The background of the slide is a close-up, high-contrast image of flames. The fire is bright yellow and orange, with dark, swirling patterns that suggest intense heat and movement. The flames are set against a dark, almost black background, which makes the fire stand out prominently.

Chapter 7

Chemical Energetics: Thermochemistry and Thermodynamics

CHAPTER ANALYSIS



FOCUS

- One of the major chapters
- 4 **key** concepts



EXAM

- Always tested
- Consist of both definition & calculations



WEIGHTAGE

- Heavy overall weightage

KEY CONCEPT

Enthalpy Change, Activation Energy & Energy Profile Diagram

Standard Enthalpy Changes

Calculating Enthalpy Change of a Reaction

Predicting the Spontaneity of a Reaction



Enthalpy Change, Activation Energy

ENTHALPY CHANGE

- Enthalpy change = energy change that occurs from **energy absorbed in bond breaking** and **released in bond forming**.
- Units = J mol^{-1} , kJ mol^{-1}

Note: +/- must be written in front of the ΔH

EXOTHERMIC REACTION, $\Delta H < 0$

Exothermic reactions are reactions or processes that **release** energy, usually in the form of heat or light. Energy is released because the **total energy of the products** < **total energy of the reactants**.

ENDOTHERMIC REACTION, $\Delta H > 0$

Endothermic reactions are reactions that require external energy, usually in the form of heat, for the reaction to proceed.

Note: Exothermic reactions are energetically more favourable than endothermic reactions as a system with lower heat content is more stable

ACTIVATION ENERGY, E_a

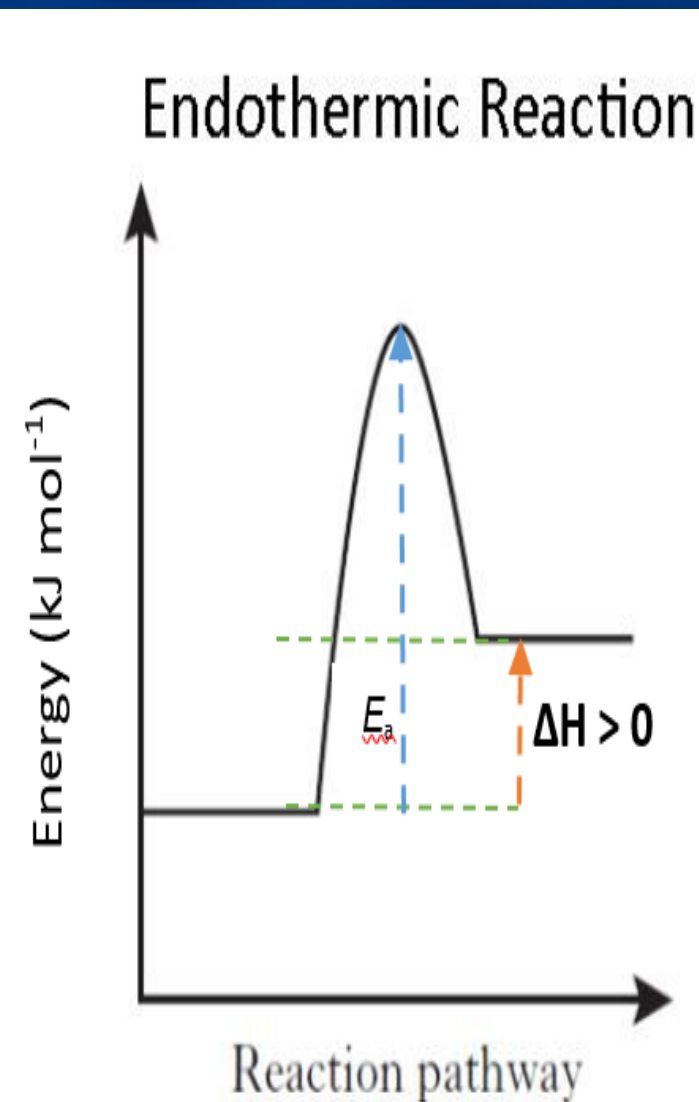
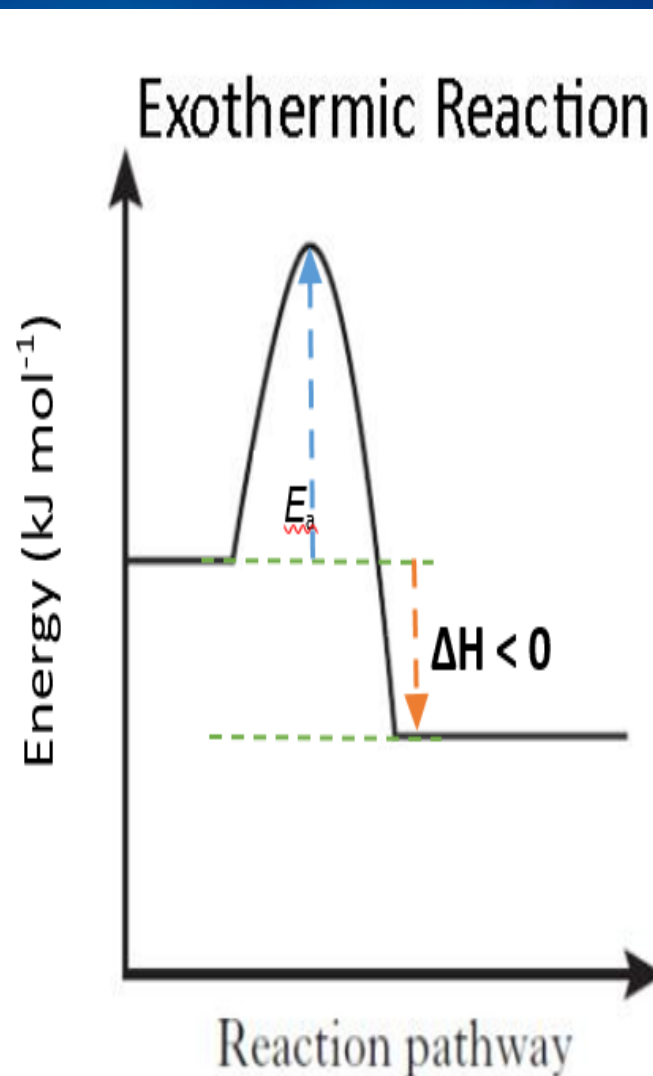
Minimum energy which reacting particles must **possess** in order to **overcome** the **activation energy barrier** before becoming **products**.

Energy Profile Diagram

ENERGY PROFILE DIAGRAM

- It is a diagram representing the energy changes that take place during a chemical reaction.
- ΔH = Energy level of products – Energy level of reactants

Note: Endothermic reaction pathway is energetically more unfavorable due to the higher E_a as compared to an exothermic reaction pathway.



STANDARD CONDITION

- **298K** (25°C), 1 bar (100,000Pa), 1.0 mol dm⁻³

Note: ≠ s.t.p! s.t.p = 273K (0°C), 1 bar (10,000Pa), 22.7 dm³mol⁻¹

Note: ≠ r.t.p! r.t.p = 293K (20°C), 1 atm (101,325Pa), 24.0 dm³mol⁻¹

THERMOCHEMICAL EQUATIONS

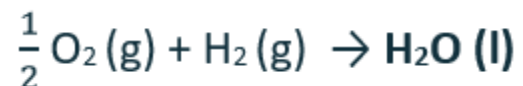
Includes ΔH (with units and sign +/-). State symbols of the reactants and products must be written.

ΔH_r (reaction)

Enthalpy change when **molar quantities of reactants** as specified by the chemical equation react to form products at 1 bar and 298K (standard conditions)

ΔH_f (formation)

- Enthalpy change when **1 mole of a substance is formed** from its **constituent elements** in their **standard states** at 1 bar and 298K (standard conditions).
- Can be both $\Delta H < 0$ and $\Delta H > 0$



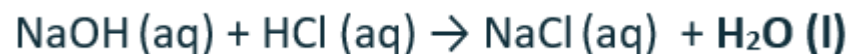
Standard Enthalpy Change

ΔH_c (combustion)

- Heat **evolved** when **1 mole of a substance is completely burnt** in **excess** oxygen at 298K and 1 bar (standard conditions).
- Is always $\Delta H < 0$.

