The parameters u = 0.235, v = 0.12 place the nearest carbon and nitrogen atoms 1.44 Å. apart. The distance between the centers of molecules is much greater; each molecule is surrounded by 8 others at a distance of 6.08 Å. and by 6 more at a distance of 7.02 Å. The distance between the nearest atoms in two adjacent molecules presumably involves the position of the hydrogen atoms, and therefore cannot be stated with accuracy.

Summary

Hexamethylene-tetramine crystals have been investigated by X-ray methods using spectral photographs and Laue photographs. The data have been accounted for by a structure with tetrahedral symmetry that may be regarded as built up of like molecules of $C_6H_{12}N_4$ in parallel orientation and on a body-centered cubic lattice whose edge is 7.02 Å. The carbon atoms are all equivalent, and likewise all the nitrogen atoms. This is in agreement with the structural formula numbered 4 in the introduction, but not with any other that has been suggested. Two nitrogen atoms are at a distance of about 1.44 Å. from each carbon atom, and at least approximately in the directions of two vertices of a tetrahedron, in agreement with the prevailing view of the tetrahedral nature of the carbon atom.

PASADENA, CALIFORNIA

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

THE REFRACTIVE INDICES OF SELENIC AND SELENIOUS ACIDS[1]

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The preparation of selenic acid has always required the formation of a dilute solution followed by concentration. For this reason a rapid and accurate method of determining the concentrations of selenic acid solutions seemed desirable. It was with this in view that the effort was made to determine the indices of refraction and the corresponding percentage compositions of the acid at frequent intervals over the whole range of possible dilutions. A similar study of selenious acid was also undertaken.

The preliminary investigation of the various methods of preparing selenic acid revealed that though it was a comparatively simple matter to make dil. selenic acid, its preparation in a pure and concentrated form was extremely difficult and in all probability had not yet been accomplished. Whether or not selenic acid was decomposed by hydrogen sulfide was uncertain, yet many of the methods for the preparation of the acid depended on the use of hydrogen sulfide, either as an important reagent in the preparation, or as a means of removing selenious acid from

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[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

the final product. Hydrogen sulfide produces a lemon-yellow precipitate of selenium sulfide with solutions containing selenious compounds, while dil. selenic acid is apparently not affected by this reagent. The work of Cameron and Macallan,[1a] and that of Morris,[2] seemed to prove that hydrogen sulfide does not decompose selenic acid. Benger,[3] and also Dennis and Koller,[4] found that hydrogen sulfide and selenic acid always yield some selenium or selenium sulfide.

Experiments in this Laboratory indicated that selenic acid previously freed from selenious acid by treatment with hydrogen sulfide, after dilution to 5% or lower concentration, could be subjected to the action of a rapid stream of hydrogen sulfide without showing the slightest trace of yellow color.

Materials

Selenium Dioxide.—The selenium dioxide used in this work was made from selenium which had been purified by dissolving crude selenium in nitric acid and subliming the selenium dioxide resulting from the evaporation of this liquid. The sublimed selenium dioxide was dissolved in distilled water and the purified selenium precipitated with sulfur dioxide. After the selenium had been washed and dried, it was reconverted to selenium dioxide as described above.

Silver Nitrate.—The silver nitrate was prepared by fusing silver chloride with sodium carbonate and dissolving the silver so obtained in nitric acid. The crystals from this solution showed no trace of black copper oxide on fusion.

Bromine.—The bromine, thoroughly mixed with sulfuric acid and potassium dichromate, was allowed to stand for several weeks and then distilled. It was then free from organic matter.

Hydrogen Sulfide.—The hydrogen sulfide was prepared by the action of 20% hydrochloric acid on sodium sulfide and was purified by being passed through 2 wash solutions containing dil. sodium sulfide solution.

