NOTES.

Air Oxidation of Titanous Sulphate Solution. Vanadous Sulphate, a New and Powerful Reducing Agent. By A. S. RUSSELL.

THE powerful reducing agent, titanous sulphate, is used less than it might be on account of the trouble of preserving it from oxidation by air. I am not aware than any worker with this reagent has said that this is unnecessary. Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 2nd ed., 1925, p. 62), who have the largest experience of this reagent, say that any results obtained without taking the precaution of preventing air oxidation are valueless. My experience is different. When a solution of titanous sulphate in $4N$-sulphuric acid is prepared from titanic sulphate by Nakazono's rapid method (*J. Chem. Soc. Japan*, 1921, **42**, 526), and kept in a burette exposed to air, I find that its titre when standardised with $N/10$-permanganate remains constant for 12 hours. It follows that precautions to exclude air are unnecessary. It is also a consequence that if titanium itself be determined by reducing titanic sulphate with zinc amalgam and titrating the liquid after separation with permanganate, the work can be carried out in air if the acidity of the titanium solution is $4N$-sulphuric acid. I confirmed this by alternately reducing with zinc amalgam and oxidising with $N/10$-permanganate four times a volume of titanic sulphate of known concentration without excluding air. The titres were constant and equal to that calculated on the assumption that the reduction was quantitative. Titanous sulphate thus resembles ferrous and uranous sulphates in being stable in air at the ordinary temperature if in $4N$-sulphuric acid.

It is not necessary to adopt the excellent but elaborate method of Knecht and Hibbert (*op. cit.*, p. 63) for preserving titanous sulphate solution for a long time. It is simpler to have a solution of titanic sulphate in $4N$-sulphuric acid and, whenever titanous sulphate is needed, to reduce the volume required with zinc amalgam for 1 minute, decant the liquid into a flask, transfer to a burette, and immediately before use standardise it against $N/10$-permanganate. I find it is not oxidised by the air when run into hot or boiling solutions reduced by it. I find also that titanous sulphate is not less powerful as a reducing agent than the chloride and that the reducing power is unaffected by the presence of the free sulphuric acid. The sulphate solution is consequently simpler to use than the chloride, because in practice back titrations are done with permanganate as well as with ferric alum.

Vanadous sulphate has not, I think, been previously used as a reducing agent. I find that it is a more powerful reducing agent than titanous sulphate, reducing with greater ease all the inorganic and organic substances reduced by the latter. It reduces titanic sulphate itself in the cold. It lies between cadmium and tin in its reducing power in $2N$-sulphuric acid, whereas titanous sulphate was found to lie between lead and copper. It is, as is to be expected, much more susceptible to air oxidation, but not to such an extent that precautions to exclude air when using it are essential. A $N/10$-solution in $10N$-sulphuric acid is not measurably oxidised by air when kept for an hour in a burette. It may therefore be used without excluding air in volumetric work which can be completed within that time. It is prepared by the same method and as quickly as titanous sulphate.—DR. LEE'S LABORATORY, CHRIST CHURCH, OXFORD. [*Received, November 3rd*, 1925.]

The Effect of Heat on Chloral Hydrate. By JAMES DENIS MOUNFIELD and JOHN KERFOOT WOOD.

THE temperature at which the dissociation of chloral hydrate commences is unknown. It is complete at 78°, and the variability of the melting point suggests that it may occur to a considerable extent at about 50°. Pope (J., 1899, **75**, 455) has suggested that two modifications of chloral hydrate may exist, but the work of Van Rossem and Jaeger (*Z. physikal. Chem.*, 1908, **62**, 701) would appear to discredit this view.

To obtain further information on these matters, the authors have conducted dilatometric and tensimetric measurements with chloral hydrate. Repeated experiments with "liquid paraffin B.P." as the indicating liquid showed that chloral hydrate suffers a change of volume at 32°; similar indications were given by samples which had been maintained at 20° and 40° for several days and which were slowly heated and cooled, respectively.

In the tensimeter experiments, the vapour pressure was measured at small intervals of temperature between 15° and 40°. The results are in Tables I and II, the former referring to rising and the latter to falling temperature; the pressures indicate millimetres of α-bromonaphthalene.

TABLE I.

Temp.	Press.	Temp.	Press.
15·65°	6·12	31·10°	17·29
18·90	8·16	31·90	18·08
19·80	8·67	33·00	19·33
21·30	9·53	34·00	20·31
23·01	10·69	34·55	21·20
24·80	11·96	35·50	22·38
26·70	13·40	36·50	23·95
27·10	13·78	37·30	24·82
28·50	14·99	37·73	25·34
29·50	15·90	38·05	26·20
30·35	16·63	38·50	26·90

TABLE II.

