be those given by the equations $\Delta F^\circ = 151{,}800 - 78.68T$, and $\Delta H =$ 151,800 calories.

At 1930°K. the free-energy change becomes zero and the actual equilibrium pressure is one atmosphere.

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[Contribution from the Chemistry Laboratory of the Missouri School of Mines and Metallurgy]

THE DETERMINATION OF SELENIUM AND TELLURIUM BY MEANS OF POTASSIUM PERMANGANATE

By W. T. Schrenk and B. L. Browning

Received June 28, 1926 Published October 6, 1926

Previous investigators have discovered that selenous and tellurous acids may be quantitatively oxidized by potassium permanganate in acid solution. Brauner[1] reported that in the reaction with tellurous acid, permanganate is not reduced to its lowest state of valence but to higher hydrated oxides. He also showed that the reaction is not quantitative in fairly concentrated sulfuric acid solution, due to loss of oxygen. Gooch and Danner[2] reduced the error to a negligible figure by carefully limiting the concentration of sulfuric acid. Gooch and Clemons[3] successfully determined selenous acid by oxidation with potassium permanganate.

The investigation showed that two difficulties must be overcome. The permanganate reacted with hydrochloric acid or chlorides present, and the manganese dioxide which precipitated was reduced very slowly by the ferrous sulfate. In many cases it was doubtful whether all the manganese dioxide was reduced at the apparent end-point, since a small amount remained as a stain on the glass.

It was found that the addition of phosphoric acid or disodium phosphate prevents the precipitation of manganese dioxide. Disodium phosphate was used since its addition does not increase the acid concentration. By dissolving the tellurium dioxide directly in sulfuric acid, the presence of chlorides was avoided and no difficulty was experienced from this source.

Procedure.—The following procedure for the determination of either selenium or tellurium was used and is recommended. A sample containing from 0.14 to 0.20 g. of the oxide is weighed and dissolved in 25 cc. of 40% sulfuric acid. In the case of tellurium dioxide, the sample must be heated until solution is complete. The solution is diluted to 150 cc., and 12 g. of disodium phosphate added. A standard solution of potassium permanganate is added to about 10 cc. in excess and the solution allowed to

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[1] Brauner, *J. Chem. Soc.*, **59**, 238 (1891).

[2] Gooch and Danner, *Am. J. Sci.*, **44**, 301 (1892).

[3] Gooch and Clemons, *ibid.*, **50**, 51 (1895).

stand for 10–30 minutes. The excess of permanganate is then titrated electrometrically with ferrous sulfate solution.

When selenium and tellurium are to be determined in the same sample, two methods are available.

1. The tellurium may be determined by oxidizing with an excess of potassium dichromate, the excess of dichromate being titrated electrometrically with ferrous sulfate by the method of Schrenk and Browning.[4] An excess of potassium permanganate is then added and the selenium determined.

2. The selenium and tellurium may be determined together by oxidation with potassium permanganate. The tellurium is then determined on a separate portion by the use of potassium dichromate, and the selenium found by difference.

The selenium dioxide and tellurium dioxide used were analyzed gravimetrically by the method of Lenher and Kao.[5]

TABLE I

TITRATION OF SELENIUM DIOXIDE

	SeO_2 taken, g.	No. of detns.	Av. error, g.	Av. dev. from av., g.
(A)	0.1372	5	−0.0003	0.0001
(B)	.1400	5	+ .0001	.0003
(C)	.1401	5	+ .0003	.0002
(D)	.1378	16	− .0001	.0003
(E)	.1371	12	− .0003	.0002
(F)	.1375	12	− .0001	.0001
(G)	.0055–0.1091	5	− .0001	.0004

In Part A the time of standing after adding potassium permanganate was 5–25 minutes. Oxidation was complete after five minutes.

In Part B the amount of disodium phosphate was varied from 1 to 12 g. In general, 12 g. of disodium phosphate prevented the precipitation of manganese dioxide. The amount necessary to prevent precipitation increases with the time of standing and with the amount of permanganate reduced.

The titrations of Part C were carried out in concentrations of sulfuric acid varying from 0.9 to 13% by weight (0.5 to 7% by volume).

In Part D the disodium phosphate added varied from 6 to 21 g., and the sulfuric acid (d., 1.84) from 10 to 25 cc. The varying of the ratio was found to be without effect.

In Part E an excess of potassium permanganate of 10 to 25 cc. was added. The amount of excess present can vary from 40 to 100% of the amount used without influencing the results of the titration.

Part F indicates the accuracy that may be expected in the use of this method.

In Part G amounts of selenium dioxide varying from 0.0055 to 0.1091 g.

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[4] Schrenk and Browning, THIS JOURNAL, **48,** 139 (1926).

