complex was found to be 0.215 ± 0.002 atm., a value which Burk states is somewhat high in comparison with other gases for different enzyme systems. In our own work the data observed were total growth and not growth rates, hence K_{N_2} cannot be precisely determined from these values. However, since under the experimental conditions used, the rate will roughly follow the final observed total growth, an approximation of K_{N_2} is possible. It would appear that K_{N_2} for the symbiotic system is below 0.10 atm. possibly in the neighborhood of 0.05 atm. Whether this difference between the dissociation constants represents a real difference in these two biological nitrogen-fixing systems is still open to question, but further experiments concerned with the character of the enzyme complex should be able to supply an answer.

Summary

The relation of the partial pressure of nitrogen to fixation of the free element by the symbiotic system in red clover has been studied over the range of pN_2 from 0.04 to 1.56 atm. in the presence of no added gas, helium and argon. Statistical analyses of data from 11 experiments indicate that the fixation of nitrogen is essentially independent of pN_2 when the latter exceeds 0.10 to 0.20 atm. but decreases rapidly with pN_2 as the latter is diminished below 0.10 atm. This pN_2 function is characteristic of the nitrogen fixing process since it is not observed in plants supplied with combined nitrogen. The implications of these observations for the mechanism of the symbiotic fixation process are discussed.

MADISON, WISCONSIN RECEIVED JANUARY 29, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Mechanism of the Dehydration of Calcium Sulfate Hemihydrate

BY HARRY B. WEISER, W. O. MILLIGAN AND W. C. EKHOLM

During the past few years several papers have appeared which reopen the question of the chemical individuality of the so-called calcium sulfate hemihydrate or plaster of Paris and the mechanism of its dehydration. Linck and Jung[1] deduced from dehydration data that plaster of Paris loses its water after the manner of zeolites. Balarew[2] at different times has been on all sides of the question. At first[2a] he claimed that the dehydration isobar would indicate that the water is present in the form of a true hydrate; later[2b] he stated that the dehydration curves show the water to be held in a new way "half-hydratic and half-zeolitic"; finally,[2c] he concluded that the water is lost in the manner of zeolites. Gibson and Holt[3] concluded from pressure–temperature curves that the water is lost continuously as in a zeolite. Parsons[4] claimed that all the water in gypsum may be lost by heating without the intermediate formation of a hemihydrate.

Jung,[5] Ramsdell and Partridge[6] and Caspari[7] reported that the x-ray diffraction pattern of calcium sulfate hemihydrate and its dehydration product[8] are identical, in agreement with the view that the hemihydrate is a zeolite. Onorato[9] and Gallitelli[10] found the hemihydrate and dehydrated hemihydrate to have the same type of structure but recognized minor differences in the powder x-radiograms. Feitknecht[11] likewise observed differences in the two patterns provided care was taken to prevent rehydration of the dehydrated hemihydrate. Feitknecht believed that Jung's dehydrated sample must have rehydrated before x-ray examination was made.

From the above survey it appears to be an open question whether "calcium sulfate hemihydrate" is a true chemical hydrate which gives a definite x-radiogram and decomposes to "dehydrated hemihydrate" which gives a different x-radiogram

---

(1) Linck and Jung, *Z. anorg. allgem. Chem.*, **137**, 407 (1924).

(2) (a) Balarew, *ibid.*, **156**, 258 (1926); (b) *Kolloid.-Z.*, **48**, 63 (1929); (c) Balarew and Koluschewa, *ibid.*, **70**, 288 (1935).

(3) Gibson and Holt, *J. Chem. Soc.*, 638 (1933).

(4) Parsons, Univ. Toronto Studies, Geol. Ser., No. 24, 1927, p. 24.

(5) Jung, *Z. anorg. allgem. Chem.*, **142**, 73 (1925).

(6) Ramsdell and Partridge, *Am. Mineral.*, **14**, 59 (1929).

(7) Caspari, *Nature*, **133**, 648 (1934).

