

## ● EARLY WORK ON THE DISPLACEMENT OF METALS AND METAL OXIDES

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WE REGRET to inform our readers of the death of Professor Vladimir N. Ipatieff, which occurred on November 29, 1952, following a short illness, just eight days after his 85th birthday.

Funeral services were held at Chicago, December 1, for this world-famed petroleum chemist and director of chemical research for Universal Oil Products Company. He had been associated with Universal for more than 23 years—ever since he left his native Russia with whose policies and philosophies he disagreed.

He was generally regarded as the world's foremost authority in the field of catalysis and it was in this area that he devoted the major portion of his remarkable career. He is particularly known for his fundamental research and development on the processes which contributed to the development of high octane aviation gasoline—alkylation, polymerization and isomerization.

It was the development of these processes which enabled the Allies to gain the upper hand in the aerial war against Germany during World War II and led to the eventual destruction of German aerial strength.

In addition to his work for Universal at their Riverside, Illinois, laboratories, Professor Ipatieff was an active member of the faculty of Northwestern University, where he set up and supervised the Ipatieff High Pressure and Catalytic Laborato-

ries, the only unit of its kind on the campus of any American university.

Professor Ipatieff was born in Moscow in 1867, and attended a number of military schools there. But throughout his schooling period he maintained an active interest in chemistry and after his graduation from the Michaelovsky Artillery Academy continued with the academy as a chemistry professor. Four years later, in 1896, the academy sent him to Germany and France for further study in chemistry.

While he achieved world-wide recognition for his chemical research in Russia, it was in the latter period of his life, spent here in the United States, that he felt he reached his greatest accomplishments.

During his lifetime he received many honors and awards for his scientific accomplishments, the most recent of which were two French citations which he received last year—one making him a Chevalier of the Cross of Lorraine and a Companion of the Resistance, and the other an appointment as a member of the French Association of the Knights of Cyprus and Jerusalem. Both these awards were granted in recognition of his work on high octane aviation gasoline during the last war.

Professor Ipatieff's widow, Varvara, outlived him by only ten days. They are survived by a son and a daughter, both of whom live in Russia.

A RECENT issue of *Chemical and Engineering News* (1) contains an article on "The chemical ore reduction process." The article describes a new method which makes it possible to separate metals from solutions of their salts by means of hydrogen at higher temperatures and pressures. It appears that three plants will be built to utilize this particular method.

It is most gratifying to me to learn of this development since my co-workers and I have published some 30 articles on this particular subject over the period from 1909 to 1930. These have been published chiefly in *Berichte der Deutscher Chemischen Gesellschaft*. It is my hope that this particular work has served as the foundation for the technological developments which have just been announced.

My colleagues at Northwestern University and at Universal Oil Products Company have urged me to review the work we carried out from 1909 to 1930 with the idea that a better understanding of the reactions taking place would be derived from such a presentation.

Since the displacement of metals from aqueous solutions of their salts by hydrogen involves the utilization of high pressures, it is first of all interesting to recall the great struggle that I had in convincing

chemists, as well as engineers, that the application of high pressures not only provides a new tool for effecting reactions heretofore believed impossible, but it also provides a safe and simple means for carrying them out.

### DISPLACEMENT OF METALS

In 1908 I had just completed a series of successful experiments on the hydrogenation of organic compounds under pressure, and conceived the idea of applying this method to the reactions of inorganic compounds. Together with my assistant, V. N. Verkhovsky (2), we started a study of the reaction of hydrogen under pressure with solutions of various salts. Prior to this, this reaction was carried out in 1859 by Academician M. N. Beketoff (3), who succeeded in replacing silver and mercury from dilute solutions in the presence of hydrogen at 10 atm. pressure; however, he was unable to precipitate copper or lead under these conditions. He indicated that copper, as well as some of the other metals, could be displaced from their solutions in the presence of platinum black; however, in this case one can easily suspect a catalytic reaction.

As can be seen from the table of the electromotive force of the metals (Table 1) each member displaces

**TABLE 1**  
**Electromotive Series of the Metals**

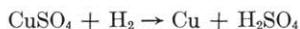
Zn 0.8	Sn 0.14	As -0.3
Fe 0.44	Pb 0.13	Cu -0.34
Cd 0.4	H <sub>2</sub> 0.0	Ag -0.8
Co 0.33	Sb -0.1	Pt -0.8
Ni 0.25	Bi -0.2	Au -1.68

from a salt solution each succeeding member, that is, metallic zinc replaces hydrogen, copper replaces silver, and platinum replaces gold, etc. It should be noted, however, that this reaction is not reversible and that the metals above hydrogen are soluble in acids while the metals below hydrogen are insoluble in acids.

