



Fig. 2.

- Dimethylbutadiene sealed *in vacuo*.  
 -▽- " + 0.5% benzoyl peroxide.  
 -△- " + 1.0% benzoyl peroxide.

dimethylbutadiene distilled and sealed *in vacuo*. It will be noticed that in the absence of catalyst there is a fall in diamagnetism over the first three hours and that thereafter there is a progressive rise in diamagnetism as is to be expected<sup>1</sup>.

We consider that measurements of this type will throw light on the nature of the induction period in polymerization reactions. Induction periods have been identified with the time of formation of polymerization nuclei; thereafter the polymerization proceeds as a chain reaction<sup>2</sup>. It is probable that the polymerization nuclei are activated molecules, and the simplest assumption to make is that they are free radicals. This would explain our magnetic result, as such free radicals would necessarily be paramagnetic, and their formation in the dimethylbutadiene would result in a fall in diamagnetism.

If the first series of results be examined further, it will be noticed that the initial fall in diamagnetism is in the neighbourhood of 13.6 per cent. It is possible to calculate the concentration of free radicals which would give this lowering if the assumption be made that the free radicals are of the type of dimethylbutadiene with one free electron. The mass susceptibility of dimethylbutadiene by this series of measurements is approximately  $-0.75 \times 10^{-6}$ . In a paramagnetic molecule with one free electron<sup>3</sup>, the paramagnetic contribution to the molecular susceptibility is theoretically  $1270 \times 10^{-6}$ . The diamagnetic contribution in this case is  $-61.5 \times 10^{-6}$ . The mass susceptibility of such a molecule will thus be  $0.133 \times 10^{-6}$ . The concentration of free radicals of this type necessary to lower the mass susceptibility of dimethylbutadiene by 13.6 per cent can now be calculated to be 0.10 mols per cent.

If the concentration of catalyst necessary to give a smooth curve be now considered, it is evident that this must be less than 1.0 per cent by weight, or, if the results for the material sealed *in vacuo* be considered, it lies somewhere between 0.5 and 1.0 per cent by weight, for there still seems to be a lowering of diamagnetic susceptibility with 0.5 per cent catalyst *in vacuo*. It is thus necessary to have a concentration of catalyst somewhere between 0.17 and 0.34 mols per cent to give a smooth curve. If we consider that all the molecules of accelerator are active in promoting the polymerization, it is a significant fact that the concentration of active centres calculated from the magnetic result should lie so near the concentration of the catalyst.

JOHN FARQUHARSON.  
P. ADY.

University College,  
Rangoon.

<sup>1</sup> Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

<sup>2</sup> Dostal and Mark, *Trans. Faraday Soc.*, **33**, 350 (1933).

<sup>3</sup> Stoner, "Magnetism and Matter", 477.

### 'Acidity' of Quartz

WHEN quartz powder, obtained by finely grinding pure Brazilian pebble, is put into neutral water the pH is rapidly lowered to about 6.4. This acidity has been attributed to silicic acid, but such an explanation seems unlikely for the following reasons.

Pure quartz has an extremely low solubility in water free from carbon dioxide, namely, only a few parts per million at room temperature, and the rate of solution would not be great enough to cause the acidity produced. Further, the dissociation constant of silicic acid<sup>1</sup> is very small (about  $10^{-10}$ ) and there is doubt whether the behaviour of silicic acid can be represented in terms of dissociation constants<sup>2</sup>. Silica sol prepared under conditions where adsorption of hydrogen ions is impossible is quite neutral<sup>3</sup>. Hence the acidity rapidly imparted to water by quartz dust is probably not due to silicic acid, and it is suggested that carbon dioxide adsorbed on the quartz is responsible for the effect.

Samples of the quartz dust were heated to about 300° C. *in vacuo* until the evolution of gas ceased. After cooling *in vacuo*, these samples were quite without effect on the pH of neutral water. An approximate computation showed that the quantity of gas evolved (all of which may not have been carbon dioxide) was ample to account for the observed acidity. The addition of pure sodium chloride (itself quite neutral in water) increased the acidity of the quartz dust-water system. This is also consistent with the view that the acidity is due to carbon dioxide, for the presence of sodium ions lowers the bicarbonate ion concentration, thus increasing the fraction of the dissolved carbon dioxide that is present as carbonic acid, with a consequent increase in the hydrogen ion concentration.

G. VAN PRAAGH.

Christ's Hospital,  
Horsham.  
June 1.

<sup>1</sup> Joseph and Oakley, *J. Chem. Soc.*, **127**, 2814 (1925).

<sup>2</sup> Britton, *J. Chem. Soc.*, **129**, 425 (1927).

<sup>3</sup> Baibaiev and Kargin, *Acta Physicochem. U.S.S.R.*, **3**, 97 (1935).

### Chelate Structure of *o,o'*-Dioxyazobenzene in Solution

THE idea that the *o*-oxyazo compounds have the chelate structure is now quite convincing. It is supported by much chemical and physical evidence, such as the slight acidity, anomalous chemical reactivities referred to phenolic hydroxyl, small association factor, slight solubility in polar solvents, molecular refraction data, absorption spectra, etc. The strongest support for the chelate structure was found by Hendricks and others<sup>1</sup> in the study of infra-red absorption spectra in carbon tetrachloride solution. On similar grounds they concluded from the absence of the absorption band at *c.*  $1.4\mu$  corresponding to the first overtone of hydroxyl vibration that *o,o'*-dioxyazobenzene has the doubly chelated *trans-trans* configuration as (I). From the chelation of both the hydroxyl groups in (I), it may be expected that the *o,o'*-dioxyazobenzene, like the *o*-mono-oxyazo compounds, is very slightly acidic. But the former is actually found to be very easily soluble in weak alkali. It may therefore be supposed that the chelate structure of the *o,o'*-dioxyazobenzene is