 **ΔH_{neut} (neutralisation)**

- Heat evolved when **1 mole of water** is formed in the **neutralisation** reaction between an acid and a base at 298K, 1 bar (standard conditions).
- Is always $\Delta H < 0$
- ΔH_{neut} (strong acid & strong base) = $-57.0 \text{ kJ mol}^{-1}$ as strong acid/base ionised completely in water
- ΔH_{neut} (weak acid or base) $< -57.0 \text{ kJ mol}^{-1}$. **Less exothermic** as some energy is absorbed to **ionise** the weak acid/base that has not been fully ionised, hence the **net heat** evolved is lesser. (*Recap: weak acid/base only dissociates partially in water*)

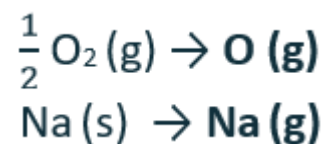


Standard Enthalpy Change

ΔH_{atom} (atomisation)

- ΔH_{atom} for an *element* is the energy required (absorbed) when 1 mole of **gaseous atoms** is formed from the **element** at 298K and 1 bar (standard conditions)
- Is always $\Delta H > 0$

Note: It is $\frac{1}{2} \times$ Bond Energy of diatomic molecules

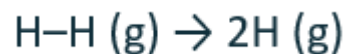


BOND ENERGY

- Bond energy (of dissociation) is the **average** energy required to break 1 mole of a **covalent bond** between two atoms in the **gaseous** state
- Is always $\Delta H > 0$

Note: It is $2 \times \Delta H_{\text{atom}}$ for diatomic molecules

Note: The greater the magnitude of the bond energy, the stronger the covalent bond



Standard Enthalpy Change

I.E. (ionisation energy)

- **First IE** is the energy required to remove 1 mole of electrons from 1 mole of **gaseous atoms** to form 1 mole of **singly charged** gaseous (cat)ions
- Is always $\Delta H > 0$



- **Second IE** is the energy required to remove 1 mole of electrons from 1 mole of **singly charged** gaseous (cat)ions to form 1 mole of **doubly charged** gaseous (cat)ions
- Is always $\Delta H > 0$



E.A. (electron affinity)

- **First EA** is the **enthalpy change** when 1 mole of electrons is added to 1 mole of **gaseous atoms** to form 1 mole of **singly charged** gaseous (an)ions
- Is always $\Delta H < 0$



- **Second EA** is the **enthalpy change** when 1 mole of electrons is added to 1 mole of **singly charged** gaseous (an)ions to form 1 mole of **doubly charged** gaseous (an)ions
- 2nd E.A. onwards is always $\Delta H > 0$



Note: This is due to the electrostatic repulsion between the negatively charged gaseous (an)ions and electrons. Energy taken in to overcome the electrostatic repulsion > Energy given out during bond formation

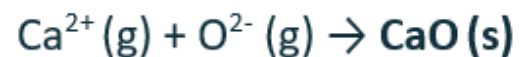
Standard Enthalpy Change

LE (Lattice energy)

- **Heat evolved** when **1 mole** of **solid ionic compound** is formed from its constituent **gaseous ions**
- Is always $\Delta H < 0$

Note: LE provide a measure of the ionic bonds present. Hence the more exothermic LE is, the stronger the ionic bonding

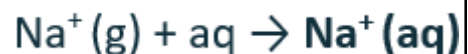
Note: If both the charge and radius increase, it will result in an overall increase in the LE due to the multiplication of the charge of the ions as compared to the addition of the radii of the ions



$$\text{Lattice energy} \propto \frac{(q+) \times (q-)}{(r+) + (r-)}$$

 ΔH_{hyd} (hydration)

- **Heat evolved** when 1 mole of **free gaseous ions** is dissolved in an infinite volume of water at 298K and 1 bar (standard conditions)
- Is always $\Delta H < 0$ due to the formation of **ion-dipole interactions** with water and ions
- **Higher** charge density = **Stronger** ion-dipole interaction hence **more** exothermic

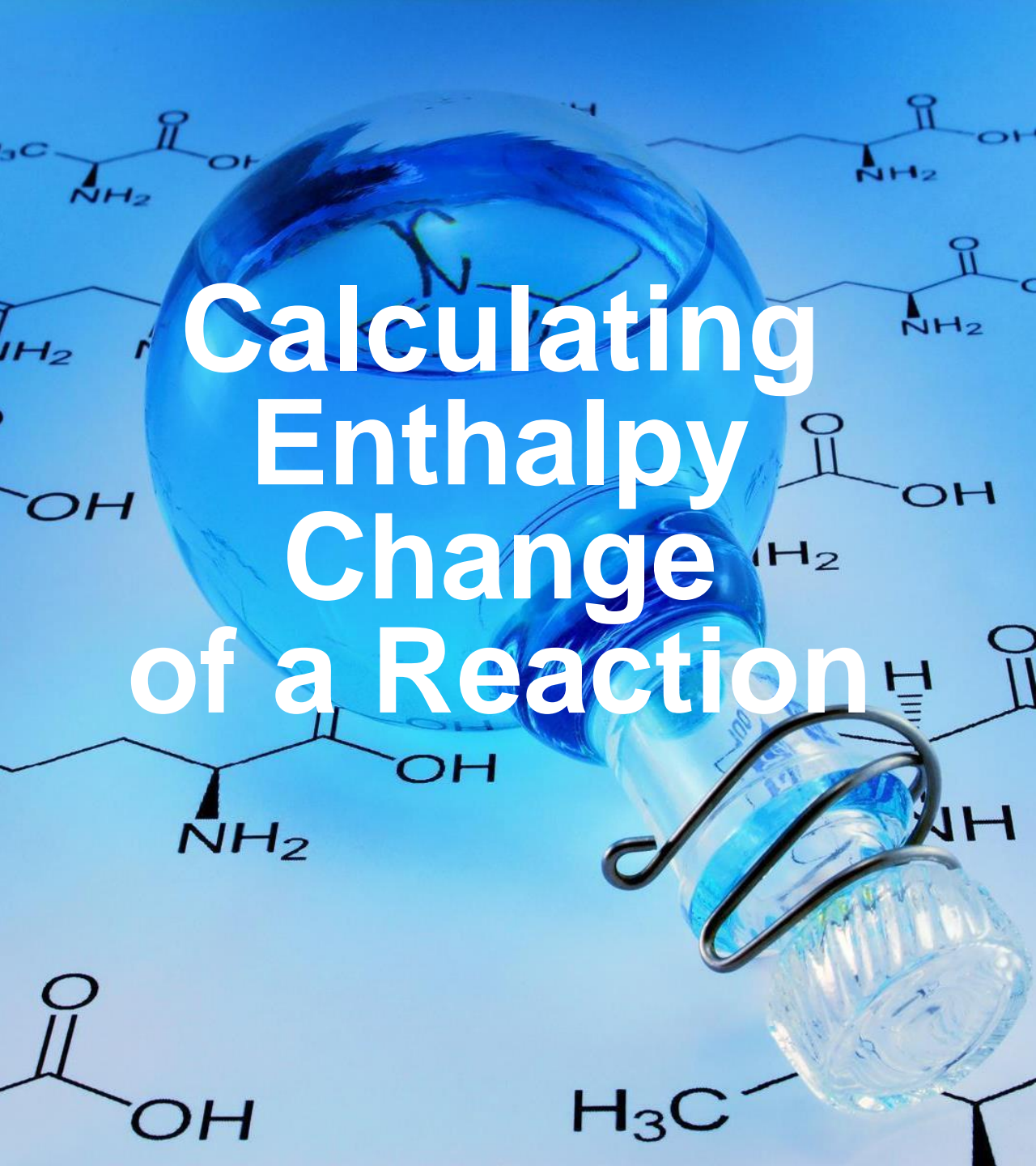
 **ΔH_{sol} (solution)**

- **Enthalpy change** when 1 mole of a **solute** (solid) is completely dissolved in an infinite volume of **solvent** at 298K and 1 bar (stp)
- When ΔH_{sol} **very endothermic**, compound is **insoluble** in water
- When ΔH_{sol} is **exothermic**, compound is **soluble** in water

Note: For ionic compounds, it will dissociate into its respective ions when dissolved in solvent