(8) It should be pointed out that van't Hoff, Henrichsen and Weigert [*Sitz. akad. Wiss.*, 570 (1901)] prepared a "soluble" form of calcium sulfate by treating gypsum with nitric acid containing 2.38 moles of water per mole of nitric acid, above 50°. This material was named "soluble anhydrite" to distinguish it from the ordinary "insoluble" anhydrite. Although the term "soluble anhydrite" is usually applied to the product formed by the dehydration of calcium sulfate hemihydrate below 200°, Balarew[2b] believes this to be distinct from the "soluble anhydrite" of van't Hoff. Both Balarew and Ramsdell and Partridge[6] prefer to apply the term "dehydrated hemihydrate" to the dehydration product, and this terminology is used in this paper.

(9) Onorato, *Periodico Min.*, **3**, 138 (1932).

(10) Gallitelli, *ibid.*, **4**, 1, 132 (1933).

(11) Feitknecht, *Helv. Chim. Acta*, **14**, 85 (1931).

or whether the system is zeolitic, yielding upon dehydration a product identical in structure with the hydrated material. In the experimental portion of this paper there will be given the results of isobaric dehydration and x-ray diffraction studies which indicate that calcium sulfate hemihydrate is not a zeolite but behaves in all essential respects like a true chemical hydrate.

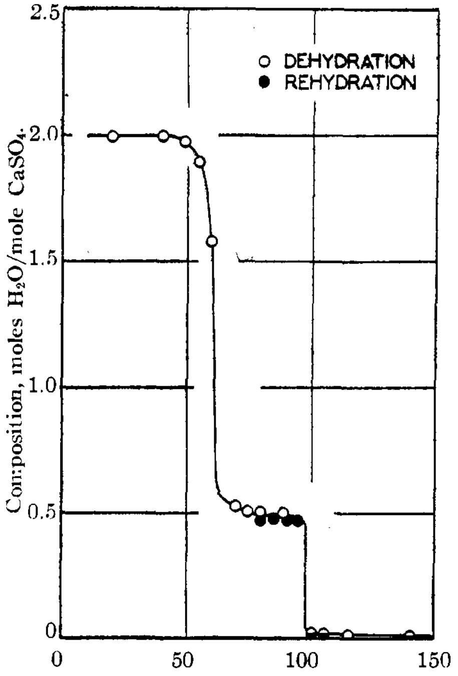

Fig. 1.

Experimental

Isobaric Dehydration.—The source of the calcium sulfate used in the experiments was clear, transparent selenite. Five samples of this material were dehydrated by raising the temperature progressively in an apparatus already described[12] at a constant aqueous vapor pressure of 23.6 mm. (water at 25°). One dehydrated sample was rehydrated by the reverse procedure. The temperature of the oven was maintained constant within ±1° for short periods of time and to within ±2° for longer periods. The samples were held at the various temperatures for days or weeks, weighing at intervals until equilibrium was attained. In some cases, the samples were held as long as five hundred hours at a given temperature. Figure 1 shows the complete dehydration–rehydration isobar for one sample. Figure 2 shows the hemihydrate portion of the dehydration for four samples. The points on the curve represent the average of values which differ by not more than ±0.006 mole of water per mole of calcium sulfate.

X-Ray Diffraction Examination.—A preliminary study was made of the x-ray diffraction patterns for (*a*) $CaSO_4 \cdot 2H_2O$ (selenite); (*b*) hemihydrate prepared by heating (*a*) to 95°; (*c*) dehydrated hemihydrate obtained by heating (*a*) to 145°, in a vacuum; and (*d*) anhydrite. Since the dehydrated hemihydrate is highly hygroscopic,[13] great care must be taken in preparing the samples for x-ray analysis. While still hot the samples were placed in thin tubes of Lindemann glass which were subsequently heated overnight in a vacuum and sealed. The sealed tubes were examined microscopically for possible leaks before placing in the diffraction apparatus. For the preliminary work the General Electric outfit (Kα Mo radiation) was employed. The films were standardized with sodium chloride in the usual way. The results are given in the form of diagrams in Fig. 3. It is apparent that each sample gives a different x-radiogram but the patterns for the hemihydrate and the dehydrated hemihydrate resemble each other rather closely.

