Ionic bonding & Lattice energy

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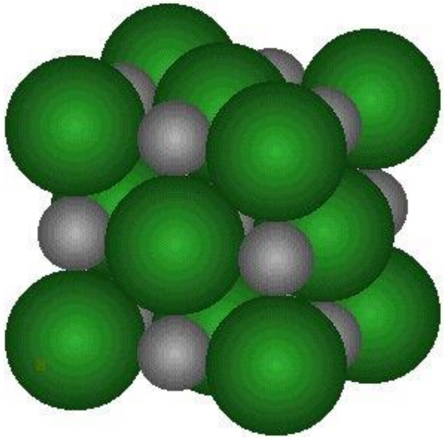
Ionic Bonding

- An ionic bond is an electrostatic attraction between oppositely charged ions
- Ionic bonding occurs between a metal and a non-metal and involves the transfer of electrons from the metal to the non-metal
- Ionic compounds are electrically neutral
- Ions attract multiple opposite charged ions
- Form crystals



Factors governing the formation of ionic bond

Ionisation Energy: Lower the ionization energy greater will be the tendency of the metal atom of change into cation and hence greater will be the ease of formation of ionic bond. That is why alkali metals and alkaline earth metals form ionic bonds easily

Electron Affinity: Higher the electron affinity more is the energy released and stable will be the anion formed and are prone to the formation of ionic bond

Lattice Energy: Greater the lattice energy, greater the strength of ionic bond. The value of lattice energy depends upon size and charge of the involved ions. Smaller the size of the cations and anions greater is the force of attraction. Greater the charge on ions greater will be the force of attraction (coulomb force). Thus, stronger is the ionic bond.

Properties of ionic compounds

- **Solids at room temperature**: On account of strong electrostatic forces between the opposite ions, these ions are locked in their allotted positions in the crystal lattice. Since they lack the freedom of movement characteristic of the liquid state, they are solids at room temperature.
- **High melting and boiling points**: MP is the temperature that a solid becomes a liquid and BP is the temperature that a liquid becomes a gas. So transforming solid to liquid (melt) or liquid to gas (boil) enough energy (temperature) is needed to break (or loosen) the strong ionic/electrostatic bonds between particles.
- **Conductors of electricity:** Solid ionic compounds are poor conductors of electricity because the ions are fixed rigidly in their positions. In the molten state and in water solutions, ions are rendered free to move about. Thus molten ionic compounds or their aqueous solutions conduct a current when placed in an electrolytic cell.
- **Hard and brittle**: Their hardness is due to the strong electrostatic forces which hold each ion in its allotted position. Ionic solids composed of positive and negative ions. Positives charges repel each other and negatives charges repel each other. Strong repulsion breaks crystal apart on applying external force

- **Soluble in water:** When a crystal of an ionic substance is placed in water, the polar water molecules detach the positive and negative ions from the crystal lattice by their electrostatic pull. These ions then get surrounded by water molecules and can lead an independent existence and are thus dissolved in water.
- **Non-directional**: Electrostatic forces are uniformly distributed in all directions and hence the bonding is non directional

Solvation energy

- Solubility of an ionic compound in any solvent depends on the Gibbs free energy ΔG^o of the process $\mathrm{MX\ (s) \rightarrow M+(sol) + X-(sol)}$
- The standard free energy change for the dissolution of the salt, $\Delta G^o s$, is related to the solubility product Ks as $\Delta G^o s = -RT \ln Ks$
- Solvation energy is the change in the Gibbs free energy of a solvent when a solute is dissolved in that solvent
- Amount of energy released when 1 mol of an ionic solid is dissolved in any solvent is defined as solvation energy or enthalpy of solvation. If it is a positive number, the dissolving process is endothermic; if it is negative, it is exothermic.
- In case of ionic solids, water is predominantly used as solvent and hence the term hydration energy or enthalpy of hydration is commonly used.
- Hydration energy (enthalpy) is defined as the amount of energy released when 1 mol of ionic solid undergo hydration
- Smaller the cation higher is the hydration energy

Lattice enthalpy

- It is the change in enthalpy (heat change) that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions. In other words, it is the amount of energy released when one mole of an ionic solid is formed from its gaseous ions.

$$M^+(g) + X^-(g) \rightarrow MX(s) + \text{Lattice energy}$$

- Lattice energy is denoted by U and is negative
- Lattice energy is inversely proportional to the size and directly proportional to the charge of the involved cations and anions.
- Hydration energy and Lattice energy are parallel to each other. When hydration energy is higher than lattice energy, the solid is soluble in water and if lattice energy is higher than hydration energy the solid is insoluble in water.
- Lattice energy can be calculated by theoretically as well as experimentally.
- Born-Lande Equation (theoretically)
- Born-Haber cycle (experimentally)

Born-Lande Equation

- The theoretical treatment of lattice energy was given by M. Born and A. Lande
- The cation and anion involved in an ionic bond (solid) can be treated as point charges, and the electrostatic (coulombic) energy, E between the two ions is given by

  $$E = -\,[Z^{+}Z^{-}e^{2}]/r \qquad (1)$$

  where Z^{+} and Z^{-} are the charges on the cations and anion respectively, E is the charge on an electron and r is the inter ionic distance
- For more than two ions, the electrostatic energy depends on the number of ions, and also on M or A (Madelung constant, depends on the geometry of the crystal) their arrangement in space. For 1 mole, the attractive energy is

  $$E = -\,[N_{A}MZ^{+}Z^{-}e^{2}]/r \qquad (2)$$

  where N_A= Avogadro's constant = $6.023\text{x}10^{23}$ mol^{-1}
- Values of Madelung constant can be calculated by summing the contribution of all the ions in the crystal lattice
- Eqn 2 suggests that an infinite amount of energy should be evolved if the distance r = 0

