

																1	2																															
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Li	Be																	B	C	N	O	F	Ne																									
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19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																															
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37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																															
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87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																															
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28

Copper, Silver and Gold

28.1 Introduction⁽¹⁾

Collectively known as the “coinage metals” because of their former usage, these elements were almost certainly the first three metals known to man. All of them occur in the elemental, or “native”, form and must have been used as primitive money long before the introduction of gold coins in Egypt around 3400 BC.

Cold-hammering was used in the late Stone Age to produce plates of gold for ornamental purposes, and this metal has always been synonymous with beauty, wealth and power. Considerable quantities were accumulated by ancient peoples. The coffin of Tutankhamun (a minor Pharaoh who was only 18 when he died) contained no less than 112 kg of gold, and the legendary Aztec and Inca hoards in Mexico and Peru were a major reason for the Spanish conquests of Central and South America in the early sixteenth century. Today, the greatest hoard of gold is the 30 000 tonnes of bullion (i.e. bars) lying in the vaults of the US Federal Reserve Bank

in New York and belonging to eighty different nations.

Estimates of the earliest use of copper vary, but 5000 BC is not unreasonable. By about 3500 BC it was being obtained in the Middle East by charcoal reduction of its ores, and by 3000 BC the advantages of adding tin in order to produce the harder bronze was appreciated in India, Mesopotamia and Greece. This established the “Bronze Age”, and copper has continued to be one of man’s most important metals.

The monetary use of silver may well be as old as that of gold but the abundance of the native metal was probably far less, so that comparable supplies were not available until a method of winning the metal from its ores had been discovered. It appears, however, that by perhaps 3000 BC a form of cupellation[†] was in operation in Asia Minor and its use gradually

[†] Cupellation processes vary but consist essentially of heating a mixture of precious and base (usually lead) metals in a stream of air in a shallow hearth, when the base metal is oxidized and removed either by blowing away or by absorption into the furnace lining. In the early production of silver, the sulfide ores must have been used to give first a silver/lead alloy from which the lead was then removed.

¹ R. F. TYLECOTE, *History of Metallurgy*, The Metals Society, London, 1976, 182 pp.

spread, so that silver coinage was of crucial economic importance to all subsequent classical Mediterranean civilizations.

The name *copper* and the symbol Cu are derived from *aes cyprium* (later Cuprum), since it was from Cyprus that the Romans first obtained their copper metal. The words *silver* and *gold* are Anglo-Saxon in origin but the chemical symbols for these elements (Ag and Au) are derived from the Latin *argentum* (itself derived from the Greek ἀργός, *argos*, shiny or white) and *aurum*, gold.

28.2 The Elements

28.2.1 Terrestrial abundance and distribution

The relative abundances of these three metals in the earth's crust (Cu 68 ppm, Ag 0.08 ppm, Au 0.004 ppm) are comparable to those of the preceding triad — Ni, Pd and Pt. Copper is found mainly as the sulfide, oxide or carbonate, its major ores being copper pyrite (chalcopyrite), CuFeS_2 , which is estimated to account for about 50% of all Cu deposits; copper glance (chalcocite), Cu_2S ; cuprite, Cu_2O and malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Large deposits are found in various parts of North and South America, and in Africa and the former Soviet Union. The native copper found near Lake Superior is extremely pure but the vast majority of current supplies of copper are obtained from low-grade ores containing only about 1% Cu.

Silver is widely distributed in sulfide ores of which silver glance (argentite), Ag_2S , is the most important. Native silver is sometimes associated with these ores as a result of their chemical reduction, while the action of salt water is probably responsible for their conversion into "horn silver", AgCl , which is found in Chile and New South Wales. The Spanish Americas provided most of the world's silver for the three centuries after about 1520, to be succeeded in the nineteenth century by Russia. Appreciable quantities are now obtained as a byproduct in the production of other metals such as copper,

and the main producers are Mexico, the former Soviet Union, Peru, the USA and Australia.

Gold, too, is widely, if sparsely, distributed both native[†] and in tellurides, and is almost invariably associated with quartz or pyrite, both in veins and in alluvial or placer deposits laid down after the weathering of gold-bearing rocks. It is also present in sea water to the extent of around 1×10^{-3} ppm, depending on location, but no economical means of recovery has yet been devised. Prior to about 1830 a large proportion of the world's stock of gold was derived from ancient and South American civilizations (recycling is not a new idea), and the annual output of new gold was no more than 12 tonnes pa. This supply gradually increased with the discovery of gold in Siberia followed by "gold rushes" in 1849 (California: as a result of which the American West was settled), 1851 (New South Wales and Victoria: within 7 y the population of Australia doubled to 1 million), 1884 (Transvaal), 1896 (Klondike, North-west Canada) and, finally, 1900 (Nome area of Alaska) as a result of which by 1890 world production had risen to 150 tonnes pa. It is now 15 times that amount, ~2300 tonnes pa.

28.2.2 Preparation and uses of the elements^(2,3)

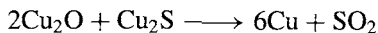
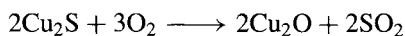
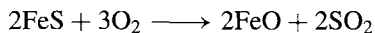
A few of the oxide ores of copper can be reduced directly to the metal by heating with coke, but the bulk of production is from sulfide ores containing iron, and they require more complicated treatment. These ores are comparatively lean (often ~0.5% Cu) and their exploitation requires economies of scale. They are therefore obtained in huge, open-pit operations employing shovels

[†] The "Welcome Stranger" nugget found in Victoria, Australia, in 1869 weighed over 71 kg and yielded nearly 65 kg of refined gold but was, unfortunately, exceptional.

² *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Interscience, New York; for Cu see Vol. 7, 1993, pp. 505–20; for Ag, Vol. 22, 1997, pp. 163–95; for Au, Vol. 12, 1994, pp. 738–67.

³ J. MARSDEN and I. HOUSE, *The Chemistry of Gold Extraction*, Ellis Horwood, Chichester, 1992, 597 pp.

of up to 25 m³ (900 ft³) and trucks of up to 250 tonnes capacity, followed by crushing and concentration (up to 15–20% Cu) by froth-flotation. (The environmentally acceptable disposal of the many millions of tonnes of finely ground waste poses serious problems.) Silica is added to the concentrate which is then heated in a reverberatory furnace (blast furnaces are unsuitable for finely powdered ores) to about 1400°C when it melts. FeS is more readily converted to the oxide than is Cu₂S and so, with the silica, forms an upper layer of iron silicate slag leaving a lower layer of copper matte which is largely Cu₂S and FeS. The liquid matte is then placed in a converter (similar to the Bessemer converter, p. 1072) with more silica and a blast of air forced through it. This transforms the remaining FeS first to FeO and then to slag, while the Cu₂S is partially converted to Cu₂O and then to metallic copper:



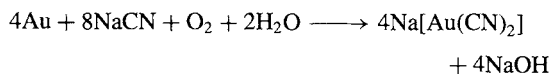
The major part of this “blister” copper is further purified electrolytically by casting into anodes which are suspended in acidified CuSO₄ solution along with cathodes of purified copper sheet. As electrolysis proceeds the pure copper is deposited on the cathodes while impurities collect below the anodes as “anode slime” which is a valuable source of Ag, Au and other precious metals.

