

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

25

Iron, Ruthenium and Osmium

25.1 Introduction

The nine elements, Fe, Ru, Os; Co, Rh, Ir; Ni, Pd and Pt, together formed Group VIII of Mendeleev's periodic table. They will be treated here, like the other transition elements, in "vertical" triads, but because of the marked "horizontal" similarities it is not uncommon for Fe, Co and Ni to be distinguished from the other six elements (known collectively as the "platinum" metals) and the two sets of elements considered separately.

The triad Fe, Ru and Os is dominated, as indeed is the whole block of transition elements, by the immense importance of iron. This element has been known since prehistoric times and no other metal has played a more important role in man's material progress. Iron beads dating from around 4000 BC were no doubt of meteoric origin, and later samples, produced by reducing iron ore with charcoal, were not cast because adequate temperatures were not attainable without the use of some form of bellows. Instead, the spongy material produced by low-temperature reduction would have had to be shaped by prolonged hammering. It seems that iron was first smelted by the Hittites in Asia

Minor sometime in the third millennium BC, but the value of the process was so great that its secret was carefully guarded and it was only with the eventual fall of the Hittite empire around 1200 BC that the knowledge was dispersed and the "Iron Age" began.⁽¹⁾ In more recent times the introduction of coke as the reductant had far-reaching effects, and was one of the major factors in the initiation of the Industrial Revolution. The name "iron" is Anglo-Saxon in origin (*iren*, cf. German *Eisen*). The symbol Fe and words such as "ferrous" derive from the Latin *ferrum*, iron.

Biologically, iron plays crucial roles in the transport and storage of oxygen and also in electron transport, and it is safe to say that, with only a few possible exceptions in the bacterial world, there would be no life without iron. Again, within the last forty years or so, the already rich organometallic chemistry of iron has been enormously expanded, and work in the whole field given an added impetus by the discovery and characterization of ferrocene.⁽²⁾

¹ V. G. CHILDE, *What Happened in History*, pp. 182–5, Penguin Books, London, 1942.

² J. S. THAYER, *Adv. Organometallic Chem.* **13**, 1–49 (1975).

Ruthenium and osmium, though interesting and useful, are in no way comparable with iron and are relative newcomers. They were discovered independently in the residues left after crude platinum had been dissolved in aqua regia; ruthenium in 1844 from ores from the Urals by K. Klaus^(2a) who named it after *Ruthenia*, the Latin name for Russia; and osmium in 1803 by S. Tennant who named it from the Greek word for odour (ὄσμη, *osme*) because of the characteristic and pungent smell of the volatile oxide, OsO₄. (CAUTION: OsO₄ is very toxic.)

25.2 The Elements Iron, Ruthenium and Osmium

25.2.1 Terrestrial abundance and distribution

Ruthenium and osmium are generally found in the metallic state along with the other “platinum” metals and the “coinage” metals. The major source of the platinum metals are the nickel–copper sulfide ores found in South Africa and Sudbury (Canada), and in the river sands of the Urals in Russia. They are rare elements, ruthenium particularly so, their estimated abundances in the earth’s crustal rocks being but 0.0001 (Ru) and 0.005 (Os) ppm. However, as in Group 7, there is a marked contrast between the abundances of the two heavier elements and that of the first.

The nuclei of iron are especially stable, giving it a comparatively high cosmic abundance (Chap. 1, p. 11), and it is thought to be the main constituent of the earth’s core (which has a radius of approximately 3500 km, i.e. 2150 miles) as well as being the major component of “siderite” meteorites. About 0.5% of the lunar soil is now known to be metallic iron and, since on average this soil is 10 m deep, there must be $\sim 10^{12}$ tonnes of iron on the moon’s surface. In the earth’s crustal rocks (6.2%, i.e. 62 000 ppm) it is the fourth most abundant element (after oxygen, silicon and aluminium) and the second most abundant metal. It is also widely distributed,

as oxides and carbonates, of which the chief ones are: haematite (Fe₂O₃), magnetite (Fe₃O₄), limonite ($\sim 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and siderite (FeCO₃). Iron pyrite (FeS₂) is also common but is not used as a source of iron because of the difficulty in eliminating the sulfur. The distribution of iron has been considerably influenced by weathering. Leaching from sulfide and silicate deposits occurs readily as FeSO₄ and Fe(HCO₃)₂ respectively. In solution, these are quickly oxidized, and even mildly alkaline conditions cause the precipitation of iron(III) oxide. Because of their availability, production of iron ores can be confined to those of the highest grade in gigantic operations.