Standard Enthalpy Change

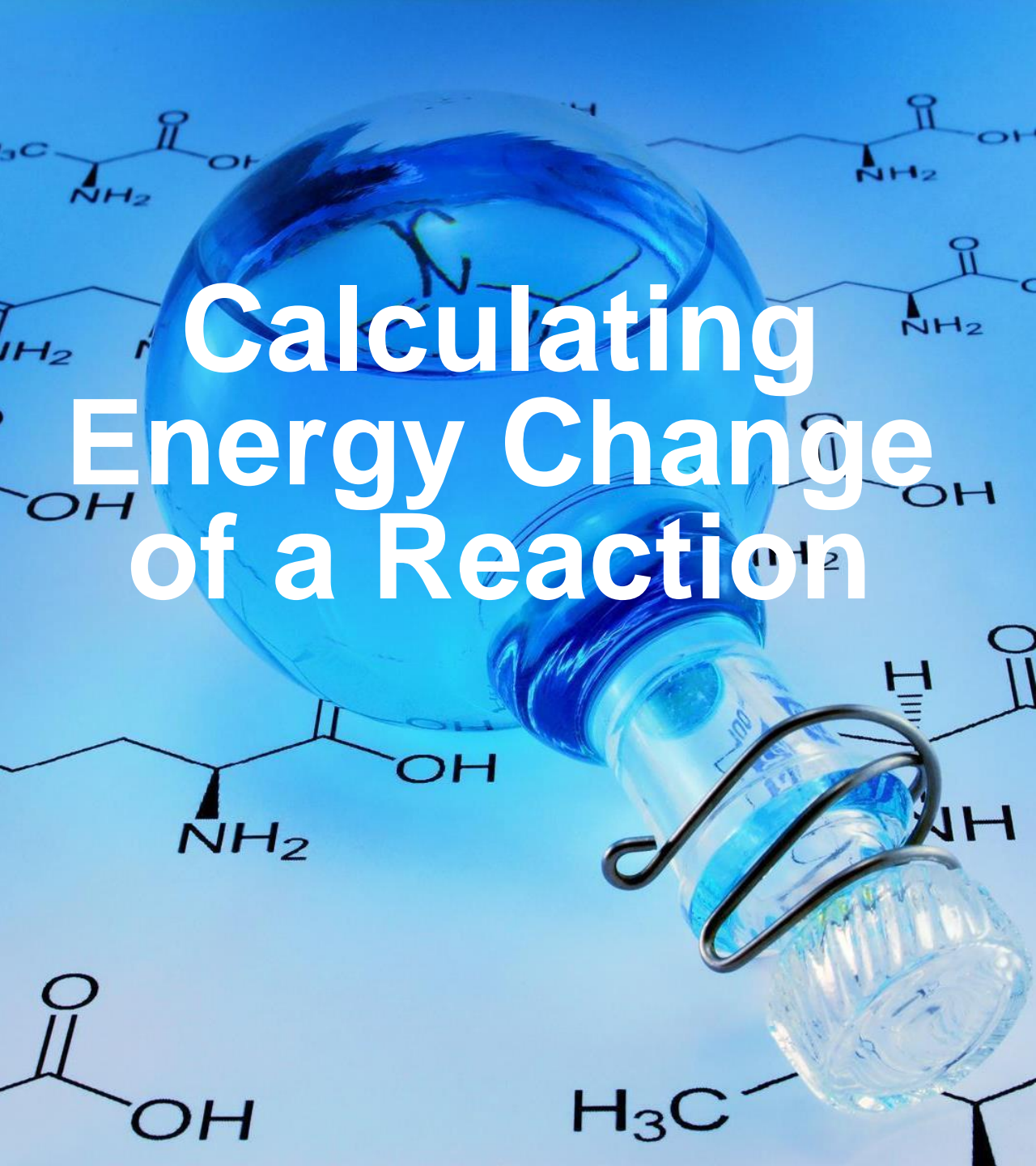


Calculating Enthalpy Change of a Reaction

HESS' LAW

- Enthalpy change (ΔH) of a reaction is determined only by the **initial and final states** of compounds/elements and is **independent** of the reaction pathway taken

5 Different Methods to Calculate Enthalpy Change



Calculating Energy Change of a Reaction

METHOD 1: ΔH_r (reaction)

Combustion

$$\Delta H_r = \sum m\Delta H_c (\text{reactants}) - \sum n\Delta H_c (\text{products})$$

Formation

$$\Delta H_r = \sum m\Delta H_f (\text{products}) - \sum n\Delta H_f (\text{reactants})$$

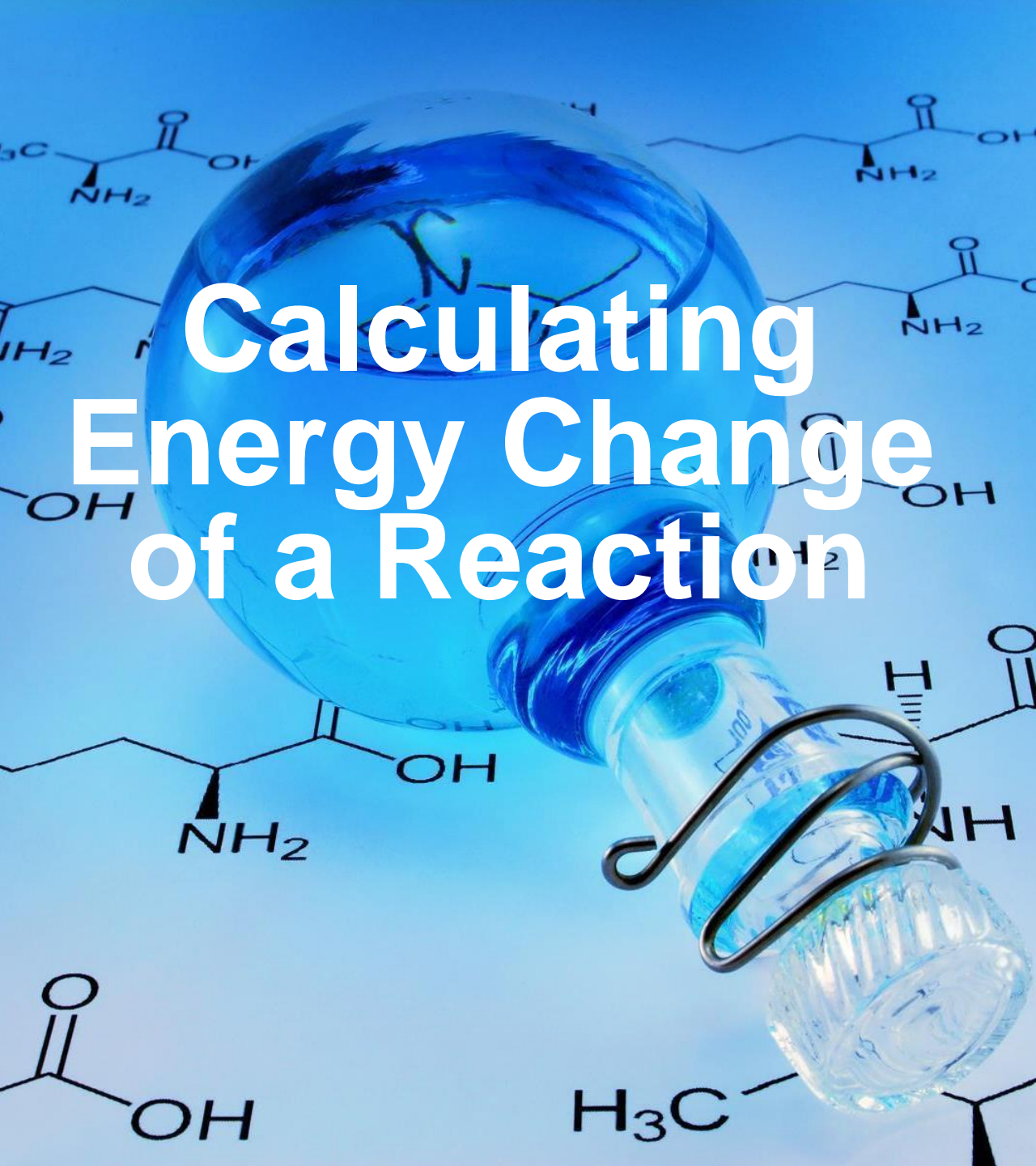
METHOD 2: USE OF BOND ENERGY VALUES

- Step 1: Identify the bonds broken and bonds formed for the compound and obtained the values from the data booklet
 - Step 2: Calculate the energy absorbed and energy released

Discrepancies between theoretical value and experimental values:

- Not in gaseous state
- Bond energy values obtained from data booklet are average values

$$\Delta H_r = \sum (\text{Energy absorbed during bond breaking (+)}) + \sum (\text{Energy released during bond formation(-)})$$



Calculating Energy Change of a Reaction

METHOD 3: EXPERIMENTAL METHOD

Using specific heat capacity

$$q = mc\Delta T$$

Units = m (g), c ($\text{J g}^{-1} \text{K}^{-1}$), q (J) ; $c = 4.18 \text{ J g}^{-1} \text{K}^{-1}$