Temp.	Press.	Temp.	Press.
37·70°	25·29	30·00°	16·20
37·25	24·60	28·70	15·22
36·43	23·61	27·60	14·08
35·90	22·72	25·70	12·59
34·95	21·70	24·00	11·20
33·60	19·80	21·80	10·00
32·50	18·60	20·85	9·21
31·50	17·81	19·45	8·42
31·20	17·56	—	—

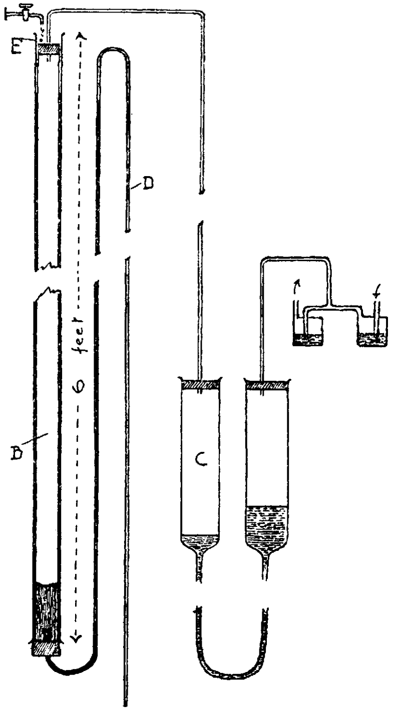
The values obtained in the two series of experiments are in agreement and show the complete absence of a break in the vapour pressure curve in the vicinity of 32°; Ramsay and Young (*Phil. Trans.*, 1886, **177**, 76), from observations made at much larger intervals of temperature, also obtained a smooth curve. From the absence of a break in the vapour pressure curve it would appear most probable that the change which occurs at 32° does not correspond to a change of modification, but marks the commencement of the dissociation of chloral hydrate.—MUNICIPAL COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, October* 10*th*, 1925.]

Preparation of Ethylene Bromohydrin. By FREDERICK HENRY McDOWALL.

IN the method of preparation of ethylene bromohydrin described by Read and Williams (J., 1917, **111**, 240) and Read and Brook (J., 1920, **117**, 359, 1214), bromine is carried over into the reaction chamber in the form of vapour by a current of air. This has several disadvantages. The ethylene becomes considerably diluted by the air, and a great deal is carried away, so that of the total amount used, only one-third is absorbed. Furthermore, the supply of bromine is not easily regulated.

These disadvantages can be obviated by dropping the bromine from a small, finely-pointed burette down a guide-tube of small bore, the lower part of which reaches to the bottom of the reaction vessel, and is placed as far as possible from the ethylene inlet. The bromine can thus be introduced slowly and, with an efficient stirrer, it becomes dissolved in the water before contact with gaseous ethylene is possible. The yields obtained in two experiments coincided with the average of those obtained by Read and Brook (*loc. cit.*, p. 1214), while the quantity of ethylene used was only slightly in excess of that absorbed. [*Received, January* 12*th*, 1926.]

An Automatic Siphonic Gas Circulator. By George M. Green.



The apparatus described is the result of an unsuccessful attempt to construct a gas-circulating device of the type communicated by Pearson and Thomas (J., 1925, **127**, 2450). It does not contain a mechanical device of the plunger variety, and the advantages claimed for it are simplicity of construction and perfect continuity of action, once started. Its disadvantages lie in its comparative slowness and its well-defined intermittency. For certain kinds of laboratory work, however, the latter might recommend themselves.

The apparatus consists of two concentric glass tubes, *B* and *E*, about 6 feet long, one of which slides within the other, the annular space between them being about 1 mm. The inner tube, about 1 inch in internal diameter, is sufficiently heavy to resist the upward-moving tendency produced by the developing hydrostatic pressure. The siphon tube, the length of which can be varied by means of rubber tubing, should be of the greatest possible diameter consistent with rapid and efficient siphonage, and be placed at a suitable height above the working bench. The inflowing water, preferably under a constant pressure head, requires careful regulation at the commencement. The diameter of the upper portions of the **U**-tube, *C*, containing the oscillating mercury is 2 inches. The valves are of the ordinary mercury seal type. With this apparatus, a constant circulation of at least 50 c.c. of gas per minute is obtainable.—Technical College, Huddersfield. [*Received, December* 28*th*, 1925.]