

4.2.2 Born–Haber and solution cycles

Name: _____ Class: _____ Date: _____

Total: 34 marks**KEY WORDS** lattice energy

Objective

Construct energy routes with the stated lattice convention and correct ion counts. Questions and marking guidance are original.

1 Key knowledge and worked examples

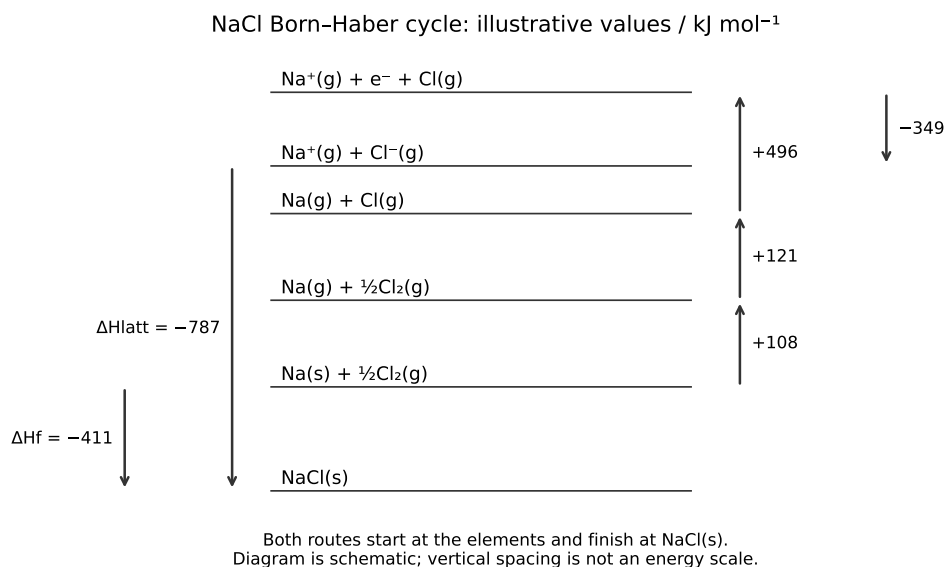
Lattice formation makes one mole of ionic solid from gaseous ions and is negative; lattice dissociation is the reverse and positive. Atomisation forms gaseous atoms from the element in its standard state. First electron affinity adds one electron to each gaseous atom; second affinity adds to an already negative ion and can be positive.

■ Worked cycle

For NaCl, illustrative values in kJ mol^{-1} are formation -411 , Na atomisation $+108$, Cl atomisation $+121$, Na ionisation $+496$ and Cl electron affinity -349 .

$$\Delta H_{\text{latt}} = -411 - [108 + 121 + 496 - 349] = -787 \text{ kJ mol}^{-1}$$

Use the same start and finish on both routes. For MgCl_2 count two Cl atomisations, two Cl electron affinities and two Mg ionisation energies. For dissolution, $\Delta H_{\text{sol}} = -\Delta H_{\text{latt,formation}} + \sum \Delta H_{\text{hyd}}$. Smaller, more highly charged ions usually have more negative lattice-formation and hydration enthalpies; competing changes prevent a one-factor solubility rule.



2 Practice

2.1 Define lattice formation enthalpy, including the required states and amount. [3]

2.2 For a salt, lattice formation = -850 and total hydration = -820 kJ mol^{-1} . Calculate solution enthalpy. [2]

2.3 Explain why the second electron affinity of oxygen is endothermic although the first is exothermic. [2]

3 Exam-style questions

3.1 For $\text{MgCl}_2(\text{s})$, use $\Delta H_f = -642$; Mg atomisation $+148$; each Cl atomisation $+121$; $\text{IE}_1 +738$; $\text{IE}_2 +1451$; each Cl electron affinity -349 , all in kJ mol^{-1} . Calculate lattice formation enthalpy. [4]

3.2 A Born–Haber lattice value is substantially more negative than a purely ionic-model estimate. Explain a possible bonding interpretation. Why can a negative solution enthalpy alone not establish solubility? [3]

3.3 Two illustrative sulfate salts A and B have lattice dissociation enthalpies $+2500$ and $+2450 \text{ kJ mol}^{-1}$, and total hydration enthalpies -2510 and $-2420 \text{ kJ mol}^{-1}$. Both have solution entropy $+40.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate each solution enthalpy and total entropy at 298 K . Use the data to explain which dissolution is favoured and why hydration alone is not the calculation. [6]

3.4 Construct a complete Born–Haber cycle for $\text{CaF}_2(\text{s})$, using these supplied illustrative enthalpies in kJ mol^{-1} : formation -1220 ; Ca atomisation $+178$; atomisation of one mole of F atoms $+79$; Ca IE_1 $+590$ and IE_2 $+1145$; first electron affinity of F -328 . Label every intermediate species/state, electron count and arrow; include the appropriate factors. Use your cycle to calculate lattice formation enthalpy. [7]

3.5 Define hydration enthalpy for chloride ions and solution enthalpy for MgCl_2 using equations, amounts and states. Construct a cycle for MgCl_2 dissolution from supplied illustrative values: lattice formation -2523 , hydration of Mg^{2+} -1920 and hydration of each Cl^- -381 kJ mol^{-1} . Calculate the solution enthalpy. [7]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Enthalpy change when one mole of ionic solid forms from its gaseous ions under stated standard conditions.

