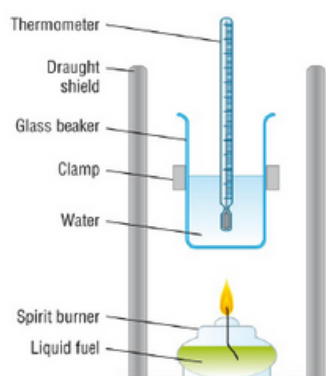
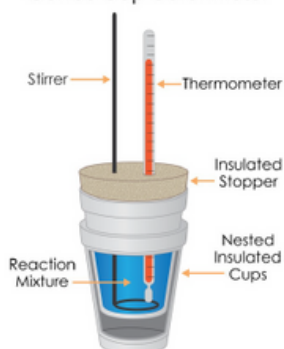


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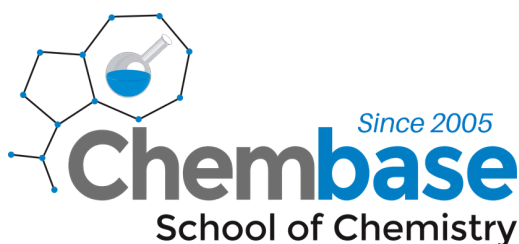
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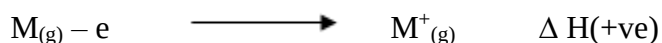
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1. Define the following terms: -

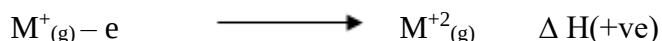
a. First ionization energy:-

The first ionization energy is the heat energy required to remove 1 mole of electrons from a mole of gaseous atoms to form a mole of uni positive gaseous ions.



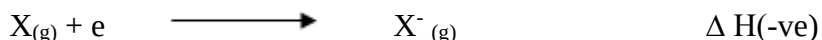
b. Second ionization energy:-

The heat energy required removing 1 mole of electrons from a mole of uni positive gaseous ions to form a mole of di positive gaseous ions.



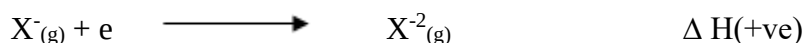
c. First electron affinity:-

The energy released when 1 mole of gaseous atoms gains one mole of electrons to form a mole of uni-negative gaseous ions. Always exothermic.



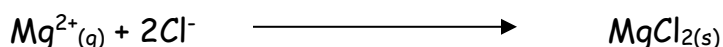
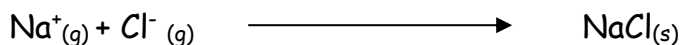
d. Second electron affinity:-

The energy absorbed when 1 mole of uni negative gaseous ions gains 1 mole of electrons to form 1 mole of di negative anions. Always endothermic.



e. Lattice enthalpy ΔH_{latt}

Lattice energy is the heat energy given out when one mole of an ionic solid is formed from its gaseous ions. The enthalpy change is always exothermic.



a) State the factors that affect the value of the lattice energies

- a. Sum of the ionic radii of the anion & cation.
- b. Charges of the ions.

b) Explain how the size of the ion effect the lattice energy

The lattice energy depends on distance between nuclei of cation & anion. The lattice energy is inversely proportional to the sum of the ionic radii.

When the sizes of the ions are smaller, the lattice energy will be larger.

E.g : $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$

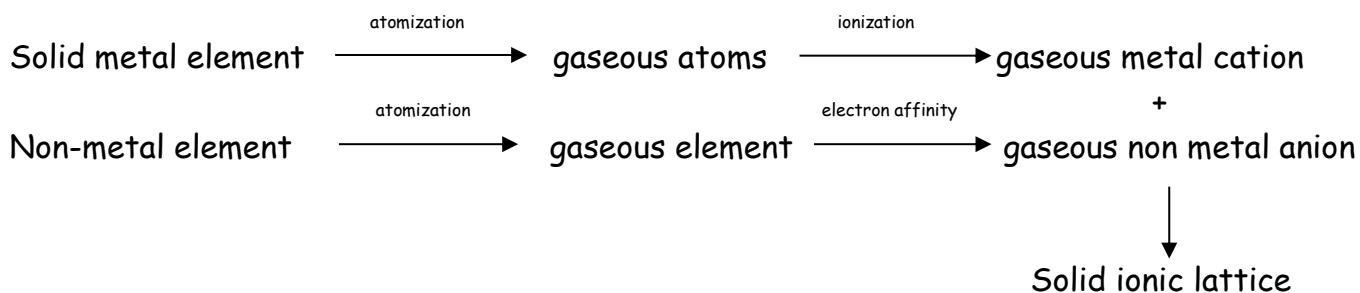
c) Explain the effect of charge on the ion on lattice energies

Lattice energy is directly proportional to charge (L.E a charge). Therefore greater the charge on the ions, larger the lattice energy.

