to the oxide and water vapor and oxygen to the hydrogen has been carried out.

2. It has been pointed out that the reaction is auto-catalytic, copper being the auto-catalyst. The reaction thus appears to take place at the copper–copper oxide interface. This is shown by the character of the reduction curve and the fact that addition of metallic copper accelerates the reaction.

3. It has been shown that the presence of water vapor in the hydrogen markedly interferes with the formation of the original copper nuclei from which the reaction zone, that is, the copper–copper oxide interface spreads out; it does not markedly affect the subsequent reaction at the interface, however.

4. The presence of oxygen in the hydrogen strongly inhibits the reaction at the interface but in all probability has no marked effect on the primary reaction, that is, the formation of the original copper nuclei.

PRINCETON, NEW JERSEY.

THE HEATS OF SOLUTION AND OF TRANSFORMATION OF THE ACIDO AND AQUO COBALT PENTAMMINES.

BY ARTHUR B. LAMB AND JOHN P. SIMMONS.*

Introduction.

The spontaneous transformations of a number of the acido cobalt pentammines into their corresponding aquo compounds have been carefully studied.[1] They have been found to go nearly to completion at ordinary temperatures in aqueous solutions and, as regards velocity, to follow the course of a monomolecular reaction. At higher temperatures the reaction becomes more evidently reversible, and it has been shown that an equilibrium is attained which strikingly resembles the dissociation equilibria of strong electrolytes in water.
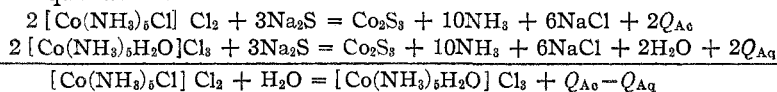
Particularly because of this wider bearing of the subject we have investigated the heat changes accompanying a number of these transformations in aqueous solution. These heat changes could be calculated from equilibria data at different temperatures, did such exist, but unfortunately there are experimental difficulties in studying these equilibria except within a narrow temperature interval. We have therefore been

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* This paper is largely based on a dissertation of the same title submitted by J. P. Simmons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, 1912.

[1] Lamb and Marden, THIS JOURNAL, **33**, 1873 (1911).

obliged to employ a direct method of measurement; direct, at least in the sense that only thermal quantities are measured. A really direct measurement of the heat of reaction would be difficult, not only because the most rapid of these transformations are relatively slow, but also because the ammines are for the most part far too insoluble to furnish solutions of adequate concentration.

The method which we have employed depends upon the use of an aqueous solution of sodium sulfide, which reacts rapidly at room temperatures with both the acido and aquo ammines, and produces the same substances in identical amount, except for the liberation of a molecule of water from the aquo ammine.

$$2 \, [\text{Co(NH}_3)_5\text{Cl}] \, \text{Cl}_2 + 3\text{Na}_2\text{S} = \text{Co}_2\text{S}_3 + 10\text{NH}_3 + 6\text{NaCl} + 2Q_{Ac}$$
$$2 \, [\text{Co(NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3 + 3\text{Na}_2\text{S} = \text{Co}_2\text{S}_3 + 10\text{NH}_3 + 6\text{NaCl} + 2\text{H}_2\text{O} + 2Q_{Aq}$$
$$\overline{[\text{Co(NH}_3)_5\text{Cl}] \, \text{Cl}_2 + \text{H}_2\text{O} = [\text{Co(NH}_3)_5\text{H}_2\text{O}] \, \text{Cl}_3 + Q_{Ac} - Q_{Aq}}$$

The difference then in its heat of reaction with an acido ammine on the one hand and with the corresponding aquo ammine on the other will evidently be equal to the heat of transformation of the acido into the aquo ammine.

The rigor of this method evidently depends on the precise identity of the products formed from the acido and the corresponding aquo ammine. The sulfide of cobalt is the only one of the products affording any possibility of dissimilarity. There was no indication whatever that such a dissimilarity existed, and yet the matter was of such fundamental importance that a careful study of the composition of the sulfide formed from the chloro- and the aquo-pentammine chlorides was made. The two sulfides were prepared under the same conditions as prevailed during an actual calorimetric determination, and were then carefully analyzed for sulfur. The chloro-pentammine for these experiments was an imported preparation which had been proved pure by repeated analyses.

