The Effect of Dissolved Oxygen on Diamagnetic Susceptibilities.

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It is shown that oxygen exerts its normal paramagnetism when dissolved in benzene and in heptane, and the true susceptibilities of these liquids are changed by about 4·5% and 8·5% respectively when they are saturated with oxygen. This effect has been overlooked by earlier workers, probably because the liquids take up atmospheric oxygen very rapidly. This is demonstrated for the particular case of toluene by spectrophotometric measurements. Diamagnetic susceptibilities of organic liquids saturated with air may therefore be in error by as much as 1·7%. Two types of Gouy tubes are described, which can be evacuated, and are suitable for use with organic liquids.

In the determination of diamagnetic susceptibilities of organic liquids, little attention appears to have been given to the effect of dissolved atmospheric oxygen, although many workers have used boiled-out distilled water for calibration. The solubility of oxygen in water is much less than in the majority of organic liquids (Seidell, " Solubility of Inorganic and Metal Organic Compounds," Van Nostrand, 1940). Broersma (*J. Chem. Phys.*, 1949, **17**, 873), who alone appears to have studied this effect experimentally, says " The presence of paramagnetic oxygen is also of great interest. For water differences up to 3 per mil were found, after boiling for some time. Hydrocarbons never showed differences larger than our precision of measurement (~ 0·1%) in this respect." However, from the recorded solubilities of oxygen, and from its paramagnetic susceptibility, it can be calculated that the expected effect is only 0·14% of the diamagnetic susceptibility for water at room temperature, but should be approximately 1% for benzene and as much as 1·7% for heptane at room temperature (Seidell, *op. cit.*). These effects are much greater than the probable error of Broersma's and other recent measurements of diamagnetic susceptibilities. It is unlikely that oxygen dissolved in organic liquids would fail to exert its normal paramagnetism, especially as it appears to behave normally in its clathrate compound with β-quinol (Evans and Richards, *J.*, 1952, 3295) and also in very dilute solutions in liquid nitrogen (Perrier and Onnes, *Leiden Communications*, **139**, *d*, 48). Experiments have therefore been made on the effect of dissolved oxygen on the susceptibilities of benzene and *n*-heptane, completely air-tight Gouy tubes being used.

Experimental

The susceptibilities of the liquids were measured by the Gouy method using the apparatus described by Evans and Richards (*loc. cit.*). It is required that the Gouy tubes should have a vacuum-tight seal which will withstand organic solvents when the tube is shaken to ensure complete saturation of the liquid with the gas used. Attempts to use ground-glass connections of suitable size and shape failed, largely owing to the poor lubricating quality of greases which are unaffected by organic solvents. Two other designs were therefore used. The first, which was satisfactory for heptane, is illustrated in Fig. 1. The Gouy tube is made from egg-shell (0·3 mm. thick) glass tubing, and is cemented with Bakelite varnish to a brass cylinder, *D*; This contains an O-ring vacuum seal (Kurie, *Rev. Sci. Instr.*, 1948, **19**, 485) through which passes a glass tube, *G*, sealed at the lower end and with a small hole, *H*, blown in the side. Small copper suspension hooks are soldered at the top of the cylinder. By raising and lowering the glass tube, *G*, the Gouy tube can be sealed or opened to a gas system connected to the top of *G*.

This tube proved unsatisfactory for benzene, because the rubber O-ring swelled when in contact with the liquid. A somewhat more complicated arrangement was therefore used as illustrated in Fig. 2. The egg-shell Gouy tube is cemented with cold-setting Araldite to a brass top *T*, which supports the copper suspension hooks. A central hole in the brass top may be closed or opened by the screw, *S*, which forms a vacuum-tight seal when screwed down against the thin annular washer, *F*, which is made of " Fluon " (polytetrafluoroethylene). When the screw is released, gases may pass in or out of the Gouy tube through the slots, *K*, in the outer screw thread. The brass top, *T*, can be connected to a vacuum system by means of a short length of transparent plastic tubing, *P*, and the sealing screw, *S*, is operated by a stainless-steel screwdriver, *D*, which passes through the O-ring seal, *O*.

FIG. 1.

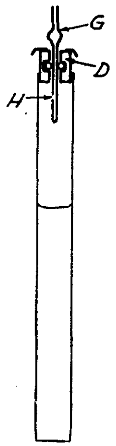
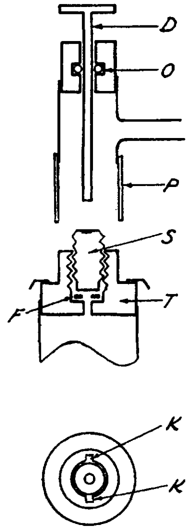


FIG. 2.



For each sample, the magnetic force was measured after saturation with (*a*) air, (*b*) nitrogen, and (*c*) oxygen. The liquids were degassed either by repeatedly cooling them to −78° and evacuating the Gouy tube (*n*-heptane) or by repeatedly opening the Gouy tube briefly to an evacuated bulb, and shaking vigorously each time after closing the seal (benzene). After this, the samples were saturated with the nitrogen or oxygen at atmospheric pressure, with frequent shaking between each exposure. Measurements were made at 21·5° ± 1°.

