# *The Polarisation of Azobenzene as a Vapour.*

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Modifications of previously used apparatus are described, making possible the taking of polarisation measurements up to temperatures of 340°. The total polarisation of azobenzene as a gas is found to be *ca.* 66 c.c.—a value of the order to be expected from the known molecular refraction, and one indicating that the atomic polarisation is about 9 c.c.

As azobenzene boils at 293° at ordinary pressures the thermostat and cell arrangements previously found satisfactory up to *ca.* 200° (cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374; Le Fèvre, Ross, and Smythe, *J.*, 1950, 276; Le Fèvre, Mulley, and Smythe, *J.*, 1950, 290) required modification as follows.

## Experimental

The gas cell has the dimensions given by Le Fèvre (" Dipole Moments," 3rd Edn., Methuen and Co. Ltd., London, 1953, p. 38), but instead of mercury-containing side-arms the emergent platinum leads are spot-welded to stout copper wires which pass through the roof of the oven. The lead from the central cylinder of the condenser is insulated by being threaded through Pyrex glass tubing, which in turn is surrounded by an earthed brass pipe which projects 1″ above and below the case of the thermostat. If the angular coaxial-cable connection holding the cable from the oscillator were soldered directly to the top of the brass tube the plastic dielectric would be affected by heat. Therefore the connector is separated from the tube by three 1″ vertical, thin, brass rods; this arrangement effectively shields the glass-insulated part of the lead. The second lead from the cell is brought out naked and soldered to the earthed outer edge of the cable connector.

The thermostat is constructed from a laboratory drying oven (internally 1′ cube) lagged with two layers of 1/4″ asbestos sheet on all six faces. Electrical heating elements are carried on asbestos boards on the left and right inner walls and the floor. The shaft of a fan stirrer, powered by an external motor, enters from underneath. The gas cell is supended from the (removable) centre of the roof by a thick brass rod to the bottom of which is screwed a " spider " upon which the cell rests. " Temperature smoothing " is effected by means of a massive aluminium cylinder, of external diameter 3·25″, which completely surrounds the cell; the cell fits snugly into a cavity of diameter 2″. To allow access to the cell, the aluminium block is split length-wise. The rear section is fixed independently of the cell to the roof and the front section is screwed to the rear section by wing nuts and bolts passing through ears. Accommodation for the gas-inlet tube of the cell is moulded in the aluminium halves. A bimetallic thermo-control is fitted through the front part of the roof; the temperature of the cell contents is read by a thermometer whose bulb is level with, and close to, the centre of the cell.

The gas-handling apparatus is indicated in the Figure. Items to the left of the manometer $M_2$ are used for the purification of the carbon dioxide or sulphur dioxide used as standard. Bulb $A$ contains phosphoric oxide supported on glass-wool. The gas is distilled from its cylinder through $A$ into trap $B$; traps $B$ and $C$ serve for the repeated cyclic distillation of the gas, which may be passed through $A$ or not, as desired. Trap $D$, which is removable, serves for the tapping-off of the first and last fractions of the distillations. Trap $B$ can also be removed, to make possible the introduction of drying agents, distillation from fresh phosphoric oxide being the most efficient. The bulbs $E$ and $E'$ contain glass-wool to prevent phosphoric oxide being carried through the apparatus when the liquid in the trap $B$ bumps while boiling: after each gas-purification, these bulbs are cut out and washed.

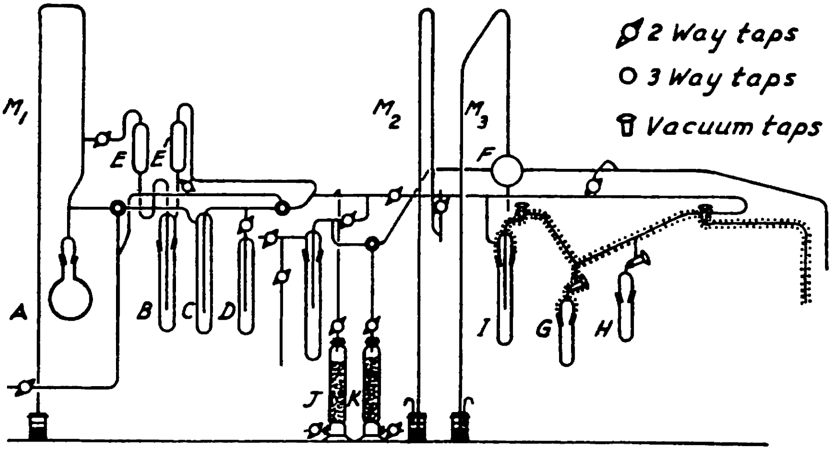
The pressure of the gas is checked at all stages by connections to the manometers $M_1$ and $M_2$. The gas is finally collected in trap $C$, and is distilled into the gas-cell when required.

