THE PERIODIC LAW

David Johnson

CHEMISTRY CASSETTE

ETG

CHEMISTRY CASSETTES

General Editor: **Peter Groves**

USING THIS CHEMISTRY CASSETTE

Please read this before you use the cassette.

This Chemistry Cassette learning programme consists of an audio-cassette,
this workbook, a set of element cards and a periodic table card. They are
designed to be used together so have them all with you as you work through the
cassette.

You will at some point in the programme be asked to cut up, and reassemble,
the periodic table card. See that you have scissors handy to do this.

The material in the workbook has been divided into numbered 'frames', each of
which contains diagrams, tables, equations, etc. Whenever Dr Johnson wants
to refer you to any of this material he will give you the appropriate frame
number.

The programme has been carefully designed for individual, self-paced learning,
and you can work through it at a rate related to your own needs and
understanding. Switch off the tape player whenever you want to think, to write
some notes, or to answer a question. Use the rewind control to revise or repeat
material that you may not fully understand on a first hearing. Always have pen
and paper with you so that you can make notes to supplement or amplify the
material contained in this workbook - this will enable you to build up a detailed
set of personal notes which will serve as your own authoritative guide to the
subject.

1

The pack contains twenty cards. On each one there is the name and symbol of a chemical element together with some of its chemical and physical properties. The compounds whose formulae appear on the cards are well-known hydrides, chlorides and normal oxides* of the elements which exist at room temperature. Sixteen of the cards have relative atomic masses printed on them, but on four of the cards the relative atomic mass is missing. To begin with, set these four to one side and pick up the remaining sixteen. Now restart the tape.

*The phrase normal oxide refers to a class of compounds which excludes peroxides and superoxides. Thus, on the sodium card the normal oxide is Na_2O. Sodium peroxide, Na_2O_2, and superoxide, NaO_2, exist but are not included. As Mendeleev noted, peroxides and superoxides are easily distinguished from normal oxides by their chemical properties, such as the reaction with acids which gives oxygen.

2

Highest hydride

    He LiH BeH_2 (BH_3) CH_4 NH_3 OH_2 FH

Highest chloride

    He LiCl $BeCl_2$ BCl_3 CCl_4 NCl_3 OCl_2 FCl

Highest normal oxide

    He Li_2O (Be_2O_2) B_2O_3 (C_2O_4) N_2O_5

Formulae in brackets have been obtained by halving or doubling formulae on the cards.

3

```
He  Li  Be  B   C   N   O   F
Ne  Na  Mg  Al  Si  P   S   Cl
```

4

Highest normal oxide

Ne Na_2O (Mg_2O_2) Al_2O_3 (Si_2O_4) P_2O_5 (S_2O_6) Cl_2O_7

Highest hydride

Ne NaH MgH_2 AlH_3 SiH_4 PH_3 SH_2 ClH

Highest chloride

Ne NaCl $MgCl_2$ $AlCl_3$ $SiCl_4$ PCl_5 SCl_2 Cl_2

Formulae in brackets have been obtained by doubling formulae on the cards.

5

Properties of scandium (scandalum)

Element: Scandium
Symbol : Sc

1 Relative atomic mass: 45.0
2 Metal
3 Melting temperature: 1539°C
4 Boiling temperature: 2831°C
5 Oxide(s): Sc_2O_3 (solid)
6 Hydride(s): ScH_3 (solid)
7 Chloride(s): $ScCl_3$ (solid)

Mendeleev's periodic table of 1871.

Series	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII – RO_4
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	-=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Co=59 Ni=59 Cu=63
5	(Cu=63)	Zn=65	-=68	-=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	-=100	Ru=104 Rh=104 Pd=106 Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	-	-	-	- - - -
9	(-)	-	-	-	-	-	-	
10	-	-	?Er=178	?La=180	Ta=182	W=184	-	Os=195 Ir=197 Pt=198 Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208			
12	-	-	-	Th=231	-	U=240	-	- - - -

A periodic table of the 1930s.

The relative atomic masses are those used in the original text. Period 1 contained only the element hydrogen and has been omitted.

Period	0	I a	I b	II a	II b	III a	III b	IV a	IV b
2	2 He 4.002	3 Li 6.940		4 Be 9.02		5 B 10.82		6 C 12.01	
3	10 Ne 20.183	11 Na 22.997		12 Mg 24.32		13 Al 26.97		14 Si 28.06	
4	18 Ar 39.944	19 K 39.096		20 Ca 40.08		21 Sc 45.10		22 Ti 47.90	
			29 Cu 63.57		30 Zn 65.38		31 Ga 69.72		32 Ge 72.60
5	36 Kr 83.7	37 Rb 85.48		38 Sr 87.63		39 Y 88.92		40 Zr 91.22	
			47 Ag 107.880		48 Cd 112.41		49 In 114.76		50 Sn 118.70
6	54 Xe 131.3	55 Cs 132.91		56 Ba 137.36		57 – 71 RARE EARTHS*		72 Hf 178.6	
			79 Au 197.2		80 Hg 200.61		81 Tl 204.39		82 Pb 207.21
7	86 Rn 222	87 –		88 Ra 226.05		89 Ac 227		90 Th 232.12	

V a	V b	VI a	VI b	VII a	VII b	VIII
7 N 14.008		8 O 16.0000		9 F 19.000		
15 P 31.02		16 S 32.06		17 Cl 35.457		
23 V 50.95		24 Cr 52.01		25 Mn 54.93		26 Fe 55.84 27 Co 58.94 28 Ni 58.69
	33 As 74.91		34 Se 78.96		35 Br 79.916	
41 Nb 92.91		42 Mo 96.0		43 Ma		44 Ru 101.7 45 Rh 102.91 46 Pd 106.7
	51 Sb 121.76		52 Te 127.61		53 I 126.92	
73 Ta 180.88		74 W 184.0		75 Re 186.31		76 Os 191.5 77 Ir 193.1 78 Pt 195.23
	83 Bi 209.00		84 Po 210.0		85 –	
91 Pa 231		92 U 238.07				

* RARE EARTHS	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il —	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.64	69 Tm 169.4	70 Yb 173.04	71 Lu 175.0

8

1 If we write the formula of the highest normal oxide as R_2O_n , then, as we move across any horizontal row of frame 7 from Group 0 to Group 8, n increases from zero in Group 0 to eight in Group 8. This trend is the most perfect of the three that we have encountered. It works for seventy-four of the ninety-one elements in frame 7. Seven of the seventeen exceptions occur in Group 8 where only ruthenium and osmium form tetroxides. Other exceptions include oxygen, fluorine, copper, silver and gold.

2 If we write the formula of the highest hydride as RH_n, then, as we move across any horizontal row of frame 7 from Group 0 to Group 7, n follows the pattern
            0, 1, 2, 3, 4, 3, 2, 1.
Notice that, this time, there is no mention of Group 8: the generalization refers only to Groups 0-7 inclusive. It works for just over sixty of the eighty-two elements in these Groups. Fifteen of the exceptions occur for elements in the a column of Groups 4, 5, 6 and 7 of frame 7.

3 If we write the formula of the highest chloride as RCl_n , then the trend in n is the same as for the hydrides in point 2 above. Again, this works for just over sixty of the eighty-two elements in Groups 0-7. Eleven of the exceptions occur for elements in the a columns of Groups 5, 6 and 7 of frame 7.

9

Bismuth has a relative atomic mass of about 209. Predict the formulae of its highest hydride, chloride and normal oxide.

10

Frame 7 tells us that bismuth occurs in Group V. Assuming bismuth is not an exception to the trends in frame 8, the formulae predicted are BiH_3, $BiCl_3$ and Bi_2O_5. The predictions are correct, although the trihydride cannot be prepared in large amounts because it decomposes very easily into bismuth and hydrogen.

11

Relative atomic masses

argon	39.95	scandium	44.96
calcium	40.08	titanium	47.90
potassium	39.10		

12

At the centre of an atom is a tiny core or nucleus. It contains two kinds of particle: protons and neutrons. The atomic number is the number of protons in the nucleus. Each proton carries a single positive charge, and the neutron no charge at all. Thus the atomic number is also equal to the positive charge on the nucleus. In frame 7, each element is immediately preceded by its atomic number. So the helium nucleus contains two protons and its charge is +2; the lithium nucleus contains three protons and its charge is +3, and so on. In terms of atomic structure it is atomic number that distinguishes one element from another.