About one-third of the copper used is secondary copper (i.e. scrap) but the annual production of new metal is nearly 8 million tonnes, the chief sources (1993) being Chile (22%), the USA (20%), the former Soviet Union (9%), Canada and China (7.5% each) and Zambia (5%). The major use is as an electrical conductor but it is also widely employed in coinage alloys as well as the traditional bronze (Cu plus 7–10% Sn), brass (Cu–Zn), and special alloys such as *Monel* (Ni–Cu).

Most silver is nowadays produced as a byproduct in the manufacture of non-ferrous metals such as copper, lead and zinc, when

the silver follows the base metal through the concentration and smelting processes. In the case of copper production, for instance, the anode slimes mentioned above are treated with hot, aerated dilute H₂SO₄, which dissolves some of the base metal content, then heated with a flux of lime or silica to slag-off most of the remaining base metals, and, finally, electrolysed in nitrate solution to give silver of better than 99.9% purity. As with copper, much of the metal used is salvage but over 10 000 tonnes of new metal were produced in 1993, mainly from Mexico (19%) the former Soviet Union, the USA and Peru (~13% each) and Australia (9%). Photography accounts for the use of about one-third of this and it is also used in silverware and jewellery, electrically, for silvering mirrors, and in the high-capacity Ag–Zn, Ag–Cd batteries. A minor though important use from 1826 until recent times was as dental amalgam (Hg/γ–Ag₃Sn).

Traditionally, gold was recovered from river sands by methods such as “panning” which depend on the high density of gold (19.3 g cm⁻³) compared with sand (~2.5 g cm⁻³)[†] but as such sources are largely worked out, modern production depends on the mining of the gold-containing rock (typically, 5–15 ppm of Au). This is crushed to a fine powder (the consistency of talcum powder) to liberate the metallic grains and these are extracted either by the cyanide process or, after gravity concentration, by amalgamation with mercury (after which the Hg is distilled off). In the former the gold and any silver present is leached from the crushed rock with an aerated, dilute solution of cyanide:



It is then precipitated by adding Zn dust. Electrolytic refining may then be used to provide gold of 99.99% purity.[‡]

[†] In ancient times, gold-bearing river sands were washed over a sheep’s fleece which trapped the gold. It seems likely that this was the origin of the Golden Fleece of Greek mythology.

[‡] Gold is commonly alloyed with other metals in order to make it harder and cheaper. (An appropriate mixture of Au

Table 28.1 Some properties of the elements copper, silver and gold

Property		Cu	Ag	Au
Atomic number		29	47	79
Number of naturally occurring isotopes		2	2	1
Atomic weight		63.546(3)	107.8682(2)	196.96655(2)
Electronic configuration		[Ar]3d ¹⁰ 4s ¹	[Kr]4d ¹⁰ 5s ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
Electronegativity		1.9	1.9	2.4
Metal radius (12-coordinate)/pm		128	144	144
Effective ionic radius (6-coordinate)/pm	V	—	—	57
	III	54	75	85
	II	73	94	—
	I	77	115	137
Ionization energy/kJ mol ⁻¹	1st	745.3	730.8	889.9
	2nd	1957.3	2072.6	1973.3
	3rd	3577.6	3359.4	(2895)
MP/°C		1083	961	1064
BP/°C		2570	2155	2808
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$		13.0	11.1	12.8
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$		307(±6)	258(±6)	343(±11)
$\Delta H_{\text{(monatomic gas)}}/\text{kJ mol}^{-1}$		337(±6)	284(±4)	379(±8)
Density (20°C)/g cm ⁻³		8.95	10.49	19.32
Electrical resistivity (20°C)/μohm cm		1.673	1.59	2.35

Total annual production of new gold is now about 2300 tonnes of which (1993) 27% comes from South Africa, 15% from the USA and 11% each from Australia and the former Soviet Union. The bulk of the gold from “Western” countries passes through the London Bullion Market which was established in 1666. Prices, which are quoted in troy oz,[†] are affected by speculative buying and can be subject to astonishing fluctuations.

The two main uses for gold are in settling international debts and in the manufacture of jewellery, but other important uses are in dentistry, the electronics industry (corrosion-free contacts), and the aerospace industry (brazing alloys and heat reflection), while in office buildings it has

been found that a mere 20 nm film on the inside face of windows cuts down heat losses in winter and reflects unwanted infrared radiation in summer.

28.2.3 Atomic and physical properties of the elements

Some important properties are listed in Table 28.1. As gold has only one naturally occurring isotope, its atomic weight is known with considerable accuracy; Cu and Ag each have 2 stable isotopes, and a slight variability of their abundance in the case of Cu prevents its atomic weight being quoted with greater precision. This is the first triad since Ti, Zr and Hf in which the ground-state electronic configuration of the free atoms is the same for the outer electrons of all three elements. Gold is the most electronegative of all metals: the value of 2.4 equals that for Se and approaches the value of 2.5 for S and I. Estimates of electron affinity vary considerably but typical values (kJ mol⁻¹) are Cu 119.2, Ag 125.6 and Au 222.8. These may be compared with values for

and Cu will maintain the golden hue.) The proportion of gold is expressed in *carats*, a *carat* being a twenty-fourth part by weight of the metal so that pure gold is 24 *carats*. In the case of precious stones the *carat* expresses mass not purity and is then defined as 200 mg. The term is derived from the name of the small and very uniform seeds of the carob tree which in antiquity were used to weigh precious metals and stones (p. 272).

[†] 1 troy (or fine) oz = 31.1035 g as distinct from 1 oz avoirdupois = 28.3495 g.

H 72.8, O 141.0 and I 295.2 kJ mol⁻¹. Consistent with this the compound CsAu has many salt-like rather than alloy-like properties and, when fused, behaves much like other molten salts. Similarly when Au is dissolved in solutions of Cs, Rb or K in liquid ammonia, the spectroscopic and other properties are best interpreted in terms of the solvated Au⁻ ion (d¹⁰s²) analogous to a halide ion (s²p⁶).

The elements are obtainable in a state of very high purity but some of their physical properties are nonetheless variable because of their dependence on mechanical history. Their colours (Cu reddish, Ag white and Au yellow) and sheen are so characteristic that the names of the metals are used to describe them.[†] Gold can also be obtained in red, blue and violet colloidal forms by the addition of various reducing agents to very dilute aqueous solutions of gold(III) chloride. A remarkably stable example is the "Purple of Cassius", obtained by using SnCl₂ as reductant, which not only provides a sensitive test for Au^{III} but is also used to colour glass and ceramics. Colloidal silver and copper are also obtainable but are less stable.

