$K(O_3 \rightleftharpoons 1^1/_2O_2)$; $K(O_2 + O \rightleftharpoons O_3)$; } Kassel, *J. Chem. Phys.*, **1,** 414 (1933).

OH: $E^\circ - E_0^\circ$; Johnston and Dawson, *loc. cit.*

Cl_2: $K(2Cl \rightleftharpoons Cl_2)$; $K(^1/_2H_2 + {}^1/_2Cl_2 \rightleftharpoons HCl)$; } Giauque and Overstreet, THIS JOURNAL, **54,** 1731 (1932).

Br_2: $E^\circ - E_0^\circ$ and K; HBr: $E^\circ - E_0^\circ$ and K; } Gordon and Barnes, *J. Chem. Phys.*, **1,** 693 (1933).

Summary

Accurate data of heat capacities and dissociation equilibria derived from band spectroscopic data of gases have been gathered and arranged in two tables. Table I contains the energy content of H_2, O_2, N_2, CO, NO, OH, CO_2, H_2O, O_3, Br_2 and HBr from 200 to 3500°K.; Table II contains equilibrium constants of numerous equilibria involving these gases and also Cl_2 and HCl from 300 to 5000°K. Complete references to sources of data are given.

PITTSBURGH, PA. RECEIVED NOVEMBER 26, 1934

The Reactions Taking Place in the Iodimetric Determination of Chromates

BY FRIEDRICH L. HAHN

It has been known for a long time that in the iodimetric titration of chromates an excess of thiosulfate is often consumed.[1] This has been attributed to an air oxidation of the iodide in acid medium. However, this explanation does not account fully for the various phenomena observed in the system dichromate–acid–iodide–thiosulfate. The excess in the quantity of thiosulfate required in *feebly* acid solutions cannot be caused by the action of atmospheric oxygen, because it is large in a rapid determination, diminishes as one prolongs the titration and disappears when some time is allowed to elapse, after having acidulated the solution before beginning the titration (Kolthoff).

The author has found that the various phenomena observed can be explained by the formation of a complex between chromic chromium and thiosulfate, this complex reacting only very slowly with iodine.[2] Chromic chromium once formed does not react with the thiosulfate, but the complex is formed when the reduction of chromate takes place in the presence of thiosulfate. This hypothesis enables us to predict phenomena verifiable by experiment.

I. If the excess of reagent consumed for feebly acid solutions is not due to an excessive formation of iodine but to an irregular fixation of the thiosulfate, it must be specific for thiosulfate as reducing agent and it ought to disappear, if the liberated iodine is reduced by another reagent; this was found on titrating the iodine with stannous chloride.

II. If the excess of thiosulfate fixed into the complex reacts slowly with iodine, the theoretical quantity of iodine will be found on titrating the colorless final solution drop by drop with iodine until the iodine color is definitively stable and by subtracting this quantity of iodine from the quantity of thiosulfate consumed. This is proved by experiments.

III. The smallest traces of thiosulfate may be detected by the catalysis of a mixture of sodium azide (NaN_3) and iodine, decolorizing the iodine and forming gaseous nitrogen.[3] This reaction reveals the presence of thiosulfate in the end solutions, although containing free iodine, of titrations in which an excess of thiosulfate has been used; this thiosulfate is furnished by decomposition of the thiosulfate–chromic complex. The reaction does not take place in solutions from exact titrations.

IV. The quantity of the complex formed in a titration ought to increase with the quantity of chromate present during the addition of the thiosulfate, and this diminishes with the concentration of H^+ or I^- ions increasing. This is in agreement with the fact that the excess of thiosulfate diminishes when the acidity of the solution increases; one may anticipate that for solutions of the same concentration in acid an increase of iodide will also diminish the thiosulfate required. This also is verified by experiment (Trials a and e, b and f on Table I).

V. Regarding quantitative relations it may be anticipated that the reactions on the sodium azide

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(1) G. Bruhns, *Z. anorg. allgem. Chem.*, **49**, 277 (1916); *J. prakt. Chem.*, **93**, 73, 312 (1916); **95**, 37 (1917); I. M. Kolthoff, *Z. anal. Chem.*, **59**, 401 (1920). Later investigations concerning the same subject, *e. g.*, K. and W. Böttger, *ibid.*, **69**, 145 (1926), or A. Friedrich and E. Bauer, *ibid.*, **97**, 305 (1934), have not contributed to solution of the problem in question.

(2) Preliminary publication, *Z. anal. Chem.*, **97**, 305 (1934).

