

CHAPTER 1

Phosphorus

Phosphorus has got itself a bit of a bad name over the years. According to Issac Asimov in his very readable *New Guide to Science*,¹ phosphorus was the impurity responsible for scuppering Henry Bessemer's initial attempts to produce high quality steel. It was also responsible for the awful medical condition known as "phossey jaw", which developed as a result of early "strike anywhere" matches that contained white phosphorus and, as we will see, this element also played a devastating part in World War II. It wasn't until the second half of the twentieth century that scientists began to get a full insight into just how vital phosphorus is for life.

1.1 PHOSPHORUS THE NON-METAL?

Phosphorus is the second member of group V in the periodic table, just below nitrogen. Its position firmly to the right of the stepped dividing line that all year 10 students draw on their periodic table places it firmly in the non-metals section of the table. However, at A level it is important to recognize that the material world rarely conforms to our hard and fast metaphysical categories, and that this line of demarcation is rather more "fuzzy" than implied at GCSE. The so-called metalloids highlight this more gradual change from metallic to non-metallic character; the semi-conducting properties of silicon and germanium are well known, but to find that phosphorus can exist

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in an allotropic form that can conduct electricity (black phosphorus) came as quite a shock. . .at least to this author!

Lesson 1: be prepared to appreciate the subtlety of chemistry. The other more common allotropes of phosphorus are white and red.

- Q1. Define the term allotrope and name one other non-metal element and one metal element that can exist as allotropes.
- Q2. A typical human body contains between 600 to 800 g of phosphorus and yet a dosage of 100 mg of white phosphorus can be fatal. How can you explain this *apparent* contradiction?

1.2 THE DISCOVERY OF PHOSPHORUS

The first isolation of phosphorus is attributed to Henning Brandt (Hamburg, 1669). The story is well known for its “yuck” factor in that Brandt required gallons of human urine, acquired from Hamburg bierkellers, which he then commenced to heat, evaporate, allow to putrefy for days, filter and heat again until samples of phosphorus vapor were condensed over and collected under water. However, at this time in history, the alchemical paradigm held sway and Brandt thought that he might have stumbled on the fabled philosopher’s stone: that which could turn base metal into gold. Brandt failed to make his fortune but was, at least, spared the horrifying epilogue to the story of Hamburg and phosphorus. The use of white phosphorus in the firebombing of Hamburg in 1943 was estimated to have killed between 50 000–100 000 men, women and children.

Q3.

- a) Calculate the number of moles of phosphorus atoms in a 14 kg bomb.
- b) Write a balanced equation for the complete combustion of phosphorus. You can assume white phosphorus exists as P_4 molecules and that the only combustion product is P_4O_{10} .
- c) Given that the ΔH_f^0 for P_4O_{10} is $-2984 \text{ kJ mol}^{-1}$, calculate the total amount of heat energy released by a 14 kg phosphorus bomb.

Another allotrope of phosphorus, as yet unmentioned, is the diatomic P_2 molecule. Sitting below nitrogen it is perhaps not surprising that P_2 molecules are linked by triple bonds ($P\equiv P$).

Q4.

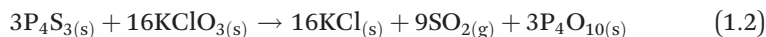
- Draw a dot and cross diagram of the $\text{P}_{2(\text{g})}$ molecule.
- The mean bond enthalpy for a single P-P bond is 198 kJ mol^{-1} and the bond enthalpy for $\text{P}\equiv\text{P}$ is 489 kJ mol^{-1} . Using a Hess's law cycle, calculate the enthalpy change for the following reaction:



- Using your answer to b) suggest which is the more stable allotrope under standard conditions.

We will return to this equation later in Q11.

No less incendiary, but rather less destructive, is the role of phosphorus in matches. Tetraphosphorus trisulfide (P_4S_3) is the fuel component of "strike anywhere" matches. The oxidizing agent, potassium chlorate (V), is added to the match head and sufficient friction initiates the following reaction:



- Q5. Calculate the mass of potassium chlorate (V) that would be required to completely combust 1 kg of P_4S_3 according to eqn 1.2.

