15.1 Energy Cycles

1st ionization energy ($\Delta H_i^\ominus$) = energy needed to form '+' ion

$$Na_{(g)} \rightarrow Na^+_{(g)} + e^-_{(g)} \quad \Delta H_i^\ominus = +496 \text{ kJ mol}^{-1}$$

(why endo?)

1st electron affinity ($\Delta H_e^\ominus$) = enthalpy change when 1 mol of (g) atoms attracts 1 mol e^-

$$Cl_{(g)} + e^-_{(g)} \rightarrow Cl^-_{(g)} \quad \Delta H_e^\ominus = -349 \text{ kJ mol}^{-1}$$

(why exo?)

Lattice Enthalpies

if add 2 above rxns, endo process

$$Na_{(g)} + Cl_{(g)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$$

$$-349 + 496 = +147 \text{ kJ mol}^{-1}$$

- stable ions w/ noble gas configurations ... why endo?

ionic lattice: exo process due to strong attraction b/w ions

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \quad \Delta H^\ominus = -790 \text{ kJ mol}^{-1}$$

$\Delta H_{lat}^\ominus$ (lattice enthalpy): formation of (g) ions from 1 mol of solid crystal (breaking into gaseous ions)

→ enthalpy change in terms of the reverse endo process

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$ $\Delta H^\circ_{lat} = +790$ kJ mol⁻¹

cannot be measured directly = use Hess's Law (measure using indirect routes) → energy cycle = Born-Haber cycle

Born Haber Cycle

Formation of ionic cmpd (from elements): takes place # of steps

☆ remember ΔH overall rxn = sum ΔH for steps

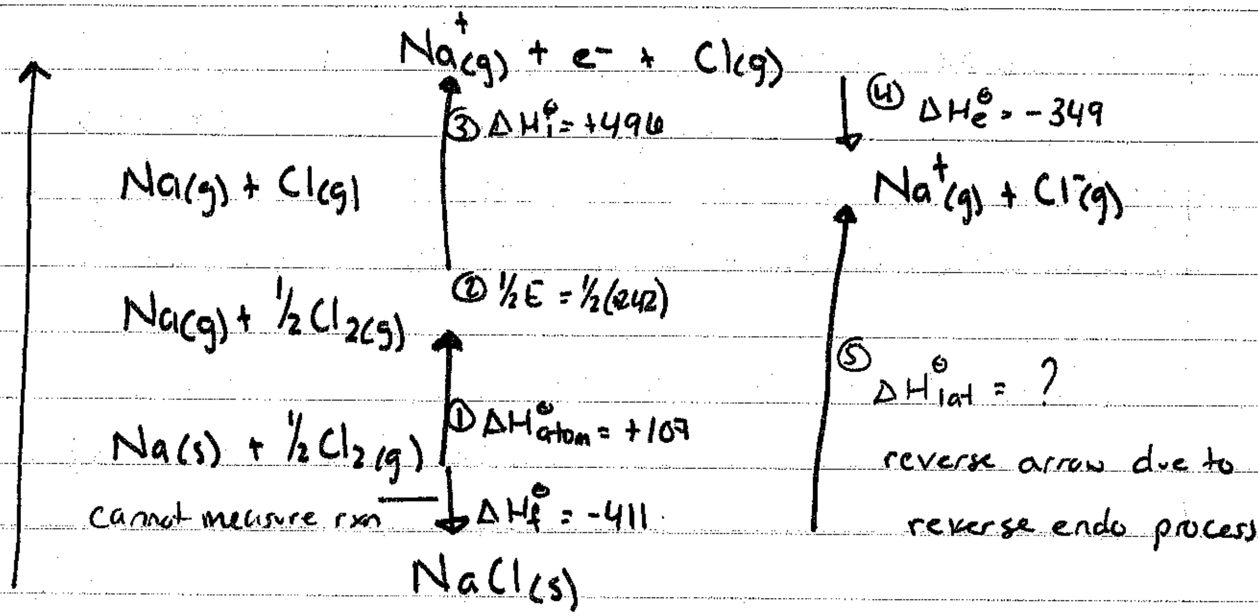
1. $\Delta H^\circ_{atomization}$: metal (s) → metal (g) (1 mol)

2. Bond enthalpy (E) : oxides / chlorides O_2 / Cl_2, need to break bond

3. $\Delta H^\circ_{ionization}$: metal (g) → $metal^+_{(g)}$ + e^- (# of e^- dependent on charge of metal)

4. $\Delta H^\circ_{electron\ affinity}$: O / Cl + e^- → O^{2-} / Cl^- (# of e^- dependent on charge of nonmetal)

5. $\Delta H^\circ_{lattice}$: unknown usually



$$\Delta H_f^\ominus = \Delta H_{atom}^\ominus + (\tfrac{1}{2})E + \Delta H_i^\ominus + \Delta H_e^\ominus - \Delta H_{lat}^\ominus$$

