To us the evidence seems conclusive that two forms of calcite do not exist, but that the heat effect at 970° in the apparatus used by Boeke and by Eitel must be due to some other material present near the thermel junction or to some condition peculiar to the furnace used.

Summary

1. An apparatus has been built with which the pressure-temperature relations in the system, calcium oxide, carbon dioxide can be studied up to 1390° and 1000 megabars pressure.

2. Equilibrium pressures have been determined which, with the previously determined data of Johnston, define the system experimentally from 587° to 1389°, and from 1.0 mm. to 779,000 mm. pressure.

3. An equation for the pressure-temperature curve which fits all data within limits of experimental error up to the eutectic point for the system, calcium carbonate–carbon dioxide is given.

4. The melting point of calcium carbonate containing only 0.38% of calcium oxide is given as 1389° at 779,000 mm. pressure. This is probably very near to the melting point of pure calcium carbonate.

5. The eutectic, experimentally determined, between calcium carbonate and calcium oxide lies at 1240° ± 1°, and 30,000 mm. ± 300 mm. The composition as judged from microscopic examination is about 50% of calcium carbonate: 50% of calcium oxide.

6. ΔH and $-\Delta F$ for the reaction, $CaCO_3 \rightleftharpoons CaO + CO_2$, have been calculated at various temperatures, and equations giving these two quantities in terms of the temperature are discussed.

7. It has been shown by thermodynamic and experimental evidence that only one crystalline form of calcium carbonate exists within the temperature range investigated.

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[Contribution from the Coastal Laboratory of the Carnegie Institution of Washington]

THE REDUCTION OF CARBON DIOXIDE BY ULTRAVIOLET LIGHT

By H. A. Spoehr

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In the many applications of chemistry to biology there is probably no other purely hypothetical suggestion which has served as such a lure for further speculation as the Baeyer[1] formaldehyde theory of photosynthesis. Attention is here confined to a discussion of some experiments on the reduction of carbonic acid to formaldehyde in glass by means of ultraviolet light. Although the conclusions drawn from these experiments can only

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[1] Baeyer, *Ber.*, 3, 63–78 (1870).

with difficulty be applied directly to the phenomenon of photosynthesis, they are nevertheless of considerable significance from a theoretical viewpoint.

During the past few years several investigators have attempted to verify the Baeyer hypothesis and have reported the reduction of carbon dioxide to formaldehyde by means of the light from the quartz mercury-vapor lamp. The results of the various investigators are, however, by no means concordant and it may facilitate a comprehension of the situation to summarize very briefly the different findings.

Usher and Priestley[2] reported that by exposing a saturated solution of carbon dioxide, in quartz tubes, to ultraviolet light they obtained "an easily recognizable quantity of formaldehyde, most of which was in the polymerized form." From this very simple experiment they conclude that "the primary products of photolysis of aqueous carbon dioxide are formaldehyde and hydrogen peroxide, that the evolution of oxygen is due to the decomposition of the latter substance by catalase, and that up to this point the process is entirely non-vital, and can be reconstructed *in vitro*." Berthelot and Gaudechon[3] found that carbon dioxide can be split into carbon monoxide and oxygen by means of ultraviolet light, and that water is split into hydrogen and oxygen. They state that they were able to obtain formaldehyde from carbon dioxide only in the presence of hydrogen.

The experiments of Stoklasa[4] and his co-workers were carried out with potassium bicarbonate and freshly prepared hydrogen. They concluded that formaldehyde is not formed from carbon dioxide and water in ultraviolet light, but only from carbon dioxide in the presence of potassium hydroxide and nascent hydrogen in ultraviolet light; the nascent condition of the hydrogen is absolutely necessary.

Recently Baly, Heilbron and Barker[5] have reported that carbonic acid and various carbonates are reduced to formaldehyde by ultraviolet light and that by the action of this light the formaldehyde is "polymerized" to hexose sugars. These pronouncements have occasioned such far-reaching deductions that an establishment of all the facts seems essential. Baly, Heilbron and Barker state that when ultraviolet light falls upon an aqueous solution of carbon dioxide there are two reactions, first the formation of formaldehyde and second the "polymerization" of this substance to carbohydrates. These two reactions are brought about by different wave lengths; the very short wave lengths ($\lambda=200\ \mu\mu$) produce the formaldehyde, while light of longer wave lengths ($\lambda=290\ \mu\mu$) condenses this to carbohydrates. In order, therefore, to obtain tests for formaldehyde from an illuminated solution of carbonic acid, it is necessary to protect the mixture "from those specific rays which cause polymerization." This Baly and his co-workers claim to have accomplished by agitating the illuminated solution or by selectively absorbing those rays which affect formaldehyde. In order to accomplish this filtering out of rays, solutions of paraldehyde or sodium phenoxide were used. It is this filtering out or protective action which, according to these investigators, explains the behavior of such "photocatalysts" as certain iron and uranium salts. These substances are thus not considered as catalysts but really as anticatalysts, in that they are assumed simply to prevent the further action of light on the formaldehyde.

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[2] Usher and Priestley, *Proc. Roy. Soc.*, **84B**, 101 (1911).

[3] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1690 (1910).