[5] Lenher and Kao, *ibid.*, **47,** 769 (1925).

were taken and 0.1997 g. of tellurium dioxide was added to each. The calculated amount of potassium permanganate required for the tellurium dioxide was subtracted from the total amount used, to find that required by the selenium.

TABLE II

TITRATION OF TELLURIUM DIOXIDE

	TeO_2 taken, g.	No. of detns.	Av. error, g.	Av. dev. from av., g.
(A)	0.0052–0.3994	25	+0.0001	0.0002
(B)	.0100– .2509	4	.0000	.0006

Part A shows the accuracy of the method for amounts of tellurium dioxide varying from 0.0050 to 0.4000 g.

In Part B amounts of tellurium dioxide varying from 0.0100 to 0.2509 g. were taken and 0.1375 g. of selenium dioxide was added to each. The calculated amount of potassium permanganate required for the selenium dioxide was subtracted from the total amount used, to find that required by the tellurium.

TABLE III

DETERMINATION OF SELENIUM DIOXIDE IN THE PRESENCE OF TELLURIUM DIOXIDE BY A COMBINATION OF METHODS

	SeO_2 taken, g.	TeO_2 taken, g.	No. of detns.	Av. error, g.
(A)	0.1379	0.1985	3	−0.0001
	.0545	.0701	3	− .0002
(B)	.1374	.0701	3	+ .0003

In Part A the selenium and tellurium were oxidized together by potassium permanganate, the tellurium was determined in a separate sample by potassium dichromate, and the amount of permanganate required by the tellurium calculated. The amount of permanganate remaining was used to calculate the selenium found. The amount of tellurium may be readily determined from the dichromate titration.

In Part B the tellurium was oxidized by potassium dichromate and the excess of the latter removed by electrometric titration with ferrous sulfate. The selenium present was then determined by oxidation with potassium permanganate.

Summary

1. Selenous and tellurous acids may be very accurately determined by oxidation with an excess of potassium permanganate. The excess of permanganate may conveniently be titrated electrometrically by the use of ferrous sulfate solution.

2. Chlorides must be absent.

3. The addition of disodium phosphate prevents the precipitation of manganese dioxide.

4. Selenous and tellurous acids in the same sample may be determined by using a combination of the dichromate and permanganate methods.

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[Contribution from the Chemical Laboratory of Cambridge University]

THE INFLUENCE OF WATER ON THE COMBINATION OF THE HALOGENS WITH HYDROGEN

By Bernard Lewis and Eric K. Rideal

Received July 23, 1926 Published October 6, 1926

In a previous communication[1] evidence was presented for the assumption that the Budde effect was brought about by the photochemical dissociation of a halogen hydrate into atoms and that this process (for high water concentrations) obeys the simple Stark-Einstein law of photochemical equivalence. The quantum efficiency, however, is zero in a thoroughly dry system. If the primary chemical action in all halogen-hydrogen reactions both photochemical and thermal is the dissociation of the excited halogen molecule into atoms through interaction with water, the subsequent reactions of the atoms being dependent on the nature of the halogen and the temperature of the system, then as shown from the Budde effect, no photochemical combination in the visible portion of the spectrum should result in completely desiccated systems. Further, if water is necessary for the dissociation of photo-excited molecules, it appears probable that the same will be true for thermo-excited halogen molecules, that is, those excited by collision, and we shall obtain no thermal combination in the dry gases.[2]

A. The Hydrogen-Chlorine Reaction.—The influence of water in this system has been studied for the thermal reaction by Mellor[3] and for the photochemical reaction by Bodenstein and Dux,[4] Tramm[5] and Coehn and Jung.[6] It was shown by the latter, employing visible light, that no combination could be detected with 10^{-7} mm. of water vapor present. At 10^{-5} mm. combination occurred. Bodenstein and Dux[4] could detect no difference in velocity at 2.3 mm. and at what was believed to be 4×10^{-3} mm. Since, however, the reaction vessel was not baked out and the chlorine contained a small quantity of oxygen which undergoes photochemical hydrogenation with chlorine as optical sensitizing agent,[7] it is quite possible that the lower limit of water vapor may have been as high as 0.1 mm. We are thus uncertain how far an increase in water vapor from 10^{-5}

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[1] Lewis and Rideal, *J. Chem. Soc.*, **129**, 583, 596 (1926).

[2] From the data of Wehn and Jung it would appear that ultraviolet light, that is, a large quantum, may effect dissociation in the absence of water.

[3] Mellor, *J. Chem. Soc.*, **81**, 1272 (1902).

[4] Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

[5] Tramm, *ibid.*, **105**, 358 (1923).

[6] Coehn and Jung, *Ber.*, **56**, 696 (1923).

[7] Norrish and Rideal, *J. Chem. Soc.*, **127**, 787 (1925).