25.2.2 Preparation and uses of the elements

Pure iron, when needed, is produced on a relatively small scale by the reduction of the pure oxide or hydroxide with hydrogen, or by the carbonyl process in which iron is heated with carbon monoxide under pressure and the Fe(CO)₅ so formed decomposed at 250°C to give the powdered metal. However, it is not in the pure state but in the form of an enormous variety of steels that iron finds its most widespread uses, the world’s annual production being over 700 million tonnes.

The first stage in the conversion of iron ore to steel is the *blast furnace* (see Panel), which accounts for the largest tonnage of any metal produced by man. In it the iron ore is reduced by coke,[†] while limestone removes any sand or clay as a slag. The molten iron is run off to be cast into moulds of the required shape or into ingots (“pigs”) for further processing — hence the names “cast-iron” or “pig-iron”. This is an

[†] The actual reducing agent is, in the main, CO. Direct reduction of the ore using H₂, CO or CO + H₂ gas (produced from natural gas or fossil fuels) now accounts for about 4% of the world’s total production of iron. With a much lower operating temperature than that of the blast furnace, reduction is confined to the ore, producing a “sponge” iron and leaving the gangue relatively unchanged. This offers a potential economy in fuel providing that the quantity and composition of the gangue do not adversely affect the subsequent conversion to steel — which is most commonly by the electric arc furnace.

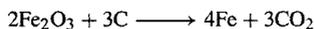
^{2a} V. N. PITCHKOV, *Platinum Metals Rev.* **40**, 181–8 (1996).

Iron^(3,4) and Steel⁽⁵⁾

About 1773, in order to overcome a shortage of timber for the production of charcoal, Abraham Darby developed a process for producing carbon (coke) from coal and used this instead of charcoal in his blast furnace at Coalbrookdale in Shropshire. The impact was dramatic. It so cheapened and increased the scale of ironmaking that in the succeeding decades Shropshire iron was used to produce for the first time: iron cylinders for steam-engines, iron rails, iron boats and ships, iron aqueducts, and iron-framed buildings. The iron bridge erected nearby over the River Severn in 1779, gave its name to the small town which grew around it and still stands, a monument to the process which "opened up" the iron industry to the Industrial Revolution.

The blast furnace (Fig. A, opposite) remains the basis of ironmaking though the scale, if not the principle, has changed considerably since the eighteenth century: the largest modern blast furnaces have hearths 14 m in diameter and produce up to 10 000 tonnes of iron daily.

The furnace is charged with a mixture of the ore (usually haematite), coke and limestone, then a blast of hot air, or air with fuel oil, is blown in at the bottom. The coke burns and such intense heat is generated that temperatures approaching 2000°C are reached near the base of the furnace and perhaps 200°C at the top. The net result is that the ore is reduced to iron, and siliceous gangue forms a slag (mainly CaSiO₃) with the limestone:



The molten iron, and the molten slag which floats on the iron, collect at the bottom of the furnace and are tapped off separately. As the charge moves down, the furnace is recharged at the top, making the process continuous. Of course the actual reactions taking place are far more numerous than this and only the more important ones are summarized in Fig. A. The details are exceedingly complex and still not fully understood. At least part of the reason for this complexity is the rapidity with which the blast passes through the furnace (~10 s) which does not allow the gas-solid reactions to reach equilibrium. The main reduction occurs near the top, as the hot rising gases meet the descending charge. Here too the limestone is converted to CaO. Reduction to the metal is completed at somewhat higher temperatures, after which fusion occurs and the iron takes up Si and P in addition to C. The deleterious uptake of S is considerably reduced if manganese is present, because of the formation of MnS which passes into the slag. For this the slag must be adequately fluid and to this end the ratio of base (CaO):acid (SiO₂, Al₂O₃) is maintained by the addition, if necessary, of gravel (SiO₂). The slag is subsequently used as a building material (breeze blocks, wall insulation) and in the manufacture of some types of cement.

