Using the born Haber cycle to explain why Calcium Chloride has the formula $CaCl_2$

N Goalby
Chemrevise.org

Why does Calcium chloride have the formula $CaCl_2$ and not CaCl or $CaCl_3$?

It is useful to draw out the born haber cycles for each potential case.

Theoretical lattice enthalpies have been calculated for each case

Theoretical lattice enthalpies
ΔH_{latt} CaCl = -719 kJ mol^{-1}
ΔH_{latt} $CaCl_2$ = -2218 kJ mol^{-1}
ΔH_{latt} $CaCl_3$ = -4650 kJ mol^{-1}

These get larger as the positive charge on the calcium ion becomes bigger.

We need to calculate an enthalpy of formation for each case.

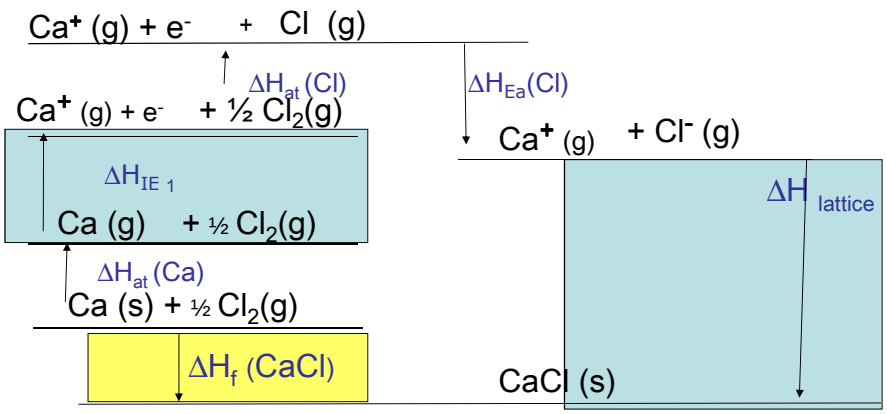
The one with the **most exothermic enthalpy of formation** will be the one that forms as it will be the most thermodynamically stable

We will need the following data

ΔH_{at} Ca = +193 kJ mol^{-1}
ΔH_{at} Cl = +121.7 kJ mol^{-1}
$\Delta H_{Ea\ 1}$ Cl = -348.8 kJ mol^{-1}

$\Delta H_{IE\ 1\ Ca}$ = + 590 kJ mol^{-1}
$\Delta H_{IE\ 2\ Ca}$ = + 1150 kJ mol^{-1}
$\Delta H_{IE\ 3\ Ca}$ = + 4940 kJ mol^{-1}

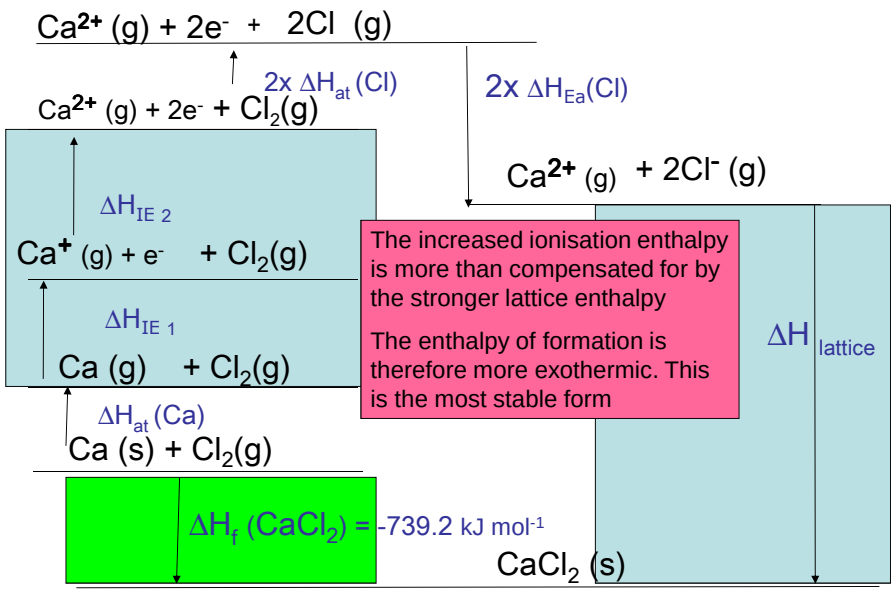
Born Haber Cycle for CaCl



The enthalpy of formation is largely a balance of the ionisation energy and lattice enthalpy.