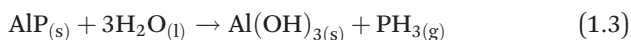
1.3 OXIDATION STATES OF PHOSPHORUS

It is clear from eqn 1.2 that phosphorus is oxidized in the reaction. However, the concept of the oxidation number is too useful to be kept only for reactions involving oxygen. With an electronegativity value of 2.1, phosphorus might be expected to form compounds with a range of formal oxidation states or numbers.

- Q6. Assign an oxidation number to phosphorus in each of the following compounds (AS level):
- P_4O_6
 - Ca_3P_2
 - H_3PO_4
 - Na_2HPO_3

A comparison of two phosphide compounds (containing the P^{3-} ion) illustrates a trend in **bond character**. Sodium phosphide (Na_3P) is an ionic black salt that is insoluble in water. Aluminium phosphide (AlP) hydrolyses on contact with water to produce highly toxic phosphine gas (PH_3).

- Q7. Explain why aluminium phosphide has a greater degree of covalent character than sodium phosphide.



Q8.

- Draw a dot and cross diagram of the PH_3 molecule, clearly showing the shape of the molecule.
- Phosphine ($M_r = 34 \text{ g mol}^{-1}$) has a boiling point of -88°C . Ammonia ($M_r = 17 \text{ g mol}^{-1}$) has a boiling point of -33°C . Account for these differences in the boiling points.

Like nitrogen, phosphorus can show oxidation states of -3 and $+3$, but the ability of phosphorus to expand its octet allows a greater chemical diversity.

Q9.

- Write out the s,p,d electronic notation for a phosphorus atom.
- Phosphorus trichloride will react further with chlorine to produce phosphorus pentachloride. Write out a balanced equation for this reaction.
- Show how sp^3d hybridization allows $\text{PCl}_{5(g)}$ to form.
- Draw a dot and cross diagram of PCl_5 and label two **different** bond angles.

1.4 THE PHOSPHORUS CYCLE

Like its periodic table neighbors, carbon, nitrogen and sulfur, phosphorus forms **acidic oxides** but, unlike them, it does not form gaseous oxides and thus does not enter the atmosphere in any significant quantities. This has considerable implications for the cycling of phosphorus on the Earth's surface, where it resides in rocks or dissolved in rivers and oceans. Issac Asimov had this to say about phosphorus:

*“We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation—but for phosphorus there is neither substitute nor replacement.”*²

Just how important phosphorus is to life can be appreciated by considering the graph taken from Chopra and Lineweaver (Figure 1.1).³

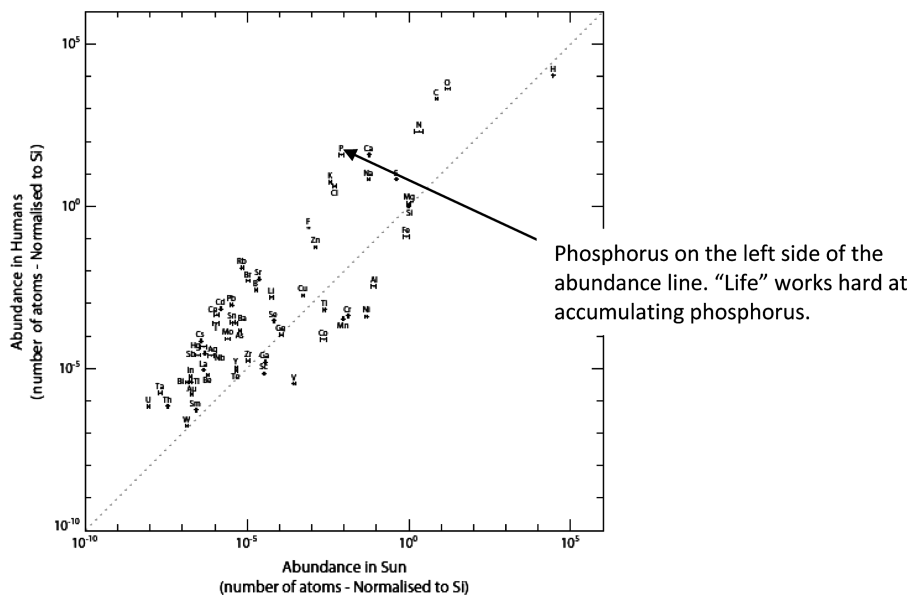


Figure 1.1 A positive correlation between elemental percentage abundances (by number of atoms), as represented by humans (y axis) and the devolatilised Sun (x axis). The abundances are normalized to silicon. Reproduced with permission of the authors, Chopra *et al.*³

