

known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form) and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN,
MADISON, November 26, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 65.]

THE GRAVIMETRIC DETERMINATION OF MERCURY AND ITS SEPARATION FROM ARSENIC, ANTIMONY, AND COPPER.

BY CHARLES J. PRETZFELD.

Received December 8, 1902.

HISTORICAL.

Mercury Weighed as Chloride.—For the determination of mercury in this form, the following reducing agents have been proposed: formic acid,¹ ferrous sulphate,² phosphorous acid,³ glucose,⁴ potassium hypophosphite,⁵ a mixture of hypophosphorous acid and peroxide of hydrogen,⁶ and hydrazine sulphate.⁷

Mercury Weighed as Oxide.—The determination of mercury in this form is unimportant, the only method known being that of Marignac.⁸

Mercury Weighed as Metal.—Under this heading, the history of mercury determination can be subdivided into three classes:

(A) By application of reducing agents in the cold.

¹ Bonsdorff : *Ann. Chem. Phys.*, **33**, 78.

² Hempel : *Ann. Chem. Pharm.*, **110**, 176.

³ Rose : *Jsb. d. Chem.*, **13**, 665.

⁴ Hager : *Ztschr. anal. Chem.*, **17**, 380.

⁵ Thompson : *J. Soc. Chem. Ind.*, **16**, 263.

⁶ Vanino and Treubert : *Ber. d. chem. Ges.*, **30**, 2808-2809.

⁷ Jannasch and Dürseleu : Doctor's Dissertation at Heidelberg, 1899.

⁸ *Jsb. d. Chem.*, (1849), p. 594.

(B) By application of heat to volatilize the mercury.

(C) By electrolytic deposition.

Under class *A* we have the methods of Mitscherlich,¹ Sieveking,² Jannasch and Alffers,³ and of Jannasch and Durselen.⁴

Under class *B* the methods of Milton,⁵ Rose,⁶ Eschka,⁷ Attwood,⁸ Schuyten,⁹ Chism,¹⁰ and of Janda¹¹ are the most important.

Under class *C* the most important methods are those of Hannay,¹² Clarke,¹³ Ludwig and Classen,¹⁴ Brand,¹⁵ Vortman,¹⁶ Rudorff,¹⁷ Smith and Moyer,¹⁸ Smith and Wallace,¹⁹ Smith and Kollock,²⁰ Perreau,²¹ and of Classen.²²

EXPERIMENTAL.

About 8 liters of a solution of mercuric nitrate were made, and used for testing the accuracy of various methods for the determination of mercury. The strength of the solution was found to be, by electrolysis, such that each cubic centimeter contained 0.01673 gram of mercury.

Estimation of Mercury as Sulphide.—The form in which mercury is most commonly weighed being the sulphide, a few experiments were conducted to find how reliable this method is.

Twenty-five cc. of the solution of mercuric nitrate were taken and the mercury precipitated, and purified according to the method of Polstorff and Bulow. The solution was diluted to a volume of 250 cc. and saturated with sulphuretted hydrogen. The precipitate was washed with water containing sulphuretted

¹ *Pogg: Ann. Phys. Chem.*, 9, 39.

² *American Chemist*, 6, 160.

³ *Ber. d. chem. Ges.*, Part II, pp. 2381-2385.

⁴ Doctor's Dissertation at Heidelberg, 1899.

⁵ *Erd. J.*, 37, 271.

⁶ *Erd. J.*, 34, 36.

⁷ *J. Chem. Soc.* (London), (1872), p. 25.

⁸ *Chem. News*, 30, 111.

⁹ *J. Soc. Chem. Ind.*, 15, 475.

¹⁰ *Trans. A. I. M. E.*, 28, 448.

¹¹ *J. Soc. Chem. Ind.*, 18, 610.

¹² *Am. Chem. J.*, 4, 193.

¹³ *Chem. News*, 38, 273.

¹⁴ *J. Chem. Soc.* (London), 1, 493.

¹⁵ *J. Soc. Chem. Ind.*, 8, 1011.

¹⁶ *Jsb. d. Chem.*, p. 2403.

¹⁷ *Ztschr. angew. Chem.*, (1892), p. 5.

