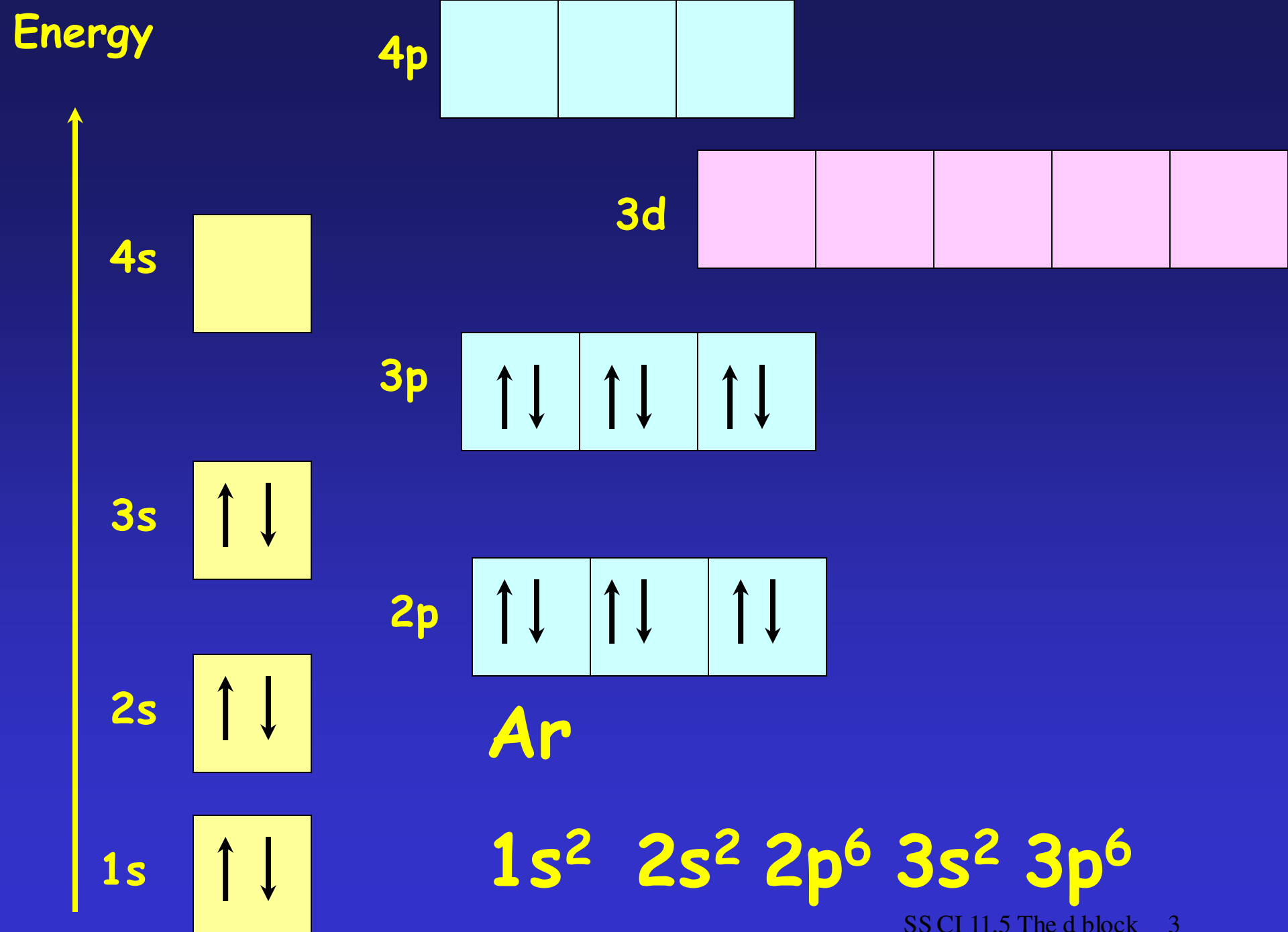


The d block:

- The d block consists of three horizontal series in periods 4, 5 & 6
 - 10 elements in each series
 - Chemistry is “different” from other elements
 - Special electronic configurations important
 - Differences within a group in the d block are less sharp than in s & p block
 - Similarities across a period are greater

Electronic Configuration

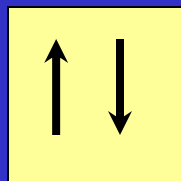
- Across the 1st row of the d block (Sc to Zn) each element
 - has 1 more electron and 1 more proton
 - Each “additional” electron enters the 3d sub-shell
 - The core configuration for all the period 4 transition elements is that of Ar
 - $1s^2 2s^2 2p^6 3s^2 3p^6$



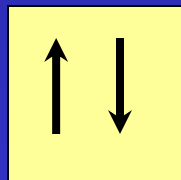
Energy



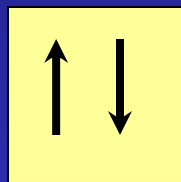
1s



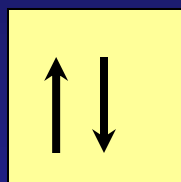
2s



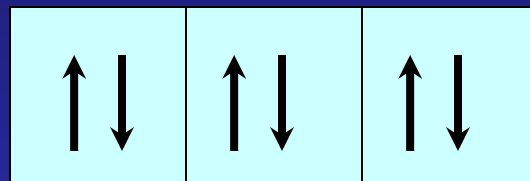
3s



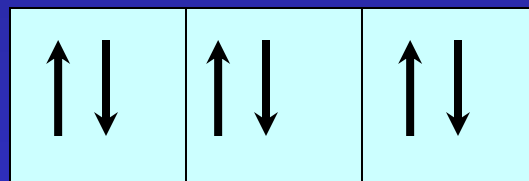
4s



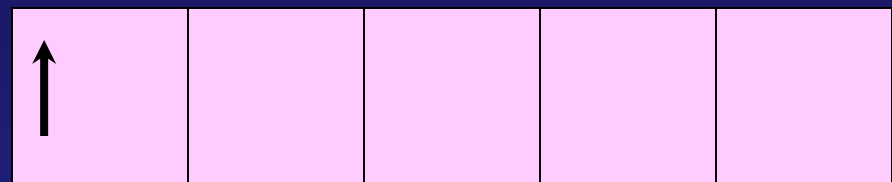
3p



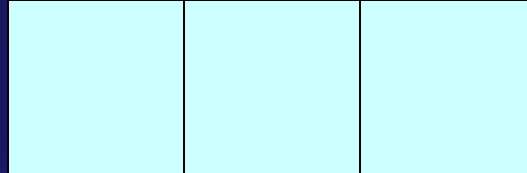
2p



3d



4p



Sc

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

Electronic Arrangement

Element	Z		3d					4s
Sc	21	[Ar]	↑					↑↓
Ti	22	[Ar]	↑	↑				↑↓
V	23	[Ar]	↑	↑	↑			↑↓
Cr	24	[Ar]	↑	↑	↑	↑	↑	↑
Mn	25	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	26	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	27	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	28	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