Traditionally, pig-iron was converted to wrought-iron by the "puddling" process in which the molten iron was manually mixed with haematite and excess carbon and other impurities burnt out. Some wrought-iron was then converted to steel by essentially small-scale and expensive methods, such as the Cementation process (prolonged heating of wrought-iron bars with charcoal) and the crucible process (fusion of wrought-iron with the correct amount of charcoal). In the mid-nineteenth century, production was enormously increased by the introduction of the *Bessemer process* in which the carbon content of molten pig-iron in a "converter" was lowered by blasting compressed air through it. The converter was lined with silica or limestone in order to form a molten slag with the basic or acidic impurities present in the pig-iron. Air and appropriate linings were also employed in the *Open-hearth process* which allowed better control of the steel's composition, but both processes have now been supplanted by the *Basic oxygen* and *Electric arc* processes.

Basic oxygen process (BOP). This process, of which there are several modifications, originated in Austria in 1952, and because of its greater speed has since become by far the most common means of producing steel. A jet of pure oxygen is blown through a retractable steel "lance" into, or over the surface of, the molten pig-iron which is contained in a basic-lined furnace. Impurities form a slag which is usually removed by tilting the converter.

Electric arc process. Patented by Siemens in 1878, this uses an electric current through the metal (direct-arc), or an arc just above the metal (indirect-arc), as a means of heating. It is widely used in the manufacture of alloy- and other high-quality steels.

World production of iron ore in 1995 was 1020 million tonnes (Mt) (China 25%, Brazil 18%, former USSR 14%, Australia 12.9%, India and USA 6% each). In the same year world production of raw steel was 748 Mt (Western Europe 22.7%, N. America 16.2%, Japan 13.6%, China 12.4%, former USSR 10.6% and S. America 4.7%).

³Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th edn., Vol. 14, pp. 829–72, Interscience, New York, 1995.

⁴Ullmann's *Encyclopedia of Industrial Chemistry*, 5th edn., Vol. A21, pp. 461–590, VCH, Weinheim, 1989.

⁵Ref. 4, Vol. A25, pp. 63–307, 1994.

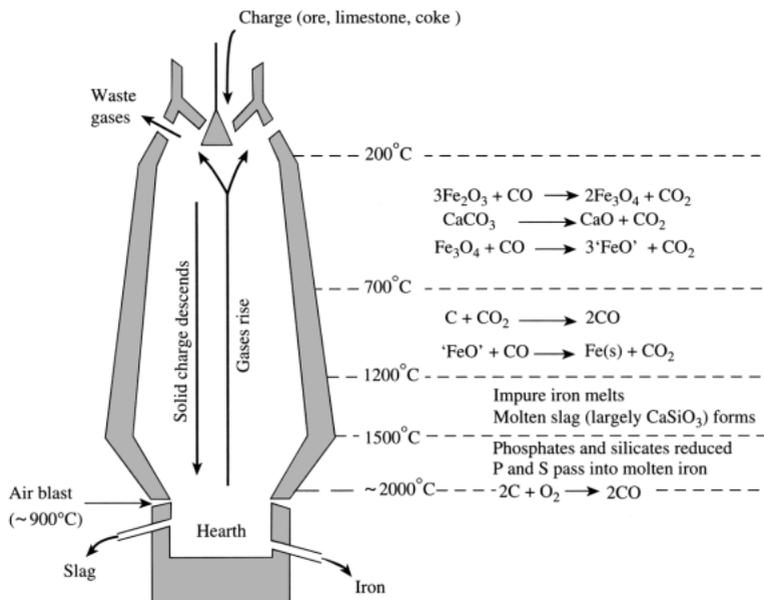


Figure A Blast furnace (diagrammatic).

impure form of iron, containing about 4% of carbon along with variable amounts of Si, Mn, P and S. It is hard but notoriously brittle. To eradicate this disadvantage the non-metallic impurities must be removed. This can be done by oxidizing them with haematite in the now obsolete “puddling process”, producing the much purer “wrought-iron”, which is tough and malleable and ideal for mechanical working. Nowadays, however, the bulk of pig-iron is converted into steel containing 0.5–1.5% C but very little S or P. The oxidation in this case is most commonly effected in one of a number of related processes by pure oxygen (basic oxygen process, or BOP), but open-hearth and electric arc furnaces are also used, while the Bessemer Converter (see Panel) was of great historical importance. This “mild steel” is cheaper than wrought-iron and stronger and more workable than cast-iron; it also has the advantage over both that it can be hardened by heating to redness and then cooling rapidly (quenching) in water or mineral oil, and “tempered” by re-heating to 200–300°C and cooling more slowly. The hardness, resilience and ductility can be controlled by varying the temperature and the

rate of cooling as well as the precise composition of the steel (see below). Alloy steels, with their enormous variety of physical properties, are prepared by the addition of the appropriate alloying metal or metals.