- Practically it is not possible, at small interionic distances repulsive force originating from mutual repulsion of electron cloud of the interacting ions starts operating.
- The repulsive force increases rapidly with decrease in r and is given by B/r^n where B is a constant that depends on the structure (number of nearest neighbour) and n is a constant known as Born exponent. For 1 gram molecule or 1 mole, the total repulsive force is N_AB/r^n
- Born exponent can be determined from compressibility measurements
- The total energy holding the crystal together, U (lattice energy) is the sum of both attractive and repulsive forces

$$U = - [N_AMZ^+Z^-e^2]/r + N_AB/r^n \qquad (3)$$

- The equilibrium distance between the ions is determined by the balance between attractive and repulsive terms.
- At equilibrium, $dU/dr = 0$ and the equilibrium distance $r = r_o$

$$dU/dr = [N_AMZ^+Z^-e^2]/r_o^2 - nN_AB/r_o^{n+1} = 0 \qquad (4)$$

- Rearranging the equation 4, an equation for repulsive coefficient B is obtained and is given by

$$B = [MZ^{+}Z^{-}e^{2}r_{o}^{n-1}]/n \qquad (5)$$

- Using eqn. (5) in eqn. (3) we heve

$$U = -\,[N_{A}MZ^{+}Z^{-}e^{2}]/r_{o}[(1-(1/n)] \qquad (6)$$

- Eqn (6) is known as the Born-Lande Equation, allows the lattice energy to be calculated from the geometry of the crystal (or Madelung constatnt), charges and the interionic distance.
- In SI unit, the equation takes the form

$$U = -\,[N_{A}MZ^{+}Z^{-}e^{2}/4\pi\varepsilon_{o}r_{o}][(1-(1/n)] \qquad (7)$$

where ε_o is the permittivity of free space = 8.854 x 10^{-12} -12 Fm^{-1}

- This estimates U = -778 kJ/mol lattice energy and experimental result for the same is found to be -775 kJ/mol

Important points of Born Lande equation

- The lattice becomes stronger, as r the interatomic distance decreases, U is proportional to 1/r
- The lattice energy depends on the product of the ionic charges, U is proportional to Z^+Z^-
- The close agreement between theoretical and experimental results for alkali metal halides does not prove the suitability of this equation
- The equation is self compensating and tends to hide the errors. Two opposing factors. Increasing the inter-ionic distance r reduces the lattice energy. It is impossible to change r without changing the structure, and therefore changing Madelung constant M or A. Increasing M increases the lattice energy; hence the effects of changing r and M may largely cancel each other.

Madelung constant

- Lattice energy can be calculated by using the following equation

$$\Delta U = \frac{Z_i Z_j}{r_0}\left(\frac{e^2}{4\pi\,\varepsilon_0}\right)$$

where Z_i, Z_j = ionic charges in electron units

r_0 = distance between ion centers

e = electronic charge = 1.602×10^{-19} C

$4\pi\,\varepsilon_0$ = permittivity of a vacuum = $1.11 \times 10^{-10}\ \mathrm{C^2J^{-1}m^{-1}}$

$$\frac{e^2}{4\pi\,\varepsilon_0} = 2.307 \times 10^{-28}\ \mathrm{J\,m}$$

- In the crystal lattice there are more interactions than the simple ion pair. Even neighboring interactions such as attraction between opposite charge, repulsion between like charges, and other longer-range interactions between the ions are also to be considered. The summation of all of these geometrical interactions is known as **Madelung constant (M/A)**
- It is a correction factor and incorporation of it produces less erroneous results in the estimation of Lattice energy.

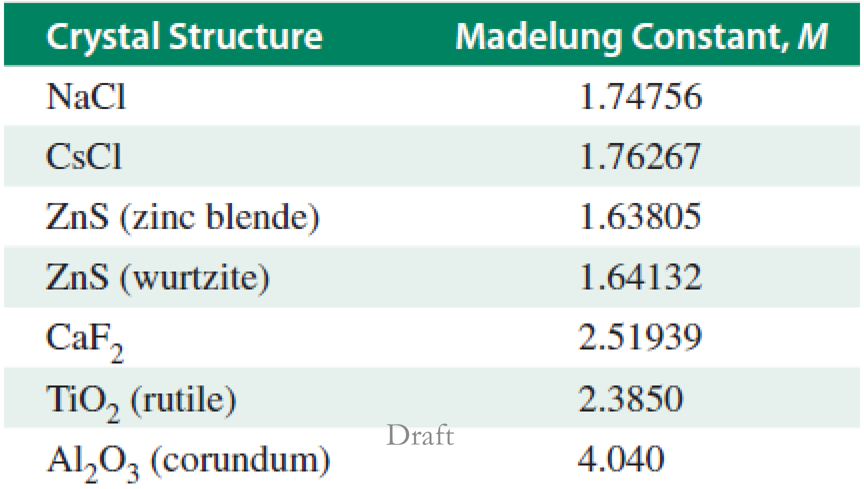
- It is used to determine the lattice energy, the net stabilization due to attraction of the ions within the lattice of one mole of a salt,

$$\Delta U = \frac{NMZ_+Z_-}{r_0}\left(\frac{e^2}{4\pi\,\varepsilon_0}\right)$$

where *N* is Avogadro's number and *M* is the Madelung constant. Repulsion between close neighbors is a more complex function, frequently involving an inverse sixth- to twelfth power dependence on the distance. The Born-Mayer equation corrects for this using only the distance and a constant, r:

$$\Delta U = \frac{NMZ_+Z_-}{r_0}\left(\frac{e^2}{4\pi\,\varepsilon_0}\right)\left(1 - \frac{\rho}{r_0}\right)$$

- For simple compounds, r = 30 pm works well when *ro* is also in pm. Lattice energies are twice as large when charges of 2 and 1 are present, and four times as large when both ions are doubly charged.