The aquo-pentammine chloride was prepared and purified by Jörgensen's method.[2] The ionizable chlorine in the chloro-pentammine was determined by precipitating with silver nitrate solution at 0°, and rapidly coagulating and filtering off the silver chloride. Two samples weighing about 0.4 g. gave 28.27 and 28.24% of chlorine, while the theoretical percentage is 28.31. The aquo-pentammine chloride was analyzed for total chlorine by warming gently with an excess of silver nitrate solution. Two 0.5g. samples gave 39.56 and 39.52% of chlorine, while the theoretical composition is 39.62% of chlorine. These analyses establish the purity of these salts.

The compositions of the cobalt sulfide precipitates were determined by starting from weighed quantities of the ammines, precipitating with sodium sulfide, washing the precipitate from sodium chloride, ammonia, and the excess of the precipitant, and oxidizing the sulfide to sulfate by an ammoniacal solution of hydrogen peroxide, acidifying, and precipitating the sulfate as barium sulfate. The chief difficulty in this analysis lies in the sensitiveness of the cobalt sulfide to oxidation to sulfate by the oxygen of the air during the process of precipitation and washing. This difficulty was successfully overcome by precipitating, washing, and filtering the sulfide in an atmosphere of hydrogen.

[2] Jörgensen, Z. anorg. Chem., 17, 455 (1898).

The apparatus for this purpose consisted of a Gooch adapter set in a suction flask by means of a tight-fitting rubber stopper. In the top of the adapter was a 3-hole rubber stopper containing a connection to a Kipp generator for hydrogen, a dropping funnel with a stopcock, and an outlet of glass tubing with a stopcock attached. By proper manipulation of the stopcocks air was expelled by hydrogen; sodium sulfide and wash water were admitted, and filtration accelerated. At the bottom of the adapter was an asbestos filter between two perforated porcelain disks.

Weighed samples of the ammines were placed upon the filter and hydrogen gas run through the apparatus for several hours. Fifty cc. of sodium sulfide solution was then introduced and the closed apparatus shaken to bring about complete reaction with the ammine. After standing for some time the solution was filtered off, freshly boiled water introduced, and the shaking and filtration were repeated. The process as a whole was then repeated several times until the wash-water no longer gave a test for sodium.

The precipitate was converted to a cobaltic ammine sulfate by standing for 48 hours in an ammoniacal solution of hydrogen peroxide. To recover any sulfate which might have entered into complex combination with the cobalt, the ammine was decomposed by boiling with sodium hydroxide until no more fumes of ammonia were given off. The resulting cobaltic hydroxide was then dissolved in an excess of hydrochloric acid, heated to boiling, and a hot solution of barium chloride added with constant stirring. The barium sulfate was filtered off after 24 hours. By this method the sulfide from the acido ammine gave 45.29% and 45.11% (mean 45.19%) of sulfur; that from the aquo ammine 45.10% and 45.06% (mean, 45.08%) of sulfur. The calculated percentages of sulfur in CoS, Co_2S_3, and CoS_2 are 35.16, 44.86 and 52.03 respectively. The results are evidently in very close agreement with the requirements of the formula Co_2S_3. The slight excess of sulfur which they indicate is scarcely more than the experimental inaccuracy, and is in the direction that would be anticipated, since any incompleteness either in the washing of the cobaltic sulfide or of the barium sulfate would tend to give too high values for the sulfur. Furthermore, the values for the sulfides from the acido and aquo salts are in still closer agreement, so that there can be no question but what the same sulfide is formed in each case.

Preliminary experiments showed that the heats of reaction with the sodium sulfide solution were very small; indeed so small that even with the saturated solution of the ammines the temperature change would amount to only a few thousandths of a degree. We were obliged therefore to work with a suspension of the solid ammines, although this complicated the measurements by the introduction of the unknown heats of solution. To obviate this difficulty we have made independent determinations of the heats of solution of the ammines concerned.

Apparatus and Method.