E.g : $\text{Al}_2\text{O}_3 > \text{MgO} > \text{CaCl}_2 > \text{NaCl}$

d) MgO solid has the same crystal structure as NaCl solid, the lattice enthalpy of NaCl is -771 kJ mol^{-1} & that of MgO is $-3889 \text{ kJ mol}^{-1}$. Account for this difference.

2. Describe the stages involved in the formation of a solid ionic crystal from its elements, hence the calculation of lattice energy



The Born-Haber cycle

3. Explain what is Born-Haber cycle & its importance

The enthalpy cycle, which is used to determine the experimental lattice enthalpy of a compound, is called the born-Haber cycle.

It is important because the experimental lattice energy of a compound cannot be determined by a direct single step. Instead, it is found by an indirect route based on Hess's law.

4. Construct a Born-Haber cycle for Sodium Chloride, hence calculate the lattice enthalpy using Hess's law
Given that:

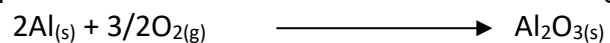
Standard enthalpy of atomization of Na	+108.4 kJ mol ⁻¹
First ionization energy of Na	+500 kJ mol ⁻¹
Standard enthalpy of atomization of Cl	+121 kJ mol ⁻¹
First electron affinity of Cl	- 364 kJ mol ⁻¹
Standard enthalpy of formation of NaCl	- 411 kJ mol ⁻¹

5. Construct a Born-Haber cycle for MgCl_2 ; hence use the data below to calculate the First electron affinity of Chlorine.

Enthalpy Change	kJ mol^{-1}
Atomization of Mg	+150
First ionization energy of Mg	+736
Second ionization energy of Mg	+1450
Formation of MgCl_2	-642
Atomization of Chlorine	+121
Lattice enthalpy of MgCl_2	-2493

6. Construct a Born-Haber cycle for MgO.

7. The equation for the heat of formation of Alumina is given as: -



Enthalpy Change	kJ mol^{-1}
Formation of Al_2O_3	-1675.7
Atomization of Al	+324.3
First ionization energy of Al	+578
Second ionization energy of Al	+1817
Third ionization energy of Al	+2745
Atomization of Oxygen	+249.2
First electron affinity of Oxygen	-141.1
Second electron affinity Oxygen	+790.8

- 8.
- a) What does the values of lattice energies tells us? Thus what can we conclude from these values?

The grater negative the value, the greater is the energetic stability of the lattice with respect to it being broken up in to separate ions. Also, the degree of ionic character can be checked by the calculation.

- b) Explain why the values of lattice energies calculated from Born-Haber cycle may differ from those calculated from purely ionic model

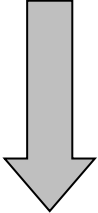
A calculation based on purely ionic model assumes that crystal is made up of perfectly spherical ions & when the geometry is determined from x-ray diffraction method. The distance between the ions will be known thus the lattice energy is calculated using an equation.

But in the calculation of more co-valent & less ionic molecules (AgI). The equation gives a lesser value than the Born-Haber cycle because the molecule is more co-valent (highly polarizable) therefore the lattice energy is less.

- c) Explain why the experimental & theoretical lattice enthalpies differ?

The lattice enthalpy of a compound obtained using Born-Haber cycle is the actual experimental lattice energy of a compound.

When the degree of co-valency of crystal greater the difference between experimental & theoretical values will be greater. Such large difference occurs when the cation has higher polarizing power & the anion has high polarisability resulting more covalent character.

E.g.:	<u>Experimental L.E</u>	<u>Theoretical L.E</u>		
AgF	-943	-925		The difference is greater as the covalent character increases.
Ag Cl	-890	-833		
Ag Br	-877	-808		
Ag I	-867	-774		

Entropy

1. State with examples why feasibility of a chemical reaction cannot be determined only by enthalpy changes

In exothermic reactions the enthalpy of the reactants are higher than the products. Therefore, the reaction is feasible at room temperature. Often assumed that endothermic reactions will not take place at room temperature due to energy of the products are greater than the reactants thus reactants are more stable also due to the activation energy barrier.

By the study of solubilities & the enthalpy of solution of many salts it can be shown that endothermic reactions also occur at room temperature & some exothermic reactions do not.

- Eg:- I) Enthalpy of solution of NH_4NO_3 is endothermic, yet it is highly soluble in water.
II) Enthalpy of solution of CaCO_3 is exothermic, yet it is insoluble in water.

Therefore, other than the enthalpies there is another factor, which influences the relative stability of a system.

When a highly ordered solid dissolves in H_2O the solid disperse throughout the liquid. The same happens with energy. The answer for the above lies in the simple concept that energy & matter tend to spread out or disperse. When the solid disperse in a liquid the solid particles get disordered. The greater the degree of disorder or randomness of a system the greater the stability.