Crystal Structure	Madelung Constant, *M*
NaCl	1.74756
CsCl	1.76267
ZnS (zinc blende)	1.63805
ZnS (wurtzite)	1.64132
CaF_2	2.51939
TiO_2 (rutile)	2.3850
Al_2O_3 (corundum)	4.040

- Evaluation of Madelung constant for a particular lattice is straight forward.
- For example, in NaCl there are attractions to the six nearest neighbors of opposite charge, repulsion by the twelve nearest neighbors of like charge, etc.
- Each Na+ ion is surrounded by six face centered neighboring Cl- ions and this distance is a characteristic distance determined by size of involved ions
- Next nearest neighbors are the twelve Na+ ion centered on the edges of that unit cell, the distance can be related to the first distance by simple geometry, as can the distance of eight Cl- ions in the next shell.
- If this process is continued until every ion in the crystal is included, the Madelung constant, M can be obtained from the summation of all interactions.
- The first three terms for the aforesaid interactions are

$$M = 6 - 12/\sqrt{2} + 8/\sqrt{3}\ldots\ldots\ldots$$

- M is only determined only by the geometry of the lattice and is independent of ionic radius and charge

Sodium fluoride adopts the NaCl type lattice. Estimate the lattice energy of NaF using an electrostatic model.

Data required:

$L = 6.022 \times 10^{23}\ \text{mol}^{-1}$ $A = 1.7476$ $e = 1.602 \times 10^{-19}\ \text{C}$
$\varepsilon_0 = 8.854 \times 10^{-12}\ \text{F m}^{-1}$ Born exponent for NaF = 7
Internuclear Na–F distance = 231 pm

The change in internal energy (the lattice energy) is given by the Born–Landé equation:

$$\Delta U(0\,\text{K}) = -\frac{LA|z_+|\,|z_-|e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

r must be in m: 231 pm = 2.31×10^{-10} m

$$\Delta U_0 = -\left(\frac{6.022 \times 10^{23} \times 1.7476 \times 1 \times 1 \times (1.602 \times 10^{-19})^2}{4 \times 3.142 \times 8.854 \times 10^{-12} \times 2.31 \times 10^{-10}}\right) \times \left(1 - \frac{1}{7}\right)$$

$$= -900\,624\ \text{J mol}^{-1}$$

$$\approx -901\ \text{kJ mol}^{-1}$$

Kapustinskii equation

- The Kapustinskii equation is used to estimate lattice enthalpies of ionic compounds and to give a measure of the thermochemical radii of the constituent ions.
- A. F. Kapustinskii observed that, if the Madelung constants (A) for a number of structures are divided by the number of ions per formula unit, N_{ion}, then approximately the same value is obtained for them all.
- He also noted that the value so obtained increases with the coordination number.
- Because ionic radius also increases with coordination number, the variation in $A/(N_{ion}d)$ from one structure to another can be expected to be fairly small.
- This observation led Kapustinskii to propose that there exists a hypothetical rock-salt structure that is energetically equivalent to the true structure of any ionic solid and therefore that the lattice enthalpy can be calculated by using the rock-salt Madelung constant and the appropriate ionic radii for 6:6 coordination.
- The resulting expression is called the **Kapustinskii equation** $U = (N_{ion}Z^{+}Z^{-}/d)\{1-(d^{*}/d)\}\kappa$ where

U is the lattice energy

N_{ion} is the number of ions in the empirical formula

$d = r^+ + r^-$ = sum of the ionic radii (pm) (thermochemical radii)

Z^+ and Z^- are the number of elementary charge of the cation and anion respectively

d* is a constant = 34.5 and

κ is a constant = 1.21×10^5 kJpm/mol

- Kapustinskii equation can be used to ascribe numerical values to the 'radii' of non-spherical molecular ions, as their values can be adjusted until the calculated value of the lattice enthalpy matches that obtained experimentally from the Born–Haber cycle.
- The self consistent parameters obtained in this way are called **thermochemical radii** that can be used to estimate lattice enthalpies, and hence enthalpies of formation, of a wide range of compounds.
- Estimate the lattice enthalpy of KNO3, if the ionic radii for the ions are 138 & 189 pm