- Note: m = the mass of the solution that changes temperature

OR

Using heat capacity

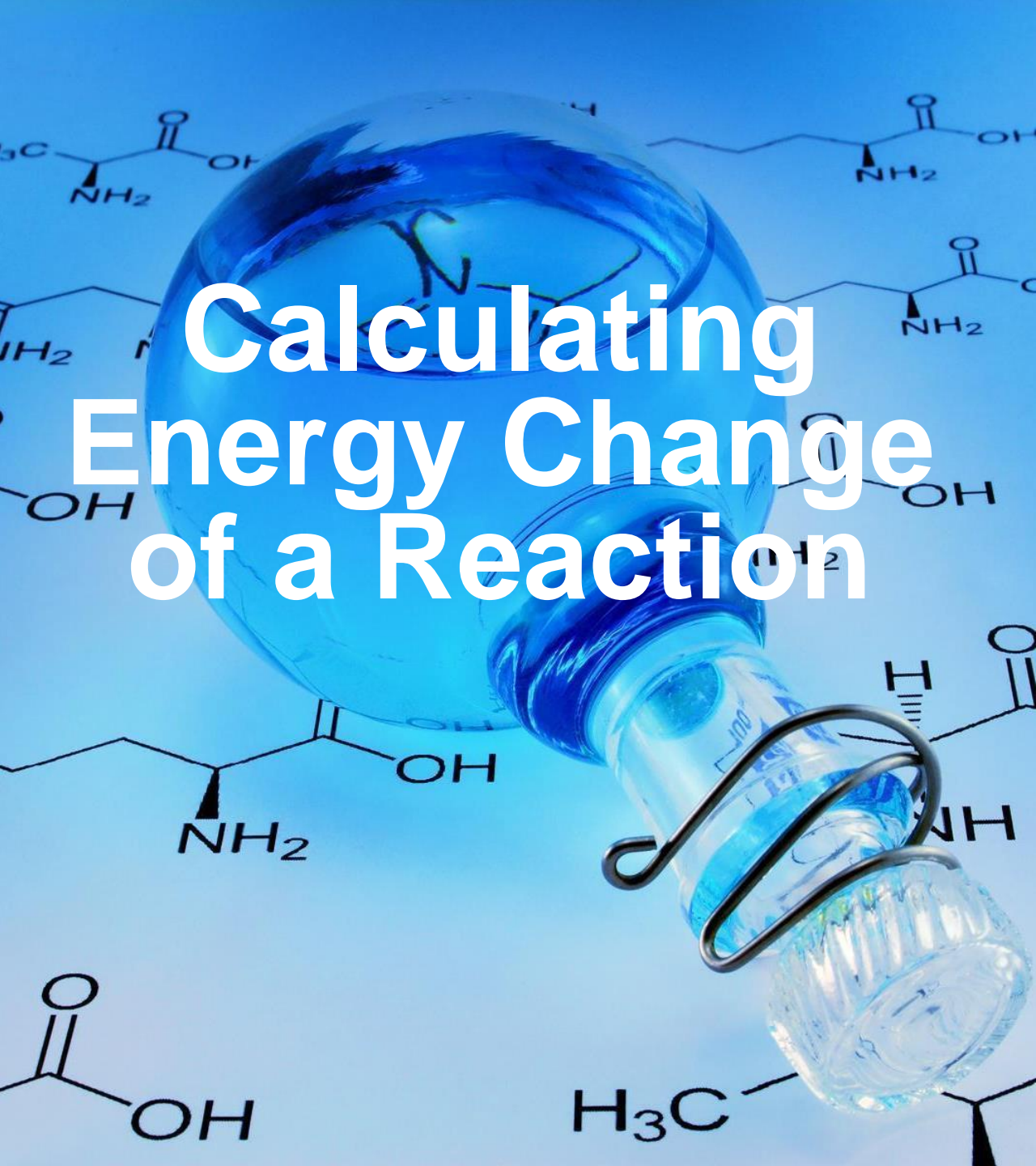
$$q = C\Delta T$$

Units = C (J K^{-1}), q (J)

Note: ΔT is the same for either in $^{\circ}\text{C}$ or in K

Note: if two solutions are mixed, the initial temperature will be different. Hence there is a need to calculate the average initial temperature of the mixture first to get ΔT

$$T_{\text{initial(average)}} = \frac{T_1V_1 + T_2V_2}{V_1 + V_2}$$



Calculating Energy Change of a Reaction

METHOD 3: EXPERIMENTAL METHOD

Relating energy obtained with enthalpy change

$$\Delta H_r = + q/n \text{ (endothermic)}$$

$$\Delta H_r = - q/n \text{ (exothermic)}$$

n = number of mols of the limiting reagent/the source of heat

Note: the mass used to calculate the number of mols might differ from the mass of the solution that changes temperature

Assumptions / Deviations from theoretical values:

- No heat lost to or heat gained from surroundings
- Heat capacity of calorimeter (polystyrene cup/container) is omitted
- Density of dilute solution 1.00 g cm^{-3} and $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$
- Complete combustion of compound for bomb calorimeter

Calculating Energy Change of a Reaction

METHOD 4: ENERGY CYCLE

- Step 1: Write out the equations given out with **state symbols**
- Step 2: Balanced the equations provided (if required)
- Step 3: Write out the equation you want to find and find similarities on both reactants and products with the rest of the other equations
- Step 4: Ensure the energy cycle diagram is closed
- Step 5: Find a starting and ending point and equate both energy value for both pathways

Enthalpy doesn't judge how you get there, as long as you do.

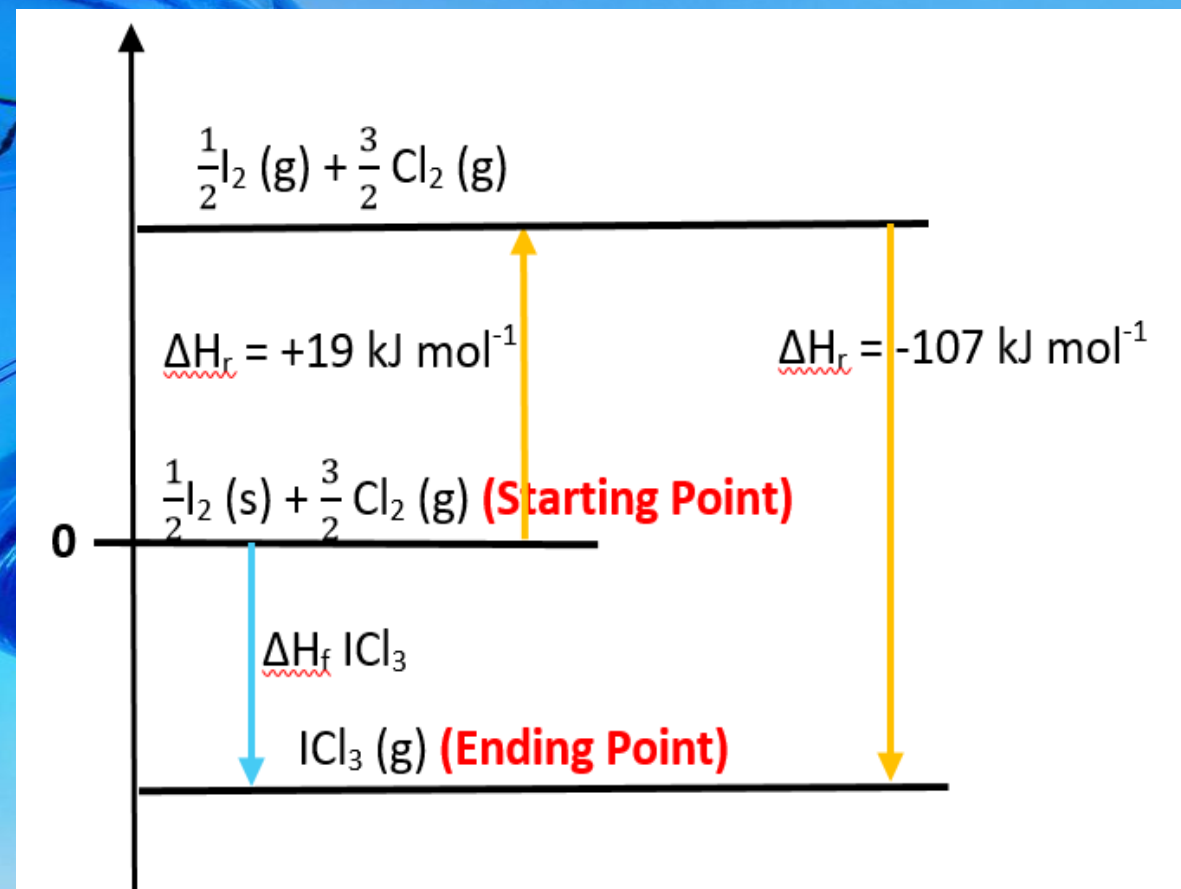


And this is why $\Delta H_1 + \Delta H_2$ gives ΔH_3 in this scenario.