Both the apparatus and the method employed in measuring the heats of solution and of transformation were very simple. The apparatus consisted of a 1-liter Dewar flask, almost completely submerged in a water thermostat and provided with a stopper

into which a Beckmann thermometer, a container for the powdered ammine and a rotary stirrer were fitted. The container consisted of a narrow glass tube extending through a hole in the rubber stopper with an enlarged cylindrical lower portion whose volume was about 10 cc. This enlarged portion was open at the bottom, but its lower rim was ground flat so that a thin microscope cover-glass could be tightly cemented to it. A glass rod extended through the narrow tube from above the stopper and worked tightly in a rubber packing placed at the entrance to the enlarged portion. By pushing this rod downward, the cover-glass could be broken and the cobalt ammine in the container projected into the surrounding water, or sodium sulfide solution. The method of procedure was simply to stir the measured volume of liquid in the Dewar flask until a constant rate of change was shown by the Beckmann thermometer; the weighed quantity of ammine in the container was then discharged into the liquid and the stirring and thermometer readings continued until a constant rate of temperature change had again been established. These readings were plotted, and by an inspection of the curves the temperature change produced by the solution or decompostion of the cobalt ammine could be ascertained.

Preliminary experiments showed that these temperature changes, particularly those produced by the decompositions, were still very small, even when several grams of the cobalt ammines was used. This could have been partially remedied by decreasing the quantity of water, or of sodium sulfide solution, and by using a smaller Dewar flask, but this would have increased the relative uncertainty in the heat capacity of the Dewar flask. The only alternative was to reduce the experimental errors as far as possible.

The uniformity in bore and the value of a degree of the Beckmann thermometer were first investigated. Fortunately, over the range used in these experiments, the bore was quite regular, no correction greater than $0.002°$ having to be applied. By comparison at two different temperatures with a standard thermometer reading to $0.001°$, which in turn had been compared with the primary standards at the Bureau of Standards in Washington, one degree of the Beckmann scale was found to be equivalent to $1.014°$ at $25°$ on the hydrogen scale. This correction has been applied in all the following measurements.

With such small heat changes to be measured the frictional heat produced by the stirring might evidently amount to a considerable fraction of the total heat change. This would not necessarily involve any error, for, by continuing the stirring after the reaction had ended, as outlined above, a correction could be applied to each experiment which would include both this effect and any heat change due to radiation or conduction. An error from this cause would creep in only if the rate of stirring were not sufficiently constant to prevent any perceptible variation in the rate at which the frictional heat was supplied. Experiments were therefore undertaken to determine the magnitude of the frictional heating effect and its variation with the rate of stirring.

In these experiments, the temperatures of the liquid in the flask and of the air in the room were brought to nearly the temperature of the thermostat $(25°)$ and kept at that temperature for some time with intermittent stirring to allow a complete equalization of the temperature throughout the flask, stirrer, container and thermometer. The small stirrer was then rotated at a constant speed and readings of the Beckmann thermometer were taken at regular intervals. The speed was determined by counting the number of revolutions per minute of the belt driving the stirrer, one revolution of the belt being equivalent to about 10 revolutions of the stirrer. With 900 cc. of a sodium sulfide solution in the Dewar flask, very small heating effects were produced, but when this solution was replaced by a similar one of the same strength which had reacted with 8 g. of acido-pentammine chloride, much larger heating effects were obtained. This, however, is not surprising in view of the fine state of subdivision of the precipitate and its rather flocculent nature, for these factors doubtless increase the viscosity very consider-

ably.   Indeed it is possible that the increased heating effect might be used as a means of measuring viscosity.   With speeds of 50 and 104 revolutions of the belt per minute heating effects of 0.0015° and 0.0060° per minute, respectively, were obtained.   Taking readings every two minutes and stirring but 10 seconds before each reading, heating effects of but 0.0003° and 0.0008°, respectively, per minute were found.   As 10 seconds' intermittent stirring at the lower rate proved sufficient to give uniform temperature readings on the thermometer, this mode of stirring was adopted in all the following measurements.   Although the frictional heat was evidently greatly reduced by this procedure its total effect over the 30 minute interval of an experiment was still relatively large and the effect of variation in speed of stirring upon it therefore required consideration.   To determine this effect, the rates of heating in the above experiments and in other similar experiments with sodium sulfide suspensions with continuous stirring, were plotted against the rates of stirring.   Nearly linear curves were obtained over the short intervals used, whose slope corresponded to an acceleration in the rate of heating of 0.00003° per minute for an acceleration in the rate of stirring of one revolution of the belt per minute; or, at a speed of 55 revolutions per minute, to about a 1% increase in the heating effect.   Since a constant rate was always attained in the following experiments within 30 minutes after the introduction of the ammine, and the heating effect in the cobalt sulfide suspensions with intermittent stirring was 0.0003° per minute, an uncertainty of 10 revolutions per minute in the rate of stirring would result in an uncertainty in temperature over this interval of less than 0.001°.   This constancy was easily attained even with intermittent stirring.