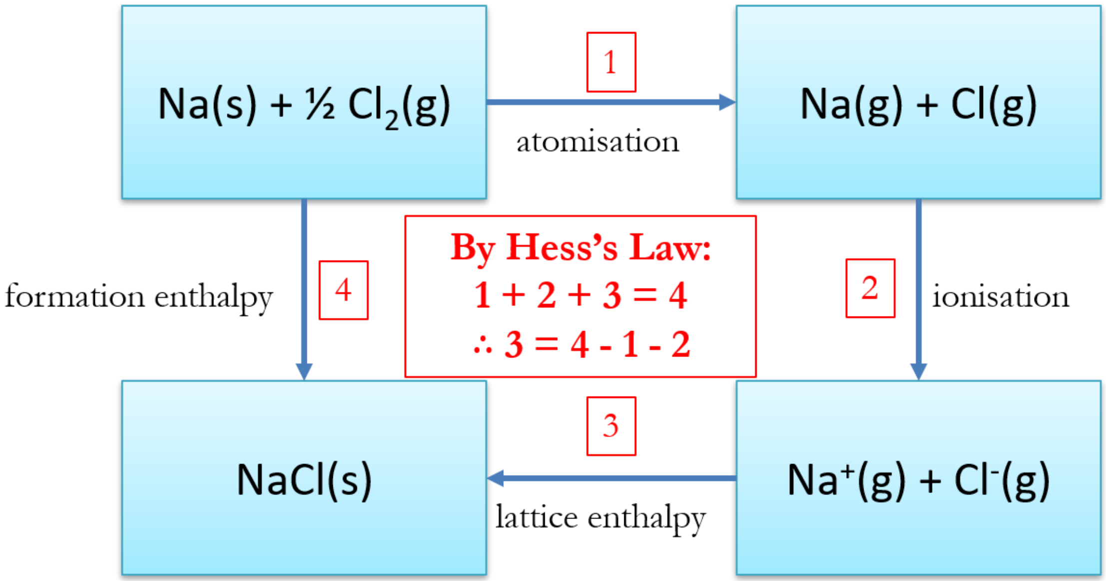
Soln: $N_{ion} = 2$, $Z^+ = 1$, $Z^- = -1$, thermochemical radii d = 138 + 189 = 327 pm, *d** = 34.5 pm

κ = 1.21×10^5 kJpm/mol. Thus, U = -622 kJ/mol (putting all the values)

Born-Haber cycle

- This cycle was devised by Born and Haber in 1919
- Lattice energies are determined experimentally using a Born-Haber cycle.
- This approach is based on Hess' law and can be used to determine the unknown lattice energy from known thermodynamic values.
- Lattice enthalpies are determined from empirical enthalpy data by using a **Born–Haber cycle**, a closed path of steps that includes lattice formation as one stage

Complete Hess's Law cycle for lattice enthalpy



lattice enthalpy = enthalpy of formation – Σeverything else

- The standard enthalpy of decomposition of a compound into its elements in their reference states is the negative of its standard enthalpy of formation, ΔH^o_f

  $M\ (s) + X\ (s, l, g) \rightarrow MX\ (s),$ $\Delta H^o_f = \text{negative}$

- For a solid element, the standard enthalpy of atomization/sublimation, $\Delta H^o_{atom/sub}$, is the standard enthalpy of sublimation, as in the process

  $M(s) \rightarrow M(g),$ $\Delta H^o_{atom/sub} = \text{positive}$

- For a gaseous element, the standard enthalpy of atomization is the standard enthalpy of dissociation, ΔH^o_{diss} (*in this case it is equal to half of dissociation energy of 1 mole* X_2)

  $X_2\ (g) \rightarrow 2X\ (g),$ $\Delta H^o_{diss} = \text{positive}$

- The standard enthalpy of formation of ions from their neutral atoms is the enthalpy of ionization (ΔH^o_{IE}) and the electron-gain enthalpy (ΔH^o_{EA})

  $M(g) \rightarrow M+(g) + e–$ $\Delta H^o_{IE} = \text{positive}$

  $X(g) + e– \rightarrow X–(g)$ $\Delta H^o_{EA} = \text{negative}$

- The value of the lattice enthalpy - the only unknown in a well-chosen cycle is found from the requirement that the sum of the enthalpy changes round a complete cycle is zero

  $\Delta H^o_f = \Delta H^o_{sub} + \Delta H^o_{diss} + \Delta H^o_{IE} - \Delta H^o_{EA} - U$

$$\begin{tikzcd}
M(s) + {}^{n}/_{2}X_2(g) \arrow[r, "\Delta_a H^o(M{,}s) + {}^{n}/_{2}D(X_2{,}g)"] \arrow[d, "\Delta_f H^o(MX_n{,}s)"'] & M(g) \arrow[d, "\Sigma IE(M{,}g)"'] & + & nX(g) \arrow[d, "n\Delta_{EA}H(X{,}g)"] \\
MX_n(s) & M^{n+}(g) \arrow[l, "\Delta_{lattice}H^o(MX_n{,}s)"'] & + & nX^{-}(g)
\end{tikzcd}$$