In the neutral atom there are electrons moving about the nucleus. Each electron carries a single negative charge and the number of electrons is equal to the positive charge on the nucleus (the atomic number). This ensures the electrical neutrality of the atom. However, although the electrons have a huge influence on the total charge, their contribution to the total mass of an atom is almost negligible. This is because the mass of an electron is well under 0.1% of that of a proton or neutron. The mass of an atom is almost entirely that of the protons and neutrons in the nucleus.

Now, the proton and neutron have nearly the same mass. The more protons there are in the nucleus, the higher its mass will tend to be, so we might hope for a correlation between atomic mass and atomic number. But this correlation need not be perfect because the mass depends upon the number of neutrons in the nucleus as well. By arranging the elements in order of relative atomic mass, Mendeleev nearly got them in order of atomic number. But not quite: at one or two points, like the argon-potassium case, the correlation breaks down. Fortunately for Mendeleev, the number of neutrons in the nucleus tends to increase as the atomic number rises: if it varied erratically the correlation would break down more often. When, in about 1914, it became possible to actually measure atomic numbers, the elements could then be arranged in order of atomic number, and the few anomalies disappeared. For those interested, more information on this topic is given in note 2 in this workbook. (p 43)

13

The exploded Mendeleev table is composed of fourteen pieces. Cut each piece out with a pair of scissors, and put them back together again to recreate the original table. To remind you of what it looked like, a copy of the figure you cut up is shown in frame 14. In frame 14 the pieces are numbered for future reference.

14
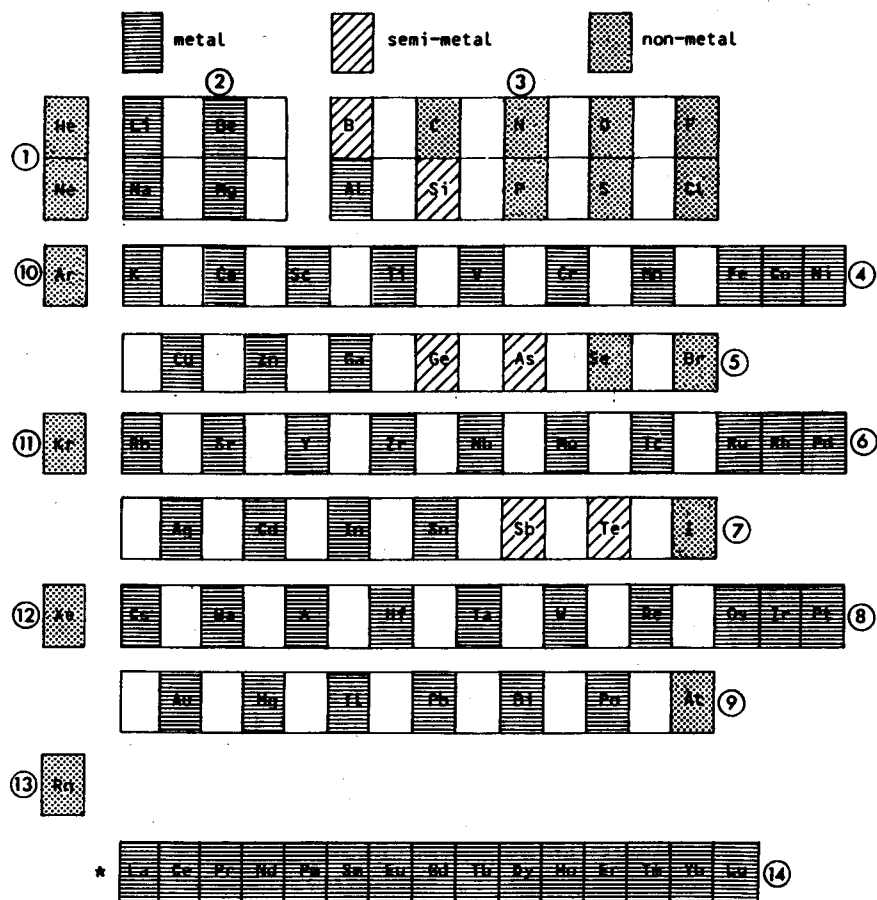
15

Set piece 14 on one side. Rearrange pieces 1 - 13 so that the following conditions are satisfied:

  (i) as before, the elements appear in order of atomic number;
 (ii) each space in the table contains one element;
(iii) elements in vertical columns in the Mendeleev table remain in vertical columns in the new table (take sub-groups a and b to be two different columns. Thus sodium and potassium fall in the same column; sodium and copper in different ones);
 (iv) in any period, any metals occur on the left, any non-metals on the right, and any semi-metals in between.

16

Move piece 5 so that pieces 4 and 5 form one long row with copper (Cu) following nickel (Ni). Now align pieces 6 and 7 in the same way in the appropriate position beneath pieces 4 and 5. Repeat by putting piece 8 beneath piece 6 and piece 9 beneath piece 7. Move piece 3 to the right so that the halogens occupy the same column, and move piece 1 to the right of piece 3 so that neon (not helium) follows fluorine. Now move pieces 10 - 13 to the right-hand end so that argon follows chlorine, krypton follows bromine, and so on.

17

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb

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18

Werner's Table (1905)

Main block (left):

H 1·008							
Li 7·03							
Na 23·05							
K 39·15	Ca 40·1						
Rb 85·4	Sr 87						
Cs 133	Ba 137·4	La 138	Ce 140	Nd 143·6	Pr 140·5		
	Ra 225		Th 232·5				

Lanthanide/actinide row:

Nd 143·6	Pr 140·5			Sm 150·3	Eu 151·79	Gd 156	Tb 160	Ho 162	Er 166		Tm 171	Yb 173
			U 239·5									

Right block:

										Be 9·1	B 11	C 12	N 14·04	O 16·00	F 19	Ne 20	He 4
										Mg 24·36	Al 27·1	Si 28·4	P 31·0	S 32·06	Cl 35·45	A 39·9	
Sc 44·1	Ti 48·1	V 51·2	Cr 52·1	Mn 55·0	Fe 55·9	Co 59·0	Ni 58·7	Cu 63·6	Zn 65·4	Ga 70	Ge 72	As 75·0	Se 79·1	Br 79·96	Kr 81·12		
Y 89·0	Zr 90·7	Nb 94	Mo 96·0		Ru 101·7	Rh 103·0	Pd 106	Ag 107·93	Cd 112·4	In 114	Sn 118·5	Sb 120	Te 127·6	I 126·95	Xe 128		
	Ta 183	W 184·0		Os 191	Ir 193·0	Pt 194·8	Au 197·2	Hg 200·3	Tl 204·1	Pb 206·9	Bi 208·5						

19

An element R is a semi-metal, forms two oxides RO_2 and RO_3, and a single hydride RH_2. Its relative atomic mass lies between 80 and 150. Identify the element, and state which group of the periodic table it lies in.

R is tellurium. The highest oxide, RO_3, suggests a Group VI element. Frame 6 shows that these elements often form a hydride RH_2, and this is confirmed by trend 2 of frame 8. Frame 7 shows that the only Group VI elements with relative atomic masses between 80 and 150 are molybdenum (Mo) and tellurium (Te). But the exploded Mendeleev table shows that of these two, only tellurium is a semi-metal.

