



Unit 5 - Energetics

Exothermic vs Endothermic, Enthalpy, Hess's Law, Born-Haber, Entropy, Spontaneity (Gibbs Free Energy)

Heating some water...

- Your job is to figure out how we can find the heat change for one mole of butane in the canister...as accurately as possible.
- You have 20 minutes to brainstorm (need materials list too!) and write a procedure ... this is not a formal lab!



Homework!!

- Write a paragraph discussing the outcome of your experiment.
- Mention REALISTIC random AND systematic errors that (actually) occurred.
- Please discuss realistic suggestions for improvement.

Thoughts..

- What type of change is this?
- What equations might we need to use?
- What can we do to minimize error?
- How many times should we do it (or different set-ups)?

Energy and Heat

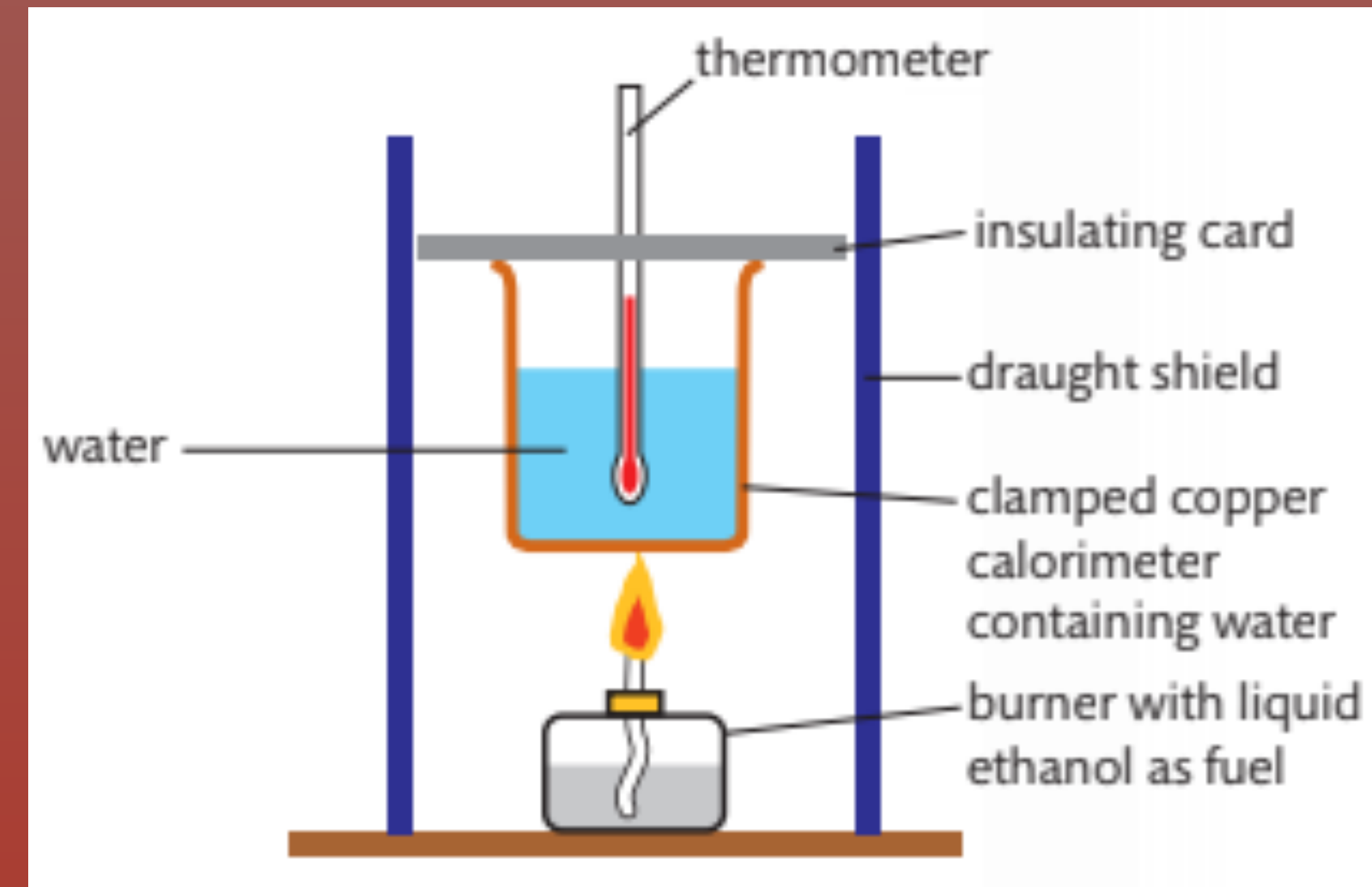
- Energy - a measure of the ability to do work
- Heat - a form of energy which is transferred as a result of a temperature difference
- System vs. Surroundings

Enthalpy

- ΔH - overall energy change in a system
- when ΔH is negative...
- when ΔH is positive...
- Standard Enthalpy Changes:
 - 100 kPa
 - Concentration of 1 mol dm^{-3}
 - all substances in standard states
 - 298 K (25°C)

Measuring Enthalpy Changes of Combustion

- Assume that all of the heat given off by the combustion is absorbed by the water.
- Enthalpy changes are usually expressed in kJ mol^{-1} .



$$\Delta H_{\text{reaction}} = -\Delta H(\text{water}) = -m(\text{H}_2\text{O}) \times c(\text{H}_2\text{O}) \times \Delta T(\text{H}_2\text{O})$$

Measuring Enthalpy Changes of Combustion

$$\Delta H_{\text{reaction}} = -\Delta H(\text{water}) = -m(\text{H}_2\text{O}) \times c(\text{H}_2\text{O}) \times \Delta T(\text{H}_2\text{O})$$

Calculate the enthalpy of combustion of ethanol from the following data. Assume all the heat from the reaction is absorbed by the water.

Compare your value with the IB data booklet value and suggest reasons for any differences.

Mass of water in copper calorimeter / g	200.00
Temperature increase in water / °C	13.00
Mass of ethanol burned / g	0.45

Measuring Enthalpy Changes of Combustion

Factors Influencing Differences:

- Not all heat produced is transferred to water.
- Combustion of ethanol not complete (oxygen availability).
- Experiment not performed under standard conditions.

Standard Enthalpy changes of reaction

- enthalpy of a reaction depends on the physical state of the reactants and products
 - Standard enthalpy changes measured @ 298K and 1.00×10^5 Pa
 - Standard Enthalpy Change (ΔH°) - when 1 mole of a substance is formed from its elements in their standard states (what they are @ 298K and 100kPa [1.00×10^5 Pa])

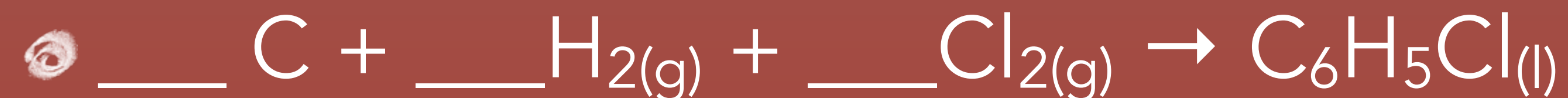
Standard enthalpy of formation

- a substance can have a ΔH_f° of zero if it exists in its "standard" state
 - ex. Li(s) , H₂(g) , S(s) , Hg(l)
- an element will have a ΔH_f° of something other than zero if it's not in its standard state
 - ex. Ca(l) , Br₂(s) , F(g)
- compounds $\Delta H_f^\circ \neq 0$

Example

- The Enthalpy of formation (ΔH_f°) of chlorobenzene is given on table 12 in your data booklet. Give the thermochemical equation which represents the ΔH_f° of chlorobenzene.
- Steps:
 1. What elements created this compound?
 2. Balance the equation