$\Delta_a H^o(M,s)$ = Enthalpy of atomization of metal M

$D(X_2,g)$ = Dissociation enthalpy of X_2 = 2 × Enthalpy of atomization of X

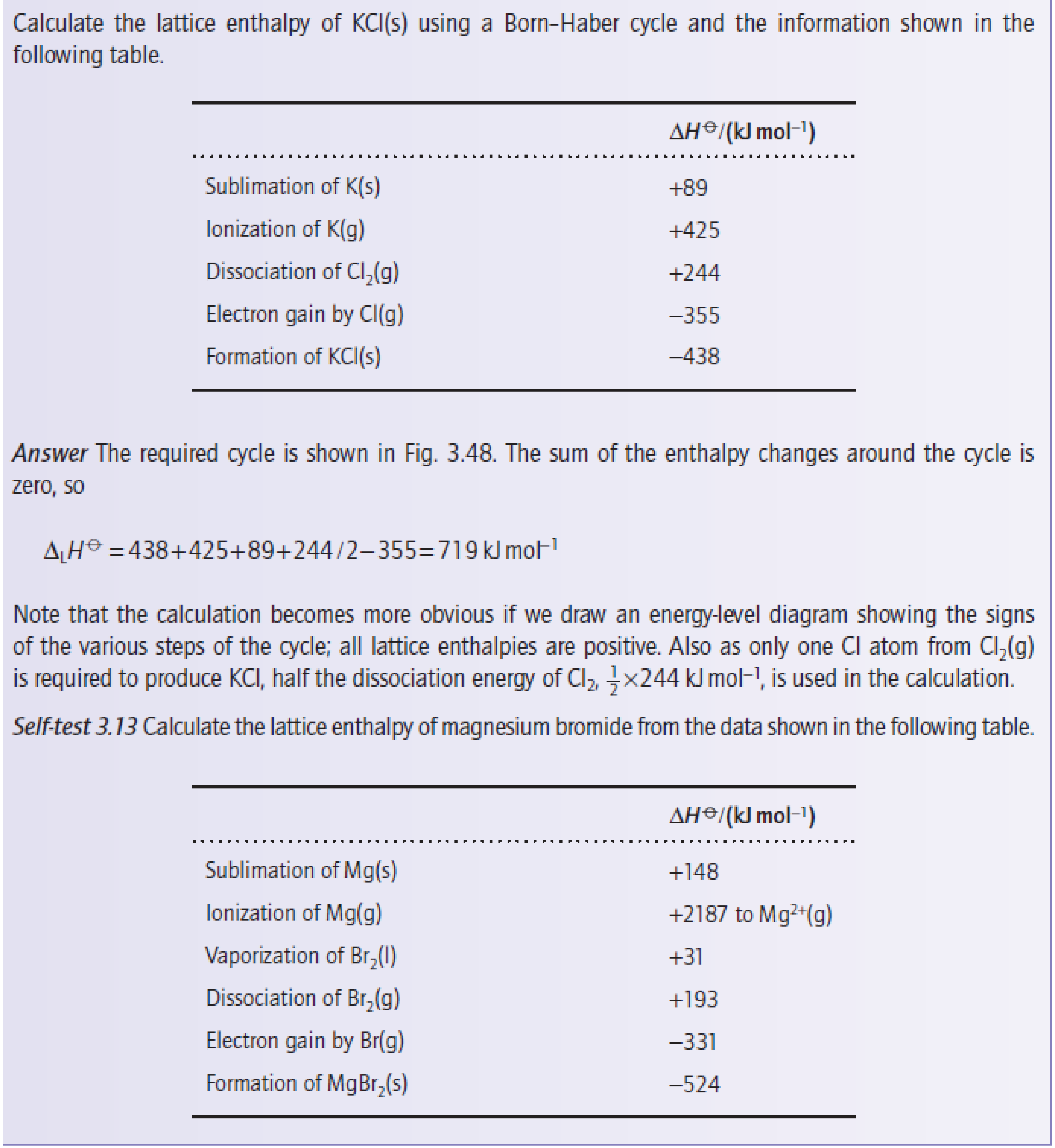
$\Sigma IE(M,g)$ = Sum of the ionization energies for the processes $M(g) \rightarrow M^+(g) \rightarrow M^{2+}(g) \ldots \rightarrow M^{n+}(g)$

$\Delta_{EA}H(X,g)$ = Enthalpy change associated with the attachment of an electron

$\Delta_f H^o(MX_n,s)$ = Standard enthalpy of formation

$\Delta_{lattice}H^o(MX_n,s)$ = Lattice enthalpy change (see text)

Use same symbol throughout



Calculate the lattice enthalpy of KCl(s) using a Born–Haber cycle and the information shown in the following table.

	$\Delta H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$
Sublimation of K(s)	+89
Ionization of K(g)	+425
Dissociation of Cl_2(g)	+244
Electron gain by Cl(g)	−355
Formation of KCl(s)	−438

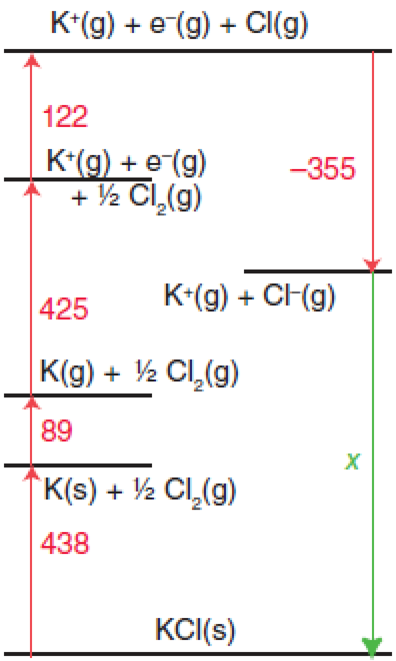
Answer The required cycle is shown in Fig. 3.48. The sum of the enthalpy changes around the cycle is zero, so

$$\Delta_L H^{\ominus} = 438 + 425 + 89 + 244/2 - 355 = 719\ \mathrm{kJ\,mol^{-1}}$$

Note that the calculation becomes more obvious if we draw an energy-level diagram showing the signs of the various steps of the cycle; all lattice enthalpies are positive. Also as only one Cl atom from Cl_2(g) is required to produce KCl, half the dissociation energy of Cl_2, $\frac{1}{2}\times 244$ kJ mol^{-1}, is used in the calculation.

Self-test 3.13 Calculate the lattice enthalpy of magnesium bromide from the data shown in the following table.