The solid metals all have the fcc structure, like their predecessors in the periodic table, Ni, Pd and Pt, and they continue the trend of diminishing mp and bp. They are soft, and extremely malleable and ductile, gold more so than any other metal. One gram of gold can be beaten out into a sheet of ~1.0 m² only 230 atoms thick (i.e. 1 cm³ to 18 m²); likewise 1 g Au can be drawn into 165 m of wire of diameter 20 μm. The electrical and thermal conductances of the

three metals are also exceptional, pre-eminence in this case belonging to silver. All these properties can be directly related to the d¹⁰s¹ electronic configuration.

28.2.4 Chemical reactivity and trends

Because of the traditional designation of Cu, Ag and Au as a subdivision of the group containing the alkali metals (justified by their respective d¹⁰s¹ and p⁶s¹ electron configurations) some similarities in properties might be expected. Such similarities as do occur, however, are confined almost entirely to the stoichiometries (as distinct from the chemical properties) of the compounds of the +1 oxidation state. The reasons are not hard to find. A filled d shell is far less effective than a filled p shell in shielding an outer s electron from the attraction of the nucleus. As a result the first ionization energies of the coinage metals are much higher, and their ionic radii smaller than those of the corresponding alkali metals (Table 28.1 and p. 75). They consequently have higher mps, are harder, denser, less reactive, less soluble in liquid ammonia, and their compounds more covalent. Again, whereas the alkali metals stand at the top of the electrochemical series (with E° between -3.045 and -2.714 V), the coinage metals are near the bottom: Cu⁺/Cu +0.521, Ag⁺/Ag +0.799, Au⁺/Au +1.691 V. On the other hand, a filled d shell is more easily disrupted than a filled p shell. The second and third ionization energies of the coinage metals are therefore *lower* than those of the alkali metals so that they are able to adopt oxidation states higher than +1. They also more readily form coordination complexes. In short, Cu, Ag and Au are transition metals whereas the alkali metals are not. Indeed, the somewhat salt-like character of CsAu and the formation of the solvated Au⁻ ion in liquid ammonia, mentioned above, can be regarded as halogen-like behaviour arising because the d¹⁰s¹ configuration is 1 electron short of the closed configuration d¹⁰s² (cf hydrogen, p. 43).

[†] The colours arise from the presence of filled d bands near the electron energy surface of the s-p conduction band of the metals (Fermi surface). X-ray data indicate that the top of the d-band is ~220 kJ mol⁻¹ (2.3 eV/atom) below the Fermi surface for Cu so electrons can be excited from the d band to the s-p band by absorption of energy in the green and blue regions of the visible spectrum but not in the orange or red regions. For silver the excitation energy is rather larger (~385 kJ mol⁻¹) corresponding to absorption in the ultraviolet region of the spectrum. Gold is intermediate but much closer to Cu, the absorption in the near ultraviolet and blue region of the spectrum giving rise to the characteristic golden yellow colour of the metal.

Copper, silver and gold are notable in forming an extensive series of alloys with many other metals and many of these have played an important part in the development of technology through the ages (p. 1173). In many cases the alloys can be thought of as nonstoichiometric intermetallic compounds of definite structural types and, despite the apparently bizarre formulae that emerge from the succession of phases, they can readily be classified by a set of rules first outlined by W. Hume-Rothery in 1926. The determining feature is the ratio of the number of electrons to the number of atoms ("electron concentration"), and because of this the phases are sometimes referred to as "electron compounds".

The fcc lattice of the coinage metals has 1 valency electron per atom ($d^{10}s^1$). Admixture with metals further to the right of the periodic table (e.g. Zn) increases the electron concentration in the primary alloy (α -phase) which can be described as an fcc solid solution

of M in Cu, Ag or Au. This continues until, as the electron concentration approaches 1.5 (i.e. 21/14), the fcc structure becomes less stable than a bcc arrangement which therefore crystallizes as the β -phase (e.g. β -brass, CuZn; see Fig. 28.1). Further increase in electron concentration results in formation of the more complex γ -brass phase of nominal formula Cu_5Zn_8 and electron concentration of $\{(5 \times 1) + (8 \times 2)\}/13 = 21/13 = 1.615$. The phase is still cubic but has 52 atoms in the unit cell (i.e. $4\text{Cu}_5\text{Zn}_8$). This γ -phase can itself take up more Zn until a third critical concentration is reached near 1.75 (i.e. 7/4 or 21/12) when the hcp ε -phase of CuZn_3 is formed. Hume-Rothery showed that this succession of phases is quite general (and also holds for Groups 8, 9 and 10 to the left of the coinage metals if they are taken to contribute no electrons to the lattice).

The reactivity of Cu, Ag and Au decreases down the group, and in its inertness gold

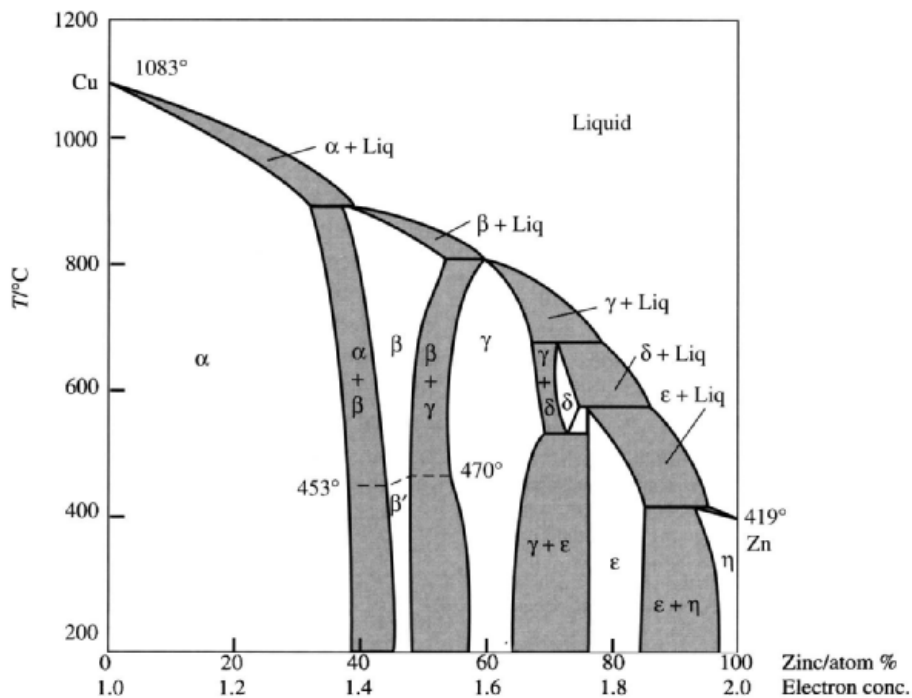


Figure 28.1 Phase diagram of the system Cu/Zn.

