TABLE 3—CHANGE OF THE MOL NUMBERS WITH THE CUBE-ROOT OF THE CONCENTRATION.

Substances.	K.	Conc.	0.005	0.01	0.02	0.05	0.1	0.2	0.5
MCl and MBr	0.292	Obs.	1.952	1.937	1.925	1.887	1.864	1.837	1.804
		Calc.	1.950	1.937	1.921	1.893	1.865	1.829	1.768
$NaClO_3$ and $NaBrO_3$	0.334	Obs.	...	...	1.902	1.883	1.852	...	...
		Calc.	...	...	1.909	1.877	1.845	...	...
$KClO_3$ and $KBrO_3$	0.418	Obs.	...	1.919	1.894	1.853	1.802	...	...
		Calc.	...	1.910	1.887	1.846	1.806	...	...
$NaIO_3$ and KIO_3	0.45	Obs.	1.940	1.915	1.886	1.835	1.769	...	...
		Calc.	1.923	1.903	1.878	1.834	1.791	...	...
Na_2SO_4 and K_2SO_4	1.10	Obs.	2.857	2.798	2.723	2.580	2.466	2.339	2.135
		Calc.	2.812	2.763	2.702	2.595	2.490	2.356	2.127
$BaCl_2$	1.00	Obs.	2.797	2.756	2.709	2.637	2.575	2.515	...
		Calc.	2.829	2.785	2.729	2.632	2.536	2.415	...
$Pb(NO_3)_2$	1.47	Obs.	2.779	2.700	2.607	2.448	2.298	2.136	1.854
		Calc.	2.749	2.684	2.602	2.459	2.318	2.140	1.833
$MgSO_4$	1.60	Obs.	1.694	1.618	1.536	1.420	1.324	1.223	1.084
		Calc.	1.726	1.655	1.566	1.411	1.258	1.064	...
$CuSO_4$	1.90	Obs.	1.616	1.545	1.455	1.318	...	...	...
		Calc.	1.675	1.592	1.485	1.301	...	...	...

differences not exceeding ½ per cent. in the case of the chlorates and bromates. In the case of the iodates and the tri-ionic salts, however, the differences at concentrations up to 0.1 normal frequently reach 1 per cent., but do not much exceed this. The bibivalent salts show deviations of several per cent., so that the principle can not be said to hold even approximately for them.

Attention may also be called to the fact that (since $K = -di/dC^{1/3}$) the value of the constant K furnishes an obvious measure of the relative rates at which the mol numbers of the various substances decrease with the increasing concentration. The regularities that exist will readily be seen by an examination of the values of K given in the table.

BOSTON, June, 1910.

SILVER NITRATE FORMED BY THE ACTION OF NITRIC ACID ON SILVER SULPHIDE.

BY HIPPOLYTE GRUENER.

Received May 30, 1910.

The statements which I have found concerning the products of the action of nitric acid on silver sulphide are incomplete and contradictory. The proportions of nitrate and sulphate formed vary widely with the conditions applied. Highly concentrated acid results in complete conversion to sulphate, while with the less concentrated acid there is formed a large percentage of nitrate. Besides concentration, temperature of the acid and time of action are influential.

In the experiments summarized in Table I, the precipitated sulphide

(0.2 g.) was treated with nitric acid (usually 15 g. of the pure acid) diluted to the proper concentration. The mixture was heated, or allowed to stand at the ordinary temperature. When the action had taken place, hot water was added to dissolve the nitrate and sulphate, the solution filtered from the sulphur and unchanged sulphide, and repeatedly evaporated to dryness. The amount of silver found in the residue determined the amount of sulphide dissolved. The nitrate formed was determined by the method of Gooch and Gruener.[1] The results are shown in Table I, which indicates the proportions of sulphide dissolved, and also the percentage of nitrate formed at different concentrations, *a*, with boiling acid, and *b* with cold acid.