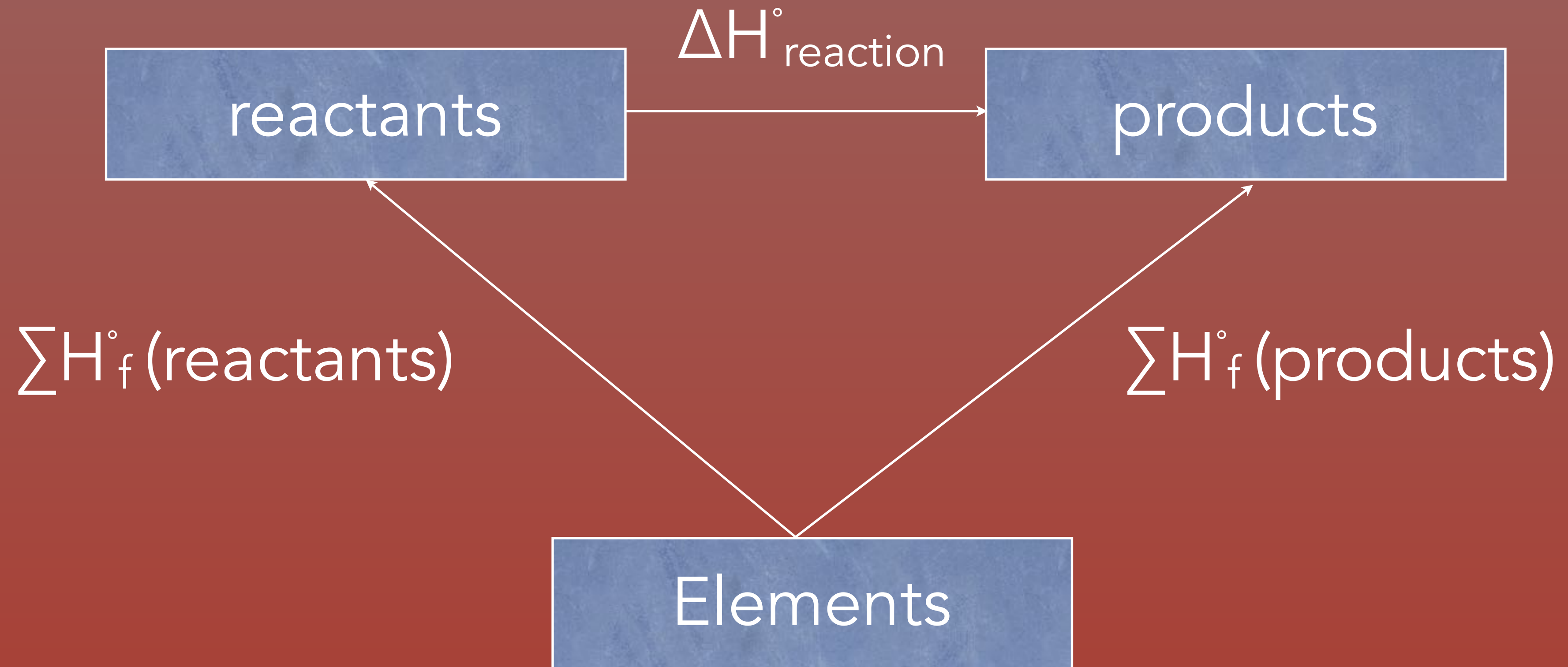
Example Continued



****Remember: only 1 mole of chlorobenzene can be made!!****



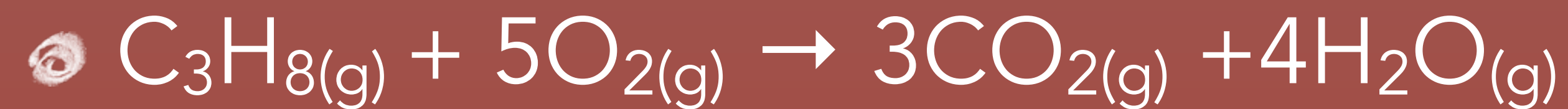
Standard Heat of Formation (any rxn)



🌀 $\Delta H^\circ_{\text{reaction}} = \Sigma H^\circ_f (\text{products}) - \Sigma H^\circ_f (\text{reactants})$

Example

• Calculate the enthalpy of formation for the reaction:



• given the following information:

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{C}_3\text{H}_{8(g)}$	-105
$\text{CO}_{2(g)}$	-394
$\text{H}_2\text{O}_{(g)}$	-286

5.2 Hess's Law

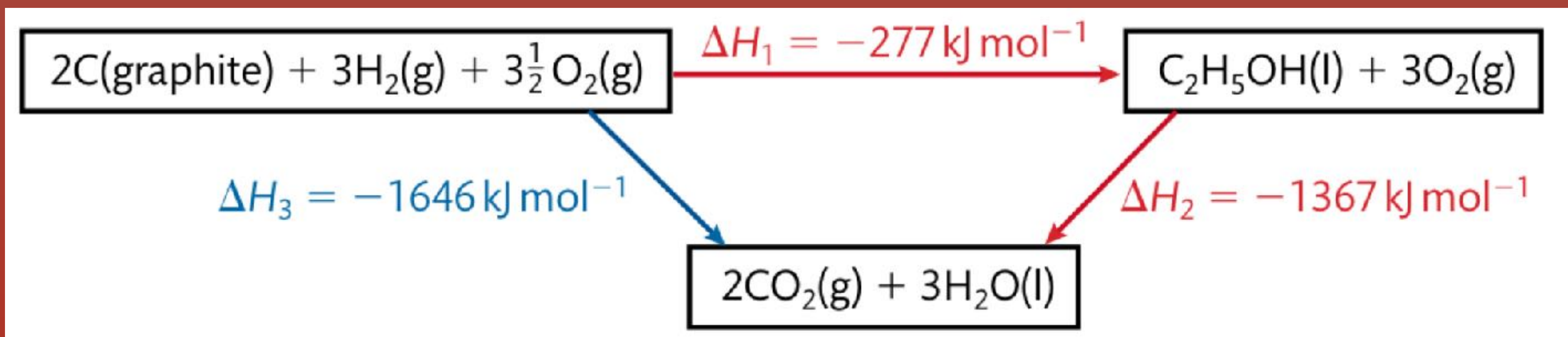
Enthalpy change for a reaction carried out in a series of steps is equal to the sum of the individual steps.
if...

