of the original crystal or liquid. Under these circumstances the position, shape and orientation of the condensed phase is maintained constant by the condition that most of it will not evaporate at all and, hence, determines the location of the phase as a whole. The matter might be made clearer if we regarded N' not as the total number of molecules in the condensed phase, but as the number of molecules in a layer on the surface of the phase taken of sufficient depth so that no change in the results would arise from an increase of depth.

Summary

In the foregoing article we have applied the methods of statistical mechanics to a determination of the entropy of crystals and supercooled glasses, and have reached the following conclusions.

1. The difference per mole in the entropy of a given substance at the absolute zero in the form of a glass and crystal can be given by an equation of the form $S_{\text{glass}} - S_{\text{crystal}} = R \log a$, where a is a small number increasing with the complexity of the molecule.
2. The exact nature of the quantity a is given by the equation, $\phi(N') = c\,a^{N'}$, which gives the number of ways in which we can arrange the mean positions of the N' molecules of a glass, when the degrees of freedom corresponding to the positional coördinates are excited to the first quantum state, excluding arrangements which could be obtained by a permutation of atoms.
3. The entropy of a perfect crystal at the absolute zero is not dependent on the complexity of the unit of crystal structure.

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THE ACTION OF SOME OXIDIZING AGENTS ON SULFITE. II

BY W. S. HENDRIXSON

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In a recent paper[1] the writer stated that he had repeated in part the work of Mayr and Peyfuss[2] on the oxidation of sulfite with nascent bromine from a known amount of bromate and an excess of bromide to the solution of which they added in order, the sulfite and hydrochloric acid. At that time the author found the oxidation to sulfite incomplete, and the presence of the bromide of little influence. These results have since been fully confirmed, and his later work shows further that sulfite may be accurately determined with bromate and a small fraction of its equivalence of iodide, or with the bromine set free by the action of known bromate on an excess of bromide.

[1] Hendrixson, THIS JOURNAL, 47, 1319 (1925).

[2] Mayr and Peyfuss, *Z. anorg. Chem.*, **127**, 123 (1923).

The titrations here recorded were carried out in a flask similar to that used by Mayr and Peyfuss; through the stopper passed the stem of a cylindrical funnel and an exit tube, each with glass stopcock. In several experiments the solution containing bromate and an excess of bromide was boiled while carbon dioxide was passed through the liquid. Later, the gas was omitted as unnecessary. By boiling the solution for a few moments, closing the stopcocks and cooling, a vacuum of more than 99% was secured; this could be maintained essentially until all danger of oxidation by air or of escape of sulfur dioxide or halogens had passed. After the liquid had been cooled, preserving the order of the experiments of Mayr and Peyfuss, a little less of sulfite solution than that required to effect complete reduction of the bromate, and boiled hydrochloric acid were added. After ten minutes, the titration was completed with iodide and thiosulfate solutions. Several experiments gave the oxidation as 97.6% of that required for complete change of the sulfite to sulfate, as based upon the known value of the sulfite determined with iodine set free from an excess of iodide by the same bromate solution, and using the same technique. A series of experiments carried out with the bromate alone gave 97.2% of oxidation, and hence the presence of the bromide must be regarded as of little value. It has been found, however, that when a little iodide instead of bromide is added to the bromate, the oxidation to sulfate ion is complete.

In the paper already mentioned[1] it is shown that sulfite can be accurately determined with iodate because the oxidation takes place almost entirely according to the reaction represented by Equation 3, following: (1) $IO_3^- + 3SO_3^= = 3SO_4^= + I^-$; (2) $IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$; (3) $3I_2 + 3SO_3^= + 3H_2O = 3SO_4^= + 6H^+ + 6I^-$. The oxidation is, therefore, practically effected by free iodine as in the ordinary iodine method. Reaction 1 is slow and, after the first few drops of sulfite are added giving free iodine, is superseded by the almost instantaneous Reactions 2 and 3, and free iodine persists to the end of the titration.

Analogous reactions do not function in the same way when bromate is used, or even with bromate and bromide, as in Mayr and Peyfuss's method in which the acid is added after the sulfite, because Reaction 2 is then very slow. When sulfite is added slowly and continuously to an acidified and agitated solution of bromate no free bromine is formed; on the other hand, free bromine is formed after the addition of a portion of sulfite and allowing the mixture to stand a few moments. In the procedure of Mayr and Peyfuss no bromine appears, after the addition of acid, until all of the sulfite has been oxidized. This indicates that the oxidation of sulfite takes place mainly according to Reaction 1. When, however, iodide even to the extent of one-sixth of an equivalent of the bromate is added to it, free iodine persists throughout the titration and the oxidation is complete to sulfate. Substitution of bromate ion for iodate ion makes it clear that the oxidation is carried out according to Reactions 2 and 3. Three series of determinations were carried out with bromate and one-half, one-fourth and one-sixth of its equivalent of iodide. The results obtained showed, respectively, 100.3, 100.4 and 99.9% of complete oxidation of sulfite to sulfate.

