

		1 H 2 He																																											
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne																												
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar																												
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr																												
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe																												
55 Cs	56 Ba	57 La	58 Hf	59 Ta	60 W	61 Re	62 Os	63 Ir	64 Pt	65 Au	66 Hg	67 Tl	68 Pb	69 Bi	70 Po	71 At	72 Rn																												
87 Fr	88 Ra	89 Ac	90 Rf	91 Db	92 Sg	93 Bh	94 Hs	95 Mt	96 Uun	97 Uu	98 Uub																																		
<table border="1"> <tr> <td>89 Ce</td> <td>90 Pr</td> <td>91 Nd</td> <td>92 Pm</td> <td>93 Sm</td> <td>94 Eu</td> <td>95 Gd</td> <td>96 Tb</td> <td>97 Dy</td> <td>98 Ho</td> <td>99 Er</td> <td>100 Tm</td> <td>101 Yb</td> <td>102 Lu</td> </tr> <tr> <td>103 Th</td> <td>104 Pa</td> <td>105 U</td> <td>106 Np</td> <td>107 Pu</td> <td>108 Am</td> <td>109 Cm</td> <td>110 Bk</td> <td>111 Cf</td> <td>112 Es</td> <td>113 Fm</td> <td>114 Md</td> <td>115 No</td> <td>116 Lr</td> </tr> </table>																		89 Ce	90 Pr	91 Nd	92 Pm	93 Sm	94 Eu	95 Gd	96 Tb	97 Dy	98 Ho	99 Er	100 Tm	101 Yb	102 Lu	103 Th	104 Pa	105 U	106 Np	107 Pu	108 Am	109 Cm	110 Bk	111 Cf	112 Es	113 Fm	114 Md	115 No	116 Lr
89 Ce	90 Pr	91 Nd	92 Pm	93 Sm	94 Eu	95 Gd	96 Tb	97 Dy	98 Ho	99 Er	100 Tm	101 Yb	102 Lu																																
103 Th	104 Pa	105 U	106 Np	107 Pu	108 Am	109 Cm	110 Bk	111 Cf	112 Es	113 Fm	114 Md	115 No	116 Lr																																

12

Phosphorus

12.1 Introduction

Phosphorus has an extensive and varied chemistry which transcends the traditional boundaries of inorganic chemistry not only because of its propensity to form innumerable covalent “organophosphorus” compounds, but also because of the numerous and crucial roles it plays in the biochemistry of all living things. It was first isolated by the alchemist Hennig Brandt in 1669 by the unsavoury process of allowing urine to putrify for several days before boiling it down to a paste which was then reductively distilled at high temperatures; the vapours were condensed under water to give the element as a white waxy substance that glowed in the dark when exposed to air.⁽¹⁾ Robert Boyle improved the process (1680) and in subsequent years made the oxide and phosphoric acid; he referred to the element as “aerial noctiluca”, but the name phosphorus soon became generally accepted (Greek $\phi\omega\varsigma$ *phos*, light; Greek $\phi\omicron\rho\omicron\varsigma$ *phoros*, bringing).

As shown in the Panel on the next page, phosphorus is probably unique among the elements in being isolated first from animal (human) excreta, then from plants, and only a century later being recognized in a mineral.

6 C	7 N	8 O
14 Si	15 P	16 S
32 Ge	33 As	34 Se

In much of its chemistry phosphorus stands in relation to nitrogen as sulfur does to oxygen. For example, whereas N₂ and O₂ are diatomic gases, P and S have many allotropic modifications which reflect the various modes of catenation adopted. Again, the ability of P and S to form multiple bonds to C, N and O, though it exists, is less highly developed than for N (p. 416), whereas the ability to form extended networks of -P-O-P-O- and -S-O-S-O-bonds is greater; this is well illustrated by comparing the oxides and oxoanions of N

¹ M. E. WEEKS, *Discovery of the Elements*, Journal of Chemical Education Publ., Easton, Pa., 1956; Phosphorus, pp. 109-39.