Maximum sub-shell populations

Principal quantum number of shell	Sub-shell	Maximum population of sub-shell	Maximum population of shell
1	1s	2	2
2	2s	2	
	2p	6	8
3	3s	2	
	3p	6	
	3d	10	18
4	4s	2	
	4p	6	
	4d	10	
	4f	14	32

Sub-shell energy level diagram.

electron capacity of sub-shell

s	p	d	f
2	6	10	14

energy increasing

6th period

5th period

4th period

3rd period

2nd period

1st period
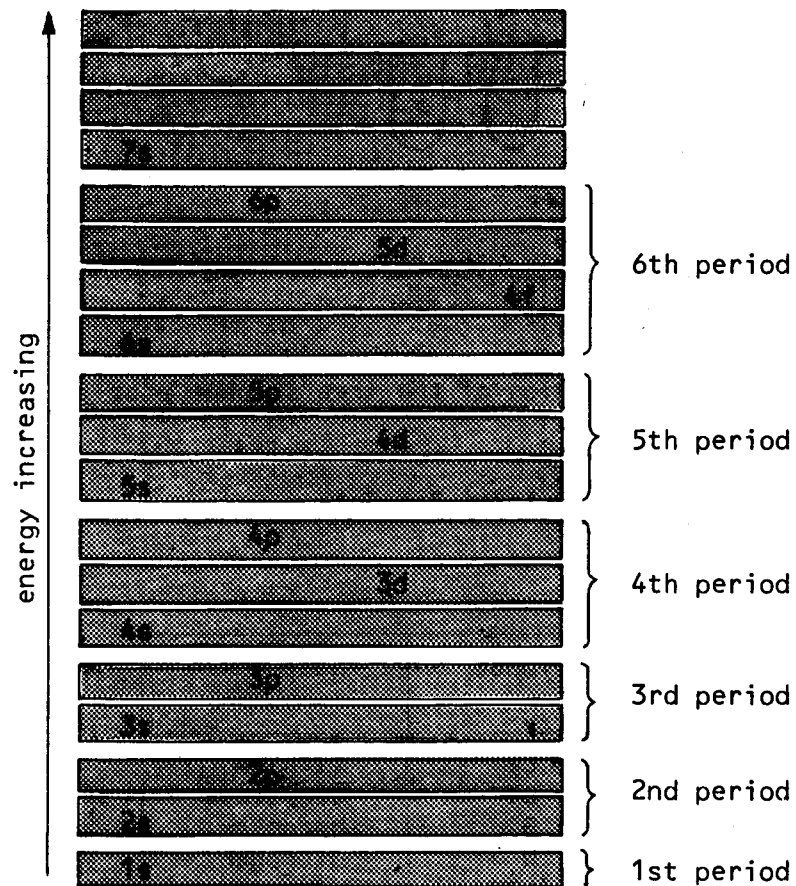
23

Order of increasing energy for sub-shells.
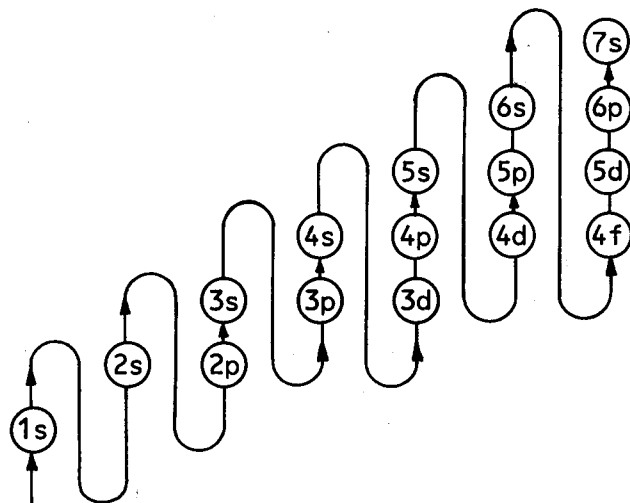
24

Electronic configuration of the free sulphur atom in the ground state

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$$
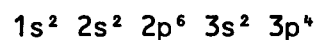
25

Atomic number	Symbol	Name
3	Li	lithium
4	Be	beryllium
5	B	boron
7	N	nitrogen
10	Ne	neon
11	Na	sodium
12	Mg	magnesium
13	Al	aluminium
15	P	phosphorus
18	Ar	argon

26

Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p^1$
N	$1s^2\ 2s^2\ 2p^3$
Ne	$1s^2\ 2s^2\ 2p^6$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

27

Li	$1s^2\ 2s^1$	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Be	$1s^2\ 2s^2$	Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
B	$1s^2\ 2s^2\ 2p^1$	Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
C	$1s^2\ 2s^2\ 2p^2$	Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
N	$1s^2\ 2s^2\ 2p^3$	P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
O	$1s^2\ 2s^2\ 2p^4$	S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
F	$1s^2\ 2s^2\ 2p^5$	Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Ne	$1s^2\ 2s^2\ 2p^6$	Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

28

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

Atomic number/symbol	Name	Atomic number/symbol	Name
19 K	potassium	27 Co	cobalt
20 Ca	calcium	30 Zn	zinc
21 Sc	scandium	31 Ga	gallium
		36 Kr	krypton

30

K	[Ar] $4s^1$
Ca	[Ar] $4s^2$
Sc	[Ar] $4s^2\ 3d^1$
Co	[Ar] $4s^2\ 3d^7$
Zn	[Ar] $4s^2\ 3d^{10}$
Ga	[Ar] $4s^2\ 3d^{10}\ 4p^1$
Kr	[Ar] $4s^2\ 3d^{10}\ 4p^6$

[Ar] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

31

3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn		31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

32

Atomic number/symbol	Name	Atomic number/symbol	Name
37 Rb	rubidium	46 Pd	palladium
38 Sr	strontium	47 Ag	silver
39 Y	yttrium	48 Cd	cadmium
40 Zr	zirconium	49 In	indium
41 Nb	niobium	50 Sn	tin
42 Mo	molybdenum	51 Sb	antimony
43 Tc	technetium	52 Te	tellurium
44 Ru	ruthenium	53 I	iodine
45 Rh	rhodium	54 Xe	xenon

33

3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn		31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd		49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe

34

57 La	lanthanum	70 Yb	ytterbium
59 Pr	praseodymium	71 Lu	lutetium
65 Tb	terbium	72 Hf	hafnium

35

La	[Xe] $6s^2$ $4f^1$
Pr	[Xe] $6s^2$ $4f^3$
Tb	[Xe] $6s^2$ $4f^9$
Yb	[Xe] $6s^2$ $4f^{14}$
Lu	[Xe] $6s^2$ $4f^{14}$ $5d^1$
Hf	[Xe] $6s^2$ $4f^{14}$ $5d^2$

36

55	Cs	caesium	72	Hf	hafnium
56	Ba	barium	73	Ta	tantalum
57	La	lanthanum	74	W	tungsten
58	Ce	cerium	75	Re	rhenium
59	Pr	praseodymium	76	Os	osmium
60	Nd	neodymium	77	Ir	iridium
61	Pm	promethium	78	Pt	platinum
62	Sm	samarium	79	Au	gold
63	Eu	europium	80	Hg	mercury
64	Gd	gadolinium	81	Tl	thallium
65	Tb	terbium	82	Pb	lead
66	Dy	dysprosium	83	Bi	bismuth
67	Ho	holmium	84	Po	polonium
68	Er	erbium	85	At	astatine
69	Tm	thulium	86	Rn	radon
70	Yb	ytterbium	87	Fr	francium
71	Lu	lutetium	88	Ra	radium

3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne

11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

19 K	20 Ca			21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

37 Rb	38 Sr			39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe

55 Cs 56 Ba 57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn

87 Fr 88 Ra

General characteristics of transition elements.

(i)   They are all metals.

(ii) Their compounds are often strongly coloured.

(iii) Their compounds are often paramagnetic: that is, if placed in proximity to a strong magnetic field, they tend to be drawn into the field. Compounds of the typical elements hardly ever behave in this way.

(iv) They often form more than one compound with other elements. In particular, they often form two or more halides of formula type RX_n (X = halide) and two or more normal oxides of formula type R_2O_n. In such cases the values of n usually differ by one. When the typical elements form two or more compounds in this way the values of n usually differ by two.

Thus iron forms a yellow-brown trichloride $FeCl_3$ and a pale green dichloride $FeCl_2$. Chromium forms the following fluorides: CrF_2, CrF_3, CrF_4, CrF_5 and CrF_6. By contrast sulphur, a typical element forms SF_2, SF_4 and SF_6.*

*Although sulphur forms a fluoride S_2F_{10} in which there are five fluorines per sulphur, the structural formula is $F_5S—SF_5$, each sulphur atom forming six bonds. So when classifying sulphur compounds by sulphur valence states, S_2F_{10} can be bracketed with SF_6.

General characteristics of the lanthanides.

(i)   They are all metals.

(ii) Their compounds are often coloured.

(iii) Their compounds are often paramagnetic.

(iv) Chemically, the elements behave rather similarly. Thus, all the metals dissolve in dilute mineral acids to give tripositive aqueous ions which are very stable to oxidation or reduction. This stability of the +3 oxidation state is quite general. All the metals give trichlorides when heated with chlorine, and all but three yield oxides of the type R_2O_3 when heated in oxygen. Because of the chemical similarity of the elements they tend to occur together in minerals, and they are hard to separate from one another.