Preparation of Selenic Acid

The method of Thompson[5] as modified by Morris[2] was selected as the one giving the highest quality of selenic acid. A solution of selenium dioxide was treated with silver nitrate, giving a white, sparingly soluble silver selenite. This salt, suspended in water, was allowed to react with bromine water and the insoluble silver bromide removed from the dil. selenic acid by collection on an asbestos filter. The selenic acid was then concentrated by distilling the water under reduced pressure at as low a temperature as possible.

Quality of Acid

The selenic acid used in this work was free from selenious acid up to a concentration of 94% as shown by the tests with hydrogen sulfide. At

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[1a] Cameron and Macallan, *Chem. News*, 59, 219, 232, 258, 267 (1889).

[2] Morris, *Trans. Wisconsin Acad. Sci. Arts Letters*, 19, [I] 369 (1918).

[3] Benger, This Journal, **39**, 2171 (1917).

[4] Dennis and Koller, *ibid.*, **41**, 960 (1919).

[5] Thompson, *Ber.*, **2**, 598 (1869).

concentrations between 94% and 99%, the acid contained small amounts of selenious acid not exceeding 0.006% of selenium dioxide in any case. This small amount was beyond the limits of detection of both the refractometer and of the gravimetric analyses used in the work, and hence could in no way affect the values obtained. A test for non-volatile residue in the most concentrated acid showed it to be practically free from such impurities. A sample of 0.5495 g. of the most concentrated selenic acid after ignition for 10 minutes gave no weighable residue.

It may be said that an excellent quality of selenic acid may be obtained by this method and that hydrogen sulfide is both efficient and necessary in the removal of the last traces of selenium dioxide.

Analytical Method

A gravimetric precipitation of the total selenium was found to be the most accurate method of determining the concentrations of the acids. For selenic acid the absence of selenious acid was always first determined by the test with hydrogen sulfide. The following procedure was used and found to give satisfactory results.

A 0.2–0.5g. sample was pipetted out and washed quantitatively from a stoppered weighing bottle into a beaker, and the quantity determined by loss of weight of the bottle. This procedure reduced to a minimum the possibility of gain or loss of moisture from contact with the atmosphere. Fifty cc. of conc. hydrochloric acid was added and the total diluted to 75–100 cc. with distilled water. The solution was then heated to boiling and 30 cc. of a saturated solution of sulfur dioxide added. The temperature of the mixture was maintained at about 90° until the red precipitate which was first formed turned black and further additions of sulfur dioxide gave no red color. After the reaction mixture had been kept for 4 or 5 hours on the sand-bath at 80° or 90°, the precipitate was collected on a prepared Gooch crucible and dried at 105–110°. Duplicate analyses were made in all cases, with an agreement which is indicated in the discussion of Table I.

Measurement of the Indices of Refraction

The indices of refraction were determined with an Abbé refractometer, but because of the danger of corrosion the usual technique was modified.

A drop of the acid under observation was placed directly on the face of the open prism by means of a pipet and the 2 halves closed. After waiting for a moment for the acid to reach the temperature of the water-cooled prism, the reading was taken. The accepted value for the refractive index was a mean of several readings agreeing to within 0.0002. The readings were obtained by adjusting the half shadow of the refractometer field with the cross hairs, first from one side and then from the other. This value was verified by a second determination after the acid had been sampled for analysis. The opportunity for the acid to gain or lose moisture from exposure to the atmosphere in the pipet during transfer to the refractometer was slight. Observations proved that the liquids gave a constant reading over a period several times as long as that required for the actual determination, so that there was no error from evaporation or condensation of atmospheric moisture while the sample was in the refractometer. Using this modified technique, the Abbé instrument incorporates practically all the features necessary for this work.

