electrodes, since there is no measurable difference of potential whether the solution be saturated with nitrogen or hydrogen.

Conclusion

Graphite and tungsten electrodes have been tested in oxidation-reduction systems. In the quinhydrone system graphite gives results identical with those obtained at blank platinum and gold-plated platinum; whereas tungsten gives entirely different values.

In the ferro-ferricyanide system graphite gives measurements one to two millivolts less than platinum; whereas those with tungsten are 5 to 10 millivolts less.

Graphite gives the same results as platinum in a dyestuff system, be it well or poorly poised; whereas tungsten gives reliable results only when the system is well poised.

The potentials of graphite and tungsten against a reversible dye system are unaffected by change from a nitrogen to a hydrogen atmosphere.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL HYGIENE, SCHOOL OF HYGIENE AND PUBLIC HEALTH, THE JOHNS HOPKINS UNIVERSITY]

THE PREPARATION OF MANGANESE-FREE MAGNESIUM

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In the course of an investigation of the possible function of manganese in animal metabolism, a number of manganese-free substances were required, among them a suitable magnesium salt. In considering magnesium salts for this purpose, it was discovered that manganese was invariably present in all of the best and C. P. labeled magnesium salts and all other magnesium preparations obtainable. Also, all magnesium compounds especially prepared with reference to freedom from manganese contained the element. The presence of manganese could be demonstrated in all these magnesium preparations by both the periodate and the spectrographic methods. Furthermore, our own efforts showed that all known methods of purifying magnesium salts were ineffective for removing such traces of manganese as could be detected by either of the above methods. The idea was then conceived of removing the manganese by first converting it into permanganate. As is well known, this can be readily done by means of potassium periodate.

The first attempt to free magnesium from manganese in the permanganate form consisted of adding in the customary manner a small amount of potassium periodate to a 10% solution of magnesium sulfate acidified with sulfuric acid and heating the resulting solution until the pink permanganate color had developed. The solution was then cooled and rendered alkaline with ammonia. The resulting precipitate of magnesium hydroxide was allowed to settle, after which the supernatant liquid was decanted as completely as possible. The precipitated magnesium hydroxide was then washed several times with distilled water which had previously been treated with sulfuric acid and potassium iodate and then rendered faintly alkaline. This procedure no doubt removed some manganese, but the magnesium hydroxide so treated always contained sufficient manganese to be detected spectrographically. Apparently, therefore, magnesium hydroxide has the capacity for adsorbing and holding in some way small amounts of manganese, which cannot be washed out. Accordingly, removal of the permanganate must take place, if at all, not after but before the magnesium hydroxide is precipitated. Electrolysis suggested itself as a possible method of separating Mg^{++} and MnO_4^- ions since they are oppositely charged and migrate to opposite poles. In a suitably designed electrolysis cell magnesium will collect as a precipitate of magnesium hydroxide at the cathode, whereas the MnO_4^- ions will concentrate at the anode. However, it is obvious that the principal consideration in the design of such a cell is an arrangement by which the original permanganate-containing solution is kept apart and separated from the cathode so that the permanganate will not be reduced by the nascent hydrogen evolved from the cathode. The design of such an arrangement was accomplished in the cell illustrated in the accompanying diagram. By means of this cell we have succeeded in preparing magnesium hydroxide which is spectrographically free from manganese. As designed and used in this Laboratory this cell consists of a two-liter pyrex beaker, a 350-ml. Erlenmeyer flask to which is fused a side arm tube in the manner indicated, a dropping funnel, a siphon tube and platinum electrodes, all assembled as indicated in the illustration. After this illustration had been prepared it was found preferable to place at a somewhat higher level the inclined tube joining the Erlenmeyer flask with the anode-containing tube. By such a design the anode pocket is made deeper, thereby making possible a more complete isolation and removal of acid hydrolysis products, *viz.*, sulfuric and permanganic acids.

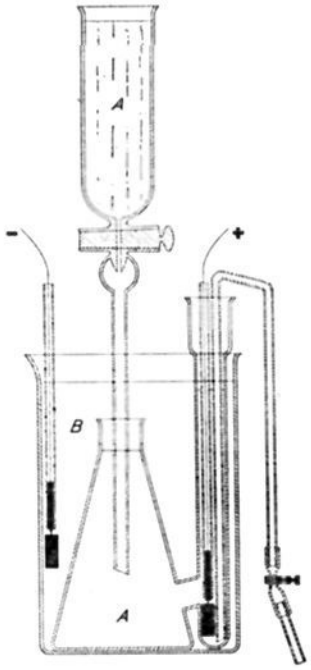

Fig. 1.—A, 10% $MgSO_4$ solution; B, 0.1% $(NH_4)_2SO_4$ solution.

