487. *An Apparatus for the Spectrophotometric Determination of Rates of Reaction in Solution down to −140°.*

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An apparatus is described by which the rates of reactions in solution involving colour changes may be measured at temperatures down to −140°.

It is often of interest to be able to determine rates of reaction in solution at as low a temperature as possible. Reactions which are otherwise too fast to measure might become accessible, for instance, complex-formation between organic molecules. Moreover, since it is possible to reduce the absolute temperature to less than half its value at room temperature, reaction rates might begin to indicate interesting deviations from the Arrhenius equation. Quantum-mechanical leakage in proton-transfer reactions, for example, is more easily detected the lower the temperature. Previous papers from this laboratory have reported results at temperatures down to −115°, the lowest practicable temperature with the apparatus then in use.[1] We have now developed an apparatus to follow reactions photometrically at temperatures down to −140°. Below this temperature, the viscosities of solvents other than hydrocarbons (in which our reactants are too sparingly soluble) become so great that solutions cannot be mixed within a reasonable time; and the solubilities of some of the solutes envisaged become too low. (Some rate measurements on reactions in a solid nitrogen glass have been reported,[2] but the choice of reactants is limited by solubility and other considerations.)

Experimental

The Thermostat Vessel and Reaction Cell.—The reaction cell is similar in principle to those previously used in this laboratory, but to improve the thermal insulation it is made in one piece with a Dewar vessel which acts as the thermostat bath. We are indebted for the glass-blowing to the Cavendish Laboratory, Cambridge. The apparatus is of Pyrex glass throughout. It is shown in vertical section and in plan in the Figure.

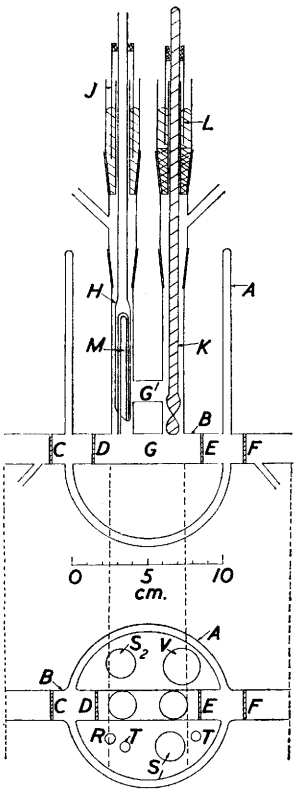
The thermostat vessel A is 10 cm. in internal diameter and 20 cm. deep. It is just large enough to contain the reaction cell, with its stirrer K and siphon tube H, a platinum thermometer R, two bath stirrers S_1 and S_2, a thermel T for temperature control, and a cooling tower V. The reaction solution is contained in the cell G, which is the central part of a tube B, of internal diameter 2 cm., sealed into the thermostat vessel; glass discs C, D, E, and F are sealed across this tube. The whole of the annular space, including that between the discs C, D and E, F, is evacuated, and the outside of the thermostat vessel is silvered; thus the reaction cell is well protected from sources of heat. To prevent any condensation on the outer windows C and F, dry air is blown over them. To cool the thermostat to −100° requires about 2 l. of liquid nitrogen, and to maintain this temperature about 3 l./hr.

A run is started as follows. With the thermostat at room temperature, one of the reactant solutions (about 40 ml.) is placed in the body of the cell (G); the other (1—4 ml.) is placed in the thin glass tube H. The two solutions are thus kept separate while being cooled; during this process, H, which carried a long mercury seal J so that it can be moved vertically, is lowered until it rests on the tube B, so as to improve thermal contact between the two liquids. When the reactants have attained thermal equilibrium, H is lifted until its lower end is only 1 cm. below the surface of the liquid in G. To initiate the reaction, the solution in tube H is blown over through the siphon tube M into the bulk of the solution, by compressing a rubber bulb, attached to the top of H, containing air free from water vapour and carbon dioxide; by manipulating the bulb, the tube H is washed out to ensure complete transfer of solution. The stirrer effects rapid mixing; with ethanol, mixing is complete in 10—15 sec. at −50°, and in less than 1 min. at −100°. During the rest of the run the stirring is continued, to ensure that the temperature of the solution is uniform.