Similar experiments were made to test the effect of variations in the temperature of the surroundings on the temperature of the liquid in the Dewar flask.   With liquid, thermostat, and air, all at very nearly 25° a constant rate of stirring was maintained for some time and regular readings of the thermometer were taken.   A constant temperature change of 0.0010° per minute was obtained under these conditions.   After this constant rate had been maintained for some time the temperature of the liquid in the flask was raised 1° and another series of readings made.   The temperature rise was found to be 0.0009° per minute.   Finally, the original temperature was re-established in the flask but the temperature of the surrounding air was lowered 5°.   The consequence was a lesser rate of temperature increase, namely 0.0003° per minute.   These results show that a temperature difference of 1° between the liquid in the flask and the thermostat produces a cooling effect of 0.0001° per minute, while a similar difference in temperature between the liquid in the flask and the air produces a cooling effect of 0.00014° per minute.   These effects are nearly negligible, but we were careful in the following experiments to keep the temperature of the air constant to a few tenths of a degree; the thermostat was kept, of course, even more constant than this.   Conduction through the neck of the flask by way of the walls, the stopper, the thermometer, etc., is evidently of somewhat more consequence than radiation and conduction across the vacuum jacket.

Heat Capacity Determinations.

The combined heat capacity of the Dewar flask, the contained liquid, the stirrer, thermometer, etc., was determined by the electrical method.   The closed container for the ammine was made into a heater for this purpose by winding non-inductively around its enlarged portion a single layer of fine, enameled, copper wire.   By closing the lower end of the container and then dipping the whole in boiling asphalt, a thin, but very tough covering was secured for the coil.   Indeed, this combination of asphalt and enamel was the only material we discovered which would withstand the joint action of the caustic sodium sulfide solution and the strong heating current.   No change in the re-

sistance of the coil could be detected after immersion in the sodium sulfide solution for several hours with the simultaneous passage of a current of several tenths of an ampere.

We did not attempt to maintain an exactly constant current, nor to measure it precisely; instead we kept the current very nearly constant by using a storage battery, a Weston milliammeter and a slide-wire resistance, closed the circuit for a measured interval of time and determined the total quantity of electricity which had passed by means of a silver coulometer.

By this method the heat evolved was obtained from the product of the resistance of the coil and the square of the weight of silver divided by the time; all quantities which could be easily and accurately determined. Since, however, we could secure only copper wire with the requisite enamel coating and copper has the high temperature coefficient of resistance characteristic of pure metals, we were obliged to measure the resistance of the coil during the passage of the heating current under the conditions of the experiment.

For this purpose an additional, open, coil of manganin wire was introduced into the circuit next to the heating coil and immersed in a stirred oil-bath. Two relatively large manganin resistances were then shunted in series around these two coils and the middle points of these two branched circuits were connected through a galvanometer. The large resistance in the ratio arms of this Wheatsone bridge arrangement obviated possible errors due to the heating effect of the current.

It was found that the resistance of the heating coil did increase perceptibly when the current was passed. A curve was constructed connecting current strength and percentage change in resistance and from it such slight corrections as were necessary were applied for the different current strengths employed in the heat-capacity determinations. Moreover, the resistance in each case was corrected to the mean temperature of the determination.

The silver coulometer consisted of a platinum dish cathode and a silver strip anode, so that the current density was kept sufficiently low.[3] The silver nitrate solution contained 40 g. of salt per 100 cc., and a small porous porcelain cup served as an anode diaphragm.