The significance of phosphorus lying to the upper left hand side of the dashed diagonal shows that all life concentrates phosphorus within itself to a higher degree than any other element. To put it another way: for any one atom of phosphorus in the universe at large, there are about 10 000 phosphorus atoms in known living systems.

Because phosphorus forms no gaseous oxides, its cycling is determined by the Earth's geological and hydrological cycles, which might be thought to limit its availability, and yet its importance to life can hardly be overstated! Consider the following examples:

- i) The HPO_4^{2-} ion is vital in buffering blood serum pH.
- ii) In phospholipids it is a major constituent of cell membranes.
- iii) It forms part of the backbone of RNA and DNA molecules.
- iv) In adenosine triphosphate (ATP), the “universal” energy molecule, it is present no less than three times.
- v) It can be found in cyclic adenosine monophosphate (AMP), nicotinamide adenine dinucleotide phosphate (NADPH), guanosine triphosphate (GTP). . .the list goes on!

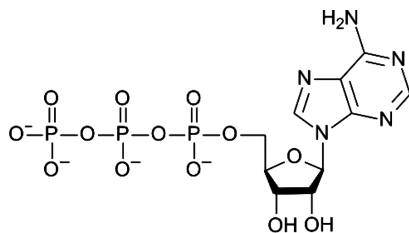


Figure 1.2 The structure of ATP.

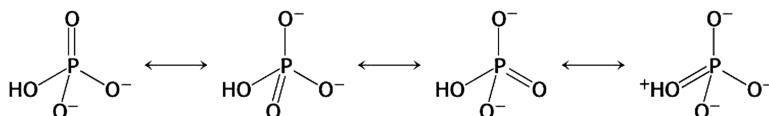


Figure 1.3 Resonance structures for HPO_4^{2-} .

It is worth dealing with a common misconception at this juncture: in chemistry lessons students are often told that bond formation is exothermic and bond breaking is endothermic. All too frequently they are then told in biology that the universal energy “unit” is generated by ATP breaking to form adenosine diphosphate (ADP) + phosphate. The hydrolysis (*i.e.*, breaking) of the P–O bond between the second and third phosphate group is **endothermic**. However, the resultant hydrogen phosphate ion (HPO_4^{2-}) then forms a resonance-stabilized structure, which is an exothermic process. You may be familiar with the consideration of the resonance stability in benzene, which makes it less reactive and thus more energetically stable than the hypothetical cyclo-1,3,5,-hexatriene (Figures 1.2 and 1.3).

The **net** result of this process has a $\Delta H_r = -30.5 \text{ kJ mol}^{-1}$ under physiological conditions. This energy can then be used to drive reactions that are thermodynamically unfavorable, such as protein synthesis.

Once released into the cytoplasm the HPO_4^{2-} has an important role to play in buffering pH. Phosphoric (V) acid has the formula H_3PO_4 . However, in the neutral conditions of the cytoplasm the following equilibrium in eqn 1.4 is important:



The reversibility of this reaction means that small additions of H^+ or OH^- can be buffered so as to retain the cytoplasmic pH at 7.0.

Q10.