An element R forms solid fluorides RF_2, RF_3, RF_4 and RF_5, their colours being blue, yellow, lime-green and colourless respectively. It also forms normal oxides R_2O_3, RO_2 and R_2O_5 respectively. Its relative atomic mass is less than 80. Identify the element and write out the electronic configuration of its atom.
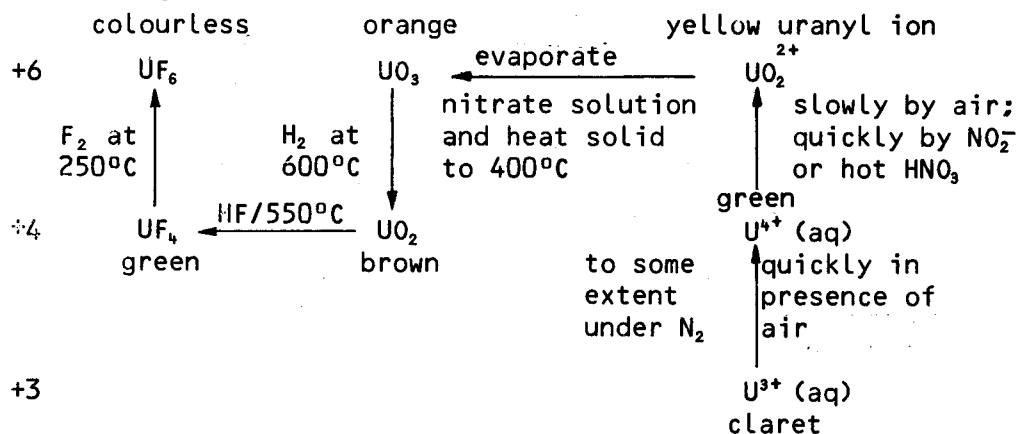
(Answer in frame 40)

40

R is vanadium. The highest oxide R_2O_5 suggests a Group V
element in Mendeleev's table, frame 7. The string of
fluorides RF_n in which the n values differ by one,
together with the striking colours suggest a transition
element. Frame 7 shows that the only Group V transition
element with a relative atomic mass less that 80 is
vanadium. From frame 23, the atomic configuration is
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$.

41

Some uranium chemistry.

Oxidation
state

	colourless	orange	yellow uranyl ion
+6	UF_6	UO_3	UO_2^{2+}

evaporate

F_2 at 250°C | H_2 at 600°C | nitrate solution and heat solid to 400°C | slowly by air; quickly by NO_2^- or hot HNO_3

green

+4 UF_4 ← HF/550°C UO_2 U^{4+} (aq)
green brown

to some extent under N_2 | quickly in presence of air

+3 U^{3+} (aq)
claret

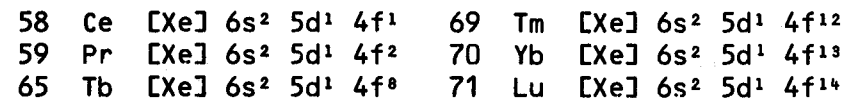**42**

To begin with, I shall just state Bohr's argument without
regard for its accuracy.

The atomic configuration of barium is [Xe] $6s^2$. For the
next element, lanthanum, Bohr guessed the configuration
to be, in effect, [Xe] $6s^2 5d^1$. He then suggested that
after lanthanum the 4f sub-shell was progressively
filled up. This would give, in modern notation,

58	Ce	[Xe] $6s^2\ 5d^1\ 4f^1$	69	Tm	[Xe] $6s^2\ 5d^1\ 4f^{12}$
59	Pr	[Xe] $6s^2\ 5d^1\ 4f^2$	70	Yb	[Xe] $6s^2\ 5d^1\ 4f^{13}$
65	Tb	[Xe] $6s^2\ 5d^1\ 4f^8$	71	Lu	[Xe] $6s^2\ 5d^1\ 4f^{14}$

Bohr suggested these configurations because, to him,
they explained the similarity of the rare earth elements.
The filling of the 5d sub-shell starts at lanthanum, but
it then stops, and the filling of the 4f level takes
over. The low principal quantum number of the 4f sub-
shell suggested to Bohr that 4f would be an inner sub-
shell: the electrons in it would be closer to the nucleus
than the outer 5d and 6s electrons. Now the chemical
properties of an atom are determined by its outer
electron configuration because reacting atoms make
contact through their outer electron regions. The
chemical properties of the elements La → Lu will there-
fore be determined by the outer $6s^2\ 5d^1$ configuration and
be largely unaffected by the filling of the inner 4f
sub-shell. This explains the long series of similar
elements like lanthanum - the lanthanide series.

When he turned to the elements beyond radium, Bohr began
by accepting Mendeleev's principles: he took the
chemistry as proof that the sequence Ac → U should be
classified with the elements Lu → W. This would mean that
after radium what we now call the 6d level was occupied.
This gives,

89	Ac	[Rn] $7s^2\ 6d^1$	91	Pa	[Rn] $7s^2\ 6d^3$
90	Th	[Rn] $7s^2\ 6d^2$	92	U	[Rn] $7s^2\ 6d^4$

But in the preceding period the filling of the 5d level stops before it is full (at lanthanum) and 4f takes over. It occurred to Bohr that at some point beyond uranium, perhaps even at uranium itself, the filling of the 6d level would stop and 5f would take over. If the change-over occurred immediately after uranium then, by analogy with the lanthanides, there would be a long series of similar elements starting with uranium – a uranide series.

You will find a comment on the accuracy of Bohr's suggested configurations, and on his general argument, in note 5 in this workbook (p 48). There is no need to bother with it now.

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Three classifications of the transradium elements.

1. Transradium elements as transition elements (after Mendeleev):

Cs	Ba	La–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	93	94	95	96	97	98	99	100				

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

2. A possible uranide series (after Bohr):

Cs	Ba	La–Lu	Hf	Ta	W	Re	Os	Ir	Pt
Fr	Ra	Ac	Th	Pa	(U–?)				

U	93	94	95	96	97	98	99	100	. . . .

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

3. Transradium elements classified with the lanthanides (after Werner):

Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Fr	Ra	Ac	Th	Pa	U	93	94	95	96	97	98	99	100			

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The discovery of neptunium.

McMillan and Abelson found that neptunium had at least
two oxidation states in aqueous solution. In the
presence of a reducing agent, like sulphur dioxide, the
neptunium activity was carried down with a precipitate
of thorium iodate $Th(IO_3)_4$. But when a strong oxidizing
agent like bromate was present the neptunium precipitated
with UO_2^{2+} in insoluble $NaUO_2(CH_2COO)_3$. They concluded,

"These properties indicate that the two valence states
are very similar to those of uranium (U^{4+} and UO_2^{2+}) ...
It is interesting to note that the new element has little
or no resemblance to rhenium; for it does not precipitate
with H_2S in acid solution ... and does not have an oxide
volatile at red heat. This fact, together with the
apparent similarity to uranium suggests that there may
be a second 'rare earth' group of similar elements
starting with uranium."

From Phys. Rev., 57, 1185 (1940)

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Common aqueous ions of plutonium.

Oxidation state	Aqueous ion
+6	orange-yellow plutonyl ion PuO_2^{2+}(aq)
+4	brown* Pu^{4+}(aq)
+3	violet Pu^{3+}(aq)

* green in fairly concentrated nitric acid.

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The actinide hypothesis (after Seaborg, 1944).

K	Ca						Lanthanide series													Sc	Ti
Rb	Sr																			Y	Zr
Cs	Ba	La	Ce	Pr	Nd	61	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb					Lu	Hf
Fr	Ra	Ac	Th	Pa	U	Np	Pu	95	96	97	98	99	100	101	102					103	104

actinide
series

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Sub-shells in order of ascending energy.

88	Ra	[Rn] $7s^2$
102	No	[Rn] $7s^2 5f^{14}$
103	Lr	[Rn] $7s^2 5f^{14} 6d^1$
104		[Rn] $7s^2 5f^{14} 6d^2$

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| Group | | I | II | | | | | | | | | | | | | | III | IV | V | VI | VII | 0 |

Period

1

2
| 3 Li | 4 Be |

3
| 11 Na | 12 Mg |

4
| 19 K | 20 Ca |

5
| 37 Rb | 38 Sr |

Lanthanides

6
| 55 Cs | 56 Ba | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb |

7
| 87 Fr | 88 Ra | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No |

Actinides

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
103 Lr	104	105

					1 H	2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Transition elements

Typical elements

Table 1   Comparison of Mendeleev's eka-aluminium with gallium.

