

MAGNETIC PROPERTIES OF COPPER AMALGAMS

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THE magnetic behaviour of copper in dilute copper amalgams has recently elicited some controversy. One of us¹ observed that dilute copper amalgams of low copper content are merely mechanical mixtures of the two metals and the magnetic susceptibility values vary from that of pure copper to that of pure mercury. Bates and Tai² observed that of all the metals which are diamagnetic in the solid state, only copper retained its diamagnetic character in amalgams of dilute concentrations, whereas elements like bismuth became paramagnetic.

Venkataramaiah³ has, however, recently reported that even copper became paramagnetic in dilute amalgams and as this claim requires further examination, the difference in the magnetic behaviour of copper in dilute amalgams observed by different workers may be due to the variations in the conditions under which the experiments might have been conducted. Amalgams were, therefore, prepared under definite conditions and the magnetic susceptibility of the samples prepared were determined on a Gouy's balance and were further checked on the Bhatnagar-Mathur Magnetic Interference Balance.⁴

Experimental

For the preparation of amalgams, pure mercury prepared by the Bijlmann⁵ method and finally distilled in a small pyrex retort was used throughout.

As the magnetic susceptibility value of mercury itself has been established correctly only recently, the value obtained by us has been compared by those obtained by other workers.

The magnetic susceptibility value of mercury observed by Honda and Owen, was different in different magnetic fields, so they applied a correction and obtained the magnetic susceptibility value of mercury as -0.184×10^{-6} . This value was taken to be correct until Vogt found that single crystal of mercury in liquid and in solid state has the magnetic susceptibility value

-0.168×10^{-6} . Since then the magnetic susceptibility value -0.168×10^{-6} for mercury has been confirmed by Bates and Tai and by Bhatnagar and Nevgi. From Table I it is clear that the value obtained by the

TABLE I

Authority	Magnetic Susceptibility $\times 10^6$
Authors	-0.165
Honda and Owen ⁶	-0.190
Owen ⁷	-0.184
Davis and Keeping ⁸	-0.189
Vogt ⁹	-0.168
Bates and Tai ²	-0.169
Bhatnagar and Nevgi ¹⁰ ..	-0.157

authors is in very good agreement with that obtained recently by other workers.

In order to prepare an amalgam by electrolysis, weighed amount of annular copper sulphate was dissolved in 20 c.c. of water in a pyrex test-tube of one inch diameter and a weighed amount of mercury was taken and made the cathode. The anode was a platinum wire which just dipped under the surface of the solution. In order to find the weight of copper that went in solution in mercury, another tube containing the same concentration of copper sulphate and having a platinum foil as a cathode and platinum wire as an anode was placed in series. The increase in weight of platinum foil after electrolysis gave the amount of copper that went in solution in mercury.

The current used was from lead storage batteries and was of the order of 10-20 milliamperes depending on the concentration of solution. The magnetic susceptibility values of the amalgams prepared by the above method are given in Table II.

TABLE II

Percentage of copper in amalgams	Magnetic Susceptibility $\times 10^6$	
	Observed	Calculated
0.5	-0.162	-0.165
1.0	-0.161	-0.164
2.0	-0.159	-0.163
3.0	-0.159	-0.162

The values given in column 3 are calculated on the mixture law, assuming the mass susceptibility value of copper to be -0.086×10^{-6} , as given in *International Critical Tables*. It is clear from the results that the observed value for magnetic susceptibility of amalgams is lower than the calculated one, indicating that the amalgams have become paramagnetic. It is argued, however, that the observed lowering of the susceptibility of amalgams may be due to the fact that magnetic susceptibility of copper actually formed during the process of electrolysis, may be different from that given in the *International Critical Tables* owing to the chances of oxidation under conditions of electrolysis.

To verify it the susceptibility value of copper, obtained by the electrolysis of annular copper sulphate, was determined and is given below in Table III, along with the values obtained by other workers.

TABLE III

Authority	Magnetic Susceptibility Value $\times 10^6$	
Honda and Shiminza	..	-0.084
Rao	..	-0.080
Inter. Crit. Tables	..	-0.083
Authors	..	-0.048

It is well known that copper at room temperature has the tendency to form oxides, which are paramagnetic. The low magnetic susceptibility value of copper may be due to the formation of such oxides, when copper sulphate solution is being electrolysed at ordinary temperature. So to avoid oxidation annalar copper sulphate was electrolysed in ice-cold solution. The susceptibility value of the samples of copper thus prepared was found to be -0.073×10^{-6} , a value higher than the previous ones, but still lower than the values observed by other workers.

Annalar copper sulphate contained 0.014 per cent. of iron, therefore, the lower value of copper observed may be due to its contamination with iron. Pure copper sulphate was, therefore, obtained by dissolving pure copper, prepared by the following method, in concentrated sulphuric acid.

Preparation of pure copper.—Rao's method of preparing copper co-agula by sparkling between the copper electrodes in a medium of inert liquid (propyl alcohol) was abandoned, because it was found that considerable amount of carbon was obtained along with copper in spite of all precautions.