↑unknown

look at # e-
multiply accordingly

$$\Delta H_{lat}^\ominus = \Delta H_{atom}^\ominus + (\tfrac{1}{2})E + \Delta H_i^\ominus + \Delta H_e^\ominus - \Delta H_f^\ominus$$
$$= +107 + \tfrac{1}{2}(+242) + 496 + (-349) - (-411)$$
$$= +786\ kJmol^{-1}$$

worked example pg 241

Theoretical lattice enthalpy (calculated from ionic model)

ionic model: only attraction is due to electrostatic forces b/w ions (assumption: spherical ions)

Trends in lattice enthalpy (energy needed to separate ions) depends on:

why? <
1. atomic radius (↑radius, ↓attraction)
2. ionic charge (↑ charge, ↑ attraction)

- theoretical values can be calculated once geometry is known

Table pg 243

☆ covalent nature → discuss (NOS : pg 243)

Enthalpies of Solutions

Def: enthalpy change when 1 mole solute is dissolved in a solvent to infinite dilution under std conditions

Ionic cmpds readily dissolve in water (polar solvent)

$\overset{\delta^+}{H}$ .... $\underset{\text{ion}}{-}$ $\overset{\delta^-}{O}$ .... $\underset{\text{ion}}{+}$

hydrated: salt ions are surrounded by H_2O

hydration enthalpy: strength of interaction b/w H_2O + ion

$\Delta H^{\ominus}_{hyd}$: enthalpy change when 1 mole of gaseous ions (from salt lattice) is dissolved to form an infinitely dilute soln

☆ difficult to measure directly

$$M^{n+}(g) \rightarrow M^{n+}(aq)$$
$$X^{m-}(g) \rightarrow X^{m-}(aq)$$

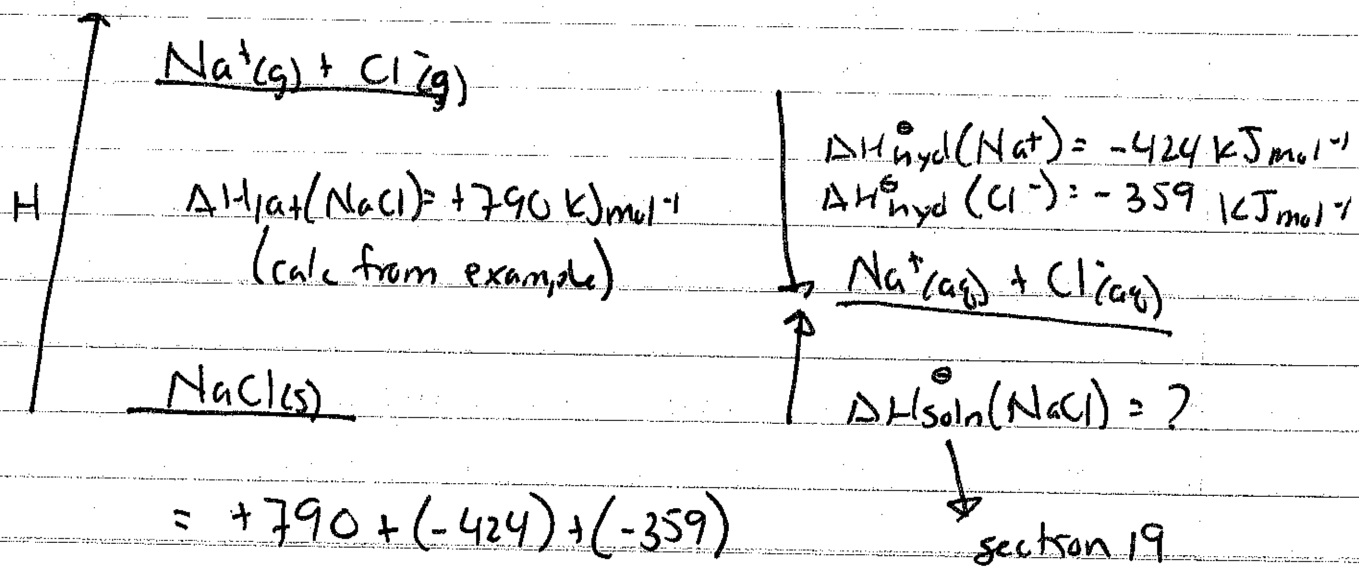
force of attraction b/w H_2O + ions ⇒ exo process
$\Delta H^{\ominus}_{hyd}$ (−) (Table pg 245)

- values less exo as groups descend + ionic radius increases (why?)

- across period 3
  metals become more exo : ionic charge ↑
  ionic radius ↓

(graphs pg 246)

$$\Delta H^\ominus_{soln}(NaCl) = \Delta H^\ominus_{latt}(NaCl) + \Delta H^\ominus_{hyd}(Na^+) + \Delta H^\ominus_{hyd}(Cl^-)$$



$= +790 + (-424) + (-359)$

$= +7\ kJ\,mol^{-}$