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end of an experiment, this procedure is followed in reverse. With the straight-through and right-angle valves closed, the lock is ventilated by the leak valve and the flange between the straight-through valve, and the adaptor is opened for sample exchange. The time required for a complete sample transfer into the system depends on the preparation and operation of the lock procedure and on the final pressure desired; for instance, the procedure may be completed within 1 h with a final pressure of 1×10^{-9} Torr.

Experimental methods at high pressures. II. A simple internal stirring system for very high pressures

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This note describes a magnetic stirring system, which can be installed inside high-pressure autoclaves. Pressures up to 4 kilobar are possible and gaseous or liquid pressurizing media can be used. The stirrer moves a magnetic stirring bar inside the sample cell in a vertical direction. Owing to its simple and efficient design, thermal side effects are very small. The effectiveness of the stirrer is demonstrated by following the rate of solution of $PbCl_2$ in water at various pressures.

Successful measurements in homogeneous reaction kinetics require verification of two fundamental experimental conditions: uniform concentration throughout the solution and precise temperature control. While in high-pressure kinetic experiments the latter is generally achieved in both liquid and gaseous pressurizing systems, the molar and thermal concentration distribution within the sample is left to natural convection and diffusion. Continuous mixing of the sample should therefore be considered if a concentration or temperature gradient in the reaction mixture is expected.

Several stirring systems have been investigated previously. None of them appear to be satisfactory for kinetic precision for reasons of contamination, temperature control, or simplicity. Commercially available stirring systems[1] usually work by means of strong external magnets, propeller stirrers utilizing internal or external propulsion, or devices which shake the whole autoclave. They are certainly useful in pilot experiments, high-pressure syntheses, or similar applications, but do not comply with the standards of purity, temperature, and pressure control which kinetic (and some nonkinetic) high-pressure experiments require. Stirring systems which have been developed for kinetic research, namely the "Magna Dash",[2,3] and other devices for *in situ* mixing, have the disadvantages of being complicated, generating heat, and thus causing thermal side effects; or they are not suitable for very high pressures.

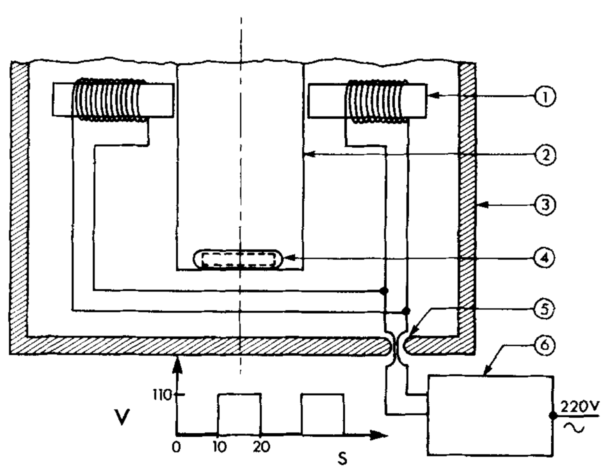

FIG. 1. Schematic diagram of the stirring system. (1)—Solenoid and core; (2)—plastic sample cell; (3)—autocalve; (4)—Teflon-coated magnetic stirring bar; (5)—high-pressure seal for electric conductors; (6)—square wave generator.

The working principle of the magnetic stirring apparatus is illustrated in Fig. 1. Its application in a high-pressure autoclave is shown in Fig. 2.

The system consists mainly of an electromagnet (1) and a Teflon-coated stirring bar (4) in the diamagnetic sample cell (2). Given the main inner dimensions of the autoclave, its diameter *a* and its length *b*, an electromagnet has to be found to yield a highly concentrated magnetic field with a negligible thermal effect on the sample. This is achieved by arranging the magnetic poles horizontally around the sample cell (Fig. 1), permitting a large number of turns in the solenoid. A space-saving practical solution for this can be found if a simple bipolar induction motor [1(a), (b) in Fig. 2] is applied (e.g., an SEL electromotor, model 2814-424 ez, 220 V, 50 Hz). The rotor is replaced by the sample cell and the solenoid is fed from a square wave generator which uses a 110-V dc power line. Electricity is supplied via a miniature conductor (di-