Time Chart for Phosphorus Chemistry

- 1669 Phosphorus isolated from urine by H. Brandt.
- 1680 R. Boyle improved the process and showed air was necessary for the phosphorescence of P.
- 1688 Phosphorus first detected in the vegetable kingdom (by B. Albino).
- 1694 P_4O_{10} and H_3PO_4 first made by R. Boyle.
- 1769 Phosphorus shown by J. G. Gahn and C. W. Scheele to be an essential constituent in the bones of man and animals, thereby revealing a plentiful source of fertilizers.
- 1779 Phosphorus first discovered in a mineral by J. G. Gahn (pyromorphite, a lead phosphate); subsequently found in the much more abundant apatite by T. Bergman and J. L. Proust.
- 1783 PH_3 first prepared by P. Gengembre (and independently in 1786 by R. Kirwan).
- 1808 PCl_3 and PCl_5 made by J. L. Gay Lussac and L. J. Thenard (and by H. Davy).
- 1811 N. L. Vauquelin isolated the first organic P compound (lethicin) from brain fat; it was characterized as a phospholipid by Gobbley in 1850.
- 1816 P. L. Dulong first clearly demonstrated the existence of two oxides of P.
- 1820 First synthesis of an organo-P compound by J. L. Lassaigne who made alkyl phosphites from $H_3PO_4 + ROH$.
- 1833 T. Graham (who later became the first President of the Chemical Society) classified phosphates as ortho, pyro or meta, following J. J. Berzelius's preparation of pyrophosphoric acid by heat.
- 1834 $(PNCl_2)_n$ made by F. Wöhler and J. von Liebig (originally formulated as $P_3N_2Cl_5$).
- 1843 J. Murray patented his production of "superphosphate" fertilizer (a name coined by him for the product of H_2SO_4 on phosphate rock).
- 1844 A. Albright started the manufacture of elemental P in England (for matches); 0.75 tonne in 1844. 26.5 tonnes in 1851.
- 1845 Polyphosphoric acids made by T. Fleitmann and W. Henneberg.
- 1848 Red (amorphous) P discovered by A. Schrötter.
- 1850 First commercial production of "wet process" phosphoric acid.
- 1868 E. F. Hoppe-Seyler and F. Miescher isolated "nuclein", the first nucleic acid, from pus.
- 1880 Modern cyclic formulation of tetrametaphosphate anion suggested by A. Glatzel. (Ring structure of metaphosphate definitely established by L. Pauling and J. Sherman 1937.)
- 1888 Electrothermal process for manufacturing P introduced by J. B. Readman (Edinburgh).
- 1898 "Strike-anywhere" matches devised by H. Sévène and E. D. Cahen in France; previously the brothers Lundström had exhibited "safety matches" in 1855, and the first P-containing striking match had been invented by F. Dérosne in 1812.
- 1929 C. H. Fiske and Y. Subbarow discovered adenosine triphosphate (ATP) in muscle fibre; it was synthesized some 20 y later by A. Todd *et al.* (Nobel Prize 1957).
- 1932 Elucidation of the glycolysis process (by G. Embden and by O. Meyerhof) followed by the glucose oxidation process (H. A. Krebs, 1937) established the intimate involvement of P compounds in many biochemical reactions.
- 1935 Radioactive ^{32}P made by (n,γ) reaction on ^{31}P .
- ~1940 Highly polymeric phosphate esters (nucleic acids) present in all cells and recognized as essential constituents of chromosomes.
- 1951 First ^{31}P nmr chemical shifts measured by W. C. Dickinson (for $POCl_3$, PCl_3 , etc. relative to aq. H_3PO_4).
- 1952 Detergents (using polyphosphates) overtake soap as main washing agent in the USA. (Heavy duty liquid detergents with polyphosphates introduced in 1955.)
- 1953 F. H. C. Crick, J. B. Watson and M. H. F. Wilkins (with Rosalind Franklin) establish the double helix structure of nucleic acids (Nobel Prize 1962).
- 1960 Concept of "pseudorotation" introduced by R. S. Berry to interpret the stereochemical non-rigidity of trigonal bipyramidal PF_5 (and SF_4 , ClF_3); the 5 F atoms are equivalent (1953) due to interconversion via a square pyramidal intermediate.
- 1961 First 2-coordinate compound of P prepared by A. B. Burg ($Me_3P=PCF_3$). First 1-coordinate P compound ($HC\equiv P$) made by T. E. Gier.
- 1966 First heterocyclic aromatic analogue of pyridine ($Ph_3C_5H_2P$) prepared by G. Märkl, followed by the parent compound C_5H_5P in 1971 (A. J. Ashe).
- 1977+ P_4 as an η^1 , η^2 , etc. ligand (see Fig. 12.9, p. 488).
- 1979 G. Wittig shared the Chemistry Nobel Prize for his development of the Wittig reaction (first published with G. Geissler in 1953).
- 1981 First stable phospho-alkyne, $Bu^iC\equiv P$ (cf. RCN).
- 1983+ Characterization of extended *conjuncto*-polyphosphide clusters (p. 491) and polyphosphanes (p. 492).

and P. "Valency expansion" is another point of difference between the elements of the first and second periods of the periodic table for, although compounds in which N has a formal oxidation state of +5 are known, no simple "single-bonded" species such as NF_5 or NCl_6^- have been prepared, analogous to PF_5 and PCl_6^- . This finds interpretation in the availability of 3d orbitals for bonding in P (and S) but not for N (or O). The extremely important Wittig reaction for olefin synthesis (p. 545) is another manifestation of this property. Discussion of more extensive group trends in which N and P are compared with the other Group 15 elements As, Sb and Bi, is deferred until the next chapter (pp. 550–4).

