Name:

Fuels and Heats of Reaction	Objectives				
21. Fuels and Heats of	define hydrogerhen				
Reaction	-define hydrocarbon -recall that coal, natural gas and petroleum are sources of hydrocarbons				
Reaction					
	-recall that decomposing animal and vegetable wastes are sources of methane				
	-recognise the hazards of methane production in slurry pits coalmines and refuse dumps				
	-discuss the contribution of methane to the greenhouse effect -define aliphatic hydrocarbon				
	-know what a homologous series is				
	-know that alkanes alkenes and alkynes are examples of homologous series				
	-apply the IUPAC system of nomenclature to the following homologous series: alkanes				
	(to C5), alkenes (to C4) and alkynes. (only ethyne to be considered) -define structural isomers				
	-draw the structural formulas and structural isomers of alkanes to C-5				
	-construct models of the alkanes (to C5), alkenes (to C4) alkynes (only ethyne to be				
	considered)				
	-draw the structural formulas of hexane, heptane, octane, cyclohexane and 2,2,4-				
	trimethylpentane				
	-draw the structural formulas and structural isomers of alkenes to C-4				
	-state the physical properties of aliphatic hydrocarbons [physical state, solubility				
	(qualitative only) in water and in non-polar solvents				
	-describe and explain what is observed during a demonstration of the solubility				
	properties of methane ethane and ethyne in polar and non-polar solvents				
	-define aromatic hydrocarbon				
	-describe the structure of benzene, methylbenzene and ethylbenzene				
	-state the physical properties of aromatic hydrocarbons [physical state, solubility				
	(qualitative only) in water and in non-polar solvents				
	-describe and explain what is observed during a demonstration of the solubility				
	properties of methylbenzene in polar and non-polar solvents				
	-recall that chemical reactions can have an associated change in temperature of the				
	system				
	-define endothermic and exothermic reactions				
	-describe and explain what is observed during a demonstration of an endothermic and				
	exothermic reaction				
	-explain why changes of state can be endothermic or exothermic				
	-define heat of reaction				
	-determine the heat of reaction of hydrochloric acid with sodium hydroxide				
	-define heat of combustion				
	-recognise that the combustion of alkanes and other hydrocarbons releases carbon				
	dioxide, water and energy				
	-write balanced chemical equations for the combustion of simple hydrocarbons				
	-relate the sign of enthalpy changes to exothermic and endothermic reactions				
	-relate energy changes to bond breaking and formation				
	-explain the concept of bond energy using the calculation of the C-H bond energy in				
	methane as an illustration				
	-define heat of combustion				
	-describe the use of the bomb calorimeter in determining calorific values of foods				
	-relate the kilogram calorific values of fuels to their uses				
	-define heat of formation				
	-state the law of conservation of energy				
	-state Hess's law				
	-calculate heat of reaction using heats of formation of reactants and products				

-calculate heat of formation using other heats of formation and one heat of reaction. (Other kinds of heat of reaction calculation not required)

- -describe the fractional distillation of crude oil
- -explain where the main fractions of crude oil (refinery gas, light gasoline, naphtha, kerosene, gas oil and residue fractions) are produced on the fractionating column -state the uses of refinery gas, light gasoline, naphtha, kerosene, and gas, oil and residue fraction
- -appreciate the rationale for the addition of mercaptans to natural gas
- -recall the composition of natural gas, liquid petroleum gas (LPG) and petrol
- -describe and explain: auto-ignition, knocking, octane number
- -relate the octane number of a fuel to its tendency to cause knocking in the internal combustion engine
- -describe the effect of chain length, degree of branching and cyclic structure on the tendency of petrol towards auto-ignition in the internal combustion engine -describe the role played by lead compounds as petrol additives in the past
- -explain isomerisation, dehydrocyclisation, catalytic cracking
- -describe the role of isomerisation, dehydrocyclisation, and catalytic cracking in the increase of the octane rating of fuel
- -oxygenates
- -prepare a sample of ethyne
- -recognise oxyacetylene welding and cutting as principle uses of ethyne (acetylene)
- -carry out an experiment to demonstrate the properties of ethyne (acetylene) [combustion, tests for unsaturation using bromine water and acidified potassium manganate(VII) solution]
- -describe the manufacture of hydrogen by:
- •electrolysis of water
- •steam reforming of natural gas (simple treatment only)
- -list some industrial uses of hydrogen including its potential as a fuel
- *Def*ⁿ: **Organic Chemistry** is the study of the compounds of carbon.
- Def^n : **Hydrocarbons** are compounds that contain carbon and hydrogen only.
- *Def*ⁿ: **Fossil Fuels** are fuels that were formed from the remains of dead plants and animals that lived millions of years ago.
- *Def*ⁿ: A **homologous series** is a series of compounds with similar chemical properties, a general chemical formula and with each successive member differing by CH₂.

