

method^{3,4}: a known mass of liquid is introduced into a sealed vessel connected to a manometer, and the gas is admitted to a predetermined pressure. The contents of the vessel are vigorously stirred, and the change in pressure is monitored. The achievement of saturation is recognised by constancy of the pressure, and the solubility of the gas is calculated from the change in pressure between the initial and the equilibrium state of the system. This procedure is not applicable to gas mixtures. All the other methods differ from the above only in the way in which the amount of dissolved gas is determined. A sample of the saturated solution of the gas in the liquid is usually taken, and analysed either chemically⁵ or physico-chemically (by chromatography^{6,7} or mass spectroscopy⁸). The main shortcoming of these methods is the difficulty of withdrawing a sample under high pressures, and yet a knowledge of the solubility under pressure is of great practical importance because many processes in the chemical industry are carried out at elevated pressures.

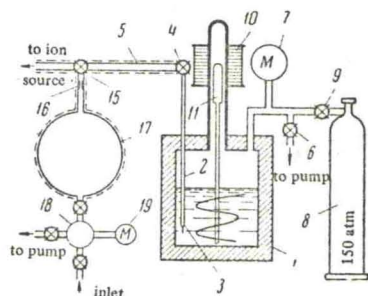


Figure 1. Diagram of apparatus

This paper describes a new mass spectroscopic method of measuring the solubility of gases and gas mixtures in volatile liquids at high pressures and over a range of temperatures. The method has a number of advantages over existing procedures: in particular, the sample can be withdrawn conveniently, the composition of the solution can be monitored directly from the high-pressure system, and the apparatus has a fast response, which enables kinetics as well as equilibria to be studied.

The method is based on a capillary system for injecting liquid samples into the mass spectrometer, developed by the present writers and G. V. Karpov⁹⁻¹¹. Its key feature is a capillary slit 1-3 mm long, 10^{-6} - 10^{-5} cm wide, and 0.3-1 mm deep. The capillary is made by flattening the end of a copper tube connected to the ionisation volume of the mass spectrometer and therefore continuously pumped to a high vacuum. A liquid mixture is analysed simply by immersing the flattened end of the tube into the mixture. The liquid rises into the capillary by the combined effects of capillarity and pressure difference, and on reaching the wider region of the copper tube it is converted into vapour, which is led to the ion source. The flow of liquid needed to ensure optimum mass spectrometric sensitivity is $\sim 10^{-8}$ g s⁻¹.

Fig. 1 shows a schematic of the overall apparatus, and Fig. 2 shows the main part of the apparatus: the working cell in which the mixture of gas and liquid is prepared. The high-pressure vessel 1 (Figs. 1 and 2) consists of a stainless steel tube 150 mm long, 12 mm outside diameter, wall

thickness 1.5 mm. The liquid is added to the vessel which is then sealed with a standard conical seal including a sleeve and retaining nut (M-16-1.5). The sleeve carries 1) a copper tube 2 with a flattened end 3 (forming the capillary sampling tube) immersed in the liquid, and the other end connected to the ionisation volume of the mass spectrometer through tap 4 and connecting tube 5; 2) three copper capillaries (0.1 mm wall thickness, 0.7 mm diameter) connecting the working volume to the manometer, rotary pump, and cylinder of experimental gas respectively. Air is removed from the pressure vessel, manometer 7, and connecting tubes by pumping through tap 6. The valve of cylinder 8 containing the experimental gas is then opened, and the desired pressure is generated in the vessel by means of regulator 9.

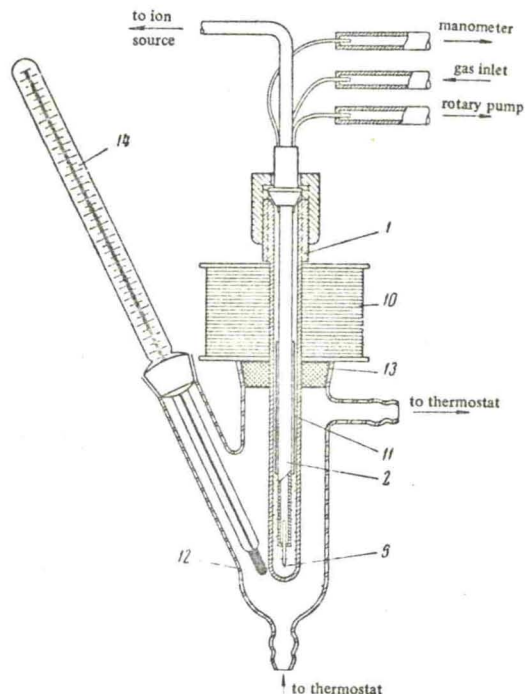


Figure 2. High-pressure vessel for studying the solubility of gases in liquids

The electromagnetic stirrer consists of a coil 10, core 11, and a steel shaft 50 mm long, 8 mm in diameter, wall thickness 0.5 mm. Temperature control is by circulating water from a U-10 thermostat through the water jacket 12, closed by a rubber stopper (13). The temperature is read on thermometer 14; temperature stability is of the order of ± 0.05 deg. The composition of the mixture of gas and liquid is continuously monitored by the mass spectrometer.

A calibration system for the mass spectrometer, of the conventional type, can be connected to the ion source by tap 15. It consists of a Break-seal 16, expansion volume 17, reservoir 18, manometer 19, and a pumping system not shown in the diagram.