- a) Write an expression for K_a for the H_2PO_4^- ion acting as an acid.
- b) Given that the K_a value for eqn 1.4 is $6.2 \times 10^{-8} \text{ mol dm}^{-3}$, calculate the ratio of $\text{H}_2\text{PO}_4^- : \text{HPO}_4^{2-}$ at $\text{pH} = 7.0$

1.5 WILL PHOSPHORUS EVER RUN OUT?

Given that one of the first principles of chemistry is that “matter is never created or destroyed in a chemical reaction”, akin to the first law of thermodynamics, which tells us that energy can never be consumed, the idea that phosphorus can be “used up” is nonsense. It should be more correctly stated that sources of phosphorus that are *economically viable to extract* can be over-consumed. Many of my students get very excited when I tell them that there are 10 million tonnes of pure gold in the world’s oceans but, at a concentration of 10 parts per 1×10^{12} , extracting the gold would cost massively more than the value of the gold extracted. However, the value of a raw material is also not fixed; for example, the price per tonne of phosphorus in 1993 was \$21.38, however, by 2008 this had climbed to \$113.00 per tonne.⁶ Clearly, a greater than five-fold increase in the price per tonne can affect the viability of a mineral resource.

We will now return to Q4 and reconsider the feasibility of the reaction shown in eqn 1.1:



Hopefully, you will have concluded that under standard conditions (1 atm. and 298 K) the reaction in eqn 1.1 is **not** feasible and yet, under certain conditions, it becomes feasible. To show this we must recall the entropy equations shown in eqn 1.5 and 1.6.

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}} \quad (1.6)$$

and that

$$\Delta S_{\text{SURROUNDINGS}} = -\Delta H/T \quad (1.5)$$

- Q11. Use the data given in Table 1.1 to calculate the temperature at which the conversion of P_4 to 2P_2 becomes feasible.

Table 1.1 Standard enthalpies of formation and standard entropy values for P_2 and P_4 .

Substance	$S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
P_2	218	144
P_4	41	0

1.6 PHOSPHORUS EXTRACTION AND “GREEN CHEMISTRY”

One of the more pressing concerns in the industrial chemistry sector these days is how to produce the desired product in the most energy-efficient way and to do so with the optimum *atom economy*. The concept of atom economy is a relatively recent one. It is defined as follows in eqn 1.7:

$$\text{Atom economy} = \frac{\text{molecular mass of desired product}}{\text{molecular mass of all reactants}} \times 100 \quad (1.7)$$

The importance of atom economy has grown as regulations involving the processing of waste materials have become more stringent and thus it has become less economically and environmentally viable to simply dump waste.

The extraction of phosphorus from a naturally occurring compound, such as calcium phosphate, is represented in eqn 1.8:



This reaction is carried out in an electric furnace at 1400 °C.

Q12.

- Calculate the atom economy for this reaction.
- How might the economic viability of this reaction be improved?

With geological resources for phosphorus becoming less economically viable, chemists are now developing methods of extracting phosphorus from animal and even human waste.

1.7 CONCLUSIONS

In the *The Periodic Table* by Primo Levi,⁴ chapter 9 is titled “Phosphorus”. “. . .It is not an emotionally neutral element,” says Levi. As the “bringer of light”, we have seen it can be the harbinger of destruction or the very spark of life. It may be that phosphorus availability is the key rate-limiting element that determines the development of life itself and yet, just as we are getting comfortable with the idea that phosphorus may indeed be life’s “bottleneck”, up pops GFAJ-1, a bacterial resident of Mono lake in California that appears to be able to substitute arsenic (As) for phosphorus in its DNA. Although it should be noted that there is still a good deal of

controversy regarding the reliability of the evidence of arsenic being incorporated into GFAJ-1's DNA. That said, we should perhaps heed lesson 1: "be prepared to appreciate the subtlety of chemistry".

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1. I. Asimov, *Asimov's New Guide to Science*, 1984, Penguin, London, pp. 278–279.
2. I. Asimov, *A Short History of Chemistry*, 1979, Anchor Books, Garden City, New York.
3. A. Chopra, C. H. Lineweaver, J. J. Brocks. T. R. Ireland, Paleocophylostoichiometrics: Searching for the elemental composition of the last universal common ancestor, *Proceedings of the 9th Space Science Conference*, Sydney, 20–30th Sept 2009, National Space Society of Australia, Sydney.
4. P. Levi, *The Periodic Table*, 1986, Abacus, London, p. 120.

Answers to the questions in this chapter can be found on pages 168–171.