The Alkanes:

This homologous series has only single bonds between the carbon atoms. They are saturated hydrocarbons and have tetrahedral geometry.

*Def*ⁿ: A **Saturated compound** is a compound in which there are only single bonds between its atoms.

In the following table showing the molecular formulae and structural formulae of the first 10 alkanes, note that each member is different to the next by CH₂ and there are only single bonds.

ALKANES:

No. of C atoms	Prefix	IUPAC Name	Molecular Formula	Structural Formula	
1	Meth-	Methane	CH ₄	H H-C-H H	
2	Eth-	Ethane	C_2H_6	H H H-C-C-H H H	
3	Prop-	Propane	C ₃ H ₈	H H H H-C-C-C-H H H H	
4	But-	Butane	C ₄ H ₁₀	H H H H-C-C-C-C-H H H H H	
5	Pent-	Pentane	C ₅ H ₁₂	H H H H 	
6	Hex-	Hexane	$\mathrm{C}_6\mathrm{H}_{14}$	H—O—C— H—O—C— H—O—C— H—O—H	
7	Hept-	Heptane	C7H16	H H H H H H 	
8	Oct-	Octane	C ₈ H ₁₈	H H H H H H H H H H H H H H H H H H H	
9	Non-	Nonane	C ₉ H ₂₀	H H H H H H H H I I I I I I I I I H-C-C-C-C-C-C-C-C-H I I I I I I I I H H H H H H H H	
10	Dec-	Decane	$C_{10}H_{22}$	H H H H H H H H H H H H H H H H H H H	

Notes:

- 1. The names of all of the alkanes end in –ane.
- 2. They all follow the general formula C_nH_{2n+2} .

Properties of Alkanes:

- 1. Soluble in non-polar solvents, e.g. cyclohexane.
- 2. Insoluble in water because the alkanes are non-polar they only have Van-der-Waals forces between the molecules.
- 3. C_1 - C_4 are gases. C_5 - C_{16} are liquids. C_{17} and above are waxy solids this is because the larger molecules have stronger Van-der-Waals forces, increasing their boiling and melting points.

*Def*ⁿ: **Structural isomers** are compounds that have the same molecular formulae but different structural formulae.

Example:

$$H - C - H$$
 $H + H + H + H + H$
 $H - C - C - C - C - H$
 $H + H + H + H - C - C - C - H$
 $H + H + H + H + H$
 $H + H + H + H$
 $H + H + H$
 $H + H + H$

The two compounds here are both made up using 4 carbon atoms and 10 hydrogen atoms. However, they are arranged differently. They are different compounds with different properties because of this and we therefore call these compounds *structural isomers* of each other.

Naming Alkanes:

Give the systematic IUPAC name for the following hydrocarbon:

Step 1: Identify the longest continuous carbon chain – name this parent molecule.

5 carbon chain \rightarrow pent-

Saturated compound – all single bonds → -ane
The parent molecule is **pentane**.

Step 2: Number the carbon chain starting from the end that gives the branches the lowest possible numbers.

Step 3: Indicate the type and position of the branches.

There are two methyl branches on C2 and C3, so we show this by writing 2,3-dimethyl

The name of the compound is **2,3-dimethylpentane**.

[Note: Put commas between numbers, dashes (-) between numbers and words, and NO spaces]

See other, more complex worked examples at https://bppchemistry.weebly.com/drawingnaming-hydrocarbons.html

Drawing Alkanes:

Draw the structural formula of 3-ethyl-2,5-dimethylhexane.

Step 1: From the name we see the parent alkane is hexane. We draw 6 carbons with single bonds between them and then number them from either side.

Step 2: Add the branches at the correct positions. The branches present (from the name) are:

- An ethyl group on C3
- A methyl group on C2
- A methyl group on C5

$$C_{2}H_{5}$$
 $C_{2}H_{5}$
 C_{3}
 C_{4}
 C_{5}
 C_{5}
 C_{6}
 C_{7}
 C_{7}
 C_{8}
 C_{8}
 C_{1}
 C_{1}
 C_{1}
 C_{1}
 C_{2}
 C_{3}
 C_{4}
 C_{5}
 C_{6}
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 C_{3}
 C_{4}
 C_{1}
 C_{1}
 C_{1}
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 C_{3}
 C_{4}
 $C_$

Step 3: Fill in hydrogens to ensure that every carbon has 4 bonds.

