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Title: History of Phosphorus

Author: Eduard Farber

Release Date: September 20, 2010 [EBook #33766]

Language: English

\*\*\* START OF THIS PROJECT GUTENBERG EBOOK HISTORY OF PHOSPHORUS \*\*\*

Produced by Chris Curnow, Joseph Cooper, Louise Pattison

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http://www.pgdp.net

Transcriber's Note.

This is Paper 40 from the Smithsonian Institution United States National

Museum Bulletin 240, comprising Papers 34-44, which will also be

available as a complete e-book.

The front material, introduction and relevant index entries from the

Bulletin are included in each single-paper e-book.

Corrections are listed at the end of the e-book.

SMITHSONIAN INSTITUTION

UNITED STATES NATIONAL MUSEUM

BULLETIN 240

[Illustration]

SMITHSONIAN PRESS

MUSEUM OF HISTORY AND TECHNOLOGY

CONTRIBUTIONS FROM THE MUSEUM OF HISTORY AND TECHNOLOGY

\_Papers 34-44\_

\_On Science and Technology\_

SMITHSONIAN INSTITUTION . WASHINGTON, D.C. 1966

\_Publications of the United States National Museum\_

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In these series, the Museum publishes original articles and monographs

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Museum of Natural History and the Museum of History and

Technology--setting forth newly acquired facts in the fields of

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organizations, and to specialists and others interested in the different

subjects.

The \_Proceedings\_, begun in 1878, are intended for the publication, in

separate form, of shorter papers from the Museum of Natural History.

These are gathered in volumes, octavo in size, with the publication date

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the United States National Herbarium\_, and since 1959, in \_Bulletins\_

titled "Contributions from the Museum of History and Technology," have

been gathered shorter papers relating to the collections and research of

that Museum.

The present collection of Contributions, Papers 34-44, comprises

Bulletin 240. Each of these papers has been previously published in

separate form. The year of publication is shown on the last page of each

paper.

FRANK A. TAYLOR \_Director, United States National Museum\_

CONTRIBUTIONS FROM

THE MUSEUM OF HISTORY AND TECHNOLOGY:

PAPER 40

HISTORY OF PHOSPHORUS

\_Eduard Farber\_

THE ELEMENT FROM ANIMALS AND PLANTS 178

EARLY USES 181

CHEMICAL CONSTITUTION OF PHOSPHORIC ACIDS 182

PHOSPHATES AS PLANT NUTRIENTS 185

FROM INORGANIC TO ORGANIC PHOSPHATES 187

PHOSPHATIDES AND PHOSPHAGENS 189

NUCLEIN AND NUCLEIC ACIDS 192

PHOSPHATES IN BIOLOGICAL PROCESSES 197

MEDICINES AND POISONS 198

\_Eduard Farber\_

HISTORY OF PHOSPHORUS

\_The "cold light" produced by phosphorus caused it to be

considered a miraculous chemical for a long time after its

discovery, about 1669. During the intervening three centuries

numerous other chemical miracles have been found, yet

phosphorus retains a special aura of universal importance in

chemistry. Many investigators have occupied themselves with

this element and its diverse chemical compounds. Further

enlightenment and insight into the ways of nature can be

expected from these efforts.\_

\_Not only is the story of phosphorus a major drama in the

history of chemistry; it also illustrates, in a spectacular

example, the growth of this science through the discovery of

connections between apparently unrelated phenomena, and the

continuous interplay between basic science and the search for

practical usage.\_

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When phosphorus was discovered, nearly three centuries ago, it was

considered a miraculous thing. The only event that provoked a similar

emotion was the discovery of radium more than two centuries later. The

excitement about the \_Phosphorus igneus\_, Boyle's \_Icy Noctiluca\_, was

slowly replaced by, or converted into, chemical research. Yet, if we

would allow room for emotion in research, we could still be excited

about the wondrous substance that chemical and biological work continues

to reveal as vitally important. It is a fundamental plant nutrient, an

essential part in nerve and brain substance, a decisive factor in muscle

action and cell growth, and also a component in fast-acting, powerful

poisons. The importance of phosphorus was gradually recognized and the

means by which this took place are characteristic and similar to other

developments in the history of science. This paper was written in order

to summarize these various means which led to the highly complex ways of

present research.

The Element from Animals and Plants

It was a little late to search for the philosophers' stone in 1669, yet

it was in such a search that phosphorus was discovered. Wilhelm Homberg

(1652-1715) described it in the following manner: Brand, "a man little

known, of low birth, with a bizarre and mysterious nature in all he

did, found this luminous matter while searching for something else. He

was a glassmaker by profession, but he had abandoned it in order to be

free for the pursuit of the philosophical stone with which he was

engrossed. Having put it into his mind that the secret of the

philosophical stone consisted in the preparation of urine, this man

worked in all kinds of manners and for a very long time without finding

anything. Finally, in the year 1669, after a strong distillation of

urine, he found in the recipient a luminant matter that has since been

called phosphorus. He showed it to some of his friends, among them

Mister Kunkel [sic]."[1]

Neither the name nor the phenomenon were really new. Organic

phosphorescent materials were known to Aristotle, and a lithophosphorus

was the subject of a book published in 1640, based on a discovery made

by a shoemaker, Vicenzo Casciarolo, on a mountain-side near Bologna in

1630.[2] Was the substance new which Brand showed to his friends? Johann

Gottfried Leonhardi quotes a book of 1689 in which the author, Kletwich,

claims that this phosphorus had already been known to Fernelius, the

court physician of King Henri II of France (1154-1189).[3] To the same

period belongs the "Ordinatio Alchid Bechil Saraceni philosophi," in

which Ferdinand Hoefer found a distillation of urine with clay and

carbonaceous material described, and the resulting product named

escarbuncle.[4] It would be worth looking for this source; although

Bechil would still remain an entirely unsuccessful predecessor, it does

seem strange that in all the distillations of arbitrary mixtures, the

conditions should never before 1669 have been right for the formation

and the observation of phosphorus.

[Illustration: Figure 1.--THE ALCHEMIST DISCOVERS PHOSPHORUS. A painting

by Joseph Wright (1734-1779) of Derby, England.]

For Brand's contemporaries at least, the discovery was new and exciting.

The philosopher Gottfried Wilhelm von Leibniz (1646-1716) considered it

important enough to devote some of his time (between his work as

librarian in Hanover and Wolfenbüttel, his efforts to reunite the

Protestant and the Catholic churches, and his duties as Privy Councellor

in what we would call a Department of Justice) to a history of

phosphorus. This friend of Huygens and Boyle tried to prove that Kunckel

was not justified in claiming the discovery for himself.[5] Since then,

it has been shown that Johann Kunckel (1630-1703) actually worked out

the method which neither Brand nor his friend Kraft wanted to disclose.

Boyle also developed a method independently, published it, and

instructed Gottfried Hankwitz in the technique. Later on, Jean Hellot

(1685-1765) gave a meticulous description of the details and a long

survey of the literature.[6]

[Illustration: Figure 2.--GALLEY-OVEN, 1869. The picture is a cross

section through the front of the oven showing one of the 36 retorts, the

receivers for the distillate, and the space in the upper story used for

evaporating the mixture of acid solution of calcium phosphate and coal.

(According to ANSELME PAYEN, \_Précis de Chimie industrielle\_, Paris,

1849; reproduced from HUGO FLECK, \_Die Fabrikation chemischer Produkte

aus thierischen Abfällen\_, Vieweg, Braunschweig, 1862, page 80 of volume

2, 2nd group, of P. BOLLEY'S \_Handbuch der chemischen Technologie\_.)]