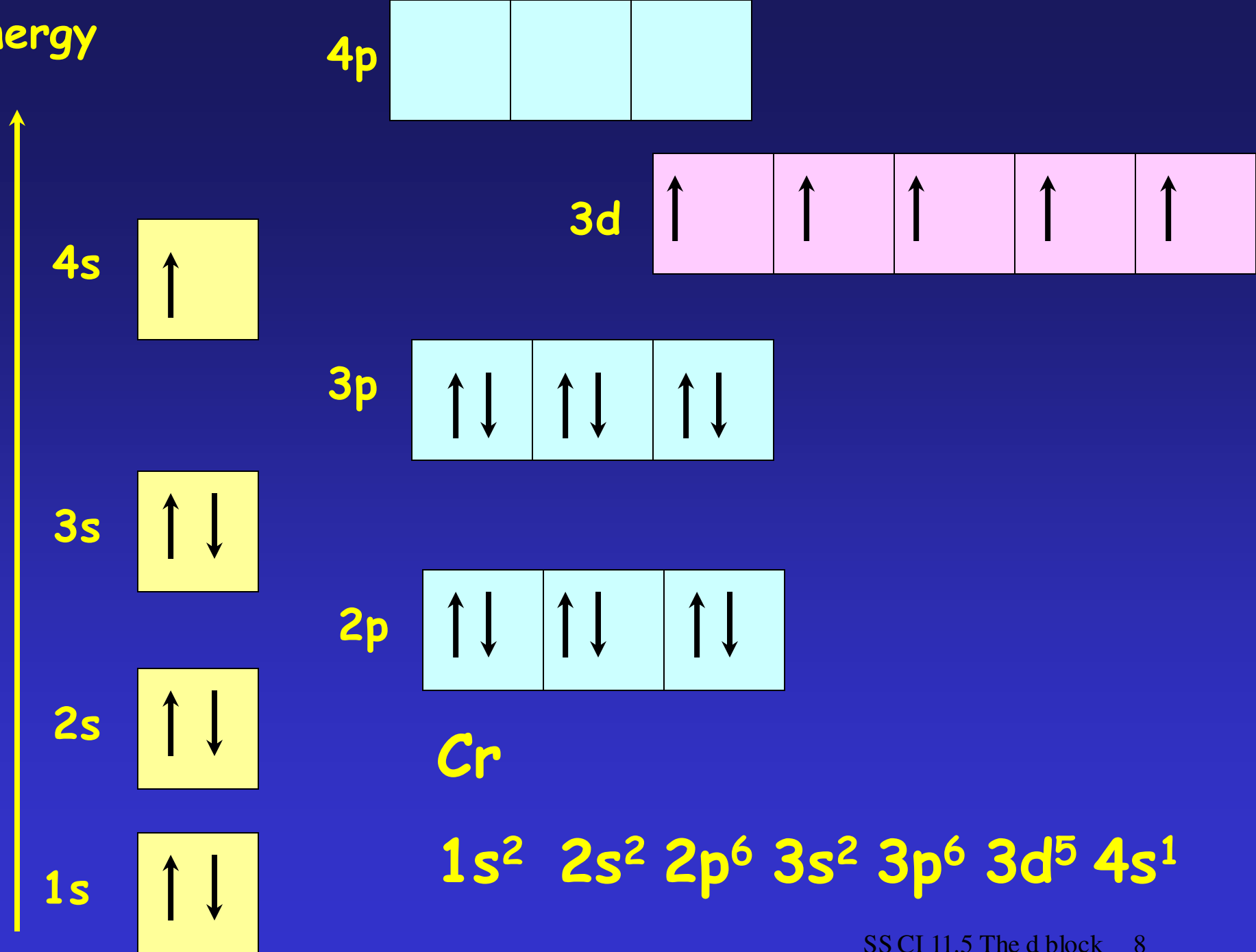
Chromium and Copper

- Cr and Cu don't fit the pattern of building up the 3d sub-shell, why?
 - In the ground state electrons are always arranged to give lowest total energy
 - Electrons are negatively charged and repel each other
 - Lower total energy is obtained with e^- singly in orbitals rather than if they are paired in an orbital
 - Energies of 3d and 4s orbitals very close together in Period 4