¹⁸ *Ztschr. anorg. Chem.*, 4, 96.

¹⁹ This Journal, 18, 169.

²⁰ Doctor's Dissertation, at Univ. of Penna., 1899.

²¹ *J. Soc. Chem. Ind.*, 19, 53.

²² "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 49.

hydrogen, and was then dissolved in a solution prepared by mixing a 15 per cent. solution of potassium sulphide with an equal volume of a 15 per cent. solution of caustic potash. The solution thus obtained was heated to 80° C. and upon addition of ammonium chloride, the mercury was reprecipitated as sulphide. This precipitate was washed with a solution of sulphuretted hydrogen, then twice with water, once with alcohol, twice with carbon bisulphide, and again with alcohol, dried at 100° and weighed.

RESULTS.

Hg(NO ₃) ₂ solution. Cc.	Calculated to Hg. Gram.	Weight of HgS found. Gram.	Calculated to Hg. Gram.
25	0.41825	0.4919	0.4239
19	0.31787	0.3734	0.3216
10	0.1673	0.1665	0.1693

Estimation of Mercury as Chloride.—The first method tried was that of Hempel, and was carried out as follows:

A known quantity of the standard solution of mercury was diluted to 150 cc.; 0.3 gram sodium chloride and 1.8 grams ferrous sulphate were then added and the solution stirred until the salts added had dissolved. Caustic soda was next added until the solution had become alkaline, and the whole was stirred for a few minutes. Sulphuric acid was then added to acid reaction and the solution again stirred. The solution was then allowed to stand over night. The precipitate was filtered off and washed once or twice with cold water, dried at 100° C., and weighed.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg ₂ Cl ₂ . Gram.	Calculated to Hg. Gram.
(A) 25	0.41825	0.4898	0.4161
(B) 25	0.41825	0.4896	0.4159
(C) 25	0.41825	0.4906	0.4167
(D) 25	0.41825	0.4905	0.4166
(E) 17	0.2844	0.3355	0.2849
(F) 15	0.2509	0.2926	0.2490

The next method tried was that of Vanino and Treubert, in which an excess of sodium chloride is added to the solution of mercury, which should have a volume of about 100 cc., and then as a reducing agent a slight excess of a mixture containing one drop of commercial hypophosphorous acid to every cubic centimeter of peroxide of hydrogen is added drop by drop, while stirring. The solution is allowed to stand one hour, filtered on balanced filters

and quickly washed with hydrochloric acid, and finally with water. The temperature used for drying was 105° C.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg ₂ Cl ₂ . Gram.	Calculated to Hg. Gram.
25	0.41825	0.4893	0.4156
25	0.41825	0.4892	0.4155
21	0.35133	0.4105	0.3486
10	0.16730	0.1955	0.1660
15	0.25096	0.2937	0.2494

By a slight modification of this method, very accurate results were obtained. Instead of converting the mercury and then reducing, the reducing agent was added first and after stirring for about one minute, an excess of sodium chloride was added. A heavy curdy precipitate, very similar in appearance to that of silver chloride, was thrown down immediately and settled very rapidly. The other conditions of the above method were maintained. The accuracy of the results obtained in this manner can be judged from the following table.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg ₂ Cl ₂ . Gram.	Calculated to Hg. Gram.
13	0.21749	0.2556	0.2171
19	0.31787	0.3736	0.3173
15	0.25095	0.2951	0.2506
15	0.25095	0.2953	0.2508
10	0.16730	0.1972	0.1675
10	0.16730	0.1972	0.1675
10	0.16730	0.1971	0.1674

The explanation for the rapid formation of this precipitate, is that mercury in the form of nitrate is reduced, and this salt of mercury being much more dissociated than the chloride, the reaction takes place in a much shorter period of time. The disadvantage of the above is, however, that mercury is usually in the form of chloride, and for this reason the method cannot be applied very generally.

The next method tried was that of H. Rose. It was conducted in exactly the same manner as that of Vanino and Treubert, the only difference being that phosphorous acid is used as a reducing agent, and that the precipitate was allowed to settle over night. The results are quite low, probably due to the strong reducing action of phosphorous acid. The precipitate had a grayish color

and also showed a tendency to run through the paper. The results obtained are as follows:

RESULTS.