All the platinum group metals are isolated from “platinum concentrates” which are commonly obtained either from “anode slimes” in the electrolytic refining of nickel and copper, or as “converter matte” from the smelting of sulfide ores.⁽⁶⁾ The details of the procedure used differ from location to location and depend on the composition of the concentrate. Classical methods of separation, relying on selective precipitation, are still widely employed but solvent extraction and ion exchange techniques are increasingly being introduced to effect the primary separations (p. 1147).

Ru and Os are usually removed by distillation of their tetroxides immediately after the initial dissolution with hydrochloric acid and chlorine. Collection of the tetroxides in alcoholic NaOH and aqueous HCl respectively yields $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2$ and $(\text{NH}_4)_3\text{RuCl}_6$ from which the metals are

⁶ Ref. 4, Vol. A21, pp. 86–105, 1992.

Table 25.1 Some properties of the elements iron, ruthenium and osmium

Property	Fe	Ru	Os
Atomic number	26	44	76
Number of naturally occurring isotopes	4	7	7
Atomic weight	55.845(2)	101.07(2)	190.23(3)
Electronic configuration	[Ar]3d ⁶ 4s ²	[Kr]4d ⁷ 5s ¹	[Xe]4f ¹⁴ 5d ⁶ 6s ²
Electronegativity	1.8	2.2	2.2
Metal radius (12-coordinate)/pm	126	134	135
Effective ionic radius/pm	VIII	36 ^(a)	39 ^(a)
(4-coordinate if marked ^(a) , VII otherwise 6-coordinate)	—	38 ^(a)	52.5
	VI	—	54.5
	V	56.5	57.5
	IV	62	63
	III	68	—
	II	—	—
MP/°C	1535	2282(±20)	3045(±30)
BP/°C	2750	extrap 4050(±100)	extrap 5025(±100)
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	13.8	~25.5	31.7
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	340(±13)	—	738
ΔH_{f} (monatomic gas)/kJ mol ⁻¹	398(±17)	640	791(±13)
Density (20°C)/g cm ⁻³	7.874	12.37	22.59
Electrical resistivity (20°C)/μohm cm	9.71	6.71	8.12

^(a)Refers to coordination number 4. ls = low spin, hs = high spin.

obtained by ignition in H₂. The metals are in the form of powder or sponge and are usually consolidated by powder-metallurgical techniques. Major uses of ruthenium are as a coating for titanium anodes in the electrolytic production of Cl₂ and, more recently, as a catalyst in the production of ammonia (p. 421). Osmium is used in dentistry as a hardening agent in gold alloys. However, Ru and Os, along with Ir, are regarded as the minor platinum metals, being obtained largely as byproducts in the production of Pt, Pd and Rh, and their annual world production is only of the order of tonnes. (Weights of Ru and Os, as of most precious metals, are generally quoted in troy ounces: 1 troy ounce = 1.097 avoirdupois ounce = 31.103 g.)

25.2.3 Properties of the elements

Table 25.1 summarizes some of the important properties of Fe, Ru and Os. The two heavier elements in particular have several naturally occurring isotopes, and difficulties in obtaining calibrated measurements of their

relative abundances limit the precision with which their atomic weights can be determined. Osmium is the densest of all elements, surpassing iridium by the tiniest of margins.⁽⁷⁾

All three elements are lustrous and silvery in colour. Iron when pure is fairly soft and readily worked, but ruthenium and osmium are less tractable in this respect. The structures of the solids are typically metallic, being hcp for the two heavier elements and bcc for iron at room temperature (α -iron). However, the behaviour of iron is complicated by the existence of a fcc form (γ -iron) at higher temperatures (above 910°), reverting to bcc again (δ -iron) at about 1390°, some 145° below its mp. Technologically, the carbon content is crucial, as can be seen from the Fe/C phase diagram (Fig. 25.1), which also throws light on the hardening and tempering

⁷Densities are calculated from crystallographic data and depend on a knowledge of the wavelength of the X-rays, Avogadro's constant and the atomic weight of the element. Using the best available data the densities of Os and Ir are calculated to be 22.587 ± 0.009 and 22.562 ± 0.009 g cm⁻³ respectively at 20°C. J. W. ARBLASTER, *Platinum Metals Rev.* **33**, 14–16 (1989). *ibid.*, **39**, 164 (1995).