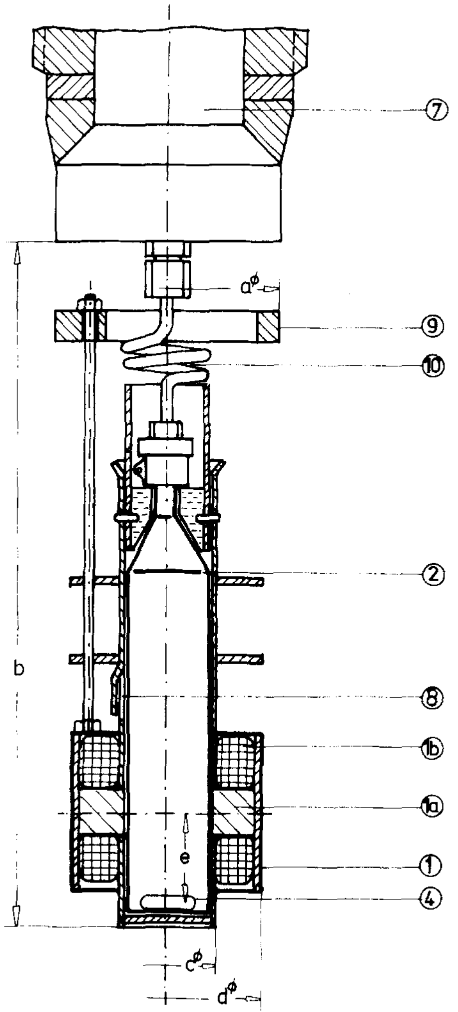

FIG. 2. Complete stirring system, numbers also corresponding to Fig. 1. (1)—Motor stator, bipolar armature; (1a)—motor core; (1b)—motor core; (1b)—solenoid; (2)—plastic sample cell; (4)—Teflon-coated magnetic stirring bar; (7)—autoclave cover with hole for sampling or additional wiring; (8)—slot for thermocouple to measure internal and sample temperature; (9)—expansion ring which is pressed against the autoclave wall and supports the whole stirring unit; (10)—flexible Teflon tubing which is replaced by electric wires for conductivity measurements. Main dimensions: $a^{\text{diam}} = 75$ mm, $b = 229$ mm, $c^{\text{diam}} = 30$ mm, $d^{\text{diam}} = 60$ mm, $e = 35$ mm.

ameter 1.5 mm, Philips Electronics) and the temperature of the sample is measured with a thermocouple (8). Both are steel-armored conductors, which can be soldered into connecting fittings and mounted through supplying holes from the bottom of the autoclave. The system is assembled and the height e of the vertical movement of the stirring bar and frequency of the square waves is adjusted to the viscosity of the fluid and the turbulence required in the sample cell. To keep the autoclave versatile and well accessible the stirring apparatus is mounted into the autoclave in the way suggested by Fig. 2, hanging on threaded brass rods suspended by the suspension ring (9), which is the only part fixed to the autoclave wall. It can be installed or removed in a short time to allow other uses of the autoclave or to replace its cheap basic parts in case of failure.

This stirring system is also applicable to other types of autoclaves, using any method of compression. For

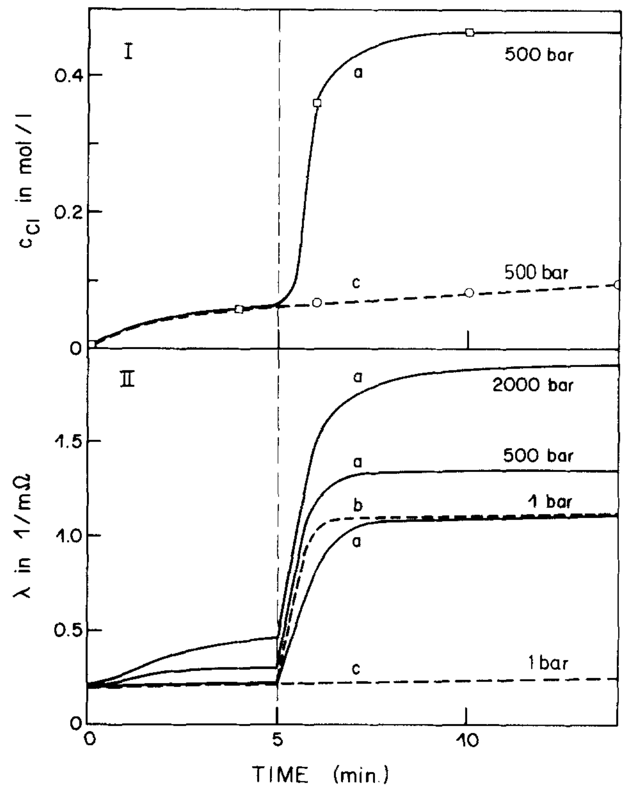

FIG. 3. Efficiency of the magnetic stirring system in a $Pb(II)Cl_2$/water mixture, (I)—measured by sampling and subsequent titration; (II)—continuously monitoring conductivity. Stirring was initiated at the 5-min mark. (a)—Curves with magnetic stirrer; (b)—curve with common laboratory stirrer at atmospheric pressure; (c)—dissolution in absence of stirring at atmospheric pressure (II) and at 500 bar (I).

high-temperature runs, solenoids with temperature resistant insulation can be utilized.

Several tests were carried out to show the effectiveness of the stirring system prior to its use in chemical reaction kinetics. The solvation of $Pb(II)Cl_2$ in water was used to compare (a) our stirrer with (b), a common laboratory stirrer, and (c), natural solvation. The results are shown in Fig. 3. The chloride concentration was followed by titration of 5-ml aliquots (I), and by monitoring the conductivity (II). The initial slope in the high-pressure runs reflects the heat of compression, which influences both solubility and conductivity. Stirring was initiated at the 5-min mark. Complete solvation was generally achieved in less than 3 min after stirring commenced. The differences of the final values after dissolution was complete were due to pressure effects.

The stirring apparatus was subsequently applied successfully to kinetic studies of homogeneous reactions in solutions, including the influence of high pressures on Friedel-Crafts alkylations.[4,5]

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[1] All major manufacturers of high-pressure equipment offer some kind of stirring system for their autoclaves.

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