The combined corrections for stirring, radiation and conduction in these heat capacity measurements, as in the subsequent calorimetric experiments, were determined in each case by taking temperature measurements over a long period before and after the heating current was applied. When these readings were plotted, the resulting curves were very smooth and permitted an accurate extrapolation over the heating interval.

Duplicate heat-capacity determinations were made, using as a liquid in the Dewar flask (1) water, (2) a 0.26 M solution of sodium sulfide, (3) water containing 8 g. of acido-pentammine chloride in solution and suspension and (4) the same sodium sulfide solution after it had reacted with 8 g. of the same ammine. These were the identical liquids employed in the subsequent calorimetric experiments, and in all the experiments the same volume of liquid (898 cc.) was taken, so that from these measurements, the heat capacity in every calorimetric experiment could be obtained. From the heat capacities of the calorimeter when the ammine was present the heat capacities of the calorimeter containing only the pure liquids can be calculated by substracting the heat capacity of the ammine. The latter quantity can be calculated with sufficient accuracy for our purpose from the atomic heats of the elements concerned, and amounts to three calories for 8 g.

The results of the heat capacity measurements are given in Table I. The average deviation from the mean of the four values for water and the four values for the sodium

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[3] Kohlrausch, "Praktische Physik," B. G. Teubner, Leipzig and Berlin, 8th ed., p. 431.

TABLE I.

HEAT CAPACITY OF CALORIMETER.

No.	Liquid.	Time. Seconds.	Resistance. Ohms.	Temperature rise. ° C.	Weight of silver. G.	Total heat cap. Cals.	Heat cap. with H₂O. Cals.	Heat cap. with Na₂S. Solution. Cals.
1	H₂O	1200	55.805	0.739	0.2794	951.9	951.9	...
2		1200	55.692	0.745	0.2804	949.1	949.1	...
3	H₂O+Am	1200	55.692	0.731	0.2787	955.5	952.5	...
4		1200	55.860	0.743	0.2806	955.8	952.8	...
5	H₂O+Na₂S	2160	56.950	0.783	0.3751	918.0	...	918.0
6		1440	51.001	0.890	0.3447	916.2	...	916.2
7	H₂O+Na₂S+Am	1260	55.346	0.810	0.2956	918.1	...	915.1
8		1140	55.346	0.766	0.2738	920.6	...	917.6
						Mean	951.6	916.7

sulfide solution is less than 0.2%, which is no greater than the probable error of the experimental data. The mean heat capacities given in this table have been used in all the subsequent calorimetric experiments after applying a small correction for the calculated heat capacities of the added ammines.

Preparation of the Ammines.

The ammines were prepared according to the improved methods of Jörgensen,[2] an imported sample of chloro-pentammine cobalt chloride, whose purity had been established by many analyses in this laboratory, serving as the starting material. Repeated analyses of salts prepared by these methods have shown them to have a high degree of purity.

Heats of Solution.

The general method of procedure has already been outlined in the section entitled Apparatus and Method. Before the actual determination was begun the stirrer was operated continuously for about an hour to secure a thorough equalization of temperature throughout the apparatus. The stirring was then cut down to 10 seconds before every 2-minute reading for a period of about 30 minutes, after which the ammine was ejected from its container. Continuous stirring was then maintained for a period of 1 minute, and this generally sufficed to bring the greater part of the finely-ground ammine into solution. The stirring was then reduced to its previous rate and continued until a perfectly uniform rate of temperature change had been established. This usually required but 3 or 4, and never more than 10 minutes. The effect of the regular, intermittent stirring was of course corrected for by extrapolation of the resulting curves; a special correction of 0.001° was applied for the one minute of continuous stirring, on the basis of the above preliminary experiments on the effect of stirring. A sample of the curves secured is shown in Fig. 1; the results as a whole are collected in Table II.
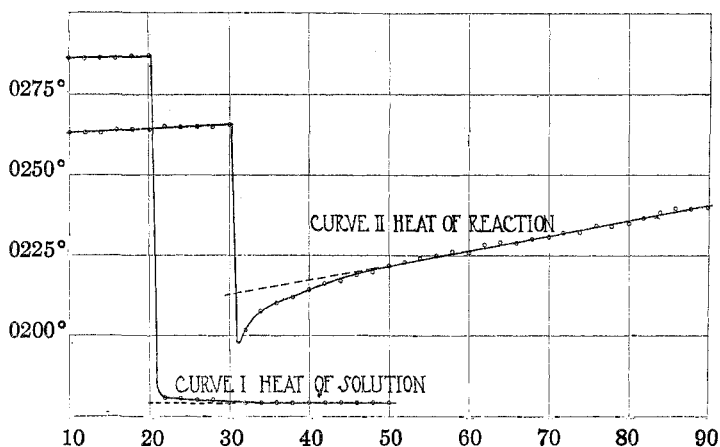
TABLE II.