Table 28.2 Oxidation states and stereochemistries of copper, silver and gold

Oxidation state	Coordination number	Stereochemistry	Cu	Ag/Au
-1 ($d^{10}s^2$)	?	?		$[\text{Au}(\text{NH}_3)_n]^-$ (liq NH_3)
0 ($d^{10}s^1$)	3	Planar	$[\text{Cu}(\text{CO})_3]$ (10 K)	$[\text{Ag}(\text{CO})_3]$ (10 K)
	4	—	$[(\text{CO})_3\text{CuCu}(\text{CO})_3]$ (30 K)	$[(\text{CO})_3\text{AgAg}(\text{CO})_3]$ (30 K)
< +1	8	See Fig. 28.10(a)		$[(\text{Ph}_3\text{P})\text{Au}\{\text{Au}(\text{PPh}_3)\}_7]^{2+}$
	10	See Fig. 28.10(c)		$[\text{Au}_{11}\text{I}_3\{\text{P}(\text{C}_6\text{H}_4\text{-4-F})_3\}_7]$
	12	Icosahedral		$[\text{Au}_{13}\text{Cl}_{12}(\text{PMe}_2\text{Ph})_{10}]^{3+}$
1 (d^{10})	2	Linear	$[\text{CuCl}_2]^-$, Cu_2O	$[\text{M}(\text{CN})_2]^-$
	3	Trigonal planar	$[\text{Cu}(\text{CN})_3]^{2-}$	$[\text{AgI}(\text{PEt}_2\text{Ar})_2]$, $[\text{AuCl}(\text{PPh}_3)_2]$
	4	Tetrahedral	$[\text{Cu}(\text{py})_4]^+$	$[\text{M}(\text{diars})_2]^+$, $[\text{Au}(\text{PMePh}_2)_4]^+$
		Square planar		$[\text{Au}\{\eta^2\text{-Os}_3(\text{CO})_{10}\text{H}\}_2]^-$
	6	Octahedral		AgX (X = F, Cl, Br)
2 (d^9)	4	Tetrahedral	$\text{Cs}_2[\text{CuCl}_4]^{(a)}$	
		Square planar	$[\text{EtNH}_3]_2[\text{CuCl}_4]^{(a)}$	$[\text{Ag}(\text{py})_4]^{2+}$, $[\text{Au}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^{2-}$
	5	Trigonal bipyramidal	$[\text{Cu}(\text{bipy})_2\text{I}]^+$	
		Square pyramidal	$[\{\text{Cu}(\text{dmgH})_2\}_2]^{(b)}$	
	6	Octahedral	$\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$	
	7	Pentagonal bipyramidal	$[\text{Cu}(\text{H}_2\text{O})_2(\text{dps})]^{2+(c)}$	
	8	Dodecahedral (dist.)	$[\text{Cu}(\text{O}_2\text{CMe})_4]^{2+}$	
3 (d^8)	4	Square planar	$[\text{CuBr}_2(\text{S}_2\text{CNBu}'_2)]$	$[\text{AgF}_4]^-$, $[\text{AuBr}_4]^-$
	5	Square pyramidal	$[\text{CuCl}(\text{PhCO}_2)_2(\text{py})_2]^{(d)}$	$[\text{Au}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2-phen})(\text{PPh}_3)]^{2+}$
	6	Octahedral	$[\text{CuF}_6]^{3-}$	$[\text{AgF}_6]^{3-}$, $[\text{AuI}_2(\text{diars})_2]^+$
4 (d^7)	6	?	$[\text{CuF}_6]^{2-}$	
5 (d^6)	6	Octahedral (?)		$[\text{AuF}_6]^-$

^(a)See text, p. 1193. ^(b) dmgH_2 = dimethylglyoxime: see also Fig. 28.6

^(c) dps = 2,6-diacetylpyridine bissemicarbazone ^(d)G. SPEIER and V. FÜLÖP *J. Chem. Soc., Chem. Commun.*, 905–6 (1990).

resembles the platinum metals. All three metals are stable in pure dry air at room temperature but copper forms Cu_2O at red heat.[†] Copper is also attacked by sulfur and halogens, and the sensitivity of silver to sulfur and its compounds is responsible for the familiar tarnishing of the metal (black Ag_2S) when exposed to air containing such substances. Under similar circumstances copper forms a green coating of a basic sulfate. In sharp contrast, gold is the only metal which will not react directly with sulfur. In general the reactions of the metals are assisted by the presence of oxidizing agents. Thus, in the absence of air, non-oxidizing acids have little effect, but

Cu and Ag dissolve in hot conc H_2SO_4 and in both dil and conc HNO_3 , while Au dissolves in conc HCl if a strong oxidizing agent is present. Thus *aqua regia*, a 3:1 mixture of conc HCl and conc HNO_3 , was so named by alchemists because it dissolves gold, the king of metals. More recently, solutions of Cl_2 and Me_3NHCl in MeCN have been shown⁽⁴⁾ to be even better solvents of gold. In addition, the metals dissolve readily in aqueous cyanide solutions in the presence of air or, better still, H_2O_2 .

Table 28.2 is a list of typical compounds of the elements, which reveals a further reduction in the range of oxidation states consequent on the stabilization of d orbitals at the end of the transition

[†] It was because of their resistance to attack by air, even when heated, that gold and silver were referred to as *noble* metals by the alchemists.

⁴ Y. NAKAO, *J. Chem. Soc., Chem. Commun.*, 426–7 (1992).

series. Apart from a single Cu^{IV} fluoro-complex and possibly one or two Cu^{IV} oxo-species, neither Cu nor Ag is known to exceed the oxidation state +3 and even Au does so only in a few Au^{V} fluoro-compounds (see below): these may owe their existence at least in part to the stabilizing effect of the t_{2g}^6 configuration. It is also significant that, in a number of instances, the +1 oxidation state no longer requires the presence of presumed π -acceptor ligands even though the M^{I} metals are to be regarded mainly as class b in character. Stable, zero-valent compounds are not found, but a number of cluster compounds with the metal in a fractional (<1) oxidation state, especially of gold, are of interest. The only aquo ions of this group are those of Cu^{I} (unstable), Cu^{II} , Ag^{I} and Ag^{II} (unstable). The best-known oxidation states, particularly in aqueous solution, are +2 for Cu, +1 for Ag, and +3 for Au. This accords with their ionization energies (Table 28.1) though, of course, few of the compounds are completely ionic. Silver has the lowest first ionization energy, while the sum of first and second is lowest for Cu and the sum of first, second, and third is lowest for Au. This is an erratic sequence and illustrates the most notable feature of the triad from a chemical point of view, namely that the elements are not well related either as three elements showing a monotonic gradation in properties or as a triad comprising a single lighter element together with a pair of closely similar heavier elements. "Horizontal" similarities with their neighbours in the periodic table are in fact more noticeable than "vertical" ones.