2. Describe the term 'entropy' (S)

Entropy is a measure of the disorder or randomness of a system. It is also the scientific term for disorder. When the molecules are ordered then the entropy is low & when the molecules are disordered the entropy is high.

The greater the disorder (entropy) the greater the stability. Thus, the total free energy of a system is the sum of the enthalpy & the entropy. Hence spontaneous changes result in increased entropy. (Second law of Thermodynamics)

3. Explain how entropy of a substance change with the change in the physical state.

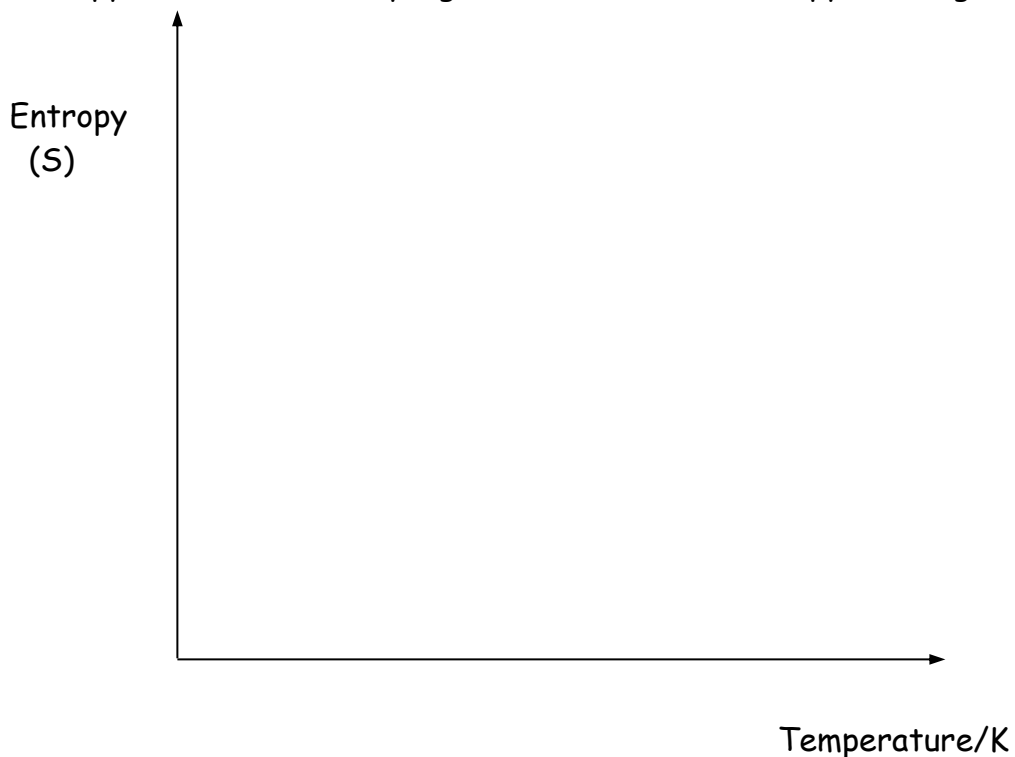
Particles in a solid are more ordered (or less disordered) than liquid or gas. Whereas particles in a liquid is more ordered than a gas. Therefore, the entropy of gas is greater than liquid, which is greater than solid.

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

4. State & explain the effect of temperature on entropy.

Entropy of a perfect crystalline substance at zero Kelvin / -273°C (absolute zero) is zero. As the temperature increases the entropy of a substance increases. During the phase change as the solid is heated there is a large jump in entropy.

As the solid is heated entropy increases until its melting point. At this point there is a large jump in entropy. Then followed by steady increase as the liquid is heated until it is reached to the boiling point. At this point there is another large jump in entropy. Thus, followed by a gradual increase in entropy as the gas is heated.



5. Explain the dependence on standard entropy of a substance on complexity of the substance.

Standard entropy is the entropy at 298K (25°C) & 1 atm pressure & is symbolized by S^{θ} . The standard entropy increases as the complexity of a substance increases.

Eg: Entropy of CaCO_3 is greater than CaO as CaCO_3 is more complex molecule than CaO
The entropy of P_4O_{10} is greater than P_4
The entropy of C_2H_6 is greater than CH_4

6. Discuss how the total entropy change (ΔS_{total}) of a reaction is found.

In an exothermic reaction the reactants give out energy to the surroundings as a result the energy of the surroundings increases by exactly the same amount. In an endothermic reaction the reactants gain energy from the surroundings thus surroundings lose an equal amount of energy.