METHOD 5: ENERGY LEVEL DIAGRAM

- Step 1: Draw and **label** the axis (Energy / kJ mol⁻¹; no x-axis; include "0" for x-axis)
- Step 2: Write out the equations given out with **state symbols**
- Step 3: Balanced the equations provided (if required)
- Step 4: Start with the elements in their standard state at point "0"
- Step 5: Find similarities of the elements with the rest of the other equations
- Step 6: Ensure the energy level diagram is closed
- Step 7: Find a starting and ending point and equate both energy value for both pathways

Note: Ensure the sign of ΔH must be consistent with arrow direction



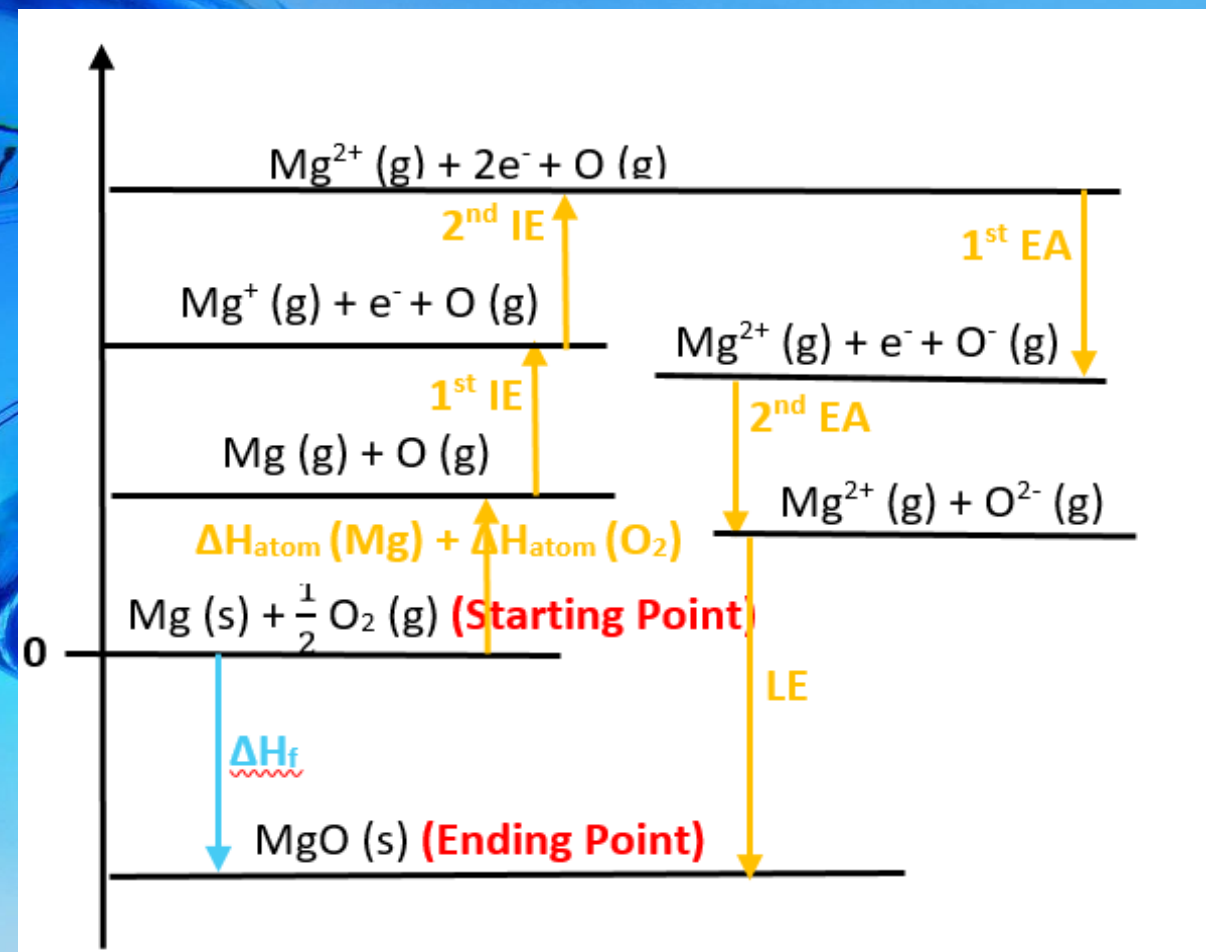
METHOD 6: BON-HABER CYCLE

- It is a type of energy level diagram used commonly to calculate LE of compounds
- Step 1: Draw and **label** the axis (Energy / kJ mol^{-1} ; no x-axis; include "0" for x-axis)
- Step 2: Write out the equations given out with **state symbols**
- Commonly used equations required: LE, EA, IE, ΔH_{atom} / Bond Energy, ΔH_f
- Step 3: Balanced the equations provided (if required)
- Step 4: Start with the elements in their standard state at point "0"
- Step 5: Find similarities of the elements with the rest of the other equations
- Step 6: Ensure the energy level diagram is closed
- Step 7: Find a starting and ending point and equate both energy value for both pathways

Discrepancies between theoretical and experimental values of LE:

- Assumed that compounds are entirely ionic. However the **degree of covalent character** (charge and ionic radii; polarisability and polarising power) in ionic compound will results in discrepancies.

Note: Comparing the difference in theoretical and experimental values of the LE gives an indication of the degree of covalent character in an ionic compound.



ENERGETICALLY STABLE VS KINETICALLY FEASIBLE (SPONTANEITY)

Exothermic reactions ($\Delta H < 0$) are **energetically more stable** and energy level of products are lower than reactants but may not be **kinetically feasible** → reaction does not occur spontaneously (naturally)

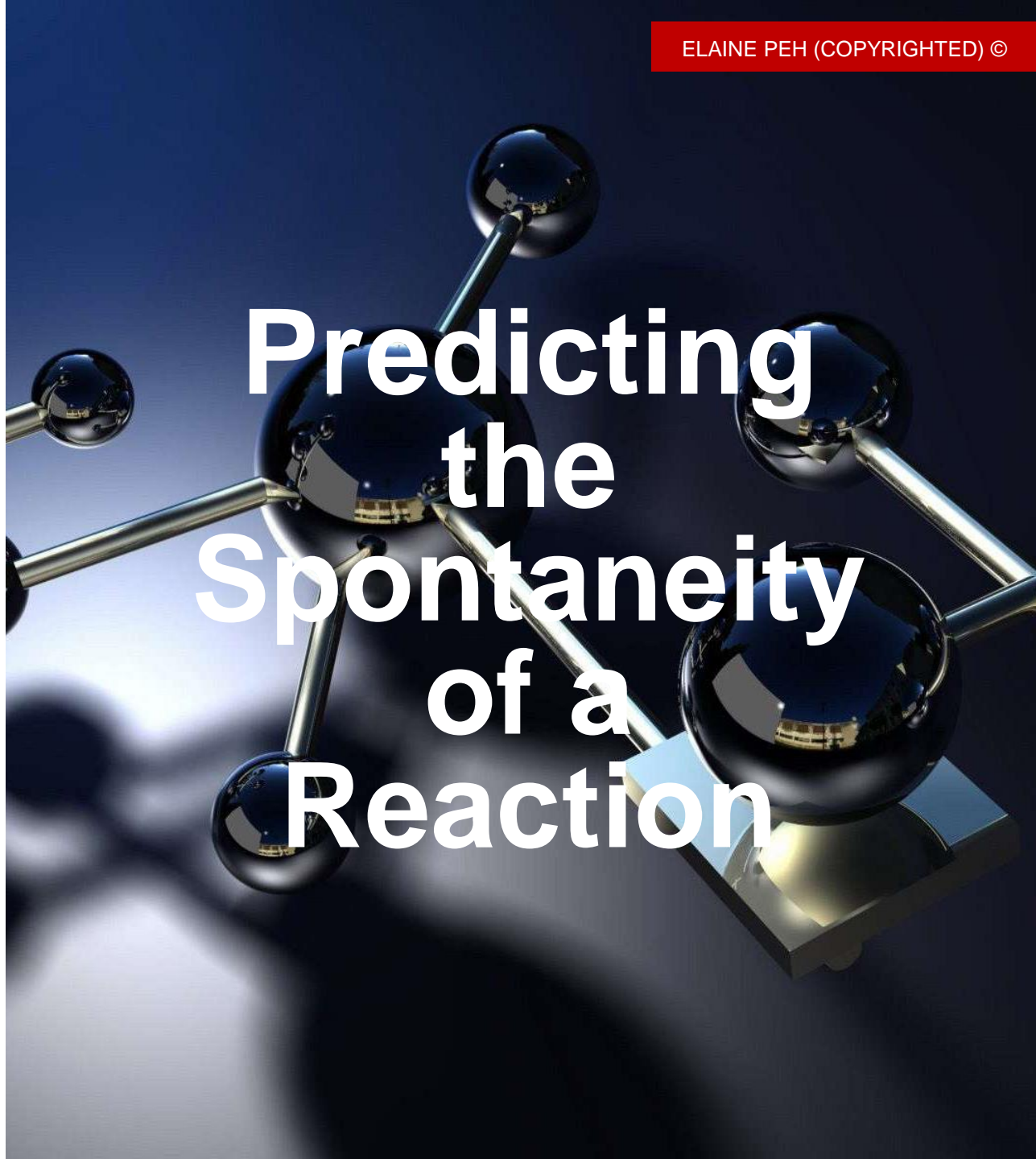
ENTROPY

Entropy 'S' is the measure of **randomness** and **disorderliness** in a **system**, reflected in the number of ways that energy in a system can be **distributed** through the **motion** of its **particles**.