The reasons are by no means certain but no doubt involve several factors, of which size is probably a major one. Thus the Cu^{II} ion is smaller than Cu^{I} and, having twice the charge, interacts much more strongly with solvent water (heats of hydration are -2100 and -580 kJ mol^{-1} respectively). The difference is evidently sufficient to outweigh the second ionization energy of copper and to render Cu^{II} more stable in aqueous solution (and in ionic solids) than Cu^{I} , in spite of the stable d^{10} configuration of the latter. In the case of silver, however, the ionic radii are both much larger and

so the difference in hydration energies will be much smaller; in addition the second ionization energy is even greater than for copper. The +1 ion with its d^{10} configuration is therefore the more stable. For gold, the stability of the 6s orbital and instability of the 5d as compared to silver, and leading respectively to the possibility of Au^{I} and enhanced stability of Au^{III} , have been convincingly ascribed to relativistic effects operating on s and p electrons.⁽⁵⁾ The high CFSE associated with square planar d^8 ions (see p. 1131) is a further factor favouring the +3 oxidation state.

Coordination numbers in this triad are again rarely higher than 6, but the univalent metals provide examples of the coordination number 2 which tends to be uncommon in transition metals proper (i.e. excluding Zn, Cd and Hg).

Organometallic chemistry (see p. 1199) is not particularly extensive even though gold alkyls were amongst the first organo-transition metal compounds to be prepared. Those of Au^{III} are the most stable in this group, while Cu^{I} and Ag^{I} (but not Au^{I}) form complexes, of lower stability, with unsaturated hydrocarbons.

28.3 Compounds of Copper, Silver and Gold

Binary carbides, M_2C_2 (i.e. acetylides), are obtained by passing C_2H_2 through ammoniacal solutions of Cu^+ and Ag^+ . Both are explosive when dry but regenerate acetylene if treated with a dilute acid. Copper and silver also form explosive azides while the even more dangerous "fulminating" silver and gold, which probably contain M_3N , are produced by the action of aqueous ammonia on the metal oxides. None of the metals reacts significantly with H_2 but the reddish-brown precipitate, obtained when aqueous CuSO_4 is reduced by hypophosphorous acid (H_3PO_2), is largely CuH .

⁵ P. PYYKKÖ and J.-P. DESCLAUX, *Acc. Chem. Res.* 12, 276-81 (1979).

28.3.1 Oxides and sulfides⁽⁶⁾

Two oxides of copper, Cu_2O (yellow or red) and CuO (black), are known, both with narrow ranges of homogeneity and both form when the metal is heated in air or O_2 , Cu_2O being favoured by high temperatures. Cu_2O (mp 1230°) is conveniently prepared by the reduction in alkaline solution of a Cu^{II} salt using hydrazine or a sugar.[†] CuO is best obtained by igniting the nitrate or basic carbonate of Cu^{II} . Addition of alkali to aqueous solutions of Cu^{II} gives a pale-blue precipitate of $\text{Cu}(\text{OH})_2$. This will redissolve in acids and also in conc alkali (amphoteric) to give deep-blue solutions probably containing species of the type $[\text{Cu}(\text{OH})_4]^{2-}$.

The lower affinities of silver and gold for oxygen lead to oxides of lower thermal stabilities than those of copper. Ag_2O is a dark-brown precipitate produced by adding alkali to a soluble Ag^{I} salt; AgOH is probably present in solution but not in the solid. It is readily reduced to the metal, and decomposes to the elements if heated above 160°C . The action of the vigorous oxidizing agent, $\text{S}_2\text{O}_8^{2-}$, on Ag_2O or other Ag^{I} compounds, produces a black oxide of stoichiometry AgO . That this is not a compound of Ag^{II} is, however, evidenced by its diamagnetism and by diffraction studies which show it to contain two types of silver ion, one with 2 colinear oxygen neighbours ($\text{Ag}^{\text{I}}-\text{O}$ 218 pm) and the other with square-planar coordination ($\text{Ag}^{\text{III}}-\text{O}$ 205 pm). It is therefore formulated as $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$. Anodic oxidation of silver salts yields two further black oxides, Ag_2O_3 ($\text{Ag}^{\text{III}}-\text{O} = 202$ pm) and, at lower potentials, Ag_3O_4 . In both of these the silver atoms are in a square planar oxygen environment. It is tempting to formulate Ag_3O_4 as $\text{Ag}^{\text{II}}\text{Ag}_2^{\text{III}}\text{O}_4$ but the average $\text{Ag}-\text{O}$ distances of 203 pm and 207 pm respectively are the wrong

way round for this and instead imply non-integral oxidation states with the lower charge on the pair of silver atoms.⁽⁷⁾ Hydrothermal treatment of AgO in a silver tube at 80°C and 4 kbar leads to an oxide which was originally (1963) incorrectly designated as $\text{Ag}_2\text{O}(\text{II})$. The compound has a metallic conductivity and the stoichiometry is, in fact, Ag_3O ; it can be described as an anti- BiI_3 structure (p. 559) in which oxide ions fill two-thirds of the octahedral sites in a hcp arrangement of Ag atoms ($\text{Ag}-\text{O}$ 229 pm; $\text{Ag}-\text{Ag}$ 276, 286, and 299 pm).

The action of alkali on aqueous Au^{III} solutions produces a precipitate, probably of $\text{Au}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which on dehydration yields brown Au_2O_3 . This is the only confirmed oxide of gold. It decomposes if heated above about 160°C and, when hydrous, is weakly acidic, dissolving in conc alkali and probably forming salts of the $[\text{Au}(\text{OH})_4]^-$ ion.

The sulfides are all black, or nearly so, and those with the metal in the +1 oxidation state are the more stable (p. 1174). Cu_2S (mp 1130°) is formed when copper is heated strongly in sulfur vapour or H_2S , and CuS is formed as a colloidal precipitate when H_2S is passed through aqueous solutions of Cu^{2+} . CuS , however, is not a simple copper(II) compounds since it contains the S_2 unit and is better formulated as $\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}(\text{S}_2)\text{S}$. Ag_2S is very readily formed from the elements or by the action of H_2S on the metal or on aqueous Ag^{I} . The action of H_2S on aqueous Au^{I} precipitates Au_2S whereas passing H_2S through cold solutions of AuCl_3 in dry ether yield Au_2S_3 , which is rapidly reduced to Au^{I} or the metal on addition of water. The relationships between the crystal structures of the oxides and sulfides of Cu , Ag and Au and the binding energies of the metals' d and p valence orbitals have been reviewed.^(7a)

The selenides and tellurides of the coinage metals are all metallic and some, such as CuSe_2 , CuTe_2 , $\text{AgTe}_{\sim 3}$ and Au_3Te_5 are superconductors at low temperature (as also are CuS and CuS_2).

