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METHODS AND TECHNIQUES OF PHYSICOCHEMICAL RESEARCH

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Tube for the Investigation of Gas-Liquid Heterogeneous Systems at Ultrahigh Pressures

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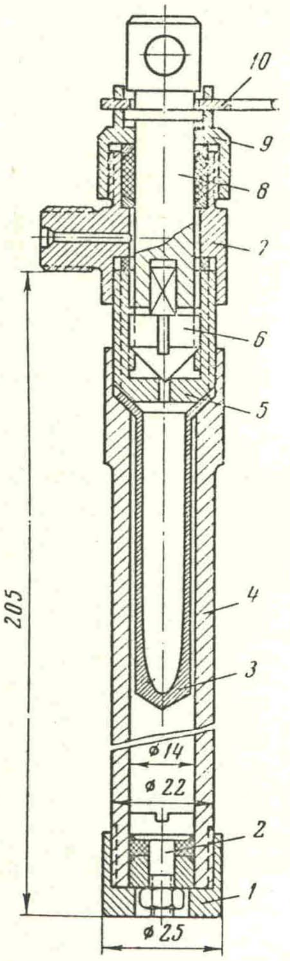
An unsealed metallic tube fixed in a steel shell with a removable valve and a mobile piston has been designed and tested. The space between the walls of the tube and the shell is filled with silicone oil, which provides a hydraulic support for the tube. Lead tubes and bellows-type and smooth stainless steel tubes have been tested. The telomerisation of ethylene by polychloromethanes has been investigated in the tube at a pressure of 2400 atm and 95°C.

Tubes made of glass (with a mercury seal[1]), lead[2], Teflon[3], and mild steel[4] are used for the investigation of liquid-phase processes at high and ultrahigh pressures; the tubes are placed in the reactor of the apparatus filled with a pressure-transmitting liquid. However, these tubes are unsuitable for the investigation of gas–liquid heterogeneous systems, since at fairly high temperatures the initial pressure within the tubes may reach several hundreds of atmospheres. Nor can one use in such investigations the sealed tube with a mobile piston described by Gonikberg and Gavrilova[5].

We designed and tested an unsealed metallic tube fixed in a steel shell with a removable valve and a mobile ground piston (see Figure). The space between the walls of the tube and the shell is filled with a silicone oil, which provides a hydraulic support for the tube. The telomerisation of ethylene by polychoromethanes was investigated in this tube at a pressure of 2400 atm and a temperature of 95°C[7]. The high-pressure apparatus was described previously[2].

Successful tests were performed on lead tubes and corrugated (bellows-type) (wall thickness 0.1 mm) and smooth (wall thickness 0.3 mm) stainless steel tubes. Tubes made of polymeric materials (Teflon) proved to be unsuitable because of the permeability of the walls to gas at a high partial pressure.

The Figure shows the steel shell with a lead tube, the upper part of which was rolled out and sealed between the shell and the head. The steel tubes were sealed by means of a sealing ring with a tail piece welded to the neck of the tube. The experimental technique, which was the same for all the tubes, consisted of the following observations. Silicone oil was poured into the steel shell and the tube, closed by a stopper, was inserted. The excess oil was removed, the neck of the tube was washed, and the head was screwed on. The tube was weighed together with the needle valve. Then the liquid telogen was introduced, the needle valve was screwed shut, and the tube was joined to a permanently fixed three-way connector. Then a rotatory spanner and a locking bracket were inserted, the telogen was freed from traces of oxygen by repeated freezing and unfreezing, the tube was disconnected, and the amount of telogen introduced was determined by reweighing. Next the tube was reconnected to the three-way connector and the spanner and the locking bracket were reintroduced. The tube was filled via the side arm of the three-way connector with ethylene freed from traces of oxygen by repeated freezing and unfreezing, the needle valve was screwed shut, the spanner was removed, and the tube was disconnected. The amount of ethylene added was found by weighing.



Apparatus for the high-pressure measurements
1) lock nut; 2) demountable moving piston operating on for principle of a seal with an uncompensated area[6]; 3) tube; 4) shell of tube; 5) head; 6) locking needle valve; 7) three-way connector; 8) rotatory spanner; 9) nut of three-way connector; 10) locking bracket [θ—diameter, the dimensions are given in millimetres (Ed. of Translation)].

