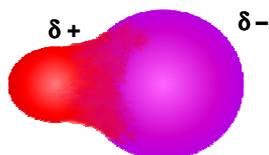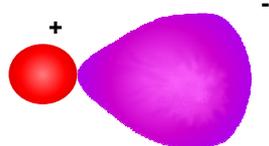# Transition from Ionic to Covalent Character
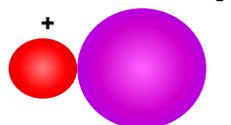
N Goalby

Chemrevise.org

Pure Covalent

Covalent with ionic character (polar covalent)

Ionic with covalent character

Pure Ionic

Fajan's Rules

- The extent of polarisation of the negative ion by the positive ion can be explained by Fajan's rules.

When the negative ion becomes distorted and more covalent we say it becomes polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.

There is a tendency towards covalent character when
- the positive ion is small
- the positive ion has multiple charges
- the negative ion is large
- the negative ion has multiple negative charges.

Examples

$AlCl_3$ shows quite large covalent character because Al has a +3 charge and is quite small, so is highly polarising.

Consider $MgCl_2$, $MgBr_2$, MgI_2.

The anions become larger and more easily polarised, so they show more covalent character

hypothetical ions   electrons attracted to Be   covalent bonds formed
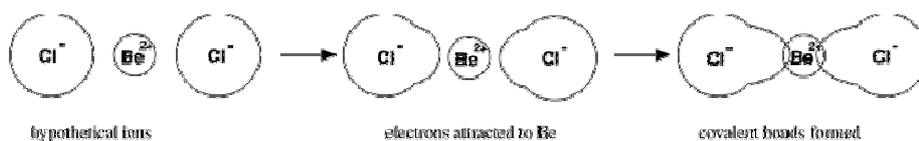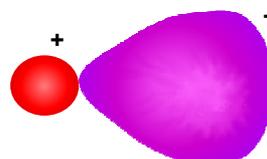
Theoretical lattice enthalpies

- Theoretical lattice enthalpies assumes a **perfect ionic model** where the ions are 100% ionic and spherical. The Born Haber lattice enthalpy is the real experimental value.

- When a compound shows covalent character the theoretical and the born Haber lattice enthalpies differ. The more the covalent character the bigger the difference between the values.

When the negative ion becomes distorted and more covalent we say it becomes polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.

100% ionic

Ionic with covalent character
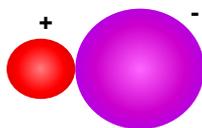
When 100 % ionic the ions are spherical.
The theoretical and the born Haber lattice enthalpies will be the same

The charge cloud is distorted. The theoretical and the experimental Born Haber lattice enthalpies will differ

Consider the following lattice dissociation enthalpy (ΔH_L) data.

	NaBr	AgBr
$\Delta H_L^{\ominus}$(experimental) / kJ mol^{-1}	+733	+890
$\Delta H_L^{\ominus}$(theoretical) / kJ mol^{-1}	+732	+758

The values of ΔH_L (experimental) have been determined from Born–Haber cycles.
The values of ΔH_L (theoretical) have been determined by calculation using a perfect ionic model.
Explain the meaning of the term *perfect ionic model*.

State what you can deduce about the bonding in NaBr from the data in the table.

State what you can deduce about the bonding in AgBr from the data in the table

Why is the magnitude of the Born Haber ΔH_L value of AgBr larger than the theoretical? What does it suggest about the strength of the bonding

	NaBr	AgBr
$\Delta H_L^{\ominus}$(experimental) / kJ mol^{-1}	+733	+890
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The data shows that the structure of silver chloride has **some contribution from covalent bonding. This appears to be bonding the structure together more tightly, as in a giant covalent structure.**

Curiously, the relative melting points indicate that the structure of silver chloride is actually weaker than that of sodium chloride. It seems as though the bonding changes its nature as the compound is heated and reverts back to a more ionic or simple covalent model.