$$\Delta H_1 = -277 \text{ kJ mol}^{-1}$$

$$\Delta H_2 = -1367 \text{ kJ mol}^{-1}$$

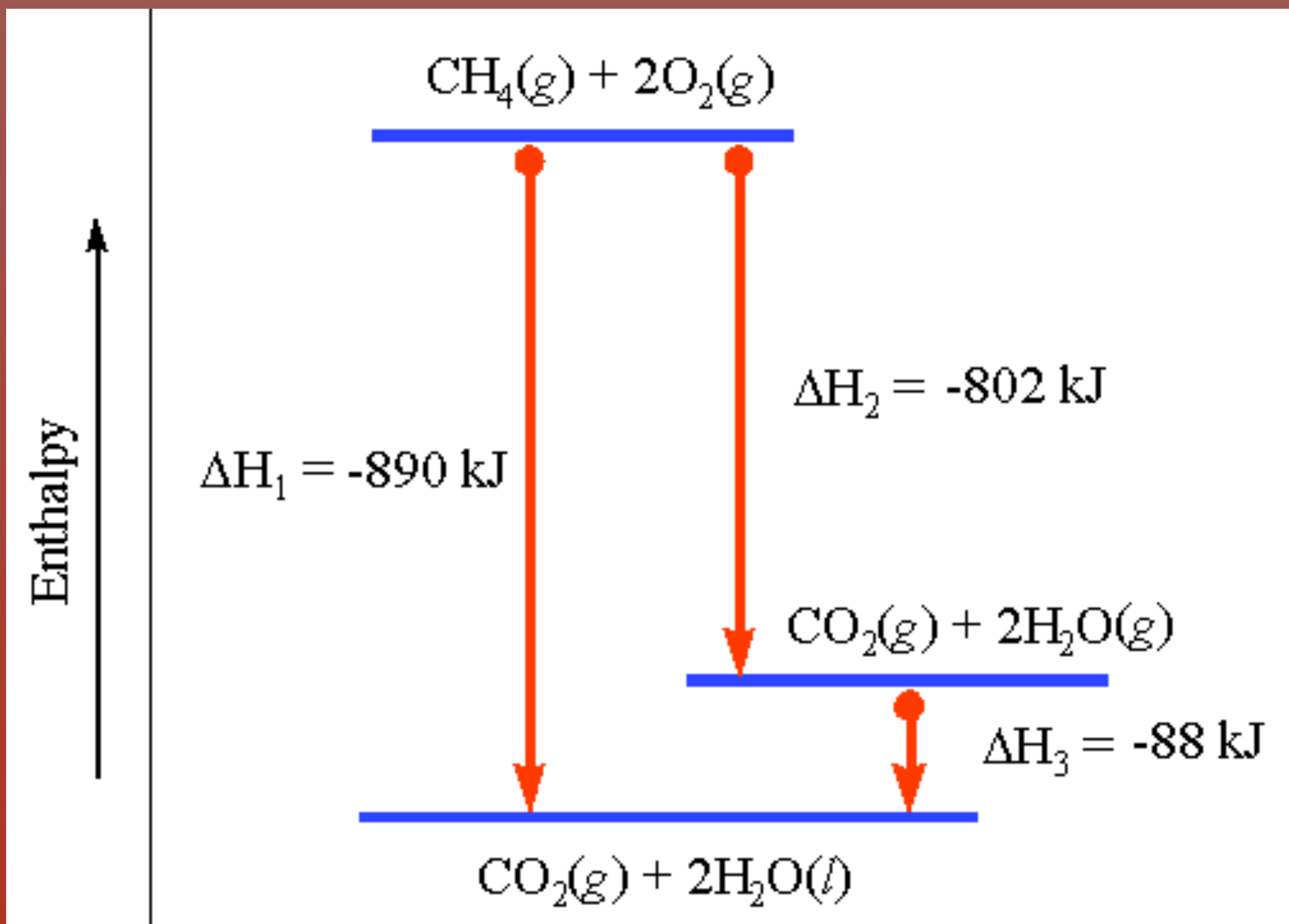
$$\Delta H_3 = -1646 \text{ kJ mol}^{-1}$$

what is the relationship between the 3?



Hess's Law

• $\Delta H_1 = \Delta H_2 + \Delta H_3$



Example...

- Calculate the ΔH value of the following rxn.
 - $\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$
- Given Steps:
 - $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta H = -242.0\text{kJ}$
 - $2\text{CO} \rightarrow 2\text{C} + \text{O}_2 \quad \Delta H = 221.0\text{kJ}$

One more....

• Calculate the ΔH value of the following rxn.



• Given:



Last one...I promise

- Using the equations below:
 - $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} \quad \Delta H = -390 \text{ kJ}$
 - $\text{Mn}_{(s)} + \text{O}_{2(g)} \rightarrow \text{MnO}_{2(s)} \quad \Delta H = -520 \text{ kJ}$
- What is ΔH (in kJ) for the following reaction?
 - $\text{MnO}_{2(s)} + \text{C}_{(s)} \rightarrow \text{Mn}_{(s)} + \text{CO}_{2(g)}$

5.3 Breaking Bonds

- What do you know about the energetics of breaking a bond?
 - Endothermic!
 - *Bond Enthalpy - the energy it takes to break one mole of bonds in a gaseous atom*
 - *why only gaseous atoms?*
 - *need to eliminate the energy needed to overcome IMFs*
 - *Ex. $\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)} \quad \Delta H = 242.0\text{kJ mol}^{-1}$*

Remember...

- in terms of bond strength:
 - single < double < triple
 - bond enthalpies will increase accordingly

Bond Formation

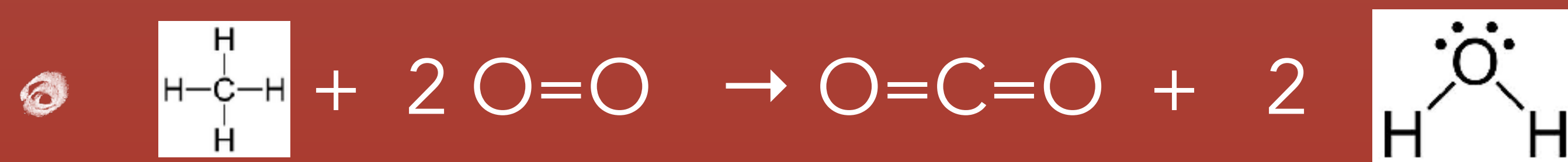
- bond making involves bringing together atoms that are attracted by an electrostatic force and releases energy...
- Exothermic!

Energy changes in reactions using bond enthalpies

• Given an equation (find the overall ΔH):



• Step 1: Write down the equation showing all the bonds



• How many of each bond?

Example Continued

- How many of each bond?
 - 4 C-H bonds, 2 O=O bonds, 2 C=O bonds, 4 H-O bonds
- IB Data Booklet - Table 11 Bond Enthalpies
 - broken bonds: endothermic (positive)
 - formed bonds: exothermic (negative)

Calculations

- C-H \rightarrow +414 x 4 bonds = +1656 kJ
- O=O \rightarrow +498 x 2 bonds = +996 kJ
- C=O \rightarrow -804 x 2 bonds = -1608 kJ
- H-O \rightarrow -463 x 4 bonds = -1852 kJ
- $\Delta H = 1656 + 996 - 1608 - 1852 = -808 \text{ kJ mol}^{-1}$
- Can also use absolute values:
 - $\Delta H = \sum \text{Bonds Broken} - \sum \text{Bonds Formed}$

Another Practice

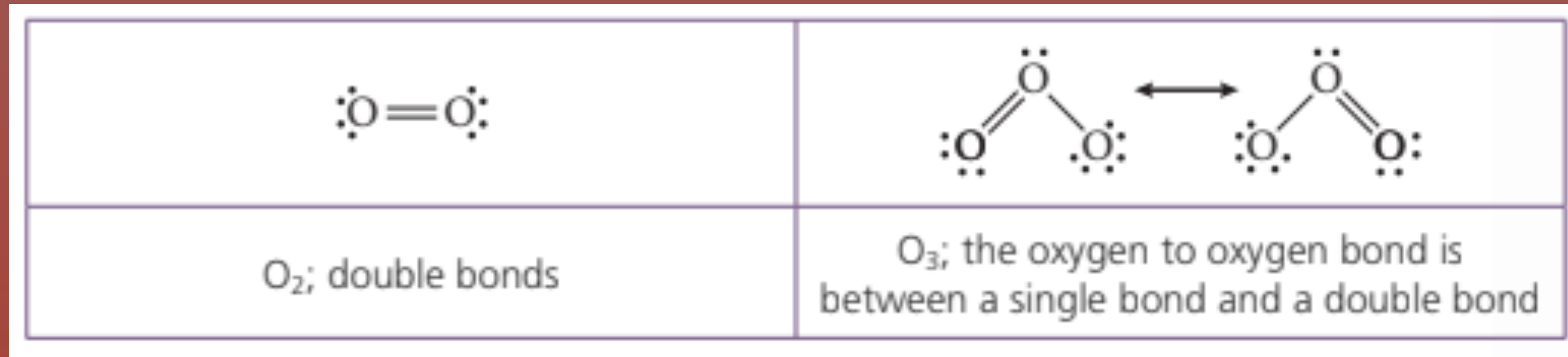


Bond	Enthalpy kJ mol^{-1}
C-C	346
C=C	614
C-H	414
H-H	436

Find ΔH for the reaction

Ozone Depletion (Again??)