The total energy change therefore should include the entropy change of the chemicals (ΔS_{system}) & also the entropy change of the surroundings (ΔS_{surr}) Therefore the total entropy change is expressed as :-

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

7. Modify the above relationship to calculate the entropy change for a reaction.

The entropy change of the system can be calculated from the below formula. The 'n' represents the Stoichiometric numbers in the chemical equation.

$$\Delta S^{\theta}_{\text{system}} = \sum nS^{\theta}_{(\text{products})} - \sum nS^{\theta}_{(\text{reactants})}$$

The above equation is similar to the equation which is used to calculate the enthalpy change of reactions (ΔH)

$$\Delta H = \sum nH_{(\text{products})} - \sum nH_{(\text{reactants})}$$

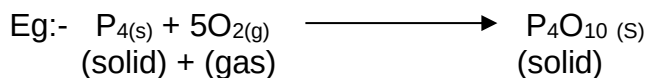
The units of ΔS is $\text{JK}^{-1} \text{mol}^{-1}$

(Note that S has joules in its units whereas ΔH has kJ)

- If the disorder increases then the ΔS will be positive. If the disorder decreases then the ΔS will be negative.

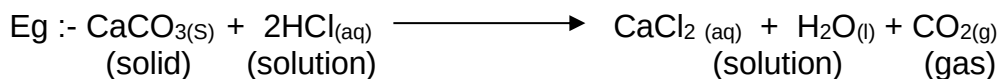
8. Describe how a reaction, which has a negative entropy change, can be feasible thus how to predict whether the entropy of the system is positive or negative by looking at the equation.

If the disorder of the reactants is replaced by the order of the products, then the reaction has negative entropy.



As the disorder of the gas is replaced by the order of the solid the extent of the disorder decreases. Therefore, ΔS_{system} is negative.

If the disorder increases then ΔS_{sys} is positive.



However, the feasibility of a reaction cannot be predicted only by the entropy of the system. The entropy of the surroundings also must be taken into account. Therefore, a reaction with negative ΔS_{sys} can also be feasible when ΔS_{surr} is considered. The reaction will only be feasible when the total entropy change (ΔS_{total}) is positive.

9. State & explain the sign for the entropy of the surroundings for exothermic & endothermic reactions.

Heat energy is transferred to the surroundings in an exothermic reaction. Therefore, the entropy changes of the surrounding increases (positive). Likewise heat energy is absorbed from the surroundings in an endothermic reaction. Therefore, the entropy changes of the surroundings decrease (negative).

- $\Delta S_{\text{surr}}^{\theta}$ is positive for all exothermic reactions.
- $\Delta S_{\text{surr}}^{\theta}$ is negative for all endothermic reactions.

10. State the equation, which demonstrate the relationship between the enthalpy change, Temperature & the entropy of the surroundings.

The entropy change of the surroundings is the negative of the enthalpy change of the system & is also inversely proportional to the temperature of the surroundings.

$$\Delta S^{\theta}_{\text{surr}} = -\frac{\Delta H}{T}$$

The ΔH is given in kJ mol^{-1} whereas T is given in Kelvin (K). The unit of $\Delta S^{\theta}_{\text{surr}}$ should be given in $\text{J K}^{-1} \text{mol}^{-1}$ not $\text{kJ K}^{-1} \text{mol}^{-1}$. Therefore, the answer has to be multiplied by 1000. You should always indicate the sign whether positive / negative for ΔS .

If the surrounding is already hot (higher temperature) then the molecules already have a higher entropy thus the entropy change will be less. Also, if the surrounding is cold the entropy change is greater.

11. Outline how to predict the feasibility of a reaction from the total entropy change.

If the total entropy change is positive the reaction is thermodynamically feasible (Thermodynamics is the study of the energy changes that occur in bulk matter)

$$\Delta S^{\theta}_{\text{total}} = \Delta S^{\theta}_{\text{system}} + \Delta S^{\theta}_{\text{surroundings}}$$

This means even the entropy change of the system is negative & if the entropy change of the surroundings is more positive the overall reaction is feasible as total entropy change is positive.

$\Delta S^{\theta}_{\text{system}}$	$\Delta S^{\theta}_{\text{surroundings}}$	Feasible
Positive Negative Negative Positive	Positive (exothermic) Negative (endothermic) Positive (exothermic) Negative (endothermic)	Always feasible Never feasible If $\Delta H / T$ is $> \Delta S^{\theta}_{\text{system}}$ feasible If $\Delta S^{\theta}_{\text{system}} > \Delta H / T$ feasible

Therefore, the reaction can occur as long as $\Delta S^{\theta}_{\text{total}}$ is positive even if one of the other entropy change is negative. Hence the feasibility of a reaction depends on the balance between $\Delta S^{\theta}_{\text{sys}}$ & $\Delta S^{\theta}_{\text{surr}}$ & at higher temperatures the magnitude of $\Delta S^{\theta}_{\text{surr}}$ decreases & its contribution to ΔS_{total} is less.