⁶ T. P. DIRKSE, *Copper, Silver, Gold and Zinc, Cadmium, Mercury Oxides and Hydroxides*, Pergamon, Oxford, 1986, 380 pp.

[†] This is the basis of the very sensitive Fehling's test for sugars and other reducing agents. A solution of a copper(II) salt dissolved in alkaline tartrate solution is added to the substance in question. If this is a reducing agent then a characteristic red precipitate is produced.

⁷ B. STANDKE and M. JANSEN, *Angew. Chem. Int. Edn. Engl.* **25**, 77-8 (1986).

^{7a} J. A. TOSSELL and D. J. VAUGHAN, *Inorg. Chem.* **20**, 3333-40 (1981).

Other phases are CuSe, CuTe; Cu_3Se_2 , Cu_3Te_2 ; AgSe, AgTe; Ag_2Se_3 , AgSe_2 ; Ag_5Te_3 ; Au_2Te_3 and AuTe_2 . Most of these are nonstoichiometric.

28.3.2 High temperature superconductors⁽⁸⁻¹⁰⁾

Without doubt the main focus of interest in the field of copper oxide chemistry has, for the past decade, been on the production of high temperature superconductors of which $\text{YBa}_2\text{Cu}_3\text{O}_7$ is the most familiar (see Panel). Like all "cuprate superconductors", it is an oxygen deficient perovskite (if it were an "ideal" perovskite its six metal atoms would require the composition $\text{YBa}_2\text{Cu}_3\text{O}_9$. This massive oxygen deficiency results in a layered structure instead of the conventional 3-dimensional array — see p. 963). As shown in Fig. 28.2, the coordination of oxygen around copper is of two types, square planar for Cu(1) and square pyramidal for Cu(2). Due to the disparate effects of the large Ba^{2+} and the smaller more highly charged Y^{3+} , the Cu(2) are not situated at the centre of the square pyramid but only 30 pm above its base. They therefore lie in "puckered" or "dimpled" CuO_2 planes connected by the apical oxygens to chains of square planar Cu(1).

Esr results indicate that both Cu(1) and Cu(2) sites have a mixture of Cu^{2+} and Cu^{3+} ions. It is generally believed that superconduction occurs via positive holes in the conduction band of the CuO_2 planes and that the concentration of these holes is controlled, through the apical oxygens, by the non-conducting chains of Cu(1) which act as reservoirs of positive and negative charge. X-ray photoelectron spectroscopy shows that the conduction band has both copper (3d) and oxygen (2p) character, presumably as a result of π

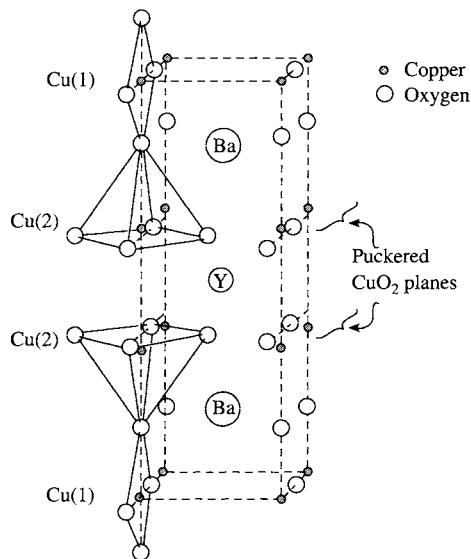


Figure 28.2 Structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

interactions which would be at a maximum in the linear O–Cu–O bonds of perfect CuO_2 planes. The extent of puckering of these planes, as well as the nature and composition of the charge reservoirs, are evidently crucial factors affecting the value of T_c . To obtain a proper understanding of these factors Y and Ba have been replaced by a range of other elements producing compounds with up to seven different elements as in $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$. $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Sr}, \text{Ba}$) and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ are other examples where the oxidation state of $\text{Cu} > (\text{II})$ and superconductivity occurs via positive holes, whereas in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, a so-called "electron superconductor", the oxidation state of $\text{Cu} < (\text{II})$ and excess electrons are the charge carriers. In each case, however, the path for conduction is provided by a CuO_2 plane.

The properties of these brittle ceramics depend critically on the preparative conditions. Intimate mixtures of the oxides, carbonates or nitrates of the relevant metals in the required proportions are heated at temperatures of 900–1000°C. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, all compositions in the range $0 \leq x \leq 0.5$ superconduct and the highest T_c is found where $x \sim 0$. For others, the oxygen content must be stringently controlled. In all cases, the most

⁸ C. N. R. RAO (Ed.), *Chemistry of High Temperature Superconductors*, World Scientific, Singapore, 1991, 520 pp.

⁹ J. T. S. IRVINE, *Superconducting Materials*, Chap. 11, pp. 275–301 in D. THOMPSON (ed.), *Insights into Speciality Inorganic Chemicals*, R.S.C., Cambridge, 1995.

¹⁰ A series of articles on Superconductivity, *Chem. in Brit.* **30**, 722–48 (1994).

Superconductivity

H. Kammerling Onnes (Nobel Prize for Physics, 1913) discovered superconductivity in Leiden in 1911 when he cooled mercury to the temperature of liquid helium. Many other materials, mostly metals and alloys, were subsequently found to display superconductivity at very low temperatures.

Two properties characterize a superconductor:

1. It is perfectly conducting, i.e. it has zero resistance.
2. It is perfectly diamagnetic, i.e. it completely excludes applied magnetic fields. This is the Meissner effect and is the reason why a superconductor can levitate a magnet.

Superconductivity exists within the boundaries of three limiting parameters which must not be exceeded: the critical temperature (T_c), the critical magnetic field (H_c) and the critical current density (J_c).

Until 1986 the highest recorded value of T_c was ~ 23 K for Nb_3Ge but in that year Bednorz and Müller, in pioneering work for which they received the 1987 Nobel Prize for Physics, reported⁽¹¹⁾ $T_c = 30$ K in an entirely new Ba-La-Cu-O ceramic system quickly identified as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. This prompted an examination of other Cu-O systems and the technologically important breakthrough in 1987 by the Houston and Alabama teams of C. W. Chu and M. K. Wu, of superconductivity at temperatures attainable in liquid nitrogen.⁽¹²⁾ $T_c = 95$ K in a material subsequently shown to be $\text{YBa}_2\text{Cu}_3\text{O}_7$, "YBCO". This, and other materials in which Y is replaced by a lanthanide, are referred to as "1,2,3" materials because of their stoichiometry. This produced a quite unprecedented explosion of activity amongst chemists, physicists and material scientists around the world. Though the highest T_c has been pushed up to 135 K (or 164 K under 350 kbar pressure) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$, YBCO is still the archetypal high temperature superconductor.

