#### Lesson 4 For Book 1

#### **Review Question --- Calculation of Free Energy**

At 298K, solid potassium nitrate dissociates when heated to produce solid potassium nitrile and gaseous oxygen,

#### with the standard enthaply change of reaction = +124 kJmol-1

The standard entropies, for the formation of each species, are shown below:

Species	S <sup>-O</sup> ( <b>JK-1 mol-1</b> )
KNO3 (s)	133
KNO2 (s)	152
O2(g)	205

- a) Write the chemical equation involving.
- b) Calculate the standard entropy change for the reaction.
- c) Calculate the standard free energy change for the reaction.
- d) Calculate the temperature at which this reaction becomes spontaneous.

Hint = Free energy change =  $\Delta H - T \Delta S$ 

(+243 JK-1 mol-1, 51.6 kJ mol-1, T=510K)

## <u>Chemical Bondings</u> → <u>Ionic bond</u>, <u>Covalent Bond</u>, <u>Metallic Bond</u>

Ionic Bond exists in \_\_\_\_\_ compounds. It is non-directional. Actually, this kind of force/bond is due to the columbic a\_\_\_\_\_ between cations and \_\_\_\_\_.

 $\rightarrow$  Factors affecting the strength:

- 1) C\_\_\_\_\_ of the ions (\_\_\_\_\_ charges, stronger bond)
- 2) S\_\_\_\_ of the ions (If the size of the ions are comparable  $\rightarrow$  better attraction  $\rightarrow$  \_\_\_\_\_ bond)
- Covalent Bond exists in \_\_\_\_\_ compounds, especially in o\_\_\_\_\_ compounds. They are due to the sharing of electrons between atom's n\_\_\_\_\_.

 $\rightarrow$  More Accurately, it is formed by the overlapping of **atmoic** o\_\_\_\_\_.

Metallic Bond exists in m\_\_\_\_\_ compounds (no matter metal, semi-metal, transition metal) → Electron-sea model :

1) Inside the lattice of metal, metal atoms loses their v\_\_\_\_\_ electrons to form cations and the electron sea.

2) There exists ionic attractions between the m\_\_\_\_\_ electrons and the metal

c\_\_\_\_\_.  $\rightarrow$  Metallic Bond

 $\rightarrow$  Factors affecting the strength:

- 1) no of valence electrons available (group 3 > 2 > 1)
- 2) size of the metal cations (go down the group, the strength will red\_\_\_\_\_)
- $\rightarrow$  More formal --- charge to radius ratio

#### **Ionic Compound (ONLY)**

- Standard Enthalpy change of Formation =  $\Delta H^{\Theta}_{f}$  the enthalpy change when one mole of the ionic compound is formed from its constituent elements (in their standard states) under standard conditions.
- $\rightarrow$  Please write down the equation for the formation of NaF (s)
- Recall that an ionic compound is formed by the "Combination" of a cation and anion. What are the enthalpy changes representing the formation of the cation (From <u>m</u>) and the anion (From halogen)

Formation of Cation (Metal(s)  $\rightarrow$  Metal (g)  $\rightarrow$  Cation(g))

→ Standard enthalpy change of **atomization** =  $\Delta H^{\bullet}$  atom is the enthalpy change when \_\_\_\_\_ mole of **gaseous** atoms is formed from an element in the standard state under standard conditions.

→ Standard enthalpy change of **ionization** =  $\Delta H^{\bullet}$  I.E. is the **energy** required to remove / enthalpy change when **one mole of electron** is re\_\_\_\_\_ from one mole of atoms or ions in the g\_\_\_\_\_

State.

→ Please write down the equation for the  $\Delta H^{-2} 2^{nd}$  I.E. of Ca(\_\_\_\_)

→ REMEMBER = It is more difficult to remove electrons from a positively charged species than from a neutral species  $\rightarrow \Delta H^{-0}$ 1st I.E.  $\Delta H^{-0}2^{nd}$  I.E. .....

Formation of Anion (Non metal e.g. oxides and halides)

→ Electron Affinity =  $\Delta H^{\bullet}E.A.$  is the enthalpy change when one mole of electrons is <u>a</u> to one mole of atoms or ions in the gaseous state.

e.g.  $O() + e \rightarrow O - ()$ 

Factors affecting the sign / magnitude of the  $\Delta H^{0}E.A.$ 

1) The electronegativity of the species (the strength of nuclear attraction)

2) The electronic configuration  $\rightarrow$  the attraction of electron is more exo\_\_\_\_\_ if

a <u>/ full</u> filled electronic configuration can be attained.

## Formation of an IONIC COMPOUND

→ Lattice enthalpy =  $\Delta H^{\bullet}$  lattice is the enthalpy change when \_\_\_\_\_ mole of an ionic c\_\_\_\_\_ (better than salt) is formed from its constituent ions in the gaseous state under standard conditions.

 $\rightarrow$  Physical meaning = a measure of **ionic bond strength**,

i.e. more negative the  $\Delta H^{\Theta}$  lattice, more strong is the electrostatic attraction between the ions.

# **×** a measure of **thermal stability**

→ In HKAL, finding  $\Delta H^{\Theta}$  lattice of an ionic crystal is typical.

## Exercise 1

Calculate the **experimental lattice enthalpy** of NaCl(s) using the following thermochemical data and the Born Haber Cycle, in which  $\Delta H^{\Theta}$ 6 represents the lattice enthalpy.