- Oxygen present in two forms O_2 and O_3



- Bond Order / Bond Strength between allotropes?
Example: The bond energy in ozone is 363 kJ mol^{-1} . Calculate the wavelength of UV radiation needed to break the bond.

Example Continued

- Remember the following relationships:

$$E_{\text{photon}} = h\nu \text{ (Planck's Equation)}$$

The wavelength (λ) is related to the frequency: $\nu = c/\lambda$ where c is the speed of light. Substituting for ν in Plank's equation:

$$E_{\text{photon}} = hc/\lambda$$

- One mole of photons is needed to break one mole of bonds.

$$L \times E_{\text{photon}} = 363 \text{ kJ} = 363000 \text{ J}$$

$$E_{\text{photon}} = 363000/6.02 \times 10^{23}$$

Substitue and solve...

Ozone Depletion Example

$$E_{\text{photon}} = 363000 / 6.02 \times 10^{23}$$

$$h = 6.63 \times 10^{-34} \text{ J s}$$

$$c = 3.0 \times 10^8 \text{ m s}^{-1}$$

Substitute and solve...

$$E_{\text{photon}} = hc/\lambda$$

$$E_{\text{photon}} = 6.03 \times 10^{-19} \text{ J} = (6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})/\lambda$$

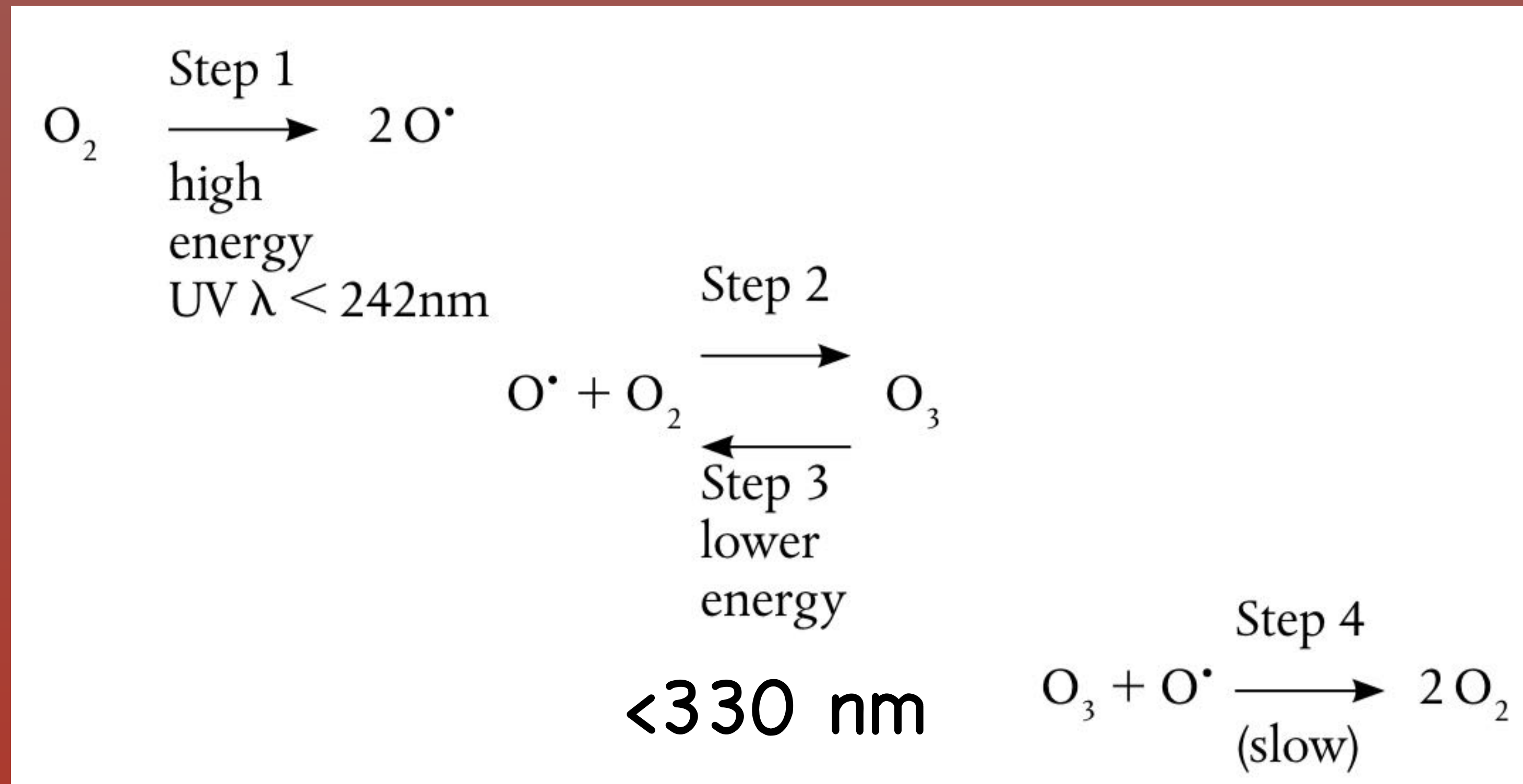
Do some math here and then rearrange...