To obtain phosphorus, a good proportion of coal (regarded as a type of

phlogiston) was added to urine, previously thickened by evaporation and

preferably after putrefaction, and the mixture was heated to the highest

attainable temperature. It was obvious that phlogiston entered into the

composition of the distillation product. The question remained whether

this product was generated \_de novo\_. In his research of 1743 to 1746,

Andreas Sigismund Marggraf (1709-1782) provided the answer. He found the

new substance in edible plant seeds, and he concluded that it enters the

human system through the plant food, to be excreted later in the urine.

He did not convince all the chemists with his reasoning. In 1789,

Macquer wrote: "There are some who, even at this time, hold that the

phosphorical ('phosphorische') acid generates itself in the animals and

who consider this to be the 'animalistic acid.'"[7]

Although Marggraf was more advanced in his arguments than these

chemists, yet he was a child of his time. The luminescent and

combustible, almost wax-like substance impressed him greatly. "My

thoughts about the unexpected generation of light and fire out of water,

fine earth, and phlogiston I reserve to describe at a later time." These

thoughts went so far as to connect the new marvel with alchemical wonder

tales. When Marggraf used the "essential salt of urine," also called

\_sal microcosmicum\_, and admixed silver chloride ("horny silver") to it

for the distillation of phosphorus, he expected "a partial conversion of

silver by phlogiston and the added fine vitrifiable earth, but no trace

of a more noble metal appeared."[8]

Robert Boyle had already found that the burning of phosphorus produced

an acid. He identified it by taste and by its influence on colored plant

extracts serving as "indicators." Hankwitz[9] described methods for

obtaining this acid, and Marggraf showed its chemical peculiarities.

They did not necessarily establish phosphorus as a new element. To do

that was not as important, at that time, as to conjecture on analogies

with known substances. Underlying all its unique characteristics was the

analogy of phosphorus with sulfur. Like sulfur, phosphorus can burn in

two different ways, either slowly or more violently, and form two

different acids. The analogy can, therefore, be extended to explain the

results in both groups in the same way. In the process of burning, the

combustible component is removed, and the acid originally combined with

the combustible is set free. Whether the analogy should be pursued even

further remained doubtful, although some suspicion lingered on for a

while that phosphoric acid might actually be a modified sulfuric acid.

Analogies and suspicions like these were needed to formulate new

questions and stimulate new experiments. They are cited here for their

important positive value in the historical development, and not for the

purpose of showing how wrong these chemists were from our point of

view, a point of view which they helped to create.

The widespread interest in the burning of sulfur and of phosphorus,

naturally, caught Lavoisier's attention. In his first volume of

\_Opuscules Physiques et Chimiques\_ (1774), he devoted 20 pages to his

experiments on phosphorus. He amplified them a few years later[10] when

he attributed the combustion to a combination of phosphorus with the

"eminently respirable" part of air. In the \_Méthode de Nomenclature

Chimique\_ of 1787, the column of "undecomposed substances" lists sulfur

as the "radical sulfurique," and phosphorus, correspondingly, as the

"radical phosphorique." The acids are now shown to be compounds of the

"undecomposed" radicals, the complete reversion of the previous concept

of this relationship. A part of the old analogy remained as far as the

acids are concerned: sulfuric acid corresponds to phosphoric; sulfurous

acid to phosphorous acid with less oxygen than in the former.[11]

Early Uses

In the 18th century, phosphorus was a costly material. It was produced

mostly for display and to satisfy curiosity. Guillaume François Rouelle

(1703-1770) demonstrated the process in his lectures, and, as Macquer

reports, he "very often" succeeded in making it.[12] Robert Boyle had

the idea of using phosphorus as a light for underwater divers.[13] A

century later, "instant lights" were sold, with molten phosphorus as the

"igniter," but they proved cumbersome and unreliable.[14] Because white

phosphorus is highly poisonous, an active development of the use in

matches occurred only after the conversion of the white modification

into the red had been studied by Émile Kopp (1844), by Wilhelm Hittorf

(1824-1914) and, in its practical application, by Anton Schrötter

(1802-1875).[15]

[Illustration: Figure 3.--DISTILLATION APPARATUS (1849) for refining

crude phosphorus. The crude phosphorus is mixed with sand under hot

water, cooled, drained, and filled into the retort. The outlet of the

retort, at least 6 cm. in diameter, is partially immersed in the water

contained in the bucket. A small dish, made from lead, with an iron

handle, receives the distilled phosphorus. (From HUGO FLECK, \_Die

Fabrikation chemischer Produkte ...\_ page 90.)]

The most exciting early use, however, was in medicine. It is not

surprising that such a use was sought at that time. Any new material

immediately became the hope of ailing mankind--and of striving

inventors.[16] Phosphorus was prescribed, in liniments with fatty oils

or as solution in alcohol and ether, for external and internal

application. A certain Dr. Kramer found it efficient against epilepsy

and melancholia (1730). A Professor Hartmann recommended it against

cramps.[17] However, in the growing production of phosphorus for

matches, the workers experienced the poisonous effects. In the plant of

Black and Bell at Stratford, this was prevented by inhaling turpentine.

Experiments on dogs were carried out to show that poisoning by

phosphorus could be remedied through oil of turpentine.[18]

[Illustration: Figure 4.--APPARATUS FOR CONVERTING WHITE PHOSPHORUS into

the red allotropic form, 1851. Redistilled phosphorus is heated in the

glass or porcelain vessel (g) which is surrounded by a sandbath (e) and

a metal bath (b). Vessel (j) is filled with mercury and water; together

with valve (k), it serves as a safety device. The alcohol lamp (l) keeps

the tube warm against clogging by solidified vapors. Because of hydrogen

phosphides, the operation, carried out at 260° C., had to be watched

very carefully. (According to Arthur Albright, 1851; reproduced from

HUGO FLECK, \_Die Fabrikation chemischer Produkte ...\_, page 112.)]

Chemical Constitution of Phosphoric Acids

In a long article on phosphorus, Edmond Willm wrote in 1876: "For a

century, urine was the only source from which phosphorus was obtained.

After Gahn, in 1769, recognized the presence of phosphoric acid in

bones, Scheele indicated the procedure for making phosphorus from

them."[19] Actually, Gahn used at first hartshorn (\_Cornu cervi

ustum\_), and Scheele doubted, until he checked it himself, that his

esteemed friend was right. A few years later, Scheele corrected Gahn's

assumption that the \_sal microcosmicum\_ was an ammonia salt; instead, it

is "a tertiary neutral salt, consisting of \_alkali minerali fixo\_ (i.e.,

sodium), \_alkali volatili\_, and \_acido phosphori\_."[20]

In the years after 1770, phosphorus was discovered in bones and many

other parts of various animals. Treatment with sulfuric acid decomposed

these materials into a solid residue and dissolved phosphoric acid. Many

salts of this acid were produced in crystalline form. Heat resistance

had been considered one of the outstanding characteristics of phosphoric

acid. Now, however, in the processes of drying and heating certain

phosphates, it became clear that three kinds of phosphoric acids could

be produced: \_ortho\_, \_pyro\_, and \_meta\_.

Berzelius cited these acids as examples of compounds which are ISOMERIC.

This word was intended to designate compounds which contain the same

number of atoms of the same elements but combined in different manners,

thereby explaining their different chemical properties and crystal

forms. It was in 1830 that Berzelius propounded this companion of the

concept, ISOMORPHISM, which was to collect all cases of equal crystal

form in compounds in which equal numbers of atoms of different elements

are put together in the same manner. Together, the two concepts of

isomerism and isomorphism seemed to cover all the known exceptions from

the simplest assumption as to specificity and chemical composition.