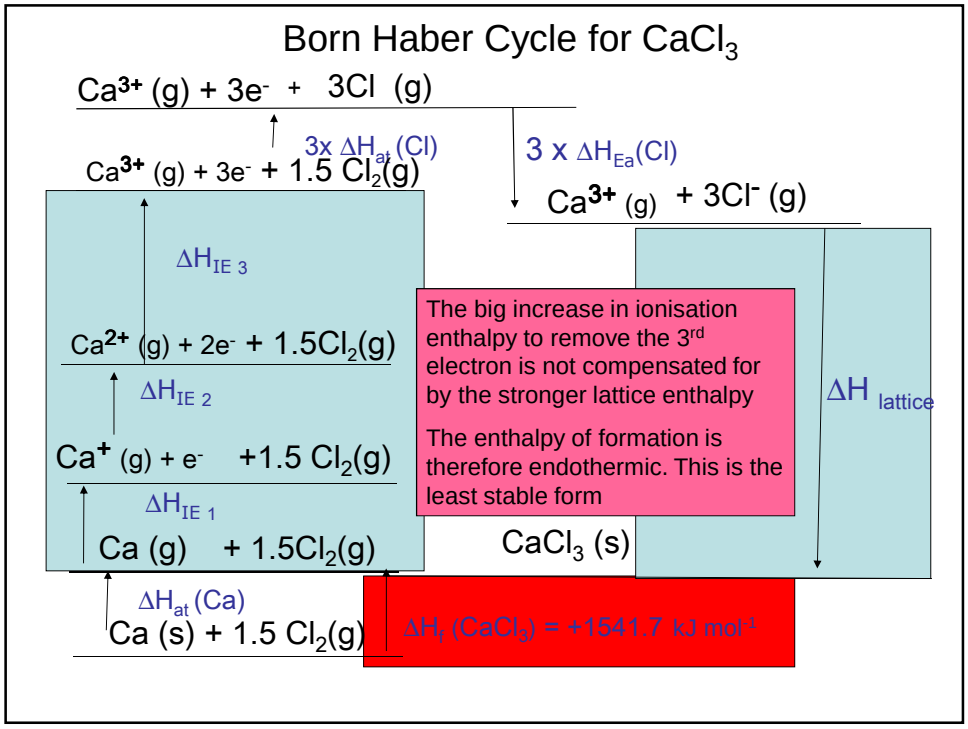
ΔH_f (CaCl) is -163.1 kJ mol^{-1}. This is exothermic.

Born Haber Cycle for $CaCl_2$



The increased ionisation enthalpy is more than compensated for by the stronger lattice enthalpy

The enthalpy of formation is therefore more exothermic. This is the most stable form


Born Haber Cycle for $CaCl_3$
$Ca^{3+}(g) + 3e^- + 3Cl(g)$
$3x\ \Delta H_{at}(Cl)$
$3 \times \Delta H_{Ea}(Cl)$
$Ca^{3+}(g) + 3e^- + 1.5\ Cl_2(g)$
$Ca^{3+}(g) + 3Cl^-(g)$
$\Delta H_{IE\ 3}$
$Ca^{2+}(g) + 2e^- + 1.5Cl_2(g)$
$\Delta H_{IE\ 2}$
$Ca^{+}(g) + e^- + 1.5\ Cl_2(g)$
$\Delta H_{IE\ 1}$
$Ca(g) + 1.5Cl_2(g)$
$CaCl_3(s)$
$\Delta H_{lattice}$
$\Delta H_{at}(Ca)$
$Ca(s) + 1.5\ Cl_2(g)$
$\Delta H_f(CaCl_3) = +1541.7\ kJ\ mol^{-1}$
The big increase in ionisation enthalpy to remove the 3rd electron is not compensated for by the stronger lattice enthalpy
The enthalpy of formation is therefore endothermic. This is the least stable form