Hg(NO ₃) ₂ taken, Cc.	Calculated to Hg. Gram.	Weight of Hg ₂ Cl ₂ . Gram.	Calculated to Hg. Gram.
25	0.4182	0.4881	0.4146
14	0.2342	0.2726	0.2316
17	0.2844	0.3311	0.2812
13	0.2175	0.2530	0.2149
17	0.2844	0.3313	0.2814
20	0.3346	0.3913	0.3324

When the reducing agent was added before converting the mercury to chloride, the following results were obtained:

RESULTS.

Hg(NO ₃) ₂ taken Cc.	Calculated to Hg. Gram.	Weight of Hg ₂ Cl ₂ . Gram.	Calculated to Hg. Gram.
10	0.1673	0.1970	0.1673
15	0.2509	0.2959	0.2514
10	0.1673	0.1968	0.1671
10	0.1673	0.1963	0.1667

The quality of the precipitate obtained in this way was the same as that obtained by similarly modifying Vanino and Treubert's method.

Estimation of Mercury as Arsenate.—Since the percentage of mercury in mercury arsenate is smaller than in mercury sulphide or chloride, the error caused by manipulation will of course be smaller than if the mercury formed a larger proportion of the precipitate. That an arsenate of mercury exists, is known,¹ but no attempt had ever been made to weigh the mercury in this form. Those conditions were consequently sought which would precipitate the metal completely and give the most accurate results. By the following method good results were obtained. To a cold solution of mercuric nitrate, of a bulk of about 100 cc., about 20 cc. of a saturated solution of sodium arsenate was added, this being an excess. A heavy yellowish-white precipitate of mercuric arsenate was immediately formed, and settled rapidly, but in order to insure complete precipitation, it was found best to allow the solution containing the precipitate to stand for about five hours. The solution was then filtered through balanced papers, and the precipitate was washed with cold water, dried at 95° C. to 100° C. and weighed.

¹ Danner's "Anorganische Chemie," II, p. 921.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Weight of Hg ₃ (AsO ₄) ₂ Gram.	Precipitate calcula- ted to Hg. Gram.
15	0.2509	0.3674	0.2509
15	0.2509	0.3677	0.2512
15	0.2509	0.3671	0.2508

These results are sufficiently accurate for any requirements, and the method is extremely simple. Unfortunately, however, the mercury is not precipitated as arsenate from a chloride solution, thus limiting the application of the method considerably. The presence of a small amount of free nitric acid did in no way interfere with the accuracy of the results.

Electrolytic Determination of Mercury.—Two methods only were used, the purpose having been more to determine the strength of the standard solution used, than to compare the methods.

In the first method the conditions proposed by E. F. Smith were tried.

RESULTS.

Hg(NO ₃) ₂ Cc.	KCN. Gram.	Dilution. Cc.	Current.	Voltage.	Tem- perature. °C.	Mercury found. Gram.
10	0.8	100	N.D. ₁₀₀ = 0.07 A	3.2	65	0.1675
10	0.8	100	N.D. ₁₀₀ = 0.07 A	3.2	65	0.1663

The other method was from a solution of the double sulphide of mercury and potassium. The conditions and results were:

Hg(NO ₃) ₂ Cc.	K ₂ S. Cc.	Dilution. Cc.	Current.	Voltage.	Tem- perature. °C.	Mercury found. Gram.
10	20-25	125-130	N.D. ₁₀₀ = 0.12 A	2½	70	0.1672
10	20-25	125-130	N.D. ₁₀₀ = 0.12 A	2½	70	0.1673

From these results, the strength of the solution in terms of mercury was 0.01673 gram for each cubic centimeter.

All of the most important methods for the gravimetric estimation of mercury having been tried, it was concluded that, when accuracy is desired, the following methods, only, will give satisfactory results.

First, the method of Vanino and Treubert, as modified, page 201.

Second, the method of Rose, as modified, page 201.

Third, the determination of mercury as arsenate, described on page 202.

Fourth, the determination of mercury by electrolysis.