(3) Reaction investigated by Fr. Feigl, *ibid.*, **76**, 376 (1928).

will become proportionally more intense as the excess of thiosulfate utilized rises. This is confirmed by experiment.

Description and Results of Experiments

The effects requiring verification will be more easily perceptible in relatively concentrated solutions; it is therefore impossible in these cases to use starch as an indicator, because the intense color of chromic salts renders the end-point invisible. The use of benzene or of chloroform, useful for avoiding this difficulty, is impracticable from the fact that it prevents a rapid titration, because it is essential, after each addition of reagent, to wait for the approximate separation of the two layers. But it is possible, though the fact is unknown to the majority of chemists, to carry out the determination without the addition of any indicator (when using decinormal solutions). The solutions containing free iodine are yellowish-green, they change to a clear blue when all the iodine is eliminated. The end-point is sharply produced by a single drop; it is still more easily seen when the determination is completed in the inverse way; in this case no doubt is possible whether the last drop does or does not change the color of the solution.

Furthermore, we have controlled potentiometrically the values of the end-point by employing the process termed "dead-stop" introduced by C. W. Foulk and A. T. Bawden;[4] the results have been excellent.

It is not necessary to include the measured values of I and II; the error never exceeds one drop and indicates no relation of excess in thiosulfate to the conditions of the determination.

III, IV, V. Increasing quantities of hydrochloric acid are added to a mixture of 10 cc. of potassium dichromate (*ca.* 0.1 *N*) and of potassium iodide, and this is decolorized by addition of thiosulfate, then iodine solution is added until a light coloration is permanent. The solution is tested by the mixture of iodine and azide to indicate any concentration in thiosulfate.

Several repetitions of this series of trials gave the same result. At the end of similar series no azide was added; it was then evident that the iodine coloration disappeared in the trials following "a" or "b" and that 1 to 3 drops of iodine were required for its permanent establishment. The coloration was stable in the trials following "c" but a single drop of thiosulfate sufficed always to make it disappear, even after an interval of several minutes. The solutions following "d" on the other hand and *a fortiori* solutions of a concentration still higher in acid, continually produce new quantities of iodine.

TABLE I

EXPERIMENTAL RESULTS

No.	Quantity added, cc.		Init. concn., HCl, *N*	Quantity added, cc.		Thiosulfate less iodine, cc.	Reaction with the azide
	Potass. iodide, *N*	HCl, 2 *N*		Thiosulfate	Iodine		
a	2	2	0.3	11.2	0.8	10.4	Strong; complete decol.
b	2	3	.4	10.4	1 (drop)	10.35	Distinct
c	2	5	.6	10.3	1 (drop)	10.25	None
d	2	10	.9	10.4	1 (drop)	10.35	None
e	6	2	.2	10.8	0.5	10.3	Feeble
f	6	3	.3	10.8	1 (drop)	10.25	None

The formation of a thiosulfate–chromic complex, in other words, the coexistence of free iodine and of thiosulfate, can be made evident by the following two trials, which are, at the same time, surprising and conclusive.

Trial "g."—Ten cc. of chromate (0.1 *N*), 8 cc. of iodide (1 *N*) and 2.5 cc. of hydrochloric acid (2 *N*) are mixed, and to the mixture is slowly added a scarcely equivalent quantity of thiosulfate (say 10.2 cc. for the above-examined solutions); a color of free iodine remains slight but stable. The thiosulfate, running into a solution of *preformed* chromic salt, does not form a complex: it serves integrally for the reduction of the iodine. The final solution does not give a reaction with azide.

Trial "h" used the same quantities of reacting substances but with the thiosulfate mixed with the iodide and the chromate and then the hydrochloric acid added. An intensely brown solution formed, containing large quantities of free iodine; this is to say that the quantity of thiosulfate practically equivalent to the iodine under the conditions of Trial "g" above, is altogether insufficient under the modified conditions. A large part of the thiosulfate placed in the presence of the *nascent* chromic salt is combined in the form of a complex and only reacts with the iodine very slowly. By pouring small quantities of the mixture into a solution of starch, and into the azide–iodine reagent, coexistence of free iodine and of thiosulfate can be proved during a period of more than three minutes; after this lapse of time the mixture is slowly decolorized by thiosulfate arising from the decomposition of the complex; as this process takes place in an acid solution, a part of this thiosulfate decomposes according to the known equation; the solution is slightly clouded by a precipitation of sulfur, and the sulfurous acid formed can reduce new additions of iodine.