$$\lambda = 3.298 \times 10^{-7} \text{ m}$$

$$\lambda = 330 \text{ nm}$$

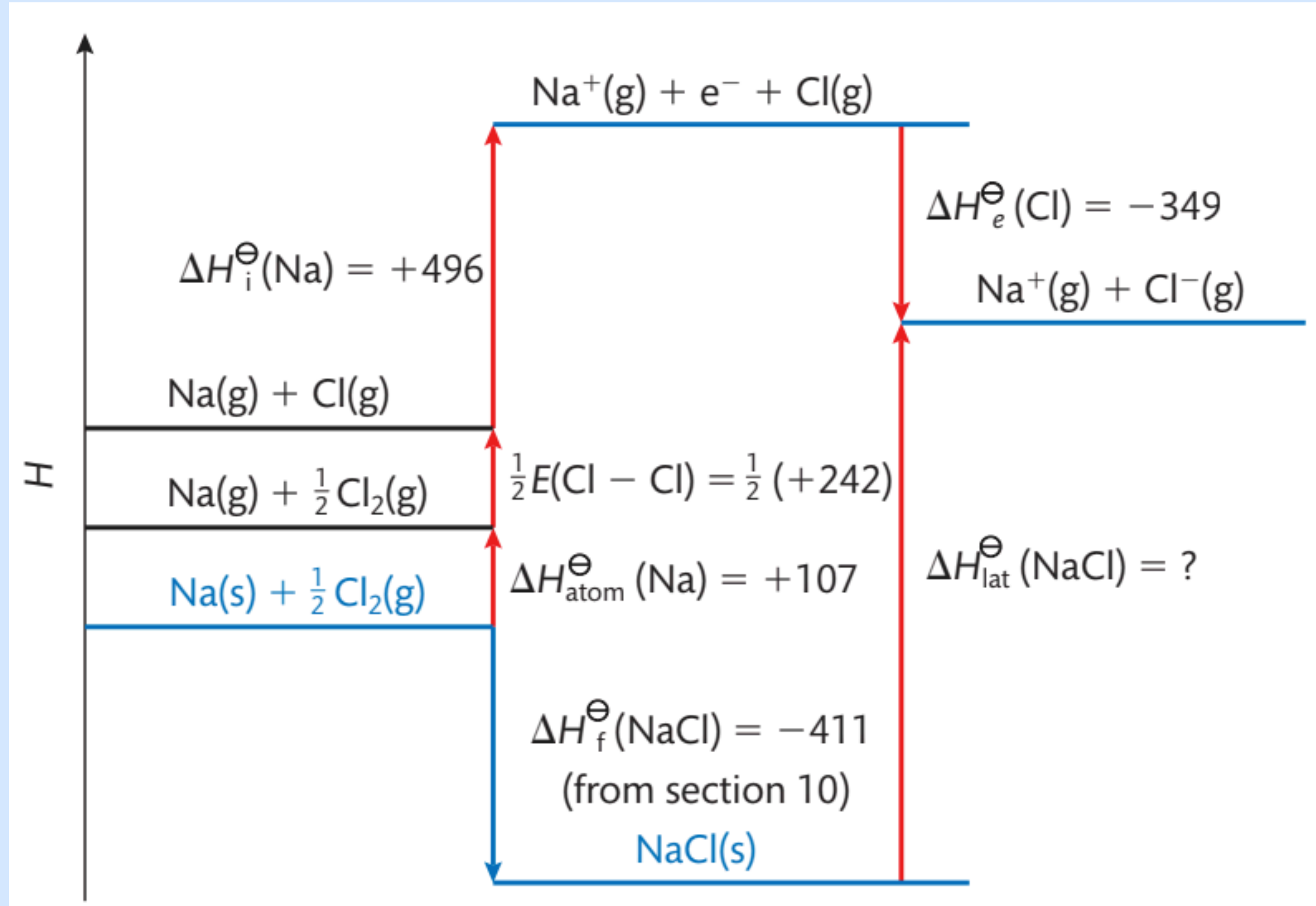
Chapman Cycle

- Level of ozone in the atmosphere (less than 10 ppm) stays constant if the rate of formation is balanced by rate of removal (steady state).



This cycle is significant because dangerous ultraviolet light has been absorbed and the stratosphere has become warmer. Both the processes are essential for the survival of life on Earth.

Born - Haber Cycles



Some Vocabulary

- Review:

- First Ionization energy - ΔH°_i - the energy needed to lose one electron in one mole of atoms in the gas phase (forming a positive ion)

- New:

- Electron affinity: (ΔH°_e) the enthalpy change when one mole of atoms attracts one mole of electrons (forming a negative ion).

Both on TABLE 8 of IB Data Booklet!!!

Some Math

- Ionization energy of sodium



- Electron affinity of chlorine



- Add the equations to find the total energy

Math Continued

- $\text{Na}_{(g)} + \text{Cl}_{(g)} \rightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \quad \Delta H^\circ = +147 \text{ kJ mol}^{-1}$
- What do you realize about this process?
- Endothermic!!
- Even though they are forming noble gas electron configurations!!

Something else must happen

- oppositely charged gaseous ions come together to form an ionic lattice structure
- $\text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \rightarrow \text{NaCl}_{(s)} \quad \Delta H^\circ = -790 \text{ kJ mol}^{-1}$
- exothermic! because there is a strong attraction between the ions

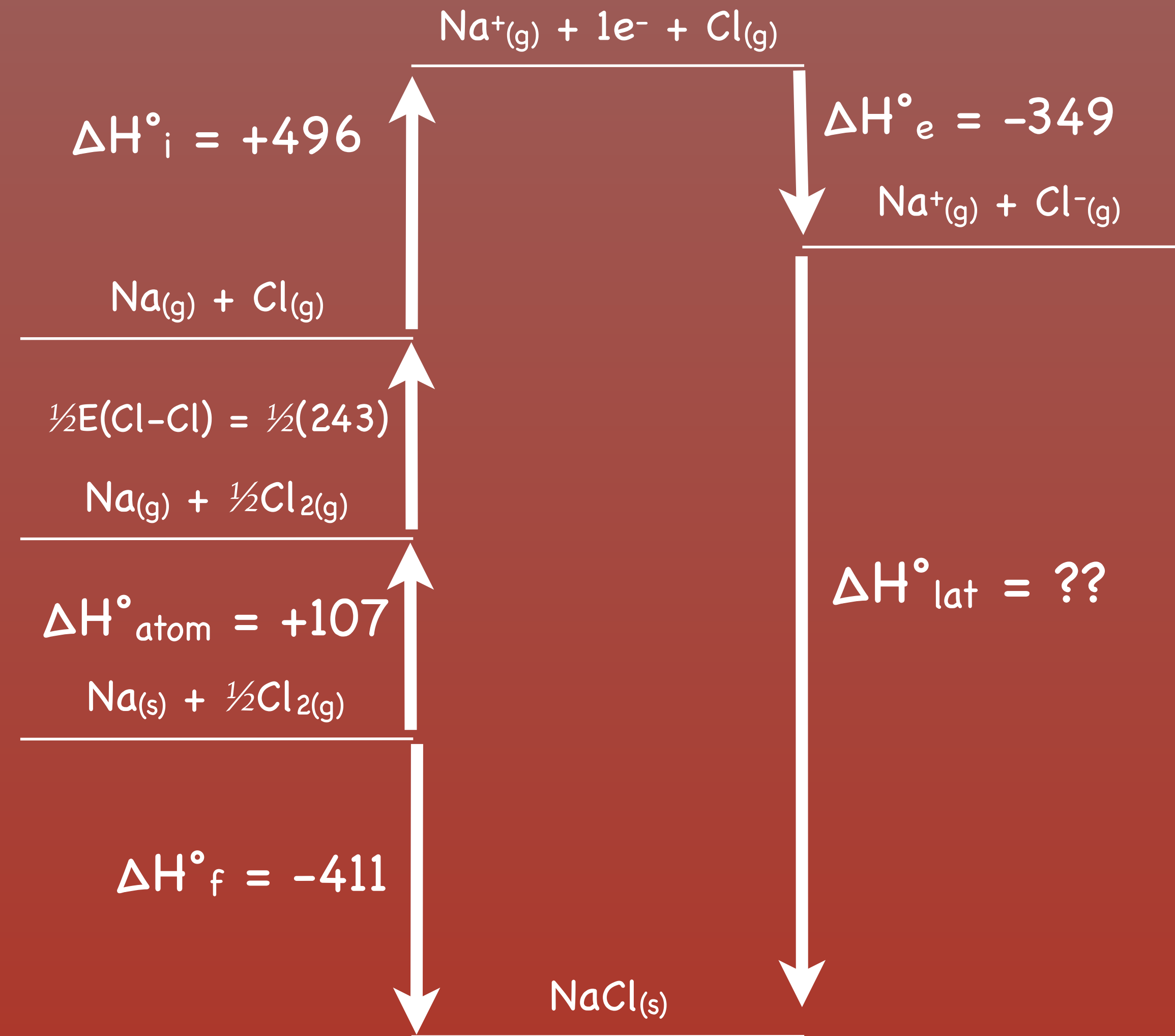
Lattice Enthalpy

- shows the enthalpy change in terms of the reverse, endothermic process - one mole of solid crystal breaking into gaseous ions
- $\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \quad \Delta H^\circ_{\text{lat}} = +790 \text{ kJ mol}^{-1}$
- How do we get from solid to an ionized gas?
 - What processes might need to occur?

Born-Haber Cycle

Step	$\Delta H^\circ/\text{kJ mol}^{-1}$
Sodium is atomized to form 1 mole of gaseous sodium ($\text{Na}_{(s)} \rightarrow \text{Na}_{(g)}$)	energy of atomization $\Delta H^\circ_{\text{atom}} = +107$
One mole of Cl atoms are formed as $\frac{1}{2}$ mole of Cl-Cl bonds break	$\frac{1}{2}E(\text{Cl-Cl}) = \frac{1}{2}(+243)$ (Table 11)
One electron is removed from the outer shell of a sodium atom $\text{Na}_{(g)} \rightarrow \text{Na}^+_{(g)} + e^-$	$\Delta H^\circ_i (\text{Na}) = +496$
One electron is added to the outer shell of a Chlorine atom $\text{Cl}_{(g)} + e^- \rightarrow \text{Cl}^-_{(g)}$	$\Delta H^\circ_e = -349$
Gaseous ions come together to form one mole of $\text{NaCl}_{(s)}$ $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}_{(s)}$	$\Delta H^\circ_{\text{lat}} = ?$

figure on page 240...