[4] Stoklasa and Zdobnicky, *Monatsh.*. **32**, 53 (1911); *Biochem. Z.*, **41**, 333 (1912).

[5] Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1025 (1921).

In 1910 the author[6] carried out extensive experiments designed to obtain a reduction of carbonic acid by means of ultraviolet light. Thereafter, also, the experiments of Usher and Priestley, Berthelot and Gaudechon, and of Stoklasa were repeated with varying conditions of light intensity, concentration of carbon dioxide, and temperature. However, a definite positive test for formaldehyde was never obtained.

Recently, since the appearance of the claims of Baly, the subject was taken up anew. The source of the ultraviolet light was a 220-volt Cooper-Hewitt quartz mercury-vapor lamp of the horizontal type; clear transparent quartz vessels of 250 cc. capacity were used; in some cases the solutions were exposed to the light in open crystallizing dishes. The solutions were agitated by a stream of washed carbon dioxide. The gas passed through the illuminated solution in the quartz flask and thence into a glass flask containing water to catch any volatile products. In some experiments quartz flasks were stoppered and shaken. Wherever rubber or cork stoppers were used, these were covered with tin foil to protect them against the action of the ultraviolet light. The distance of the quartz flasks from the quartz mercury-vapor lamp was varied from 2 to 15 cm., and the time of illumination from 1 to 60 hours.

The tests for formaldehyde were the following: *p*-dihydrazine-diphenyl (Neuberg[7]); diphenylamine in sulfuric acid (Grafe[8]); 5% resorcinol and 40% sodium hydroxide solutions (Lebbin[9]); rosaniline in sulfurous acid plus hydrochloric acid (Fincke, Willstätter[10]), and the Schryver test.[11] The essential precautions in applying these tests are given in the literature cited.

Neither carbonic acid, potassium bicarbonate, calcium bicarbonate, magnesium bicarbonate, all of which Baly and his co-workers state give "strong reactions for formaldehyde," yielded this substance. The carbonic acid solutions used were saturated at 15°. The concentration of the other substances ranged from saturated to extreme dilution. As catalysts ferric chloride, uranium salts, and colloidal ferric hydroxide were again tried but all of the results were negative regarding formaldehyde and sugar. The question of the selective light filters was also taken up.

It was found that paraldehyde itself in water solution breaks down readily in ultraviolet light. The illuminated solution, besides containing acetaldehyde, reduces Fehling and Benedict solutions in the cold. All

[6] Spoehr, *Biochem. Z.*, **57,** 110 (1913); *Plant World,* **19,** 12 (1916).

[7] Neuberg, *Ber.*, **32,** 189, 196 (1899).

[8] Grafe, *Oesterr. bot. Z.*, **64,** 289 (1906).

[9] Lebbin-Abderhalden, "Handbuch der Biochem. Arbeitsmethoden," Urban and Schwarzenberg, Berlin, **1910,** vol. II, p. 15.

[10] Fincke, *Biochem. Z.*, **52,** 219 (1913). Willstätter, "Untersuchungen über die Assimilation der Kohlensäure, Julius Springer, Berlin, **1918,** p. 386.

[11] Moore, "Biochemistry," Longmans, Green and Co., **1921,** 44.

indications point to the formation of glyco-aldehyde which, already at 60°, goes over into a hexose sugar and reduces Benedict solution in the cold. Thus, paraldehyde, far from being a protection against sugar formation, itself, quite independent of the presence of carbon dioxide yields substances which reduce alkaline copper solutions. No evidence was obtained of the reduction of carbon dioxide itself to formaldehyde.

Summary and Conclusions

Unfortunately, in none of the work which has appeared on this subject have the experimental conditions and apparatus been described with the precision and care which the importance of the subject demands. In view of the fact that it was impossible to detect any reduction of carbon dioxide to formaldehyde by means of ultraviolet light, the only possible conclusion is that in those experiments in which a direct reduction of carbon dioxide to formaldehyde by means of ultraviolet light was reported, there existed certain essential conditions or factors not described in the publications or that there is some misinterpretation of experimental observations.

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THE SEPARATION OF TIN AND ARSENIC

BY LEROY W. MCCAY

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Introduction

When a moderately dilute hydrochloric or sulfuric acid solution of tin in the higher and arsenic in the lower state of oxidation is mixed with a little hydrofluoric acid and then treated with a current of hydrogen sulfide, arsenious sulfide is completely and alone precipitated.

The above observation was referred to in my paper on the "Separation of Tin and Antimony,"[1] also in the one on the "Analysis of Tin-Antimony Alloys,"[2] and N. Howell Furman[3] has utilized it in his scheme for the qualitative analysis of the tin group. The method of procedure is analogous to that employed in separating antimony from tin.

Experimental Part

The solution of the stannic and arsenious compounds, to which from 2 to 5 cc. of 48% hydrofluoric acid has been added, is brought at once into a large platinum dish, heated gently for a few minutes, cooled, diluted to

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[1] McCay, THIS JOURNAL, **31**, 374 (1909).

[2] McCay, *ibid.*, **32**, 1244 (1910).

[3] Furman, *ibid.*, **40**, 902 (1918).