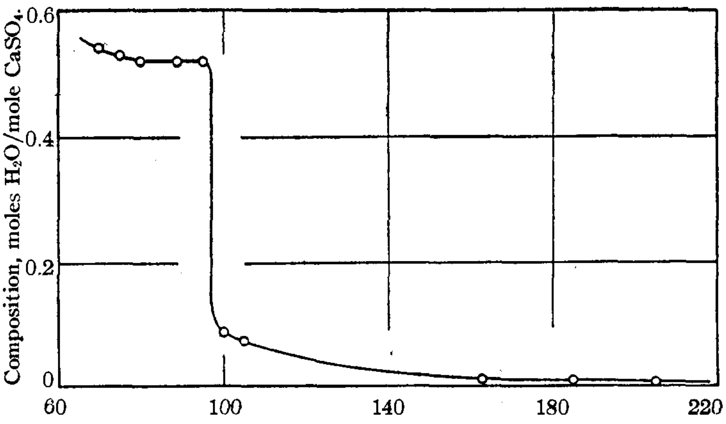

Fig. 2.

In order to make a quantitative study of the differences between the similar patterns of the hemihydrate and dehydrated hemihydrate, diffraction patterns were obtained with a Seemann

---

(12) Weiser and Milligan, *J. Phys. Chem.*, **38**, 513 (1934).

(13) (a) Bower, *Bur. Standards J. Research*, **12**, 241 (1934); (b) Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 653 (1933).

crystal analysis apparatus using Kα Cu radiation filtered through nickel foil. A precision Debye–Scherrer camera, 115.3 mm. in diameter, was employed. For purposes of calibration, pure nickelous oxide[14] prepared by igniting nickel nitrate in a current of nitrogen was mixed with the samples.

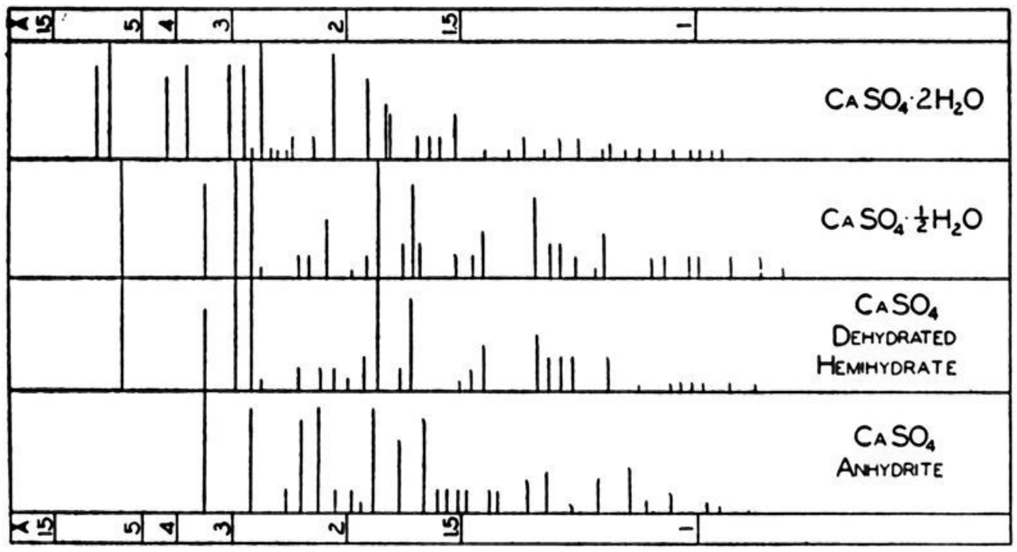

Fig. 3.

Fairly long exposures were required because of the low symmetry of the material, the small primary particle size, the large size and small aperture of the camera, and the need for obtaining a large number of lines. The usual exposure time was thirty to thirty-five hours at 60 m. a. and 40 k. v. Some typical negatives are reproduced in Fig. 4 and the data are shown diagrammatically in Fig. 5.

