

acting on it is a function of the difference in volume susceptibilities of the test-piece (K_0) and of the surrounding solution (K_1). In order to eliminate errors from variations in field intensity the test-piece was made of glass filled with gadolinium oxide so that $K_0=K_1$. The apparatus was sensitive to 0.005 per cent, apparently about four times less sensitive than Specchia's apparatus. The light sources were a 100 watt microscope lamp, and a carbon arc. Cupric chloride solution was used to filter out the infra-red. The results obtained in every case confirmed those of Gorter; no increase was observed, but a slow decrease took place. The temperature increase due to radiation absorption was about 0.0002° per second, which was roughly that expected to cause the observed decrease in susceptibility. A marked movement of the test-piece occurred on exposure to light from which the infra-red had not been thoroughly screened off. This was doubtless due to a radiometer effect. It could be almost eliminated by making the light path strictly parallel to the test-piece.

It may be worth mentioning that the explanation of the increase in susceptibility given by Bose and Raha⁷ seems to be open to the following objection. They suggest that the light causes a temporary breakdown of the l -coupling between paramagnetic ion and associated solvent molecules, thereby reducing the orbital moment damping. Such a mechanism could scarcely give rise to their observed increase of the same order of magnitude in didymium salts, as in say ferric chloride, because in the former case the 4f electrons which are responsible for the paramagnetism are almost completely screened from external influences, while for elements of the first transition series the orbital moments are usually strongly if not completely damped by the electrons of neighbouring ions or molecules.

P. W. SELWOOD.

Frick Chemical Laboratory,
Princeton, N.J.

¹ Bose and Raha, *NATURE*, **127**, 520, April 4, 1931.

² Bose and Raha, *NATURE*, **130**, 544, Oct. 8, 1932.

³ Specchia, *NATURE*, **130**, 697, Nov. 5, 1932.

⁴ Specchia, *Nuovo Cimento*, N.S., **8**, 391; 1931.

⁵ Gorter, *NATURE*, **130**, 60, July 9, 1932.

⁶ Decker, *Ann. Physik*, **79**, 324; 1926.

⁷ Bose and Raha, *Z. Physik*, **80**, 361; 1933.

Supersaturation of Liquids with Gases

ALTHOUGH it is well known that liquids may be supersaturated with gases, the extent to which a gas may be retained in supersaturated solution does not seem to be generally realised, and no quantitative information about the phenomenon is given in most textbooks on physical chemistry.

We recently had occasion to repeat some experiments by E. C. Gilbert¹ on the oxidation of hydrazine by potassium ferricyanide, in which the course of the reaction was followed by measuring the rate at which nitrogen gas was evolved. The velocity constants obtained were much higher than those recorded by Gilbert at the same temperature and with the same initial concentrations of reagents. It was found that the rate of evolution of gas was controlled mainly by the rate of stirring, increasing with the latter up to about 1,000 r.p.m. (The rate of stirring in Gilbert's experiments was 250 r.p.m.)

That this result was due to supersaturation of the aqueous solution by the nitrogen produced in the reaction, and not to genuine variation of the reaction

rate with stirring, was shown by allowing the reaction to proceed for some time in unstirred solution, and then stirring vigorously. Rapid evolution of gas occurred, and the total volume evolved soon equalled that which would have been obtained if the solution had been stirred from the beginning. In some cases the amount of nitrogen which accumulated in the unstirred solution was seven or eight times the normal solubility of the gas.

Since the course of many reactions is followed, in quantitative work on chemical kinetics, by noting the rate of evolution of a gaseous product, it is important to emphasise the fact that supersaturation, unless broken down by adequate means, is likely to invalidate completely results obtained in this way.

The extent to which supersaturation may occur in solutions saturated with gases under pressure has already been demonstrated in papers which appear to have received less attention than they deserve.

K. S. Wyatt² found that an aqueous solution of nitrogen, saturated at a pressure exceeding 100 atmospheres at air temperature, could be brought to atmospheric pressure without the immediate formation of bubbles in the liquid, and F. B. Kenrick, K. L. Wismer, and K. S. Wyatt³ obtained similar results with oxygen, nitrogen and carbon dioxide. J. Metschl⁴ investigated the supersaturation of water and various organic solvents with oxygen, nitrogen, hydrogen and carbon dioxide at five atmospheres pressure, and found that the resulting solutions were very stable at atmospheric pressure, vigorous agitation being required before all the excess gas could be removed. Metschl's paper contains references to earlier work on the subject, mostly of a qualitative nature.

When a solution is supersaturated with a solid, introduction of a crystal of the solid immediately induces crystallisation, but in the case of a solution supersaturated with a gas, the presence of bubbles of the gas is not similarly effective. For example, in the oxidation of hydrazine by ferricyanide, gas is slowly but continuously evolved, even when the solution is unstirred, without breaking down the supersaturation.

Further work is being carried out on this reaction.

T. N. RICHARDSON.

KENNETH C. BAILEY.

Trinity College,

Dublin.

March 28.

¹ *J. Phys. Chem.*, **35**, 3631; 1931.

² *Trans. Roy. Soc. Canada*, [iii], **18**, 127; 1924.

³ *J. Phys. Chem.*, **28**, 1308; 1924.

⁴ *J. Phys. Chem.*, **28**, 417; 1924.

Alkylanilines with Tertiary Alkyl Groups

THE preparation of alkylanilines containing tertiary alkyl groups by the reaction of tertiary alkyl halides with aniline is known to present serious difficulties. Thus Nef¹ obtained only a poor yield of tertiary butylaniline in this way and his attempts to prepare tertiary amylaniline furnished only an impure product. By using suitable modifications of Nef's method, it has been possible to obtain tertiary butylaniline, tertiary amylaniline and tertiary hexyl aniline in a state of purity.

An examination of the reactions of these amines has revealed some surprising abnormalities. The tertiary alkyl group is split off by heating the amines