Appended will be found analyses of several parts of a single horse. These are not given to show anything about the accuracy of the method, but to increase the data relating to the amount of glycogen in different cuts of horse meat. The horse was one which had been killed in an accident, three days before the analysis was made.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen corresponding to dextrose.	Glycogen in each of the preceding columns, calculated to fat-free, water-free basis.	
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
1	Second cut of round..	74.36	3.27	0.49	0.00	2.19	0.00
2	First cut of round....	73.77	3.23	0.27	0.05	1.17	0.22
3	Shoulder clod........	73.54	5.27	0.58	0.05	2.73	0.23
4	Cross ribs............	73.86	6.30	0.32	0.04	1.62	0.20
5	Chuck...............	68.00	15.39	0.34	0.00	2.05	0.00
6	Plate	52.16	33.66	0.41	0.00	2.89	0.00
7	Brisket	66.70	12.16	0.46	0.006	2.17	0.03

I would like to express my thanks to Dr. W. D. Bigelow, of this Division, for putting at my disposal a very complete bibliography of glycogen. Since his work will shortly appear in print, I will not attempt to go into the literature of the subject.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 15.]

THE ELECTROLYTIC DEPOSITION OF BRASS.

BY J. LIVINGSTON R. MORGAN.

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BRASS plating by electrolysis was discovered in 1841, and the original process, with a few modifications, is still in use at the present time. The formulas for the preparation of the bath are entirely empirical, the subject, so far as I know, having never been treated from the theoretical standpoint. The purpose of this paper is to consider the reaction by the light of our present knowledge of electrochemistry, and to present the theory of the process which results.

When a metal with a high electrolytic solution pressure (Zn) is placed in an acid solution and connected by a wire to a plate of platinum, immersed in the same liquid, hydrogen gas is given off, at the platinum side, in the form of bubbles. The chemical reaction is

$$M + \overset{+}{H} + \overset{-}{A} = \overset{+}{M} + \overset{-}{A} + H\text{gas},$$

where M represents a monovalent metal, and HA a monobasic acid, which is dissociated into the ions $\overset{+}{H}$ and $\overset{-}{A}$. The process consists, essentially, in, the formation of metallic ions, which force ions of hydrogen out of the solution. A certain difference of potential results from this reaction which may be calculated by aid of the formula

$$\pi = \frac{0.0002}{n} T \log.\frac{P}{p} - 0.0002\ T \log.\frac{P_1}{p_1} \text{ volts},$$

where n is the valence of the metal, P its electrolytic solution pressure, and p the osmotic counter pressure of the metallic ions in solution, while P_1 and p_1 are the corresponding figures for hydrogen. The end of such a reaction will be reached, of course, when the solution is saturated with ions of the metal; *i. e.*, when all ions of hydrogen have disappeared.

When a metal possessing a low electrolytic solution pressure (Cu) is placed in acid, no hydrogen gas is given off, and ions of this metal in a solution would precipitate in the metallic form upon the plate.

When the metal plate in the above arrangement is used as the anode of a decomposition cell the general action of a metal with a high electrolytic solution pressure is the same, only intensified. With a metal of low electrolytic solution pressure the action is reversed so that if the electromotive force is made sufficiently high the metal acts as one of the former class and separates hydrogen from the acid. The value of the term P then can always be increased by an external electromotive force. Thus by reversing a Daniell cell and sending a current from the copper to the zinc, through the liquid, copper is dissolved and zinc precipitated. If a solution of a copper salt is electrolyzed with a copper anode, the value of P is increased until it exceeds the value p; *i. e.*, the osmotic counter pressure of the copper ions. At the cathode the copper ions accumulate, and are forced out of a solution upon the plate. With copper this would naturally take place even without a great accumulation of ions, but with a metal of high electrolytic solution pressure the ions would separate only when the term p is made greater than P. The work necessary for plating with a metal of high electrolytic solution pressure is thus seen to be done at the cathode, for there P must be exceeded by p, while for one with a low electrolytic solution pressure it is done at the anode for there it is necessary for P to exceed p in value. In other words metals like zinc, in simple solutions, need the current to separate them from the solution, while those like copper need it to cause the anode to dissolve. If the decomposing electromotive force is great enough, hydrogen will also be separated at the cathode, for ions of hydrogen will accumulate then and be evolved as gas when the electromotive force causes p_1 to exceed P_1 in value. With a small electromotive force, however, this will not take place so that for our purposes we may leave it out of consideration entirely.