The remainder of the apparatus is provided for the handling of substances, which (melted if necessary) can be boiled in the tubes $G$ and $H$. The glass tubing, taps, and ground-glass joints between the tubes and the cell are wound with Nichrome resistance wire (0·0285″ diam., 10 turns/in.). The heating system is supplied with current from a 240 v, 9 A, variable transformer set at 170—230 v, depending on the desired temperature. The liquid is first frozen in the tube *G* or *H*, the apparatus is evacuated, and, on melting, the liquid may be vapourised by heating it with a Bunsen burner. After measurement, the vapour is collected in the liquid-air trap *I*. The vacuum-taps in the high-temperature sections of the apparatus are lubricated with Silicone grease (Imperial Chemical Industries Limited). Even so, entrainment of the grease by the vapours at high tempertures necessitates the occasional dismantling, washing, and re-assembly of the hot-vapour handling system.

The manometer $M_3$ measures the pressure of air which, in the glass-diaphragm gauge to be described below, balances the pressure exerted by the vapour in the cell. The bulb *F* both increases the volume of the balancing system and acts as a splash-trap for mercury in the event of accidents to $M_3$.

The towers *J* and *K* serve to admit air (dried by $CaCl_2$ or $P_2O_5$) to the gas-handling and pressure-balancing systems, respectively.

For the applications now intended it is necessary to measure the pressure of a vapour at a high temperature, without allowing condensation to take place on cooler parts of the apparatus. The vapour must therefore be separated from the manometer on which the pressure readings are taken. In addition, the pressure must be known with an accuracy of ±1 mm. Hg, and measurements must be possible over the ranges 0—760 mm. Hg and 20—300° or above. Speed of manipulation of the measuring device is important.



The small number of potentially useful devices has been reviewed by Partington (" Advanced Treatise on Physical Chemistry," London, 1949, Vol. I, p. 560). Eventually, a glass-diaphragm gauge of the type described by Lockspeiser (*J. Sci. Inst.*, 1930, **7**, 145), who used silica as the material, or by Klemenc (*J. Amer. Chem. Soc.*, 1925, **47**, 2173) was constructed and is part of the apparatus.

The vapour is confined inside a small (1″-diam.) glass bulb inside the thermostat and is connected to the outlet from the gas-cell. One side of the glass bulb, whose walls are extremely thin (*ca.* 0·1 mm.) has been carefully flattened by heating in a cool flame; this forms a diaphragm, tightly stretched across the decapitated bulb, which responds with a movement of 1—2 mm. at the centre to variations of the pressure difference between its two sides. Of over 200 diaphragms thus made, only two survived a pressure difference of 1 atm. at 200—300°.

The bulb is sealed by a ring-seal into the lower end of a glass cylinder, which projects through the roof of the oven and is connected to the bulb *F* and manometer $M_3$. The balancing pressure may be lowered by pumping or raised by admission of air through a phosphoric oxide tower.

A light metal spring rests on the upper surface of the diaphragm. In the equilibrium position, this spring just touches a rigidly supported platinum-wire point, making an electrical circuit which lights a small bulb fastened on the scale of $M_3$. The pressure reading is thus made whenever the light " goes on."

The pressure gauge is calibrated before each series of readings, *i.e.*, at every temperature, since electrical contact is not necessarily made when the known and the unknown pressure are equal; a small difference usually exists. Calibration is easily achieved by admitting known pressures of air—measured on $M_2$—into the cell, and then observing on $M_3$ the value at which the bulb lights. The calibration also measures the consistency of the readings. Under the extreme condition of 320°, readings were consistent to within 3 mm., and the mean of four readings usually gave a value which was not altered much by further readings. Nevertheless, sudden changes in the calibration factor did occur in several runs at temperatures above 220°, and half-hourly re-calibrations are part of the measuring routine. The gauge cannot be used with the apparatus described at temperatures above 320°, which is thus the effective upper limit to the temperature of measurement. At this point the thermostat arrangements have been found usually to hold the cell temperature constant to 0·25°, though slow drifts of up to 1° per hour sometimes take place; these can easily be counterbalanced by manual adjustment of the regulator.