Materials.—The *n*-heptane was a pure sample prepared synthetically, which was kindly lent by Dr. F. J. Stubbs.

A sample of Kahlbaum's benzene " for molecular weight determinations " was fractionally distilled, and the middle fraction, boiling over a range of 0·2°, was collected. The oxygen and nitrogen were obtained from commercial cylinders.

Results.—The apparatus was calibrated with air-saturated benzene, the susceptibility of which was assumed to be $-0{\cdot}7020 \times 10^{-6}$ (Angus and Tilston, *Trans. Faraday Soc.*, 1947, **43**, 235; Selwood *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 3168; 1940, **62**, 2765, 3055). The values for the diamagnetic susceptibility, χ, of heptane are given in Table 1. The value found for the ratio of the susceptibilities of air-saturated heptane to air-saturated benzene agrees exactly with that found by Broersma (*loc. cit.*), but the ratio for the de-oxygenated liquids differs by about 1%.

TABLE 1. *Susceptibilities of heptane.**

Saturated with :	$-10^6\chi$	$-10^6\chi_M$	Saturated with :	$-10^6\chi$	$-10^6\chi_M$	Saturated with :	$-10^6\chi$	$-10^6\chi_M$
nitrogen	0·8665	86·65	air	0·8513	85·13	oxygen	0·7944	79·44

TABLE 2. *Susceptibilities of benzene.**

Saturated with :	$-10^6\chi$	$-10^6\chi_M$	Saturated with:	$-10^6\chi$	$-10^6\chi_M$	Saturated with :	$-10^6\chi$	$-10^6\chi_M$
itrogen	0·7081	55·22	air	0·7020 †	54·76	oxygen	0·6756	52·70

* χ = Specific susceptibility; χ_M = molar susceptibility. † Assumed.

DISCUSSION

It is clear from the above results that oxygen exerts a paramagnetic effect when dissolved in these solvents. In the case of heptane, the change of susceptibility on removal of dissolved *air* is $1{\cdot}7_9\%$, in good agreement with the value of 1·73% calculated from the Bunsen coefficient, α, for oxygen in heptane of 0·332 at 20°, reported by Glendinning and Bedwell ("Solubility of atmospheric gases, hydrogen and carbon monoxide," Unpublished Ministry of Supply Report), and the paramagnetic susceptibility of gaseous oxygen at 21·5° ($+106 \times 10^{-6}$; Burris and Hause, *J. Chem. Phys.*, 1943, **11**, 442). Furthermore, using the value of the susceptibility of *n*-heptane saturated with oxygen, and allowing for the impurities in cylinder oxygen (about 2%), we calculate a value for the susceptibility of dissolved oxygen at 21·5° of $+111 \times 10^{-6}$. This compares favourably with the value for gaseous oxygen at this temperature of 106×10^{-6}.

The change of susceptibility of benzene on removal of dissolved air is 0·87%, compared with the calculated value of 0·96%, using a value for the Bunsen coefficient α for oxygen in benzene at 20° of 0·206. This is an average of the values quoted by Glendinning and Bedwell (0·207) (*loc. cit.*) and by Horiuti (0·204) (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1931, **17**, 125.) From the measurements on benzene saturated with oxygen, a value for the paramagnetic susceptibility of oxygen at 21·5° is obtained of 110×10^{-6}.

From these two examples, it seems likely that dissolved oxygen exerts its usual paramagnetism in organic solvents. The failure of Broersma (*loc. cit.*) to observe any effect of this kind is probably due to the great rapidity with which these substances appear to take up oxygen from the air. This was shown qualitatively, by using the absorption band in the near ultra-violet region of the spectrum, which is shown by oxygen in aromatic solvents (Evans, *J.*, 1953, 345). Quartz absorption cells of thickness 1 cm., fitted with C 10 sockets, were filled with toluene, which was degassed and then saturated with nitrogen. One cell was then opened to the air, and the increase in optical density at 2850 Å observed on a Unicam SP 500 spectrophotometer, without moving the cells in any way. After 10 min. the optical density was about 40% of that corresponding to complete saturation with air, and after 20 min. about 70% of that value. The effect of shaking was particularly marked. If the toluene saturated with nitrogen was poured quickly into another absorption cell, its optical density measured immediately was already 65% of that expected for complete saturation with air. During the measurement of diamagnetic susceptibilities the samples are often exposed to the air for much longer periods than these, and so complete saturation would presumably be obtained, even if the sample had been previously degassed.

It seems likely, therefore, that many measurements of diamagnetic susceptibilities reported in the past are in error by an amount corresponding to the effect of dissolved oxygen, which may be as great as 1·7%. Since there are few recorded values for the solubility of oxygen in organic liquids, it is clearly desirable that accurate measurements of susceptibilities should be made in the absence of air.

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