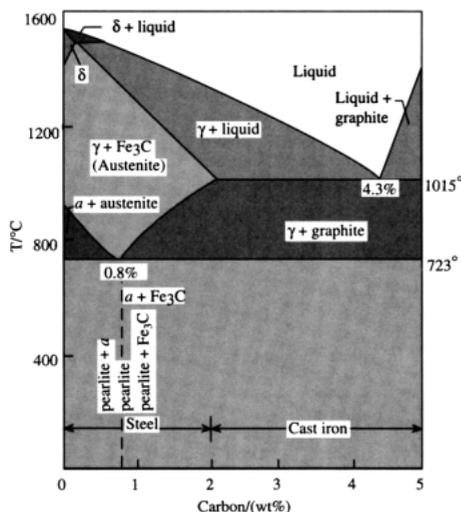


Figure 25.1 The iron-carbon phase diagram for low concentrations of carbon.

processes already referred to. The lowering of the mp from 1535° to 1015°C when the C content reaches 4.3%, facilitates the fusion of iron in the blast furnace, and the lower solubility of Fe_3C (“cementite”) in α -iron as compared to δ - and γ -iron leads to the possibility of producing metastable forms by varying the rate of cooling of hot steels. At elevated temperatures a solid solution of Fe_3C in γ -iron, known as “austenite”, prevails. If 0.8% C is present, slow cooling below 723°C causes Fe_3C to separate forming alternate layers with the α -iron. Because of its appearance when polished, this is known as “pearlite” and is rather soft and malleable. If, however, the cooling is rapid (quenching) the separation is suppressed and the extremely hard and brittle “martensite” is produced. Reheating to an intermediate temperature tempers the steel by modifying the proportions of hard and malleable forms. If the C content of the steel is below 0.8% then slow cooling gives a mixture of pearlite and α -iron and, if higher than 0.8% a mixture of pearlite and Fe_3C . Varying the proportion of carbon in the steel thereby further extends the range of physical properties which can be attained by appropriate heat treatment.

The magnetic properties of iron are also dependent on purity and heat treatment. Up to 768°C

(the Curie point) pure iron is ferromagnetic as a result of extensive magnetic interactions between unpaired electrons on adjacent atoms, which cause the electron spins to be aligned in the same direction, so producing exceedingly high magnetic susceptibilities and the characteristic ferromagnetic properties of “saturation” and “hysteresis”. The existence of unpaired electrons on the individual atoms, as opposed to being delocalized in bands permeating the lattice, can be rationalized at least partly by supposing that in the bcc lattice the metal d_{z^2} and $d_{x^2-y^2}$ orbitals, which are not directed towards nearest neighbours, are therefore nonbonding and so can retain 2 unpaired electrons on the atom. On the other hand, electrons in the remaining three d orbitals participate in the formation of a conduction band of predominantly paired electrons. At temperatures above the Curie temperature, thermal energy overcomes the interaction between the electrons localized on individual atoms; their mutual alignment is broken, and normal paramagnetic behaviour ensues. This is sometimes referred to as β -iron ($768\text{--}910^{\circ}$) though the crystal structure remains bcc as in ferromagnetic α -iron. For the construction of permanent magnets, cobalt steels are particularly useful, whereas for the “soft” irons used in electric motors and transformer cores (where the magnetization undergoes rapid reversal) silicon steels are preferred.

The mps and bps and enthalpies of atomization indicate that the $(n-1)d$ electrons are contributing to metal bonding less than in earlier groups although, possibly due to an enhanced tendency for metals with a d^5 configuration to resist delocalization of their d electrons, Mn and to a lesser extent Tc occupy “anomalous” positions so that for Fe and Ru the values of these quantities are actually higher than for the elements immediately preceding them. In the third transition series Re appears to be “well-behaved” and the changes from $\text{W} \rightarrow \text{Re} \rightarrow \text{Os}$ are consequently smooth.