Unfortunately the first, second and third methods above re-

ferred to cannot be used when the mercury is in the form of chloride, the first and second yielding low results, and the third being impossible since no precipitate is formed. The precipitation of mercury as sulphide, on the other hand, permits of very wide application. The precipitation as such is always rapid as well as complete, but if weighed in this form it yields high results on account of the separated sulphur present. The precipitation in this form is however of great value, not only because it acts in many cases as a separation, but also because the precipitate can easily be dissolved and electrolyzed from the solution thus obtained, yielding most satisfactory results. This method was used in the succeeding work on the separation of mercury.

The Separation of Mercury from Arsenic, Antimony and Copper.—The most important methods for this separation are those of Rose,¹ Fresenius,² Polstorff and Bülow,³ v. Uslar,⁴ Jannasch and Lenhart,⁵ Jannasch and Devin,⁶ and Jannasch and Durselen.⁷

As these methods either afford low results or require an excessive amount of manipulation, a simpler and more accurate method was sought.

EXPERIMENTAL.

Separation of Mercury from Antimony and Copper by the Use of Sulphuretted Hydrogen in a Cyanide Solution.

Separation of Mercury from Copper.—Although it was already known that mercury could be separated from copper by saturating a cyanide solution of the two metals with sulphuretted hydrogen,⁸ no attempt has been made to separate mercury from antimony and arsenic by a method based on the same, or on a similar principle. Before going further, it was considered advisable to test the accuracy of the method of Haidlen and Fresenius for the separation of mercury from copper. The results were found to be satisfactory.

¹ *Jsb. d. Chem.*, **13**, 665.

² *Ztschr. anal. Chem.*, **2**, 343 (1863).

³ *Ibid.*, **31**, 697.

⁴ *Ibid.*, **34**, 411.

⁵ *Ztschr. anorg. Chem.*, **12**, [5], 359-364.

⁶ *Ber. d. chem. Ges.*, **31**, 2, 2377-2385.

⁷ Doctor's Dissertation, Heidelberg, 1899; *Ibid.*, Heidelberg, 1899.

⁸ Haidlen and Fresenius: *Ann. Chem. Pharm.*, **43**, 144 (1842).

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Hg(NO ₃) ₂ calcu- lated to Hg. Gram.	Cu taken. Gram.	Hg found. Gram.
9	0.1505	0.05	0.1497
10	0.1673	0.05	0.1666
10	0.1673	0.05	0.1670
10	0.1673	0.05	0.1667
10	0.1673	0.15	0.1672
10	0.1673	0.15	0.1674
10	0.1673	0.30	0.1671
10	0.1673	0.30	0.1670

Separation of Mercury from Antimony and Copper.—The above method was tried for the separation of mercury from solutions containing antimony and copper, and although good results were obtained, the process was inconvenient owing to the partial precipitation of antimony, upon adding potassium cyanide. In the presence of tartaric acid, it was found that antimony remains completely in solution and that upon saturating the solution with sulphuretted hydrogen, only mercury is precipitated.

Separation of Mercury from Antimony, Arsenic and Copper by the Use of Tartaric Acid, Potassium Cyanide and Sulphuretted Hydrogen.

Separation of Mercury from Antimony and Copper.—To a clear solution of the three metals, about 30 cc. of a saturated solution of tartaric acid was added and the solution stirred for one or two minutes. Potassium cyanide was then added in small amounts at a time, until the solution became clear. While adding the latter reagent, it was found necessary to stir the solution continually in order to dissolve the potassium cyanide. Hydrogen sulphide was then led into the solution, until saturated, and the precipitate of mercury sulphide was allowed to settle. This precipitation was performed in the cold, as there is some danger of losing a little mercury with the escaping fumes. The precipitate of mercury sulphide was then filtered, dissolved and electrolyzed.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Sb taken. Gram.	Cu taken. Gram.	Hg found. Gram.
10	0.1673	0.10	0.10	0.1672
10	0.1673	0.10	0.10	0.1665
8	0.1338	0.20	0.20	0.1328
9	0.1505	0.20	0.20	0.1509
11	0.1840	0.30	0.30	0.1840
12	0.2007	0.30	0.30	0.2005
9	0.1505	0.10	0.30	0.1510
10	0.1673	0.10	0.30	0.1669
8	0.1338	0.30	0.10	0.1339
11	0.1840	0.30	0.10	0.1844