Indices of Refraction of Selenic Acid

Table I shows the observed values for the index of refraction of the various concentrations of selenic acid towards the sodium line D. The value in each case is the result of duplicate determinations, each of which is a mean of several readings checking to within 0.0002. The corresponding percentages of selenic acid are means of two and sometimes three independent determinations of the selenium content calculated to selenic acid. The acid had been tested previously for selenious acid by means of hydrogen sulfide. Out of 76 duplicate determinations, 32 pairs agreed to within 0.1% of their selenic acid content, 47 agreed to within 0.2%, and 56 to within 0.3%. This is a very satisfactory agreement when one considers that with an average sized sample of 80% selenic acid an error of 0.0001 g. in the final weighing, when calculated to selenic acid percentage, is equal to 0.1.

TABLE I

INDICES OF REFRACTION OF SELENIC ACID

Results by Determination for the Sodium Line D at 20°

Index	%	Index	%	Index	%
1.3330	0.00	1.3901	40.52	1.4811	79.75
1.3383	4.62	1.3916	41.68	1.4860	81.33
1.3409	6.66	1.3947	43.24	1.4906	83.08
1.3443	9.28	1.3980	44.77	1.4946	84.31
1.3476	11.99	1.4013	46.62	1.4950	84.69
1.3491	13.25	1.4078	50.53	1.4973	85.33
1.3503	14.32	1.4115	52.09	1.4993	86.20
1.3527	15.85	1.4149	54.19	1.5006	86.79
1.3553	17.87	1.4151	54.24	1.5010	87.10
1.3565	18.40	1.4189	55.76	1.5047	88.20
1.3586	20.00	1.4221	57.38	1.5065	88.91
1.3610	21.77	1.4258	58.90	1.5079	89.64
1.3621	22.29	1.4289	60.41	1.5088	90.16
1.3636	23.73	1.4322	61.88	1.5122	91.95
1.3660	25.21	1.4352	63.05	1.5136	92.75
1.3685	27.09	1.4382	64.33	1.5146	93.39
1.3691	27.53	1.4416	65.89	1.5155	94.31
1.3706	28.63	1.4461	67.18	1.5158	94.41
1.3723	29.68	1.4499	68.71	1.5168	95.63
1.3751	31.05	1.4538	70.27	1.5168	95.89
1.3780	33.22	1.4572	71.39	1.5172	97.28
1.3794	33.84	1.4616	73.22	1.5171	98.17
1.3817	35.00	1.4659	74.75	1.5170	98.36
1.3834	36.18	1.4696	76.01	1.5160	98.70
1.3856	38.01	1.4728	77.17	1.5160	98.98
1.3881	39.34	1.4792	79.21	....	...

Using the observed values of Table I, the indices of refraction were plotted against the corresponding percentages on a scale well beyond the limits of experimental error. The small units on the ordinates were assigned a value of 0.0002 unit of index of refraction and those on the abscissas 0.2% composition. The data plotted on this scale gave a curve from which the interpolated data presented in Table II was taken. As these figures represent a mean of the observed values, they should be more nearly correct than the experimental data of Table I.

A study of Table II reveals that a difference of 1% concentration is equal to 0.0010 in the index of refraction at the lower concentrations, gradually increasing to 0.0040 at 80%, and dropping off again to 0.0010 at 90%. As the limiting error of the refractometer is 0.0002, this corre-