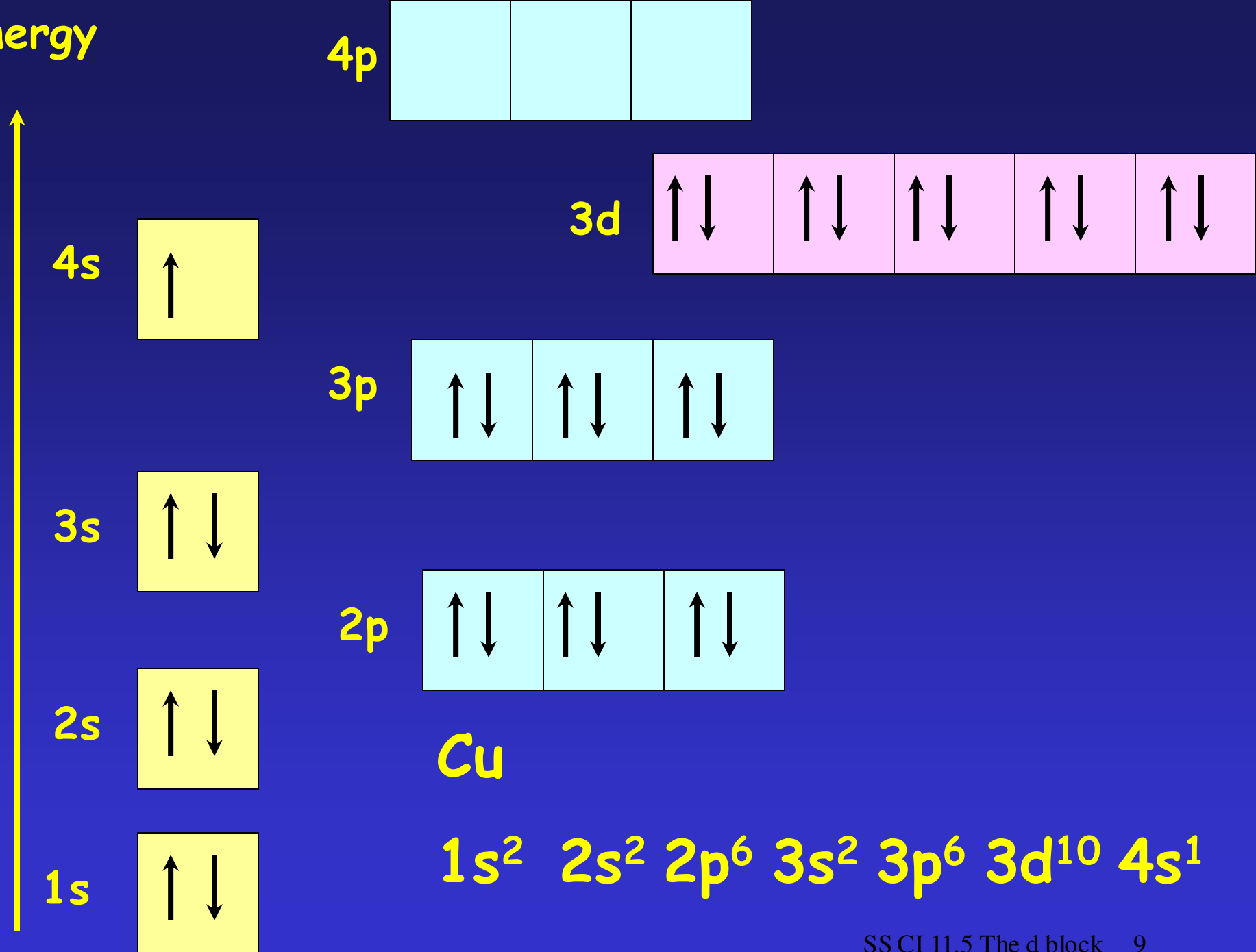
Chromium and Copper

- At Cr
 - Orbital energies such that putting one e^- into each 3d and 4s orbital gives lower energy than having 2 e^- in the 4s orbital
- At Cu
 - Putting 2 e^- into the 4s orbital would give a higher energy than filling the 3d orbitals

Energy



Energy



What is a transition metal?

- Transition metals [TM's] have characteristic properties
 - e.g. coloured compounds, variable oxidation states
- These are due to presence of an inner incomplete d sub-shell
- Electrons from both inner d sub-shell and outer s sub-shell can be involved in compound formation

What is a transition metal?