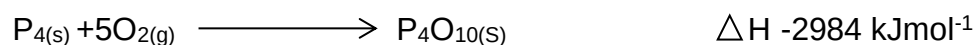
- ❖ If ΔS_{total} is positive the change is said to be Thermodynamically spontaneous. Thus, the change will take place. Suppose if ΔS_{total} is negative the forward reaction will not be feasible but the reverse reaction will be Thermodynamically spontaneous.
- ❖ Altering the temperature can alter the value of the total entropy change. As for exothermic reactions an increase temperature will cause ΔS_{surr} to become less positive hence will make ΔS_{total} less positive. Thus, a negative ΔS_{surr} becomes less negative.

12. Use the below data table to answer the questions that follow.*

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Gas	Entropy $S^{\theta}/$ $\text{J K}^{-1} \text{mol}^{-1}$	Liquid	Entropy $S^{\theta}/$ $\text{J K}^{-1} \text{mol}^{-1}$	Solid	Entropy $S^{\theta}/$ $\text{J K}^{-1} \text{mol}^{-1}$
H_2	131	$\text{C}_2\text{H}_5\text{OH}$	161	P_4	164
O_2	205	CCl_4	216	P_4O_{10}	229
N_2	192	C_6H_6	174	C	5.7
$\text{H}_2\text{O}(\text{g})$	189	$\text{H}_2\text{O}(\text{l})$	70	$\text{H}_2\text{O}(\text{s})$	43
CO_2	214			CaO	40
NH_3	192			CaCO_3	93
CH_4	186				
C_2H_6	230				

- a) Calculate the standard entropy change for the reaction between Phosphorous & Oxygen to produce P_4O_{10}

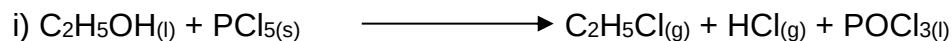


b) Calculate the entropy change of the surroundings when 1mol of Phosphorus burns in air.

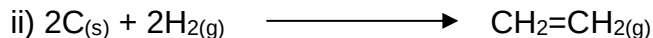
c) Calculate the total entropy change for the combustion of Phosphorus. The entropy change of the system is $-960 \text{ JK}^{-1} \text{ mol}^{-1}$ & the entropy change of the surroundings is $+10,000 \text{ JK}^{-1} \text{ mol}^{-1}$

d) Calculate the value of ΔS_{surr} at 25°C & at 100°C for a reaction with $\Delta H = -123 \text{ kJ mol}^{-1}$

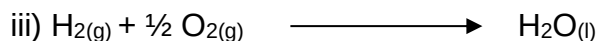
e) Comment on the feasibility of the following reactions occurring at a temperature of 298 K



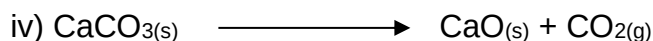
$$\Delta H = -107 \text{ kJ mol}^{-1} ; \Delta S_{\text{system}} = +368 \text{ JK}^{-1} \text{ mol}^{-1}$$



$$\Delta H = +52.2 \text{ kJ mol}^{-1} ; \Delta S_{\text{system}} = -184 \text{ JK}^{-1} \text{ mol}^{-1}$$



$$\Delta H = -286 \text{ kJmol}^{-1} ; \quad \Delta S_{\text{system}} = -45 \text{ JK}^{-1} \text{ mol}^{-1}$$



$$\Delta H = +178 \text{ kJmol}^{-1} ; \quad \Delta S_{\text{system}} = +164 \text{ JK}^{-1} \text{ mol}^{-1}$$

13. Discuss the difference between the concepts of thermodynamic stability & kinetic inertness in terms of total enthalpy change.

In an exothermic reaction the reactants are higher in energy than the products. Therefore, reactants are thermodynamically unstable with respect to products. Thus ΔS_{total} is positive means that the reactants are thermodynamically unstable relative to products.

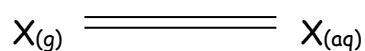
Likewise negative ΔS_{total} means that the reactants are thermodynamically stable with respect to products. As the reactants are low in enthalpy & it absorb heat from the surroundings.

Kinetic Stability is based on the activation energy. A large activation energy means that the reactants are stable with respect to products & a small activation energy means that the reactants are kinetically unstable with respect to products.

Solubility

1. Explain the entropy change that occurs when a gas is dissolved.

Dissolving a gas results in the system to be more ordered. Hence dissolving a gas always results in a negative ΔS_{system} . This means heat is given out thus gas dissolves exothermically & surroundings become more disordered.



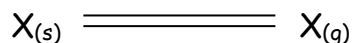
When temperature is increased the above Equilibria will be shifted to left. Therefore, gases are less soluble in hot water than in cold water.