Eka-aluminium, Ea (1871 prediction)	Gallium, Ga (discovered in 1875)
Relative atomic mass 68	Relative atomic mass 69.72
Metal of density 5.9 g cm^{-3} and low melting point. It will be involatile and unaffected by air. It will decompose steam at red heat and dissolve slowly in acids and alkalies.	Metal of density 5.91 g cm^{-3} melting at 29.8°C. It is involatile and does not react with air. It decomposes steam on strong heating and it dissolves slowly in acids and alkalies.
There will be an oxide Ea$_2$O$_3$ of density 5.5g cm^{-3}. This will react with HCl to form a salt EaCl$_3$. The hydroxide will be soluble in acids and alkalies.	Ga$_2$O$_3$ has a density of 5.9 g cm^{-3}. It reacts with HCl to form GaCl$_3$. Ga(OH)$_3$ is soluble in acids and alkalies.
The sulphate should form alums; the sulphide will be precipitated from aqueous solution by H$_2$S; and the chloride, EaCl$_3$, will be more volatile than ZnCl$_2$.	Alums such as KGa(SO$_4$)$_3$.12H$_2$O are known. Ga$_2$S$_3$ is precipitated by H$_2$S, and GaCl$_3$ is more volatile than ZnCl$_2$.
The element will probably be discovered by spectrum analysis.	Gallium was first detected by observing a new violet line in the spark spectrum of zinc blende.

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Notes

1 Mendeleev's predictions

Between 1869 and 1871 Mendeleev used the periodic law to make precise predictions of the chemistry of three undiscovered elements. These were the elements with relative atomic masses 44, 68 and 72 (frame 6). Mendeleev called them eka-boron, eka-aluminium and eka-silicon respectively. The left hand column of table 1 shows the predictions made in the case of eka-aluminium.

In 1875 a French chemist, Lecoq de Boisbaudran discovered a new element in a sample of zinc blende from the Pyrenees. He called it gallium and published a few of its properties. Mendeleev, whose work was unknown to Boisbaudran, saw instantly that gallium was his eka-aluminium and pointed this out in a note which he sent to France. Particularly important was the fact that the published density of the metal (4.7 g cm^{-3}) was significantly less than Mendeleev's predicted value (5.9 g cm^{-3}). De Boisbaudran at first resisted Mendeleev's claim but he subsequently found that his first sample of gallium had been contaminated by sodium which he had used as a reducing agent. When the metal was purified of sodium, and the density redetermined, he found the value was identical with Mendeleev's prediction. As the right hand column of table 1 shows, equally striking agreement was obtained in the case of the other properties.

Chemists were astonished to find a theoretician providing information on a new element which was more accurate than that supplied by the actual discoverer. Equal success was achieved with the discovery of eka-boron by L F Nilson in 1879, and of eka-silicon by C A Winkler in 1886. Eka-boron was named scandium and is identical with the element 'scandalum' discussed on the tape. Eka-silicon was named germanium. Table 2 shows predicted and observed properties of germanium. Mendeleev's success with gallium had gained widespread assent for his periodic law and, unlike de Boisbaudran,

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Table 2 Comparison of Mendeleev's eka-silicon with germanium.

Eka-silicon, Es (1871 prediction)	Germanium, Ge (discovered in 1886)
Relative atomic mass 72	Relative atomic mass 72.32
Density 5.5 g cm^{-3}	Density 5.47 g cm^{-3}
Atomic volume 13 cm^3	Atomic volume 13.22 cm^3
Element will be dirty grey, and on heating in air will give a white powder of EsO_2.	Element is greyish white, and on heating in air gives a white oxide GeO_2.
Element will decompose steam with difficulty.	Element does not decompose steam.
EsO_2 will be refractory and have a density of 4.7 g cm^{-3}.	GeO_2 is refractory and has a density of 4.703 g cm^{-3}.
Eka-silicon will form a tetrachloride, which will be a liquid, boiling under 100°C, with a density of 1.9 g cm^{-3}	Germanium tetrachloride, $GeCl_4$, boils at 86°C and has a density of 1.887 g cm^{-3}.
Eka-silicon will form a fluoride, EsF_4, which will not be gaseous.	Germanium tetrafluoride, GeF_4, is a white solid, hydrolysed by water to H_2GeF_6.

both Nilson and Winkler recognised that their new elements had been predicted by Mendeleev.

It is important to recognise that Mendeleev's system gave a completely wrong idea of the undiscovered elements (frame 6) with relative atomic masses between 140 and 178. Although he never made detailed predictions for this region, which was subsequently filled by the rare-earth elements, he would clearly have made mistakes if he had tried. Nor was Mendeleev the only discoverer of the periodic system. The Dutch historian, J W van Spronsen, recognises six independent discoverers, of which Mendeleev was the last. But what gives Mendeleev pre-eminence is his boldness in predicting the chemistry of unknown elements. More than anything else, the triumphant vindication of these predictions persuaded chemists that the periodic law was an invaluable intellectual instrument. In a revealing comment on his own boldness, made in his famous Faraday Lecture, Mendeleev remarked that "the periodic law, by insisting on the necessity for a revision of the supposed facts, exposed itself at once to destruction in its very origin." According to the philosopher, Sir Karl Popper, bold conjectures that wantonly expose themselves to experimental refutation are the most effective way of hastening scientific progress. Mendeleev's remark suggests that to some extent he saw his own achievement in these terms.

2 Relative atomic mass and atomic number

As noted in frame 12, what really distinguishes one element from another is the atomic number, the number of protons in the nucleus. But the relative atomic mass is fixed by the sum of the number of protons and the number of neutrons in the nucleus. It follows that we can have atoms of the same element which differ in relative atomic mass because they contain different numbers of neutrons.

As an example consider naturally occurring magnesium. This contains three types of magnesium atom. Each type

contains a different number of neutrons in the nucleus: twelve in the first case, thirteen in the second, and fourteen in the third. The three types are called isotopes of magnesium. Despite the differences in the number of neutrons, in a chemical sense they behave very nearly identically - all three types are magnesium. This is because all three contain twelve protons in the nucleus and it is this common number of protons that makes them magnesium atoms. Each magnesium nucleus thus carries a positive charge of +12. If a naturally occurring element consists of more than one isotope then the relative atomic mass of the element will depend, among other things, on the relative proportions of the different isotopes.

It should now be clear that it is possible for the atoms of one element to contain both a larger number of protons and a smaller number of neutrons than those of another. In extreme cases this can mean that although the atomic number of the first element is larger than that of the second, its relative atomic mass is less. It is in cases like this that the anomalies in Mendeleev's table materialise. Because argon was not discovered until 1892, the argon-potassium case was not relevant in the crucial period when the periodic law was struggling for acceptance. The important instance here occurs halfway down Groups VI and VII (frame 7). Tellurium occurs in Group VI and iodine in Group VII. The chemistry of the elements shows clearly that this is the right choice, but the relative atomic mass of tellurium is greater than that of iodine. During the 1880s many attempts were made to remove this anomaly. Frequent redeterminations of the relative atomic mass of tellurium were performed, and samples of tellurium were investigated for traces of some undiscovered element of higher relative atomic mass. No convincing evidence for a reversal of the iodine-tellurium order was obtained. This raised some doubts about the truth of the periodic law, but for most chemists the success in other fields far outweighed this failing.

In 1913 all this was altered by the research of an English phycicist, Henry Moseley. When elements are bombarded with a stream of fast moving electrons they then emit X-ray radiation, at particular wavelengths which are characteristic of the element. Moseley showed how these wavelengths could be used to determine the atomic number. His work revealed that in cases like that of tellurium and iodine the atomic numbers were in reverse order of the relative atomic masses. Anomalies of this sort then disappeared. Less than two years later, in August 1915, Moseley was killed in action on the Gallipoli peninsula at the age of 27.

3 Electrons in atoms

The language used in the introduction to electronic configurations included terms such as 'shell', 'sub-shell', 'planetary system' and 'orbiting electron'. Quantum-mechanical ideas established after Bohr's pioneering work show that these terms are misleading if their conventional meanings are retained. For example, we cannot establish the orbit of an electron in a sense that allows us to predict precise positions of the electron at successive intervals of time. The best we can do is to give the probability of finding the electron at some particular point in space. Spectroscopic and theoretical investigations of electron distributions in atoms suggest that it is possible to speak of a shell structure but only in the sense that as one moves outward from the nucleus one encounters successive regions where the probability of finding electrons is high, separated by regions where the probability is low. The successive regions of high probability correspond to the shells with principal quantum numbers 1, 2, 3, 4, etc. However, the shells cannot be sharply distinguished from each other because in the intervening regions the probability of finding electrons, although low, is almost always finite. Moreover, the fairly simple spatial division of the electron distribution into shells cannot be duplicated within the shells themselves, because the variation of the spatial probability function for the component sub-shells is too complicated.