- Not all d block elements have incomplete d sub-shells
 - e.g. Zn has e.c. of $[\text{Ar}]3\text{d}^{10}4\text{s}^2$, the Zn^{2+} ion ($[\text{Ar}] 3\text{d}^{10}$) is not a typical TM ion
 - Similarly Sc forms Sc^{3+} which has the stable e.c of Ar. Sc^{3+} has no 3d electrons

What is a transition metal?

- For this reason, a transition metal is defined as being an element which forms at least one ion with a partially filled sub-shell of d electrons.
 - In period 4 only Ti-Cu are TM's!
 - Note that when d block elements form ions the s electrons are lost first

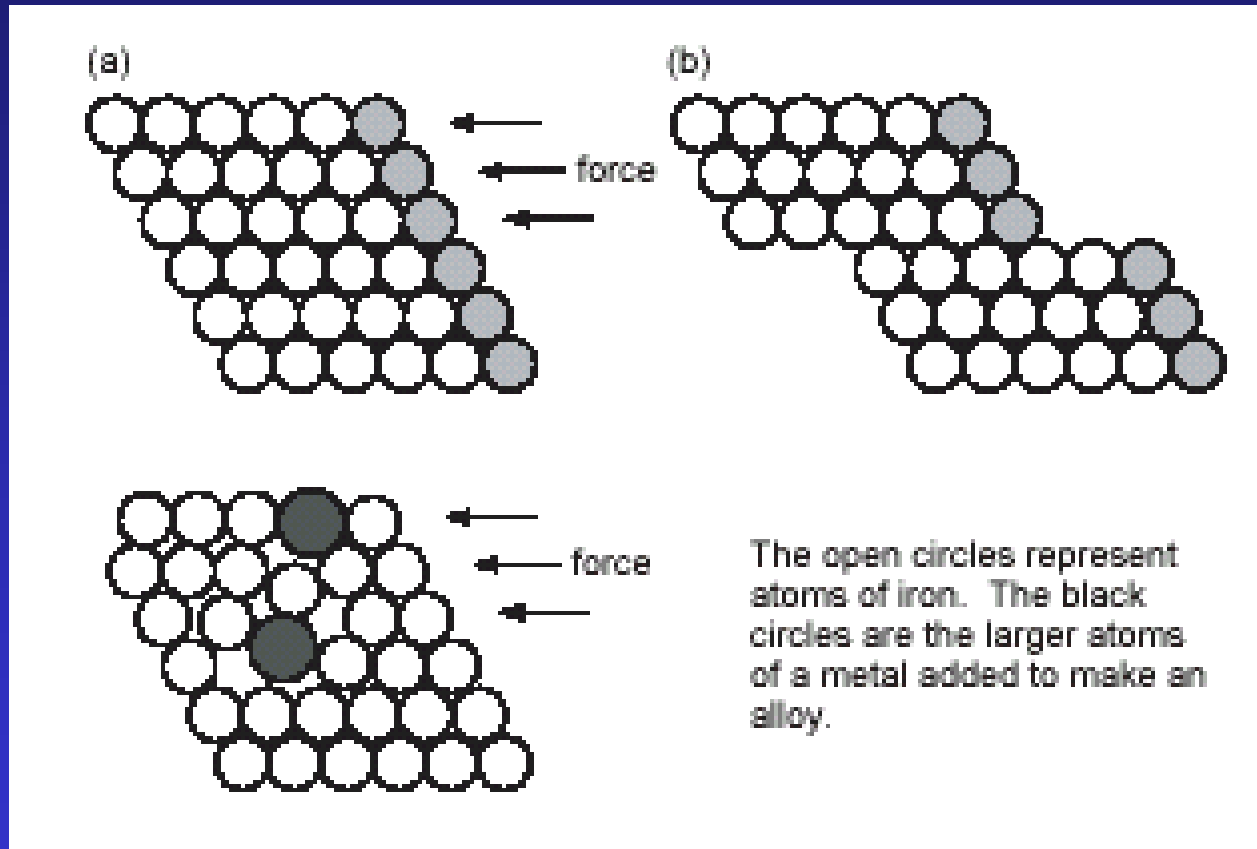
What are TM's like?