2. Similarly explain the entropy change when a solid is dissolved.

When solid is dissolved the particles of solid move in to the solvent to form a solution. Thus, the system becomes more disordered, but dissolving solids does not always result in positive ΔS_{system} .

The entropy of the solute becomes more positive as it turns from highly ordered solid to a more random solution. Simultaneously the solvent may turn to be more ordered due to the forces of attraction between the solute & the solvent. This usually happens when compounds with high charge density dissolve in water.

The enthalpy of solution (ΔH_{sol}) can be either negative or positive. If it is negative then the heat is given out thus the entropy of the surroundings becomes more positive. If it is positive the entropy decreases.



If the ΔH_{sol} is exothermic the above Equilibria is driven to left thus the substance becomes less soluble. If the ΔH_{sol} is endothermic the Equilibria will shift to right thus the solution will be more soluble.

3. Explain the concept of solubility in terms of forces between solvent & solute particles.

In order for a substance to be soluble, the solute particles should be separated & each particle should be surrounded by solvent particles.

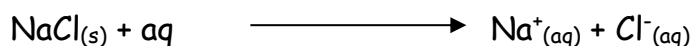
Therefore, the forces between the solute & solvent must be stronger in order to overcome the solvent-solvent & solute-solute forces.

4. Define the term hydration & hydration energy.

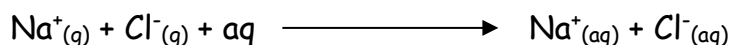
When an ionic substance is dissolved in water the cation will be surrounded by the partial negative 'O' atom of water & the anions will be surrounded by the partial positive 'H' of water. This process is called as hydration & the energy released during this process is known as hydration energy.

5. Define enthalpy of solution & enthalpy of hydration.

The Enthalpy of solution ΔH_{sol} is the enthalpy change when 1 mole of the solid is dissolved in excess solvent resulting an infinitely dilute solution. (Infinitely dilute solution is a solution where further dilution does not cause any heat change)



The enthalpy of Hydration ΔH_{hyd} of an ion is the enthalpy change when 1 mol of gaseous ions are dissolved in excess solvent resulting an infinitely dilute solution.



6. With the help of a Hess law cycle derive the relationship between lattice enthalpy, enthalpy of solution & hydration.

From the above equation it can be said that: -

- When the lattice energy become more exothermic, the enthalpy of solution becomes more endothermic.
- Also, when either hydration enthalpy become more exothermic the enthalpy of solution become more exothermic.
- Therefore, the sign of the enthalpy of solution depends on the difference on magnitude between lattice energy & the sum of the hydration energy.

7. Comment on the magnitude of lattice energy & hydration energy for exothermic & endothermic solvation.

For exothermic solvation the magnitude of the sum of the hydration energy will be greater than the lattice energy. Similarly for endothermic solvation the magnitude of the lattice energy will be greater than the sum of the hydration enthalpies.

- 8.
- Use the given data to calculate the enthalpy of solution of KI (Lattice enthalpy of KI -629 kJmol^{-1} , Enthalpy of hydration of K^+ -322 kJmol^{-1} , Enthalpy of hydration of I^- -364 kJmol^{-1})
 - Use the given data to calculate the enthalpy of solution of MgCl_2 (Lattice enthalpy of MgCl_2 -2500 kJmol^{-1} , Enthalpy of hydration of Mg^{2+} -1920 kJmol^{-1} , Enthalpy of hydration of Cl^- -364 kJmol^{-1})
9. State & explain the factors that affect the values of enthalpy of hydration & the lattice energy of an ionic compound.
- The magnitude of the lattice energy:
 - Is directly proportional to the product of the charges on the ions. Larger the product of the charges on the cation & anion greater the lattice energy
 - Is inversely proportional to the sum of the radii of the cation & the anion. Greater the sum smaller the magnitude of the lattice energy.
 - The extent of co-valency. The greater the extent of covalency the greater the magnitude of the lattice energy.
 - The magnitude of the lattice energy decreases down the group as the size of the cation & anion increase.
 - Also, the magnitude of the lattice energy increases as the charge on either or both the cation & the anion increases.

□ Factors which affect the hydration enthalpy;

- a) The hydration energy is directly proportional to the magnitude of the charge on the ion. The greater the charge the greater the hydration energy.
- b) The hydration energy is inversely proportional to the radius of the ion. Smaller the radius greater the hydration energy.

If the radius of the ions increases the hydration energy becomes less exothermic

10. State & explain the factors, which determine the extent of solubility of an ionic compound.

Solubility of a solid is determined by the total entropy change for 1 mol of the solid. An ionic solid to dissolve the total entropy change should be a positive value. The total entropy change depends on the entropy change of the system & the enthalpy change.

$$\Delta S_{\text{total}}^{\theta} = \Delta S_{\text{sys}}^{\theta} + \Delta S_{\text{surr}}^{\theta}$$

$$\Delta S_{\text{total}}^{\theta} = \Delta S_{\text{sys}}^{\theta} + (-\Delta H_{\text{sol}}^{\theta} / T)$$

Therefore, solubility of an ionic compound is determined by the entropy change of the system & the enthalpy change of the reaction.