Because of the great importance of phosphorus and its compounds in the chemical industry, several books and reviews on their preparation and uses are available.^(2–10) Some of these applications reflect the fact that P is a vital element for the growth and development of all plants and animals and is therefore an important constituent in many fertilizers. Phosphorus compounds are involved in energy transfer

processes (such as photosynthesis (p. 126), metabolism, nerve function and muscle action), in heredity (via DNA), and in the production of bones and teeth.^(11–14) Topics in phosphorus chemistry are regularly reviewed.⁽¹⁵⁾

12.2 The Element

12.2.1 Abundance and distribution

Phosphorus is the eleventh element in order of abundance in crustal rocks of the earth and it occurs there to the extent of ~1120 ppm (cf. H ~1520 ppm, Mn ~1060 ppm). All its known terrestrial minerals are orthophosphates though the reduced phosphide mineral schriebersite $(\text{Fe,Ni})_3\text{P}$ occurs in most iron meteorites. Some 200 crystalline phosphate minerals have been described, but by far the major amount of P occurs in a single mineral family, the apatites, and these are the only ones of industrial importance, the others being rare curiosities.⁽¹⁶⁾ Apatites (p. 523) have the idealized general formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaX}_2$, that is $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, and common members are fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, chloroapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, and hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. In addition, there are vast deposits of amorphous phosphate rock, phosphorite, which approximates in composition to fluoroapatite.^(11,17) These deposits are widely

² J. EMSLEY and D. HALL, *The Chemistry of Phosphorus*, Harper & Row, London 1976, 534 pp.

³ A. F. CHILDS, Phosphorus, phosphoric acid and inorganic phosphates, in *The Modern Inorganic Chemicals Industry*, (R. THOMPSON, ed.), pp. 375–401, The Chemical Society, London, 1977.

⁴ *Proceedings of the First International Congress on Phosphorus Compounds and their Non-fertilizer Applications, 17–21 October 1977 Rabat, Morocco*, IMPHOS (Institut Mondial du Phosphat), Rabat, 1978, 767 pp.

⁵ L. D. QUIN and J. D. VERKADE (eds.), *Phosphorus Chemistry: Proceedings of the 1981 International Conference*, ACS Symposium Series No. 171, 1981, 640 pp.

⁶ H. GOLDWHITE, *Introduction to Phosphorus Chemistry*, Cambridge University Press, Cambridge, 1981, 113 pp.

⁷ E. C. ALYEA and D. W. MEEK (eds.), *Catalytic Aspects of Metal Phosphine Complexes*, ACS Symposium Series No. 196, 1982, 421 pp.

⁸ D. E. C. CORBRIDGE, *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 5th edn. Elsevier, Amsterdam, 1995, 1208 pp.

⁹ A. D. F. TOY and E. N. WALSH, *Phosphorus Chemistry in Everyday Living*, (2nd edn). Washington, ACS, 1987, 362 pp.

¹⁰ E. N. WALSH, E. J. GRIFFITH, R. W. PARRY and L. D. QUIN (eds.), *Phosphorus Chemistry: Developments in American Science*, ACS Symposium Series No. 486, 1992, 288 pp.

¹¹ J. R. VAN WAZER (ed.), *Phosphorus and its Compounds*, Vol. 2, *Technology, Biological Functions and Applications*, Interscience, New York, 1961, 2046 pp.

¹² F. H. PORTUGAL and J. S. COHEN, *A Century of DNA. A History of the Discovery of the Structure and Function of the Genetic Substance*, MIT Press, Littleton, Mass., 1977, 384 pp.

¹³ R. L. RAWIS, *Chem. and Eng. News*, Dec. 21, 1987, pp. 26–39.

¹⁴ J. K. BARTON, *Chem. and Eng. News*, Sept. 26, 1988, pp. 30–42.

¹⁵ *Topics in Phosphorus Chemistry*, Wiley, New York, Vol. 1 (1964)–Vol. 11 (1983).

¹⁶ J. O. NRIAGU and P. B. MOORE (eds.), *Phosphate Minerals*, Springer Verlag, Berlin, 1984, 442 pp.

¹⁷ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, (transl. D. R. TERRELL), VCH, Weinheim, 1989, Phosphorus, pp. 68–105.

Table 12.1 Estimated reserves of phosphate rock (in gigatonnes of contained P)

Continent	Main areas	Reserves/10 ⁹ tonnes P
Africa	Morocco, Senegal, Tunisia, Algeria, Sahara, Egypt, Togo, Angola, South Africa	4.6
North America	USA (Florida, Georgia, Carolina, Tennessee, Idaho, Montana, Utah, Wyoming), Mexico	1.6
South America	Peru, Brazil, Chile, Columbia	0.4
Europe	Western and Eastern	0.7
Asia/Middle East	Kola Peninsula, Kazakhstan, Siberia, Jordan, Israel, Saudi Arabia, India, Turkey	1.4
Australasia	Queensland, Nauru, Makatea	0.4
Total		9.1

spread throughout the world as indicated in Table 12.1 and reserves (1982 estimates) are adequate for several centuries with present technology. The phosphate content of commercial phosphate rock generally falls in the range (72 ± 10)% BPL [i.e. "bone phosphate of lime", Ca₃(PO₄)₂] corresponding to (33 ± 5)% P₄O₁₀ or 12–17% P. The USA is the principal producer, having produced one-third of the total world output in 1985, and Morocco is the largest exporter, mainly to the UK and continental Europe. World production is a staggering 151 million tonnes of phosphate rock per annum (1985), equivalent to some 20 million tonnes of contained phosphorus (p. 480).