However, only a few years later Thomas Graham (1805-1869) proved that

the three phosphoric acids are not isomeric. He used the proportion of 2

P to 5 O in the oxide which Berzelius had thought justified at least

until "an example of the contrary could be sufficiently

established."[21] Refining the techniques of Gay-Lussac (1816) and

several other investigators, Graham characterized the three phosphoric

acids as "a terphosphate, a biphosphate, and phosphate of water."

Actually, this was the wrong terminology for what he meant and

formulated as trihydrate, bihydrate, and monohydrate of phosphorus

oxide. In his manner of writing the formulas, each dot over the symbol

for the element was to indicate an atom of oxygen; thus, he wrote:

... :: .. ... . .

H^{3} P H^{2} P and H P.[22]

[Illustration: Figure 5.--OVEN FOR THE CALCINATION OF BONES, about 1870.

"The operation is carried out in a rather high oven, such as shown....

The fresh bones are thrown in at the top of the oven, B. First, fuel in

chamber F is lighted, and a certain quantity of bones is burnt on the

grid D. When these bones are burning well, the oven is gradually filled

with bones, and the combustion maintains itself without addition of

other fuel. A circular gallery, C, surrounds the bottom of the oven and

carries the products of combustion into the chimney, H. The calcined

bones are taken out at the lower opening, G, by removing the bars of

grid B." (Translation of the description from FIGUIER, \_Merveilles de

l'industrie\_, volume 3, 1874, page 537.)]

[Illustration: Figure 6.--AN ADVERTISEMENT with view of plant for

manufacturing superphosphate about 1867. (From E. T. FREEDLEY,

\_Philadelphia and its Manufacturers in 1867\_, page 288.)]

Graham had come to this understanding of the phosphoric acids through

his previous studies of "Alcoates, definite compounds of Salts and

Alcohol analogous to the Hydrates" (1831). Liebig started from analogies

he saw with certain organic acids when he formulated the phosphoric

acids with a constant proportion of water (aq.) and varying proportions

of "phosphoric acid" (P) as follows:

2 P 3 aq. phosphoric acid

3 P 3 aq. pyrophosphoric acid

6 P 3 aq. metaphosphoric acid.

[Illustration: Figure 7.--FLORIDA HARD-ROCK PHOSPHATE MINING. (From

Carroll D. Wright, \_The Phosphate Industry of the United States\_, sixth

special report of the Commissioner of Labor, Government Printing Office,

Washington, 1893, plate facing page 43.)]

Salts are formed when a "basis," i.e., a metal oxide, replaces water.

When potassium-acid sulfate is neutralized by sodium base, the acid-salt

divides into Glauber's salt and potassium sulfate, which proves the

acid-salt to be a mixture of the neutral salt with its acid. Sodium-acid

phosphate behaves quite differently. After neutralization by a potassium

"base" (hydroxide), the salt does not split up; a uniform

sodium-potassium phosphate is obtained. Therefore, phosphoric acid is

truly three-basic![23]

This result has later been confirmed, but the analogy by means of which

it had been obtained was very weak, in certain parts quite wrong.

The acids from the two lower oxides of phosphorus were also considered

as three-basic. Adolphe Wurtz (1817-1884) formulated them in 1846,

according to the theory of chemical types:

(PO)···

O^{3} phosphoric acid

H^{3}

(PHO)··

O^{2} phosphorus acid

H^{2}

(PH^{2}O)·

O hypophosphorous acid.[24]

H

Further proof for these constitutions was sought in the study of the

esters formed when the acids react with alcohols.

Among the analogies and generalizations by which the research on

phosphoric acid was supported, and to the results of which it

contributed a full share, was the new theory of acids. Not oxygen,

Lavoisier's general acidifier, but reactive hydrogen determines the

character of acids. In this brief survey, it seems sufficient just to

mention this connection without describing it in detail.

The study of phosphoric acids led to important new concepts in

theoretical chemistry. The finding of polybasicity was extended to other

acids and formed the model that helped to recognize the

polyfunctionality in other compounds, like alcohols and amines. The

hydrogen theory of acids was fundamental for further advance. In another

dimension, it is particularly interesting to see that large-scale

applications followed almost immediately and directly from the new

theoretical insight. The first and foremost of these applications was in

agriculture.

Phosphates as Plant Nutrients

One hundred years after the discovery of "cold light," the presence of

phosphorus in plants and animals was ascertained, and its form was

established as a compound of phosphoric acid. This knowledge had little

practical effect until the "nature" of the acid, in its various forms,

was explained through the work of Thomas Graham. From it, there started

a considerable technical development.

At about that time (1833), the Duke of Richmond proved that the

fertilizing value of bones resided not in the gelatin, nor in the

calcium, but in the phosphoric acid. Thus, he confirmed what Théodore de

Saussure had said in 1804, that "we have no reason to believe" that

plants can exist without phosphorus. Unknowingly at first, the farmer

had supplied this element by means of the organic fertilizers he used:

manure, excrements, bones, and horns. Now, with the value of phosphorus

known, a search began for mineral phosphates to be applied as

fertilizers. Jean Baptiste Boussingault (1802-1887), an agricultural

chemist in Lyons, traveled to Peru to see the guano deposits. Garcilaso

de la Vega (ca. 1540 to ca. 1616) noted in his history of Peru (1604)

that guano was used by the Incas as a fertilizer. Two hundred years

later, Alexander von Humboldt revived this knowledge, and Humphry Davy

wrote about the benefits of guano to the soil. Yet, the application of

this fertilizer developed only slowly, until Justus Liebig sang its

praise. Imports into England rose and far exceeded those into France

where, between 1857 and 1867, about 50,000 tons were annually received.

The other great advance in the use of phosphatic plant nutrients started

with Liebig's recommendation (1840) to treat bones with sulfuric acid

for solubilization. This idea was not entirely new; since 1832, a

production of a "superphosphate" from bones and sulfuric acid had been

in progress at Prague. At Rothamsted in 1842, John Bennet Lawes

obtained a patent on the manufacture of superphosphate. Other

manufactures in England followed and were successful, although James

Muspratt (1793-1886) at Newton lost much time and "some thousands of

pounds" on Liebig's idea of a "mineral manure."

[Illustration: Figure 8.--FLORIDA LAND-PEBBLE PHOSPHATE MINING. (From

Carroll D. Wright, \_The Phosphate Industry of the United States ...\_,

plate facing page 58.)]

It was difficult enough to establish the efficacy of bones and

artificially produced phosphates in promoting the growth of plants under

special conditions of soils and climate; therefore, the question as to

the action of phosphates in the growing plant was not even seriously

formulated at that time. The beneficial effects were obvious enough to

increase the use of phosphates as plant nutrients and to call for new

sources of supply. Active developments of phosphate mining and treating

started in South Carolina in 1867, and in Florida in 1888.[25]

In a reciprocal action, more phosphate application to soils stimulated

increasing research on the conditions and reactions obtaining in the

complex and varying compositions called soil. The findings of

bacteriologists made it clear that physics and chemistry had to be

amplified by biology for a real understanding of fertilizer effects.

After 1900, for example, Julius Stoklasa (1857-1936) pointed out that

bacterial action in soil solubilizes water-insoluble phosphates and

makes them available to the plants.[26]

[Illustration: Figure 9.--FLORIDA RIVER-PEBBLE PHOSPHATE MINING. (From

Carroll D. Wright, \_The Phosphate Industry of the United States ...\_,

plate facing page 64.)]