Gibbs Free Energy (G^θ)

1. What is Gibbs free energy & why it is important?

The total entropy which includes the system & surrounding was used previously to predict the feasibility of a reaction. In chemical thermodynamics it's often preferred to focus on the system than the surroundings. Free energy enables us to do this for changes that occur at constant temperature and pressure. (Not necessary at standard conditions).

Gibbs free energy refers to the amount of energy of the system available to do work. This energy is referred to as the "FREE" energy as it is the remaining energy of the system after it had used some of its energy for entropy. Since this was discovered by J. Willard Gibbs it is called as Gibbs Free Energy. Symbolized by ΔG .

Gibbs free energy is important to predict the feasibility of a reaction where feasibility cannot be predicted when enthalpy & entropy is considered together. Eg: Reaction which is feasible with respect to enthalpy but not entropy (exothermic reaction with negative entropy) or Feasible with respect to entropy but not enthalpy. (Endothermic reaction with positive entropy)

2. Define Standard Gibbs free energy change, ΔG^θ

Gibbs free energy / Gibbs function is the combination of entropy and enthalpy. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system. And can be defined by the following equation:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

Where, ΔH^θ is the standard enthalpy change of the reaction. (298K, 1atm)

T is the temperature in Kelvin

ΔS^θ is the standard entropy change of the system.

ΔG^θ is the standard Gibbs free energy. Remember that the superscript θ on ΔG^θ indicates that the numerical value of Gibbs free energy is based on the reaction at standard conditions and it refers to 1M concentrated solution & 1 atm pressure. **Temperature is NOT a part of standard conditions for ΔG^θ .**

3. Derive the Gibbs free energy equation from total entropy equation. Gibbs free energy change is given by the equation $\Delta G = -T\Delta S_{\text{total}}$

4. Define the term Standard molar Gibbs free energy of formation.

Standard molar Gibbs free energy of formation is the free energy change which accompanies the formation of one mole of a compound from its elements in their standard state.

Symbolized by ΔG°_f and units are kJmol^{-1}

5. Explain how ΔG determines the direction & extent of a chemical change hence spontaneity.

$\Delta G < 0$ reaction can spontaneously proceed to the **right**: $A \rightarrow B$

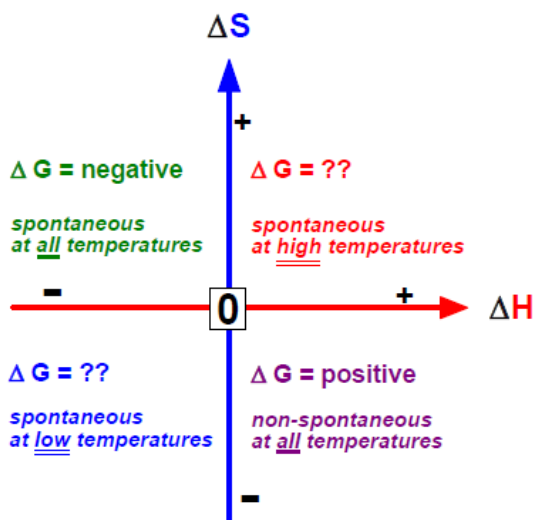
$\Delta G > 0$ reaction can spontaneously proceed to the **left**: $A \leftarrow B$

$\Delta G = 0$ the reaction is at *equilibrium*; the quantities of A and B will not change

Thus negative ΔG indicates that the reaction is spontaneous, a positive ΔG indicates a non-spontaneous reaction and if ΔG is zero the reaction is at equilibrium. ΔG°_f is a measure of the stability of the compound. Greater the negative value greater the stability thus difficult to decompose and vice versa.

➤ The ΔG°_f of an element under standard condition is zero. (Eg: $\text{H}_2, \text{O}_2, \text{Br}_2, \text{C}, \text{Mg}, \text{Na}$)

6. Discuss the effect of temperature on spontaneity of a reaction



As $\Delta G = \Delta H - T\Delta S$, ΔG changes with temperature.

ΔH could be negative (an exothermic reaction) or positive (an endothermic reaction). Similarly, ΔS could be either positive or negative. Thus, there are four possible combinations of the signs of ΔH and ΔS

a. ΔH is negative and ΔS is positive:

As both ΔH and $-T\Delta S$ terms are negative irrespective of the temperature, ΔG is also will to be negative. **The reaction will be spontaneous at all temperatures.**

b. ΔH is positive and ΔS is negative :

As both ΔH and $-T\Delta S$ terms are positive irrespective of the temperature, ΔG is also will be positive. **The reaction will not be spontaneous at any temperature.**

c. ΔH is positive and ΔS is positive :

ΔH is positive. $-T\Delta S$ is negative.

