

and their mean value for the given temperature is calculated  $[h'_{\text{mean}} = (h'_1 + h'_2)/2]$ . The thermostat is then re-set, and  $h'_{\text{mean}}$  is measured at some other temperatures.

The pycnometer is then removed from the thermostat, weighed, cut open, emptied, carefully dried, and re-weighed. The mass of the calibrating liquid present in the pycnometer is found from the weight difference. Knowing the density of the calibrating liquid, the volumes corresponding to the measured heights can be calculated. Hence we can write the first pycnometric equation in the form

$$V' = a' + b'h'_{\text{mean}} + c'(h'_{\text{mean}})^2, \quad (1)$$

where the constants  $a'$ ,  $b'$ , and  $c'$  are calculated by least squares.

Using exactly the same procedure, the pycnometer is calibrated a second time with enough liquid to reach to the mark 5. The distances  $h''_1$  and  $h''_2$  for the liquid menisci in tubes 4 and 10 are measured, and the mean values  $h''_{\text{mean}} = (h''_1 + h''_2)/2$  are calculated for the chosen calibration temperatures. From these results we obtain the second pycnometric equation

$$V'' = a'' + b''h''_{\text{mean}} + c''(h''_{\text{mean}})^2. \quad (2)$$

After calibration, the apparatus is washed and dried, and used to measure the density of two liquids with limited mutual solubility. The heavier liquid is added through tube 2, followed by the lighter liquid, in amounts such that the interface is in tube 7 and the meniscus of the lighter liquid is above mark 5. Tube 2 is again sealed off, the apparatus is clamped in a rotary shaker, and placed in the thermostat.

When the apparatus has reached the desired temperature, it is rotated round an axis perpendicular to the plane of the paper through  $180^\circ$  anticlockwise, and then returned to the vertical position, using a hydraulic device or a servo-motor. This motion causes mixing of the liquids in the mixing reservoir 1, and no liquid enters tube 2. Mixing is continued for several hours at the chosen temperature until mutually saturated solutions are obtained. The pycnometer is returned to the vertical position, and the liquids are allowed to settle until interfacial boundaries appear in tubes 7 and 10. The pycnometer is rotated round an axis perpendicular to the plane of the paper, and some of the lighter liquid is poured out of tube 10 so as to bring the interface to the middle section of tube 7. The apparatus is allowed to reach thermostat temperature for several hours, until the positions of the menisci have become stable, and the density measurement is begun. The distances from the mark 3 to the menisci of the lighter ( $h_{l_1}$  and  $h_{l_2}$ ) and the heavier ( $h_{h_1}$  and  $h_{h_2}$ ) liquid in tubes 4, 7, and 10 are noted.

Using the calibrating equations (1) and (2), the volume  $V_1$  of the heavier liquid is determined by inserting into Eqn. (1) the value  $h_{1\text{mean}} = (h_{h_1} + h_{h_2})/2$ , and the total volume  $V$  by inserting into Eqn. (2) the value  $h_{1\text{mean}} = (h_{l_1} + h_{l_2})/2$ . The volume of  $V_1$  of the lighter liquid is obtained by difference. We can write the two equations

$$V_1\rho_1 + V_2\rho_2 = m, \quad (3)$$

$$(h_{h_2} - h_{l_2})\rho_1 = \Delta h\rho_2 + (h_{h_1} - h_{l_1})\rho_1. \quad (4)$$

where  $m$  is the combined mass of the two liquids,  $\Delta h$  is the difference between the levels of the solution of the heavier liquid in the heavier liquid in tubes 7 and 10,  $\rho_1$  and  $\rho_2$  are the densities of the saturated solutions of the heavier in the lighter liquid and vice-versa.

Inserting values of  $V_1$ ,  $V_2$ ,  $m$ ,  $h_{l_2}$ ,  $h_{h_1}$ ,  $h_{h_2}$ ,  $h_{l_1}$ , and  $\Delta h$  in Eqns. (3) and (4), the densities  $\rho_1$  and  $\rho_2$  are determined by solving the equations simultaneously. An important feature of the present pycnometer is the fact that the masses of the individual liquid phases (which vary with temperature because of solubility differences) do not need to be separately known. The total mass, however, remains constant irrespective of temperature, and is readily determined by weighing at the end of the experiment.

