NOTES.

Note on the Solubility of Sulphur Dioxide in Sulphuric Acid and the Existence of the Monohydrate. By JOHN ALBERT NEWTON FRIEND.

THE solubility of sulphur dioxide in aqueous solutions of sulphuric acid of concentrations ranging from 55·1 to 98·5% was determined by Miles and Fenton (J., 1920, **117**, 59). Upon plotting the observed solubility against the percentage of acid up to 84·2%, a straight line is obtained if the small deviations are regarded as due to experimental error. By extrapolation the solubility in pure water is approximately 10·0 g. of sulphur dioxide per 100 g. of water. This is a little lower than the value, *viz.*, 10·64 g., found by Hudson (J., 1925, **127**, 1340); the difference, which is immaterial for present purposes, is in part attributable to Hudson's results being calculated to a partial pressure of 760 mm. of sulphur dioxide, whereas the results of Miles and Fenton appear to refer to a total pressure of 760 mm. The curve also gives a solubility of approximately 2·8 g. of sulphur dioxide per 100 g. of solution containing 84·5% of sulphuric acid, a composition corresponding to H_2SO_4,H_2O.

If, now, we assume * that aqueous solutions of sulphuric acid of the high concentrations under discussion consist essentially of a mixture of water and H_2SO_4,H_2O, the solubility of sulphur dioxide in any particular concentration of acid may be regarded as made up of two quantities, namely, that in the free water and that in the monohydrate. From the above extrapolated data we can then calculate the solubility. Thus, consider the solubility S in a solution containing 68·9% H_2SO_4, equivalent to 81·5% H_2SO_4,H_2O. The free water is 100 — 81·5 or 18·5 g. Then

$$S = \frac{18{\cdot}5 \times 10{\cdot}0}{100} + \frac{81{\cdot}5 \times 2{\cdot}8}{100} = 4{\cdot}13 \text{ g.} \quad . \quad . \quad . \quad (1)$$

The observed value was 4·16 g.

The following results have been obtained in this way :

H_2SO_4 (%)	55·1	59·6	61·6	68·9	74·1	78·3	80·2	82·5	84·2
S (calc.)	5·31	4·92	4·76	4·13	3·69	3·33	3·17	2·97	2·83
S (obs., Miles and Fenton)	5·13	4·90	4·82	4·16	3·63	3·23	3·12	2·99	2·88

Apart from the first result, the agreement is very close, and supports the assumption made above. The curve shows that the observed value for 55·1% acid is slightly too low, hence the discrepancy; the calculated figure being probably more correct.

Equation (1) may be generalised, for x% of H_2SO_4, to

$$S = 10{\cdot}0 - 0{\cdot}0852x.$$

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* Analogous assumptions with entirely different solutions were made by Baur (*Ahrens' Sammlung*, 1903, **8**, 466) and by Philip (J., 1907, **91**, 711).

5-Bromo- and 5 : 4′-Dibromo-3-nitro-4-acetamidodiphenyls. A Correction. By FRANK BELL.

3-NITRO-4-ACETAMIDODIPHENYL on bromination was stated to give a mixture of 5-bromo- and 5 : 4′-dibromo-3-nitro-4-acetamidodiphenyls (Bell and Robinson, J., 1927, 1130); this conclusion is based on an analytical error: actually the free bases are produced. These may be crystallised unchanged from acetic anhydride, but addition of a drop of sulphuric acid readily effects acetylation. 5-*Bromo-3-nitro-4-acetamidodiphenyl* crystallises from acetic acid in colourless needles, m. p. 223° (Found : Br, 24·3. $C_{14}H_{11}O_3N_2Br$ requires Br, 23·9%), and the 5 : 4′-*dibromo*-compound separates from the same solvent in almost colourless needles, m. p. 251° (Found : C, 40·4; H, 2·6. $C_{14}H_{10}O_3N_2Br_2$ requires C, 40·5; H, 2·4%). This corrected result harmonises with that of Scarborough and Waters (J., 1927, 1138) and indicates that Hinkel and Hey's 5-bromo- and 5 : 4′-dibromo-3-nitro-4-acetamidodiphenyls (J., 1928, 1838) were unacetylated bases.—BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 1st,* 1931.]