- TM's are metals
- They are similar to each other but different from s block metals eg Na and Mg
- Properties of TM's
 - Dense metals
 - Have high T_m and T_b
 - Tend to be hard and durable
 - Have high tensile strength
 - Have good mechanical properties

What are TM's like?

- Properties derive from strong *metallic bonding*
- TM's can release e^- into the pool of mobile electrons from both outer and inner shells
 - Strong metallic bonds formed between the mobile pool and the +ve metal ions
 - Enables widespread use of TMs!
 - Alloys very important: inhibits slip in crystal lattice usually results in increased hardness and reduced malleability

Effect of Alloying on TM's

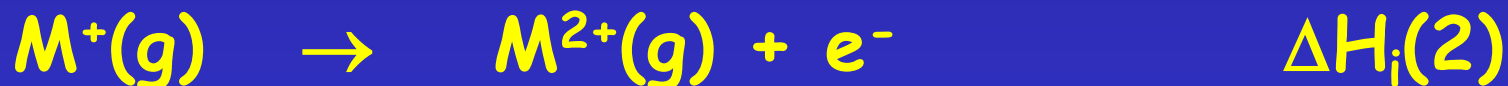
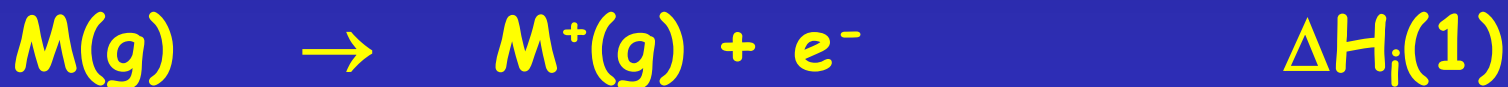


TM Chemical Properties

- Typical chemical properties of the TM's are
 - Formation of compounds in a variety of oxidation states
 - Catalytic activity of the elements and their compounds
 - Strong tendency to form complexes
 - See CI 11.6
 - Formation of coloured compounds
 - See CI 11.6

Variable Oxidation States

- TM's show a great variety of oxidation states cf s block metals
- If compare successive ionisation enthalpies (ΔH_i) for Ca and V as follows



ΔH_i for Ca and V

Element	Ionisation Enthalpies [kJ mol ⁻¹]			
	$\Delta H_i(1)$	$\Delta H_i(2)$	$\Delta H_i(3)$	$\Delta H_i(4)$
Ca [Ar]4s ²	+596	+1152	+4918	+6480
V [Ar]3d ³ 4s ²	+656	+1420	+2834	+4513

ΔH_i for Ca and V

- Both Ca & V always lose the 4s electrons
- For Ca
 - $\Delta H_i(1)$ & $\Delta H_i(2)$ relatively low as corresponds to removing outer 4s e^-
 - Sharp increase in $\Delta H_i(3)$ & $\Delta H_i(4)$ cf $\Delta H_i(2)$ due to difficulty in removing 3p e^-
- For Sc
 - Gradual increase from $\Delta H_i(1)$ to $\Delta H_i(4)$ as removing 4s then 3d e^-

Oxidation States of TM's

- In the following table
 - Most important OS's in boxes
 - OS = +1 only important for Cu
 - In all others sum of $\Delta H_i(1) + \Delta H_i(2)$ low enough for $2e^-$ to be removed
 - OS = +2, where 4s e^- lost shown by all except for Sc and Ti
 - OS = +3, shown by all except Zn

Oxidation States of TM's

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
		+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4		+4					
		+5							
			+6	+6	+6				
				+7					

Oxidation States of TM's

- No of OS's shown by an element increases from Sc to Mn
 - In each of these elements highest OS is equal to no. of 3d and 4s e^-
- After Mn decrease in no. of OS's shown by an element
 - Highest OS shown becomes lower and less stable
 - Seems increasing nuclear charge binds 3d e^- more strongly, hence harder to remove