Phosphorus also occurs in all living things and the phosphate cycle, including the massive use of phosphatic fertilizers, is of great current interest.^(18–20) The movement of phosphorus through the environment differs from that of the other non-metals essential to life (H, C, N, O and S) because it has no volatile compounds that can circulate via the atmosphere. Instead, it circulates via two rapid biological

cycles on land and sea (weeks and years) superimposed on a much slower primary geological inorganic cycle (millions of years). In the inorganic cycle, phosphates are slowly leached from the igneous or sedimentary rocks by weathering, and transported by rivers to the lakes and seas where they are precipitated as insoluble metal phosphates or incorporated into the aquatic food chain. The solubility of metal phosphates clearly depends on pH, salinity, temperature, etc., but in neutral solution Ca₃(PO₄)₂ (solubility product ~10⁻²⁹ mol⁵ l⁻⁵) may first precipitate and then gradually transform into the less soluble hydroxyapatite [Ca₅(PO₄)₃(OH)], and, finally, into the least-soluble member, fluorapatite (solubility product ~10⁻⁶⁰ mol⁹ l⁻⁹). Sedimentation follows and eventually, on a geological time scale, uplift to form a new land mass. Some idea of actual concentrations of ions involved may be obtained from the fact that in sea water there is one phosphate group per million water molecules; at a salinity of 3.3%, pH 8 and 20°C, 87% of the inorganic phosphate exist as [HPO₄]²⁻, 12% as [PO₄]³⁻ and 1% as [H₂PO₄]⁻. Of the [PO₄]³⁻ species, 99.6% is complexed with cations other than Na⁺.⁽²¹⁾

The secondary biological cycles stem from the crucial roles that phosphates and particularly organophosphates play in all life processes. Thus organophosphates are incorporated into the backbone structures of DNA and RNA which regulate the reproductive processes of cells, and they

¹⁸ B. H. SVENSSON and R. SÖDERLUND (eds.), *Nitrogen, Phosphorus, and Sulfur—Global Biogeochemical Cycles*, SCOPE Report, No. 7, Sweden 1976, 170 pp.; also SCOPE Report No. 10, Wiley, New York, 1977, 220 pp. and SCOPE Newsletter 47, Jan. 1995, pp. 1–4.

¹⁹ E. J. GRIFFITH, A. BEETON, J. M. SPENCER, and D. T. MITCHELL (eds.), *Environmental Phosphorus Handbook*, Wiley, New York, 1973, 718 pp.

²⁰ Ciba Foundation Symposium 57 (New Series), *Phosphorus in the Environment: Its Chemistry and Biochemistry*, Elsevier, Amsterdam, 1978, 320 pp.

²¹ E. T. DEGENS, *Topics in Current Chem.* **64**, 1–112 (1976).

are also involved in many metabolic and energy-transfer processes either as adenosine triphosphate (ATP) (p. 528) or other such compounds. Another role, restricted to higher forms of life, is the structural use of calcium phosphates as bones and teeth. Tooth enamel is nearly pure hydroxyapatite and its resistance to dental caries is enhanced by replacement of OH^- by F^- (fluoridation) to give the tougher, less soluble $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$. It is also commonly believed that the main inorganic phases in bone are hydroxyapatite and an amorphous phosphate, though many crystallographers favour an isomorphous solution of hydroxyapatite and the carbonate-apatite mineral dahllite, $[(\text{Na},\text{Ca})_5(\text{PO}_4,\text{CO}_3)_3(\text{OH})]$, as the main crystalline phase with little or no amorphous material. Young bones also contain brushite, $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$, and the hydrated octacalcium phosphate $[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}]$ which

is composed, essentially, of alternate layers of apatite and water oriented parallel to (001).⁽²¹⁾

The land-based phosphate cycle is shown in Fig. 12.1.⁽²²⁾ The amount of phosphate in untilled soil is normally quite small and remains fairly stable because it is present as the insoluble salts of Ca^{II} , Fe^{III} and Al^{III} . To be used by plants, the phosphate must be released as the soluble $[\text{H}_2\text{PO}_4]^-$ anion, in which form it can be taken up by plant roots. Although acidic soil conditions will facilitate phosphate absorption, phosphorus is the nutrient which is often in shortest supply for the growing plant. Most mined phosphate is thus destined for use in fertilizers and this accounts for up to 75% of phosphate rock in technologically advanced countries and over 90% in less advanced (more

²² J. EMSLEY, *Chem. Br.* 13, 459–63 (1977).