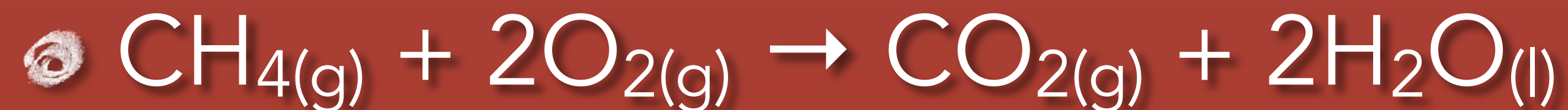
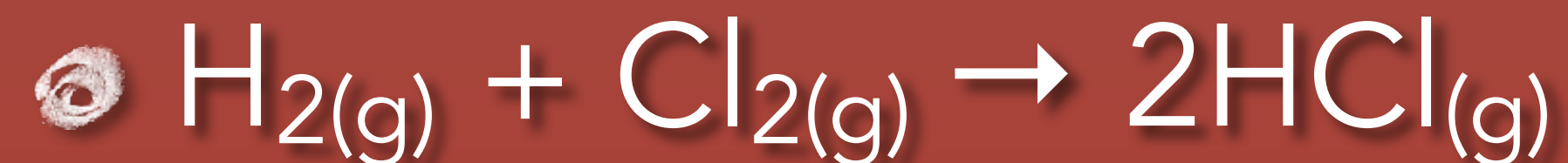
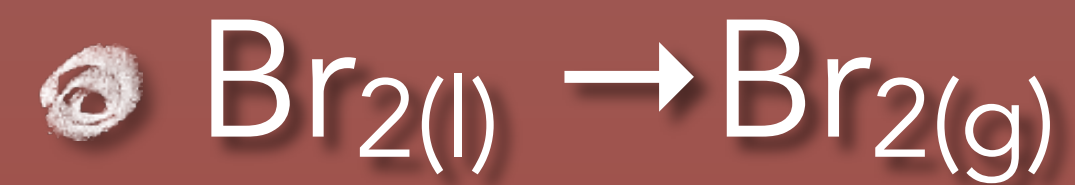
Your job now...

- Split into groups of 2-3 (MAX!)
- work through the example on page 241 #45
- Find out how a lattice enthalpy can be calculated from the ionic model
- Do practice problem #21
- Compare the difference between theoretical and experimental lattice energies (discuss ionic character)

Entropy

- degree of disorder in a system
- solid < liquid < aqueous < gas
- energy and matter tend to disperse and the universe becomes more disordered
- as time moves forward, matter and energy become more disordered, and the total entropy of the universe increases
- second law of thermodynamics

How does the entropy change?



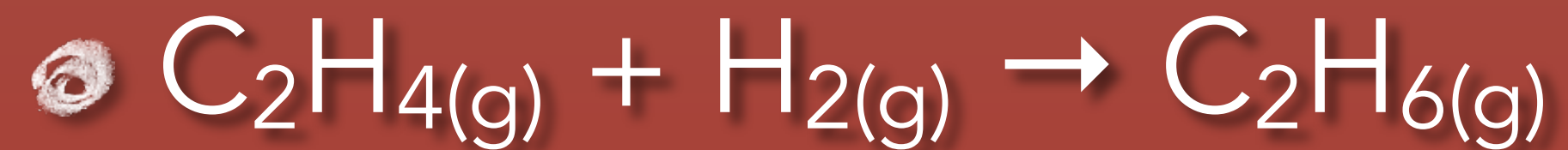
Absolute Entropy (S°)

- can be calculated (@ Standard condition)
- depends on temperature, pressure
- a perfectly ordered solid @ absolute zero has an absolute entropy of zero
- $\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$

Example...

- Calculate the entropy change for the hydrogenation of ethene using the entropy values given in Table 12 of your data booklet

$$\Delta S^\circ_{\text{Hydrogen}} = 131 \text{ J K}^{-1} \text{ mol}^{-1}$$



- Blue Problems: #54-61

Spontaneity (Gibbs Free Energy)

- Using enthalpy and entropy to determine the feasibility of a reaction

How does this increase entropy of the universe?



- $\Delta H^{\circ}_{\text{sys}} = -217 \text{ kJ mol}^{-1}$

- $\Delta S^{\circ}_{\text{sys}}$ approximately equal to zero

Some relationships....

- entropy directly proportional to enthalpy

- $\Delta S^\circ_{\text{surroundings}} \propto -\Delta H^\circ_{\text{system}}$

- entropy inversely proportional to absolute temperature

- $\Delta S^\circ_{\text{surroundings}} \propto 1/T$

Explaining the units of entropy

- $\Delta S_{\text{surroundings}} = -\Delta H_{\text{system}}/T$ (must be in Kelvin)

- $\text{J mol}^{-1} \text{K}^{-1}$

Using ΔG_{sys} to predict feasibility of change

- $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$
- Temperature can be thought of as the variable that adjusts the significance of ΔS_{sys}
- At low temperature: $\Delta G_{\text{sys}} \cong \Delta H_{\text{sys}}$ (as $T\Delta S \cong 0$)
 - \therefore all exothermic reactions can occur at low T
- At high temperature: $\Delta G_{\text{sys}} \cong -T\Delta S_{\text{sys}}$ (the T is high enough to make ΔH_{sys} negligible)
 - \therefore all reactions which have a positive ΔS_{sys} can be feasible at high temperatures even if they are endothermic

Gibbs Free Energy

$$\Delta H < 0$$

$$\Delta H > 0$$

$$\Delta S > 0$$

Spontaneous
at all T ($\Delta G < 0$)

Spontaneous
at high T
(when $T\Delta S$ is
large)

$$\Delta S < 0$$

Spontaneous
at low T (when
 $T\Delta S$ is small)

Non-
spontaneous
at all T ($\Delta G > 0$)

Spontaneity Scenarios

- Not! for memorization - should be able to work through the data to decide spontaneity

ΔH^\ominus	ΔS^\ominus	T	ΔG	Spontaneity
positive (endothermic)	positive (more disordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
positive (endothermic)	negative (more ordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous
negative (exothermic)	positive (more disordered products)	low	negative $\approx \Delta H^\ominus$	spontaneous
negative (exothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	low	negative $\approx -T\Delta S^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous

- (a) Give an equation for the boiling of water.
- (b) Predict a sign for the enthalpy change and entropy change for this process.
- (c) Predict a value for the sign of ΔG at low and high temperatures.
- (d) Suggest why water boils at 100 °C.
- (e) Use the entropy values in the table on page 252 to calculate the entropy change for this process.
- (f) Use the data below to calculate the enthalpy change for the process.

	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}(\text{l})$	-286
$\text{H}_2\text{O}(\text{g})$	-242

- (g) Deduce the boiling point of water from your calculations. Describe any assumptions you have made.

Calculating ΔG

- Two Routes:
- At temp other than 298K
 - $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$
- At standard conditions
 - $\Delta G_{\text{rxn}} = \sum \Delta G^{\circ}_f (\text{products}) - \sum \Delta G^{\circ}_f (\text{reactants})$
 - (same way ΔH°_f can be calculated)

Example:

• Calculate $\Delta G^\circ_{\text{rxn}}$ for the following reaction:



COMPOUND	ΔG°_f kJ mol ⁻¹
$\text{Fe}_2\text{O}_{3(s)}$	-742
$\text{Al}_2\text{O}_{3(s)}$	-1582

One more example..