Operation

The Erlenmeyer flask is filled to a level about three-fourths to one inch from its mouth with a 10% solution of magnesium sulfate (A) whose manganese has previously been oxidized to the permanganate form in the usual manner by potassium periodate. The flask is then placed inside the two-liter beaker, after which the electrodes, the siphon and the dropping funnel are placed as indicated in the figure. A 0.1% solution of ammonium sulfate (B) is then carefully introduced into the space between the beaker and the Erlenmeyer flask, including the space within the neck of the flask not filled by (over) the magnesium sulfate solution, the level of the ammonium sulfate solution being adjusted to a point about three-quarters to one inch higher than the mouth of the Erlenmeyer flask. The dropping funnel is next filled with another portion of the same 10% solution of magnesium sulfate, indicated by A in the illustration (previously treated with potassium periodate) as that already contained in the flask. Operation may now be started by connecting the electrodes directly with a 110-volt direct current, which was found suitable for this particular cell. Within a few minutes magnesium hydroxide can be observed to deposit around the cathode, which is in the space within the beaker but outside the flask. At the same time sulfuric and permanganic acids will concentrate in the pocket of the side arm containing the anode. These acids must be drawn off at approximately the same rate as they are formed in order to maintain the efficiency of the process. This removal of the acid is accomplished by means of the siphon which reaches to the bottom of the anode-containing pocket. It is difficult to ascertain with any exactness the proper rate of flow of this siphon. However, we have found by experience that a flow of 15 to 20 drops per minute yields satisfactory results in this particular cell. The rate at which the solution so withdrawn, together with the rate of electrolysis, determines the rate at which additional permanganate-containing magnesium sulfate solution must be introduced from the dropping funnel. Obviously, this rate is maintained by adjusting the drip from this funnel so that the liquid junction between the permanganate-containing magnesium sulfate solution in the Erlenmeyer flask and the overlying solution, which was originally ammonium sulfate, is approximately at the same level as at the start, that is, three-fourths to one inch from the mouth of the Erlenmeyer flask. It will usually require three or four readjustments of the stopcock in the dropping funnel before the rate of inflow through the funnel will balance the combined rates of outflow through the siphon and the electrolysis. An inflow of about 25 drops per minute will nearly strike the balance when the outflow is 15 to 20 drops and the electrolyzing current is 110 volts. When this balance has been attained, as indicated by the constancy of the level of the liquid junction between the permanganate-containing magnesium sulfate solution and the overlying solution in the neck of the Erlenmeyer flask, electrolysis will proceed with little need for attention. The above liquid junction is always so conspicuous and clear-cut that there is never any difficulty in locating it with the eye. An inspection of the cell about once an hour is sufficient. After six or seven hours, a large and voluminous drift of magnesium hydroxide will have deposited on the bottom of the beaker and this will be found spectrographically free from manganese.

Summary

Apparently all of the highest grade and C. P. labeled magnesium compounds contain traces of manganese which cannot be removed by ordinary methods of purification. A new method has been developed by which magnesium salts can be rendered manganese-free. This method consists

of an oxidation of the manganese to the permanganate form by means of potassium periodate, followed by electrolysis in a specially designed cell in which magnesium hydroxide deposits in a cathode-containing compartment and the permanganate in an anode-containing compartment. An essential feature of this cell is an arrangement whereby hydrogen from the cathode is kept out of contact with the permanganate.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXXIV. TRIMETHYL GERMANIUM BROMIDE[1]

BY L. M. DENNIS AND W. I. PATNODE

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Halogenated aryl compounds of germanium of the type R_3GeX have been prepared by several investigators.[2] These compounds are solids which can readily be purified by crystallization from organic solvents. Comparatively little work has been done on the germanium alkyl compounds, and no halogenated alkyl of the above type has been announced. Trimethyl germanium bromide was chosen as a typical representative of this class. It was to be expected that the compound would be somewhat more difficult to prepare and purify than the corresponding aryl compounds since it probably would be a liquid that is rapidly attacked by atmospheric moisture. Consequently, the method of halogenation developed by Dennis and Judy[3] was used.

Materials.—Germanium tetrachloride was converted to germanium tetramethyl by the method of Dennis and Hance.[4] Hydrogen bromide was prepared by the reduction of bromine by hydrogen sulfide.

Procedure.—The apparatus was similar to that used by Dennis and Judy[3] for the halogenation of monogermane. Anhydrous aluminum bromide was introduced into the reaction bulb in the manner there described. About 15 g. of germanium tetramethyl was distilled into one of the smaller bulbs of the vacuum chain, after its purity had been established by determination of its vapor tension at 0°. Slightly less than the theoretical amount of hydrogen bromide required by the equation

$$HBr + Ge(CH_3)_4 = Ge(CH_3)_3Br + CH_4$$

was condensed in another bulb of the apparatus, and was then distilled over into the bulb that contained the germanium tetramethyl. The two

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[2] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925); Kraus and Foster, THIS JOURNAL, **49**, 457 (1927); Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927).

[3] Dennis and Judy, *ibid.*, **51**, 2321 (1929).

[4] Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).