Temperature Control and Measurement.—The cooling tower (V) consists of two concentric

[1] Ainscough and Caldin, preceding paper; *J.*, 1956, 2546, and earlier papers.
[2] Pimentel, *J. Amer. Chem. Soc.*, 1958, **80**, 62.

glass tubes about 30 cm. long, with liquid nitrogen in the inner tube; the level of the liquid is maintained constant by a simple manometric device. Part of the space between the two tubes is occupied by isopentane; by varying the depth of immersion of the inner tube in the isopentane, the rate of cooling can be controlled. Round the base of the outer tube is wound a coil of resistance wire (Kanthal D), which acts as an intermittent heater. This is brought into operation by a thermo-regulator which consists of a thermel, mirror galvanometer, photocell, and relay. The thermel comprises two sets of 20 junctions; one set is kept in ice, the other (T) is in two halves in the bath. All electrical components are placed on an earthed equipotential shield.[3]



Thermostat vessel and reaction cell; vertical section through diameter along axis of reaction cell, and plan (to scale).

The temperature of the bath is measured by means of a platinum-resistance thermometer, constructed by one of us (R. A. J.). This is a four-terminal compensated-lead instrument, with the platinum helix wound on a mica former as desctibed by Meyers.[4] It was calibrated at the oxygen point,[5] the triple point of water,[6] the steam point, and the sulphur point.[7] We are indebted to the Physics Department for facilities and advice. When the thermometer is in use, its resistance is measured by passing a current (2 mA) through it in series with a standard 25-ohm resistance, and comparing the p.d.s. across the two resistances by means of a Diesselhorst potentiometer. Calculation shows that the current raises the temperature by only 0·008°.[8]

The temperature of the bath is uniform within ±0·01°, except close to the cooling tower or the surface. The variation over a period of time is within ±0·02°. The temperature of a liquid in the reaction cell (with the stirrer in operation) has been shown by experiments with a bare thermel to be uniform and to remain constant within ±0·002° at all temperatures down

[3] White, in "Temperature, its Measurement and Control in Science and Industry," Reinhold Publ. Corp., 1941, p. 279.
[4] Meyers, *Bur. Stand. J. Res.*, 1932, **9**, 807.
[5] Scott, ref. 3, p. 213.
[6] Barber, Handley, and Harrington, *Brit. J. Appl. Physics*, 1954, **5**, 41.
[7] Mueller and Burgess, *J. Amer. Chem. Soc.*, 1919, **41**, 745.
[8] Smith, *N.P.L. Collected Papers*, 1913, **9**, 228.

to −140°. It is a few hundredths of a degree higher than the measured bath temperature. All sources of uncertainty being taken into account, the temperature in the reaction cell can be determined within ±0·03°.

The Photometer.—A photoelectric photometer and appropriate filters are used. (*a*) In work on the reaction between the trinitrotoluene anion and hydrofluoric acid (following paper), a 30-watt tungsten lamp run from a constant-volts transformer has been used as a source, and a photocell (Type V.A. 39, made by Cinema Television Ltd.) as detector. The light passed through a rotating sector, so that a.c. was generated. The amplifier circuit was modified from that of Kalmus and Saunders.[9] Several different gains were available, each covering about 0·4 unit of optical density. The relation between measured optical density (*i.e.*, logarithm of galvanometer reading) and concentration was tested by using Indian ink and a red filter (Chance OR2) [10] and found to be linear within about ±0·01 unit of optical density over the range 0·2—1·8. There was a slight lag in the response of this system, but calculation showed that it would not affect the rate constants of even the fastest runs by more than 1%. (*b*) In later work, by Mr. E. Harbron, a photomultipler has been used in place of the photocell, with a logarithmic circuit modified from that of Ashmore, Levitt, and Thrush.[11] The advantage of this system, apart from its stability and rapid response, is that the galvanometer reading varies linearly with the optical density between 0 and 1·4, and hence linearly with the concentration of coloured species.

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The University, Leeds, 2. [*Received, December 4th*, 1959.]

[9] Kalmus and Saunders, *Electronics*, July 1950, p. 84.
[10] Withrow, *Ind. Eng. Chem. Anal.*, 1935, **8**, 214.
[11] Ashmore, Levitt, and Thrush, *Trans. Faraday Soc.*, 1956, **52**, 830, and personal communication.