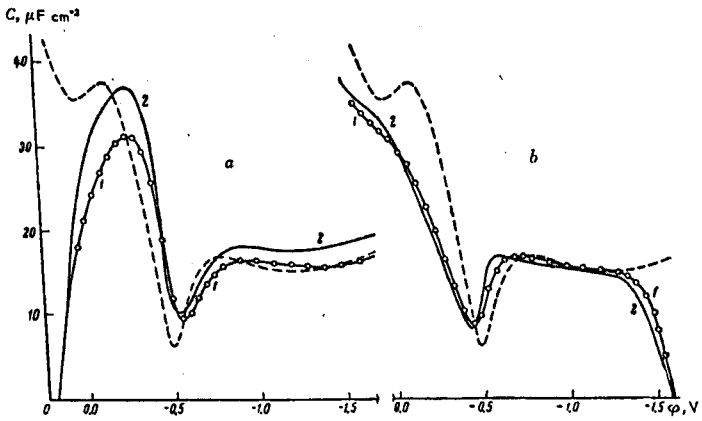

Fig. 2. Curves showing the variation in capacitive current in 0.001 *N* Na_2SO_4 with a linear change in voltage: *a*) negative variation in potential (φ_{init} = 0.2 V); *b*) positive variation in potential (φ_{init} = -1.6 V); v = 16 V sec^{-1}; arrests between drops 4 sec; 1) calculated from Eqn. (2); 2) experimental curve; broken curve — variation in differential capacity (bridge method, 400 c/s).

layer[2]. The method of measuring this capacity in concentrated electrolyte solutions by means of an oscillographic polarograph was worked out in ref. 3, and was applied to a study of the adsorption of a series of saturated alcohols on mercury[4].

In the case of dilute solutions, however, the quantity R is large, and Eqn. (1) must be solved to find I_C. If the variation of the capacity of the double layer with the electrode potential φ is allowed for, $C = C(\varphi) = C(t)$, the solution of Eqn. (1) is of the form

$$I_C = \frac{v}{R}\exp\left(-\frac{\rho}{R}\right)\theta, \qquad (2)$$

where

$$\rho = \int_0^t \frac{dt}{C(t)} \text{ and } \theta = \int_0^t \exp\left(\frac{\rho}{R}\right)dt.$$

Substitution of C = const in the expression for ρ leads to a trivial equation for the capacitive current passing through a circuit having constant capacity and resistance when a linearly varying voltage is applied to it‡:

$$I_C = vC(1 - e^{-t/RC}) = vC(1 - 10^{-|\varphi - \varphi_{init}|/2{,}3RCv}). \qquad (3)$$

The variation of the capacitive current with time according to Eqn. (2) cannot at present be expressed analytically, since in general the dependence of C on φ, and hence on t, cannot be represented by any algebraic equation. However, the variation of the capacity of the double layer with potential can be determined experimentally, from bridge measurements for example, and then it is not difficult to calculate ρ and θ by numerical integration of plots of $1/C(t)$ and $\exp(\rho/R)$ against t. If the values of ρ and θ obtained in this way are substituted in Eqn. (2), it is possible to calculate the dependence of I_C on t.

We have determined the differential-capacity curves at a dropping mercury electrode in 0.001 *N* Na_2SO_4 solution by an impedance-bridge method[6], and from the results have calculated by means of Eqn. (2) the dependence of the capacitive current on time. The value of R was at all potentials 11.8×10^3 ohms. The results are plotted in Fig. 2, where the ordinates also represent I_C/vS (S = surface area of electrode) for comparison with the differential-capacity curve. The graph includes also experimental curves which we obtained in 0.001 *N* Na_2SO_4 with a TsLA oscillographic polarograph (model 01);[7] Fig. 2*a* corresponds to the cathodic "tooth" (φ_{init} = 0.2 V relative to the saturated calomel electrode), and Fig. 2*b* to the anodic voltage (φ_{init} = -1.6 V). The rate of change of voltage v was 16 V sec^{-1} in our experiments§. An individual sawtooth pulse (Fig. 1*b*), synchronised with the separation of the drop, was applied with arrests of 4 sec between drops. This was possible since the TsLA oscillographic polarograph allows the supply of a sawtooth pulse to be synchronised with the separation of a mercury drop in quite dilute solutions (0.001 *N*). If, however, synchronisation is impossible, measurements must be made with continuous scanning, in which sawtooth pulses are supplied at fixed intervals (0.5 or 1.0 sec).

Doubly distilled water and mercury were used in the work; the Na_2SO_4 was recrystallised twice from the redistilled water, and then ignited. The solution was carefully freed from dissolved oxygen by means of hydrogen which had passed through a liquid-nitrogen trap.

‡ A more complicated solution is obtained when a high-frequency sawtooth voltage is used (Fig. 1*c*)[5].

§ It is evident from Eqn. (3) that the deviation of the recorded capacitive current from the value vC is smaller, the lower is v and the greater the interval from the initial potential φ_{init}. In differential-capacity measurements with an oscillographic polarograph, therefore, comparatively low values of v should be used, as was done in refs. 2-5. On the other hand, diminution in v leads to an undesirable distortion of the results owing to the presence of a residual faradaic current I_f, due to the reduction of traces of impurities in the solution and proportional to $v^{\frac{1}{2}}$, so that $I_C/I_f \propto v^{\frac{1}{2}}$. Therefore in measurements of the variation of I_C with t by means of an oscillographic polarograph it is necessary to purify the solutions carefully from traces of impurities and to use an optimum value of v.

Fig. 2 shows a considerable divergence between the curves of C and of I_C/vS plotted against φ, although the latter also show a minimum close to the zero-charge point[8]. For the anodic change in potential, the experimental results agree well with calculation (Fig. 2*b*). For the cathodic change in potential, the agreement between calculation and experiment is not quite as good, since during the arrest before application of a "tooth" the electrode is maintained at $\varphi_{init} = 0.2$ V (relative to saturated calomel electrode), at which potential there is apparently some dissolution of the mercury, leading to an increase in the residual current and hence to distortion of the plot of I_C against φ.

It follows from Eqn. (1) that at extremal points on the $I_C-\varphi$ (or I_C-t) curves $C = I_C/v$, since at these points $dI_C/dt = 0$. It can be seen from Fig. 2 that the calculated curves of I_C/vS against φ actually intersect the $C-\varphi$ curve at the maxima and minima. In addition, it follows from Fig. 2 that the values of I_C/vS at the minima close to the zero-charge point only slightly exceed the minimum values of the capacity on the $C-\varphi$ curves, while the potentials of the minima in the capacitive current with cathodic and anodic voltages (φ'_{min} and φ''_{min}) differ by approximately 40–50 mV (on the negative and the positive sides respectively) from the potential of the minimum in the $C-\varphi$ curve, which in the absence of specific adsorption corresponds to the zero-charge point (φ_0). Therefore we can assume with some degree of approximation that

$$\varphi_0 \simeq \frac{1}{2}(\varphi'_{min} + \varphi''_{min}). \qquad (4)$$

In fact the potentials of the minima in the experimental curves are respectively $\varphi'_{min} = -0.54$ V and $\varphi''_{min} = -0.44$ V, whence according to Eqn. (4) $\varphi_0 \simeq -0.49$ V (relative to the saturated calomel electrode), which coincides with the potential of the minimum in the $C-\varphi$ curve (Fig. 2), and agrees satisfactorily with the accurate value of the zero-charge point in Na_2SO_4 solution, -0.473 V.[9]

Thus when the conditions of an ideally polarisable electrode are realised and a sawtooth voltage is used, the recording of oscillograms in dilute solutions of electrolytes which are not adsorbed can serve as a method for the approximate determination (to within 10–20 mV) of zero-charge potentials. In virtue of the rapidity of this method, it may prove useful in determining zero-charge points of solid metals, where the surface changes occurring with time make it difficult to measure $C-\varphi$ curves by means of an impedance bridge.

In conclusion we express our deep gratitude to Academician A. N. Frumkin for a thorough check of the manuscript.

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A STABILISED RECTIFIER FOR THE POWER SUPPLY TO MEASURING CIRCUITS

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The anodic voltage of the valves in measuring circuits supplied from the mains is usually stabilised by means of a gas-discharge tube. The current supplied through the heaters is not stabilised, however, which in many cases lowers the overall stability of the instrument.

The circuit shown in Fig. 1 ensures stabilisation of both the anodic voltage and the voltage across the heaters. The primary coil of the rectifier transformer *Tr* is connected in series with the coil *4–4* of the choke *Ch*, the inductive impedance of which depends on the currents flowing through the magnetising coils of the choke, *5–5* and *6–6*. During mains voltage variations the current in the *6–6* coil, connected in series with the stabilitron, alters also and, by changing the inductance of the choke, maintains the voltage across the primary coil of the transformer constant.

The saturable reactor *Ch* is constructed on a three-rod former (Fig. 2). The a.c. coil *4–4* is mounted on the two outer rods. The d.c. coils *5–5* and *6–6* are mounted on the central rod and are connected in such a way that their magnetic fluxes are opposed. However, coil *5–5* has a greater number of ampere-turns than coil *6–6* and ensures constant magnetisation of the choke.

With increase in the mains voltage, the rectified voltage also increases and the current passing through the stabilitron and the control coil *6–6* becomes several times greater. The overall magnetisation of the choke is reduced, its inductive impedance increases, and the excess mains voltage is damped out by the choke. With a decrease in the mains voltage, the demagnetising current through coil *6–6* is

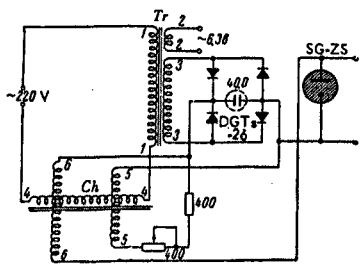

Fig. 1.