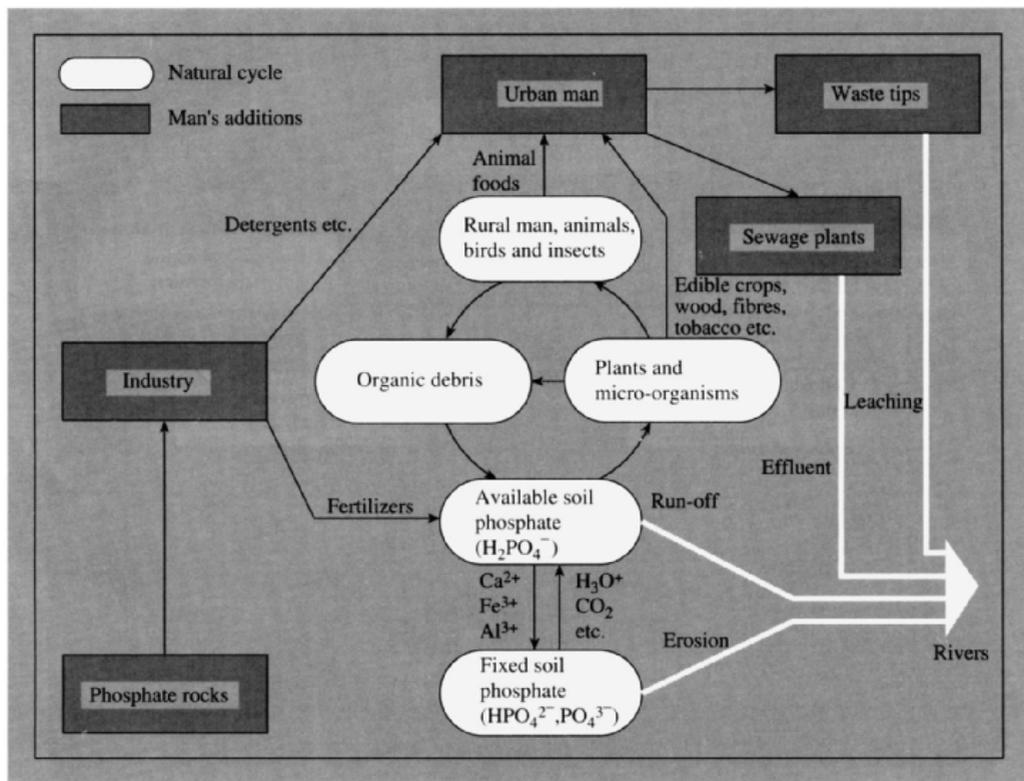


Figure 12.1 The land-based phosphate cycle.

agriculturally based) countries. Moderation in all things, however: excessive fertilization of natural waters due to detergents and untreated sewage in run-off water can lead to heavy overgrowth of algae and higher plants, thus starving the water of dissolved oxygen, killing fish and other aquatic life, and preventing the use of lakes for recreation, etc. This unintended over-fertilization and its consequences has been termed eutrophication (Greek $\epsilon\upsilon$, *eu*, well; $\tau\rho\acute{\epsilon}\phi\epsilon\iota\nu$, *trephain*, to nourish) and is the subject of active environmental legislation in several countries. Reclamation of eutrophied lakes can best be effected by addition of soluble Al^{III} salts to precipitate the phosphates.

As just implied, the land-based phosphorus cycle is connected to the water-based cycle via the rivers and sewers. It has been estimated that, on a global scale, about 2 million

tonnes of phosphate are washed into the seas annually from natural processes and rather more than this amount is dumped from human activities. For example in the UK some 200 000 tonnes of phosphate enters the sewers each year: 100 000 tonnes from detergents (now decreasing), 75 000 from human excreta, and 25 000 tonnes from industrial processes. Details of the subsequent water-based phosphate cycle are shown schematically in Fig. 12.2. The water-based cycle is the most rapid of the three phosphate cycles and can be completed within weeks (or even days). The first members of the food chain are the algae and experiments with radioactive ^{32}P (p. 482) have shown that, within minutes of entering an aquatic environment, inorganic phosphate is absorbed by algae and bacteria (50% uptake in 1 min. 80% in 3 min). In the seas and oceans the various phosphate anions