In 1892 Tammann and Nernst(4) tried to precipitate copper from copper sulfate by using hydrogen under pressure up to about 40 atm. In a great many cases their experiments terminated in an explosion, while those that survived the experimental conditions still did not show separation of copper from copper sulfate. Until our work in 1908 this was the last attempt to separate copper and other metals by means of hydrogen.

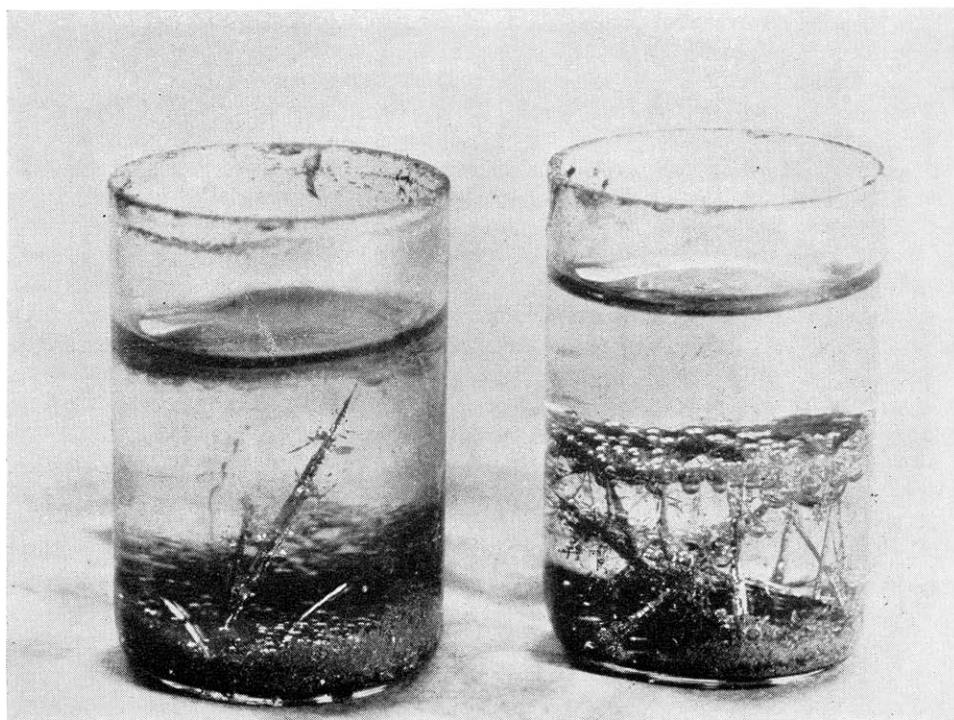
In our experiments we started with the study of the effect of hydrogen pressure on the displacement of metals from their salts at room temperature. A 0.1 N solution of copper sulfate was placed in a glass or quartz tube and inserted into the Ipatieff autoclave, and then hydrogen was pumped in. In order to prevent the loss of water by evaporation the tube was equipped with a stopper having a capillary opening. In these experiments it was found that although pressures of 200, 580, and 600 atm. were used, and the experiments were carried out for several days, there was no trace of any separation of copper from the solution. In other experiments we have tried other salts of copper, as well as the salts of other metals, such as nickel, cobalt, and cadmium. However, despite the use of high pressure, none of these experiments showed any displacement of the metals from their solutions at 25°C. We decided to heat the bomb, or autoclave, to higher temperatures, and only then did we observe deposits at the bottom of the tubes. The composition of these deposits depended upon the temperature at which the experiment was carried out. For example, copper sulfate at 90°C. and 25 atm. pressure gave a crystalline material having a composition CuSO<sub>4</sub>·2Cu(OH)<sub>2</sub>, while after longer times of contact

the separation of Cu<sub>2</sub>O was found to take place. When the experiment was continued for 40 to 50 hours crystals of copper separated out along with Cu<sub>2</sub>O, while after seven days of heating the only product found was metallic copper, according to the equation:



At 200 atm. pressure and 90°C. pure copper separates out readily. The effect of temperature is quite pronounced. For example, at 50°C. and 700 atm. pressure, copper sulfate does not produce cuprous oxide; however, at 60°C. and 600 atm., cuprous oxide does precipitate out. These experiments showed that the formation of the basic salts and metal oxides takes place through the hydrolysis of the salts, while the precipitation of the metals by means of hydrogen is a separate reaction. This was proved by the addition of sulfuric acid to a solution of copper sulfate, thereby providing sufficient hydrogen ions to repress hydrolysis and to result in the precipitation of pure copper by treatment with hydrogen. It was finally found that for each metal there is a certain critical temperature and pressure which permits the displacement of the metal from its solution by means of hydrogen.

Further experiments showed also that at atmospheric pressure an increase in temperature does not bring out the separation of the metal; thus the cooperative action of both temperature and pressure is essential. It should be noted, of course, that when we talk of critical temperatures and pressures, there is no connection at all with the critical temperatures and pressures governing the behavior of gases. As stated above, the hydrolysis reaction requires one set of conditions, and this is



Copper Crystals Recovered from Autoclave



V. N. Ipatieff in 1915 as a Lieutenant General of the Russian Army

followed by the precipitation of the metal from the solution. Our definition of the critical temperature for the replacement of a given metal from a water solution of its salt is the temperature at which a metal is precipitated out rapidly and to completion at a minimum hydrogen pressure. If one makes the supposition that the reaction of the replacement of metals takes place at all temperatures, but very slowly, it should be noted that the reaction-rate constants calculated by my son, V. V. Ipatieff (5), indicate that exceedingly long times are required for the reaction to take place. For example, in order to precipitate one per cent of the metal from a normal solution at 20°C. and 100 atm., the required times are as follows: bismuth, 37 years; antimony, 160 years; and arsenic, 1140 years. Using the very approximate formula which states that the reaction rate doubles for each 10°C., we should expect that the precipitation of the metal would take place in a reasonably short time at relatively low temperatures. However, experiments have shown that the separation does not take place until a certain critical temperature is reached.

The same reasoning can be applied to the pressure factor; if one considers electropotential values one would expect that bismuth, for example, could be displaced from a solution at relatively low pressures and at a temperature of 175°C. However, actually there is no precipitation at 15 atm. of hydrogen pressure, and the displacement only takes place at considerably higher pressures. In an actual experiment it was found that 60 per cent of the bismuth is precipitated at 150 atm. pressure after heating for 23 hours at 175°C. It is interesting to note that further increases of pressure raise the separation extent to only 62 per cent and complete

precipitation of bismuth from a solution requires considerably more severe conditions.

As is known, in order to explain the reaction of the displacement of metals by hydrogen Nernst proposed an equation which makes it possible to calculate the pressure required for carrying out the reaction. This pressure must be greater than the electrolytic solution pressure of the metal.

$$\log P = \frac{\pi \times Ne}{0.058} \log p$$

Where  $P$  is the electrolytic solution pressure,  $\pi$  is the electropotential difference,  $Ne$  is the potential of the cation, and  $p$  is the osmotic pressure of the cation. However, this equation does not include the effect of temperature and therefore requires some modification. I recall a lecture which I delivered before the German Chemical Society in 1923. Following the lecture, Dr. Nernst invited me to come to his laboratory in order to discuss further the mechanism of the reaction, but after long discussions we could not arrive at a reasonable hypothesis. I also recall that at the Seventh International Chemical Congress in London in 1909, Arrhenius, who was the Chairman of the meeting, indicated that some changes must be made in our theoretical viewpoints on the calculation of the electrolytic solution pressure of metals. For example, for the separation of cadmium from its nitrate, the calculated required pressure of hydrogen is 10,000 atm.; however, our experiments showed that a 2-N solution of this salt at 270°C. and a pressure of 220 atm. in a quartz tube yields hexagonal crystals of metallic cadmium in 10 hours.

It should be noted that in our experiments the choice of required temperature also governed our choice of the reaction vessel. At temperatures in excess of 250°C. we were compelled to use a quartz tube instead of an ordinary glass tube, while at temperatures in excess of 300°C. the reaction was carried out in gold and platinum tubes. At high temperatures water vapors act on the quartz tube, with the result that under these conditions we were able to obtain hexagonal quartz crystals. Very recently I had the pleasure of seeing the beautiful large quartz crystals prepared by the excellent method worked out by the Bell Telephone Laboratories for the preparation of large-size quartz crystals at high temperatures and high pressures (A. C. Walker and E. Buehler (6)). The procedure involves the seeding of an aqueous phase above a silica phase with a minute quartz crystal and permitting the crystal to grow evenly and slowly.