Determination of Sulfite with Free Bromine

It was evident that use of the special flask mentioned afforded opportunity to study the oxidation of sulfite by free bromine without the possible loss of bromine vapor. The procedure was the same as that of Mayr and Peyfuss except that acid was added to the bromate and the excess of bromide and, after sufficient time had been allowed for the complete reduction of the bromate, the sulfite was added until nearly all of the bromine had disappeared, after which iodide was added and the titration was completed with thiosulfate solution. The true concentration of the sulfite was determined in the same way but by substitution of an excess of iodide for the bromide. The flask was exhausted with a high vacuum pump until the solution, a little above room temperature, boiled freely for some moments, since this method had been already proved to be quite as efficacious as boiling under ordinary pressure. Four determinations with iodine and four with bromine were made in the same morning and none was rejected. The agreement and uniformity were remarkable as shown by the following results expressed in normality of the sulfite solution: (1) determinations with free iodine, 0.13063, 0.13079, 0.13084, 0.13068 *N*; (2) determinations with free bromine, 0.13087, 0.13073, 0.13066, 0.13087 *N*.

In this case, of course, there can be no question of the interpretation of the results. The oxidations of sulfite must have proceeded entirely by Reaction 3, with the substitution of bromine for iodine in the second series. Since the halogens cause oxidation indirectly, through the oxygen of water, it is not surprising that they should give the same result.

Oxidation of Sulfite with Permanganate, Dichromate and Fractional Equivalents of Iodide

Although complete oxidation of sulfite to sulfate has not been obtained with permanganate or dichromate alone, it has been secured, as in the case of bromate, by the addition of a fractional equivalent of iodine and for the same reason. In each case the acidified solution of oxidant was boiled in a vacuum, and the boiled normal solution of iodide and, after some moments, the sulfite solution were added until only a little iodine remained, which was determined with thiosulfate solution. With one-half an equivalent of iodide, permanganate gave 99.9% of oxidation to sulfate, while the permanganate alone on the same day gave 91%. Dichromate and one-half an equivalent of iodide gave 100% oxidation, and one-third of an equivalent gave 99.9%.

Summary

1. Sulfite cannot be determined with bromate, dichromate or permanganate alone, since they do not oxidize it completely to sulfate.

2. Sulfite may be determined accurately by titration with iodate alone or with bromate, permanganate or dichromate, by the addition to those oxidants of half their equivalent (or, in the case of bromate, even one-sixth of an equivalent) of iodide. It may also be determined with free bromine.

3. All titrations in the experiments recorded here were carried out in a vacuum flask of Pyrex glass to avoid action of air or escape of sulfur dioxide or halogens. Such a flask is to be recommended in work involving possible disturbance of a reaction by air or loss of gases.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE

III. FAILURE TO OBTAIN A COMPOUND CONTAINING ONLY NITROGEN AND CHLORINE FROM OXIDES OF NITROGEN

BY W. A. NOYES

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In 1913[1] an account was given of experiments which seemed to indicate the possibility of a chloride of nitrogen in which the chlorine is in the negative form, or tends to separate from the nitrogen in the negative form, in contrast with ordinary nitrogen trichloride, from which, in its normal reactions, the chlorine separates in the positive form. In 1921[2] it was reported that no conditions had been found under which a compound of nitrogen and chlorine could be obtained by passing the gases through an electric arc.

Since 1913 a considerable number and variety of experiments have been tried in the endeavor to replace the oxygen of oxides of nitrogen by chlorine. Ninety-two such experiments and 176 analyses of mixed gases have failed to show, conclusively, the formation of any chloride of nitrogen which does not contain oxygen. Nitrosyl chloride, from which the chlorine separates easily in the negative form, was obtained in many of the experiments and, at times, there seemed to be some evidence of the formation of a nitrogen dichloride, NCl_2. It seems difficult to understand why such a compound, corresponding to nitric oxide, NO, should not be formed, but the conclusion was finally forced upon me that when nitrogen and oxygen atoms separate the nitrogen atom has a greater affinity for another nitrogen atom than it has for chlorine. Apparently only nitrogen in the form of

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[1] Noyes, THIS JOURNAL, **35**, 767 (1913).

[2] Noyes, *ibid.*, **43**, 1774 (1921).