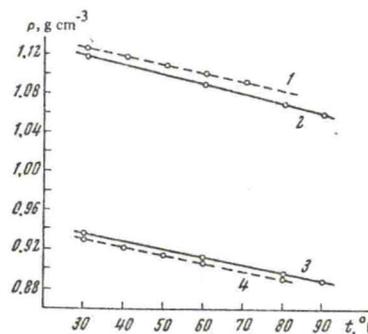


Figure 2. Density polytherms for the PEG-DBS system: 1) for pure PEG; 2) for a saturated solution of DBS in PEG; 3) for a saturated solution of PEG in DBS; 4) for pure DBS

The pycnometer has been used in our laboratory to measure the density of a number of systems. In particular, the following polytherm equations have been obtained for the density in the poly(ethylene glycol)-dibutyl sebacate (PEG-DBS) system (see Fig. 2):

$$\rho_{\text{DBS}} = 0.9504 - 0.0005619t + 0.000001731t^2, \quad (5)$$

$$\rho_{\text{PEG}} = 1.14704 - 0.0014236t + 0.000001485t^2. \quad (6)$$

The mean scatter of the experimentally measured densities from these curves is less than  $0.0001 \text{ g cm}^{-3}$ .

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### Mass-spectrometric Assembly for Studying the Solubility of Gases and Gas Mixtures in Liquids at High Pressures

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A fast mass-spectrometric procedure for measuring the solubility of gases and gas mixtures in volatile liquids at different temperatures and at pressures between 1 and 150 atm has been developed. The mass spectrometer has a capillary sample injection system which allows the composition of the liquid in the high-pressure vessel to be determined by continuously sampling the liquid at a rate of  $\sim 10^{-8} \text{ g s}^{-1}$ . Plots of the solubility of argon in benzene and in toluene as a function of pressure at  $20 \pm 1$  and  $17.3 \pm 0.2^\circ\text{C}$  are given.

Several methods of measuring the solubility of gases in liquids are known<sup>1,2</sup>, but they all suffer from serious shortcomings. The most widely used is the manometric

method<sup>3,4</sup>: 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 chemically<sup>5</sup> or physico-chemically (by chromatography<sup>6,7</sup> or mass spectroscopy<sup>8</sup>). 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.

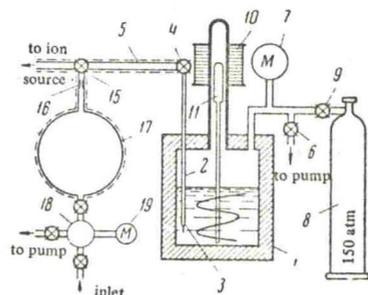


Figure 1. Diagram of apparatus

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. Karpov<sup>9-11</sup>. 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<sup>-1</sup>.

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.

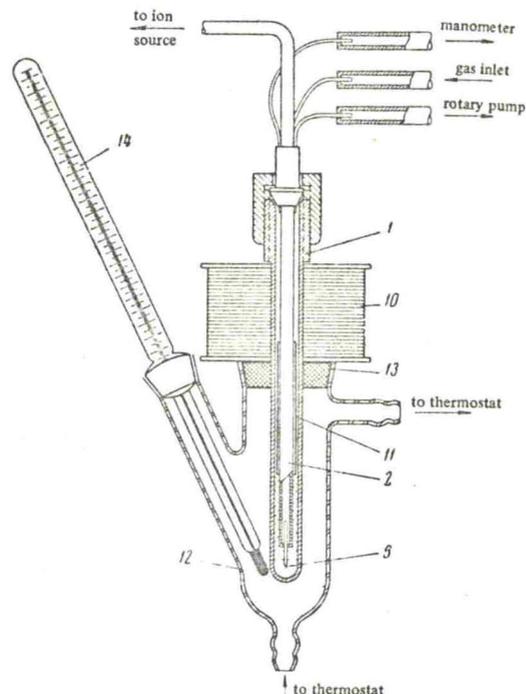


Figure 2. High-pressure vessel for studying the solubility of gases in liquids

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  $\pm 0.05$  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.