TABLE II

INDICES OF REFRACTION OF SELENIC ACID

Results by Interpolation for the Sodium Line D at 20°

Index	%	Index	%	Index	%
1.3330	0.00	1.3794	34	1.4449	67
1.3341	1	1.3810	35	1.4475	68
1.3352	2	1.3826	36	1.4502	69
1.3364	3	1.3842	37	1.4529	70
1.3377	4	1.3858	38	1.4556	71
1.3389	5	1.3875	39	1.4584	72
1.3401	6	1.3892	40	1.4612	73
1.3413	7	1.3909	41	1.4640	74
1.3425	8	1.3926	42	1.4668	75
1.3437	9	1.3943	43	1.4696	76
1.3450	10	1.3960	44	1.4724	77
1.3463	11	1.3978	45	1.4753	78
1.3476	12	1.3996	46	1.4784	79
1.3488	13	1.4014	47	1.4810	80
1.3501	14	1.4032	48	1.4850	81
1.3514	15	1.4050	49	1.4879	82
1.3527	16	1.4068	50	1.4907	83
1.3541	17	1.4086	51	1.4935	84
1.3555	18	1.4106	52	1.4962	85
1.3569	19	1.4126	53	1.4989	86
1.3583	20	1.4146	54	1.5013	87
1.3597	21	1.4166	55	1.5038	88
1.3611	22	1.4188	56	1.5062	89
1.3625	23	1.4210	57	1.5085	90
1.3639	24	1.4232	58	1.5106	91
1.3654	25	1.4255	59	1.5124	92
1.3669	26	1.4278	60	1.5140	93
1.3684	27	1.4301	61	1.5153	94
1.3699	28	1.4325	62	1.5163	95
1.3714	29	1.4349	63	1.5169	96
1.3730	30	1.4373	64	1.5171	97
1.3746	31	1.4398	65	1.5172	98
1.3762	32	1.4423	66	1.5160	99
1.3778	33	....	..	....	..

sponds with the least favorable case to 0.2%, which is the limiting error in the analytical method used. The refractometric method is, therefore, at least as accurate as the best analytical method.

The peculiar decrease in the refractive property above 97% makes the index of refraction of no value in determining exact concentrations above this point, and values as low as 95% would be uncertain. Sulfuric acid also shows a similar decrease in the refractive property at high concentrations. Values quoted in Landolt and Börnstein "Tabellen" indicate this at two points. The figures quoted from Le Blanc[6] reveal a decrease at 94.11% while those of Hess,[7] show the same tendency at 100%. It has been suggested that the decrease in refractivity is due to the greater refractive power of the monohydrate of selenic acid. However, this is not possible since the maximum index of refraction should be found at a concentration of 88.96% (the concentration of selenic acid in the monohydrate) instead of 97.28%, as is actually the case. The sharp falling off in the refractive index corresponds to the concentrations at which selenic acid is in a highly supercooled condition. Anhydrous selenic acid, prepared by Cameron and Macallan[1] and also by Benger[3] melted at 58°. A sample of 98.3% acid used in this work crystallized spontaneously and was found to melt at 55–60°.

Index of Refraction of Selenious Acid

The selenium dioxide thus prepared always contained some water, even after several sublimations. This was proved by analysis for total selenium dioxide content and also by direct determination of the water content. These findings agree with those of Meyer,[8] who determined the vapor pressures of both selenium dioxide and selenious acid at temperatures ranging from 20° to 320°. The slight differences in this property of these two compounds caused him to conclude that selenium dioxide could not be freed from water even by a number of sublimations.

An approximately saturated solution of selenious acid was prepared. The index of refraction was then taken and the selenious acid content estimated by a gravimetric determination of the selenium content as previously described. These determinations were repeated at frequent intervals of concentration as shown in Table III.

Discussion of Selenious Acid Tables.—The accuracy of the refractometer in determining the concentration of pure aqueous solutions of selenious acid is equally as great as for selenic acid; 1% of concentration in the lower ranges is equal to 0.0010 unit of index of refraction, increasing to 0.0039 in the case of the saturated solution. Therefore, even in the least

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[6] Le Blanc, *Z. physik. Chem.*, **4**, 553 (1889) (quoted from Landolt and Börnstein).

[7] Hess, *Wein Anz.*, **1905**, 312 (quoted from Landolt and Börnstein).

[8] Meyer, *Z. Elektrochem.*, **19**, 833 (1913).

sensitive portions, 0.0002 unit of index of refraction, which is the limiting error of the refractometer used, is equal to 0.2% difference in the percentage composition. Since 0.2% is as good agreement as is to be expected from our best analytical method, the index of refraction furnishes a very satisfactory and rapid method of determining the concentration of selenious acid solutions.