The conditions for this separation were found to be very broad, thus rendering the method one which can be carried out with great facility. The minimum amount of potassium cyanide required is an excess of 1 or 2 grams. It is safer to add an excess of 2 or 3 grams so that the solution will be strongly alkaline. Any excess beyond this amount does no harm. The dilution also permits of wide limits. The smallest bulk which was used in the above determinations was about 150 cc. and the largest about 500 cc. In both of these experiments the results were accurate. Furthermore, the solution, alkaline with potassium cyanide, was allowed to stand for more than two hours, with no perceptible change. Nor did standing for two or three hours after precipitation with hydrogen sulphide interfere in any way with the final result. The advantage of the tartaric acid in the solution, over the method first attempted, where no tartaric acid was used, is firstly, that no precipitate of antimony is formed, thereby avoiding the necessity of an additional filtration, and in case a determination of antimony is required, the solution of this precipitate is avoided. The red color formed in the former method is completely absent in the presence of this acid. In most, if not all cases, however, the solution becomes pale orange, which is not in the least an objection. Again when no tartaric acid is used, it is always fatal to use potassium cyanide, containing sulphur¹ since mercury is precipitated as sulphide and is consequently filtered off with the antimony and copper. When, on the other hand, tartaric acid is present, a black precipitate of mercury sulphide is formed which can be filtered off with the main precipitate of mercury sulphide, precipitated by hydrogen sulphide.

Separation of Mercury from Arsenic, Antimony and Copper.—The next separation attempted under these same conditions was the separation of mercury from arsenic. A solution of sodium arsenate was made up of a strength of about 1 per cent. of metal. The results of the separations were very satisfactory.

RESULTS.

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	As taken Gram.	Hg found. Gram.
8	0.1338	0.05	0.1342
10	0.1673	0.05	0.1670
11	0.1840	0.30	0.1833
9	0.1506	0.30	0.1511

¹ Potassium cyanide free from sulphur is a very expensive reagent.

To determine if mercury could be separated from antimony, arsenic and copper, experiments were made with the following results:

Hg(NO ₃) ₂ taken. Cc.	Calculated to Hg. Gram.	Cu taken. Gram.	Sb taken. Gram.	As taken. Gram.	Hg found. Gram.
9	0.1506	0.05	0.05	0.05	0.1509
9	0.1506	0.05	0.05	0.05	0.1507

It was also attempted to separate mercury from tin but the results were very low. This, although it could not be accounted for, is of interest, since, in the method of Polstorff and Bülow where mercury is separated by dissolving the sulphide in alkaline sulphide and then reprecipitating it as sulphide on addition of ammonium chloride, some mercury is also withheld by tin if present.¹ The method of v. Uslar,² in which phosphorous acid is used to separate mercury from the metals of the fifth and sixth group is useless also, if tin is present. Bismuth and lead, if present, are completely precipitated with the mercury as sulphides, from which they are separated by digestion with an alkaline sulphide.

MERCURIAL ORES.

A. Analysis of Cinnabar.—Cinnabar, being the most important ore of mercury, it seemed well worth while to compare one or two of the most important methods for the determination of that metal therein.

The most important methods for the determination of mercury in cinnabar are those of Classen,³ Rising and Lenher,⁴ Smith and Wallace,⁵ Chism⁶ and a number of distillation methods.

By the method of Smith and Wallace, the ore was found to contain 16.0 per cent. and 16.02 per cent. of mercury. Chism's method was tried with various modifications, yielding the following results:

Ore taken. Gram.	Hg found. Per cent.
0.29755	13.81
0.22440	13.68
0.1661	15.35
0.1301	15.14
0.1384	15.32
0.1384	13.87
0.4625	13.91

¹ Classen: "Ausgewählte Methoden der Analytischen Chemie," p. 63.

² *Ztschr. anal. Chem.*, **34**, 391 (1895).

³ "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 50.