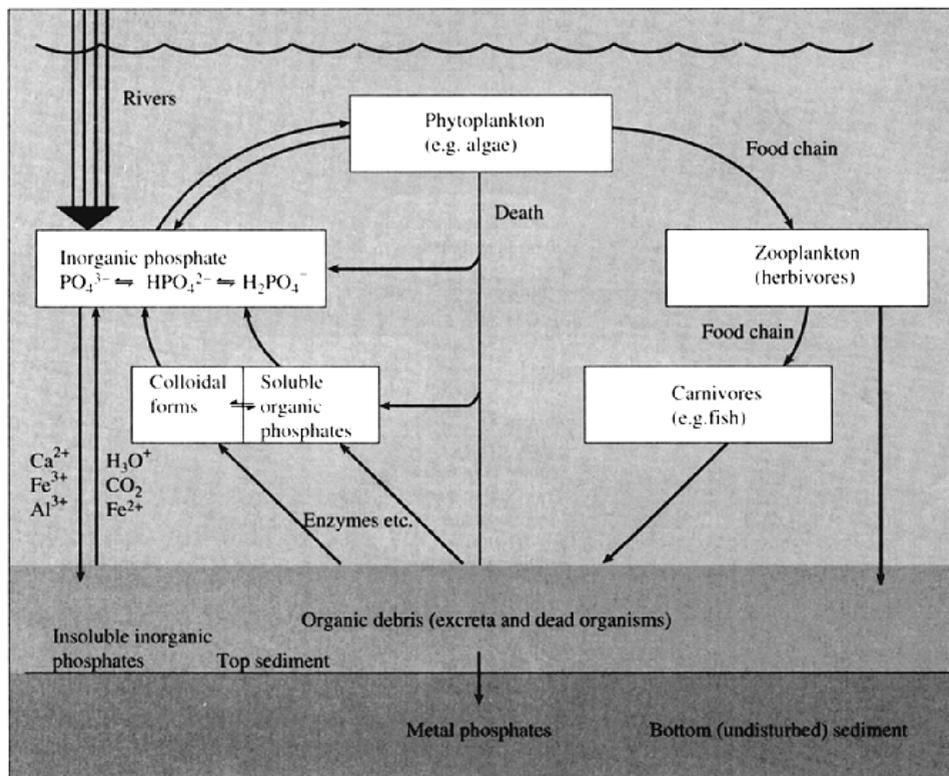
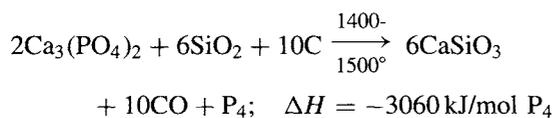


Figure 12.2 The water-based phosphate cycle.⁽²²⁾

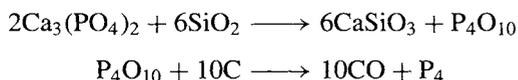
form insoluble inorganic phosphates which gradually sink to the sea bed. The concentration of phosphate therefore increases with depth (down to about 1000 m, below which it remains fairly constant); by contrast the sunlight, which is necessary for the primary photosynthesis in the food chain, is greatest at the surface and rapidly diminishes with depth. It is significant that those regions of the sea where the deeper phosphate-rich waters come welling up to the surface support by far the greatest concentration of the world's fish population; such regions, which occur in the mid-Pacific, the Pacific coast of the Americas, Arabia and Antarctica, account for only 0.1% of the sea's surface but support 50% of the world's fish population.

12.2.2 Production and uses of elemental phosphorus

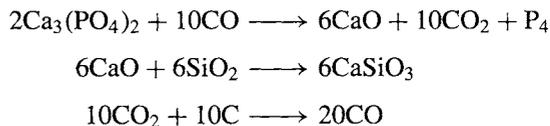
For a century after its discovery the only source of phosphorus was urine. The present process of heating phosphate rock with sand and coke was proposed by E. Aubertin and L. Boblique in 1867 and improved by J. B. Readman who introduced the use of an electric furnace. The reactions occurring are still not fully understood, but the overall process can be represented by the idealized equation:



The presence of silica to form slag which is vital to large-scale production was perceptively introduced by Robert Boyle in his very early experiments. Two apparently acceptable mechanisms have been proposed and it is possible that both may be occurring. In the first, the rock is thought to react with molten silica to form slag and P_4O_{10} which is then reduced by the carbon:



In the second possible mechanism, the rock is considered to be directly reduced by CO and the CaO so formed then reacts with the silica to form slag:



Whatever the details, the process is clearly energy intensive and, even at 90% efficiency, requires ~15 MWh per tonne of phosphorus (see Panel).

12.2.3 Allotropes of phosphorus⁽²³⁾

Phosphorus (like C and S) exists in many allotropic modifications which reflect the variety of ways of achieving catenation. At least five crystalline polymorphs are known and there are also several "amorphous" or vitreous forms (see Fig. 12.3). All forms, however, melt to give the same liquid which consists of symmetrical P_4 tetrahedral molecules, P–P 225 pm. The same molecular form exists in the gas phase (P–P 221 pm), but at high temperatures (above ~800°C) and low pressures P_4 is in equilibrium with the diatomic form $\text{P}\equiv\text{P}$ (189.5 pm). At atmospheric pressure, dissociation of P_4 into 2P_2 reaches 50% at ~1800°C and dissociation of P_2 into 2P reaches 50% at ~2800°.