Increasing the temperature will result $-T\Delta S$ will become more negative, and will eventually outweigh ΔH thus the reaction will be spontaneous.

But at low temperatures, ΔG becomes positive thus the reaction will be non spontaneous. Eg : Decomposition of CaCO_3

d. ΔH is negative and ΔS is negative :

ΔH is negative. $-T\Delta S$ is positive.

As temperature increases, $-T\Delta S$ will become more positive, and will eventually outweigh the effect of ΔH thus reaction will be non spontaneous. But at low temperatures ΔG will be negative thus be spontaneous.

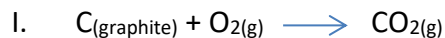
7. State the factors which is to be considered when Calculating ΔG° hence explain how ΔG of a reaction is calculated.

ΔG° and ΔH° are both measured in kJ mol^{-1} whereas the entropy change is calculated in $\text{JK}^{-1}\text{mol}^{-1}$, Thus one must change the entropy change value into kJ before when calculating ΔG° .

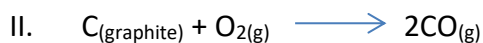
Similar to enthalpies and entropies the standard Gibbs free energy of a reaction can be calculated as to the below equation:

$$\Delta G^\circ = \sum n \Delta G^\circ_{(\text{products})} - \sum n \Delta G^\circ_{(\text{reactants})} \quad n = \text{no.of moles}$$

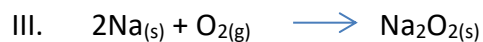
8. Calculate the ΔG° in below examples hence comment on the feasibility of the reaction.



Calculate ΔG° for CO_2 at 298 K. $\Delta H_f^\circ(\text{CO}_2) = -393 \text{ KJ/mol}$, $S^\circ(\text{O}_2) = 205 \text{ J/mol.K}$, $S^\circ(\text{C}) = 6 \text{ J/mol.K}$, $S^\circ(\text{CO}_2) = 213 \text{ J/mol.K}$



Calculate ΔG° for CO at 298 K. $\Delta H_f^\circ(\text{CO}) = -110 \text{ KJ/mol}$, $S^\circ(\text{O}_2) = 205 \text{ J/mol.K}$, $S^\circ(\text{C}) = 6 \text{ J/mol.K}$, $S^\circ(\text{CO}) = 198 \text{ J/mol.K}$



Calculate ΔG° for the reaction at 298 K. $\Delta H = -510 \text{ KJ/mol}$, $S^\circ(\text{Na}) = 51.2 \text{ J/mol.K}$, $S^\circ(\text{Na}_2\text{O}_2) = 95.0 \text{ J/mol.K}$, $S^\circ(\text{O}_2) = 205.0 \text{ J/mol.K}$

9. Calculate ΔG° for the following Reactions, Given that;

$$\Delta G^\circ_f (\text{SO}_{2, \text{g}}) = -300 \text{ kJ/mol}$$

$$\Delta G^\circ_f (\text{H}_2\text{SO}_{4, \text{l}}) = -690 \text{ kJ/mol}$$

$$\Delta G^\circ_f (\text{H}_2\text{O, l}) = -237 \text{ kJ/mol}$$

$$\Delta G^\circ_f (\text{SO}_{3, \text{g}}) = -371 \text{ kJ/mol}$$

$$\Delta G^\circ_f (\text{H}_2\text{SO}_{4, \text{aq}}) = -742 \text{ kJ/mol}$$

$$\Delta G^\circ_f (\text{H}_2\text{S, g}) = -34 \text{ kJ/mol}$$



10. Calculate the temperature above at which the following non spontaneous reaction becomes spontaneous. (Assume that ΔH° and ΔS° does not change much with temperature)



$$\Delta S^\circ = +552 \text{ J/molK}$$

$$\Delta G^\circ = +301 \text{ kJ/mol (at 298 K)}$$

11. With the help of a Gibbs free energy cycle calculate ΔG°_f for the below decomposition, hence comment on the feasibility.



The relevant ΔG°_f values are :

$$\Delta G^\circ_f[\text{NaHCO}_{3(s)}] = -850 \text{ kJmol}^{-1}$$

$$\Delta G^\circ_f[\text{CO}_{2(g)}] = -390 \text{ kJmol}^{-1},$$

$$\Delta G^\circ_f[\text{H}_2\text{O}_{(l)}] = -235. \text{ kJmol}^{-1}$$

$$\Delta G^\circ_f[\text{Na}_2\text{CO}_{3(s)}] = -1045 \text{ kJmol}^{-1}$$