367. *Heats of Formation and of Solution of Some Isomeric Cobaltammines.*

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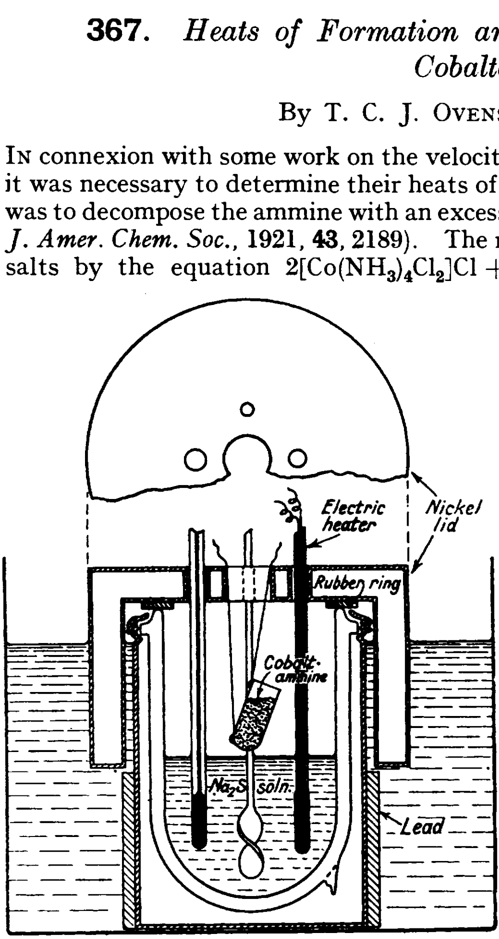
IN connexion with some work on the velocity of transformation of isomeric cobaltammines, it was necessary to determine their heats of formation in solution, and the method adopted was to decompose the ammine with an excess of M-sodium sulphide (cf. Lamb and Simmons, *J. Amer. Chem. Soc.*, 1921, **43**, 2189). The reaction can be represented for the tetrammine salts by the equation $2[Co(NH_3)_4Cl_2]Cl + 3Na_2S = Co_2S_3 + 8NH_3 + 6NaCl + 2Q$ cals. If, now, the heats of formation in solution of sodium sulphide and chloride and ammonia (or ethylenediamine) and the heat of formation of solid cobaltic sulphide are known, then the required heat of formation can be calculated from Q. The necessary values were obtained from "International Critical Tables," that for solid cobaltic sulphide being a theoretical one, however, as there is no simple method for its direct determination.



EXPERIMENTAL.

The apparatus used is shown in the diagram. It consisted of a 1-litre Dewar flask almost completely submerged in a small tank of water; the rotary stirrer was driven by a motor at a constant speed, and the thermometer was a standard instrument capable of being read to 0·001°. The electrical heater was constructed of no. 38 gauge Eureka wire, possessing a negligible temperature–resistance coefficient. Some difficulty was encountered in coating this coil. Bakelite was first tried, but it would not withstand the action of sodium sulphide solution. The most satisfactory method was to grind some asphalt in a little benzene, allow the solution to evaporate until it became syrupy, paint the syrup on the coil, and allow it to dry in the air. This gave a polished coating which would keep in good condition for a few weeks. The same volume of solution (398 ± 0·4 c.c.) was used in each experiment.

The heat capacity of the Dewar flask and its contents was found by passing a steady current through the heating coil for a known time. The constancy of the current was assured by the use of large-capacity accumulators, and was measured by means of a silver coulometer. The resistance of the heater was determined separately by the bridge method, and checked between each experiment in which it was used. The combined effects of stirring, radiation, and conduction were allowed for by taking temperature measurements over long periods before and after the heating current was applied, the true rise in temperature being determined graphically. The actual values obtained were : (*a*) with *M*-sodium sulphide in the calorimeter, 431·0, 429·7, 432·9, mean 431·2 cals.; (*b*) with water in the calorimeter, 435·7, 437·0, 436·8, mean 436·5 cals. In the actual measurements the heat capacity of the cobaltammine had to be added to the above values. This was calculated with sufficient accuracy from the atomic heats of the elements concerned, and was found to be 0·31w for the tetrammine and 0·33w for the bisethylenediamine isomerides, w being the weight of ammine used.

Heats of Reaction.—The method of introduction of the salt is evident from the diagram, trouble from splashing being obviated in this way. The small container was weighed before and after being tipped. The stirring, which was commenced about one hour before addition of the salt, was fairly vigorous. The initial temperature inside the calorimeter was arranged to be about 2° higher than that of the water in the tank. The temperature readings prior to the reaction fell slowly, the heating effect of the stirrer not being enough to counteract the cooling due to conduction and radiation. After addition of the cobaltammine, the stirring was continued at the same rate, but its heating effect was considerably increased owing to the formation of the cobaltic sulphide precipitate. The readings at the end of the experiment, however, rose quite gradually, and no difficulty was experienced in determining the true temperature change. Most of the reaction took place immediately on dropping the salt into the liquid, but generally about 10 minutes elapsed before readings became uniform, probably owing to small particles of salt becoming covered with a layer of sulphide. The composition of the latter was determined each time by analysis to ensure that it was Co_2S_3.

The results are summarised in the following table. The agreement for the tetrammine isomerides was good, but for the bisethylenediamine derivatives the maximum deviation was as much as 3·8%.

Salt.	Wt. (g.).	Temp. rise.	Heat capacity, cals.	Heat of reaction, cals.	Mean, cals.
trans-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	2·1122	0·340°	431·9	16,270	16,300
	2·1983	0·356	431·9	16,330	
cis-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	0·9961	0·167	431·5	16,890	16,930
	1·4009	0·236	431·6	16,970	
trans-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$	1·3820	0·154	431·7	13,730	14,060
	2·0941	0·241	431·9	14,180	
	0·9906	0·112	431·5	13,930	
	1·6098	0·188	431·7	14,390	
cis-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$	1·6994	0·186	431·8	13,490	13,150
	1·0925	0·121	431·6	13,650	
	1·4831	0·153	431·7	12,710	
	1·4869	0·154	431·7	12,760	

These values lead to the following heats of formation in the solid state :

Salt.	Heat of formation (cals.).	Salt.	Heat of formation (cals.).
trans-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	214,800	*trans*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$	171,920
cis- ,,	214,170	*cis*- ,,	172,830

Owing to the limited accuracy of the values for the other salts involved in the calculations, the above values are probably correct to only three significant figures; the differences between the pairs of isomerides, however, are more accurate than this.

Heats of Solution.—The same apparatus was used for the determination of the heats of solution, water being substituted for the sodium sulphide solution. A difficulty is caused by a slow reaction with water to give aquo-salts. With the bisethylenediamine salts, this reaction is comparatively small at 10°, and no appreciable error is introduced by working at this temperature. The tetrammines react more readily, however, but the determinations for the *cis*-isomeride were successfully carried out at 3° ; owing to the slight solubility of the *trans*-form at this temperature, it was necessary to work at 8°. No appreciable error is introduced by regarding the heats of solution at 20° as the same as at the temperature actually used. The results are summarised below.

Salt.	Heat of formation, cals.	Heat of solution, cals.	Heat of formation in solution, cals.
trans-$[Co(NH_3)_4Cl_2]Cl$	214,800	−8290	206,510
cis- ,,	214,170	−9510	204,660
trans-$[Co\ en_2Cl_2]Cl$	171,920	−5340	166,580
cis- ,,	172,830	−8010	164,820

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