Table 2 shows some of the typical results obtained in the precipitation of copper and other metals by means of hydrogen under pressure. The indicated temperatures and pressures do not represent the critical temperatures and pressures.

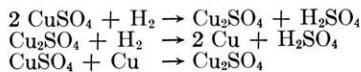
These experiments showed that the addition of an acid to a neutral solution of the salt has a profound effect on the displacement of the metal by hydrogen at constant temperature. For example, a neutral solution of cupric acetate at 100°C. and 40 atm. hydrogen pressure yielded cupric oxide; when the tempera-

TABLE 2  
Displacement of Metals from 1/10 N Aqueous Solutions

Salt	Temp., °C.	Pressure, atm.	Product analysis
CuSO <sub>4</sub>	20	580	No Cu
CuSO <sub>4</sub>	160	118	100.0% Cu
CuSO <sub>4</sub>	122	120	99.93% Cu
H <sub>2</sub> SO <sub>4</sub>			
NiSO <sub>4</sub>	207	123	99.74% Ni
CoSO <sub>4</sub>	230	150	100.0% Co
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	240	150	100.0% Pb
Bi(NO <sub>3</sub> ) <sub>3</sub>	248	150	100.0% Bi
K <sub>2</sub> H <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub>	330	200	100.0% Sb

ture was increased to 180–190°C. at the same pressure only traces of cuprous oxide were found in cupric oxide. In order to obtain the separation of metal with copper it is essential that the solution contain a definite concentration of hydrogen ions. As long as the concentration of the acid does not exceed 75–76 per cent (12.5-N), hydrogen displaces only cuprous oxide. Higher concentrations of acid in the salt solution stop the hydrolysis and result in the separation of pure metallic copper. In this particular case the solution at 20°C. has a pH of 1.12, which corresponds to a hydrogen ion concentration of 0.075.

An investigation (?) of the solution remaining after the precipitation of metal from copper sulfate showed that it also contained some cuprous sulfate, Cu<sub>2</sub>SO<sub>4</sub>. The question was immediately raised as to what conditions are required for the conversion of cupric sulfate into cuprous sulfate. A number of experiments showed that under no conditions was it possible to obtain only Cu<sub>2</sub>SO<sub>4</sub>; moreover, it was not possible to separate metallic copper by hydrogen without leaving in the solution some cuprous and cupric ions, although in some cases the amounts present were negligible. This would indicate that under the experimental conditions the displacement of copper by hydrogen never goes to completion, and the residual solution still contains traces of copper ions. Table 3 gives the data which confirm the precipitation of metallic copper from cupric sulfate with a formation of both cuprous and cupric ions in the residual solution. The reactions which govern this are most likely the following:



The last reaction can be written:



There is no doubt that the entire system appears to be in a dynamic equilibrium involving hydrogen and both cuprous and cupric ions.

The above experiments were carried out in the Ipatieff rotating autoclave or in autoclaves equipped with mechanical agitators. For example, a solenoid in the head of the bomb was connected to a rod provided with horizontal discs; the rod was moved continuously up and down through the solution by action of the solenoid. Other autoclaves, equipped with stirrers re-

TABLE 3  
Effect of Hydrogen Ion Concentration on Separation of Copper from 1.0 N Copper Sulfate Solutions. Time: 24 hours, Temp.: 100°C.

<i>H<sub>2</sub> Pressure, atm.</i>	<i>Conc. of H<sub>2</sub>SO<sub>4</sub></i>	<i>Distribution of Cu based on original CuSO<sub>4</sub></i>		
		<i>as Cu<sup>++</sup></i>	<i>as Cu<sup>+</sup></i>	<i>as Cu metal</i>
100	None added	54	15	31
100	1.0 N	30	35	35
100	2.0 N	52.5	27	20
100	4.0 N	55.5	22	22.5
100	14.0 N	40.5	47	12.5
20	None added	37.5	40	22.5
20	1.0 N	33	53.5	13.5
20	2.0 N	41	56	3
20	4.0 N	77.5	22.5	0
20	14.0 N	98.5	1.5	0

volving at 200 r. p. m., also provided for a reasonably good mixing of the solutions.