The insight into the importance of phosphorus in organisms, especially

since Liebig's time, is reflected in the work of Friedrich Nietzsche

(1844-1900). This "re-valuator of all values" who modestly said of

himself: "I am dynamite!" once explained the human temperaments as

caused by the inorganic salts they contain: "The differences in

temperament are perhaps caused more by the different distribution and

quantities of the inorganic salts than by everything else. Bilious

people have too little sodium sulfate, the melancholics are lacking in

potassium sulfate and phosphate; too little calcium phosphate in the

phlegmatics. Courageous natures have an excess of iron phosphate." (See

volume 12 of \_Nietzsche's Works\_, edit. Naumann-Kröner, Leipzig, 1886.)

In this strange association of inorganic salts with human temperaments,

the role of iron phosphate as a producer of courage is particularly

interesting. What would a modern philosopher conclude if he followed the

development of insight into the composition and function of complex

phosphate compounds in organisms?

From Inorganic to Organic Phosphates

By the middle of the 19th century, the source of phosphorus in natural

phosphates and the chemistry of its oxidation products had been

established. The main difficulty that had to be overcome was that these

oxidation products existed in so many forms, not only several stages of

oxidation, but, in addition, aggregations and condensations of the

phosphoric acids. Once the fundamental chemistry of these acids was

elucidated, the attention of chemists and physiologists turned to the

task of finding the actual state in which phosphorus compounds were

present in the organisms. It had been a great advance when it had been

shown that plants need phosphates in their soil. This led to the next

question concerning the materials in the body of the plant for which

phosphates were being used and into which they were incorporated.

Similarly, the knowledge that animals attain their phosphates from the

digested plant food called, in the next step of scientific inquiry, for

information on the nature of phosphates produced from this source.

The method used in this inquiry was to subject anatomically separated

parts of the organisms to chemical separations. The means for such

separations had to be more gentle than the strong heat and destructive

chemicals that had been considered adequate up to then. The

interpretation of the new results naturally relied on the general

advance of chemistry, the development of new methods for isolating

substances of little stability, of new concepts concerning the

arrangements of atoms in the molecules, and of new apparatus to measure

their rates of change.

In the system of chemistry, as it developed in the first half of the

19th century, the new development can be characterized as the turn from

inorganic to organic phosphates, from the substance of minerals and

strong chemical interactions to the components in which phosphate groups

remained combined with carbon-containing substances.

[Illustration: Figure 10.--ELECTRIC FURNACE FOR PRODUCING ELEMENTAL

PHOSPHORUS, invented by Thomas Parker of Newbridge, England, and

assigned to The Electric Construction Corporation of the same place. The

drawing is part of United States patent 482,586 (September 13, 1892).

The furnace was patented in England on October 29, 1889 (no. 17,060); in

France on June 23, 1890 (no. 206,566); in Germany on June 17, 1890 (no.

55,700); and in Italy on October 23, 1890 (no. 431). The following

explanation is cited from the U.S. patent:

Figure 1 [shown here] is a vertical section of the furnace, and Fig. 2

is a diagram to illustrate the means for regulating the electro-motive

force or quantity of current across the furnace.

F is the furnace containing the charge to be treated. It has an

inlet-hopper at \_a\_, with slides AA, by which the charge can be admitted

without opening communication between the interior of the furnace and

the outer air.

B is a screw conveyer by which the charge is pushed forward into the

furnace.

\_c´c´\_ are the electrodes, consisting of blocks or cylinders or the like

of carbon fixed in metal socket-pieces \_c c\_, to which the

electric-circuit wires \_d\_ from the dynamo D are affixed. The current,

as aforesaid, may be either continuous or alternating. \_c^{2}c^{2}\_ are

rods of metal or carbon, which are used to establish the electric

circuit through the furnace, the said rods being inserted into holes in

conductors \_c^{3}\_ (in contact with the socket-pieces \_c\_) and in the

furnace, as shown.

\_g\_ is the outlet for the gas or vapor, \_h\_ the slag-tap hole, and \_x\_

the opening for manipulating the charge, the said openings being closed

by clay or otherwise when the furnace is at work.

I use coke or other form of carbon in the charge between the electrodes

\_c´\_, the said coke being in contact with the said electrodes, so that

complete incandescence is insured.

A means for varying the electro-motive force or quantity of current

across the furnace with the varying resistance of the charge is

illustrated by the diagram, Fig. 2. \_c´ c^{2}\_ indicate the electrodes

in the furnace, as in Fig. 1, and D is the dynamo and T its terminals. E

represents the exciting-circuit. R R are resistances, and R S is the

resistance-switch, which is operated to put in more or less resistance

at R as the resistance of the charge in the furnace lessens or

increases. This switch may be automatically operated, and a suitable

arrangement for the purpose is a current-regulator such as is described

in the specification of English Letters Patent No. 14,504, of September

14, 1889, granted to William Henry Douglas and Thomas Hugh Parker.]

[Illustration:

T. PARKER.

ELECTRICAL FURNACE.

Patented Sept. 13, 1892.

FIG. 1.]

[Illustration: FIG. 2.

\_Inventor

Thomas Parker\_

\_By his attorneys

Howson and Howson\_

\_Witnesses:

George Baumann

John Revell\_]

[Illustration: Figure 11.--DIPPING OF MATCHSTICKS in France, about 1870.

The frame which holds the matches so that one end protrudes at the

bottom, is lowered over a pan containing molten sulfur. The

sulfur-covered matches are then dropped into a phosphorous paste. See

figure 12. (From FIGUIER, \_Merveilles de l'industrie\_, volume 3, 1874,

page 575.)]

Phosphatides and Phosphagens

The important phosphorus compounds in organisms are much more complex

than the simple salts, to which Nietzsche attributed such influence on

man's character. Long before he wrote, it was known that phosphoric acid

combines not only with inorganic bases to form salts, but with alcohols

to form esters. In the middle of the 19th century, Théophile Juste

Pelouze (1807-1867) extended this knowledge to an ester of glycerol.

This proved to be significant in several respects. Glycerol had been

shown by Michel Chevreul (1786-1889) as the substance in fats that is

released in the process of soap boiling, when the fatty acids are

converted into their salts. That it has the nature of an alcohol had

been demonstrated by Marcellin Berthelot. Instead of one "alcoholic"

hydroxyl group, OH, like ethanol (the alcohol of fermentation), or two

hydroxyl groups (like ethylene glycol), glycerol contains three such

groups. It was the only "natural" alcohol known at that time. That this

alcohol would combine with phosphoric acid could be predicted, but that

the ester, as obtained by Pelouze, still contained free acidic functions

and formed a water-soluble barium salt was a new experience.

[Illustration: Figure 12.--PAN FOR DIPPING MATCHSTICKS into phosphorus

paste, about 1870. The letters on the picture are: A, matches; B, water

bath; C, frame; D, plate; E, phosphorus paste; F, oven. The phosphorus

paste of Böttger, 1842, contained 10 phosphorus, 25 antimony sulfide,

12.5 manganese dioxide, 15 gelatin. According to Figuier (page 579), R.

Wagner substituted lead dioxide for the manganese dioxide. (From

FIGUIER, volume 3, 1874, page 576.)]