The commonest form of phosphorus, and the one which is usually formed by condensation from the gaseous or liquid states, is the waxy, cubic, white form $\alpha\text{-P}_4$ (d 1.8232 g cm⁻³ at 20°C). This, paradoxically, is also the most volatile and reactive solid form and thermodynamically the least stable. It is the slow phosphorescent oxidation of the vapour above these crystals that gives white phosphorus its most characteristic property. Indeed, the emission of yellow-green light from the oxidation of P_4 is one of the earliest recorded examples of chemiluminescence, though the details of the reaction

²³ D. E. C. CORBRIDGE, *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, 1974, 542 pp.

Production of White Phosphorus^(3,11,17)

A typical modern phosphorus furnace (12 m diameter) can produce some 4 tonnes per hour and is rated at 60–70 MW (i.e. 140 000 A at 500 V). Three electrodes, each weighing 60 tonnes, lead in the current. The amounts of raw material required to make 1 tonne of white phosphorus depend on their purity but are typically 8 tonnes of phosphate rock, 2 tonnes of silica, 1.5 tonnes of coke, and 0.4 tonnes of electrode carbon. The phosphorus vapour is driven off from the top of the furnace together with the CO and some H₂; it is passed through a hot electrostatic precipitator to remove dust and then condensed by water sprays at about 70° (P₄ melts at 44.1°). The byproduct CO is used for supplementary heating.

As most phosphate rock approximates in composition to fluoroapatite, [Ca₅(PO₄)₃F], it contains 3–4 wt% F. This reacts to give the toxic and corrosive gas SiF₄ which must be removed from the effluent. The stoichiometry of phosphate rock might suggest that about 1 mole of SiF₄ is formed for each 3 moles of P₄, but only about 20% of the fluorine reacts in this way, the rest being retained in the slag. Nevertheless, since a typical furnace can produce over 30 000 tonnes of phosphorus per year this represents a substantial waste of a potentially useful byproduct (~5000 tonnes SiF₄ yearly per furnace). In some plants the SiF₄ is recovered by treatment with water and soda ash (Na₂CO₃) to give Na₂SiF₆ which can be used in the fluoridation of drinking water.

Another troublesome impurity in phosphate rock (1–5%) is Fe₂O₃ which is reduced in the furnace to "ferrophosphorus", an impure form of Fe₂P. This is a dense liquid at the reaction temperature; it sinks beneath the slag and can be drained away at intervals. As every tonne of ferrophosphorus contains ~0.25 tonne of P, this is a major loss, but is unavoidable since the Fe₂O₃ cannot economically be removed beforehand. The few uses of ferrophosphorus depend on its high density (~6.6 g cm⁻³). It can be mixed with dynamite for blasting or used as a filler in high-density concrete and in radiation shields for nuclear reactors. It is also used in the manufacture of special steels and cast-irons, especially for non-sparking railway brake-shoes. The other substantial byproduct, CaSiO₃ slag, has little economic use and is sold as hard core for road-fill or concrete aggregate; about 7–9 tonnes are formed per tonne of P produced.

World capacity for the production of elemental P is ~1.5 million tonnes per year. Some figures for 1984 are as follows:

Country	USSR	USA	Germany	Netherlands	Canada	France
ktonne/y	615	412	95	90	90	39
Country	China	Japan	Mexico	India	South Africa	
ktonne/y	35	20	10	10	6	

About 80–90% of the elemental P produced is reoxidized to (pure) phosphoric acid (p. 521). The rest is used to make phosphorus oxides (p. 503), sulfides (p. 506), phosphorus chlorides and oxochloride (p. 496), and organic P compounds. A small amount is converted to red phosphorus (see below) for use in the striking surface of matches for pyrotechnics and as a flame retarding agent (in polyamides). Bulk price for P₄ is ~\$2.00/kg.

mechanism are still not fully understood: the primary emitting species in the visible region of the spectrum are probably (PO)₂ and HPO; ultraviolet emission from excited states of PO also occurs.⁽²⁴⁾ At -76.9° and atmospheric pressure the α-form of P₄ converts to the very similar white hexagonal β-form (*d* 1.88 g cm⁻³), possibly by loss of rotational disorder; Δ*H*(α→β) = 15.9 kJ (mol P₄)⁻¹. White phosphorus is insoluble in water but exceedingly soluble (as P₄) in CS₂ (~880 g per 100 g CS₂ at 10°C). It is also very soluble in PCl₃, POCl₃, liquid SO₂, liquid

NH₃ and benzene, and somewhat less soluble in numerous other organic solvents. The β-form can be maintained as a solid up to 64.4°C under a pressure of 11 600 atm, whereas the α-form melts at 44.1°C. White phosphorus is highly toxic and ingestion, inhalation or even contact with skin must be avoided; the fatal dose when taken internally is about 50 mg.

Amorphous red phosphorus was first obtained in 1848 by heating white P₄ out of contact with air for several days, and is now made on a commercial scale by a similar process at 270°–300°C. It is denser than white P₄ (~2.16 g cm⁻³), has a much higher m.p.