#### SEPARATION OF METALS

In view of the fact that various metals have different electrode potentials, and since it was indicated that different temperatures and pressures are required for displacing the metals from their solutions, it would be reasonable to expect that the action of hydrogen under pressure on solutions containing different metal ions could result in the separation of the metals. It would be expected that the metal with the lowest electrode potential would be separated first. For example (8), if one has a mixture of copper sulfate and zinc sulfate solutions, or copper sulfate with iron salts, such as Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O], the initial precipitate is metallic copper. The separation of copper occurs at temperatures and pressures somewhat higher than those required for precipitation of copper from solutions containing no other metal ion. In order to prevent the hydrolysis of other salts it is necessary in some cases to add sulfuric acid to the system.

A number of experiments have been carried out by my son, V. V. Ipatieff (9), on the separation of arsenic, bismuth, and antimony at 100 atm. hydrogen pressure and temperatures ranging from 175 to 225°C. In order to separate arsenic from bismuth, a 2-N hydrochloric acid solution was employed; at the end of 18 hours arsenic had separated completely, while the residual solution contained the bismuth chloride.

In the separation of arsenic from antimony he used an apparatus equipped with a stirrer and a solution of the chlorides of the metals with a normality of 0.5 and an additional hydrochloric acid concentration of 2 N. At the end of 22 hours of heating, all the arsenic was recovered in the deposit, while the antimony was retained in the solution. It was found, however, that if the system was subjected to further heating after the precipitation of arsenic there was some deposit of antimony; however, there was no re-solution of the arsenic deposited in the early stages of the experiment. The separation of antimony from bismuth takes place only partially, an observation which may be explained by the very small difference in electropotential between the two metals in solutions of equal concentration. Fur-

ther experiments made by V. V. Ipatieff, concerned the separation of the metals of the platinum family.

#### BASIC SALTS AND METAL OXIDES

The precipitation of crystalline basic salts and metal oxides under hydrogen pressure occurs via hydrolysis. In this case one may also ascribe to water an oxidizing action which becomes more and more intense as the temperature is increased.

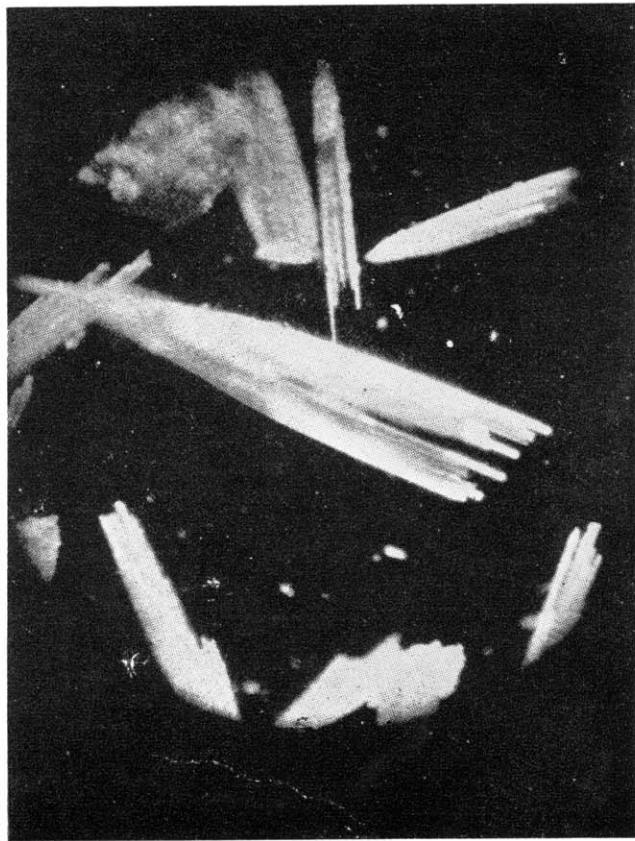
In our experiments we approached 360°C. as the upper limit in order to maintain a liquid phase. We were unable to precipitate metallic iron because its critical temperature of precipitation is above 360°C., and under those conditions water tends to oxidize the iron back to an oxide. The same applies to other members of the iron group.