ALCOHOLIC FERMENTATION

(C\_{6}H\_{10}O\_{5})\_{\_n\_} C\_{6}H\_{12}O\_{6} C\_{6}H\_{12}O\_{6}

glycogen glucose fructose

^| ^| ^|

|| H\_{3}PO\_{4} || <-- ATP || <--ATP

|v |v |v

---------------+ ------+

H--C--OPO\_{3}H\_{2}| H--C--OH | H \_{2}C--OH

| | | | |

H--C--OH | H--C--OH | C--(OH)--+

| | | | | |

HO--C--H O <==> HO--C--H O <=======> HO--C--H |

| | | | | O

H--C--OH | H--C--OH | H--C--OH |

| | | | | |

H--C--------------+ H--C-----+ H--C--------+

| | |

CH\_{2}OH H\_{2}C--OPO\_{3}H\_{2}+ADP H\_{2}C--OPO\_{3}H\_{2}+ADP

glucose-1-phosphate glucose-6-phosphate fructose-6-phosphate

(Cori-ester) (Robison-ester) (Neuberg-ester)

^ |

| | <-- ATP

+----| |

| +------|

| |

| v

H\_{2}C--OPO\_{3}H\_{2}

|

C(OH)--+

| |

HO--C--H |

fructose-1,6-diphosphate | O

(Harden-Young-ester) H--C--OH |

| |

H--C------+

|

H\_{2}C--OPO\_{3}H\_{2} + ADP

^|

|| O

|| //

CH\_{2}OPO\_{3}H\_{2} || CH

| |v | 3-phosphoglycer-aldehyde

dihydroxyacetone-phosphate C=O <=============> CHOH (Fischer-ester)

| |

CH\_{2}OH CH\_{2}OPO\_{3}H\_{2}

|| + coenzyme + H\_{3}PO\_{4}

O=C--OPO\_{3}H\_{2}

|

1,3-diphosphoglyceric acid CHOH + dihydro-coenzyme

(Negelein-ester) |

CH\_{2}OPO\_{3}H

^|

ADP --> ||

|| O

|v//

C--OH

| +---+

3-phosphoglyceric acid CHOH + |ATP|

(Nilsson-ester) | +---+

CH\_{2}OPO\_{3}H\_{2}

^|

|v

COOH

2-phosphoglyceric acid |

CHOPO\_{3}H\_{2}

|

CH\_{2}OH

^|

|v

COOH

|

phosphopyruvic acid COPO\_{3}H\_{2}

(enol-) ||

CH\_2

ADP --> ||

COOH

+------+ | +---+

|CO\_{2}| + CH\_3CHO <-------- C=O + |ATP|

+------+ acetaldehyde | +---+

carbon | CH\_{3}

dioxide | + dihydro-coenzyme pyruvic acid

|

v

+----------------+

| CH\_{3}CH\_{2}OH | + coenzyme

+----------------+

ethyl alcohol

[Illustration: Figure 13.--SURVEY OF ALCOHOLIC FERMENTATION, 1951. The

"well-known scheme of alcoholic fermentation" according to Albert Jan

Kluyver (1888-1956), presented before the Society of Chemical Industry

in the Royal Institution, March 7, 1951. In \_Chemistry & Industry\_,

1952, page 136 ff., Kluyver restates that "... the fermentation of one

molecule of glucose is indissolubly connected with the formation of two

molecules of adenosine triphosphate (ATP) out of two molecules of

adenosine diphosphate (ADP)."]

Shortly after this experience had been gained, it became valuable for

understanding the chemical nature of a new substance extracted from a

natural organ. This substance was named lecithin by its discoverer,

Nicolas Théodore Gobley[27] (1811-1876), because he obtained it from egg

yolk (in Greek, \_lékidos\_). He used ether and alcohol for this

extraction. Had he used water and mineral acid instead, he would not

have found lecithin, but only its components. As Gobley and, slightly

later, Oscar Liebreich (1839-1908), subjected lecithin to treatment with

boiling water and acid, they separated it into three parts. One of them

was the glycerophosphoric acid of Pelouze, the second was the well-known

stearic acid of Chevreul, but the third was somewhat mysterious. This

third substance was the same as one previously noticed when nerves had

been subjected to an extraction by boiling water and acid and,

therefore, called nerve-substance or neurine. Adolf Friedrich Strecker

(1822-1871) established the identity of this neurine with a product he

had extracted from bile and which went under the name of choline.

Adolphe Wurtz (1817-1884) succeeded in synthesizing this substance from

ethylene oxide, CH\_2.O.CH\_2 and trimethylamine N(CH\_3)\_3.[28] Thus, all

three parts were identified, and Strecker put them together to construct

a chemical formula for lecithin, glycerophosphoric acid combined with a

fatty acid and with choline (a hydrate of neurine).

{ OH }

N { (CH\_3)\_3 } Choline

{ C\_2H\_4O }

C\_18H\_33O\_2 } HO }

} } PO

C\_16H\_31O\_2 } C\_3H\_5O }

Fatty Acids Glycerophosphate

\--------v-------/

Lecithin

according to Strecker

This formula was not quite correct. Richard Willstätter showed that an

internal neutralization takes place between the amino group and the free

acidic residue. This is expressed in his lecithin formula of 1918.

CH\_{2}·O·R

|

CH\_{2}·O·R\_2

|

| O·CH\_{2}·CH\_{2}

| / \

CH\_{2}·O--P=O N(CH\_{3})\_{3}

\ /

\---O----/

[Illustration: Lecithin (1918)]

When the aim was to distill elementary phosphorus out of an organic

material, it did not matter whether this was fresh or putrified. For

obtaining lecithin out of egg yolk and similar materials, it was

essential to use it in fresh condition. Otherwise, enzymes would have

decomposed it. Through more recent work, four enzymes have been

separated, which act specifically in decomposing lecithin. Enzyme A

removes one fatty acid and leaves a complex residue, called

lysolecithin, intact. Enzyme B attacks this residue and splits off the

remaining fatty acid group from it, enzyme C liberates only the choline

from lecithin, and enzyme D opens lecithin at the ester bond between

glycerol and phosphoric acid. This is shown in the following diagram.

ENZYMATIC SPLITTING OF LECITHINS

ENZYME SUBSTRATE PRODUCTS

A Lecithin Lysolecithin and fatty

acids.

B Lysolecithin Glycero-phospho-choline

and fatty acids.

C Lecithin Phosphatidic acid and

choline.

D Lecithin Phosphoryl choline and

diglyceride.

Several fatty acids can be present in lecithin from various sources:

palmitic and oleic acid, besides the stearic acid which at first had

been thought the only one involved. In another group of extracts from

brain or nerve tissue, amino-ethanol H\_{2}NCH\_{2}CH\_{2}OH is found

instead of the choline of lecithin. The variations include the alcohol,

to which the fatty acids and choline phosphate are attached, for

example, glycerol can be replaced by the so-called meat-sugar, inositol,

which has six hydroxyl groups in its hexagon-shaped molecule

C\_{6}H\_{6}(OH)\_{6}.

[Illustration: Figure 14.--EDUARD BUCHNER (1860-1917) received the Nobel

Prize in Chemistry for his discovery of cell-free fermentation, the

first step in finding the role of phosphate in fermentations (1907).]

The generally similar behavior of these phosphate-and fat-containing

substances was emphasized by Ludwig Thudichum (1829-1901). He coined the

name phosphatides for this group of substances from seeds and

nerves.[29] His work on the phosphates in brain substance aroused

particular interest. When William Crookes drew his highly imaginative

picture of an "evolution" of the chemical elements, he put into it

"phosphorus for the brain, salt for the sea, clay for the solid

earth...."[30] But phosphatides occur in many places of organisms, in

bacteria, in leaves and roots of plants, in fat and tissues of animals.