Oxidation States of TM's

- In general
 - Lower OS's found in simple ionic compounds
 - E.g. compounds containing Cr^{3+} , Mn^{2+} , Fe^{3+} , Cu^{2+} ions
 - TM's in higher OS's usually covalently bound to electronegative element such as O or F
 - E.g VO_3^- , vanadate(V) ion; MnO_4^- , manganate(VII) ion
 - Simple ions with high OS's such as V^{5+} & Mn^{7+} are not formed

Stability of OS's

- Change from one OS to another is a redox reaction
- Relative stability of different OS's can be predicted by looking at Standard Electrode Potentials
 - E° values

Stability of OS's

- General trends
 - Higher OS's become less stable relative to lower ones on moving from left to right across the series
 - Compounds containing TM's in high OS's tend to be oxidising agents e.g MnO_4^-
 - Compounds with TM's in low OS's are often reducing agents e.g V^{2+} & Fe^{2+}

Stability of OS's

- General trends (continued)
 - Relative stability of +2 state with respect to +3 state increases across the series
 - For compounds early in the series, +2 state highly reducing
 - E.g. $V^{2+}(aq)$ & $Cr^{2+}(aq)$ strong reducing agents
 - Later in series +2 stable, +3 state highly oxidising
 - E.g. Co^{3+} is a strong oxidising agent, Ni^{3+} & Cu^{3+} do not exist in aqueous solution.

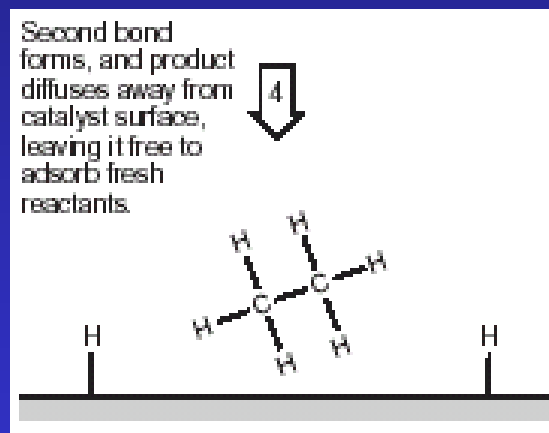
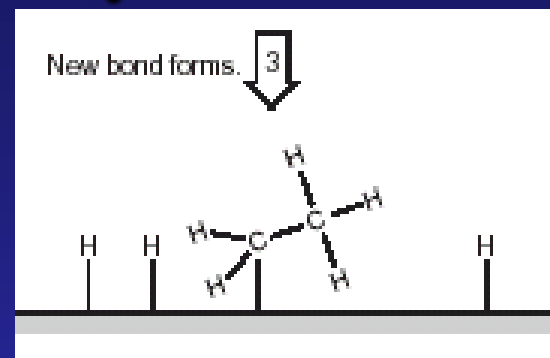
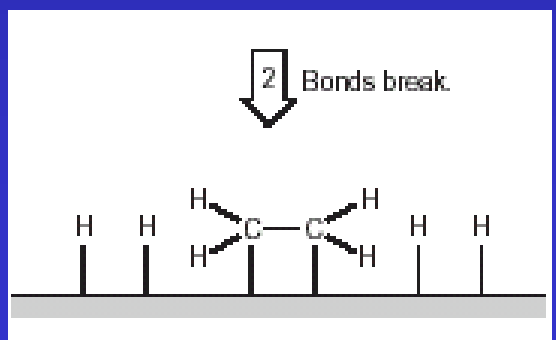
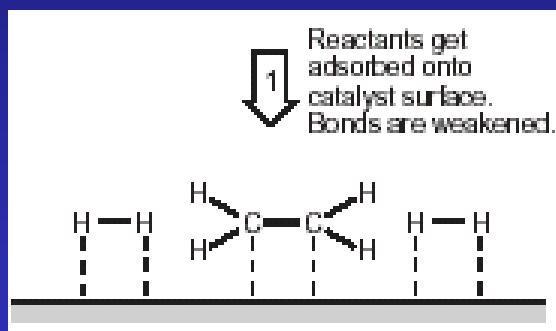
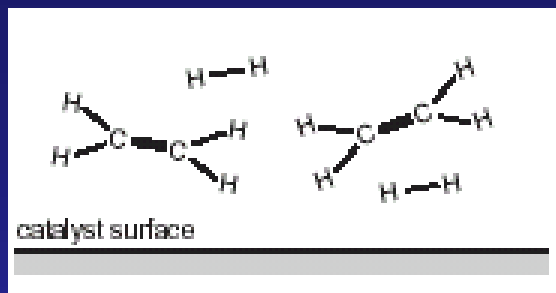
Catalytic Activity