	$\Delta H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$
Sublimation of Mg(s)	+148
Ionization of Mg(g)	+2187 to Mg^{2+}(g)
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron gain by Br(g)	−331
Formation of $MgBr_2$(s)	−524



Given that the standard enthalpy of formation at 298 K of CaF_2 is $-1228\,\mathrm{kJ\,mol^{-1}}$, determine the lattice energy for CaF_2 using appropriate data from the Appendices.

First, construct an appropriate thermochemical cycle:

$$\begin{tikzcd}
\mathrm{Ca(s)} + \mathrm{F_2(g)} \arrow[r, "\Delta_a H^\circ(\mathrm{Ca,s}) + D(\mathrm{F_2,g})"] \arrow[d, "\Delta_f H^\circ(\mathrm{CaF_2,s})"] & \mathrm{Ca(g)} \arrow[d, "IE_1 + IE_2\ (\mathrm{Ca,g})"'] & + 2\mathrm{F(g)} \arrow[d, "2\Delta_{EA}H(\mathrm{F,g})"] \\
\mathrm{CaF_2(s)} & \mathrm{Ca^{2+}(g)} \arrow[l, "\Delta_{lattice}H^\circ(\mathrm{CaF_2,s}) \approx \Delta U(0\ \mathrm{K})"'] & + 2\mathrm{F^-(g)}
\end{tikzcd}$$

Values that need to be found in the Appendices are:

Appendix 10: $\Delta_a H^\circ(\mathrm{Ca,s}) = 178\,\mathrm{kJ\,mol^{-1}}$
$D(\mathrm{F_2,g}) = 2\Delta_a H^\circ(\mathrm{F,g}) = 158\,\mathrm{kJ\,mol^{-1}}$
Appendix 8: $IE_1(\mathrm{Ca,g}) = 590$; $IE_2(\mathrm{Ca,g}) = 1145\,\mathrm{kJ\,mol^{-1}}$
Appendix 9: $\Delta_{EA}H(\mathrm{F,g}) = -328\,\mathrm{kJ\,mol^{-1}}$

Use of Hess's Law gives:

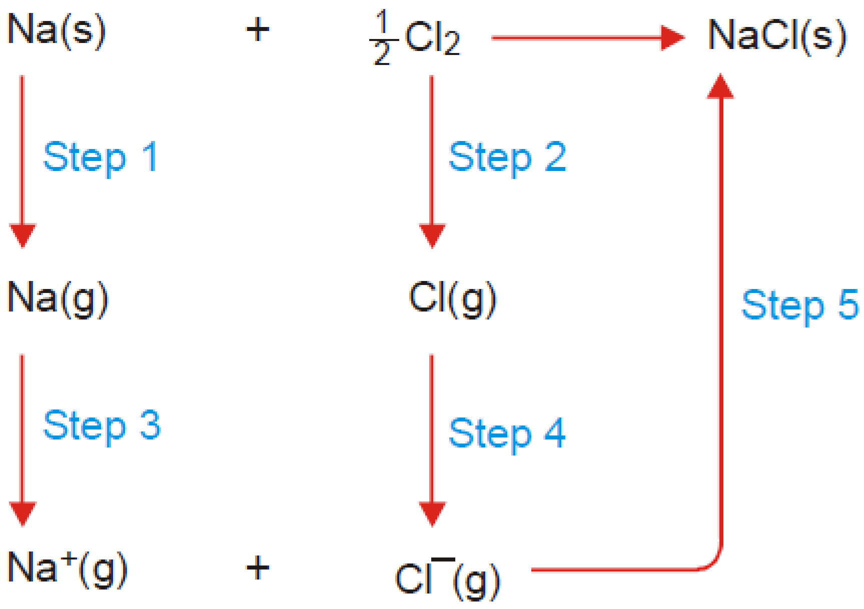
$$\begin{aligned}
\Delta U(0\,\mathrm{K}) &\approx \Delta_f H^\circ(\mathrm{CaF_2,s}) - \Delta_a H^\circ(\mathrm{Ca,s}) \\
&\quad - D(\mathrm{F_2,g}) - \Sigma IE(\mathrm{Ca,g}) - 2\Delta_{EA}H(\mathrm{F,g}) \\
&\approx -1228 - 178 - 158 - 590 - 1145 + 2(328)
\end{aligned}$$

$$\Delta U(0\,\mathrm{K}) \approx -2643\,\mathrm{kJ\,mol^{-1}}$$

- Lattice energy estimation using Born Haber cycle can be illustrated from the formation of NaCl crystal from its elements

Enthalpy change for direct formation: The enthalpy change for the direct formation of sodium chloride from sodium metal and chlorine is – 411 kJ.

$$\text{Na (s)} + \tfrac{1}{2}\text{Cl}_2\text{ (g)} \rightarrow \text{NaCl (s)}, \qquad \Delta H^{o}_{f} = -\,411\text{ kJ}$$



For MX just replace Na by M and Cl by X and use the same cycle

Enthalpy change by indirect steps: The direct enthalpy change of NaCl stated above is equal to enthalpy changes of five steps by which the formation of NaCl can be accomplished

Step 1. Conversion of sodium metal to gaseous atoms (sublimation).

$\mathrm{Na}(s) \rightarrow \mathrm{Na}(g),$ $\Delta H^{o}_{sub} = + 108\ \mathrm{kJ}$

Step 2. Dissociation of chlorine molecules to chlorine atoms. The enthalpy of dissociation is 121 kJ per mole of chlorine.