Other topics that were given short shrift on the tape were the sub-shell labels and capacities. These are best

seen as a consequence of rules which restrict the values of the quantum numbers that electrons can have. On the tape only one quantum number was introduced explicitly - the principal quantum number, n. Any electron within a particular shell has the principal quantum number of the shell. In addition, it has three other quantum numbers. the first of which is the <u>azimuthal quantum number</u>, l.

If the principal quantum number of the shell is n, then l can take all integral values in the range zero to (n-1). Thus if n = 3, l can be 0, 1 or 2. The value of l denotes the type of sub-shell to which the electron belongs. If l = 0 the characteristic letter is s; if l = 1 it is p; if l = 2 it is d; and if l = 3 it is f. Note that for any shell the number of possible values of l is equal to n. On the tape I expressed this by saying that in any shell the number of sub-shells is equal to the principal quantum number of the shell.

At this point you can see that all the electrons in a particular sub-shell have the same values of n and l. Within a sub-shell the electrons differ in their values of the magnetic quantum number m_l, and the spin quantum number m_s. The possible values of m_l within a sub-shell are integral and run from l down through zero to $-l$. Thus for a p sub-shell, l =1 and m_l can be 1, 0 or -1. The spin quantum number m_s always takes one of only two values which, for reasons we do not go into here, are denoted $+\frac{1}{2}$ and $-\frac{1}{2}$. In table 3, by following the rules of this section, we give all the possible sets of values of the four quantum numbers for the electrons in a 3p sub-shell. Note that there are six such sets. Thus, if we decide to give each electron a different set of quantum numbers, we can only get six electrons into the sub-shell: to get seven electrons in we would have to duplicate one of the sets of values. An important principle of quantum mechanics is the Pauli exclusion principle. This states that within a particular atom, no two electrons can have the same four quantum numbers. Thus the exclusion principle, allied with the quantum number rules of this section, determines the maximum capacities of the sub-shells which were introduced on the tape.

To check that you have understood this write out a table corresponding to table 3 for electrons with n = 4 and l = 2. By doing this you can show that, like all d sub-shells, the 4d sub-shell can accommodate no more than ten electrons. The answer appears in table 4 on page 48.

Table 3 <u>Possible sets of quantum numbers for electrons in a 3p sub-shell.</u>

Principal n	Azimuthal l	Magnetic m_l	Spin m_s
3	1	1	$+\frac{1}{2}$
3	1	1	$-\frac{1}{2}$
3	1	0	$+\frac{1}{2}$
3	1	0	$-\frac{1}{2}$
3	1	-1	$+\frac{1}{2}$
3	1	-1	$-\frac{1}{2}$

4 <u>Imperfections in the periodicity in the ground electronic configurations of atoms.</u>

Suppose that frame 23 (or frame 47), allied with the procedure described on the tape, always gave the correct electron configuration of atoms. Then a long periodic table could be constructed so that atoms in vertical columns always had similar outer electron configurations. These conditions are not always fulfilled for the transition elements. If frame 23 always gave correct electron configurations the atoms of the first, second and third transition series would have outer electron configurations of the types $4s^2 3d^n$, $5s^2 4d^n$ and $6s^2 5d^n$ respectively, where n runs form 1 to 10. A table of ground state electronic configurations appears in Appendix I: the expected outer configurations occur for only twenty of the thirty elements in the three transition series. For example, in a column of the

Table 4 **Possible sets of quantum numbers for electrons with n = 4 and l = 2.**

Principal n	Azimuthal l	Magnetic m_l	Spin m_s
4	2	2	$+\frac{1}{2}$
4	2	2	$-\frac{1}{2}$
4	2	1	$+\frac{1}{2}$
4	2	1	$-\frac{1}{2}$
4	2	0	$+\frac{1}{2}$
4	2	0	$-\frac{1}{2}$
4	2	-1	$+\frac{1}{2}$
4	2	-1	$-\frac{1}{2}$
4	2	-2	$+\frac{1}{2}$
4	2	-2	$-\frac{1}{2}$

periodic table which contains nickel, palladium and platinum, the atoms have the outer electron configurations $4s^2 3d^8$, $4d^{10}$ and $6s^1 5d^9$ respectively. Other imperfections of this sort occur among the lanthanides and actinides and are discussed in notes 6 and 8.

All instances where frames 23 and 47 fail to give the correct ground state configurations of atoms are marked in Appendix II with an asterisk. For elements 1 - 102 there are nineteen such failures. Like periodicities in chemical properties the periodicity in the ground electronic configuration of atoms is imperfect.

5   Niels Bohr and the atomic configurations of the rare earths and transradium elements.

Bohr guessed the atomic configuration of the elements Ce → Lu to be [Xe] $6s^2 5d^1 4f^n$ where n runs form 1 to 14. This guess was prompted by the chemistry of these elements and the belief that the 4f electrons in them

were inner electrons. Frame 38 shows that the dominant oxidation state is +3. Using an ionic formulation, then in, say, the chlorides, there are M^{3+} and Cl^- ions. Bohr would have said that this happened because the three outer electrons in the 5d and 6s levels are fairly easily lost, but subsequent loss of the 4f electrons was more difficult. Thus oxidation states above +3 are not readily formed.

This part of the argument has a fatal weakness because the atomic configurations are not [Xe] $6s^2 5d^1 4f^n$. In agreement with frame 23, all but three of them turned out to be [Xe] $6s^2 4f^{n+1}$. Bohr's reasoning now predicts the dominant oxidation state to be +2.

Today we know that there are two related weaknesses in the argument. First, the 4f electrons in the free atoms are not inner electrons to the extent that Bohr believed. Second, and more generally, the relation between the chemistry of an element and its atomic configuration is not as straightforward as he implies.

Of course, such hindsights must not blind us to the brilliance of Bohr's overall achievement. Note that there is much truth in the details of his final suggestion: the filling of the 5f shell does begin in the region of uranium although, as Appendix II shows, the changeover from 6d to 5f is less abrupt than he anticipated.

6   Classifying the actinide elements.

As noted on the tape, the highest and most prominent oxidation state of the sequence Ac → U is equal to what would be the Mendeleev group number if the elements were classified in the first arrangement of frame 43. Indeed, we can now include element 93, neptunium, in this sequence. Although, like McMillan and Abelson, no one has succeeded in establishing the existence of a heptoxide akin to $Re_2 O_7$, in 1969 alkaline solutions of $NpO_5^{3-}(aq)$ and solid compounds such as $Li_3 NpO_5$ were successfully prepared. Although these species are

rather easily reduced, they contain neptunium in oxidation state +7.

The belief in a uranide series, a series of elements very like uranium, was made possible by the very limited experimental information which was available when neptunium and plutonium were first prepared. For example, we now know that the elements U → Am all form aqueous ions of the type $MO_2^{2+}(aq)$ and $M^{3+}(aq)$. However, the relative stability of these two ions changes drastically between uranium and americium. The values of $E^{\ominus}$ for the redox system

$$MO_2^{2+}(aq) + 4H^+(aq) + 3e = M^{3+}(aq) + 2H_2O(l)$$
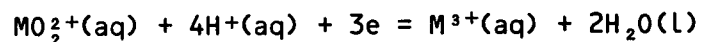
are Ov for uranium, 0.68v for neptunium, 1.02v for plutonium and 1.69v for americium.

This is just one example of a general trend: as we move from uranium to curium, oxidation states above +3 become progessively less stable with respect to the tripositive state. Thus if sodium nitrite is added to the aqueous tripositive ions of the elements U → Am the products are $UO_2^{2+}(aq)$, $NpO_2^+(aq)$, $Pu^{4+}(aq)$ and $Am^{3+}(aq)$.