The whole apparatus has been in use for several years, measurements on 1 : 8-cineole (Freeman, Le Fèvre, and Maramba, *J.*, 1952, 1649), methylene dibromide and bromoform (Buckingham and Le Fèvre, *J.*, 1953, 3432), benzyl alcohol (Buckingham, Le Fèvre, and Holland, *J.*, 1954, 1646), and various non-polar substances (Le Fèvre and Rao, *Australian J. Chem.*, 1954, **7**, 135; 1955, **8**, 39) being made with it. As standardising gases sulphur dioxide, carbon dioxide, or benzene has been employed at different times; lately, from experience, we have come to prefer the last substance. Polarisations are taken as follow: for $SO_2$, $P = 10·9 + 16160/T$ (cf. *J.*, 1950, 276); for $CO_2$, $P = 7·341$ c.c. (cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374); for $C_6H_6$, $P = 27·0$ c.c. (cf. Le Fèvre and Rao, *loc. cit.*).

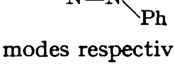
*Polarisations of Azobenzene.*—The azobenzene was recrystallised from alcohol (in the dark) then dried and stored in a blackened desiccator; it had m. p. 68°. Measurements are tabulated under the usual headings, $x$ and $x'$ being the limiting values of $\Delta C/p$ as $p$ approaches zero for the vapourised azobenzene and the standard gas ($CO_2$) respectively (see Le Fèvre, *op. cit.*, and other references given above).

*Polarisations of azobenzene at various temperatures.*

| Temp. (°K) | $x/x'$ | $p$ range (cm. Hg) | No. of obstns. | $P$ (c.c.) |
|---|---|---|---|---|
| 509·4 | 9·48 | 5—11 | 9 | 69·2 |
| 513 | 9·32 | 3—14 | 16 | 68·4 |
| 529·5 | 9·16 | 4—17 | 11 | 67·3 |
| 541 | 9·06 | 6—19 | 16 | 66·5 |
| 569 | 9·10 | 5—17 | 19 | 66·8 |
| 587 | 9·48 | 3—19 | 17 | 69·6 |
| 611 | 8·91 | 6—23 | 18 | 65·4 |

The departure from constancy is greater than that usually experienced with non-polar dielectrics at lower temperatures. Noting that our higher temperatures exceed those recorded by Coop and Sutton (*J.*, 1938, 1269) by some 50°, we consider our results to be fairly satisfactory when judged against those shown by these authors for certain acetylacetone complexes (*e.g.*, of Cr, 127·5—133·7 c.c., or of Al, 129·3—132·8 c.c.). The mean, with standard variation, of the above seven determinations is therefore 67·6 ± 1·5 c.c.

Such a conclusion is in harmony with the $_{\infty}(P_2)$ of 67 c.c. found in benzene as solvent by Hartley and Le Fèvre (*J.*, 1939, 531). It is also compatible with the known refractivities (in c.c.) of azobenzene. These, determined on molten material or on solutions in various solvents, have ranged between $R_{\alpha} = 62·28$ c.c. for the melt to $R_D = 65·33$ in acetic acid (Duval, *Compt. rend.*, 1911, **153**, 875; Auwers and Heimke, *Ber.*, 1928, **61**, 1030; Auwers, *Ber.*, 1938, **71**, 611). The nearness of the above wave-lengths to absorption lines will invalidate the usual extrapolations to $R_{\infty}$, but—noting that $R_{\alpha}$ or $R_D$ is calculated from bond constants by Auwers (*loc. cit.*) as around 57 c.c.—we may infer that the atomic polarisation is about 10 c.c. (*i.e.*, roughly 17% of $_EP$).



That such an estimate is reasonable may be demonstrated as follows. Considering *trans*-azobenzene as the 4-point system inset, and applying parallel arguments to those used by Le Fèvre and Rao (*locc. cit.*), we compute $_AP$ as the sum of three terms due to stretching, in-plane bending, and twisting modes respectively:

$$_{A}P = \frac{8\pi N e^2}{9k_1} + \frac{8\pi N\mu^2}{9k_{\delta}} + \frac{8\pi N\mu^2}{9k_r}$$

where $e$ is the electronic charge, $\mu$ is the link moment $\mu_{Ph-N}$, and $k_1$, $k_{\delta}$, or $k_r$ the appropriate force constants. The last are, of course, unknown for azobenzene. Their order of magnitude being assumed to be $k_1 = 10^5$ dynes/cm., and $k_\delta$ or $k_r = 2{\cdot}10^{-12}$ ergs/radian², ${}_{\mathrm{A}}P$ emerges—with $\mu = 2$ D (cf. Le Fèvre and Vine, *J.*, 1938, 431)—as around 7 c.c., to which *ca.* 2 c.c. may be added for the phenyl groups (Le Fèvre and Rao, *loc. cit.*), making 9 c.c. in all.

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