HEATS OF SOLUTION OF PENTAMMINE COBALT SALTS IN WATER AT 25°.

Pentammine. Salt.	Weight taken. G.	Molar concentration.	Temperature change. Observed. °C.	Temperature change. Corrected. °C.	Heat cap. cals.	Molar ht. of sol. obs. cals.	Molar ht. of sol. av. cals.
Chloro chloride........	2	0.00890	-0.105_5	-0.106_7	950.8	12700	
	2	0.00890	-0.101_0	-0.101_9	950.8	12140	-12420
Aquo chloride..........	4	0.01661	-0.099_3	-0.099_7	951.6	6367	
	8	0.03322	-0.203_3	-0.205_1	953.1	6560	-6460
Bromo bromide........	1	0.00290	-0.035_2	-0.034_7	950.3	12660	
	1	0.00290	-0.035_2	-0.034_7	950.3	12660	-12660
Aquo bromide.........	3	0.00832	-0.073_0	-0.073_0	950.9	9305	
	3	0.00832	-0.071_5	-0.071_5	950.9	9114	-9220
Nitrato nitrate.........	2	0.00738	-0.102_6	-0.103_0	950.9	14800	
	2	0.00738	-0.104_0	-0.104_4	950.9	15000	-14900
Aquo nitrate...........	5	0.01741	-0.250_0	-0.252_5	952.3	15400	
	4	0.01393	-0.200_0	-0.201_8	951.8	15370	-15380

Average deviation of mean ± 200 cals.

Heats of Solution Calculated from Solubility Measurements.

Heats of solution are readily calculated from solubility measurements made at different temperatures by use of Van't Hoff's equation. There are difficulties, however, in applying this method to the cobalt ammines. In the first place, time is required for a precise attainment of saturation, and within this period there will be, even at 0°, a conversion of the acido (purpureo) salt into the corresponding aquo(roseo) salt, and vice-versa, which will vitiate the solubility measurements. In the second place, to apply Van't Hoff's equation requires a knowledge which we do not possess of the percentage dissociation of the dissolved salt. This latter difficulty can only be avoided in the case of the slightly soluble ammines whose percentage dissociation is high, and hence can be estimated with

sufficient accuracy from the known percentage dissociation of other salts of the same type.

In view of these difficulties we have only applied this method to chloro-pentammine cobalt chloride, which is not only but slightly soluble, but also changes more slowly than the corresponding bromo or nitrato am-mines into the aquo salt. The solubility measurements on this salt were made at three temperatures, 0°, 30°, and 50°, saturation being reached from opposite sides in duplicate experiments. The salt was ground to moderate fineness before use and the suspension was rapidly stirred in a thermostat, but the results at the highest temperature were very dis-cordant, due presumably to partial conversion into aquo salt and to incomplete saturation, and were therefore discarded. At given intervals some of the clear liquid was drawn off through a filter-pipet, its specific gravity was determined and a weighed portion was evaporated to dryness. The ammine was then converted into cobalt sulfate according to Gibbs' procedure[4] and weighed. The results are collected in Table III. It will

TABLE III.

SOLUBILITY OF CHLORO-PENTAMMINE COBALT CHLORIDE IN WATER.