From curium to nobelium the elements are lanthanide-like: with one exception, the most prominent oxidation state is +3, and this is very stable to oxidation or reduction. The exception is nobelium where the important oxidation state is +2: $No^{3+}(aq)$ exists but its oxidizing powers are roughly on a par with permanganate or dichromate, and it is easily reduced to $No^{2+}(aq)$. Even here, however, there are grounds for comparison with the lanthanides because, in the second half of the lanthanide series, ytterbium which is grouped above nobelium, is the only element to form a well-characterized dipositive aqueous ion.

Thus, when we make element by element comparisons, it is only in the second half of the actinide series that we find strong chemical reasons for a classification with the lanthanides. At the beginning the highest oxidation state follows the pattern of a normal (outer) transition series. In between there is a transition stage between the initial and final phases: between uranium and curium the higher oxidation states become progressively less stable with respect to the lower +3 state.

The strongest reason for classifying the actinides with the lanthanides is a macroscopic one; the lengths of the two series match. Thus, after nobelium comes lawrencium which can be classified as a transition element under lutetium because the only known oxidation state is +3. Even more important, the only known oxidation state of element 104 is +4, so it can be grouped under hafnium. It is interesting that this vital last piece of evidence was obtained in 1970, sixty-five years after Werner classified the transradium elements with the lanthanides in an essentially modern table, and twenty-six years after Seaborg made the actinide hypothesis explicit.

Finally, we need to glance at the electronic configurations of actinide atoms which were established after the crucial chemical studies. Appendix II shows that actinium and thorium have transition element configurations: plutonium and the succeeding actinides have lanthanide-like structures. Thus, as we move across the series, the drift in electronic configuration and the change in oxidation state pattern are not exactly matched. For example, although the filling of the 5f sub-shell begins at protoactinium, the highest oxidation state is +5 in line with the values obtained from the elements Fr → Th. Again, lanthanide-like configurations appear well before curium where the very strong chemical resemblance to the lanthanides begins.

7 The overall structure of frame 48.

The general shape of the periodic table in frame 48 is different from that of the tables which appear in most text books. The chief difference lies in the disposition of the lanthanide and actinide elements.

In frame 48 the lanthanides and actinides appear in the main body of the table, whereas in many textbooks they appear beneath it as a sort of footnote. The footnote device is explained, I think, by the limited size of

pages in books. It is hard to cram a full long table into the width of one page, so it has to be broken up. Memories of 1930s Meneleev-type arrangements, in which the lanthanides appeared as a footnote, encouraged writers to break off the lanthanides and actinides and plant them beneath the rest of the table. I take such arrangements to be a kind of shorthand for tables like frame 48 in which the lanthanides and actinides are treated like other elements and included in the main body of the table.

A second difference from most textbook tables lies in the actual definition of the lanthanides and actinides. This is discussed in note 8a.

8   Defining blocks of elements.

Three kinds of consideration can influence the membership of the blocks of elements which appear in frame 48: electronic configurations, the structure of the chosen periodic table, and similarities or patterns in chemical and physical properties. Universal agreement on the content of the blocks of elements would be possible if all three lines of argument led unambiguously to identical conclustions. Unfortunately they do not! Each pathway has its ambivalent moments, and the various conclusions do not always coincide: sometimes they merely overlap. This leaves room for individual judgment and individual preference. One crucial way of exercising this preference is through the different priority given to the three kinds of consideration.

On the tape much consideration was devoted to the first. The members of each block share common features in the electronic configurations of atoms. For example, I pointed out that the transition elements span regions of the periodic table in which a d sub-shell in the free atom is being filled up. However, in actually designating the content of the different blocks, priority was given mainly to the second of the three considerations rather than the first. Frame 48 was my preferred periodic table: the blocks of elements were then defined from its structure.

Thus the general shape of frame 48 is such that the following breakdown is a fairly natural one. The typical or main group elements are those which occupy groups (columns) containing five or more members. They fall into two blocks at the extremes of the table. Two kinds of element bridge (form a transition) across the gap; the transition elements which occupy columns containing three or four members, and the lanthanides and actinides, sometimes called the inner transition elements, which occupy columns containing two members.

This argument contains a potential ambiguity because the content of the blocks depends, to some extent, upon which periodic table is chosen to represent the periodic law. Thus the terms typical element and transitional element were introduced by Mendeleev to describe characteristics of periodic tables that he invented. These tables differ from those which are popular today. Consequently, in modern textbooks, the two families of elements have a membership which is different from, and larger than that assumed in Mendeleev's writings. This then is the sort of ambiguity inherent in the second of our three considerations. Those associated with the first and third exist because generalizations made about periodicity in electronic configuration and about chemical properties are often imperfect. These ambiguities, allied with the problem of weighting the three considerations, mean that one person's designation of a block of elements can differ from that of another's. The next two sections deal with specific differences of this kind.

(a) The lanthanides and actinides.   Frame 48 differs from most textbook tables in the actual definition of the lanthanides and actinides. Most chemists agree that there are fourteen lanthanides, because fourteen electrons are needed to fill the 4f shell. Now the first element whose atom has a ground state electronic configuration with a full 4f shell is element 70, ytterbium. The configuration is [Xe] $6s^2 4f^{14}$ in line with frame 23. I have therefore defined the lanthanides as ytterbium plus the thirteen preceding elements. This gives us elements 57 - 70 (lanthanum - ytterbium) inclusive.

The problem with this definition is the ground state configuration of the lanthanum atom. In frame 35 we deduced this to be [Xe] $6s^2 4f^1$ by applying frame 23. As Appendix II shows, the actual configuration is [Xe] $6s^2 5d^1$. This is one of the nineteen cases when frame 23 (or 47) does not work, and our first lanthanide does not contain a 4f electron in its atomic ground state. The first 4f electron only appears at the next element, cerium, where the configuration is [Xe] $6s^2 5d^1 4f^1$. Because of this many chemists begin the lanthanide series with cerium. They define their fourteen lanthanides as the elements 58 - 71 (cerium - lutetium) inclusive. This scheme, however, also has a weakness. Because the 4f sub-shell now becomes full at the penultimate lanthanide, ytterbium, then in moving from ytterbium to the last lanthanide, lutetium, a 5d and not a 4f electron is added.

These difficulties arise because, although we require fourteen lanthanides, the filling of the 4f sub-shell spans only thirteen elements. Both solutions have matching drawbacks. I prefer the first for two main reasons. First, if we adopt the second and define the lanthanides as Ce → Lu, then lanthanum becomes a transition element. Consequently lanthanum must be grouped under scandium and yttrium, which are the other transition elements with outer electronic configurations of the type $s^2 d^1$. Frame 48 would then have to be changed by moving scandium and yttrium to the left so that they lie above lanthanum. The transition elements would then be split into two parts: one part would consist of a single column (Sc, Y and La) and the other would consist of the remaining nine columns. The two parts would be separated by the lanthanide and actinide elements. By defining the lanthanides as the series La → Yb this split is avoided and the transition metals are concentrated into a single block.

A second reason for preferring this definition is that it establishes a useful analogy between the electronic configurations of the lanthanides, actinides and transition elements. If these elements are defined as in frame 48 then all their atoms can have outer electron configurations of the type $s^2 x^n$, where x = d and n runs from 1 to 10 for the transition elements, and x = f and n runs from 1 to 14 for the lanthanides and actinides. It is true, of course, that when frames 23 and 47 fail, these will not be the ground state configurations. The $s^2 x^n$ configuration can then only be attained by exciting electrons. Nevertheless it can exist. In any case, as Appendix II shows, $s^2 x^n$ is the ground state configuration for the majority of cases (thirty-nine out of the fifty-eight elements in question).

(b) <u>The transition elements.</u> According to the procedure followed at the beginning of note 8, the first three transition series are the sequences Sc → Zn, Y → Cd and Lu → Hg. Ten-member transition series of this sort are adopted by many authors, especially in the United States. However, generalizations 2, 3 and 4 of frame 38 work better if the first and last members of these series are excluded. Some authorities therefore assign less than ten elements to a transition series. Here, priority is given to the third of the three considerations listed at the start of note 8, although attempts are often made to rationalize the policy by a definition stated in terms of electronic configuration. Thus the International Union of Pure and Applied Chemistry (IUPAC) defines a transition element as "an element whose atom has an incomplete d sub-shell, or which gives rise to a cation or cations with an incomplete d sub-shell."

The intention here seems to be to designate, say, the first transition series as the elements Sc → Cu. However, the supporting definition is not sufficiently specific: it would allow a typical element like germanium to be included among the transition elements, because the ion $Ge^{5+}(g)$ has been studied by atomic spectroscopy and shown to contain an incomplete 3d shell. The main justification of the designation lies in the imperfect trends and patterns in chemical properties of the sort listed in frame 38. The same comment can be made of textbook authors who define the first transition series as the sequence Ti → Cu.