Copper was, therefore, prepared by shaking a ten per cent. solution of annalar copper sulphate with extra pure granulated zinc metal. When copper had been completely displaced from the solution, *i.e.*, when the solution became colourless, the precipitate was washed with distilled water and refluxed with conc. hydrochloric acid and later on boiled, washed with dilute, pure hydrochloric acid (1:1) two or three times. It was kept under very dilute hydrochloric acid, so that if any oxide was formed, it was at once redissolved in it and in this manner, copper could be kept without oxidation for about a fortnight. The copper was washed free of hydrochloric acid and then washed with alcohol and subsequently with ether and was ultimately dried under vacuum at about 60° C. Its magnetic susceptibility value was found to be -0.085×10^{-6} which is in very good agreement with the value obtained by other workers.

This copper was dissolved in pure sulphuric acid and diluted with water to get pure copper sulphate solution, which was used as an electrolyte to prepare amalgams by electrolysis at low temperatures.

The percentage of copper present in the amalgams prepared from the pure copper sulphate was determined iodometrically and also by electro-deposition method. The results obtained by both the methods were in excellent agreement.

The magnetic susceptibility values of these amalgams are given in Table IV.

TABLE IV

Percentage of copper in amalgams	Magnetic Susceptibility $\times 10^6$	
	Observed	Calculated
0.49	-0.164	-0.165
0.99	-0.164	-0.164
1.25	-0.163	-0.163
2.00	-0.162	-0.163
3.00	-0.161	-0.161
4.00	-0.160	-0.160
5.00	-0.159	-0.160
7.5 (Hard)	-0.139	-0.159
10.00 (Hard)	-0.125	-0.157

Amalgams upto 5 per cent. concentration of copper took a few hours to be prepared and remained fluids, but those containing higher percentage of copper took two to three days to be prepared and these hardened during the course of electrolysis.

It is clear from the above table that as long as the amalgams could be obtained in the fluid state, *i.e.*, upto 5 per cent. of copper concentration their observed and the calculated susceptibility values agree very well, but the amalgams of higher concentrations which solidify give lower susceptibility values than the calculated ones. This lowering in the values may be due to the oxidation of copper to some paramagnetic compounds during the course of electrolysis for a long time or due to a change in crystal structure which imparts the hardened structure.

Therefore amalgams containing higher percentage of copper were alternatively prepared by grinding the components in right proportions under very dilute analytically pure sulphuric acid.

The magnetic susceptibility value of fresh and dry amalgams prepared by the above method are tabulated below and in column 3 are given the calculated values according to the mixture law.

TABLE V

Percentage of copper in gm. in amalgams	Magnetic Susceptibility $\times 10^6$	
	Observed	Calculated
10	- 0.156	- 0.157
20	- 0.147	- 0.148
30	- 0.140	- 0.140
34	- 0.138	- 0.138
40	- 0.131	- 0.132
50	- 0.125	- 0.125
60	- 0.116	- 0.117
70	- 0.109	- 0.110
80	- 0.099	- 0.100
90	- 0.091	- 0.091

From the results, it is clear that the observed magnetic susceptibility values of the freshly prepared amalgams are in very good accord with the calculated ones. It was, however, observed that amalgams hardened on keeping and their magnetic susceptibility value diminished very much.

The magnetic susceptibility values of some of these are given below in Table VI.

TABLE VI

Percentage of copper amalgams	Magnetic Susceptibility $\times 10^6$	
	After keeping for a week	Calculated
40	- 0.071	- 0.141
50	- 0.059	- 0.131
60	- 0.051	- 0.117

It may be contended that the lowering in magnetic susceptibility value of amalgams on keeping in air may be due to the oxidation of copper. Therefore, in order to avoid the oxidation of copper freshly prepared amalgams were either kept under ether or in a vacuum desiccator. In spite of this it was observed that the magnetic susceptibility value of these amalgams went on decreasing. These samples were analysed to find if any oxide was formed and it revealed that the hardened black and brittle sample of amalgam containing 34 per cent. copper, after keeping under ether, contained 33.03 per cent. of copper and the other after keeping in vacuum contained 33.98 per cent. of copper. The fall in the percentage of copper in the samples kept in air is probably due to the formation of some oxides. Therefore, the greater fall in susceptibility value of the samples kept in air seems to be due to the formation of copper oxide which is known to be paramagnetic. Fresh amalgams prepared by grinding method were therefore at once sealed under vacuum in pyrex tubes which had been previously heated upto about 500° C. to expel all occluded oxygen and other gases from the glass lest the occluded gases should affect the amalgams in any way. The viscosity and colour of such amalgams remained nearly the same for about two days but after that they became more viscous and finally solid and then their colour faded. Their magnetic susceptibilities were determined in terms of pull per gram on the Gouy's balance from day to day, till the deflection became constant. The susceptibility values determined from these observations are tabulated in Table VII along with the susceptibility value of freshly prepared amalgams. In column 4 are given the difference between the susceptibilities of fresh and aged amalgams.