2.2 $\Delta H_{sol} = +850 - 820 = +30 \text{ kJ mol}^{-1}$.

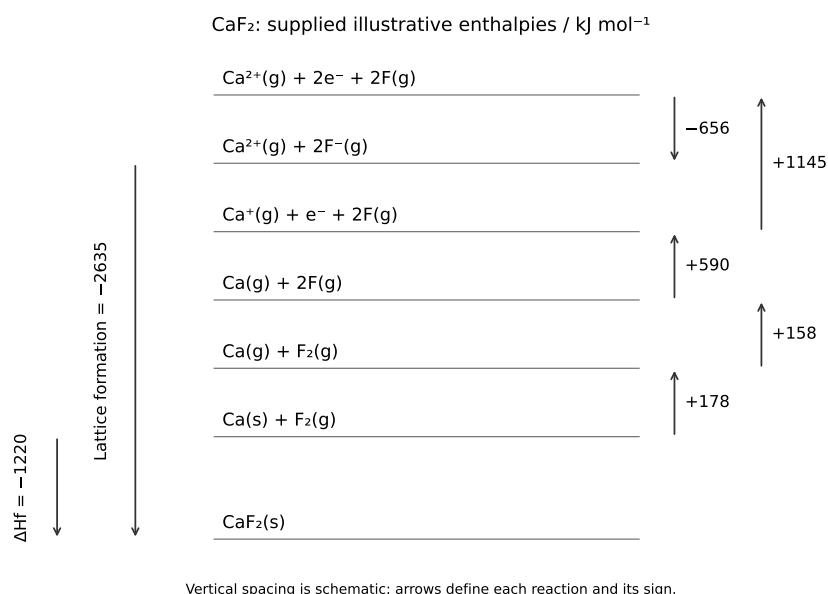
2.3 An electron approaches an already negative O^- ion; energy is needed to overcome electron-ion repulsion.

3.1 $-642 = 148 + 2(121) + 738 + 1451 + 2(-349) + \Delta H_{latt}$. Other steps sum to 1881, giving $\Delta H_{latt} = -2523 \text{ kJ mol}^{-1}$.

3.2 Extra stabilisation can support covalent character, from cation polarisation of anion electron density. Dissolution also involves entropy, so enthalpy alone does not determine the total entropy change.

3.3 For A, $\Delta H_{sol} = 2500 - 2510 = -10 \text{ kJ mol}^{-1}$; for B, $2450 - 2420 = +30 \text{ kJ mol}^{-1}$. A: $\Delta S_{total} = 40 - (-10000/298) = +73.6 \text{ J mol}^{-1} \text{ K}^{-1}$. B: $40 - 30000/298 = -60.7 \text{ J mol}^{-1} \text{ K}^{-1}$. A has favourable positive total entropy; hydration and lattice terms compete and entropy must also be included. These are illustrative data, not measured values assigned to named salts.

3.4 A complete construction is shown below. Ca atomisation contributes +178 and two fluorine atomisations +158 with correct gaseous-atom states. Both calcium ionisations contribute +590 +1145, with $\text{Ca}^+/\text{Ca}^{2+}$ and one/two electrons correctly shown. Two electron affinities contribute -656 and produce two gaseous F^- ions. The formation arrow goes from $\text{Ca(s)} + \text{F}_2(\text{g})$ to $\text{CaF}_2(\text{s})$, -1220; lattice formation goes from $\text{Ca}^{2+}(\text{g}) + 2\text{F}^-(\text{g})$ to the solid. Hess route: $-1220 = 178 + 2(79) + 590 + 1145 + 2(-328) + \Delta H_{latt}$, hence $\Delta H_{latt} = -2635 \text{ kJ mol}^{-1}$. Accept an equivalent complete cycle with directions and signs consistent.



3.5 Hydration: $\text{Cl}^-(\text{g}) \rightarrow \text{Cl}^-(\text{aq})$, for one mole of gaseous chloride ions under stated

standard conditions. Solution: $\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$, for one mole of solid in sufficient water that further dilution causes no enthalpy change, under stated standard conditions. The cycle separates the lattice to $\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g})$, +2523, then hydrates one Mg^{2+} and two Cl^{-} ions. Total hydration = $-1920 + 2(-381) = -2682 \text{ kJ mol}^{-1}$. The solution arrow and indirect route have matching initial/final species and signs, giving $\Delta H_{\text{sol}} = 2523 - 2682 = -159 \text{ kJ mol}^{-1}$.