ENTROPY CHANGE, ΔS

- Measure the change in **randomness** and **disorderliness** in a **system**.
- Units = $\text{J mol}^{-1} \text{K}^{-1}$
- $\Delta S > 0$, increase in disorderliness
- $\Delta S < 0$, decrease in disorderliness

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$



Predicting the Spontaneity of a Reaction

FACTORS AFFECTING ENTROPY

1. Temperature

- **Increase** in temperature result in an increase in average Kinetic Energy and range of energy increases, hence there are more ways to disperse the energy / **distribute the particles**
- *Note: can link to Maxwell-Boltzman distribution curve in Reaction Kinetics Chapter*

2. Change in **phase** (solid → liquid → gas)

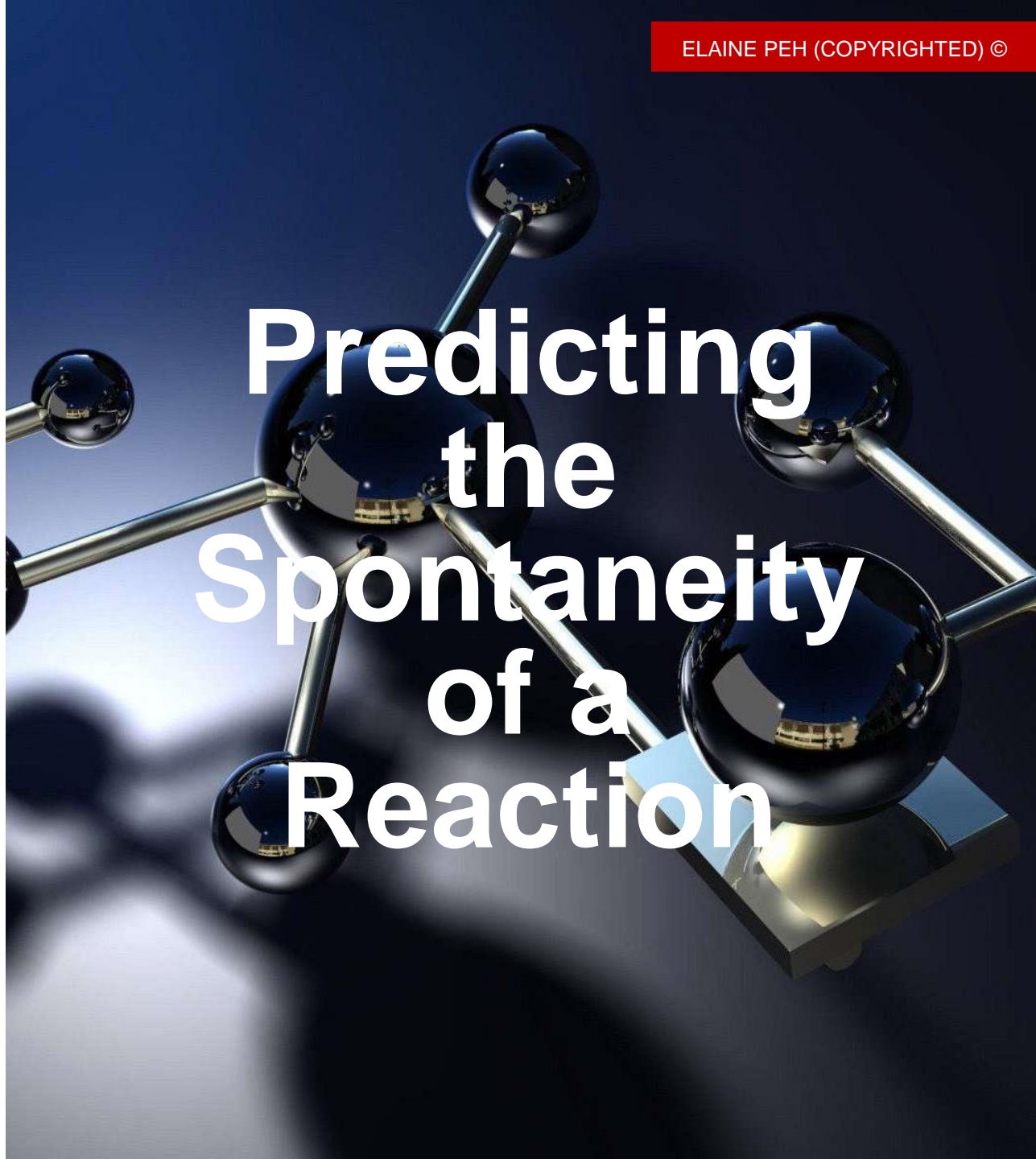
- During melting and boiling, particles move more freely from solid to liquid and from liquid to gaseous state, hence become more disordered. There are now **more ways to distribute the particles and their energy**, thus an increase in entropy

Note: Entropy of solid < liquid << gas

3. Change in **number** of particles (only for **gaseous systems** in chemical reactions)

- A chemical reaction resulting in an **increase** in gaseous particles increases the overall entropy as particles in gas are most disordered; there are now more ways to distribute particles

*Note: There must be a **net** increase in number of mols of gaseous products as compared to gaseous reactants*

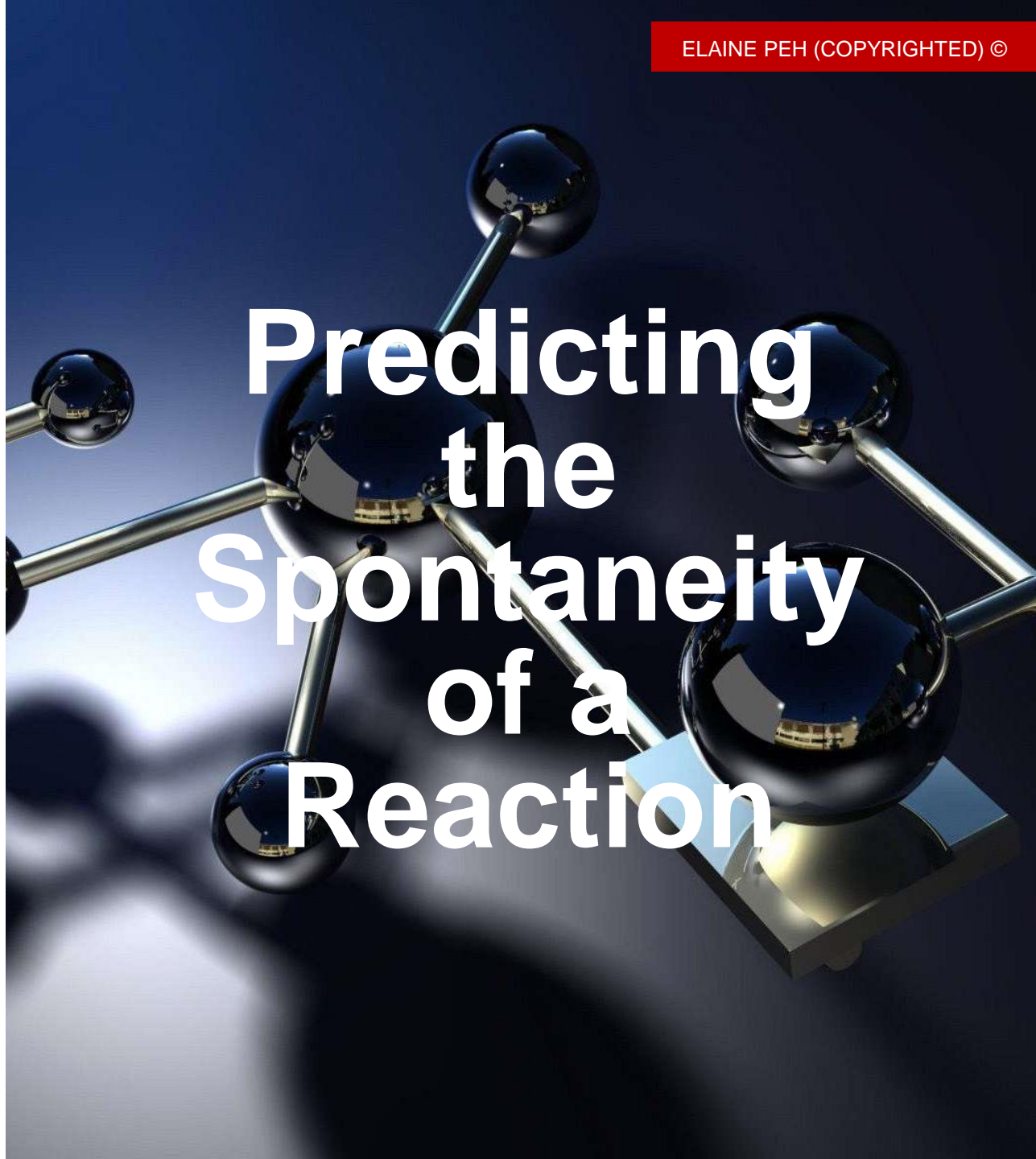


Predicting
the
Spontaneity
of a
Reaction

FACTORS AFFECTING ENTROPY

4. **Mixing** of gaseous particles (only under **CONSTANT PRESSURE**)
 - Entropy only increase when **volume increases** due to mixing under constant pressure. As volume increase there are now more ways to distribute the gas particle.
 - Entropy does not change when gaseous particles are mixed under **constant volume** as the number of ways to distribute the gas particles remain constant.