The Alkenes:

This homologous series has a double bond between two of the carbon atoms. They are unsaturated hydrocarbons and have planar geometry.

 Def^n : An **Unsaturated compound** is a compound which contains one or more double or triple bonds between its atoms.

In the following table showing the molecular formulae and structural formulae of the first 4 alkenes, note that each member is different to the next by CH_2 and there is a double bond.

ALKENES:

No. of C atoms	Prefix	Double Bond Location	IUPAC Name	Molecular Formula	Structural Formula
2	Eth-	C1	Ethene	C_2H_4	H H C=C H H
3	Prop-	C1	Propene	C ₃ H ₆	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
4	But-	C1	But-1-ene	C_4H_8	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
4	But-	C2	But-2-ene	C_4H_8	H H H H

Notes:

- 1. The names of the alkenes end in —ene, with the carbon where the double bond begins appearing in the name.
- 2. They all follow the general formula C_nH_{2n} .

Properties of Alkenes:

- 1. Soluble in non-polar solvents, e.g. cyclohexane.
- 2. Insoluble in water because the alkenes are non-polar they only have Van-der-Waals forces between the molecules.
- 3. C₁-C₃ are gases. C₄-C₁₄ are liquids. C₁₅ and above are waxy solids this is because the larger molecules have stronger Van-der-Waals forces, increasing their boiling and melting points.

Naming Alkenes:

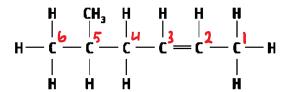
Give the systematic IUPAC name for the following hydrocarbon:

$$H - C - C - C - C = C - C - H$$

Step 1: Identify the longest continuous carbon chain containing the C=C double bond. This is the parent molecule.

6 carbon chain → hex-Unsaturated compound – C=C double bond → -ene The parent molecule is **hexene**.

Step 2: Number the carbons in the parent molecule from the side closest to the double bond. Put the position of where the C=C double bond *begins* into the name of the compound.



C=C begins on C2 \rightarrow Hex-2-ene

Step 3: Indicate the type and position of the branches.

There is a methyl branch on C5, so we show this by writing **5-methyl**

The name of the compound is **5-methylhex-2-ene**.

Cyclic Hydrocarbons:

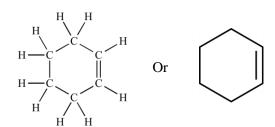
When a hydrocarbon's longest chain of carbon atoms forms a closed ring, we begin its IUPAC name with "cyclo".

For example:

$$\begin{array}{c|c}
H & H & H \\
H & C & C & H \\
H & C & C & H \\
H & C & C & H \\
H & H & H
\end{array}$$
Or

Cyclohexane contains six carbon atoms, singly bonded, in a closed ring.

Note: In the second structure, each point/vertex represents a carbon atom, each line represents a single bond, and hydrogens are left out.



Cyclohexene contains six carbon atoms, with a C=C double bond, in a closed ring.

Note: The double-line in the second structure represents the C=C double bond.

The Alkynes:

This homologous series has a triple bond between two of the carbon atoms. They are unsaturated hydrocarbons. They have planar geometry.

There is only one alkyne on the LC course and it is ethyne (old name *acetylene*)

No. of C atoms	Prefix	IUPAC Name	Molecular Formula	Structural Formula
2	Eth-	Ethyne	C_2H_2	H—C≡C—H

Notes:

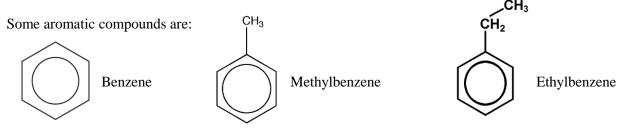
- 1. The names of the alkenes end in –yne.
- 2. They all follow the general formula C_nH_{2n-2} .
- 3. Ethyne is used in *oxyacetylene* for welding and cutting metal. Ethyne and oxygen burn at a very high temperature.

Properties of Alkynes:

- 1. Soluble in non-polar solvents, e.g. cyclohexane.
- 2. Insoluble in water because the alkynes are non-polar they only have Van-der-Waals forces between the molecules.