⁴ *This Journal*, **18**, 96 (1896).

⁵ *Ibid.*, **18**, 169 (1896).

⁶ *Trans. A. I. M. E.*, **28**, 148 (1898).

Another method tried on cinnabar was the distillation of a large amount of mercury from the ore, which had been mixed with iron filings. An ordinary glass retort was used and the mercury was caught in very dilute hydrochloric acid. The purification of the mercury was carried out by treatment with successive portions of dilute hydrochloric acid. It was finally poured into a weighed porcelain crucible and dried after having been washed with alcohol, two or three times.

RESULTS.

Ore taken. Grams.	Iron filings taken. Grams.	Hg found. Grams.	Hg found. Per cent.
22.5214	175	3.5163	15.61
24.1709	180	3.7402	15.47

B. Analysis of Mercurial Tetrahedrite.—Although earnest and repeated efforts were made to procure specimens of mercurial tetrahedrite, the only one that could be obtained contained but 0.3 per cent. of mercury. This was considered too low to show a just comparison of the methods, so a mixture of cinnabar and tetrahedrite was made and analyzed in the same way.

In applying the method in which tartaric acid and potassium cyanide are used, the decomposition of the mineral and mixture were effected in the manner described by Rose and Wöhler. The solution obtained was then filtered. To the filtrate, tartaric acid was added, then potassium cyanide and this was followed by the addition of sulphuretted hydrogen. The precipitate of mercuric sulphide was then filtered from the solution and treated as already described. If lead and bismuth are present, they also will be precipitated and can be separated from the mercuric sulphide by any of the well-known methods. All of the other metals likely to be found in tetrahedrite remain in solution.

RESULTS.

Amount of mineral taken. Gram.	Mercury found. Gram.	Mercury. Per cent.	
0.9153	0.0012	0.13	} Method of Rose and Wöhler.
1.0474	0.0014	0.13	
1.0500	0.0015	0.14	
1.1986	0.0042	0.35	} Tartaric acid and potas- sium cyanide method.
1.0278	0.0039	0.38	
0.8581	0.0756	8.81	} Method of Rose and Wöhler.
0.8989	0.0805	8.95	
1.0310	0.0931	9.03	
0.8853	0.0845	9.54	} Tartaric acid and potas- sium cyanide method.
0.9139	0.0874	9.56	
0.8592	0.0814	9.47	

These results show conclusively that the separation of mercury from arsenic, antimony, and copper, by the use of tartaric acid and potassium cyanide is more complete and consequently more accurate than by the use of ammonium sulphide.

Chism's method also was tried on the tetrahedrite, with good results. This seems to prove this method very good for ores running low in mercury.

The results obtained by Chism's method were 0.27 per cent. and 0.33 per cent. of mercury.

As this work was carried out under the suggestion and guidance of Professor E. H. Miller, it is but just and proper, that any merit which it may possess be associated with his name.

QUANTITATIVE LABORATORY,
May, 1902.

NOTE CONCERNING THE CALCULATION OF THERMOCHEMICAL RESULTS.

BY THEODORE WILLIAM RICHARDS.

Received December 10, 1902.

It is well known that the heat capacities of the majority of reacting substances change during their reaction. The magnitude of these changes and their significance are nevertheless often neglected.

A serious error may arise from this neglect. For example, according to the results of Thomsen, the neutralization of an approximately half normal solution of sodium hydroxide by an equivalent solution of hydrochloric acid involves an increase of heat capacity of 1.27 per cent.¹ The question now arises, since the solutions themselves are the capacities being warmed, What value for the total heat capacity shall be used in the calculation of the heat of reaction? Obviously the energy-change will be found to be 1.27 per cent. greater if the final, rather than the initial, heat capacity is used. The answer to this question is variously given in the different authorities upon thermochemistry. Ostwald and Luther in their admirable handbook² use the sum of the initial heat capacities; Thomsen often uses the capacity of the water alone; Berthelot commonly considers the capacity as equal to that

¹ Thomsen: "Thermochemische Untersuchungen," I, p. 67 (1882).

² Ostwald-Luther: *Physiko-Chemische Messungen*, (1902), p. 214.