If an alloy, made up of two metals one of which has a very high electrolytic solution pressure, while the other has a very low one, is placed in acid the constituent with the high pressure will dissolve, separating hydrogen gas upon a platinum plate, while the other will be unaffected. The end of the reaction will be reached when the acid is saturated with the ions of the one metal or if there is an excess of acid, when the one metal is entirely dissolved. Using such an alloy as the anode of a decomposition cell, both constituents will go into solution. The amounts dissolved will be proportional to the values of the electrolytic solution pressure. If the electrolyte in the cell contains ions of each constituent, then at any one decomposing electromotive force the amounts dissolved will be proportional to the electrolytic solution pressures divided by the osmotic counter pressures of the metallic ions. If the alloy contains 50 per cent. of each constituent it will be necessary for its solution in unchanged ratio, that $\frac{P}{p}=\frac{P'}{p'}$, where P and P' are the electrolytic solution pressures of the two metals and p and p' the osmotic pressures of their ions. In other words it is necessary that the ionic concentration of the metals be proportional to the electrolytic solution pressures. This relation is shown most plainly by the following diagram :

$$\left.\begin{matrix}\text{Cu}\\ \text{Zn}\end{matrix}\right\}\text{50 per cent.}\ \left\|\ \begin{array}{l} \rightarrow P_{\text{Cu}} = 4.8 \times 10^{-20}\,\text{At.}\\ \leftarrow p_{\text{Cu}} = 4.8 \times 10^{-20}\,\text{At.}\\ \leftarrow p_{\text{Zn}} = 9.9 \times 10^{+18}\,\text{At.}\\ \rightarrow P_{\text{Zn}} = 9.9 \times 10^{+18}\,\text{At.}\end{array}\right.$$

The two opposing pressures, osmotic and electrolytic solution, are thus equalized for each of the two metals; hence an electromotive force applied to the alloy as anode will cause equal amounts of copper and zinc to be dissolved. Such a mixture would be made if a saturated solution of a zinc salt were in contact with a plate of the 50 per cent. alloy, and the alloy, when made the anode, would dissolve evenly. It is necessary now, however, to consider the cathode upon which the metal will be precipitated. Here we will not get, at any current density, the alloy we expect so that the relation between the zinc and copper ions in the solution will change, and consequently the two constituents will then be dissolved from the anode in another ratio. *For the deposition of any alloy, then, we see that it is necessary that the following conditions be fulfilled: 1. That the solution have such an ionic concentration of the two metals that the correct amount of each constituent dissolves from the anode; i. e., that the alloy dissolves as such. 2. That the correct alloy separates at the cathode, so that the composition of the liquid is not altered in such a way that the first condition is unfulfilled.* With alloys of copper and zinc we see that, for simple salt solutions, the first condition can be fulfilled, but the second can not.

A solution from which brass may be deposited and which will retain this power, by dissolving the correct proportions of copper and zinc from the anode, must have the following properties, which are self-evident from what has already been said: *1. It must contain ions of zinc and copper in such a proportion that 30 per cent. of zinc, and 70 per cent. of copper will be dissolved from the anode; i.e.,* $\frac{P}{p} : \frac{P'}{p'} :: 30 : 70$. *2. It must contain complex ions of zinc and copper, from which these metals may be separated.* These are necessary, for we have seen that simple metallic ions cause changes in the composition of the solution and thus vary the composition of the alloy dissolved. There is also less work needed to separate metals from complex ions than from simple ones. *3. For economy, the maximum concentration of copper* *ions should be as small as possible in order that copper may be separated easily from the anode.*

All these conditions are fulfilled by a solution of the mixed salts of copper and zinc in potassium cyanide solution. We have first an extremely small concentration of zinc and copper ions. The absolute value of the concentration of copper ions can be appreciated from the consideration of the following experiment: When a solution of potassium cyanide is poured upon the copper side of a Daniell cell, the poles are reversed ; *i. e.*, copper becomes the negative pole. In order to do this, it is necessary that

$$\frac{P}{p}\,(\mathrm{ZnSO_4}) < \frac{P'}{p'}\,(\mathrm{CuSO_4 \text{ in } KCN});$$

i. e., that the value of p becomes so small that $P'(= 4.8 \times 10^{-20})$ exceeds it and copper goes into solution. We have the complex ions $\overset{-}{\mathrm{Zn}}(\overset{-}{\mathrm{CN}})_4$ and $\overset{-}{\mathrm{Cu}}(\overset{-}{\mathrm{CN}})_4$, from which zinc and copper may be deposited in varying proportions according to the current density, for zinc needs a greater current density than copper. In other words from our theoretical knowledge we can predict that such a solution would serve our purpose.