	$\Delta H^{\bullet}$ (kJmol-1)	$Na_{(s)} + \frac{1}{2}$	Cl <sub>2(g)</sub> ΔH <sub>1</sub>	→ Na <sup>+</sup> CL <sub>2</sub>
$\Delta H^{\Theta}$ atom of Na(s)	108	(3)		(s)
$\Delta H^{\bullet} 1^{st} IE \text{ of Na (g)}$	495	ΔH <sub>2</sub>	∆H <sub>3</sub>	ΔH <sub>6</sub>
Bond dissociation enthalpy			ΔH <sub>4</sub>	
of Cl <sub>2</sub> (g)	239	Na <sub>(g)</sub> + (		$Cl_{(g)} \neq Na_{(g)}$
$\Delta H^{\Theta} EA \text{ of } Cl (g)$	-349		∆⊓ <u>5</u>	
$\Delta H^{\Theta}$ f of NaCl(s)	-411	Fig 1.		(c) doc brown at www.docbrown.info

(-784.5 kJmol-1)

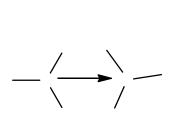
 $\rightarrow$  The theoretical lattice enthalpy of NaCl(s) is -770kJmol-1. If the ionic crystal is in a good agreement with the **Perfect ionic model**, these two values should be close to each other.

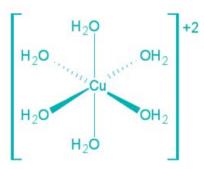
# **Covalent Compound (only)**

- Recall that a covalent bond, which is directional, is formed by the overlapping of atomic o\_\_\_\_\_. For elements in period 3 or above, octet can be extended as they have low l\_\_\_\_\_ vacant d o\_\_\_\_\_\_, ie, the atoms can form more than four covalent bonds. E.g. PF<sub>5</sub>, a colourless gas at room temperature and pressure
- As for the covalent bond, there is a type called **dative covalent bond**.

→ It is formed by the o\_\_\_\_\_ of an empty orbital of an atom with an orbital occupied by a l\_\_\_\_\_ pair of electrons of another atom.

 $\rightarrow$  it is important for you to know that, in later chapter about the formation of **metal complex**, the bond between the metal centre and the **ligand** is dative covalent in nature.





• **Bond dissociation enthalpy**,  $\Delta H^{\bullet}$  B.E., for convalent compound (especially

and

for organic compound), is the enthalpy change when **one mole of a particular** 

**bond** in a particular environment is broken under standard conditions.

- $\rightarrow$  the data given for you to do calculation are just an **average** value only.
- The enthalpy change of **atomization** of an organic compound =  $\Delta H^{\Theta}$  atom is the enthalpy change of the breaking down of one \_\_\_\_\_\_ of the gaseous compound into its cinstituent atoms in the g\_\_\_\_\_\_ state.

e.g.  $H_2C \longrightarrow CH_2(g) \rightarrow 2C(g) + 4H(g)$ 

• \*\* 
$$\Delta H^{\bullet}$$
 reaction = sum of average bond enthalpies of reactants –

sum of average bond enthalpies of products

(not frequently used)

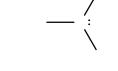
#### Drawing of covalent compounds --- Lewis Structure

Illustration e.g. NH3

- 1) Allocate the central atom , i.e. the least **electronegative** atom
- Count the total no of valence electrons, i.e., it is equal to the no of group of the atoms. That is, N has \_\_\_\_\_; H has <u>one</u>.
- 3) Then, draw the brief lewis structure without considering the actual shape of the compoound.

Now, there is only \_\_\_\_\_ valence electrons H - N - H

4) Since **Two** valence electrons remain unused, we add them to the central N atom and hence there is one lone pair electron of N atom.



p.s.  $\rightarrow$  Negative Ion: Add the number of electrons equal to the negative charge on the ion. E.g. no of valence electron of NH<sub>2</sub><sup>-</sup> = 8+1 = 9

→ Positive Ion: Subtract the number of electrons equal to the positive charge on the ion. E.g. no of valence electron of  $NH_4^+ = 8 - 1 = 7$ 

 $\rightarrow$  If the central atom can extent its octet, double bond or even triple bond can be formed

 $\rightarrow$  When **resonance is possible**, more than one Lewis structure can be drawn **REMEMBER** = more Lewis structure / Resonance structure, more stable is the compound.

1) Draw Lewis structures for the following molecules or polyatomic ions.

**Revision Notes** 

a) H<sub>2</sub>O

b) BF<sub>3</sub>

c) PCl<sub>5</sub>

d)  $H_2S$ 

e) SOCl<sub>2</sub> f) IO<sub>3</sub><sup>-</sup> (S is the central atom, O and Cl are both bonded to S)

g) CH<sub>3</sub>CH<sub>2</sub>OH

h) CH<sub>3</sub>OCH<sub>3</sub>

2. Draw Lewis structures for the following molecules or polyatomic ions:

a. N<sub>2</sub>

b. CH<sub>3</sub>COOH (acetic acid) (Be sure to use the correct skeletal arrangement for the –COOH group. It is **NOT** straight chain C–O–O–H.)

c. HNO<sub>3</sub> (nitric acid)

d.  $H_2SO_4$ 

e. CO<sub>2</sub>

 $f. N_2H_2$ 

g. CO

h.  $O_3$  (Structure is not a ring, it is a chain.)