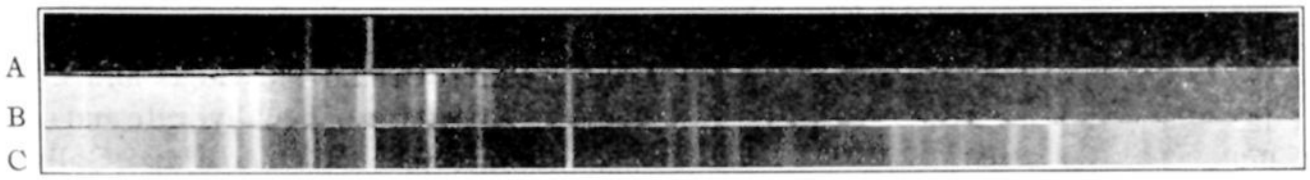

Fig. 4.—A, NiO; B, $CaSO_4 \cdot 0.5H_2O$; C, $CaSO_4$ (Dehydrated hemihydrate).

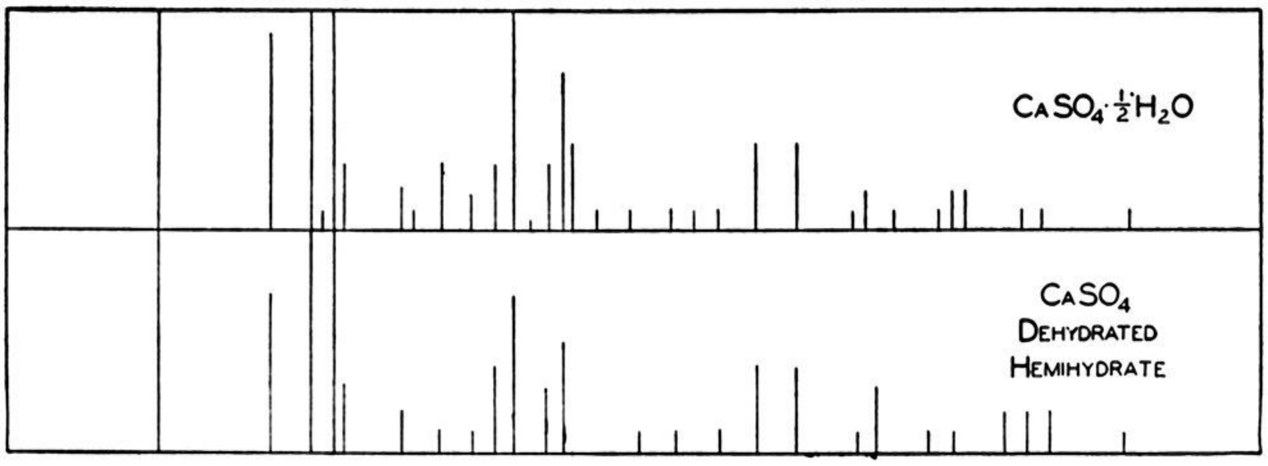

Fig. 5.

For purposes of comparison the corrected data are given in Table I. The interplanar spacings in Å. are denoted by d_{hkl} and the visually estimated, relative intensities by I.

Additional samples for x-ray examination were prepared by dehydrating selenite for twenty-four hours in a vacuum at 134, 159, 180 and 219°. The average composition of these samples was found to be $CaSO_4 \cdot \pm 0.01H_2O$. To avoid any possibility of rehydration, the same procedure for filling and sealing the sample tubes was used as described above. All the patterns, using molybdenum radiation, were identical with those for dehydrated hemihydrate. This indicates the absence of any detectable amount of undecomposed hemihydrate or anhydrite. The samples dehydrated at 159 and 219° were allowed to rehydrate in air for several days. The compositions became, respectively, 0.63 and 0.60 mole of water per mole of calcium sulfate. After rehydrating the sample dehydrated to 134°, it was examined by x-rays, giving a pattern identical with that of hemihydrate.

Discussion of Results

The dehydration isobars for calcium sulfate hemihydrate are typical of those for a definite hydrate which adsorbs a small amount of water and gives a dehydration product which likewise adsorbs water. Since the hemihydrate and es-

---

(14) Cairns and Ott, THIS JOURNAL, **55**, 527 (1933).