In spite of its long history, it was not until 1957 that Bardeen, Cooper and Schrieffer⁽¹³⁾ provided a satisfactory explanation of superconductivity. This "BSC theory" suggests that pairs of electrons (Cooper pairs) move together through the lattice, the first electron polarizing the lattice in such a way that the second one can more easily follow it. The stronger the interaction of the two electrons the higher T_c , but it turns out as a consequence of this model that T_c should have an upper limit ~ 35 K. The advent of high-temperature superconductors therefore necessitated a new, or at least modified, explanation for the pairing mechanism. Various suggestions have been made but none has yet gained universal acceptance.

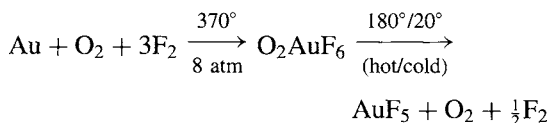
homogeneous products with the best grain alignment and the highest current density J_c , require the most careful control of sintering temperature, annealing and quenching rates. The major problems preventing large-scale practical applications therefore lie in the field of material processing. At present thin films of "YBCO" (see Panel), obtained for instance by its deposition on metal coated with ZrO_2 to provide flexible tapes, appear to offer the most promising way forward.

28.3.3 Halides

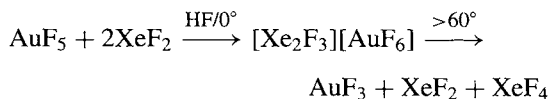
Table 28.3 is a list of the known halides: only gold forms a pentahalide and trihalides and, with

the exception of AgF_2 , only copper (as yet) forms dihalides.

AuF_5 is an unstable, polymeric, diamagnetic, dark-red powder, produced by heating $[\text{O}_2][\text{AuF}_6]$ under reduced pressure and condensing the product on to a "cold finger":



The compound tends to dissociate into AuF_3 and, when treated with XeF_2 in anhydrous HF solution below room temperature, yields yellow-orange crystals of the complex $[\text{Xe}_2\text{F}_3][\text{AuF}_6]$:



Again, in the +3 oxidation state, only gold is known to form binary halides, though AuI_3 has not been isolated. The chloride and the

¹¹ J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys. B* **64**, 189–93 (1986).

¹² M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58**, 908–10 (1987).

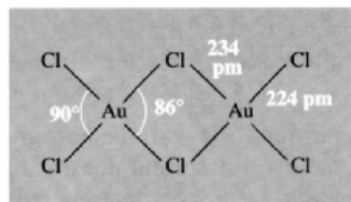
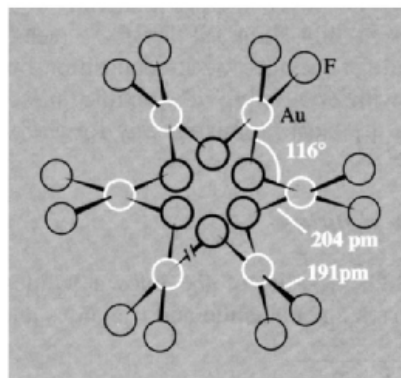
¹³ J. BARDEEN, L. N. COOPER and J. R. SCHRIEFFER, *Phys. Rev.* **106**, 162–4 (1957).

Table 28.3 Halides of copper, silver and gold (mp/°C)

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+5	AuF ₅ red (d > 60°)			
+3	AuF ₃ orange-yellow (subl 300°)	AuCl ₃ red (d > 160°)	AuBr ₃ red-brown	
+2	CuF ₂ white (785°) AgF ₂ brown (690°)	CuCl ₂ yellow-brown (630°)	CuBr ₂ black (498°)	
+1	— AgF yellow (435°) —	CuCl white (422°) AgCl white (455°) AuCl yellow (d > 420°)	CuBr white (504°) AgBr pale yellow (430°) AuBr yellow	CuI white (606°) AgI yellow (556°) AuI yellow
+ $\frac{1}{2}$ (0,+1)	Ag ₂ F yellow-green (d > 100°)			

bromide are red-brown solids prepared directly from the elements and have a planar dimeric structure in both the solid and vapour phases. Dimensions for the chloride are as shown in Structure (1). On being heated, both compounds lose halogen to form first the monohalide and finally metallic gold. Au₂Cl₆ is one of the best-known compounds of gold and provides a convenient starting point for much coordination chemistry, dissolving in hydrochloric acid to give the stable [AuCl₄]⁻ ion. Treatment of Au₂Cl₆ with F₂ or BrF₃ also affords a route to AuF₃, a powerful fluorinating agent. This orange solid consists of square-planar AuF₄ units which share *cis*-fluorine atoms with 2 adjacent AuF₄ units so as to form a helical chain (Structure (2)).

No halides are known for gold in the +2 oxidation state and silver only forms the difluoride; this is obtained by direct heating of silver in a stream of fluorine. AgF₂ is thermally stable but is a vigorous fluorinating agent used especially to fluorinate hydrocarbons. For copper, on the other hand, 3 dihalides are stable and the anhydrous difluoride, dichloride and dibromide can all be obtained by heating the elements. The white ionic CuF₂ has a distorted rutile structure

(1) Au₂Cl₆(2) Unique helical chain structure of AuF₃

(p. 961) with four shorter equatorial distances (Cu-F 193 pm) and two longer axial distances (Cu-F 227 pm). A similar distortion is found in

the d^4 compound CrF_2 (p. 1021). When prepared from aqueous solution by dissolving copper(II) carbonate or oxide in 40% hydrofluoric acid, blue crystals of the dihydrate are obtained; these are composed of puckered sheets of planar *trans*- $[\text{CuF}_2(\text{H}_2\text{O})_2]$ groups linked by strong H bonds to give distorted octahedral coordination about Cu with 2 Cu–O 194 pm, 2 Cu–F 190 pm, and 2 further Cu–F at 246.5 pm; the O–H...F distance is 271.5 pm. With anhydrous CuCl_2 and CuBr_2 their increasing covalency is reflected in their polymeric chain structure, consisting of planar CuX_4 units with opposite edges shared, and by the deepening colours of brown and black respectively. The chloride and bromide are both very soluble in water, and various hydrates and complexes can be recrystallized. The solutions are more conveniently obtained by dissolution of the metal or $\text{Cu}(\text{OH})_2$ in the relevant hydrohalic acid.