TABLE VII

Percentage of copper in amalgam	Magnetic Susceptibility $\times 10^6$		Difference 10
	Fresh amalgam	Old amalgam	
5.0	-0.159	-0.093	0.066
10.0	-0.156	-0.087	0.069
20.0	-0.147	-0.070	0.077
30.0	-0.140	-0.055	0.085
34.0	-0.136	-0.047	0.089
40.0	-0.132	-0.051	0.081
50.0	-0.124	-0.048	0.076
60.0	-0.116	-0.046	0.070
70.0	-0.107	-0.041	0.066
80.0	-0.099	-0.035	0.064
90.0	-0.091	-0.029	0.062

Discussion of Results

From the results tabulated in Table IV it is clear that freshly prepared amalgams obey the mixture law and on hardening the magnetic susceptibility value falls ; the difference between the magnetic susceptibility values of the freshly prepared and hardened amalgams varies with the varying concentrations, being maximum in the case of amalgam containing 34 per cent. copper.

One of us (S. S. Bhatnagar) while working on very dilute copper amalgams prepared by electrolysis, found that the magnetic susceptibility values of amalgams vary linearly from that of mercury to that of copper. Bates and Tai² determined the magnetic susceptibility of series of amalgams of dilute concentrations of manganese, bismuth, chromium and copper and found that with the exception of copper, all the metals which are diamagnetic in solid state, became paragmanetic in dilute amalgams. The

paramagnetism of the metal in amalgams is attributed by them to the increase of free electrons in dilute amalgams. This view is further supported by the work of Skaupy,¹¹ who refers to the well-known fact that conductivities of such amalgams containing the metals like lead, zinc, cadmium, etc., are greater than those of pure mercury, whereas the conductivities of solid solutions or of mixed crystals are always less than that of solvent metal. He attributes this conductivity behaviour of amalgams to the increase in number of the free electrons. Venkataramaiah³ has also studied recently the magnetic properties of dilute amalgams of copper and has found that the observed magnetic susceptibility value of dilute copper amalgam is lower than the calculated ones. He has attributed this change to the increase in the number of free electrons in dilute amalgams of copper as in those of other metals.

These results of his are contrary to those observed by Bates and Tai and by the authors. He prepared the amalgams by the electrolysis of pure copper sulphate and assumed the magnetic susceptibility of copper to be -0.083×10^{-6} from the International Critical Tables. It has been shown by us that this procedure is not justified as in the process of prolonged electrolysis in presence of air and due to heat generated, copper gets oxidised and there is no justification in amalgams so prepared to employ the value for copper given in the International Critical Tables.

Fresh support in favour of our work comes from the work of Terry and Wright¹² who have investigated the crystal structure of concentrated copper amalgams by X-ray study and have found that freshly prepared amalgams of copper are mechanical mixtures but that they change the crystal structure on hardening. They have also found that there is a special change in the crystal structure in amalgams ranging from 30-35 per cent. of copper, indicating the formation of a compound at these concentrations.

From the magnetic data given in Tables IV and V, it is evident that freshly prepared amalgams are just mechanical mixtures and that on hardening, they form compounds and that in case of 34 per cent. of copper amalgam, the change is more marked and hence shows the formation of a compound at that concentration.

Summary

Magnetic properties of dilute as well as concentrated amalgams have been investigated. It has been shown that when dilute amalgams are prepared by prolonged electrolysis at room temperature the diamagnetic susceptibility of the amalgams prepared is lower than that calculated on the

mixture law and the results are in line with those of Venkataramiah ; but if the amalgams are prepared at low temperature, 0° C., within 4-5 hours or by grinding the components according to the method of Terry and Wright susceptibility value of the amalgams obeys the mixture law. This difference in the susceptibility has been explained by the authors, by suggesting the formation of paragmanetic oxides formed during prolonged electrolysis at high temperatures. Amalgams of higher concentrations prepared by grinding method, when fresh obey the mixture law but on keeping, even under vacuum, become less diamagnetic and the maximum difference, in susceptibility values between a fresh and an aged amalgam is observed in one which contains 34 per cent. copper. This is supposed to be due to the formation of compound.

REFERENCES

1. Bhatnagar and Mathur *Physical Principles and Applications of Magneto-Chemistry*, p. 341.
2. Bates and Tai .. *Proc. Phys. Soc.*, 1926, **48**, 795.
3. Venkataramiah .. *Proc. Ind. Acad. Sci.*, 1937, **5 A**, 532.
4. Bhatnagar and Mathur *Phil. Mag.*, 1929, **8**, 1041.
5. Bijnmann .. *J. Agric. Sci.*, 1924, **14**, 232.
6. Honda .. *Ann. Phys. Lpz.*, 1910, **32**, 1027.
7. Owen .. *Ibid.*, 1912, **37**, 657.
8. Davies and Keeping .. *Phil. Mag.*, 1929, **7**, 145.
9. Vogt .. *Ann. Phys. Lpz.*, 1932, **14**, 1.
10. Bhatnagar and Nevgi .. *Curr. Sci.*, August 1937.
11. Skaupy, F. .. *Phys. Z.*, 1920, **21**, 597.
12. Terry and Wright .. *Phil. Mag.*, 1928, **28**, 1055.