II. "On Chemical Affinity, and the Solubility of the Sulphate of Baryta in Acid Liquors." By F. Crace Calvert, Esq. Communicated by William Allen Miller, M.D., F.R.S. Received October 27, 1855.

Solubility of the Sulphate of Baryta.

The author observes that sulphate of baryta is not an insoluble salt, as is generally admitted, for he has found that 1000 grs. of nitric acid, of spec. grav. 1·167, are capable of dissolving 2 grs. of sulphate of baryta; and what renders the knowledge of this fact still more useful in analytical chemistry is, that the insolubility of this salt is affected even by the weakest nitric or hydrochloric acids; for whilst 0·062 gr. of sulphate of baryta only requires 1000 grs. of nitric acid, of spec. grav. 1·032, to hold it in solution, the same quantity of salt requires 50·000 grs. of pure distilled water to dissolve it.

What is not less useful to know is, that the solubility of sulphate of baryta is affected in a higher degree by the bulk of the acid than by its strength. The two following tables, taken from amongst many others contained in the paper, will not only illustrate this fact, but will also give an insight into the way in which the experiments were conducted. The first table illustrates the influence which increasing bulks of the same nitric acid exert on the formation of sulphate of baryta, and the second table the action which increasing strengths of acid have:—

Table XVI.

Order of jars.	Number of divisions of the alkalimeter of nitric acid, spec. grav. 1·167.	Number of divisions of the alkalimeter of water added.	Spec. grav. of the bulk of acid.	Sulphate of potash dissolved in the acid.	Nitrate of baryta poured in, previously dissolved in 20 grs. of water.	Time required for a precipitate to appear.	Quantity of sulphate of baryta precipitated.	Quantity of sulphate of baryta dissolved.
1	20	20	1·167	3·34	5·00	3 min.	4·28	Average
2	20	40	1·120	...	...	...	4·34	quantity
3	20	60	1·085	...	...	...		dissolved
4	20	80	1·067	...	...	...		equal
5	20	100	1·057	...	...	...	4·35	0·10 gr.
6	20	120	1·050	...	...	...	4·35	
7	20	140	1·044	...	...	...	4·36	
8	20	160	1·039	...	...	...		
9	20	180	1·035	...	...	...		
10	20	200	1·032	...	...	...	4·38	

TABLE II.

Order of jars.	Number of divisions of the alkalimeter.	Corresponding weight of nitric acid, sp. gr. 1·167.	Quantity of sulphate of potash.	Quantity of nitrate of baryta.	Weight of sulphate of baryta.	Time required for a precipitate to appear.	Quantity of sulphate of baryta dissolved.
1	40	466·8	3·34	5·00	4·46	Instantly	0·02
2	80	933·6	...	...	...	20 minutes	1·29
3	120	1400·4	...	...	...	2 hours	2·34
4	160	1867·2	...	...	...	8½ hours	3·66
5	200	2334·0	...	...	...	24 hours	
6	240	2800·8	...	...	...	No precip.	
7	280	3267·6	...	...	...		
8	320	3734·4	...	...	...		
9	360	4201·2	...	...	...		
10	400	4668·0	...	...	...		

These tables clearly show the influence which a given strength of nitric acid has on the solubility of the sulphate of baryta; for there is a precipitate in three minutes in all the jars of the first table, whilst we have a precipitate only in the first four jars of Table II.

Another fact which is observed in these tables is, that whilst 240 divisions of the alkalimeter of nitric acid, spec. grav. 1·167, are capable of dissolving, or preventing the formation of, 4·46 grs. of sulphate of baryta, 240 divisions of an acid, of spec. grav. 1·032, only retained in solution 0·086 gr. It follows from these facts, that in future the practice of rendering liquors acid with nitric or hydrochloric acids, must be discontinued when sulphates are to be determined, or separated from chromates, phosphates, &c.

Influence of Mass on Chemical Affinity.

The researches of the author, to illustrate the influence which mass exerts on chemical affinity, are extensive; a few of the results arrived at are here given.

The following table will clearly show the marked influence which increasing volumes of nitric acid have in preventing the formation of sulphate of baryta :—

TABLE IV.