Table III shows the percentage composition and the corresponding index of refraction of various solutions of selenious acid towards the sodium line D at 20°, from that of a saturated solution down to that of pure water. The data presented in Table IV were obtained from a curve

TABLE III

INDICES OF REFRACTION OF SELENIOUS ACID

Results by Determination for the Sodium Line D at 20°

Index	%	Index	%	Index	%
1.3330	0.00	1.3681	27.60	1.4065	48.11
1.3371	3.97	1.3701	28.68	1.4112	50.22
1.3408	7.09	1.3727	30.27	1.4152	52.33
1.3438	9.59	1.3742	31.25	1.4212	54.42
1.3461	11.68	1.3761	32.32	1.4280	57.02
1.3480	13.03	1.3784	33.64	1.4364	60.09
1.3490	13.85	1.3803	34.84	1.4431	62.71
1.3513	15.56	1.3837	36.95	1.4494	64.66
1.3532	16.96	1.3350	37.62	1.4562	66.44
1.3551	18.61	1.3871	38.71	1.4631	68.91
1.3562	19.54	1.3883	39.39	1.4683	70.70
1.3586	21.11	1.3912	40.74	1.4771	72.91
1.3599	21.96	1.3931	41.66	1.4830	74.43
1.3621	23.40	1.3946	42.59	1.4889	75.77
1.3640	24.87	1.3961	43.17	1.4965	77.64
1.3640	25.53	1.3962	43.44	1.5012	79.14
1.3665	26.57	1.4011	45.22	....	...

TABLE IV

INDICES OF REFRACTION OF SELENIOUS ACID

Results by Interpolation for the Sodium Line D at 20°

Index	%	Index	%	Index	%
1.3330	0	1.3673	27	1.4205	54
1.3340	1	1.3689	28	1.4230	55
1.3350	2	1.3705	29	1.4255	56
1.3360	3	1.3721	30	1.4280	57
1.3371	4	1.3738	31	1.4305	58
1.3382	5	1.3755	32	1.4331	59
1.3394	6	1.3772	33	1.4358	60
1.3406	7	1.3789	34	1.4386	61
1.3417	8	1.3806	35	1.4414	62
1.3429	9	1.3823	36	1.4443	63
1.3441	10	1.3840	37	1.4474	64
1.3454	11	1.3858	38	1.4505	65

TABLE IV (*Continued*)

Index	%	Index	%	Index	%
1.3467	12	1.3876	39	1.4537	66
1.3480	13	1.3895	40	1.4570	67
1.3492	14	1.3915	41	1.4603	68
1.3504	15	1.3935	42	1.4636	69
1.3517	16	1.3956	43	1.4670	70
1.3530	17	1.3977	44	1.4705	71
1.3543	18	1.3998	45	1.4741	72
1.3556	19	1.4020	46	1.4778	73
1.3570	20	1.4042	47	1.4816	74
1.3584	21	1.4064	48	1.4853	75
1.3698	22	1.4086	49	1.4893	76
1.3613	23	1.4109	50	1.4932	77
1.3628	24	1.4132	51	1.4971	78
1.3643	25	1.4156	52	1.5010	79
1.3658	26	1.4180	53	....	..

based on the observed values of Table III. For this curve one unit on the abscissas was assigned a value of 0.2% and one unit on the ordinates a value of 0.0002 unit of index of refraction. This made possible an interpolation of data, well beyond the experimental limits of error, which is shown in Table IV.

Summary

1. The indices of refraction of various strengths of selenic acid solutions and the corresponding percentage compositions have been determined. This furnishes a basis for determining the concentration of selenic acid solutions by means of an Abbé refractometer which is rapid and accurate.

2. Tables of the refractive indices and percentage compositions of selenious acid solutions are presented. These tables offer a rapid and accurate means of determining the concentration of such solutions.

The author wishes to acknowledge his appreciation of the inspiration and many helpful suggestions received from Professor Victor Lenher under whose direction this work was carried out.

MADISON, WISCONSIN