And where phosphatides are found, there are also enzymes that

specifically act on them. They are called phosphatases to imply that

they split the phosphatides. In addition, enzymes are present, which

transfer phosphate groups from one compound to another. They are more

abundant in seeds of high fat content than in the more starch-containing

seeds, but even potatoes and orange juice have phosphatases.[31]

Thus, from phosphatides, phosphoric acid is generated, and they could

also be called phosphagens. Since 1926, however, the name phosphagens

has been reserved for a group of organic substances that release their

phosphoric acid very readily. The link between phosphorus and carbon is

provided by oxygen in the phosphatides, by nitrogen in the phosphagens.

In vertebrates, the basis for the phosphoric acid is creatine, whereas

invertebrates have arginine instead.

H OH OH

| / /

N--P=O NH--P=O

/ \ / \

C=NH OH C=NH OH

\ \

N--CH\_{2}COOH NH

| |

CH\_{3} CH\_{2}

|

Creatine phosphate CH\_{2}

|

CH\_{2}

|

CHNH\_{2}

|

COOH

Arginine phosphate

Nuclein and Nucleic Acids

All parts of an organism are essential for life. Only with this in mind

does it make sense to say that the most important part of the cell is

its nucleus. From the nuclei of cells in pus and in salmon sperm, Johann

Friedrich Miescher (1811-1887) obtained a peculiar kind of substance,

which he named nuclein (1868). Its phosphate content was easily

discovered, but to find the exact proportions and the nature of the

other components required special methods of separation from

phosphatides and other proteins. It was difficult to develop such

methods at a time when little was known about the properties, and

particularly the stability, of a nuclein. For preparing nuclein from

yeast cells, Felix Hoppe-Seyler (1825-1895) described the following

details: Yeast is dispersed in water to extract soluble materials, like

salts or sugars. After a few hours, the insoluble material is separated,

washed once more with water, and then extracted with a very dilute

solution of sodium hydroxide. The slightly alkaline solution, freed from

insoluble residues, is slowly added to a weak hydrochloric acid. A

precipitate forms which is separated by filtration, washed with dilute

acid, then with cold alcohol, and finally extracted by boiling alcohol.

The dried residue is the nuclein.[32] It contains six percent

phosphorus. A little more washing with water, a slightly longer

treatment with acid or alcohol gives products of lower phosphorus

content. Many experimental variations were necessary to establish the

procedure that leads to purification without alteration of the natural

substance.

This was also true for the methods of chemical degradation, carried out

in order to find the components of nucleins in their highest state of

natural complexity. It was learned for example, that the special kind of

carbohydrate present in nucleins was very susceptible to change under

the conditions of hydrolysis by acids. Phoebus Aaron Theodor Levine

(1869-1940), therefore, used the digestion by a living organism. With E.

S. London, he introduced a solution of nucleic acid into, e.g., the

gastrointestinal segment of a dog through a gastric fistula and withdrew

the product of digestion through an intestinal fistula. Fortunately, the

products obtained in such degradations were not new in themselves. The

carbohydrate in this nucleic acid proved to be identical with D-ribose,

which Emil Fischer had artificially made from arabinose and named ribose

to indicate this relationship (1891). The nitrogenous products of the

degradation were identical with substances previously prepared in the

long study of uric acid. In the course of this study, Emil Fischer

established uric acid and a number of its derivatives as having the

elementary skeleton of what he called "pure uric acid," abbreviated to

purine. Out of Adolf Baeyer's work on barbituric acid came the knowledge

of pyrimidine and its derivatives.

[Illustration: Figure 15.--ALBRECHT KOSSEL (1853-1927) received the

Nobel Prize in Medicine and Physiology in 1910 for his work on nucleic

substances, which contain a high proportion of phosphorus. The chemical

bonds of this phosphorus in the molecules of nucleic substances were

determined in later work. (\_Photo courtesy National Library of Medicine,

Washington, D.C.\_)]

From these findings, together with what Oswald Schmiedeberg (1838-1921)

had established concerning the presence of four phosphate groups in the

molecule (1899), Robert Feulgen (1884-1955) constructed the following

scheme of a nucleic acid. Feulgen's formula of 1918 is:

Phosphoric acid--Carbohydrate--Guanine

Phosphoric acid--Carbohydrate--Cytosine

Phosphoric acid--Carbohydrate--Thymine

Phosphoric acid--Carbohydrate--Adenine

Of the four basic components on the right, thymine occurs in the nucleic

acid from the thymus gland. Yeast contains uracil instead. The

difference between these two bases is one methyl group: thymine is a

5-methyluracil. In all of these basic substances, the structure of urea

NH\_{2}

/

C=O

\

NH\_{2}

is involved, and they form pairs of oxidized and reduced states:

PURINE PYRIMIDINE

(reduced) Adenine + (oxidized) Thymine

(oxidized) Guanine + (reduced) Cytosine

3N = CH4

| |

2H--C CH5

|| ||

1N--CH6

Pyrimidine

1N==CH6

| | H

| | 7/ N==C--NH\_{2}

2H--C C--N | |

|| ||5 \ H--C C--NH

|| || \ || || \

|| || CH8 || || CH

|| || // || || //

3N--C--N N--C--N

4 9

Adenine

Purine

HN--C=O

| |

NH\_{2}--C C--NH N==C--NH\_{2} H--N--C=O

|| || \ | | | |

|| || CH O=C C--H O=C CH

|| || // | || | ||

N--C--N H--N--CH HN--CH

Guanine Cytosine Uracil

The carbohydrate is ribose or deoxyribose.

CHO CHO

| |

H--C--OH HO--C--H

| |

HO--C--H HO--C--H

| |

HO--C--H HO--C--H

| |

CH\_{2}OH CH\_{2}OH

Arabinose L-Ribose

Fischer and Piloty, 1891

H

\(1)/-----O-----\(4) (5)

C CH--CH\_{2}OH

/ \(2) (3)/

HO CH\_{2}--HC(OH)

Deoxyribose

The exact position of phosphoric acid was established after long work

and verified by synthesis.[33]

A compound of adenine, ribose, and phosphoric acid was found in yeast,

blood, and in skeletal muscle of mammals. From 100 grams of such muscle,

0.35-0.40 grams of this compound were isolated. If the muscle is at

rest, the compound contains three molecules of phosphoric acid, linked

through oxygen atoms. It was named adenosine triphosphate or

adenyltriphosphoric acid,[34] usually abbreviated by the symbol ATP. It

releases one phosphoric acid group very easily and goes over in the

diphosphate, ADP, but it can also lose 2 P-groups as pyrophosphoric acid

and leave the monophosphate, AMP.

N==C--NH\_{2}

| |

HC C--N +----O----+

|| || \\ | |

|| || CH | OH OH | H OH

|| || / | | | | | /

N--C--N-----C--C---C--C--C--O--P=O

| | | | | \

H H H H H OH

\---------/\---------------/\--------/

Adenine D-Ribose Phosphoric

acid

This change of ATP was considered to be the main source of energy in

muscle contraction by Otto Meyerhof.[35] The corresponding derivatives

of guanine, cytosine, and uracil were also found, and they are active in

the temporary transfer of phosphoric acid groups in biological

processes.

Thus, the study of organic phosphates progressed from the comparatively

simple esters connected with fatty substances of organisms to the

proteins and the nuclear substances of the cell. The proportional amount

of phosphorus in the former was larger than in the latter; the actual

importance and function in the life of organisms, however, is not

measured by the quantity but determined by the special nature of the

compounds.

[Illustration: Figure 16.--OTTO MEYERHOF (1884-1951) received one-half

of the Nobel Prize in Medicine and Physiology in 1922 for his discovery

of the metabolism of lactic acid in muscle, which involves the action of

phosphates, especially adenosine duophosphates. (\_Photo courtesy

National Library of Medicine, Washington, D.C.\_)]

[Illustration: Figure 17.--ARTHUR HARDEN (1865-1940), left, AND HANS A.