Ground state electronic configurations[†] of the atoms of the elements.

Atomic number	Symbol	Name of element	Ground state electronic configuration of atom
1	H	hydrogen	$1s^1$
2	He	helium	$1s^2$
3	Li	lithium	$[He]2s^1$
4	Be	beryllium	$[He]2s^2$
5	B	boron	$[He]2s^2 2p^1$
6	C	carbon	$[He]2s^2 2p^2$
7	N	nitrogen	$[He]2s^2 2p^3$
8	O	oxygen	$[He]2s^2 2p^4$
9	F	fluorine	$[He]2s^2 2p^5$
10	Ne	neon	$[He]2s^2 2p^6$
11	Na	sodium	$[Ne]3s^1$
12	Mg	magnesium	$[Ne]3s^2$
13	Al	aluminium	$[Ne]3s^2 3p^1$
14	Si	silicon	$[Ne]3s^2 3p^2$
15	P	phosphorus	$[Ne]3s^2 3p^3$
16	S	sulphur	$[Ne]3s^2 3p^4$
17	Cl	chlorine	$[Ne]3s^2 3p^5$
18	Ar	argon	$[Ne]3s^2 3p^6$
19	K	potassium	$[Ar]4s^1$
20	Ca	calcium	$[Ar]4s^2$
21	Sc	scandium	$[Ar]4s^2 3d^1$
22	Ti	titanium	$[Ar]4s^2 3d^2$
23	V	vanadium	$[Ar]4s^2 3d^3$
24	Cr	chromium	*$[Ar]4s^1 3d^5$
25	Mn	manganese	$[Ar]4s^2 3d^5$
26	Fe	iron	$[Ar]4s^2 3d^6$
27	Co	cobalt	$[Ar]4s^2 3d^7$
28	Ni	nickel	$[Ar]4s^2 3d^8$
29	Cu	copper	*$[Ar]4s^1 3d^{10}$
30	Zn	zinc	$[Ar]4s^2 3d^{10}$
31	Ga	gallium	$[Ar]3d^{10} 4s^2 4p^1$
32	Ge	germanium	$[Ar]3d^{10} 4s^2 4p^2$
33	As	arsenic	$[Ar]3d^{10} 4s^2 4p^3$
34	Se	selenium	$[Ar]3d^{10} 4s^2 4p^4$

Atomic number	Symbol	Name of element	Ground state electronic configuration of atom
35	Br	bromine	$[Ar]3d^{10} 4s^2 4p^5$
36	Kr	krypton	$[Ar]3d^{10} 4s^2 4p^6$
37	Rb	rubidium	$[Kr]5s^1$
38	Sr	strontium	$[Kr]5s^2$
39	Y	yttrium	$[Kr]5s^2 4d^1$
40	Zr	zirconium	$[Kr]5s^2 4d^2$
41	Nb	niobium	*$[Kr]5s^1 4d^4$
42	Mo	molybdenum	*$[Kr]5s^1 4d^5$
43	Tc	technetium	$[Kr]5s^2 4d^5$
44	Ru	ruthenium	*$[Kr]5s^1 4d^7$
45	Rh	rhodium	*$[Kr]5s^1 4d^8$
46	Pd	palladium	*$[Kr]4d^{10}$
47	Ag	silver	*$[Kr]5s^1 4d^{10}$
48	Cd	cadmium	$[Kr]5s^2 4d^{10}$
49	In	indium	$[Kr]4d^{10} 5s^2 5p^1$
50	Sn	tin	$[Kr]4d^{10} 5s^2 5p^2$
51	Sb	antimony	$[Kr]4d^{10} 5s^2 5p^3$
52	Te	tellurium	$[Kr]4d^{10} 5s^2 5p^4$
53	I	iodine	$[Kr]4d^{10} 5s^2 5p^5$
54	Xe	xenon	$[Kr]4d^{10} 5s^2 5p^6$
55	Cs	caesium	$[Xe]6s^1$
56	Ba	barium	$[Xe]6s^2$
57	La	lanthanum	*$[Xe]6s^2 5d^1$
58	Ce	cerium	*$[Xe]6s^2 4f^1 5d^1$
59	Pr	praseodymium	$[Xe]6s^2 4f^3$
60	Nd	neodymium	$[Xe]6s^2 4f^4$
61	Pm	promethium	$[Xe]6s^2 4f^5$
62	Sm	samarium	$[Xe]6s^2 4f^6$
63	Eu	europium	$[Xe]6s^2 4f^7$
64	Gd	gadolinium	*$[Xe]6s^2 4f^7 5d^1$
65	Tb	terbium	$[Xe]6s^2 4f^9$
66	Dy	dysprosium	$[Xe]6s^2 4f^{10}$
67	Ho	holmium	$[Xe]6s^2 4f^{11}$
68	Er	erbium	$[Xe]6s^2 4f^{12}$
69	Tm	thulium	$[Xe]6s^2 4f^{13}$
70	Yb	ytterbium	$[Xe]6s^2 4f^{14}$

Atomic number	Symbol	Name of element	Ground state electronic configuration of atom
71	Lu	lutetium	$[Xe]4f^{14} 6s^2 5d^1$
72	Hf	hafnium	$[Xe]4f^{14} 6s^2 5d^2$
73	Ta	tantalum	$[Xe]4f^{14} 6s^2 5d^3$
74	W	tungsten	$[Xe]4f^{14} 6s^2 5d^4$
75	Re	rhenium	$[Xe]4f^{14} 6s^2 5d^5$
76	Os	osmium	$[Xe]4f^{14} 6s^2 5d^6$
77	Ir	iridium	$[Xe]4f^{14} 6s^2 5d^7$
78	Pt	platinum	*$[Xe]4f^{14} 6s^1 5d^9$
79	Au	gold	*$[Xe]4f^{14} 6s^1 5d^{10}$
80	Hg	mercury	$[Xe]4f^{14} 6s^2 5d^{10}$
81	Tl	thallium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
82	Pb	lead	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$
83	Bi	bismuth	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
84	Po	polonium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
85	At	astatine	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$
86	Rn	radon	$[Xe]4f^{14} 5d^{10} 6s^2 6p^6$
87	Fr	francium	$[Rn]7s^1$
88	Ra	radium	$[Rn]7s^2$
89	Ac	actinium	*$[Rn]7s^2 6d^1$
90	Th	thorium	*$[Rn]7s^2 6d^2$
91	Pa	protactinium	*$[Rn]7s^2 5f^2 6d^1$
92	U	uranium	*$[Rn]7s^2 5f^3 6d^1$
93	Np	neptunium	*$[Rn]7s^2 5f^4 6d^1$
94	Pu	plutonium	$[Rn]7s^2 5f^6$
95	Am	americium	$[Rn]7s^2 5f^7$
96	Cm	curium	*$[Rn]7s^2 5f^7 6d^1$
97	Bk	berkelium	$[Rn]7s^2 5f^9$
98	Cf	californium	$[Rn]7s^2 5f^{10}$
99	Es	einsteinium	$[Rn]7s^2 5f^{11}$
100	Fm	fermium	$[Rn]7s^2 5f^{12}$
101	Md	mendeleevium	$[Rn]7s^2 5f^{13}$
102	No	nobelium	$[Rn]7s^2 5f^{14}$
103	Lr	lawrencium	$[Rn]5f^{14} 7s^2 6d^1$

† When a sub-shell is being filled it is written last in the configuration. Thus cobalt is part of a series in which the 3d sub-shell is filling, and the configuration is written $[Ar]4s^2 3d^7$. However, once the sub-shell has

finally become completely filled, then in the <u>succeeding</u> elements, it and the other completely filled sub-shells are arranged in order of principal quantum number. Thus the 3d and 4s levels are full at zinc, so at the next element, gallium, the configuration is written $[Ar]3d^{10}4s^24p^1$, the full 3d and 4s sub-shells being in the reverse of their order at cobalt and zinc.

* These configurations are the ones that cannot be predicted by the application of frame 47.

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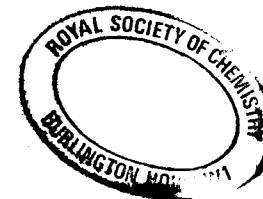
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