

VERSATILE AUTOMATIC COULOMBMETER

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Abstract

The apparatus is suitable for following reactions in which one of the reaction partners is a gas, the consumption of this being replaceable by electrolysis. The volume of gas reacted can be determined from the measured charge values. The equipment consists of a glass apparatus comprising an electrolysis cell and the reaction vessel, which can be thermostated, together with the electrical unit and the magnetophone for the recording of the results: this permits rapid subsequent evaluation

By definition coulombmetry is a method whereby extremely small amounts of materials can be determined conveniently and quickly. The method has the very great advantage that the appropriate apparatus can readily be automated.

The method can also be used to advantage in biological and biochemical examinations; this will be exemplified below.

Since the measurement of the amount of charge can be traced back to the measurement of time, the electrodes must be connected to constant current. If modern electronic elements are utilized it is not difficult nowadays to construct supply sources of very high stability.

Apart from the coulombmeter reported in the present paper, attention is paid to the construction of an apparatus which functions continuously and possesses a closed regulation circuit. In this system the value of the current strength passing depends on the pressure, or on the difference in levels, which is proportional to the pressure. By the application of an appropriate correlation between the current strength and the difference in levels, it is possible to achieve very high accuracy and excellent dynamic properties.

However, the construction of such an apparatus is very expensive, and is justified only if it is necessary to follow rapid changes in a wide range.

We set out to construct an automatic instrument, which is easy to handle, contains the most modern elements and requires little space. The instrument is suitable for investigations in which one of the reactants is a gas.

Experimental technique and Methods

For homogeneous hydrogenation a coulombmeter was first used by NAGY and SIMÁNDI (1962), the stabilized supply source and recorder being prepared on the basis of the paper of TELCS and NAGY (1961).

BECK and GIMESI (1963) investigated the effect of F^- on the activation of molecular H_2 . This work was repeated coulombmetrically by BECK and GAÁL, an

the same activation enthalpy and entropy values were found, proving the reliability of the method.

The rate of reduction of Ag^+ was calculated by means of the relation given by NAGY and SIMÁNDI (1962):

$$W = f \cdot I_0 \cdot \text{tg } \alpha$$

in which the value of f in the case of H_2 is 5.18×10^{-7} (solution volume in ml $0.5/96\,500 = 5.18 \times 10^{-7}$). The dimensions of the rate are mole/litre·sec. I_0 is the strength of the current measured in milliamperes. The value of $\text{tg } \alpha$ is obtained by plotting the total time of electrolysis as a function of the reaction time and taking the quotient of the differences.

The apparatus works on the principle that when the solution reacts with the gas, then the pressure in the gas space above the solution decreases. As a result of the fall in pressure the liquid level rises in the arm of the electrolysis cell connected to the closed space, and in the other arm the liquid moves away from the Pt contact. Consequently, the relay connects constant current to the Pt electrodes.

The gas evolved equalizes the pressure and the cycle is repeated.

The apparatus of NAGY and SIMÁNDI (1962) has been modified in that the reaction vessel is connected via the stopper to the coulombmeter proper, so that it can be removed easily to facilitate cleaning (Fig. 1).

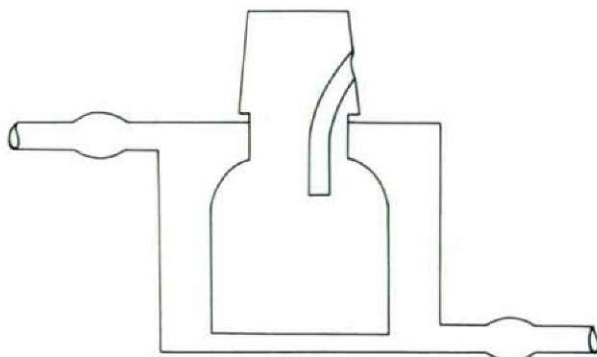


Fig. 1. Reaction vessel of glass apparatus, connected via stopper to the instrument.

The reaction mixture may be stirred with a magnetic stirrer.

The two electrodes are contained in vessel *b*, as shown in Fig. 2, there also being a Pt auxiliary electrode in that part open to the atmosphere; this serves for the development of the contact. The purpose of the U-tube in part *a* is to make the apparatus suitable for the measurement of the consumption of a gas reaction partner not prepared by electrolysis. A convenient sealing fluid is placed in the U-tube and the part leading to the reaction vessel is filled with the actual gas. The volume of the reaction space is 100 ml, only two-thirds of this generally being used.

In other cases this U-tube can also be used to effect the adsorption of carbon dioxide released in the course of the uptake of oxygen by biological materials.

If it is desired to measure the rate of the reaction on a non-linear section of the function, then the actual amount of oxygen can be calculated from the well-known formula

$$m = \frac{M}{n \cdot F} \cdot i \cdot t$$

where M is the formula weight, n the change in the number of electrons, F the Faraday number, i the current strength in amperes, and t the time in seconds.

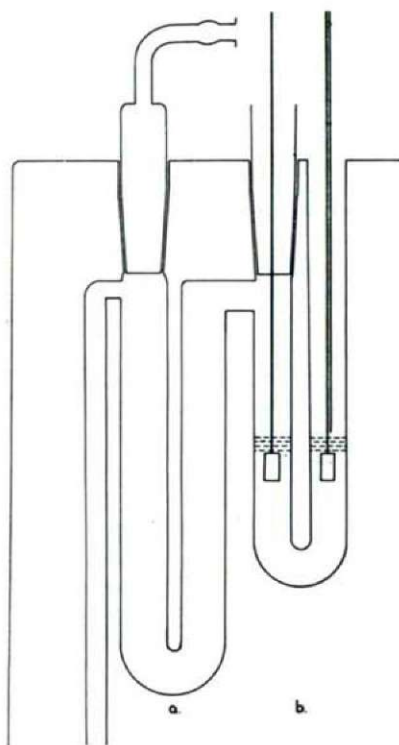


Fig. 2. a) sealing fluid in U-tube, b) the electrolysis cell with electrodes and contact.

Supply source

An outline of the integrated-circuit, stabilized supply source can be seen in Fig. 3.

The range of operation of the supply source is 0.5 mA—1 A, with a maximum output voltage of 15 V. The stability of the supply source is better than 0.1% ensured by a precision voltage-regulating integrated circuit (FAIRCHILD U6A7723393).

The current strength can be established by variation or switch-over of resistance R . The value of R may be determined from the approximate formula

$$R(\Omega) = \frac{7,15 V}{I_{\text{out}} (A)}$$

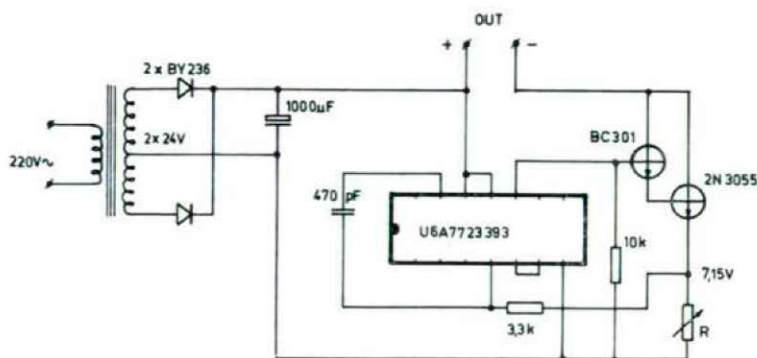


Fig. 3

To ensure the stability it is advisable to use stable resistances with low temperature coefficients.

Change in the liquid level in the electrolysis cell (Fig. 2b) is sensed via one of the electrolysis electrodes and an auxiliary electrode.

On the making of the contact, the 50 Hz alternating potential at the auxiliary electrode gives rise to a current only in the microampere range, and this causes no electrolysis. As mentioned above, however, when the circuit is closed the electrolysis ceases, for the amplified and rectified alternating current interrupts the electrolysis by switching out a relay.

The reaction time and the amount of charge used during the reaction are measured by counter relays. The time is measured in seconds. The counter relays are controlled by a 50-fold attenuation of the mains frequency, with the aid of digital integrated circuits. The first counter relay continuously measures time from the beginning until the end of the experiment. The other two relays in turn measure only the time of the electrolysis. Depending on the position of the switch, the switch-over can be made at 0.5, 1, 2, 4 or 8-minute intervals. The current strength can similarly be adjusted by switch, to 10, 20, 50, 100 or 200 mA. The experimental results can be comfortably read off the non-operating relay by suitable arrangement of the switch-over time.

For the acceleration of the evaluation in long-time experiments it is practical to automate the apparatus, i.e. to provide the possibility that the amounts of charge relating to the various time values be read off subsequently too.

The apparatus developed affords two possibilities for this: by connection to a recorder or to a magnetophone.

Recorder connection

The apparatus can be connected to a 10 mV recorder, by means of which the time of electrolysis can be recorded as a function of the reaction time.

When the current-stabilizer is switched on, the apparatus sends a 6–7 mV signal to the recorder, and this lasts until the time of switching off. The instrument produces a small mark on the recorder chart at previously determined time intervals, and this permits the exact reaction time to be established.

Magnetophone connection

Recording of the signal on a magnetophone seems to be the most convenient and accurate procedure. At the end of the reaction the result of the experiment can be played back at any desired time, at a rate much higher than the rate of recording. It is practical, therefore, to record at the lowest rate.