TABLE I

X-RAY DIFFRACTION DATA

Hemihydrate $CaSO_4 \cdot 0.5H_2O$		Dehydrated hemihydrate $CaSO_4$	
d_{hkl}	I	d_{hkl}	I
6.000	10	6.000	10
3.468	9	3.468	7
3.002	10	3.012	10
2.898	1		
2.797	10	2.793	10
2.703	3	2.711	3
(NiO) 2.407	7	(NiO) 2.407	7
2.337	2	2.335	3
2.272	1		
2.131	2	2.138	1
(NiO) 2.084	9	(NiO) 2.084	9
2.002	1	1.995	1
1.905	3	1.870	4
1.848	10	1.844	7
1.792	1		
1.732	3	1.741	3
1.692	7	1.692	5
1.662	4		
1.602	1		
1.527	1	1.506	1
(NiO) 1.474	10	(NiO) 1.474	10
1.441	1	1.432	1
1.394	1		
1.353	1	1.349	1
1.296	4	1.292	4
(NiO) 1.257	5	(NiO) 1.257	5
1.238	4	1.237	4
(NiO) 1.203	5	(NiO) 1.203	5
1.167	1	1.161	1
1.153	2	1.142	3
1.122	1		
1.079	1	1.090	1
1.068	2	1.065	1
1.056	2		
(NiO) 1.042	3	(NiO) 1.042	3
		1.026	2
1.011	1	1.009	2
0.9969	1	0.9918	2
(NiO) .9563	4	(NiO) .9563	4
.9418	1	.9441	1
(NiO) .9321	4	(NiO) .9321	4

pecially the dehydrated hemihydrate are known to adsorb water, the evidence seems conclusive that when $CaSO_4 \cdot 2H_2O$ is dehydrated isobarically, a definite hydrate $CaSO_4 \cdot 0.5H_2O$ which adsorbs a small amount of water is first formed and this in turn dehydrates in stepwise fashion to give dehydrated hemihydrate, calcium sulfate, which adsorbs water that is not removed completely at a vapor pressure of 23.6 mm. until well above the decomposition temperature. There is no indication that the water is present in the zeolitic form unless one wishes to apply the term "zeolitic" to the very small amount of water adsorbed first by the very finely divided hemihydrate and later by the resulting dehydrated hemihydrate. The failure of some investigators to obtain a clearly defined reversible step-curve for the decomposition of the hemihydrate is probably due to their failure to wait until equilibrium was established at each temperature.

The conclusions drawn from the dehydration data are supported by the x-ray diffraction studies. Since distinct characteristic differences exist between the x-ray patterns of hemihydrate and dehydrated hemihydrate, it would follow that the two are definite chemical individuals. The close agreement between many strong reflections shows that the type of lattice and the size of the unit cell are similar and that the hemihydrate lattice does not rearrange very much upon loss of the one-half molecule of water. This is the only way in which the hemihydrate resembles a zeolite. The characteristic changes in the pattern which take place on dehydration and rehydration show, however, that the water molecules in the hemihydrate are in a fixed position in the lattice and that the compound is not a zeolite.

The x-ray observations confirm qualitatively those of Feitknecht[11] but since the latter reported his data only in rough graphical form it is impossible to make a quantitative comparison. Since Jung,[5] Ramsdell and Partridge[6] and Caspari[7] believed the patterns of hemihydrate and dehydrated hemihydrate to be the same and Gallitelli[10] and Onorato[9] state that the structures are the same but recognize minor differences in the powder photographs, it would appear that these investigators failed to recognize the existence or the significance of the small but characteristic differences upon dehydration. This may be due to the small size of the cameras employed, the use of molybdenum radiation in some cases, and the failure to use a reference material for standardizing the films. However, there can be no doubt that significant differences exist between the x-radiograms of the two substances when use is made of a relatively large camera, copper radiation, and a standardizing material, and when special care is taken to avoid rehydration of the dehydrated hemihydrate.

