

XCI.—*The Constitution of Ammonium Amalgam.*

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THE study of the so-called ammonium amalgam has formed the subject of numerous researches, which have resulted in throwing a considerable amount of light on its properties, but have led to no very satisfactory conclusions as to its constitution. Recently Moissan (*Compt. rend.*, 1901, 133, 803) has published an elaborate memoir on this subject in which he describes a convenient method of preparing the amalgam, gives an account of its chemical and physical properties, and in discussing the latter leaves it an open question as to whether it is to be considered to be a solution of "ammonium" in mercury or an emulsion of ammonia, hydrogen, and mercury. With a view to the solution of this problem we decided to determine the freezing points of a series of preparations of the amalgam of different concentrations. If the amalgam were a true solution, that is to say, a homogeneous mixture of ammonium and mercury, its freezing point should decrease linearly with the concentration of the ammonium present in it; if the latter explanation held good, either the freezing point would be identical with that of pure mercury, or a paste of crystals might be formed at some higher temperature.

The amalgam was prepared by Moissan's method (*loc. cit.*). Sodium amalgam (400—600 grams), containing a quantity of sodium equivalent to the concentration of the ammonium amalgam required for the experiment, was cooled in a flask with a long and narrow neck to a temperature just above its freezing point. Anhydrous ammonia was then condensed in the flask, and in this liquid excess of ammonium iodide was dissolved. The mixture was shaken from time to time, the temperature being kept constant by adding small quantities of liquid air to the alcohol in which the flask was cooled. After about an hour, the ammonia was allowed to evaporate, and the liquid amalgam was then filtered several times through an ordinary

folded filter paper with a hole pierced in the bottom of it. It was finally transferred to the experimental tube, particular care being taken to keep the temperature as near to the freezing point as possible during the manipulations to which it was subjected.

The freezing point of mercury, and afterwards of the amalgam, was determined by means of an arrangement similar to that commonly employed in molecular weight determinations. The amalgam was contained in a cylindrical tube, 30 cm. long and 3.5 cm. in diameter, rounded at the lower end. It was surrounded for the greater part of its length by an outer tube, the two being kept apart by rings of flannel. The temperature was measured by means of a Callendar resistance thermometer. The resistance, galvanometer, &c., were the same as had already been employed by one of us in the comparison of the platinum and hydrogen scales of temperature (*Proc. Roy. Soc.*, 1905, 74, 528). The thermometer consisted of a coil of silk-covered platinum wire, soldered at its ends to copper leads. The coil fitted fairly tightly into the bottom of a glass tube, 8 mm. in diameter, which also surrounded the main and "compensating" leads. Its resistance at the ice-point was 17.52 ohms; the coefficient of change of resistance with temperature was 0.0036647, a value which indicates that the metal was not pure platinum. However, as the freezing point of mercury was found to be -39.40° on the scale of this thermometer, it appears that over the range of our experiments the observed temperatures are so nearly coincident with temperatures on the Centigrade scale as to make the application of a correction unnecessary.

In conducting an experiment, the alcohol-bath surrounding the experimental tube was maintained at a temperature about 5 or 10 degrees below the freezing point of the amalgam. There was not the least difficulty in determining the freezing point, though when a very small trace of free ammonia was present with the amalgam the latter appeared to become slightly pasty at its freezing point. This difficulty was overcome by carefully purifying the amalgam.

After determining the freezing point, the thermometer and stirrer were removed from the tube and a rubber stopper with two holes was fitted to it. Through the holes passed tubes, so that air could be drawn through the experimental tube and afterwards through an absorption apparatus containing a normal solution of hydrochloric acid. After some hours, the tube was warmed to accelerate the evolution of the ammonia, and finally the mercury was itself gently warmed with the acid solution; the slight evolution of gas showed that even the action of heat only slowly decomposed very dilute solutions of ammonium in mercury. The quantity of ammonia evolved was determined by titration, and the solution was always examined for the presence of sodium,

which was only found in one experiment which we have not recorded. At the end of each experiment, the mercury was dried and weighed.

The following are the results of our experiments :

Freezing Point of Mercury on Platinum Scale, -39.40° .

Grams of NH_4 in 100 grams of mercury (α).	Freezing point of amalgam.	$D = \frac{\Delta}{\alpha} \times 18.$
0.084	-41.605°	470
0.507	-45.61	220
0.415	-44.82	230
0.079	-40.81	320 *
0.027	-40.01	410
0.0094	-39.62	420
0.0117	-39.67	420

* Probably inaccurate.

It appears that with low concentrations the value of " D " is between 410 and 470, and that it first increases and then decreases rapidly as the concentration increases. Tammann (*Zeit. physikal. Chem.*, 1889, **3**, 440) obtained similar results in the case of the amalgams of certain common metals. For sodium he obtained as a mean value of " D " the number 420, corresponding to concentrations between 0.022 and 0.112 gram of sodium in 100 grams of mercury. His results for potassium amalgam are stated below :

α .	D .
0.018	600
0.030	560
0.091	320
0.112	360
0.137	280

The resemblance in the behaviour of sodium amalgam and ammonium amalgam is very marked, and leaves no room for doubt that the latter is really a solution of ammonium in mercury. This view is supported by the fact that the amalgam continues to evolve ammonia and hydrogen after it has been allowed to stand for many hours at the temperature of the experiment. Further, if the temperature of the amalgam is allowed to rise until the volume begins to increase, and the amalgam is then cooled, it appears to return to its original state ; hence it is not impossible that "ammonium" can exist transitorily in the free state.

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