²⁴ R. J. VAN ZEE and A. U. KHAN, *J. Am. Chem. Soc.* **96**, 6805–6 (1974).

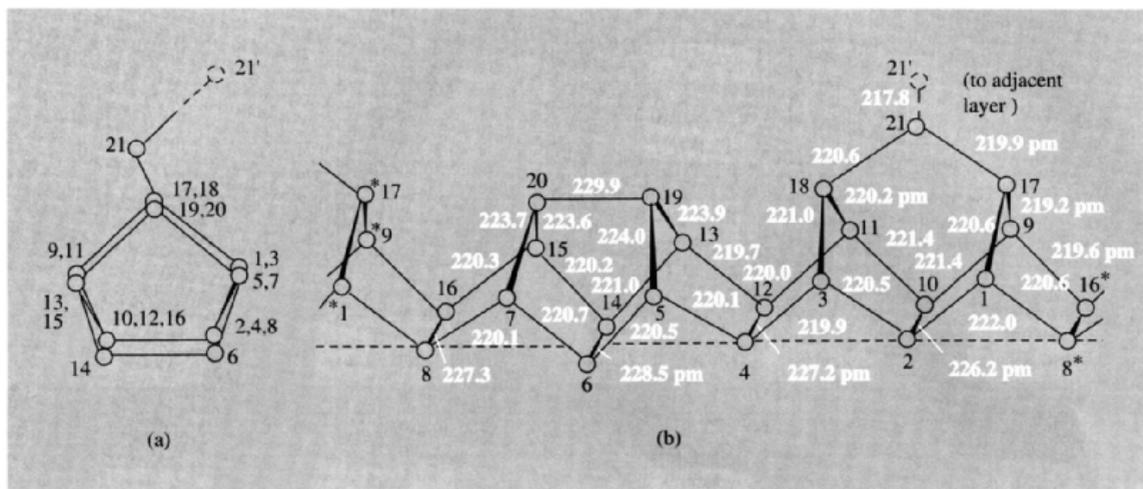


Figure 12.4 Structure of Hittorf's violet monoclinic phosphorus showing (a) end view of one pentagonal tube, (b) the side view of a single tube (dimensions in pm).

same as in P_4) but the average P-P-P angle is 101° (instead of 60°).

Black phosphorus, the thermodynamically most stable form of the element, has been prepared in three crystalline forms and one amorphous form. It is even more highly polymeric than the red form and has a correspondingly higher density (orthorhombic 2.69 , rhombohedral 3.56 , cubic 3.88 g cm^{-3}). Black phosphorus (orthorhombic) was originally made by heating white P_4 to 200° under a pressure of $12\,000 \text{ atm}$ (P. W. Bridgman, 1916). Higher pressures convert it successively to the rhombohedral and cubic forms (Fig. 12.3). Orthorhombic black P (mp $\sim 610^\circ$) has a layer structure which is based on a puckered hexagonal net of 3-coordinate P atoms with 2 interatomic angles of 102° and 1 of 96.5° (P-P 223 pm). The relation of this form to the rhombohedral and cubic forms is shown in Fig. 12.5. Comparison with the rhombohedral forms of As, Sb and Bi is also instructive in showing the increasing tendency towards octahedral coordination and metallic properties (p. 551). Black P is semiconducting but its electrical properties are probably significantly affected by impurities introduced during its preparation.

12.2.4 Atomic and physical properties⁽²⁶⁾

Phosphorus has only one stable isotope, ^{31}P , and accordingly (p. 17) its atomic weight is known with extreme accuracy, $30.973\,762(4)$. Sixteen radioactive isotopes are known, of which ^{32}P is by far the most important; it is made on the multikilogram scale by the neutron irradiation of $^{32}\text{S}(n,p)$ or $^{31}\text{P}(n,\gamma)$ in a nuclear reactor, and is a pure β -emitter of half life 14.26 days , $E_{\text{max}} 1.709 \text{ MeV}$, $E_{\text{mean}} 0.69 \text{ MeV}$. It finds extensive use in tracer and mechanistic studies. The stable isotope ^{31}P has a nuclear spin quantum number of $\frac{1}{2}$ and this is much used in nmr spectroscopy.⁽²⁷⁾ Chemical shifts and coupling constants can both be used diagnostically to determine structural information.

In the ground state, P has the electronic configuration $[\text{Ne}]3s^2 3p_x^1 3p_y^1 3p_z^1$ with 3 unpaired

²⁶ Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, Suppl. 3, *Phosphorus*, Longman, London, 1971, 1467 pp.

²⁷ D. G. GORENSTEIN (ed.) *Phosphorus-31 NMR; Principles and Applications* Academic Press, London, 1984, 604 pp. J. G. VERKADE and L. D. QUIN (eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH Publishers, Weinheim, 1987, 717 pp.