The tube was placed in a thermostatted reactor of the high-pressure apparatus and in the course of 7 min the pressure was raised to 2400 kgf cm^{-2}. After the experiment the pressure was released, the tube was removed from the reactor, cooled, and washed. The space between the cone of the needle valve and the head was washed through slits cut in the needle. The agreement between the weights of the tube before and after the experiments indicated the absence of leakage of the reaction mixture.

The excess ethylene was slowly released, with the needle smoothly screwed out, and the reaction mixture was extracted from the tube with the aid of a syringe.

The lead and smooth steel tubes must be changed after each experiment because of irreversible distortion occurring when the contents of the tube are compressed (to 40% in certain experiments). On removing the pressure, the lead tubes form microcracks, through which a small amount of their contents passes into the interior of the shell. The bellows-type tubes do not suffer from these disadvantages. In the presence of a core, the degree of compression of the tube may reach up to 50% without irreversible distortion. This makes it possible to use one tube repeatedly without extracting it from the shell. A disadvantage of the bellows-type tubes is the complexity of the mechanical cleaning of the inner surface.

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High-sensitivity Pirani Gauge with Automatic Recording

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A recording Pirani gauge for the measurement of gas pressures in the range 1×10^{-6}–1 torr has been described.

In laboratory practice Pirani gauges have come to be widely used because of a number of advantages such as small size, simplicity of design, wide range of pressures recorded, the possibility of continuous automatic recording of the readings, etc. However, in many cases their maximum sensitivity and the lower limit of measurable pressure, which is usually 10^{-3}–10^{-4} torr,[1,2], are inadequate. The attempts to improve these parameters usually lead to a considerable increase in the complexity and cost of the apparatus.

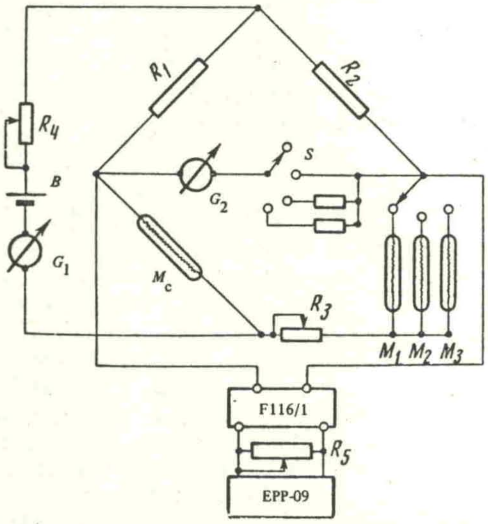

Figure 1. Measuring circuit of the gauge.

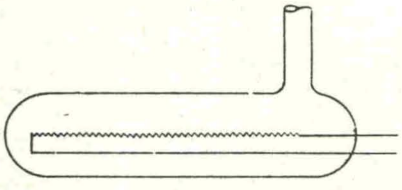

Figure 2. Pressure transducer.

For a number of years we have successfully employed automatically recording Pirani gauges of simple design with a sensitivity up to 1×10^{-6} torr. The measuring circuit of these gauges, which is of the usual bridge type, is presented in Fig. 1. It provides for a possibility of alternate inclusion of three pressure transducers (M_1, M_2, and M_3) located in various parts of the vacuum apparatus. To compensate the variation in room temperature and in the current supplied, a compensation cell M_c is employed; R_1 and R_2 and 300 Ω bifilar Manganin resistances. The bridge is balanced with a resistance box R_3 of type R-33 or R-333.

The bridge is supplied from a d.c. source *B* with a stabilised voltage of 12 V. The supply current (40 mA) is set by means of a variable wire resistance R_4 and is measured with a milliammeter G_1. The out-of-balance bridge current, which flows when the pressure in the transducer changes, is amplified by a photoamplifier of type F-116/1 and is automatically recorded with an EPP-09 pen recorder. To regulate the degree of amplification, a variable resistance R_5 is included in the external circuit of