$\tfrac{1}{2}\mathrm{Cl}_2\ (\mathrm{g}) \rightarrow \mathrm{Cl}\ (\mathrm{g}),$ $\Delta H^{o}_{diss} = + 121\ \mathrm{kJ}$ (*stoichiometry*)

Step 3. Conversion of gaseous sodium to sodium ions by losing electrons. The enthalpy of ionization or the ionization energy, 495 kJ/per mole of sodium atoms.

$\mathrm{Na}(g) \rightarrow \mathrm{Na+}(g) + e–$ $\Delta H^{o}_{IE} = + 495\ \mathrm{kJ}$

Step 4. Chlorine atoms gain an electrons to form chloride ions. The energy released is the electron affinity of chlorine –348 kJ.

$\mathrm{Cl}(\mathrm{g}) + e– \rightarrow \mathrm{Cl–}(g)$ $\Delta H^{o}_{EA} = – 348\ \mathrm{kJ}$

Step 5. Sodium and chloride ions get together and form the crystal lattice. The energy released in this process is the negative of lattice energy.

$\mathrm{Na+}(g) + \mathrm{Cl–}(g) \rightarrow \mathrm{NaCl}(s)$ U = (lattice energy)

The lattice energy can be calculated by equating the enthalpy of formation of NaCl, – 411 kJ, to the sum of the enthalpy changes for the five steps.

- Thus, According to Hess's law we have

$$\Delta H^o_f = \Delta H^o_{sub} + \Delta H^o_{diss} + \Delta H^o_{IE} - \Delta H^o_{EA} - U \qquad (\mathit{\Delta H^o_{diss}} = \tfrac{1}{2} E_{diss})$$

- Using the enthalpies of the individual steps and as a whole, lattice energy for the ionic solid can easily be estimated experimentally.

Application of Born Haber cycle

1. Born Haber cycle helps un in understanding the stability of many ionic compounds
2. Estimation of electron affinities: Electron affinity can be estimated from lattice energy of a suitable compound with Born Haber cycle
3. Estimation of proton affinities: It is the energy released when a proton is added to a species, also gaseous
4. Estimation of heat of formation:
5. Explanation of the high oxidation states of metals:

Consequences of lattice enthalpies

Thermal stabilities of ionic solids: Lattice enthalpies may be used to explain the chemical properties of many ionic solids, including their thermal decomposition (decomposition of Gr. II metal carbonate can be extended suitably to others) $MCO_3(s) \rightarrow MO(s) + CO_2(g)$

$MgCO_3$, for instance, decomposes when heated to about 300° C, whereas $CaCO_3$ decomposes only if the temperature is raised to over 800° C. The decomposition temperatures of thermally unstable compounds (such as carbonates) increase with cation radius.

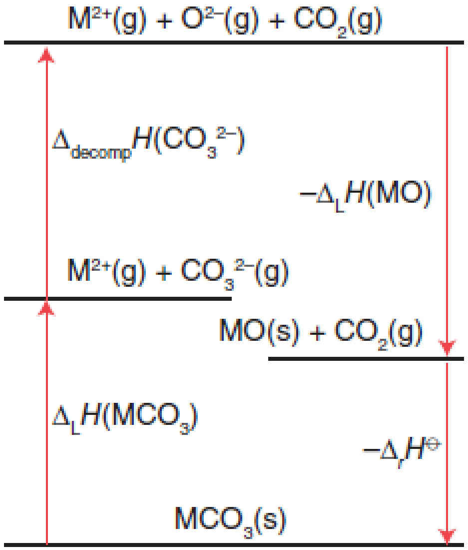
The stabilizing influence of a large cation on an unstable anion can be explained in terms of trends in lattice enthalpies. The decomposition temperatures of solid inorganic compounds can be discussed in terms of their Gibbs energies of decomposition into specified products and it will be negative when T is sufficiently high.

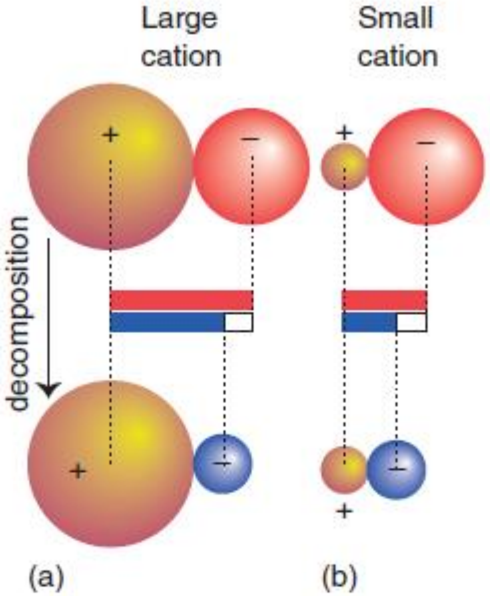
Reaction enthalpy also plays a major role (compared to entropy). Enthalpy of decomposition of CO_3^{2-} in gas phase is large and positive, and is less strongly positive if lattice enthalpy of the oxide is significantly greater than that of carbonate.

$CO_3^{2-}(g) \rightarrow O^{2-}(g) + CO_2(g)$

The decomposition temperature will be low for oxides that have relatively high lattice enthalpies compared with their parent carbonates

- This is applicable especially for small, highly charged cations (such as Mg2+). A small cation has a more significant influence on the change in the lattice enthalpy as the cation size is varied. If the cation is small, however, the relative change in lattice parameter is large, resulting in a larger increase in lattice enthalpy, and decomposition is thermodynamically more favourable.
- The difference in lattice enthalpy between MOn and (MCO3)n is also magnified by a larger charge on the cation, as $U \propto Z+Z-/d$, so the thermal decomposition of a carbonate will occur at lower temperatures if it contains a higher-charged cation. M(II) carbonate decomposes at lower temperature than M(I) carbonates.