- Calculate the ΔG_{rxn} for the thermal decomposition of calcium carbonate @ 298K from the following data

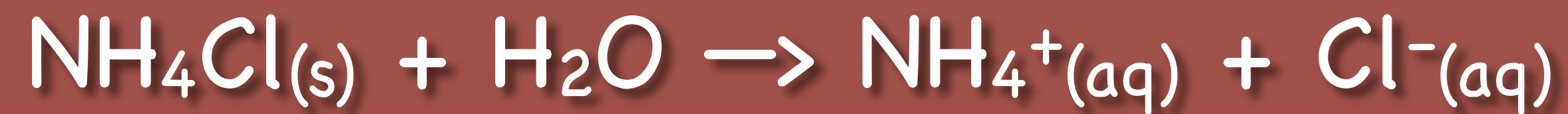
Compound	ΔH°_f kJ mol ⁻¹	ΔS°_f J K ⁻¹ mol ⁻¹
CaCO _{3(s)}	-1207	92.9
CaO _(s)	-635	39.7
CO _{2(g)}	-394	214

Hint: calculate ΔH , ΔS then ΔG

Compound	ΔH°_f kJ mol ⁻¹	ΔS°_f J K ⁻¹ mol ⁻¹
CaCO _{3(s)}	-1207	92.9
CaO _(s)	-635	39.7
CO _{2(g)}	-394	214



Enthalpies of Solution

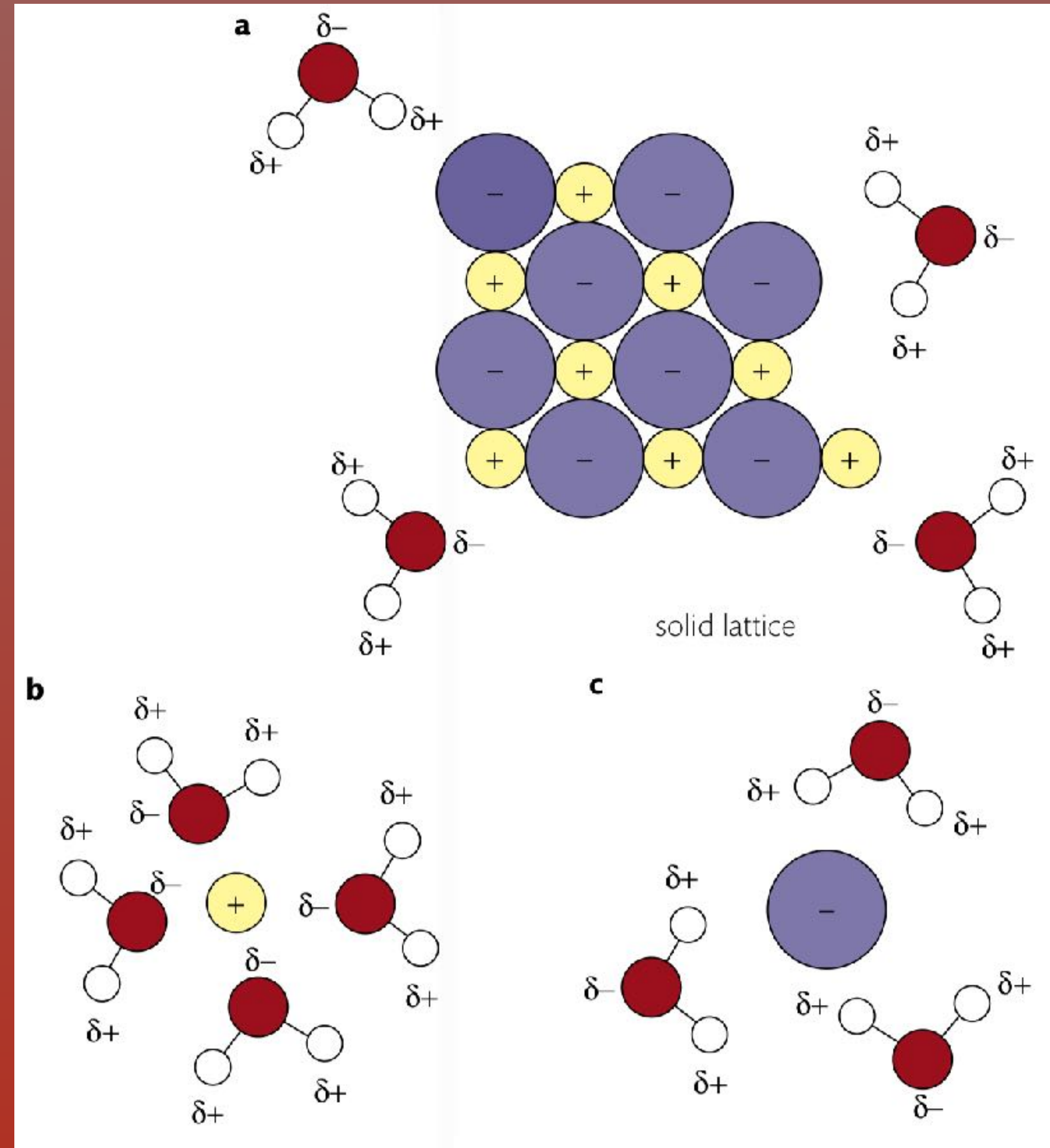


$$\Delta H^{\circ}_{\text{sol}} = +14.78 \text{ kJ mol}^{-1}$$

- Calculated by measuring temperature change in solution.
- Enthalpy of solution refers to the ideal situation of infinite dilution.

Enthalpies of Solution...continued

- NaCl and NH_4Cl dissolve readily due to strong attractions to the polar solvent water.
- Ions separate from the lattice are said to be **hydrated**.
- The strength of the interaction is given by **hydration enthalpy**.



Hydration Enthalpy

- Enthalpy changes when one mole of GASEOUS ions dissolve.
- Difficult to measure directly so... (done with a spectral technique)
- We use $\Delta H^0_{\text{hyd}} = H^+$



- Combine this value with hydration enthalpy of different compounds for individual ions.

Hydration Enthalpy

- Enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinitely dilute solution of one mole of aqueous ions.



- Exothermic process so enthalpy changes are negative.

Hydration Enthalpy

Cations	$\Delta H_{\text{hyd}}^{\ominus} / \text{kJ mol}^{-1}$	Anions	$\Delta H_{\text{hyd}}^{\ominus} / \text{kJ mol}^{-1}$
Li ⁺	-538	F ⁻	-504
Na ⁺	-424	Cl ⁻	-359
K ⁺	-340	Br ⁻	-328
Rb ⁺	-315	I ⁻	-287