S. VON EULER-CHELPIN (b. 1875), right, shared the Nobel Prize in

Chemistry in 1929. Harden received it for his research in fermentation,

which showed the influence of phosphate, particularly the formation of a

hexose diphosphate. Euler-Chelpin received his award for his research in

fermentation. He found coenzyme A which is a nucleotide containing

phosphoric acid.]

[Illustration: Figure 18.--GEORGE DE HEVESY (b. 1885) received the Nobel

Prize in Chemistry in 1943 for his research with isotopic tracer

elements, particularly radiophosphorus of weight 32 (ordinary phosphorus

is 31).]

[Illustration: Figure 19.--CARL F. CORI (b. 1896) AND HIS WIFE, GERTY T.

CORI (1896-1957) received part of the Nobel Prize in Medicine and

Physiology in 1947 for their study on glycogen conversion. In the course

of this study, they identified glucose 1-phosphate, now usually referred

to as "Cori ester," and its function in the glycogen cycle. (\_Photo

courtesy National Library of Medicine, Washington, D.C.\_)]

The study of this function is the newest phase in the history of

phosphorus and represents the culmination of the previous efforts. This

newest phase developed out of an accidental discovery concerning one of

the oldest organic-chemical industries, the production of alcohol by the

fermentative action of yeast on sugar. A transition of carbohydrates

through phosphate compounds to the end products of the fermentation

process was found, and it gradually proved to be a kind of model for a

host of biological processes.

Specific phosphates were thus found to be indispensable for life. In

reverse, the wrong kind of phosphates can destroy life. As a result, an

important part of the new phase in phosphorus history consisted in the

study--and use--of antibiotic phosphorus compounds.

Phosphates in Biological Processes

The first indication that phosphorus is important for life came from the

experience that plants take it up from the substances in the soil. They

incorporate it in their body substance. What makes phosphorus so

important that they cannot grow without it? The next insight was that

animals acquire it from their plant food. It is then found in bones, in

fat and nerve tissue, in all cells and particularly in the cell nuclei.

What are its functions there?

The answers to such questions were developed from the study of a

long-known process, the conversion of carbohydrates into carbon dioxide

and alcohol by yeast. It started with Eduard Buchner's discovery of

1890, that fermentation is produced by a preparation from yeast in which

all living cells have been removed. When yeast is dead-ground and

pressed out, the juice still has the ability to produce fermentation.

It is strange, but in many ways characteristic for the process of

science, that the "riddle" of phosphorus in life was solved by first

eliminating life. In such "lifeless" fermentations, Arthur Harden found

that the conversion of sugar begins with the formation of a hexose

phosphate (1904). The "ferment" of yeast, called zymase, proved to be a

composite of several enzymes. Hans von Euler-Chelpin isolated one part

of zymase, which remains active even after heating its solution to the

boiling point. From 1 kilogram of yeast, he obtained 20 milligrams of

this heat-stable enzyme, which he called cozymase and identified as a

nucleotide composed of a purine, a sugar, and phosphoric acid.[36] In

the years between the two World Wars, zymase was further resolved into

more enzymes, one of them the coenzyme I, which was shown to be ADP

connected with another molecule of ribose attached to the amide of

nicotinic acid, or diphosphopyridine nucleotide:

^ NH\_{2}

/ \\ |

/ \\ N ^

|| |-CONH\_{2} //\ / \\

|| | | || N

\ // | || |

N\_{+} N--+ |

| | \//

| | N

H--C------+ H--C------+

| | | |

H--C--OH | H--C--OH |

| O | O

H--C--OH | H--C--OH |

| | | |

H--C------+ O O H--C------+

| || || |

CH\_{2}--O--P--O--P--O--CH\_{2}

| |

O- OH

Coenzyme I

[Illustration: Figure 20.--FRITZ A. LIPMANN (b. 1899) shared with Hans

Adolf Krebs the Nobel Prize in Medicine and Physiology in 1953 for his

work on coenzyme A. He discovered acetyl phosphate as the substance in

bacteria, which transfers phosphate to adenylic acid.]

[Illustration: Figure 21.--ALEXANDER R. TODD (b. 1907) received the

Nobel Prize in Chemistry in 1957 for his research on nucleotides. He

determined the position of the phosphate groups in the molecule and

confirmed it by synthesis of dinucleotide phosphates.]

Its function is connected with the transfer of hydrogen between

intermediates formed through phosphate-transferring enzymes.

Fermentation proceeds by a cascade of processes, in which phosphate

groups swing back and forth, and equilibria between ATP with ADP play a

major role.

Many of the enzymes are closely related to vitamins. Thus, cocarboxylase

A, which takes part in the separation of carbon dioxide from an

intermediate fermentation product, is the phosphate of vitamin B\_{1}.

Others of the B vitamins contain phosphate groups, for example those of

the B\_{2} and B\_{6} group, and in B\_{12}, one lonely phosphate forms a

bridge in the large molecule that contains one atom of cobalt:

C\_{63}H\_{90}N\_{14}O\_{14}PCo. The formation of vitamin A from carotine

occurs under the influence of ATP.

The first stages in fermentation are like those in respiration, which

ends with carbon dioxide and water. These two are the materials for the

reverse process in photosynthesis. When light is absorbed by the

chlorophyll of green plants, one of the initial reactions is a transfer

of hydrogen from water to a triphosphopyridine nucleotide, which later

acts to reduce the carbon dioxide. Under the influence of ATP,

phosphoglyceric acid is synthesized and further built up by way of

carbohydrate phosphates to hexose sugars and finally to starch. In many

starchy fruits, a small proportion of phosphate remains attached to the

end product.

The synthesis of proteins is under the control of deoxyribonucleic acid

or ribonucleic acid, abbreviated by the symbols DNA and RNA. The genes

in the nucleus are parts of a giant DNA molecule. RNA is a universal

constituent of all living cells. Where protein synthesis is intense, the

content in RNA is high. Thus, the spinning glands of silkworms are

extraordinarily rich in RNA.[37]

In his research on the radioactive isotope P^32, George de Hevesy gained

some insight into the surprising mobility of phosphates in organisms: "A

phosphate radical taken up with the food may first participate in the

phosphorylation of glucose in the intestinal mucose, soon afterwards

pass into the circulation as free phosphate, enter a red corpuscle,

become incorporated with an adenosine triphosphoric-acid molecule,

participate in a glycolytic process going on in the corpuscle, return to

circulation, penetrate into the liver cells, participate in the

formation of a phosphatide molecule, after a short interval enter the

circulation in this form, penetrate into the spleen, and leave this

organ after some time as a constituent of a lymphocyte. We may meet the

phosphate radical again as a constituent of the plasma, from which it

may find its way into the skeleton."[38] Much has been added in the last

30 years to complete this picture in many details and to extend it to

other biochemical processes, including even the changes of the pigments

in the retina in the visual process, or in the conversion of chemical

energy to light by bacteria and insects.

Medicines and Poisons

In the delicate balance of these processes, disturbances may occur which

can be remedied by specific phosphate-containing medicines. Thus,

adenosine phosphate has been recommended in cases of angina pectoris

and marketed under trade names like sarkolyt, or in compounds named

angiolysine. A considerable number of physiologically active organic

phosphates can be found in the patent literature.[39] Yeast itself is

considered to be a valuable food additive.

On the other hand, there are phosphate compounds that act as poisons.