It would seem necessary, next, to find just what proportion of zinc and copper salt should be present in the cyanide solution, to give the correct ratio of ions. This, however, is not necessary, as is shown by the following consideration, for this ratio adjusts itself automatically during the reaction. In practice, at times, a bath is made up as follows: A solution of potassium cyanide is electrolyzed, at the correct density to deposit brass, for several hours with brass electrodes, the liquid being drawn off and used as the bath. From the brass anode ions of zinc and copper ions are given off into the solution forming the salts $\mathrm{K_2ZnCN_4}$ and $\mathrm{K_2CuCN_4}$. These salts dissociate, to a very large extent, into $2\overset{+}{\mathrm{K}}$ and $\mathrm{M}\overset{--}{\mathrm{CN}}_4$, where M represents either copper or zinc. There is also a further dissociation, to a very slight degree, into $2\overset{+}{\mathrm{K}}$, $\overset{++}{\mathrm{M}}$ and $4\overset{-}{\mathrm{CN}}$. The zinc, on account of its high electrolytic solution pressure, will dissolve to a greater extent than the copper, so that there will be more ions of $\overset{--}{\mathrm{ZnCN}}_4$ than of $\overset{--}{\mathrm{CuCN}}_4$. Only 30 parts of zinc, however, at this current density can separate to every 70 parts of copper so that there is also a concentration of $\overset{-\;-}{\mathrm{ZnCN}_4}$ ions on the cathode side; this takes place after hydrogen has been given off for a time. The equilibrium in the solution is fixed by certain equations. By these only a certain amount of free zinc ions can exist in the solution, all over this amount being transformed into $\overset{-\;-}{\mathrm{ZnCN}_4}$, and of this latter a relatively small portion only can separate at the cathode. For this reason when the solution becomes saturated with $\overset{-\;-}{\mathrm{ZnCN}_4}$ ions, it exerts the same counter pressure with its free zinc ions as it would if the solution were saturated with zinc ions, since any more zinc ions would supersaturate the solution. For this reason zinc can only dissolve to the same amount in which it separates.

The copper ions in the solution are so few that, as before observed, the metal acts as though it possessed a high electrolytic solution pressure. There is a larger number of $\overset{-\;-}{\mathrm{CuCN}_4}$ ions and since these break up and separate copper to a greater extent than those of $\overset{-\;-}{\mathrm{ZnCN}_4}$ separate zinc, and since the solution never becomes saturated with them, the terms $\frac{P}{p}$ and $\frac{P'}{p'}$ become of the same order, and are related as 30 : 70. It is thus seen that the regulation of the relative concentration of zinc and copper dissolved is automatic and depends upon the current density which regulates the ratio deposited. In few words we may sum up the behavior as follows: The solution is saturated with zinc, since no more can exist either as Zn or as $\overset{-\;-}{\mathrm{ZnCN}_4}$, except as Zn from $\overset{-\;-}{\mathrm{ZnCN}_4}$ separates. The relation $\frac{P'}{p'}$ is increased by the exceedingly small value of p' so that ions of copper can form, but as they form they separate on the other side, removing the saturated condition with respect to zinc, so that the correct relative amount of this also can separate and dissolve, etc.

Another method consists in dissolving equal weights of copper and zinc salts in a solution of potassium cyanide. The action, of course, is exactly similar to that given above for potassium cyanide solution alone, so that it will not be necessary for us to consider it.

It is thus possible from purely theoretical knowledge, and a few appropriate simple experiments to find just what solutions must be used for baths for the deposition of any alloy. The contrast between this method and the old empirical one of trying all combinations until a lucky hit is made, the true reasons for which are unknown, is striking, but it is just what is being experienced to-day in all branches of chemistry by the application of theory to practice. The other ingredients which are used in the baths are to produce a fine smooth coating and have nothing to do with the theory of the method. Of course there are other solutions which behave just as the double cyanides do, but as the theory is the same, the only idea of a change would be for economy and that is a question for the technical side of the subject. Such another solution which is used is made by dissolving zinc and copper salts in an excess of ammonia. Here we have just as before Zn and Cu ions, and also complex ones which behave just as $\overline{\mathrm{Cu}}\,\overline{\mathrm{C}}\mathrm{N}_4$ and $\overline{\mathrm{Zn}}\,\overline{\mathrm{C}}\mathrm{N}_4$.

Another liquid which causes copper to act as a metal of high electrolytic solution pressure is a solution of potassium sulphide.

THE DETERMINATION OF SULPHUR IN BITUMENS.

By A. C. Langmuir.

Received November 24, 1899.

In the September number of this Journal, S. F. and H. E. Peckham criticize a paper by E. H. Hodgson which appeared in November, 1898, and describe, in some detail, their own method slightly modified.

The authors claim for their method that it is "simple, reasonably rapid and accurate" and state that it is "susceptible of great accuracy, if *conducted with care.* It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant."

It is but fair to Mr. Hodgson to call attention to certain features in Messrs. Peckham's method which cannot inspire chemists with confidence and which may possibly indicate that the authors themselves have not bestowed on their method the great care which they miss in Mr. Hodgson's work.

A brief review of the method is necessary: Approximately