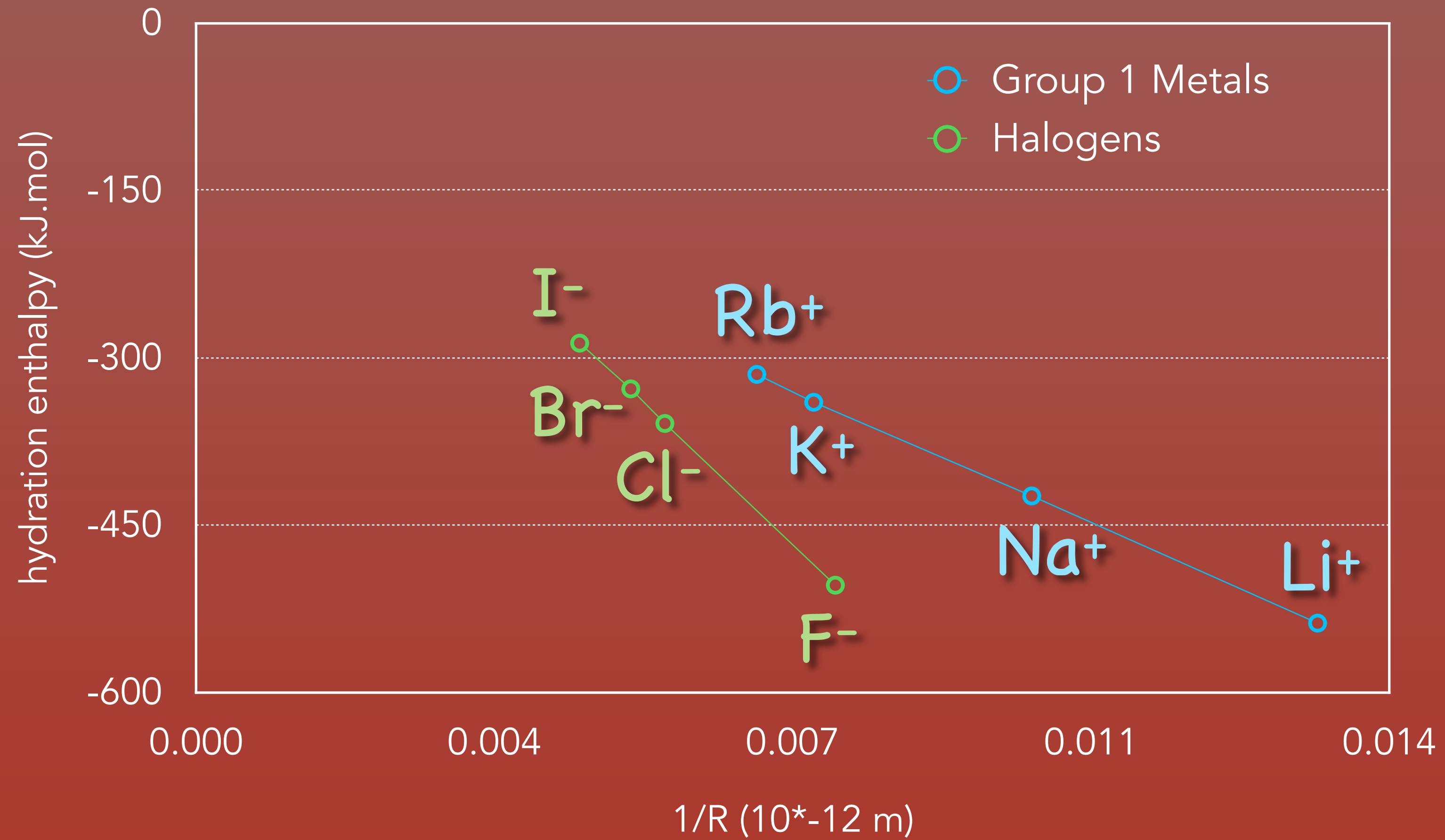
- Values become less exothermic as ionic radius increases.

$$\Delta H_{\text{hyd}}^{\ominus} \approx \frac{-A}{R_{\text{ionic}}}$$

Cations	$\Delta H_{\text{hyd}}^{\ominus} / \text{kJ mol}^{-1}$
Na ⁺	-424
Mg ²⁺	-1963
Al ³⁺	-4741

As charge increases, ionic radius decreases for Period 3 metals

Hydration Enthalpies



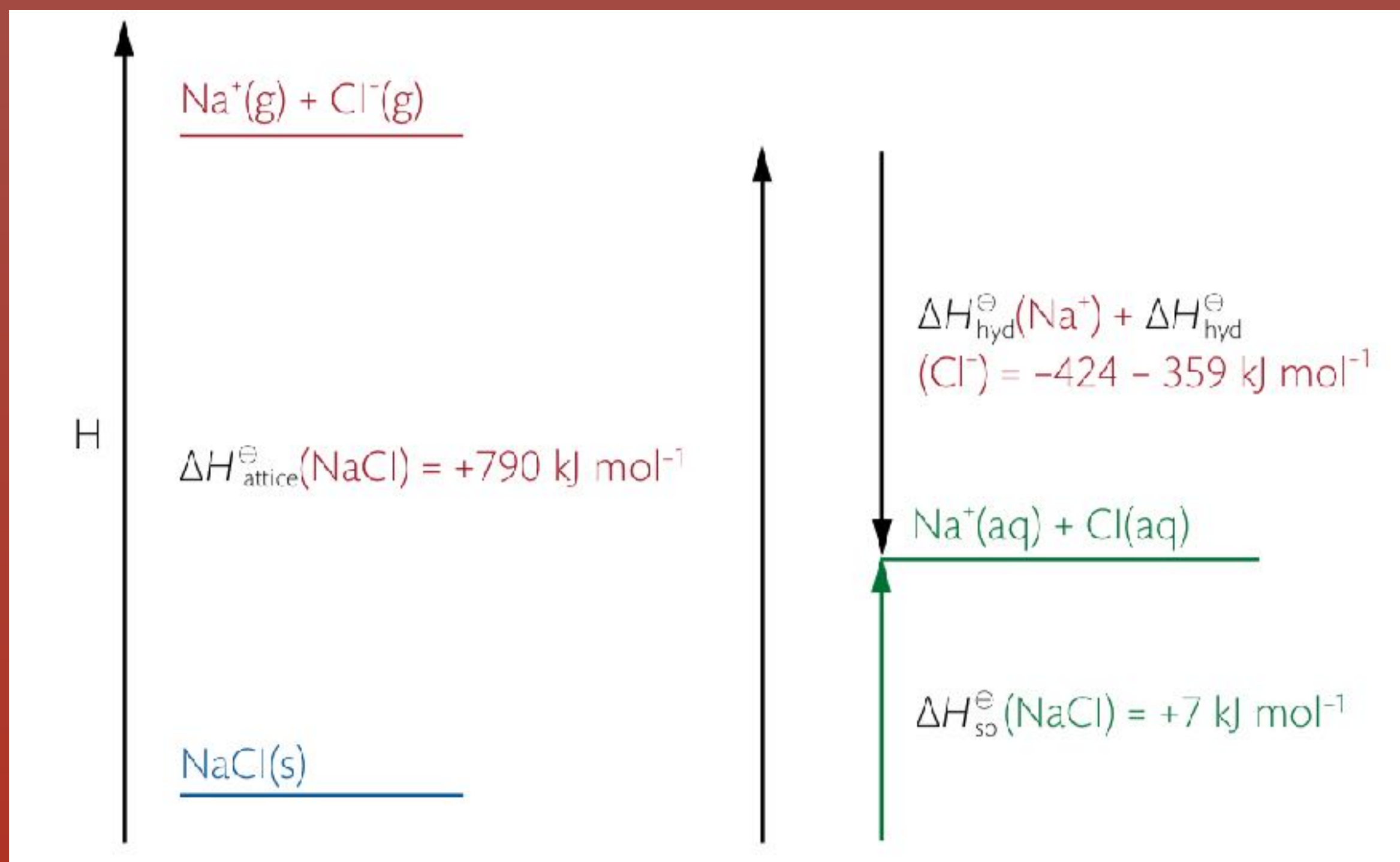
Hydration & Lattice Enthalpies

- Solid sublimed to gaseous ions and then plunged into water.

$$\Delta H^{\ominus}_{\text{sol}}(\text{NaCl}) = \Delta H^{\ominus}_{\text{lattice}}(\text{NaCl}) + \Delta H^{\ominus}_{\text{hyd}}(\text{Na}^+) + \Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$$

$$\Delta H^{\ominus}_{\text{sol}}(\text{NaCl}) = +790 - 424 - 359 \text{ kJ mol}^{-1}$$

$$\Delta H^{\ominus}_{\text{sol}}(\text{NaCl}) = +7 \text{ kJ mol}^{-1}$$



- Compare this value to that found in Table 19 of your data booklet.