

experiments¹¹ show, however, that the presence of a large excess of ammonium oxalate prevents the complete precipitation of this organic salt of magnesium. All the results were too low when much oxalate was present.

Neubauer,¹² Gooch and Austin,¹³ Järvinen,¹⁴ and Smitz have all found that the precipitation of magnesium succeeds in the presence of considerable ammonium salt, but it is evident that they never tried the experiment with as much ammonium oxalate present as recommended by Bobtelsky. In giving beginners a sample of dolomite to analyze for calcium and magnesium, the results obtained are usually good when the directions of Richards or of Blasdale are followed and a single precipitation of calcium oxalate made, or when, according to the directions of Fresenius,¹⁵ a double precipitation of calcium oxalate is made. Occasionally, however, we have noticed that a student fails to get all of the magnesium precipitated as magnesium ammonium phosphate. In the light of these experiments it seems probable that this is the result of using too large an excess of ammonium oxalate. These experiments indicate that 75 cc. of 0.5 *N* ammonium oxalate solution is sufficient for the precipitation of 0.3 g. of calcium ions in a volume of 500 cc., but the same quantity of reagent should be used when only 0.02 g. of calcium is present in the presence of considerable magnesium (0.12 g.).

Summary

For the precipitation of calcium oxalate in the presence of magnesium ions an excess of ammonium oxalate is necessary. If this excess is properly regulated, it is possible to precipitate pure calcium oxalate. If, however, a very large quantity of ammonium oxalate is present, the precipitation of magnesium ammonium phosphate is incomplete even after long standing.

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NOTE

The Rate of Reaction of Liquid and Gaseous Zinc with Carbon Monoxide.¹—The data of Maier and Ralston² on the free energy of zinc oxide and Lewis and Randall's³ equation for the free energy of carbon monoxide indicate that at all except extremely small partial pressures,

¹¹ Performed by Mr. Waite.

¹² Neubauer, *Z. angew. Chem.*, **9**, 435 (1896).

¹³ Gooch and Austin, *Am. J. Sci.*, [4] **7**, 187 (1899).

¹⁴ Järvinen, *Z. anal. Chem.*, **44**, 333 (1905).

¹⁵ Cf. Hillebrand, "Analysis of Silicate and Carbonate Rocks."

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² Maier and Ralston, *THIS JOURNAL*, **38**, 364 (1926).

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 576.

zinc vapor and carbon monoxide should react to give zinc oxide and carbon at about 700° , the temperature of the condenser in zinc smelter practice. Viewed otherwise, carbon monoxide should at 700° change to carbon dioxide and carbon almost completely, and the carbon dioxide should oxidize the zinc to zinc oxide. As the formation of carbon dioxide and carbon from carbon monoxide is, in the absence of a catalyst, extremely slow at 700° , it appeared to be of interest to determine whether or not the rate of the direct reduction of carbon monoxide by zinc was appreciable. The appearance of some carbon during experiments of Maier and Ralston at higher temperatures suggested that zinc oxide might catalyze the decomposition of carbon monoxide into carbon and the dioxide.

Pure zinc was made by fractional distillation of electrolytic zinc *in vacuo*. Pure carbon monoxide was made from concentrated sulfuric acid and 60% formic acid, passed over soda lime, and allowed to stand for two days in contact with molten sodium at 130° .

In a system of about 200 cc. in volume, 20 g. of zinc was distilled in two hours through carbon monoxide at 0.5 atm. Vaporization took place in the center of a horizontal silica tube furnace, the gas passed through about 20 cm. of the tube kept at 750° by a separate winding, and condensation took place near the end of the furnace. The distilled zinc contained no free carbon detectable when 1 g. was dissolved in hydrochloric acid, and no zinc oxide could be found on the walls of the tube. The hydrogen evolved was not tested for hydrocarbons. The pressure did not drop.

About 5 g. of zinc was refluxed in a silica tube in 0.5 atm. of carbon monoxide for five days. The volume of the system was about 100 cc. and the temperature was 690° . A total decrease in pressure of 0.006 atm. occurred. Some zinc condensed in the section of the tube at the upper end of the furnace, changing to a finely divided solid in the colder part of the tube and to large crystals in the hotter part.

A silica tube containing 0.1 g. of zinc and 3 pieces of red fire brick about 1 mm. in diameter was evacuated, heated to 680° , and filled with carbon monoxide at 0.4 atm. The volume of the system was about 100 cc. In five days the pressure dropped 0.06 atm. The fire brick became sooty, and a coating of zinc oxide covered the inner wall of the tube. Fire brick freed from iron showed no catalytic effect whatever; negative results were also obtained with aluminum oxide and zinc oxide.

Zinc containing 0.04% of iron was refluxed in carbon monoxide in the same way as the pure zinc, with the same result.

These experiments indicate (1) that the reaction $\text{CO} + \text{Zn}_{(l \text{ or } g)} = \text{ZnO} + \text{C}$ is extremely slow at 600 to 700° in the absence of a catalyst, (2) that it is possibly slower than the reaction $2\text{CO} = \text{CO}_2 + \text{C}$ under the same conditions and (3) that zinc reduces carbon dioxide rapidly at the given temperatures.

The production of zinc oxide in the zinc condenser is due, then, to the oxidation of the zinc by carbon dioxide, or water vapor, both of which are present in considerable quantities in the gases issuing from the retort when reduction first starts. Additional carbon dioxide may be produced by the reaction $2\text{CO} = \text{CO}_2 + \text{C}$, which is catalyzed by the clay present in the condenser walls. Pure carbon monoxide is an excellent atmosphere in which to distil zinc, provided the walls of the apparatus are free of iron.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF DENVER]
A MODIFICATION OF THE SKRAUP SYNTHESIS OF QUINOLINE

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The Skraup synthesis of quinoline occupies a position of interest in organic chemistry because it offers a ready method of synthesis of the quinoline group of compounds.

Several modifications have been proposed since the method was inaugurated in 1880. The most important advance has been the enlargement of the yield. The ferrous sulfate modification is outstanding in this phase of the development.¹ The original Skraup method and all of the modifications to date possess one disadvantage in common. The reaction is usually vigorous and at times violent. Clarke and Davis writing in "Organic Syntheses" say, "In the Skraup synthesis of quinoline the principal difficulty has always been the violence with which the reaction generally takes place; it occasionally proceeds relatively smoothly, but in the majority of cases gets beyond control."¹ The occasional violence of the reaction renders the experiment objectionable as a routine laboratory experiment. The authors have succeeded in eliminating this danger by the addition of acetic acid to the reaction mixture, and have studied the effect of variations in the conditions upon the yield of quinoline obtained.

The safety attained by this modification is attested by the fact that the reaction has been carried out in our Laboratories by large classes of students observing no special precaution and the reaction has never become violent.

During the course of the investigation an unsuccessful attempt was made to render the reaction safe by dilution of the sulfuric acid. The method

⁴ Associate chemist.

¹ H. T. Clarke and Anne W. Davis, "Organic Syntheses," John Wiley and Sons, New York, 2, 79 (1922).