A final experiment may refute any possible objection that the preceding trials differed too largely from analytical conditions.

Trial "i."—To 200 cc. of water are added 10 cc. of chromate (0.1 *N*), 10 cc. of iodide (1 *N*), a scarcely

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[4] Foulk and Bawden, THIS JOURNAL, **48**, 2045 (1926).

equivalent quantity of thiosulfate (10.2 cc.) and finally, with constant stirring, 50 cc. of hydrochloric acid (2 *N*). The solution acquires at once the color of bichromate; then, after a lapse of several seconds, instantly that of iodized starch. This second color fades very slowly; after six minutes it is still very pronounced; it requires about twelve minutes to disappear completely. During the whole of this period the presence of thiosulfate in the solution can be verified by its reaction on sodium azide.

Summary

The excess of thiosulfate used in the iodimetric titration of chromate in feebly acid solution is attributed to the formation of a complex chromic thiosulfate during the reduction of the chromate. This complex reacts slowly with free iodine.

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À LA SORBONNE
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Tertiary Butyl Alcohol as a Solvent for Cryoscopic Molecular Weight Determinations

BY GEORGE S. PARKS, GRANT E. WARREN AND EARNEST S. GREENE

This investigation was carried out a few years ago to determine the suitability of tertiary butyl alcohol as a solvent for molecular weight determinations by the Beckmann freezing point method. As this alcohol can now be produced cheaply and in a very pure form as a by-product of oil cracking processes by several companies in the United States, the publication of our results appears to be timely.

The principal earlier investigation on the subject is that of Atkins,[1] whose alcohol was probably much less pure than the material now available. At any rate his results, with *p*-dibromobenzene, acetanilide, thiocarbamide, *p*-toluidine and α-naphthylamine as solutes, did not appear very satisfactory and the values thereby obtained for the cryoscopic constant of *t*-butyl alcohol varied from 7.3 to 15.4. To explain his rather erratic data Atkins suggested that the butyl alcohol probably exists in two crystalline modifications, one of which may be very unstable with a heat of fusion of about 13.8 calories per gram. In our present study we also made measurements with acetanilide and *p*-toluidine but failed to obtain the highly abnormal results reported in this earlier investigation.

Method and Apparatus

The Beckmann freezing point method, as described in standard laboratory manuals such as those of Findlay[2] and Daniels, Mathews and Williams,[3] was used in all our molecular weight determinations. Of course, the hygroscopic character of the solvent and its rather pronounced tendency to undercool before crystallization had to be taken into consideration in the experimental procedure. In order to prevent entrance of moisture from the air, the inner freezing tube was equipped with tightly fitting rubber stoppers and the wire stirrer was operated within a sleeve of thin, flexible rubber, which thus made an air-tight seal. To avoid an excessive amount of undercooling of the entire butyl alcohol solution, a small piece of platinum wire was fused through the bottom of this inner tube. During a determination crystallization could then be started at any desired degree of undercooling by removing the tube and touching the external portion of this wire for an instant to a soldering copper which had been previously chilled in ice or solid carbon dioxide. A three-liter Dewar jar, filled with water which was kept about 1.5° below the freezing point of the alcohol solutions, served as the external cooling bath.

The freezing point depressions for the molecular weight determinations were always measured with a Beckmann thermometer which had been previously calibrated by the U. S. Bureau of Standards. Other temperature measurements, including the melting point of the purified *t*-butyl alcohol and the freezing points in our study of the *t*-butyl-*t*-amyl alcohol system, were made with a similarly calibrated mercury thermometer which could be read to ±0.04°.

Materials

Several liters of *t*-butyl alcohol, m. p. about 20°, were generously given to us for this investigation by the Standard Oil Development Company. This material was first dehydrated by two fractional distillations over lime and was then subjected to ten fractional crystallizations. About two liters of final product, melting at 25.4°, was thus obtained.

The various solutes employed in this investigation were for the most part samples of the substances which have have been previously used in specific heat studies at Stanford University. Details concerning the preparation of the methyl, ethyl, *n*-propyl, isopropyl and *t*-amyl alcohols, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, *n*- and *t*-butylbenzenes, ethyl benzene, *p*-cymene, diphenylmethane, acetic acid, acetone and phenol have been given in

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[1] Atkins, *J. Chem. Soc.*, **99**, 10 (1911).

[2] Findlay, "Practical Physical Chemistry," Longmans, Green and Co., London, 1931, p. 119.

[3] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1934, p. 61.