

Lattice Enthalpy and Born–Haber Cycles

Answer key with worked solutions

A. Definitions

1. Lattice enthalpy.

(a) The enthalpy change when 1 mol of an ionic solid forms from its gaseous ions under standard conditions. (b) Lattice: $\text{K}^+(\text{g}) + \text{Br}^-(\text{g}) \longrightarrow \text{KBr}(\text{s})$. Formation: $\text{K}(\text{s}) + \frac{1}{2} \text{Br}_2(\text{l}) \longrightarrow \text{KBr}(\text{s})$ (bromine is a liquid in its standard state).

2. Endothermic or exothermic.

(a) endothermic (b) **exothermic** (c) **endothermic** (d) endothermic (e) exothermic

B. Calculations

3. LiF.

Steps to the gaseous ions:

$$\begin{aligned} & 159.3 + 520.2 + 79.4 - 328.2 \text{ (kJ/mol)} \\ & = +430.7 \text{ kJ/mol} \\ & \Delta H_{\text{latt}}^\circ \\ & = -616.0 \text{ kJ/mol} - 430.7 \text{ kJ/mol} \\ & = \mathbf{-1046.7 \text{ kJ/mol}} \end{aligned}$$

4. EA of bromine.

$$\begin{aligned} \Delta H_{\text{f}}^\circ &= \Delta H_{\text{sub}}(\text{K}) + \text{IE}_1 + \Delta H_{\text{atom}}(\text{Br}) + \text{EA} + \Delta H_{\text{latt}}^\circ, \text{ so:} \\ \text{EA} &= -393.8 - 89.0 - 418.8 \\ &\quad - 111.9 - (-689.0) \text{ (kJ/mol)} \\ &= \mathbf{-324.5 \text{ kJ/mol}} \end{aligned}$$

C. Trends

5. Order.

KCl, NaCl, CaO, MgO (least to most negative). KCl and NaCl have 1+ and 1- ions; K^+ is larger than Na^+ , so KCl is less negative. CaO and MgO have 2+ and 2- ions, so their attractions are about four times stronger; Mg^{2+} is smaller than Ca^{2+} , so MgO is the most negative.

6. Second electron affinity of oxygen.

(a) Steps other than EA_2 :

$$\begin{aligned} &177.8 + 589.8 + 1145.4 \\ &\quad + 249.2 - 141.0 \text{ (kJ/mol)} \\ &= +2021.2 \text{ kJ/mol} \\ EA_2 &= -634.9 - 2021.2 \\ &\quad - (-3414) \text{ (kJ/mol)} \\ &= +758 \text{ kJ/mol} \end{aligned}$$

(b) It is **endothermic**: the electron is added to O^- , which is already negative, so it is repelled and energy must be put in.

D. Challenge

7. Hypothetical MgCl.

(a)

$$\begin{aligned} \Delta H_f^\circ &= 147.1 + 737.7 + 121.3 \\ &\quad - 348.6 - 753.0 \text{ (kJ/mol)} \\ &= -95.5 \text{ kJ/mol} \end{aligned}$$

(b) Products minus reactants:

$$\begin{aligned} \Delta H &= (1 \text{ mol})(-641.3 \text{ kJ/mol}) \\ &\quad - (2 \text{ mol})(-95.5 \text{ kJ/mol}) \\ &= -450.3 \text{ kJ} \end{aligned}$$

(c) MgCl would be stable relative to the elements, but it would release a lot of energy by turning into Mg and $MgCl_2$. Removing the second electron costs 1450.7 kJ/mol, but the much more negative lattice enthalpy of $MgCl_2$ (2+ ions) more than repays it, so $MgCl_2$ forms.

8. Ionic model.

NaCl is almost purely **ionic**: the model of separate spherical ions describes it well. In AgI, the large, easily polarized I^- ion is distorted by Ag^+ , so some electron density is shared between them: the bonding has **covalent character**, which adds extra attraction not included in the ionic model.