No.	Temp. °C.	Time. Hours.	Density. $t/4°$.	Solubility, g. per 100 g. of H_2O. From undersat.	From supersat.	Mean.	Av.	Solubility g. per liter.
1	0	0.5		0.2137	0.2300	0.2219		
2	0	1		0.2130	0.2328	0.2229		
3	0	1.5	1.00096	0.2237	0.2220	0.2228	0.2228	2.244
4	0	1.5		0.2274[a]	0.2474[a]	....		
5	0	3.0		0.2222	0.2229	0.2226		
6	0	3.0		0.2215	0.2242	0.2229		
7	29.7	0.5	0.9994	0.6098	0.6070	0.6085	0.6088	6.047
8	29.7	1.0		0.6091	0.6090	0.6090		
9	50	1.0	0.9945	1.056	1.082	1.069	1.025[b]	10.01
10	50	2.0		1.110	1.127	1.113		

[a] Not included in taking the mean.

[b] Extrapolated to zero time in view of the evident slight formation of roseo salt.

be seen that the solubilities are concordant and independent of the time, indicating a precise attainment of saturation and a negligible conversion into aquo salt.

The heat of solution was calculated from the data given in Table IV using the equation of Van't Hoff[5] in its differential form where

$$L = RT^2i \left(\frac{d \log_e iS}{dT} \right)$$

in which L represents the molecular heat of solution, R the gas constant,

[4] Gibbs, "Researches on the Ammonia Cobalt Bases," Smithsonian Contributions to Knowledge, Washington, 1856.

[5] Van't Hoff, Z. physik. Chem., 17, 147 and 546 (1895). See also Noyes and Sam-met, Z. physik. Chem., 43, 513 (1903).

i the Van't Hoff coefficient and S the solubility in grams per liter, i is the only term for which no immediate data are available; approximate values for it and for di/dt were obtained on the very generally justified assumption that this salt would resemble, in this respect, the similarly constituted salt, barium chloride; i and $di/i\ dt$ were calculated for barium chloride from the conductivity measurements of Kohlrausch and Gruneisen,[6] and Deguisne,[7] and were found to be 2.610 and -0.000038 respectively at 25°. To evaluate d log S/dt, the logarithm of the observed values of S were plotted against the temperature and were found to lie on a slightly curved line. The equation for the symmetrical parabola passing most nearly through these points was then computed; it was log $S = 0.3517 + 0.01657\ t - 0.00007054\ t^2$. This equation, when differentiated, gave d log S/dt at 25° $= 0.01304$. Substituting these values, and $R = 1.985$ cal. per degree and $T = 298$ in the above equation the result $L = 13440$ cal. was obtained, which agrees as well as could be expected with the experimentally determined value of 12400 cal. This is especially true when one recalls that the calculated value is the *integral* heat of solution,[8] while that experimentally determined is very nearly the *initial* heat of solution, and these will differ somewhat in value except in very dilute solution.

Heats of Reaction.

The procedure in determining the heats of reaction was practically identical with that followed in the case of the heats of solution, except that a 0.26 M solution of sodium sulfide was used in place of the water. The stirring was made continuous for one minute after the ejection of the ammine and a correction of 0.001° was applied for the extra heating effect. The temperature rise did not usually become uniform until after about 20 minutes; probably the particles of the ammine became coated with a layer of the sulfide. Temperature readings were then continued for some 40 minutes to obtain with certainty the temperature rise per minute. The readings of a typical experiment are plotted in Curve II of Fig. 1. The results of all measurements are collected in Table IV. It will be seen from this table that the average discrepancy between the heat capacities found in duplicate experiments corresponds to an average discrepancy in the temperature change of about 0.001°. It will also be seen that in some cases the reaction is decidedly exothermic, in others endothermic.

[6] Gruneisen, *Sitzber. Ber. Akad.*, 1904, 1215. Landolt-Börnstein-Roth, "Tabellen," 1912, p. 1103.

[7] Deguisne, *Dissertation*, Strassburg, 1895. Landolt-Börnstein-Roth, "Tabellen," 1912, p. 1116.

[8] Roozeboom, *Rec. trav. chim.*, 5, 335–392 (1886); van Deventer and van der Stadt, *Z. physik. Chem.*, 9, 43 (1892).

TABLE IV.

HEATS OF REACTION OF SOLID PENTAMMINE COBALT SALTS WITH SODIUM SULFIDE
SOLUTION AT 25°.