Q. Present an argument to account for the fact that, when they burn in oxygen, lithium forms the oxide Li2O but sodium forms the peroxide Na2O2 .

Answer: The role of the relative sizes of cations and anions in determining the stability of a compound is to be considered. Because the small Li+ ion results in Li2O having a more favorable lattice enthalpy (in comparison with M2O2) than Na2O, the decomposition reaction M2O2(s)→ M2O(s) + O2(g) is thermodynamically more favorable for Li2O2 than for Na2O2 .

Q. Predict the order of decomposition temperatures of alkaline earth metal sulfates in the reaction MSO4 (s) → MO(s) + SO3 (g).

- **The stabilities of oxidation states:** The relative stabilities of different oxidation states in solids can often be predicted from consideration of lattice enthalpies
- High metal oxidation states are stabilized by small anions
- F has a greater ability than the other halogens to stabilize the high oxidation states of metals. Thus, the only known halides of Ag(II), Co(III), and Mn(IV) are the fluorides.
- The process MX (s) + ½ X2 (g) → MX2 (s) is strongly spontaneous if X = F.
- One contribution to the reaction enthalpy is the conversion of ½ X2 to X− . Despite F having a lower electron affinity than Cl, this step is more exothermic for X = F than for X = Cl because the bond enthalpy of F2 is lower than that of Cl2.
- The lattice enthalpies, however, play the major role
- In the conversion of MX to MX2 , the charge number of the cation increases from +1 to +2, so the lattice enthalpy increases. As the radius of the anion increases, however, this difference in the two lattice enthalpies diminishes, and the exothermic contribution to the overall reaction decreases too. Hence, both the lattice enthalpy and the X− formation enthalpy lead to a less exothermic reaction as the halogen changes from F to I (provided entropy factors are similar)
- Thermodynamic stability of MX relative to MX2 on going from X = F to X = I increases

- **Solubility:** The solubilities of salts in water can be rationalized by considering lattice and hydration enthalpies.
- Lattice enthalpies play a role in solubilities, as the dissolution involves breaking up the lattice
- Compounds with widely different radii are soluble and with similar radii are least in water. Difference in size favors solubility in water
- In gravimetric analysis, Ba2+ is used to precipitate SO42-, and the solubilities of the Group 2 sulfates decrease from MgSO4 to BaSO4. In contrast, the solubility of the Group 2 hydroxides increases down the group: Mg(OH)2 is the sparingly soluble ‘milk of magnesia’ but Ba(OH)2 can be used as a soluble hydroxide for preparation of solutions of OH−. The first case shows that a large anion requires a large cation for precipitation. The second case shows that a small anion requires a small cation for precipitation.
- If the cation has a larger hydration enthalpy than its anion partner (reflecting the difference in their sizes) or vice versa, then the dissolution of the salt is exothermic (reflecting the favourable solubility equilibrium).
- The lattice enthalpy is inversely proportional to the distance between the centers of the ions $U \alpha 1/(r^{+} + r^{-})$ and the hydration enthalpy (each ion being hydrated individually) is proportional to the sum of individual ion contributions $H \alpha [1/r^{+} + 1/r^{-}]$

- If the radius of one ion is small, the term in the hydration enthalpy for that ion will be large. However, in the expression for the lattice enthalpy, one small ion cannot make the denominator of the expression small by itself. Thus, one small ion can result in a large hydration enthalpy but not necessarily lead to a high lattice enthalpy, so ion size asymmetry can result in exothermic dissolution. If both ions are small, then both the lattice enthalpy and the hydration enthalpy may be large, and dissolution might not be very exothermic.

Q. What is the trend in the solubilities of the Gr 2 metal carbonates (Mg to Ra)?

Answer The role of the relative sizes of cations and anions is to be considered. The CO32− anion has a large radius and has the same magnitude of charge as the cations M2+ of the Group 2 elements. The least soluble carbonate of the group is predicted to be that of the largest cation, Ra2+. The most soluble is expected to be the carbonate of the smallest cation, Mg2+. Although magnesium carbonate is more soluble than radium carbonate, it is still only sparingly soluble.

Q. Which can be expected to be more soluble in water, NaClO4 or KClO4 ?

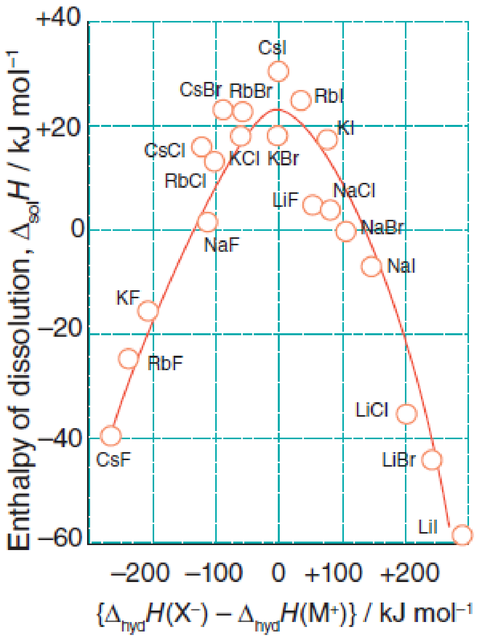


Figure 3.51 The correlation between enthalpies of solution of halides and the differences between the hydration enthalpies of the ions. Dissolution is most exothermic when the difference is large.