One group of such compounds was discovered in 1929 by W. Lange, who

wrote: "Of interest is the strong action of mono-fluorophosphate esters

on the human body--the effect is produced by very small quantities."[40]

Diisopropyl fluorophosphate has since become a potential agent for

chemical warfare. It inactivates an enzyme which controls the

transmission of nerve impulses to muscle, acetylcholine esterase.

Organic esters of phosphoric acids are used as insecticides. The

hexa-ethylester of tetraphosphoric acid, prepared by Gerhard Schrader by

heating triethylphosphate with phosphorus oxychloride,[41] actually

contains tetraethylpyrophosphate (TEPP) among others. Bayer's Dipterex,

the dimethyl ester of 2,2,2-trichloro-1-hydroxyethyl-phosphonate, has

been modified to dimethyl-2,2-dichlorovinyl-phosphate and is especially

active against the oriental fruit fly.[42]

[Illustration: Figure 22.--ARTHUR KORNBERG (b. 1918) AND SEVERO OCHOA

(b. 1905) shared the Nobel Prize in Medicine and Physiology in 1959.

Kornberg received it for research on the biological synthesis of

deoxyribonucleic acid. In particular, he found that four triphosphate

components and a small amount of the end product as a "template" had to

be present for the enzymatic synthesis. Ochoa received his share of the

prize for research in ribonucleic acid and deoxyribonucleic acid. In

particular, Ochoa synthesized polyribonucleotides and used the

radioactive isotope, P^{32}. The synthetic polyribonucleotides were

found to resemble the natural substances in all essentials.]

Cl H O

| | || OCH\_{3}

| | ||/

Cl--C--C--P Bayer's L 13/59

| | \ (Dipterex)

| | OCH\_{3}

Cl OH

(CH\_{3})\_{2}N O O N(CH\_{3})\_{2}

\|| ||/

P--O--P Schradan

/ \

(CH\_{3})\_{2}N N(CH\_{3})\_{2}

Octamethylpyrophosphoramide

[Illustration: Figure 23.--MELVIN CALVIN (b. 1911) received the Nobel

Prize in Chemistry in 1961 for his research in photosynthesis, in which

he specified the function of phosphoglyceric acid as an intermediate in

the synthesis of carbohydrates from carbon dioxide and water by green

plants.]

The story of phosphorus, which began 300 years ago, has acquired new

importance in this century. Many scientists have contributed to it: 13

of them have received Nobel Prizes for work directly bearing on the

chemical and biological importance of phosphorus compounds. In

chronological order, they are: Eduard Buchner, Albrecht Kossel, Otto

Meyerhof, Arthur Harden, Hans von Euler-Chelpin, George de Hevesy, Carl

F. Cori, Gerty T. Cori, Fritz Lipmann, Lord Alexander Todd, Arthur

Kornberg, Severo Ochoa, and Melvin Calvin. The developers of industrial

production and commercial utilization of phosphate compounds have had

other rewards.

Some impression of the continuing growth in this field[43] can be gained

from the following data.

PHOSPHATE ROCK

annually "sold or used by producer" in the United States in million long

tons (2,240 lbs.)

1880 0.2

1890 0.5

1900 1.5

1910 2.655

1920 4.104

1930 3.926

1940 4.003

1945 5.807

1950 11.114

1955 12.265

1955 (world: about 56)

1960 17.202

1962 19.060

Sources: U.S. Bureau of the Census. \_Historical Statistics of the United

States 1789-1945\_ (1949); \_Statistical Abstract of the United States.\_

ELEMENTAL PHOSPHORUS

annually produced in the United States in short tons (2,000 lbs.)

1939 43,000

1944 85,679

1950 153,233

1956 312,200

1958 335,750

1959 366,350

1960 409,096

1961 430,617

1962 451,970

Source: U.S. Department of Commerce.

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INDEX

Aristotle, 179

Baeyer, Adolf, 193

Bechil, Achild, 179

Berthelot, Marcellin, 189

Berzelius, Jöns Jakob, 182

Black and Bell, plant at Stratford, 182

Boussingault, Jean Baptiste, 185

Boyle, Robert, 178, 179

Brand, H., 178, 179

Buchner, Hans, 197, 200

Calvin, Melvin, 200

Casciarolo, Vicenzo, 179

Chevreul, Michel, 189

Cori, Carl F., 200

Cori, Gerti T., 200

Crookes, William, 192

Davy, Sir Humphry, 185

De Hevesy, George, 198, 200

De la Vega, Garcilaso, 185

De Saussure, Théodore, 185

Euler-Chelpin, Hans von, 197, 200

Fernelius, Jean, 179

Feulgen, Robert, 193

Fischer, Emil, 193

Gahn, Johann Gottlieb, 182

Gay-Lussac, Joseph Louis, 182

Gobley, Nicolas Théodore, 191

Graham, Thomas, 182, 183, 185

Hankwitz, Gottfried, 180

Harden, Arthur, 197, 200

Hartmann, Immanuel Peter, 181

Hellot, Jean, 180

Henry II, King of France, 179

Hittorf, Wilhelm, 181

Hoefer, Ferdinand, 179

Holmberg, Wilhelm, 178

Hoppe-Seyler, Felix, 193

Humboldt, Alexander von, 185

Huygens, Christiaan, 179

Incas, 185

Kletwich, Johann Christopher, 179

Koppe, Émile, 181

Kornberg, Arthur, 200

Kossel, Albrecht, 200

Kraft, Johann Daniel, 179

Kramer, Dr. ----, 181

Kunckel, Johann, 179

Lange, W., 199

Lavoisier, Antoine Laurent, 181, 185

Laws, John Bennet, 186

Leibnitz, Gottfried Wilhelm von, 179

Lennox, Charles, third Duke of Richmond, 185

Leonhardi, Johann Gottfried, 179

Levine, Phoebus Aaron Theodor, 193

Liebig, Justus, 183, 185, 186

Liebreich, Oscar, 191

Lipmann, Fritz, 200

London, E. S., 193

Macquer, Peter Joseph, 180

Marggraf, Andreas Sigismund, 180

Meyerhof, Otto, 194, 200

Miescher, Johann Friedrich, 192

Muspratt, James, 186

Nietzsche, Friedrich, 186, 187, 189

Ochoa, Severo, 200

Pelouze, Théophile Juste, 189

Rouelle, Guillaume François, 181

Scheele, Karl W., 182

Schmiedeberg, Oswald, 193

Schrader, Gerhard, 199

Schrötter, Anton, 181

Stoklasa, Julius, 186

Strecker, Adolf Friedrich, 191

Thudichum, Ludwig, 192

Todd, Lord Alexander, 200

Willm, Edmond, 182

Willstätter, Richard, 191

Wurtz, Adolphe, 185, 191

Transcriber's Notes

The following typographical errors have been corrected:

Page 180 "\_Abfällen\_, Vieweg, Braunschweig," - had "Viewig".

Page 188 "wires \_d\_ from the dynamo D" - had "dynano".

Page 191 "phosphate are attached, for example," - had "attached, For".

Page 192 "But phosphatides occur" - had "phosphatide soccur".

Page 193 "the nucleic acid from the thymus" - had "nucleidic".

Page 199 "acetylcholine esterase." - had "acetylcholin".

Page 200 "George de Hevesy, Carl F. Cori," - comma added after Hevesy.

Footnote [39] "See, e.g., \_Chemical Week\_, vol. 77" - had "See. e.g."

Index Entry: "Gahn, Johann Gottlieb, 182" - had "Gähn"

The spelling of "Bertholet" [Claude Louis Berthollet] is as given on the

original title page of the work referenced in this paper.

Inconsistent hyphenation of chemical names has been retained.

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