5. **Dissolution of ionic solid** (effect on ΔS varies)
 - **Entropy increase**; ions are now free to move in solution, increasing the number of ways to distribute the particles.
 - **Entropy decrease**; water molecules now become restricted in motion as they arrange themselves around the ions via ion-dipole interaction
→ *magnitude of each determines whether entropy increases or decreases*



Predicting
the
Spontaneity
of a
Reaction

GIBBS FREE ENERGY

- It combines enthalpy and entropy into a single value.

CHANGE IN GIBBS FREE ENERGY, ΔG

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

- $\Delta H = \text{J mol}^{-1}, \text{kJ mol}^{-1}$
- $\Delta S = \text{J mol}^{-1} \text{K}^{-1}$
- $T = \text{K}$
- $\Delta G = \text{J mol}^{-1}, \text{kJ mol}^{-1}$

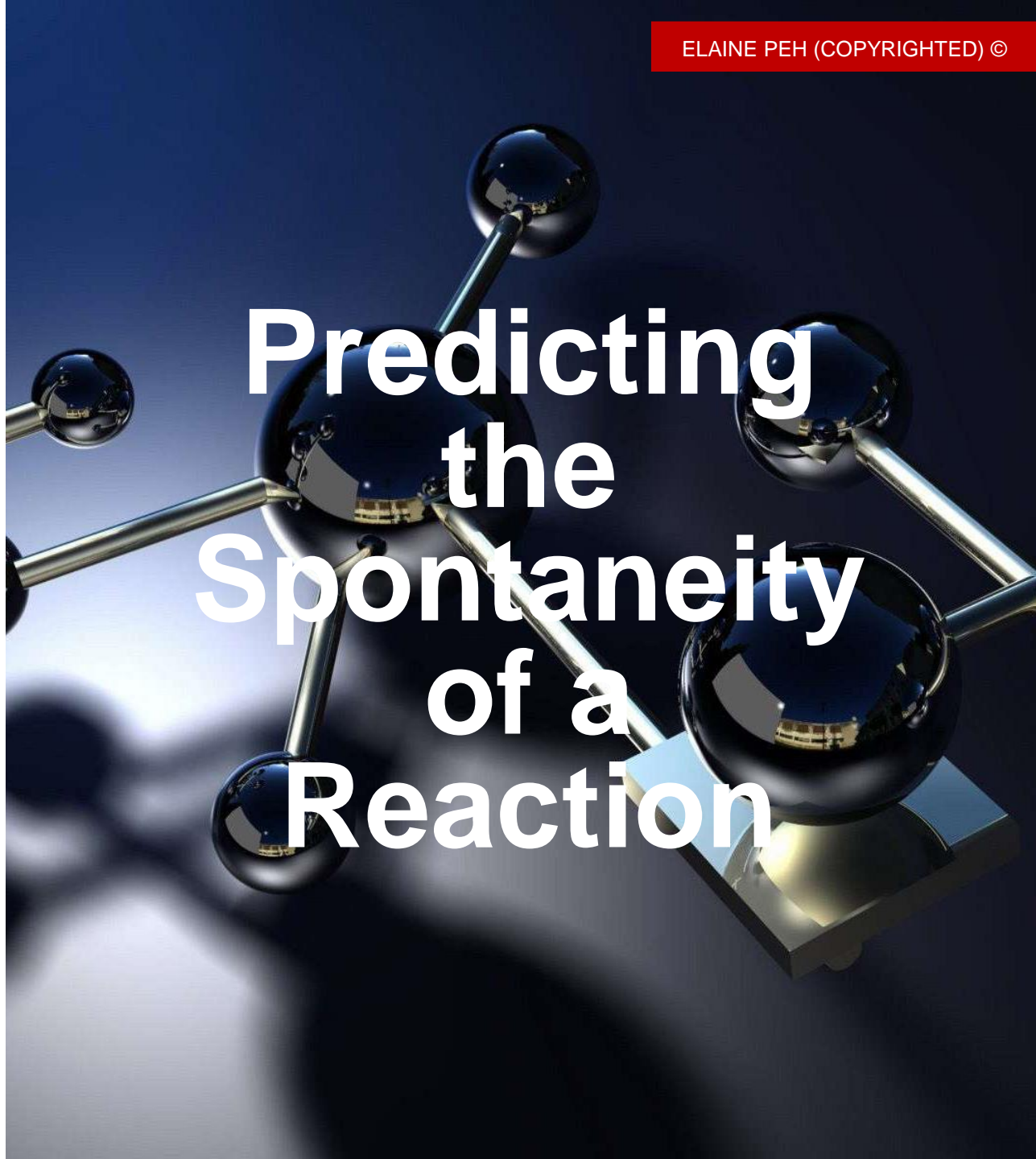
Note: The unit for ΔS is usually $\text{J mol}^{-1} \text{K}^{-1}$ and for ΔH is usually kJ mol^{-1} , remember to convert all to the same units during calculation!

- $\Delta G > 0$, reaction is spontaneous in the forward reaction
- $\Delta G < 0$, reaction is not spontaneous in the forward reaction
- $\Delta G = 0$, system at equilibrium, no net reaction in forward or backward direction

Note: this occur during phase change (melting and boiling)

Limitations in using ΔG to predict spontaneity of a reaction:

1. Valid only Standard Conditions
2. Assumed that ΔH and ΔS are constant as temperature changes
3. ΔG only indicates the thermodynamic feasibility of a reaction. It gives no information about the kinetic feasibility. Thermodynamically / energetically feasible does not equate to kinetically feasible due to high E_a .



Predicting the Spontaneity of a Reaction

Predicting the Spontaneity of a Reaction

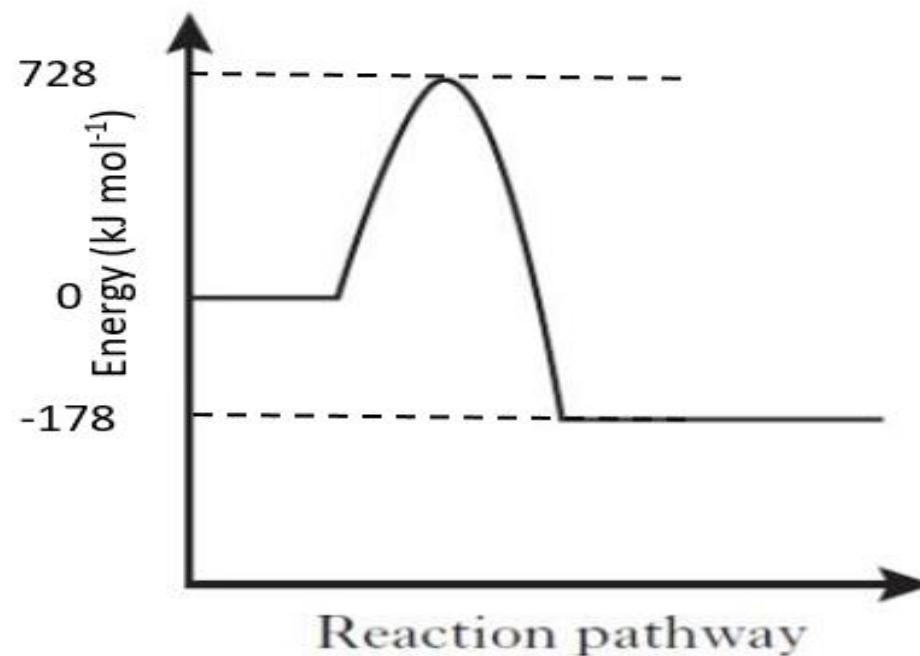
$$\Delta G = \Delta H - T\Delta S$$

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous	Spontaneous at high temps
$\Delta S < 0$	Spontaneous at low temps	Not Spontaneous

	$\Delta H > 0$	$\Delta H < 0$
$\Delta S > 0$	Spontaneity depends on T (spontaneous at higher temperatures)	Spontaneous at all temperatures
$\Delta S < 0$	Nonspontaneous (proceeds only with a continuous input of energy)	Spontaneity depends on T (spontaneous at lower temperatures)

Practice Questions

Question: Determine the ΔH and E_a of the following reaction pathway



Answer:
 $\Delta H = -178 \text{ kJ mol}^{-1}$
 $E_a = 728 \text{ kJ mol}^{-1}$

Practice Questions

Question: Compare the LE between MgCl_2 and NaCl

Answer: *LE of MgCl_2 will be more exothermic than LE of NaCl .*

Question: Compare the LE between CaO and NaF

Answer: *The LE of CaO is more exothermic than NaF*

Question: What is the relationship between LE, ΔH_{hyd} and ΔH_{sol} of MgO ?