The Basic Character of 3-Chloro-4-nitrosophenol and the Acidic Nature of 3-Chlorobenzoquinone-4-oxime. By HERBERT HENRY HODGSON.

IN a previous paper (this vol., p. 1495) it was pointed out that 3-chloro-4-nitrosophenol readily forms a picrate, whereas its oximic isomeride does not, and that this behaviour was in accord with electronic considerations which postulated a negative (basic) character for the nitroso-group and an acidic character for the oxime group. Further support to this view is afforded by the work of Hammick and Illingworth (J., 1930, 2363) and of Le Fèvre (this vol., p. 810), which shows that the nitroso-group in non-hydroxylic compounds is *m*-directing in acid solution but *op*-directing in neutral solution (see also Ingold, J., 1925, **127**, 513), whilst the bromine atom in *p*-bromonitrosobenzene does not react with aniline.

The above characteristics, if sufficiently intense, should be manifested in double-salt formation, and some evidence of this has been obtained; *e.g.*, 3-chloro-4-nitrosophenol forms *molecular compounds* with 2 : 4 : 6-trinitro-*m*-cresol [light yellow plates, m. p. 160° (decomp.) (Found : Cl, 8·7. $C_{13}H_9O_9N_4Cl$ requires Cl, 8·8%)], 3-fluoro-2 : 4 : 6-trinitrophenol [yellow plates, m. p. 147—150° (decomp.) (Found : Cl, 8·7. $C_{12}H_6O_9N_4FCl$ requires Cl, 8·8%)], 3-chloro-2 : 4 : 6-trinitrophenol [yellow plates, m. p. 163° (decomp.) (Found : Cl, 16·66. $C_{12}H_6O_9N_4Cl_2$ requires Cl, 16·86%)], 3-bromo-2 : 4 : 6-trinitrophenol [yellow prisms, m. p. 172—175° (decomp.) (Found : Cl + Br, 24·5. $C_{12}H_6O_9N_4ClBr$ requires Cl + Br, 24·8%)], and 3-iodo-2 : 4 : 6-trinitrophenol [yellow prisms, m. p. 177° (decomp.) (Found : Cl + I, 31·4. $C_{12}H_6O_9N_4ClI$ requires Cl + I, 31·7%)], but crystallises unchanged from methyl-alcoholic solutions of *o*-, *m*-, and *p*-nitrophenol, 2 : 4-dinitrophenol, 4-nitro-1-naphthol, 1-nitro-2-naphthol, 3-chloro-2 : 4 : 6-tribromophenol, benzoic, oxalic, and gallic acids.

3-Chlorobenzoquinone-4-oxime forms molecular compounds with *urea* [slender light brown needles, m. p. 160° (decomp.) (Found : Cl, 16·1. $C_7H_8O_3N_3Cl$ requires Cl, 16·3%)] and *acridine* [slender light yellow-brown needles, m. p. 174° (Found : Cl, 10·4. $C_{19}H_{13}O_2N_2Cl$ requires Cl, 10·5%)], but crystallises unchanged from methyl-alcoholic solutions containing aniline, acetamide, or benzamide.

Neither isomeride forms double compounds with *s*-trinitrobenzene or *s*-trinitrotoluene.

Molecular-weight determinations of the double compounds showed them to be largely dissociated in the solvents employed. The values recorded are the means of several determinations.

		M,	
Substance.	Solvent.	Obs.	Calc.
3-Chloro-4-nitrosophenol picrate	Phenol	204·2	386·5
,, ,, ,,	Nitrobenzene	212	386·5
3-Chlorobenzoquinone-4-oxime–urea	Phenol	78·7	217·5
,, ,, ,,	*o*-Cresol	93	217·5
,, ,, ,,	Naphthalene	142	217·5
,, ,, ,,	Nitrobenzene	Urea crystallised first.	
3-Chlorobenzoquinone-4-oxime–acridine	Phenol	168·2	336·5
,, ,, ,,	*o*-Cresol	254	336·5

Double Compound of 3-*Chloro*-4-*Nitrosophenol with* 3-*Chlorobenzoquinone*-4-*oxime*.—When equal quantities of these substances are dissolved in hot methyl alcohol and cooled, greenish-yellow needles separate which decompose at 145°, depressed by addition of either component. A mixture of equal weights of the isomerides decomposes at 136—138°. In phenol and in acetophenone the compound is dissociated.

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