*Iron.* A solution of iron nitrate produced octahedral crystals of  $\text{Fe}_3\text{O}_4$ ; the same well-developed crystals were obtained from potassium ferrocyanide. However, in the latter case we also obtained in the solution some formic acid, ammonia, and carbonic acid. The formation of these products is to be expected.

Of considerable interest was the formation of crystalline basic salts of iron, produced from ferric phosphate (10). The products contained both di- and trivalent iron in the molecule, having the general formula of



and, depending upon the composition, the resulting



Zinc Silicate Crystals Formed by the Reaction of Zinc Nitrate with Quartz (Ber., 59, 1418 (1926))

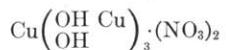
salts had various colors ranging from green to blue to black. These products correspond to the naturally occurring mineral vivianite. Ferric arsenate at 355°C. and 260 atm. produces scorodite ( $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$ ).

*Manganese* (11). Both potassium permanganate,  $\text{KMnO}_4$ , and manganese nitrate,  $\text{Mn}(\text{NO}_3)_2$ , at 300°C. and 150 atm. yielded beautifully developed cubic crystals of  $\text{Mn}_3\text{O}_4$ , identical with the natural mineral hausmannite. Manganese chloride at 360°C. and 350 atm. gave  $\text{MnO} \cdot \text{H}_2\text{O}$ , which is readily oxidized by air.

*Chromium.* Chromium nitrate gave the crystalline chromium oxide hydrate  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

*Nickel and Cobalt* (12). An aqueous solution of nickel cyanide,  $\text{Ni}(\text{CN})_2$ , at 150 to 160°C. and a hydrogen pressure of 80 atm. produces a crystalline deposit of the anhydrous  $\text{NiO}$ ; this compound has yet to be obtained from other salts of nickel. Furthermore, this experiment shows that we are as yet unable to obtain a higher nickel oxide,  $\text{Ni}_2\text{O}_3$ , contrary to our experience with cobalt. In the latter case, a solution of the cobalt salt in the presence of hydrogen under pressure and 260°C. produces  $\text{Co}_2\text{O}_3$ .

*Copper* (13). It was found that 1 and 2-N solutions of copper nitrate at 168°C. and an initial hydrogen pressure of 100 atm. gave a basic salt insoluble in acids and mixtures of acids. The salt was formed in well-developed green crystals analyzing as  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ , the structure of which, according to Werner's theory, is:



This product is found in nature under the name of gerhardtite. It should be noted that if one substitutes nitrogen for hydrogen, the reaction does not take place.

Experiments with copper arsenite under the same conditions gave the mineral domeykite,  $\text{Cu}_3\text{As}$ .

*Zinc* (14). According to the electrolytic solution pressure equation, the replacement of zinc from the water solutions of its salts requires a hydrogen pressure in excess of 50,000 atm. Our experiments have shown that a 1-N solution of zinc nitrate at 350°C. and 350 atm. hydrogen pressure produces the precipitation of metallic zinc, which deposits upon previously formed crystals of zinc oxide. At lower temperatures zinc nitrate produces well-developed needles of zinc oxide with a slight greenish coloration. Zinc sulfate at 290°C. and 250 atm. yielded zinc sulfide crystals,  $\text{ZnS}$ , identical with the naturally occurring mineral zinc blende. It is interesting to note that in several experiments on the precipitation of zinc oxide in quartz tubes, well-developed crystals are formed which upon analysis showed a composition of  $\text{ZnSiO}_3 \cdot 3\text{H}_2\text{O}$ . This compound can be obtained also from a 2-N solution of zinc nitrate if it is heated to 320°C. at 250–300 atm. using unpolished quartz tubes. Similarly it was found that upon heating magnesium and manganese salts with water glass similar crystalline silicates are formed.

The results discussed above provide an indication of the tremendous scope of the study of reactions of inorganic compounds at high pressures and temperatures.

Such a study should explain not only the mechanism of these particular reactions but also the formation of naturally occurring minerals. Such investigations would therefore be of considerable help in geological work. As a matter of fact, in 1912, following one of the reports of the work described above, a well-known geologist predicted that such work would have in the future not only experimental but also commercial application. This was a correct prediction; just at the time of my departure for the United States in 1930 I was asked by the Bayerische Stickstoff Werke in Germany to undertake a continuation of the experiments on the displacement of metals from solutions, since even at that time there was considerable interest in the production of copper from copper sulfate solutions.

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