Summary

1. Contrary to the conclusions of Linck and Jung, Balarew, Gibson and Holt, and others, the dehydration curve of calcium sulfate hemi-

hydrate gives a definite step indicating that the compound is a true chemical hydrate and not a zeolite.

2. Contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Gallitelli, Onorato and others, calcium sulfate hemihydrate and "dehydrated hemihydrate" do not have identical structures. The x-radiograms of the two substances are similar, showing that the structures are similar; but the existence of definite characteristic differences between the two patterns indicates that the water molecules in the hemihydrate occupy fixed position in the lattice. These observations likewise support the view that calcium sulfate hemihydrate is a chemical individual and that the process of dehydration is not zeolitic in character.

HOUSTON, TEXAS RECEIVED APRIL 27, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 546]

Strong Oxidizing Agents in Nitric Acid Solution. I. Oxidation Potential of Cerous–Ceric Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Plan of these Investigations

In connection with the recent investigations made by Noyes, Hoard, Pitzer and Dunn[1,2] of argentic salts in nitric acid solution, electromotive force measurements were made by Noyes and Kossiakoff[3] to determine the oxidation potential of argentous–argentic salts (Ag^{I}, Ag^{II}); and the result (1.914 volts) was compared with those of other strong oxidizing agents for which reliable data exist. As these data are rather limited, it seemed desirable to carry out researches on the oxidation potential of other powerful oxidizing substances; and it is the purpose of this series of papers to present the results obtained with cerous–ceric salts (Ce^{III}, Ce^{IV}), with thallous–thallic salts (Tl^{I}, Tl^{III}), and with cobaltous–cobaltic salts (Co^{II}, Co^{III}) in nitric acid solution.

The method of measurement was much the same as that used for argentous–argentic salts by Noyes and Kossiakoff, to whose article reference should be made for certain details of procedure. The conditions are simpler, however, in the case of ceric nitrate or thallic nitrate, in that these substances, unlike argentic nitrate, do not undergo at room temperature spontaneous reduction to cerous or thallous salt.

In this first paper are presented the results of measurements on cerous–ceric cells. Such cells were first measured by Baur and Glaessner.[4] They used cells containing cerous and ceric salts in nitric and sulfuric acid solutions; but carried out the work at "room temperature," and eliminated the liquid potential only to the extent that this is accomplished by inserting a saturated solution of potassium chloride between the cerium and the calomel electrodes. A satisfactory value therefore cannot be calculated for the oxidation potential from their data.

More recently, Kunz[5] studied the formal potential of cerous–ceric salts in 0.5 and 1.0 formal sulfuric acid solutions.

In order to determine the value in nitrate solution, which is likely to form complexes to a less extent, and to eliminate largely the liquid potential, we measured at 25 and at 0° cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \mathrm{atm.}),\ \mathrm{HClO_4}\,(c'),\ \left\{\mathrm{HNO_3}\,(c) + \begin{matrix}\mathrm{Ce^{IV}}\,(c_2)\\ \mathrm{Ce^{III}}\,(c_1)\end{matrix}\right\},\ \mathrm{Pt}$$

These experiments will now be described.

Apparatus and Materials

Preparation and Analysis of Solutions.—In preparing the stock solutions of cerous and ceric nitrate, C. P. hydrated cerous nitrate was used to make up a solution approximately 0.1 *f* in cerous nitrate and 1 *f* in nitric acid (to prevent subsequent hydrolysis). A 17-cm. layer of this solution gave no absorption spectrum, showing the absence of other rare-earth elements. The solution was then divided into two nearly equal portions.

A solution of ceric nitrate was prepared by electrolytic oxidation of one of these portions with a current of 2 amperes at 6–8 volts, till samples removed and titrated with ferrous sulfate solution showed that the oxidation was nearly complete.

The ceric nitrate solution thus prepared was analyzed as

---

[1] Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221–1229 (1935).

[2] Noyes, Pitzer and Dunn, *ibid.*, **57**, 1229–1237 (1935).

[3] Noyes and Kossiakoff, *ibid.*, **57**, 1238–1242 (1935).

[4] Baur and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

[5] Kunz, THIS JOURNAL, **53**, 98 (1931).