Answer: $\Delta H_{\text{sol}} = -LE + \Delta H_{\text{hyd of ions}}$

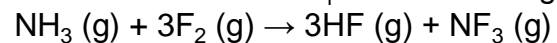
Question: Find the ΔH_{f} of the formation of CH_4 gas given the following data:

Answer: $-74.6 \text{ kJ mol}^{-1}$

Thermochemical Equation	$\Delta H_{\text{c}} (\text{kJ mol}^{-1})$
$\text{CH}_4 (\text{g}) + 2\text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l})$	-890.2
$\text{C} (\text{s}) + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$	-393.4
$\text{H}_2 (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{l})$	-285.7

Practice Questions

Question: Find the ΔH_r of the following reaction using the Bond Energy Values given and from the Data Booklet



$\text{N-F} = 272 \text{ kJ mol}^{-1}$

Answer: -858 kJ mol^{-1}

Question: 250 cm^3 of 0.5 mol dm^{-3} NaOH was added to 250 cm^3 of 0.8 mol dm^{-3} of H_2SO_4 in a calorimeter. The initial temperature of the two solutions were 15°C . After the reaction, the temperature rose to a maximum of 21.7°C . Calculate the enthalpy change of neutralization of the reaction.

Answer: $-112.024 \text{ kJ mol}^{-1}$

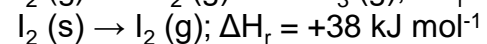
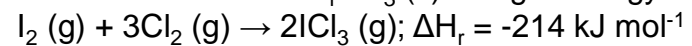
Question: By using the data given, determine the mean P-Cl bond energy using a energy cycle

Answer: -331 kJ mol^{-1} (3 sf)

	$\Delta H_r (\text{kJ mol}^{-1})$
$\Delta H_f \text{ PCl}_3 (\text{g})$	-315
$\Delta H_{\text{atomization}}$ of Phosphorous	+314
$\Delta H_{\text{atomization}}$ of Chlorine	+121

Practice Questions

Question: Find the ΔH_f ICl_3 (s) using a energy level diagram with the following data



Answer: -88 kJ mol^{-1}

Question: Find the LE of sodium fluorine using a Bon Haber cycle using the data given and from Data Booklet

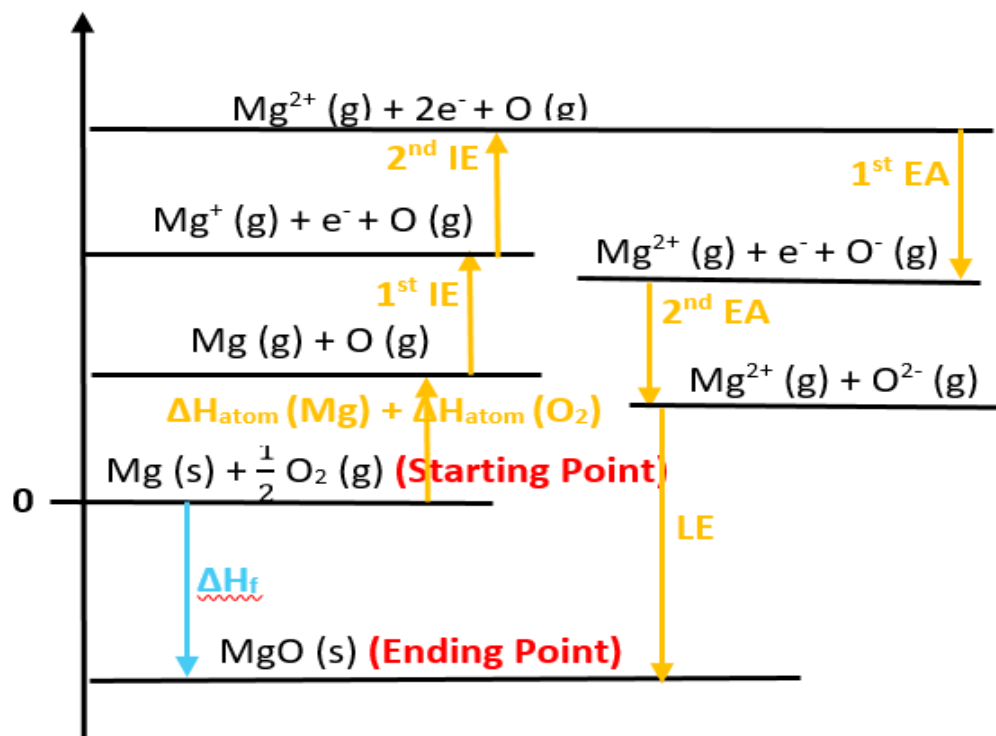
	ΔH_r (kJ mol ⁻¹)
$\Delta H_{\text{atom}} \text{Na (s)}$	+107
1 st EA of $\text{F}_2 (\text{g})$	-328
$\Delta H_f \text{NaF (s)}$	-574

Answer: -928 kJ mol^{-1} (3 sf)

Practice Questions

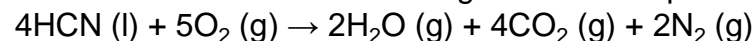
Question: Construct a Bon Haber cycle to illustrate the steps required to find the LE of MgO(s)

Answer:



Practice Questions

Question: Consider the following reaction and predict if the reaction would occur spontaneously at room temperature (298K)?



$$\Delta H_r = -1558 \text{ kJ mol}^{-1}$$

$$\Delta S = +336.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

Answer: Since $\Delta G < 0$, reaction would be spontaneous at room temperature.

Question: Consider the dissociation of $\text{N}_2\text{O}_4 \text{ (g)}$:



By considering the enthalpy and entropy changes, explain why little or no dissociation occurs at low temperature but is highly favoured at high temperatures.

Answer: For the above reaction, ΔH and ΔS are both positive. $\Delta G = \Delta H - T\Delta S$. At low temperature, magnitude of $T\Delta S$ will be less than magnitude of ΔH , hence $\Delta G > 0$, reaction is non-spontaneous at low temperature. At high temperature, magnitude of $T\Delta S$ will be greater than magnitude of ΔH , hence $\Delta G < 0$, reaction is spontaneous at high temperature.

Practice Questions

Question: Magnesium oxide is produced by the decomposition of magnesium carbonate.



$$\Delta H_r = +101 \text{ kJ mol}^{-1}$$

$$\Delta S = +159 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (a) Calculate ΔG for the reaction at 298K
- (b) Calculate the temperature at which the decomposition will take place.
- (c) Explain why magnesium carbonate decompose at around 500K instead of the temperature calculated in (b)?

Answer:

(a) $\Delta G = +53.6 \text{ kJ mol}^{-1}$

(b) $T = 635\text{K}$

(c) *In the calculation of (b), the ΔH and ΔS used were measured at standard conditions and not at the decomposition temperature. Thus the calculated temperature differs from the actual.*

Test yourself!

- (a) explain that most chemical reactions are accompanied by energy changes, principally in the form of heat usually associated with the breaking and forming of chemical bonds; the reaction can be exothermic (ΔH negative) or endothermic (ΔH positive)
- (b) construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy
- (c) explain and use the terms:
- (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation
 - (ii) *bond energy* (ΔH positive, i.e. bond breaking)
 - (iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)
- (d) calculate enthalpy changes from appropriate experimental results, including the use of the relationship:
heat change = $mc\Delta T$

Test yourself!

- (e) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy
- (f) apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:
 - (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion
 - (ii) the formation of a simple ionic solid and of its aqueous solution
 - (iii) average bond energies
- (g) explain and use the term *entropy*

Test yourself!

(h) discuss the effects on the entropy of a chemical system by the following:

- (i) change in temperature
 - (ii) change in phase
 - (iii) change in the number of particles (especially for gaseous systems)
 - (iv) mixing of particles
- [quantitative treatment is **not** required]

(i) predict whether the entropy change for a given process or reaction is positive or negative

(j) state and use the equation involving *standard Gibbs free energy change of reaction*, $\Delta G = \Delta H - T\Delta S$

(k) state whether a reaction or process will be spontaneous by using the sign of ΔG

(l) understand the limitations in the use of ΔG to predict the spontaneity of a reaction

(m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

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