The Aromatic Hydrocarbons:

Defⁿ: Aromatic compounds are compounds which contain a benzene ring. (More detail given in Ch. 22)

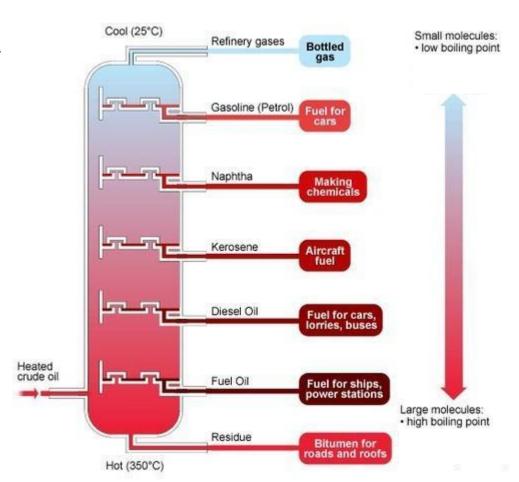


OIL REFINING:

Crude oil is made up of a mixture of different hydrocarbons. **Fractional distillation** is used to separate these different hydrocarbons into groups called fractions, based on their boiling points.

<u>How does fractional distillation</u> <u>work?</u>

- 1. Hot, vaporised crude oil enters the bottom of the column.
- 2. The column has a high temperature at the bottom and a low temperature at the top.
- 3. Larger molecules have higher boiling points.
- 4. Large molecules condense and are collected near the bottom of the column.
- Smaller molecules condense and are collected further up the column where it is cooler.



Note: The refinery gas fraction is collected and bottled under pressure as **LPG** (**Liquified Petroleum Gas**). This consists of propane and butane and is used for cooking. Sulphur compounds called **mercaptans** are added to LPG in order to give it a smell so that leaks can be detected.

Natural gas does **not** come from the fractional distillation of crude oil. It is found on its own in in porous rock deep underground. Natural gas consists of methane and ethane and also has **mercaptans** added.

OCTANE NUMBER:

Defⁿ: The **octane number** of a fuel is a measure of its tendency to resist autoignition (knocking).

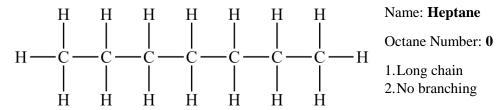
Defⁿ: Autoignition is the premature ignition of a fuel-air mixture before a spark is produced.

When a petrol engine uses a fuel with a low octane number, the fuel can autoignite, causing:

- 1. Excess wear on the engine
- 2. Loss of power.

Reference Hydrocarbons:

There are two reference hydrocarbons used to give a fuel its octane number:



Name: 2,2,4-trimethylpentane

Octane Number: 100

Short chain
 Branching

When you see a petrol pump that says "Octane 95", that means the fuel has the same tendency to autoignite as a mixture of 95% 2,2,4-trimethylpentane and 5% heptane.

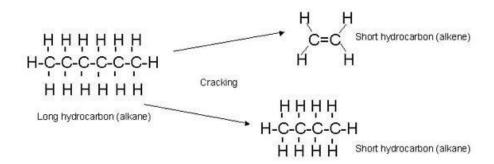
Factors that affect Octane Number:

- 1. Length of chain: Shorter carbon chains have higher octane numbers.
- 2. **Degree of branching:** The more branching a hydrocarbon has, the higher its octane number.
- **3. Presence of rings:** Ring structures give a fuel a higher octane number. Benzene rings have higher octane numbers again.

Processes that Raise the Octane Number of a Fuel:

1. Isomerisation: This involves changing straight chain alkanes into their branched isomers to raise octane number.

2. Catalytic Cracking: This involves using heat and a catalyst to break down long chain hydrocarbons into short chain molecules. This is done because there is higher demand for shorter chain molecules with higher octane numbers. One of the products of catalytic cracking will always be an alkene.



3. Dehydrocyclisation: This involves using catalysts to change linear molecules into cyclic molecules, and cyclic molecules into aromatic compounds. Hydrogen gas is also formed.

- **4. Adding Oxygenates:** This is the addition of oxygen-containing compounds to a fuel in order to raise its octane number and make it burn "cleaner" as less carbon monoxide is formed when it is burned. Examples of oxygenates are *methanol*, *ethanol* and *MTBE* (*methyl tertiary-butyl ether*).
- 5. Addition of lead (Pb) [BANNED in 2000]: Lead compounds (tetraethyl lead) used to be added to petrol to increase its octane number. This has been banned because lead is a poisonous health hazard and poisons the metals in a car's catalytic converter. This is why petrol pumps say "Unleaded".