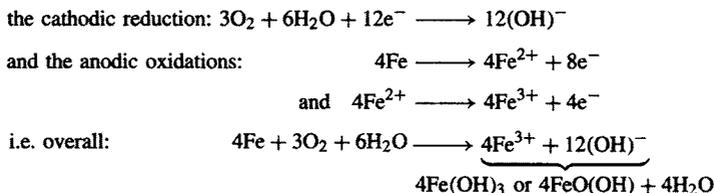
25.2.4 Chemical reactivity and trends

As expected, contrasts between the first element and the two heavier congeners are noticeable,

Rusting of Iron⁽⁸⁾

The economic importance of rusting can scarcely be overestimated. Although precision is impossible, it is likely that the cost of corrosion is over 1% of the world's economy.

Rusting of iron consists of the formation of hydrated oxide, $\text{Fe}(\text{OH})_3$ or $\text{FeO}(\text{OH})$, and is evidently an electrochemical process which requires the presence of water, oxygen and an electrolyte — in the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50% provides the necessary amount of water. The mechanism is complex⁽⁹⁾ and will depend in detail on the prevailing conditions, but may be summarized as:



The presence of the electrolyte is required to provide a pathway for the current and, in urban areas, this is commonly iron(II) sulfate formed as a result of attack by atmospheric SO_2 but, in seaside areas, airborne particles of salt are important. Because of its electrochemical nature, rusting may continue for long periods at a more or less constant rate, in contrast to the formation of an anhydrous oxide coating which under dry conditions slows down rapidly as the coating thickens.

The anodic oxidation of the iron is usually localized in surface pits and crevices which allow the formation of adherent rust over the remaining surface area. Eventually the lateral extension of the anodic area undermines the rust to produce loose flakes. Moreover, once an adherent film of rust has formed, simply painting over gives but poor protection. This is due to the presence of electrolytes such as iron(II) sulfate in the film so that painting merely seals in the ingredients for anodic oxidation. It then only requires the exposure of some other portion of the surface, where cathodic reduction can take place, for rusting beneath the paint to occur.

The protection of iron and steel against rusting takes many forms, including: simple covering with paint; coating with another metal such as zinc (galvanizing) or tin; treating with "inhibitors" such as chromate(VI) or (in the presence of air) phosphate or hydroxide, all of which produce a coherent protective film of Fe_2O_3 . Another method uses sacrificial anodes, most usually Mg or Zn which, being higher than Fe in the electrochemical series, are attacked preferentially. In fact, the Zn coating on galvanized iron is actually a sacrificial anode.

both in the reactivity of the elements and in their chemistry. Iron is much the most reactive metal of the triad, being pyrophoric if finely divided and dissolving readily in dilute acids to give Fe^{II} salts; however, it is rendered passive by oxidizing acids such as concentrated nitric and chromic, due to the formation of an impervious oxide film which protects it from further reaction but which is immediately removed by acids such as hydrochloric. Ruthenium and osmium, on the other hand, are virtually unaffected by non-oxidizing acids, or even aqua regia. Iron also reacts fairly easily with most non-metals whereas ruthenium and osmium do so only with difficulty at high temperatures, except in the case of

oxidizing agents such as F_2 and Cl_2 . Indeed, it is with oxidizing agents generally that Ru and Os metals are most reactive. Thus Os is converted to OsO_4 by conc nitric acid and both metals can be dissolved in molten alkali in the presence of air or, better still, in oxidizing flux such as Na_2O_2 or KClO_3 to give the ruthenates and osmates $[\text{RuO}_4]^{2-}$ and $[\text{OsO}_2(\text{OH})_4]^{2-}$ respectively. If the aqueous extracts from these fusions are treated with Cl_2 and heated, the tetroxides distil off, providing convenient preparative starting materials as well as the means of recovering the elements.

Ruthenium and Os are stable to atmospheric attack though if Os is very finely divided it gives off the characteristic smell of OsO_4 . By contrast, iron is subject to corrosion in the form of rusting which, because of its great economic importance, has received much attention (see Panel above).