Pentammine. Salt.	Weight. G.	Temperature change. Obs. °C.	Corrected °C.	Heat capacity. Cals.	Heat of reaction. Obs. cals.	Heat of reaction Av. cals.
Chloro chloride	7.5475	$+0.088_0$	$+0.089_2$	919.3	2659	2650
	7.5098	$\pm 0.087_0$	$+0.085_8$		2639	
Aquo chloride	8.0000	$+0.207_0$	$+0.207_9$	919.4	6415	6476
		$+0.210_0$	$+0.211_9$		6536	
Bromo bromide		$+0.007_0$	$+0.005_1$	917.1	613	635
	3.0000	$+0.007_5$	$+0.005_6$		657	
Aquo bromide		$+0.021_3$	$+0.019_3$	917.2	2373	2384
		$+0.021_4$	$+0.019_5$		2396	
Nitrato nitrate	2.0000	-0.016_5	-0.018_3	917.4	-2608	-2560
	6.0000	-0.051_6	-0.054_4	919.0	-2518	
Aquo nitrate	4.0000	-0.045_6	-0.048_3	918.0	-3548	-3526
		-0.045_0	-0.047_7	918.0	-3504	

Average deviation of mean ± 30 cal.

By subtracting the heats of solution from the heats of reaction of the
solid salts the heats of reaction in solution may be obtained. By sub-
tracting the heats of reaction of the aquo from the corresponding acido
salts in solution the heats of transformation are finally obtained. The
results of these calculations are collected in Table V.

TABLE V.

HEATS OF REACTION AND TRANSFORMATION OF PENTAMMINE COBALT SALTS IN AQUEOUS
SOLUTION AT 25°.

Ammine.	Heat of reaction. Cals.	Heat of transformation. Cals.
Chloro chloride......................	15070	2140
Aquo chloride.......................	12930	
Bromo bromide......................	13290	1690
Aquo bromide.......................	11600	
Nitrato nitrate......................	12340	480
Aquo nitrate........................	11860	

Discussion of Results.

The heats of transformation are in reverse order as compared with the
velocities of transformation;[1] that is, of the ammines the chloro changes
the least rapidly, the bromo next, and the nitrato the most rapidly into
the corresponding aquo compound. They follow, in all probability, the
same reverse order as compared to the free energy of transformation, al-
though this latter quantity has only been measured in the case of the
chloride and bromide. This is of interest, because not only are the
magnitude and sign of the heat of transformation the same as has been
found for the heats of ionization of salts in water but there, too, the
more highly dissociated have, in general, the lesser heats of ionization. All

of these considerations seem then to emphasize the similarity pointed out before between the transformation of the acido (purpureo)-pentammine salts in aqueous solution into the aquo(roseo)-pentammine salts and the electrolytic dissociation of the strong electrolytes in water.

Summary.

1. A method of calorimetry has been developed in which only observations on a silver coulometer, and of time and electrical resistance are required.

2. It has been shown that the same sulfide of cobalt (Co_2S_3) is produced by the action of sodium sulfide on chloro- and aquo-pentammine cobalt chloride in aqueous solution.

3. The solubility of chloro-pentammine cobaltic chloride has been measured at several temperatures, and its heat of solution has been computed from these data, and found to be in fair agreement with the directly measured values.

4. The heats of solution in water of a number of acido- and aquo-pentammine cobaltic salts, and their heats of reaction with aqueous solutions of sodium sulfide have been measured. From these data the heats of transformation of the solid acido to the corresponding solid aquo ammines have been calculated.

5. The heats of transformation have been found to be antibat to the velocities of transformation, but probably symbat to the free energies of transformation, a reaction similar to that shown by the ionization of salts in water.

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NOTE.

An Interesting Colloid Gel.[1]—The structure of gels has been a question which has given rise to numerous investigations and we are still far from unanimity of opinion. Probably one of the factors which contributes to the difficulties of the problem is the complexity of the disperse material. Gelatin, for example, has been used in many investigations, but when we realize how inadequate our knowledge is regarding the chemical configuration of the gelatin molecule, and how easily proteins may be altered by physical or chemical factors, it is not surprising that the experimental results have been found to differ widely when different samples of gelatin are used. The same objections apply to agar-agar as apply to gelatin.

Aside from the complex organic substances, such as proteins, gums,

[1] Published with the approval of the Director as Paper No. 263, Journal Series, Minnesota Agricultural Experiment Station.