HYDROGEN AS A FUEL:

There are two ways to produce hydrogen gas for use as a fuel:

1. Steam Reforming of Natural Gas:

Steam is reacted with natural gas using a catalyst:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

2. Electrolysis of Water:

An electric current is passed through water:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

This method of producing hydrogen is too expensive to be practical.

Uses of hydrogen:

- 1. Used to produce ammonia (NH₃) [see Ch. 17)
- 2. Used to hydrogenate vegetable oils to produce margarine.
- 3. Burned as a fuel because it is environmentally friendly its only waste product is water:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Note: Hydrogen forms a very explosive mixture with air and is therefore difficult to store and transport safely, without risk of explosion.

THERMOCHEMISTRY:

*Def*ⁿ: An **exothermic** reaction is one that gets hotter (produces heat).

*Def*ⁿ: An **endothermic** reaction is one that gets cooler (absorbs heat).

 Def^n : **Heat of reaction** (Δ **H**) is the heat change when the number of moles of the reactants indicated in the balanced chemical equation for the reaction react completely.

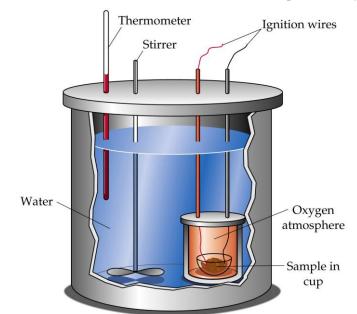
Notes:

- 1. If the ΔH value is negative, the reaction is exothermic and gets hotter.
- 2. If the ΔH value is positive, the reaction is endothermic and gets cooler.

Heat of Combustion:

 Def^n : **Heat of combustion** (Δ **H**) is the heat change when *one mole* of a substance is burned completely in excess oxygen.

The heat of combustion of a substance can be experimentally measured using a *Bomb Calorimeter*:



- 1. The sample to be tested is placed into the metal bomb along with pressurised oxygen gas.
- 2. Ignition wires ignite the sample.
- 3. The burning sample heats the water up.
- 4. The stirrer ensures the heat is evenly spread.
- 5. The thermometer reads the increase in the water temperature.
- 6. The heat of combustion can then be calculated. $\Delta H = mc\Delta T$ [used later in experiment 22]

Writing Balanced Equations for Heat of Combusion:

Write a balanced equation for the combustion of propane.

Note: All hydrocarbons need oxygen to combust, and the products formed will always be carbon dioxide and water. Therefore, combustion equations will always be of the form:

FUEL +
$$O_2 \rightarrow CO_2 + H_2O$$

So our equation is:

$$C_3H_8 + O_2 \rightarrow CO_2 + H_2O$$

Finally, balance this equation: [Hint – balance C first, then H, and finally O atoms]

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Note: You MUST have only 1 mole of fuel in your equation, as Heat of Combustion is defined in terms of 1 mole of fuel.

*Def*ⁿ: The **Kilogram Calorific Value** of a fuel is the heat energy produced when 1 kg of the fuel is burned completely in oxygen.

Bond Energy:

 ΔH comes from the fact that, in a reaction, covalent bonds are broken and new ones are formed. Breaking bonds requires energy. Making bonds releases energy. By calculating how much energy is needed to break the bonds and how much energy is given off by making the new bonds, we can calculate ΔH .

*Def*ⁿ: **Bond Energy** is the average energy required to break one mole of a particular covalent bond and to separate the neutral atoms completely from each other.

Heat of Neutralisation:

 Def^n : **Heat of Neutralisation** (Δ **H**) is the heat change when *one mole* of H⁺ ions from an acid reacts with *one mole* of OH⁻ ions from a base.

Note: 1 mole of HCl will produce 1 mole of H⁺ ions when in solution, which makes calculations straightforward.

However, 1 mole of H_2SO_4 produces 2 moles of H^+ ions when in solution, meaning the ΔH calculated must be divided by 2, as the definition specifies that Heat of Neutralisation involves 1 mole of H^+ .

Heat of Formation:

 Def^n : The **Heat of Formation** (Δ **H**) of a compound is the heat change that takes place when *one mole* of the compound is formed from its elements in their standard states.