The ratio of the concentrations of the gas and of the liquid in the mixture is

$$n(g)/n(l) = \eta_{rel} [M(l)/M(g)]^{1/2} i(g)/i(l),$$

where  $i(g)/i(l)$  is the observed intensity ratio of the mass-spectral lines which characterise the gas and the liquid † respectively;  $\eta_{rel}$  is the relative sensitivity of the mass spectrometer towards the liquid and the gas;  $[M(l)/M(g)]^{1/2}$  is a factor which accounts for the molecular flow regime in the capillary inlet system;  $M(l)$  and  $M(g)$  are the molecular weights of the liquid and the gas.

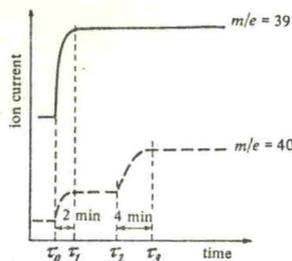


Figure 3. Kinetics of the change of intensity of the mass-spectral lines (argon in toluene experiment)

Fig. 3 shows a typical kinetic plot of the mass-spectral line intensities obtained in the present apparatus. As a concrete example, the experiment on the solubility of argon in toluene is shown. The full line labelled  $m/e = 39$  corresponds to the liquid, the broken line ( $m/e = 40$ ) to the gas. The argon is admitted from the gas cylinder to the vessel containing toluene at time  $\tau_0$ . This increases the pressure difference across the capillary inlet system, and causes an increase in the intensity of both the  $m/e = 39$  (toluene) line and the  $m/e = 40$  line, also present in the toluene mass spectrum. The diffusion time of the argon molecules to the inlet split is very large on the present scale, and therefore the intensity ratio of the  $m/e = 39$  and  $m/e = 40$  lines is characteristic of pure toluene and does not indicate the presence of argon. The electromagnetic stirrer was switched on at time  $\tau_2$ : the intensity of the  $m/e = 39$  toluene line was unaffected, but that of the  $m/e = 40$  line began to increase as the gas dissolved in the liquid. At time  $\tau_3$  equilibrium was achieved and the solution became saturated.

Fig. 4 shows the measured solubilities of argon in benzene and in toluene as a function of argon pressure. The mole fraction of argon in the solution is plotted vertically. The measurements were made on different days, and the temperature was  $20 \pm 1^\circ\text{C}$  for benzene and  $17.3 \pm 0.2^\circ\text{C}$  for toluene. The liquids were of "analytically pure" grade, the argon contained 0.1%  $\text{N}_2$  and 0.01%  $\text{O}_2$  impurities. The experiments confirm that Henry's law applies to the present solutions (mean scatter of the points from the straight lines  $\pm 3\%$ ). The solubility at 1 atm is numerically

† Since the mass spectra of the gas and the liquid are superimposed, a correction must be applied for any contribution of the liquid to lines characteristic of the gas.

equal to the slope of the experimental straight lines. These results are consistent with those of previous workers (with the exception of Eremina<sup>12</sup>) within experimental error:

Mixture	$10^4 N_{\text{Ar}}$ , mole fraction Ar	
	this work	published data
Argon-benzene	$8.44 \pm 0.25$	$7.94 \pm 0.08$ (Ref.12)
		$8.73 \pm 0.18$ (Ref.13)
		$8.77 \pm 0.20$ (Ref.14)
Argon-toluene	$10.42 \pm 0.31$	$9.41 \pm 0.09$ (Ref.12)
		$10.74 \pm 0.21$ (Ref.13)
		$10.897 \pm 0.015$ (Ref.15)

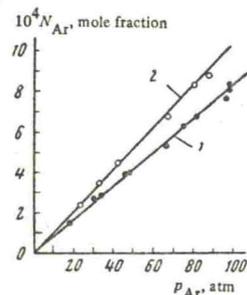


Figure 4. Solubility of argon as a function of gas pressure in 1) benzene and 2) toluene

The slight disagreement with published data may be ascribed to systematic error in the methods used by the previous workers<sup>12-15</sup>, since our procedure appears to exclude the possibility of systematic errors from uncontrolled loss of material during sampling.

Thus, the method described offers new possible applications of the mass spectrometer in thermodynamic and kinetic studies of liquids, arising from the choice of a capillary liquid inlet system.

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