- TM's and their compounds effective and important catalysts
 - *Industrially and biologically!!*
- The “people in the know” believe
 - catalysts provide reaction pathway with lower E_A than uncatalysed reaction (see CI 10.5)
- Once again,
 - availability of 3d and 4s e^-
 - ability to change OS
 - among factors which make TM's such good catalysts

Heterogeneous Catalysis

- Catalyst in different phase from reactants
 - Usually means solid TM catalyst with reactants in liquid or gas phases
- TM's can
 - use the 3d and 4s e^- of atoms on metal surface to form weak bonds to the reactants.
 - Once reaction has occurred on TM surface, these bonds can break to release products
- Important example is hydrogenation of alkenes using Ni or Pt catalyst

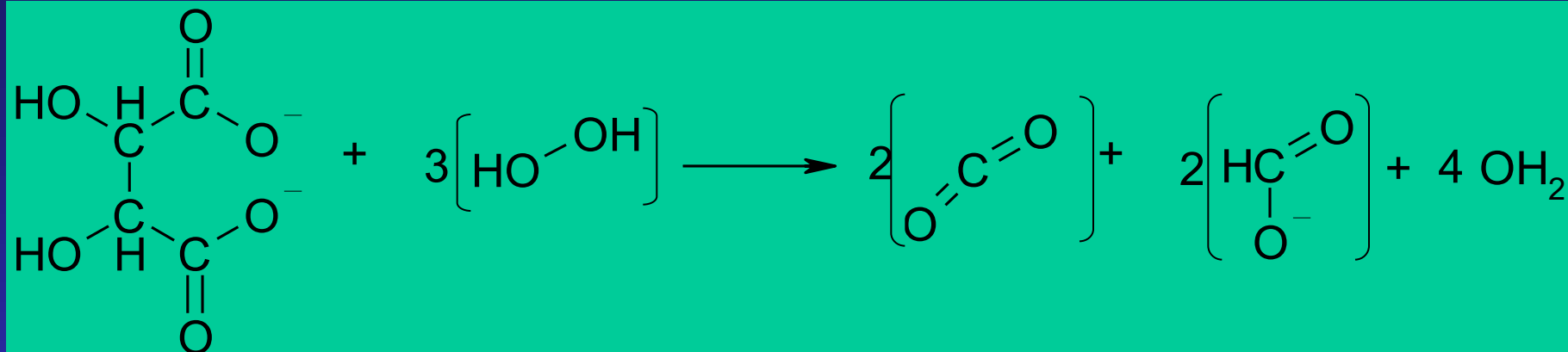
Heterogeneous Catalysis



Homogeneous Catalysis

- Catalyst in same phase as reactants
 - Usually means reaction takes place in aqueous phase
 - Catalyst aqueous TM ion
- Usually involves
 - TM ion forming *intermediate compound* with one or more of the reactants
 - Intermediate then breaks down to form products

Homogeneous Catalysis



- Above reaction is that used in Activity SS5.2
 - 2,3-dihydroxybutanoate ion with hydrogen peroxide
 - Reaction catalysed by Co^{2+}

Suggested Mechanism