TABLE I.

		a. Acid boiling.			*b*. Acid cold.		
No. of expt.	Conc. of HNO_3. Per cent.	Time of action.	Per cent. Ag_2S dissolved.	Per cent. of possible nitrate formed.	Time of action.	Per cent. Ag_2S dissolved.	Per cent. of possible nitrate formed.
1....	94	50 min.	98.6	0	6 days	100	0
2....	71	5 min.	99.9	3.6	18 hours	95.0	7.2
3....	65	....	...	..	4 days	99.4	22.6
4....	55	10 min.	100	35.2	4 days	99.5	29.0
5....	45	3 min.	98.4	57.9	4 days	99.5	58.4
6....	35	3 min.	99.4	71.9	6 days	99.7	77.0
7....	25	5 min.	98.8	87.8	6 days	99.3	91.5
8....	20	until action was complete	98.9	94.7	11 days	98.6	95.9
9....	15	until action was complete	98.9	90.9	11 days	98.8	97.0
10....	10	until action was complete	97.2	90.7	11 days	98.3	92.7
11....	7.5	15 min.	99.0	..	7 mos.	98.8	92.3
12....	5	30 min.	96.4	88.9	7 mos.	98.8	84.4
13....	2.5	4 hours	75.0	74.8	7 mos.	89.0	75.8
14....	1.25	20 hours	86.0	60.4	7 mos.	7.3	0

The complete conversion of the sulphide to sulphate by the strongest acid used suggests the other extreme, namely, complete conversion to nitrate. But the maximum formation of nitrate is found at about 20 per cent. acid, and with greater dilution the amount of nitrate is found to diminish. The advantage of the cold acid from the standpoint of the nitrate is apparent, for the average yield when the action takes place at ordinary temperature is about 10 per cent. greater than when the acid is heated.

The time of contact of the reacting substances is important. When the sulphur liberated by the first action is promptly removed, *i. e.*, by dilution and filtration, the percentage of nitrate is conspicuously greater than when longer contact is allowed. When the time of contact is less-

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[1] *Am. J. Sci.*, 44, 117.

ened to increase the amount of nitrate, there is also a diminution of the amount of sulphide dissolved. These points are shown in Table II.

TABLE II.

HNO_3 = 71 per cent. Ag_2S = 0.2g.

Acid boiling				Acid cold.			
No. of expt.	Time of action.	Per cent. Ag_2S dissolved.	Per cent. nitrate formed.	No. of expt.	Time of action.	Per cent. Ag_2S dissolved.	Per cent. nitrate formed.
21........	Heated just to boiling	62	39.5	31	1 hour	37.0	32.8
22........	15 sec.	97.5	37.5	32	3.5 hrs.	53.6	20.8
23........	30 sec.	96.6	21.1	33	9 hours	85.2	22.9
24........	1 min.	91.4	8.4	34	18 hours	95	7.2
25........	5 min.	99.7	3.6	35	42 hours	99.7	0.8
26........	70 min.	100	1.1	36	66 hours	99.8	0.3

Summary.

Nitric acid, when of concentration above 5 per cent., dissolves precipitated silver sulphide rapidly. Very strong acid yields silver sulphate alone, while acid of lower concentration forms some nitrate in proportion to its dilution. 20–15 per cent. acid yields the maximum, about 95 per cent. nitrate, greater dilution again resulting in a smaller percentage. Heating the acid, or prolonging its time of action is unfavorable to the formation of nitrate.

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GRAHAMITE, A SOLID NATIVE BITUMEN.

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Received June 24, 1910.

Grahamite is a solid native bitumen, the type of which was first found in Ritchie County, West Virginia, in the early sixties of the last century. It was named for the Messrs. Graham, who were interested in the commercial development of the deposit, by Henry Wurtz. The early literature of the subject[1] is largely devoted to the origin of the material and to its relations to coal, asphalt and albertite, as the latter occurs in Nova Scotia.[2] It is largely controversial, which is not surprising in view of the fact that there had been little opportunity up to that time of studying and differentiating the native bitumens.

In 1890 Prof. Wm. P Blake, who had been interesting himself in the solid native bitumen found in such large amounts in veins in Utah and

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[1] J. P. Leslie, *Proc. Am. Phil. Soc.*, 9, 183 (1863). Henry Wurtz, *Am. J. Sci.*, [2] 42, 420 (1865); *Proc. A. A. A. S.*, 18, 124 (1869); *Am. Gas Light J.*, 11, 98. S. F. Peckham, *Am. Gas Light J.*, 11, 164 (1869). W. M. Fontaine, *Am. J. Sci.*, [3] 6, 409 (1873). J. P. Kimball, *Am. J. Sci.*, [3] 12, 277 (1876).

[2] Wetherill, *Trans. Am. Phil. Soc.*, 1852, 353.