Iodide ions reduce Cu^{II} to Cu^{I} , and attempts to prepare copper(II) iodide therefore result in the formation of CuI . (In a quite analogous way attempts to prepare copper(II) cyanide yield CuCN instead.) In fact it is the electronegative fluorine which fails to form a salt with copper(I), the other 3 halides being white insoluble compounds precipitated from aqueous solutions by the reduction of the Cu^{II} halide. By contrast, silver(I) provides (for the only time in this triad) 4 well-characterized halides. All except AgI have the rock-salt structure (p. 242).[†] Increasing covalency from chloride to iodide is reflected in the deepening colour white \rightarrow yellow, as the

[†] At room temperature the stable form of silver iodide is γ - AgI which has the cubic zinc blende structure (p. 1210). β - AgI , which has the hexagonal ZnO (or wurtzite) structure (p. 1210), is the stable form between 136° and 146° . This structure is closely related to that of hexagonal ice (p. 624) and AgI has been found to be particularly effective in nucleating ice crystals in super cooled clouds, thereby inducing the precipitation of rain. β - AgI has another remarkable property: at 146° it undergoes a phase change to cubic α - AgI in which the iodide sublattice is rigid but the silver sublattice “melts”. This has a dramatic effect on the (ionic) electrical conductivity of the solid which leaps from 3.4×10^{-4} to $1.31 \text{ ohm}^{-1} \text{ cm}^2$, a factor of nearly 4000. The iodide sublattice in α - AgI is bcc and this provides 42 possible sites for each 2Ag^+ , distributed as follows:

energy of the charge transfer ($\text{X}^- \text{Ag}^+ \rightarrow \text{XAg}$) is lowered, and also in increasing insolubility. In the latter respect, however, AgF is quite anomalous in that it is one of the few silver(I) salts which form hydrates ($2\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$). That it is soluble in water is understandable in view of its ionic character and the high solvation energy of the small fluoride ion, but the *extent* of its solubility (1800 g per litre of water at 25°C) is astonishing. All 4 AgX can be prepared directly from the elements but it is more convenient to prepare AgF by dissolving AgO in hydrofluoric acid and evaporating the solution until the solid crystallizes; the others can be made by adding X^- to a solution of AgNO_3 or other soluble Ag^{I} compound, when AgX is precipitated. The most important property of these halides, particularly AgBr , is their sensitivity to light (AgF only to ultraviolet) which is the basis for their use in photography, discussed below.

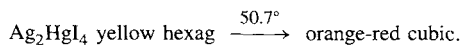
All four monohalides of gold have been prepared but the fluoride only by mass spectrometric methods.⁽¹⁴⁾ AuCl and AuBr are formed by heating the trihalides to no more than 150°C and AuI by heating the metal and iodine. At higher temperatures they dissociate into the elements. AuI is a chain polymer which features linear 2-coordinate Au with Au–I 262 pm and the angle Au–I–Au 72° .

28.3.4 Photography

Photography is a good example of a technology which evolved well in advance of a proper understanding of the principles involved (see

6 sites having 2I^- neighbours at 252 pm
 12 sites having 3I^- neighbours at 267 pm
 24 sites having 4I^- neighbours at 286 pm

The silver ions are almost randomly distributed on these sites, thus accounting for their high mobility. Many other fast ion conductors have subsequently been developed on this principle, e.g.



¹⁴ D. SCHRODER, J. HRUŠAK, I. C. TORNIEPORTH-OETTING, T. M. KLAPOČKE and H. SCHWARTZ. *Angew. Chem. Int. Edn. Engl.* **33**, 212–4 (1994).

History of Photography

In 1727 J. H. Schulze, a German physician, found that a paste of chalk and AgNO_3 was blackened by sunlight and, using stencils, he produced black images. At the end of the eighteenth century Thomas Wedgwood (son of the potter Josiah) and Humphry Davy used a lens to form an image on paper and leather treated with AgNO_3 , and produced pictures which unfortunately faded rather quickly.

The first permanent images were obtained by the French landowner J. N. Niépce using bitumen-coated pewter (bitumen hardens when exposed to light for *several hours* and the unexposed portions can then be dissolved away in oil of turpentine). He then helped the portrait painter, L. J. M. Daguerre, to perfect the “daguerreotype” process which utilized plates of copper coated with silver sensitized with iodine vapour. The announcement of this process in 1839 was greeted with enormous enthusiasm but it suffered from the critical drawback that each picture was unique and could not be duplicated.

Reproducibility was provided by the “calotype” process, patented in 1841 by the English landowner W. H. Fox Talbot, which used semi-transparent paper treated with AgI and a “developer”, gallic acid. This produced a “negative” from which any number of “positive” prints could subsequently be obtained. Furthermore it embodied the important discovery of the “latent image” which could be fully developed later. Even with Talbot’s very coarse papers, exposure times were reduced to a few minutes and portraits became feasible, even if uncomfortable for the subject.

Though Talbot’s pictures were undoubtedly much inferior in quality to Daguerre’s, the innovations of his process were the ones which facilitated further improvements and paved the way for photography as we now know it. Sir John Herschel, who first coined the terms “photography”, “negative” and “positive”, suggested the use of “hyposulphite” (sodium thiosulfate) for “fixing” the image, and later the use of glass instead of paper — hence, photographic “plates”. F. S. Archer’s “wet collodion” process (1851) reduced the exposure time to about 10 s and R. L. Maddox’s “dry gelatin” plates reduced it to only 0.5 s. In 1889 G. Eastman used a roll film of celluloid and founded the American Eastman Kodak Company.

Meanwhile the Scottish physicist, Clerk Maxwell (1861), recognizing that the sensitivities of the silver halides are not uniform across the spectrum, proposed a three-colour process in which separate negatives were exposed through red, green and blue filters, and thereby provided the basis for the later development of colour photography. Actually, the sensitivity is greatest at the blue end of the spectrum; a fact which seriously affected all early photographs. This problem was overcome when the German, H. W. Vogel, discovered that sensitivity could be extended by incorporating certain dyes into the photographic emulsion. “Spectral sensitization” at the present time is able to extend the sensitivity not only across the whole visible region but far into the infrared as well.

Panel). Most of the basic processes were established almost a century and a half ago, but a coherent theoretical explanation was not available until the publication in 1938 of the classic paper by R. W. Gurney and N. F. Mott. (*Proc. Roy. Soc. A164*, 151–67 (1938)). Since then the subject has stimulated a vast amount of fundamental research in wide areas of solid-state chemistry and physics.

A photograph is the permanent record of an image formed on a light-sensitive surface, and the essential steps in producing it are:

- (a) production of light-sensitive surface;
- (b) exposure to produce a “latent image”;
- (c) development of the image to produce a “negative”;
- (d) making the image permanent, i.e. “fixing” it;
- (e) making “positive” prints from the negative.

(a) In modern processes the light-sensitive surface is an “emulsion” of silver halide in gelatine, coated on to a suitable transparent film, or support. The halide is carefully precipitated so as to produce small uniform crystals, ($<1 \mu\text{m}$ diameter, containing $\sim 10^{12}$ Ag atoms), or “grains” as they are normally called. The particular halide used depends on the sensitivity required, but AgBr is most commonly used on films; AgI is used where especially fast film is required and AgCl and certain organic dyes are also incorporated in the emulsion.

(b) When, on exposure of the emulsion to light, a photon of energy $h\nu$ impinges on a grain of AgX , a halide ion is excited and loses its electron to the conduction band, through which it passes rapidly to the surface of the grain where it is able to liberate an atom of silver:

