An Automatic Apparatus for Following Slow Reactions by Continuous Sampling and Titration

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Reactions with half lives of several hours present a troublesome problem for a research worker who has not the time nor the patience for manual sampling. Fortunately, several instrumental methods are nowadays at hand, the most common of which is perhaps the spectrophotometric method. However, in several cases the sample-and-titrate method is the only possible procedure. In those cases where the addition of the titrant to the reaction mixture has no detrimental effect, the "pH-static" or "potentiostatic" method may be advantageously employed. In this method the potential between two electrodes immersed in the reaction mixture is maintained constant by continuous titration. Very often, however, the titrant gives rise to side reactions, which prevent the use of the potentiostatic method. For this reason, a new version of the potentiostatic method was devised. In this method the reaction mixture is loaded into a thermostated syringe and injected at a constant rate into a vessel where it is diluted and titrated continuously as in the conventional potentiostatic method. This method has been advantageously used by the author to determine rate coefficients of some zero-order catalytic reactions,[1] but the apparatus has not been previously described in detail. To demonstrate the apparatus and procedure, we have taken the reaction between benzyl chloride and dimethyl aniline, the rate of which has been previously determined.[2] The reaction was followed by titrating the chloride ion liberated during the reaction.

Apparatus. Fig. 1 shows the reaction syringe and the accessories. The part A is an Agla micrometer syringe (Burroughs Wellcome & Co.) with a total volume of 0.5 ml. The whole syringe is equipped with a jacket C held at a constant temperature by water circulating from a constant temperature bath. The piston of the syringe is driven at a constant rate by a synchronous motor D connected to a micrometer screw E *via* a gear box F. The speed of the micrometer screw was 0.04 rpm which gave a flow rate of 6.666 nl/s. The nozzle B of the syringe is inserted into a hole in the bottom of the titration vessel G. To maintain also the titration solution at a constant temperature, the vessel is equipped with a water jacket H. The Teflon stopper I of the vessel supports a glass stirrer J, the electrodes K, and a thin capillary tube L through which the titrant is added.

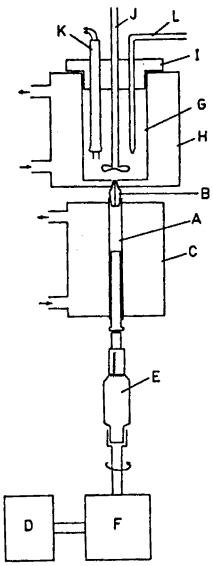

Fig. 1. Apparatus for following slow reactions. For notation, see text.

Because of the low chloride concentrations produced, the titration was performed by the bipotentiometric method of Tölg.[3] In this method a weak polarizing current is passed between two small silver-silver chloride electrodes. Silver nitrate solution is used as a titrant and the end point is indicated by a sharp potential peak. The electrodes were made by fusing two short platinum wires into one end of a glass tube so that the lengths of the protruding wires were 5 mm and the distance between them 5 mm. The platinum surfaces were purified by electrolysis in nitric acid solution and rinsing with water. A thin layer of silver was electrolyzed onto them from a solution of potassium dicyanoargentate. The electrolysis voltage was 6 V, the current 0.4 mA, and the time 1.5 h. The electrodes were rinsed with water and a layer of silver

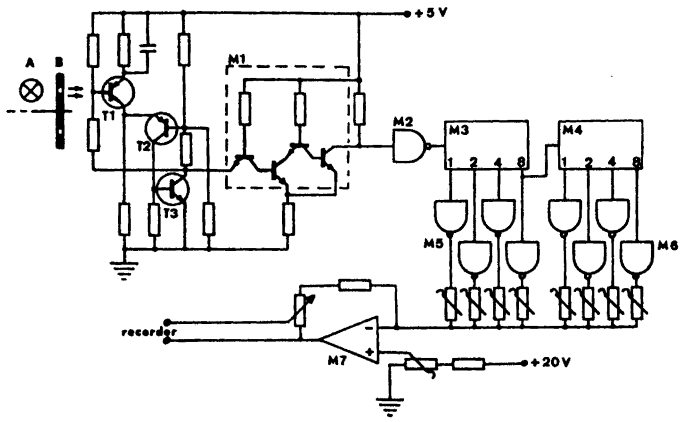

Fig. 2. Schematic diagram of the buret movement recording system. T1 is Philips OCP70, T2 is Siemens AFY11, T3 is Philips BFY51, M1 is National DM8060 (SN7460), M2, M5, and M6 are National DM8000 (SN7400), M3 and M4 are National DM8530 (SN7490), and M7 is Fairchild μA709C.

chloride was electrolyzed onto them in 0.5 M hydrochloric acid. In this case the electrolysis current was 0.4–0.5 mA and the time 10 min. The electrodes were rinsed with water and stored in glacial acetic acid. A polarizing current was supplied to the electrodes by a 9 V source in series with a 550 MΩ resistor. The potential between the electrodes was measured by a Radiometer TTT1 titrator. The titrator was connected to a Radiometer ABU 12 motor-driven buret which added small aliquots of the titrant to the titration vessel to maintain the potential constant. The buret could be mechanically coupled to a recorder. However, the readability of the titrant consumption would have been too low and another recording method was devised. A schematic diagram of the recording system is shown in Fig. 2. The movement of the buret piston is mechanically coupled to a disk B which has 10 equidistant holes arranged in a circle. The disk is mounted between an electric bulb A and a phototransistor T1. Thus each revolution of the disk gives 10 light pulses. One revolution of the disk corresponds to the delivery of 10 μl of the titrant and so 1 μl corresponds to one pulse. The signal from T1 is fed to a Schmitt trigger composed of transistors T2 and T3 and an integrated circuit M1 and then to the decade counters M3 and M4. The outputs of the decades are coupled to quadruple NAND gates M5 and M6 whose outputs in turn are connected *via* resistors to the inverting input of an operational amplifier M7. A part of the voltage across the feedback resistor of the amplifier is taken to a recorder. The output span can be adjusted with a potentiometer. The NAND gates, resistors, and the operational amplifier form a simple digital-to-analog converter. The voltage across the recorder terminals is a stair-case voltage, which returns to zero after every 100 μl. Compared with a digital printer, this method has the advantage of maintaining the same resolution and at the same time allowing continuous monitoring of the titrant delivery.

Performance of the kinetic run. The thermostats circulating water through the jackets of the reaction syringe and the titration vessel were adjusted to 35°C and 20°C, respectively. A small vial was charged with *ca.* 1 ml of a 0.395 M solution of redistilled dimethylaniline (E. Merck) in dry methanol containing 0.0176 mol of redistilled benzyl chloride (E. Merck) per liter. The vial was closed with a screw cap equipped with a silicone rubber septum and placed into a constant temperature bath at 35°C for a short time. The contents of the vial were drawn into the reaction syringe through a hypodermic needle. The needle was removed and the nozzle of the syringe was fitted into the hole in the bottom of the titration vessel and 10 ml of glacial acetic acid which was 0.01 M in perchloric acid was pipetted into the vessel. Stirring was started and the potential was manually adjusted to −30 mV by adding a 0.00254 M solution of silver nitrate in acetic acid. This potential

is on the steep slope of the potential peak on the side of excess silver nitrate. Although the potential change is steeper at more negative potentials, the smaller fluctuations due to slow response to titrant addition led to the choice of this potential. The synchronous motor and the recorder were started and the titrator was set to the "pH-stat" mode. The reaction was followed for 12 h.

Treatment of data. It is easily shown that the consumption V of the titrant is given by

$$V = \frac{v}{n} \int_{t_0}^{t+t_0} x \, dt \qquad (1)$$

where x denotes the concentration of the chemical which is liberated or destroyed during the reaction and which is continuously titrated, v is the flow rate of the reaction mixture and n is the normality of the titrant. For a second-order reaction we have

$$kt = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \qquad (2)$$

where a and b are the initial concentrations of the reactants. This equation gives

$$x = ab \frac{\exp[kt(b-a)]-1}{b \exp[kt(b-a)]-a} \qquad (3)$$

Substitution into eqn. (1) and integration gives

$$V = \frac{v}{n} \left\{ bt - \frac{1}{k} \ln \frac{b \exp[k(t+t_0)(b-a)]-a}{b \exp[kt_0(b-a)]-a} \right\} \qquad (4)$$

In the experiment, 72 data points were taken at equal time intervals. Eqn. (4) was fitted to the data by the method of least squares allowing k and t_0 to be adjustable parameters. The sum of least squares was minimized by the general minimization program of Chandler [4] on a Univac 1108 computer. The standard error of k was estimated using Quenouille's method.[5] The obtained value, $(5.91 \pm 0.04) \times 10^{-5}$ l mol^{-1} s^{-1}, of the rate coefficient at 35°C is in excellent agreement with the value 5.83×10^{-5} l mol^{-1} s^{-1} reported by Peacock and Po Tha.[2]

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Electrical and Magnetic Properties of PdSb and PtSb

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Many intermetallic phases not only have room temperature electrical resistivities comparable with those of pure metals, but also surprisingly low residual resistivities, implying a high degree of perfection of atomic arrangement in the crystal lattice. The consequently low electron scattering and/or high carrier mobility at low temperatures implies that de Haas-van Alphen oscillations in magnetic susceptibility corresponding to sections of the Fermi surface should be observable; although the interpretation of the experimental data may be difficult in the actual case. The possibility of experimental exploration of the geometry of the Fermi surface in such phases suggests that it could be rewarding to perform electrical and magnetic measurements on suitable representatives.

The present paper concerns the electrical and magnetic properties of PdSb and PtSb, which crystallize [1-3] with the NiAs type structure. The PdSb and PtSb phases are reported to exhibit metallic properties,[4-6] transformations to superconducting states occurring at 1.5 and 2.1 K, respectively. The de Haas-van Alphen effect has been observed [7] for PdSb at