Number of jars.	Number of divisions of the alkalimeter.	Corresponding weight of acid, sp. gr. 1·167.	Quantity of sulphate of potash.	Quantity of nitrate of baryta.	Weight of sulphate of baryta.	Time when precipitate appeared.
1	40	466·8	5·12 grs.	8·00	7·13	Instantly
2	80	933·6	...	...	...	2 minutes
3	120	1400·4	...	...	...	14 minutes
4	160	1867·2	...	...	...	1 hour
5	200	2334·0	...	...	...	1 hour 15 minutes
6	240	2800·8	...	...	...	4 hours
7	280	3267·6	...	...	...	8 hours [cloud)
8	320	3734·4	...	...	...	21 hours (only a
9	360	4201·2	...	...	...	None
10	400	4668·0	...	...	...	None

Thus in this table we perceive, that as the bulk of acid increases, more time is required for a precipitate to appear, although there is a large excess of substance employed on the quantity necessary to give an instantaneous precipitate; and it is curious to observe how wide is the space of time in each successive jar for a precipitate to appear, and in jars numbers 9 and 10 no deposits were formed after twenty-four hours. As the quantity of precipitate decreased rapidly in each successive jar, they were gathered, and their amount determined with due care; and these are the facts observed:—

TABLE V.

Number of jars.	Number of divisions of the alkalimeter.	Corresponding weight of nitric acid, sp. gr. 1·167.	Quantity of sulphate of baryta precipitated.	Quantity of sulphate of baryta dissolved.	Quantity of sulphate of baryta dissolved per 1000 grs.
1	40	466·8	6·86	0·27	0·591
2	80	933·6	5·63	1·50	1·615
3	120	1400·4	4·66	2·47	1·767
4	160	1867·2	3·22	3·91	2·099
5	200	2334·0	2·33	4·80	2·059
6	240	2800·8	1·10	6·03	2·155
7	280	3267·6	0·14	6·99	2·141

The results contained in this table, especially those in the last column, clearly show the influence of mass on chemical affinity, for there is no difference in any of the jars excepting the increasing bulk of the acid; and still we have in jar No. 1 only 0·591 of sulphate of baryta dissolved per 1000 grs. of acid, whilst we have 2·099 in No. 4 jar.

But the relative bulk of acid is not the only influence which affects the affinity of sulphuric acid for baryta, as the relative quantities of nitrate of baryta and sulphate of potash put in presence also exert an action. This fact is illustrated by the following results, taken from three different tables, in which the same quantities of acid were used, but different proportions of salts :—

TABLE IV. E.

Number of table.	Quantities of acid, sp. gr. 1·167.	Sulphate of potash.	Nitrate of baryta.	Sulphate of baryta.	Time before a precipitate appeared.
No. 1	466·8	0·753	1·121	1·00	12 hours
	933·6	0·753	1·121	1·00	None
No. 2	466·8	3·34	5·00	4·46	Instantly
	933·6	3·34	5·00	4·46	2 hours
No. 4	466 8	5·12	8·00	7·13	Instantly
	933·6	5·12	8·00	7·13	2 minutes

This point is again brought out in the following table, which is also taken from several series of experiments :—

TABLE IV. A.

Number of table.	Order of jar.	Quantities of fluid.	Total quantities of sulphate of baryta susceptible of being produced.	Quantity of acid represented.	Quantities of sulphate of baryta dissolved in 1000 grs.	Increased ratio of solubility.
No. 1	2	933·6	1·00	1000	1·071	0·
No. 2	6	2800·8	4·46	...	1·593	0·522
No. 4	9	4201·2	7·13	...	1·912	0·841

These facts, and others described in the paper, demonstrate that the solubility of the sulphate of baryta, or its non-formation, is not only influenced by the respective bulks of an acid of spec. grav. 1·167, and the respective quality of salts employed, but that the relative quantity of matter put in presence has a decided influence on chemical affinity; and these observations not only corroborate perfectly the results obtained by Mr. Bunsen on the influence of volumes on the combination of gases, and the observations which show a like influence on the carbonates, but also are, I believe, the first instance which has been noticed of irregularity of solubility of a substance in increased multiple bulks of a liquid.