Note: By "elements in their standard states" we mean how they exist in nature. Remember, for "Hydrogen and the Secret 7" the elements exists as diatomic molecules (e.g. H₂, N₂, O₂, Cl₂, etc.,). All other elements are monoatomic (e.g. C, Na, Al, Ca, etc.,)

Writing Balanced Equations for Heat of Formation:

Write balanced equation for the formation of methane from its elements in their standard states.

To approach this, we look at the elements present in methane (CH₄): C and H.

The standard state of each of these elements are C and H_2 . \leftarrow These will become the left hand side of our equation:

$$C + H_2 \rightarrow CH_4$$

Finally, balance, making sure methane has a coefficient of 1, to keep with the definition:

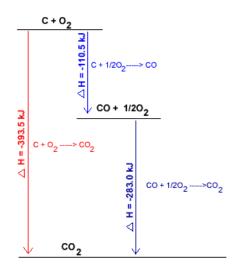
$$C + 2H_2 \rightarrow CH_4$$

Hess's Law:

*Def*ⁿ: **Hess's Law** states that the heat change for a reaction is independent of the pathway taken.

*Def*ⁿ: The **Law of Conservation of Energy** states that energy cannot be created or destroyed, but can be converted from one form to another.

Using Hess's Law we can calculate the heat change for reactions, if we are given the heat changes for related reactions.



Hess's Law Calculation:

Calculate the heat of formation of methane given that the heats of formation of carbon dioxide and water, respectively, are -393 kJ mol⁻¹ and -286 kJ mol⁻¹ and the heat of combustion of methane is -879 kJ mol⁻¹.

Step 1: Identify what you are being asked to calculate. This will ALWAYS either be (i) a heat of reaction for a given balanced equation, (ii) a heat of formation or (iii) a heat of combustion. This may involve writing your own chemical equation.

We are asked here to calculate the heat of formation of methane. We were not given a balanced chemical equation so we need to write the balanced equation for the formation of methane from its elements in their standard states. Methane's chemical formula is CH₄.

$$C + 2H_2 \rightarrow CH_4$$

Step 2: Write down the balanced chemical equations for the other pieces of information we have been given. We need to write down the formation equations for carbon dioxide and water, and the combustion equation for methane.

		$\Delta H (kJ \text{ mol}^{-1})$
1.	$C + O_2 \rightarrow CO_2$	-393
2.	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-286
3.	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-879

Step 3: Match one element/compound in each of the 3 equations above to our main equation. If, in one of the 3 equations, there are two chemicals that also appear in the main equation, use the more complicated of the two.

For eqⁿ 1:

C appears in both eqⁿ 1 and the main equation. They both have the same coefficient (1 in this case) and they both appear on the same side of the arrow (both on the left). This means we can keep eqⁿ as it is:

Eqⁿ 1:
$$C + O_2 \rightarrow CO_2$$
 $\Delta H = -393 \text{ kJ mol}^{-1}$

For eqⁿ 2:

 H_2 appears both in eqⁿ 2 and in the main equation. They both appear on the same side of the arrow (both on the left). To make their coefficients match we need to multiply eqⁿ by 2. To do this we multiply everything in eqⁿ by 2, including the value for ΔH .

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2 O$$
 $\Delta H = -286 \text{ kJ mol}^{-1}$ (x2)
 $Eq^n 2: 2H_2 + O_2 \rightarrow 2H_2 O$ $\Delta H = -572 \text{ kJ mol}^{-1}$

For eqⁿ 3:

 CH_4 appears in both eqⁿ 3 and in the main equation. They have the same coefficient, so we don't need to multiply. However, they appear on opposite sides of the arrow. This means we "flip" eqⁿ 3 around the arrow, and change the sign of ΔH .

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
 $\Delta H = -879 \text{ kJ mol}^{-1}$ (flip)
 $Eq^n 3: CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$ $\Delta H = +879 \text{ kJ mol}^{-1}$

Step 4: Rewrite your adjusted 3 equations and add: [cancel species that appear on both sides of the arrow]

		$\Delta H (kJ \text{ mol}^{-1})$
1.	$C + \mathcal{O}_2 \rightarrow C\mathcal{O}_2$	-393
2.	$2H_2 + Q_2 \rightarrow 2H_2O$	-572
3.	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	+879
•	$C + 2H_2 \rightarrow CH_4$	-86

Note: We know this is the correct solution as our final equation is the same as our main equation.

See other, more complex worked examples at https://bppchemistry.weebly.com/hesss-law-calculations.html