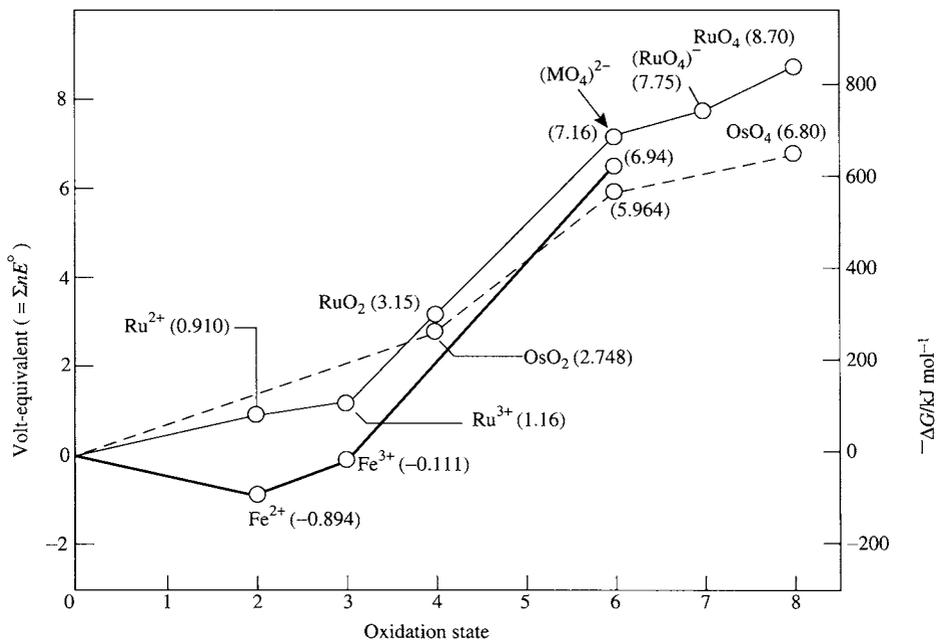
⁸ U. R. EVANS, *An Introduction to Metallic Corrosion*, Arnold, London, 3rd edn, 1981, 320 pp.

⁹ T. E. GRAEDEL and R. P. FRANKENTHAL, *J. Electrochem. Soc.* **137**, 2385–94 (1990).

Table 25.2 Standard reduction potentials for iron, ruthenium and osmium in acidic aqueous solution^(a)

Half reaction	E°/V	Volt-equivalent
$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.447	-0.894
$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$	-0.037	-0.111
$(\text{FeO}_4)^{2-} + 8\text{H}^+ + 3e^- \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O}$	2.20	6.49
$\text{Ru}^{2+} + 2e^- \rightleftharpoons \text{Ru}$	0.455	0.910
$\text{Ru}^{3+} + e^- \rightleftharpoons \text{Ru}^{2+}$	0.249	1.159
$\text{RuO}_2 + 4\text{H}^+ + 2e^- \rightleftharpoons \text{Ru}^{2+} + 2\text{H}_2\text{O}$	1.120	3.150
$(\text{RuO}_4)^{2-} + 8\text{H}^+ + 4e^- \rightleftharpoons \text{Ru}^{2+} + 4\text{H}_2\text{O}$	1.563	7.162
$(\text{RuO}_4)^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Ru}^{2+} + 4\text{H}_2\text{O}$	1.368	7.750
$\text{RuO}_4 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{RuO}_2 + 2\text{H}_2\text{O}$	1.387	8.698
$\text{OsO}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{Os} + 2\text{H}_2\text{O}$	0.687	2.748
$(\text{OsO}_4)^{2-} + 8\text{H}^+ + 6e^- \rightleftharpoons \text{Os} + 4\text{H}_2\text{O}$	0.994	5.964
$\text{OsO}_4 + 8\text{H}^+ + 8e^- \rightleftharpoons \text{Os} + 4\text{H}_2\text{O}$	0.85	6.80

(a) See also Table A (p. 1093) and Table 25.8 (p. 1101).

**Figure 25.2** Plot of volt-equivalent against oxidation state for Fe, Ru and Os in acidic aqueous solution.

In moving across the transition series, iron is the first element which fails to attain its group oxidation state (+8). The highest oxidation state known (so far) is +6 in $[\text{FeO}_4]^{2-}$ and even this is extremely easily reduced. On the

other hand, ruthenium and osmium do attain the group oxidation state of +8, though they are the last elements to do so in the second and third transition series, and this is consequently the highest oxidation state for any element (see also

Xe^{VIII}, p. 894). Ruthenium(VIII) is significantly less stable than Os^{VIII} and it is clear that the second- and third-row elements, though similar, are by no means as alike as for earlier element-pairs in the transition series. The same gradation within the triad is well illustrated by the reactions of the metals with oxygen. All react on heating, but their products are, respectively, Fe₂O₃ and Fe₃O₄, Ru^{IV}O₂ and Os^{VIII}O₄. In general terms it can be said that the most common oxidation states

for the three elements are +2 and +3 for Fe, +3 for Ru, and +4 for Os. And, while Fe (and to a lesser extent Ru) has an extensive aqueous cationic chemistry in its lower oxidation states, Os has none. Table 25.2 and Fig. 25.2 summarize the relative stabilities of the various oxidation states in acidic aqueous solution.