An M11 magnetophone was used. The gearings were arranged so as to give a quotient of the recording playing-back rated of 8. Thus, the subsequent play-back is eight times shorter than the total reaction time.

The coulombmeter causes a short impulse to be recorded on the tape every second, while in addition to these impulses a 700 Hz A.C. signal is also recorded when the current-stabilizer is switched on.

When the magnetophone is played back it must be connected to the coulombmeter, which senses the signals recorded on the tape and accelerated eight times, and causes the counting relays to operate as in the recording.

The magnetophone need not be stopped during the playback, for as mentioned earlier the relays can be preset to switch over periodically, and there is always sufficient time to read off the value from the non-operating relay.

Sources of error

1. Variation of the temperature can give rise to a considerable change in the pressure of the gas in the reaction space, and it is therefore essential to maintain the temperature constant.

2. The change in the course of the electrolysis of the volume of the electrolyte solution is negligible, for the few ml of gas evolved correspond to only a very small volume of liquid.

3. Pressure correction. In measurements lasting for a long time a barometer correction must be made if the atmospheric pressure changes appreciably meanwhile. Increase of the air pressure results in an increased time of electrolysis and this causes a positive error.

If the volume of oxygen resulting from the change in the external air pressure is $V(t)$, the volume of the reaction space is V_0 , the initial atmospheric pressure is P_0 , and that at time t is $P(t)$, then

$$V(t) = \frac{P(t) - P_0}{P_0} \cdot V_0.$$

If the volume of gas taken up is plotted as a function of time, the actual volume (V_{act}) is the difference of the measured volume and $V(t)$.

Use of the apparatus

The apparatus can be employed to measure the oxygen-uptakes of plant and animal tissues. As plant material barley was grown to the age of 10 days, and the shoots then homogenized in phosphate buffer of pH 6. The results are illustrated in Fig. 4.

For material of animal origin the apparatus was used to study the oxygen-uptake of snail heart. The snail heart was placed in Ringer solution as reported by RIPPLINGER and HEROLD (1970). The experimental results are shown in Fig. 5.

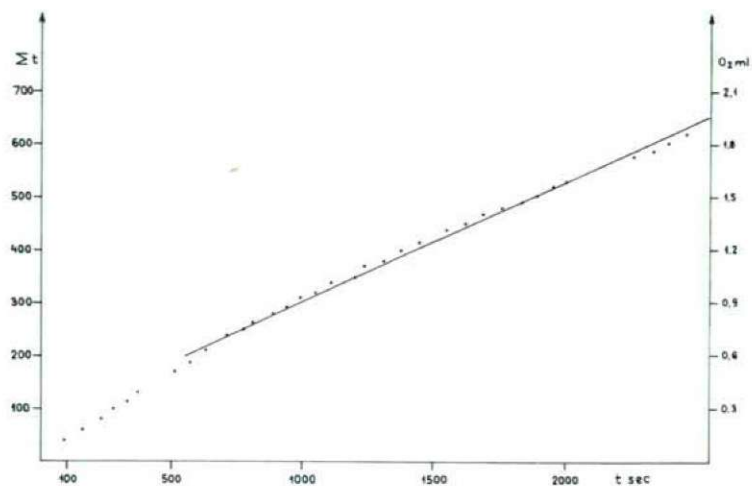


Fig. 4. Oxygen-uptake of barley homogenizate in phosphate buffer of pH 6 at 29 °C. $I_o = 50$ mA.

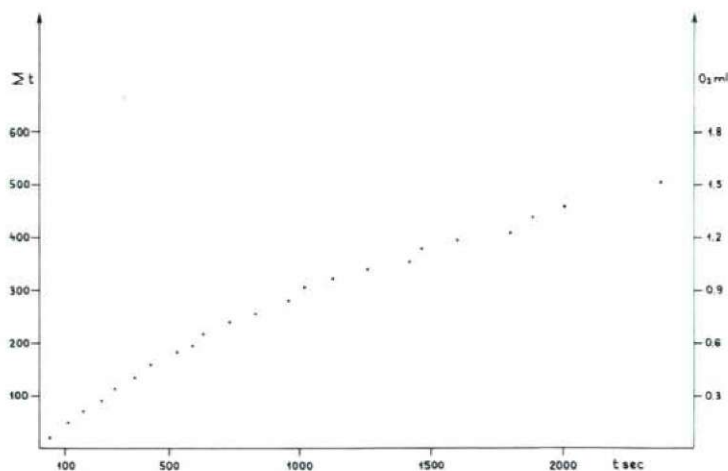


Fig. 5. Oxygen-uptake of smail heart at 29 °C. $I_o = 50$ mA.

Among many other possibilities, the method is excellently suited to the following of enzymatic hydroxylation with molecular oxygen (6).

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