

## 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

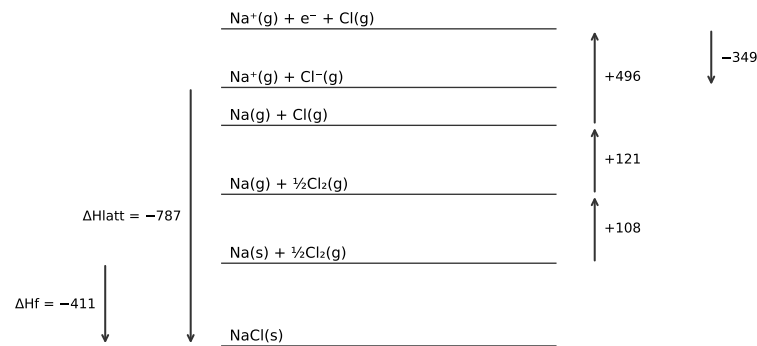
Lattice formation makes one mole of ionic solid from gaseous ions and is negative; lattice dissociation is the reverse and positive. Atomisation forms gaseous atoms from the element in its standard state. First electron affinity adds one electron to each gaseous atom; second affinity adds to an already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

#### ■ Worked cycle

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

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

Use the same start and finish on both routes. For  $\text{MgCl}_2$  count two Cl atomisations, two Cl electron affinities and two Mg ionisation energies. For dissolution,  $\Delta H_{sol} = -\Delta H_{latt, formation} + \sum \Delta H_{hyd}$ . Smaller, more highly charged ions usually have more negative lattice-formation and hydration enthalpies; competing changes prevent a one-factor solubility rule.

NaCl Born–Haber cycle: illustrative values /  $\text{kJ mol}^{-1}$ 

Both routes start at the elements and finish at NaCl(s).  
Diagram is schematic; vertical spacing is not an energy scale.

### 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 =  $-820 \text{ kJ mol}^{-1}$ . 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  $\text{kJ mol}^{-1}$ . 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  $298 \text{ K}$ . 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  $\text{kJ mol}^{-1}$ : formation  $-1220$ ; Ca atomisation  $+178$ ; atomisation of one mole of F atoms  $+79$ ; Ca  $\text{IE}_1 +590$  and  $\text{IE}_2 +1145$ ; 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  $\text{MgCl}_2$  using equations, amounts and states. Construct a cycle for  $\text{MgCl}_2$  dissolution from supplied illustrative values: lattice formation  $-2523$ , hydration of  $\text{Mg}^{2+}$   $-1920$  and hydration of each  $\text{Cl}^-$   $-381 \text{ kJ mol}^{-1}$ . 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**  $\Delta H_{sol} = +850 - 820 = +30 \text{ kJ mol}^{-1}$ .

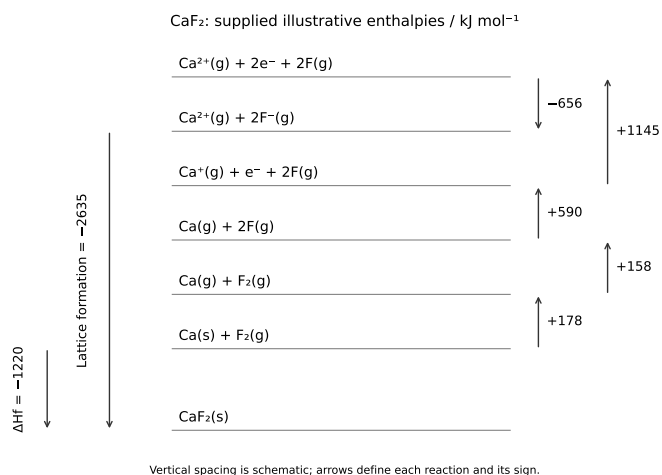
**2.3** An electron approaches an already negative  $\text{O}^-$  ion; energy is needed to overcome electron-ion repulsion.

**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  $\text{F}^-$  ions. The formation arrow goes from  $\text{Ca}(\text{s}) + \text{F}_2(\text{g})$  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  $\text{Mg}^{2+}$  and two  $\text{Cl}^-$  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  $\Delta H_{sol} = 2523 - 2682 = -159 \text{ kJ mol}^{-1}$ .