A selection of representative examples of compounds of the three elements is given in Table 25.3. As in the preceding group there is

Table 25.3 Oxidation states and stereochemistries of some compounds of iron, ruthenium and osmium

Oxidation state	Coordination number	Stereochemistry	Fe	Ru, Os
-2 (d ¹⁰)	4	Tetrahedral	[Fe(CO) ₄] ²⁻	[M(CO) ₄] ²⁻
-1 (d ⁹)	5	Trigonal bipyramidal	[Fe ₂ (CO) ₈] ²⁻	
0 (d ⁸)	5	Trigonal bipyramidal	[Fe(CO) ₅]	[M(CO) ₅](?)
	6	Octahedral (D ₃)	[Fe(bipy) ₃]	
	7	Face-capped octahedral	[Fe ₂ (CO) ₉]	
1 (d ⁷)	2	Linear	[FeO ₂] ³⁻	
	6	Octahedral	[Fe(NO)(H ₂ O) ₅] ²⁺	[Os(NH ₃) ₆] ⁺
	9	(See Fig. 25.15(a))	[(Fe(η ⁵ -C ₅ H ₅)(CO)(μ-CO)) ₂]	
2 (d ⁶)	4	Tetrahedral	[FeCl ₄] ²⁻	[RuH{N(SiMe ₃) ₂ }(PPh ₃) ₂]
		Square planar	BaFeSi ₄ O ₁₀	
	5	Trigonal bipyramidal	[FeBr{N(C ₂ H ₄ NMe ₂) ₃ }] ⁺	
		Square pyramidal	[Fe(OAsMe ₃) ₄ (ClO ₄)] ⁺	[RuCl ₂ (PPh ₃) ₃]
	6	Octahedral	[Fe(H ₂ O) ₆] ²⁺	[M(CN) ₆] ⁴⁻
	7	(p. 174)	[Fe(η ⁴ -B ₄ H ₈)(CO) ₃]	
	8	(See Fig. 25.15c)	[Fe(η ¹ -C ₅ H ₅)(η ⁵ -C ₅ H ₅)(CO) ₂]	
	10	Sandwich	[Fe(η ⁵ -C ₅ H ₅) ₂]	[M(η ⁵ -C ₅ H ₅) ₂]
3 (d ⁵)	3	Planar	[Fe{N(SiMe ₃) ₂] ₃]	
	4	Tetrahedral	[FeCl ₄] ⁻	
	5	Square pyramidal	[Fe(acac) ₂ Cl]	
	6	Octahedral	[Fe(CN) ₆] ³⁻	[MCl ₆] ³⁻
	7	Pentagonal bipyramidal	[Fe(edta)(H ₂ O)] ⁻	
	8	Dodecahedral	[Fe(NO ₃) ₄] ⁻	
4 (d ⁴)	6	Octahedral	[Fe(diars) ₂ Cl ₂] ²⁺	[MCl ₆] ²⁻
	4	Tetrahedral		OsCy ₄
5 (d ³)	4	Tetrahedral	[FeO ₄] ³⁻	
	6	Octahedral		[MF ₆] ⁻
6 (d ²)	4	Tetrahedral	[FeO ₄] ²⁻	[RuO ₄] ²⁻
	5	Square pyramidal		[OsNCl ₄] ⁻
		Trigonal bipyramidal		[RuO ₅] ^{4-(a)}
	6	Octahedral		[OsO ₂ (OH) ₄] ²⁻
7 (d ¹)	4	Tetrahedral		[MO ₄] ⁻
	6	Octahedral		[OsOF ₅]
	7	Pentagonal bipyramidal		OsF ₇
8 (d ⁰)	4	Tetrahedral		MO ₄
	6	Octahedral		[OsO ₄ F ₂] ²⁻

^(a)Both tetrahedral and trigonal bipyramidal Ru^{VI} occur in the single compound, CsK₅[RuO₅][RuO₄]; D. FISCHER and R. HOPPE, *Z. anorg. allg. Chem.* **617**, 37-44 (1992).