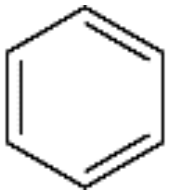
UNDERSTANDING BENZENE STRUCTURE

LESSON 3 **SOME FURTHER EVIDENCE**

From the last two LESSONS, you have discovered that;



- the **molecular formula of benzene is C_6H_6**
- There are many possible structures that could have the formula **C_6H_6**
- ***Kekulé*** suggested a structure that we refer to as ***Kekulé benzene.***
- There are reasons to doubt this proposed theoretical structure. These include,
    - Failure to react with **bromine water**
    - **Bond lengths between carbons are all equal** AND **between the length of a C-C and C=C**

Stretch and Challenge conclusions also show that $\Delta_a H$ data can be used in conjunction with **mean bond enthalpies** to show that ***Kekulé benzene*** is **thermodynamically less stable than real benzene. This evidence is not required by OCR!**

This week we will look at another key piece of evidence that you will need to know and understand. This will cast further doubt on the ***Kekulé benzene*** structure.

3. Enthalpy of Hydrogenation

Hydrogenation is a very important reaction in organic chemistry. The simplest example is:

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$

1. What type of organic reaction is this? addition
2. What catalyst is typically used in this reaction? nickel
3. What is the atom economy of this reaction? 100%
4. 7.00g of ethene was placed in a reactor vessel with a catalyst.

   Hydrogen was then added from a container in which it was stored at **5000 kPa** and at **18°C**. What **volume** of hydrogen in cm^3 would need to be added if it was at this temperature and pressure?

   V= *n*RT/p

   n=7.00g / 28.0g mol^{-1}= **0.250**mol

   ***R*= 8.314** *J $mol^{-1}K^{-1}$*

   T= 18+ 273 = **291** K

   ***P*= 5 x 10^6** Pa V= **0.25 x 8.314 x 291/5 x 10^6** = **1.21 x $10^{-4}m^3$**

   1.21 x 10^{-4}x 1 000 000 = **121 cm^3** of gas produced

Volume of hydrogen **121 cm^3**

Consider the following hydrogenation reaction:

5. Draw the skeletal formula of the product of the reaction in the space, above.

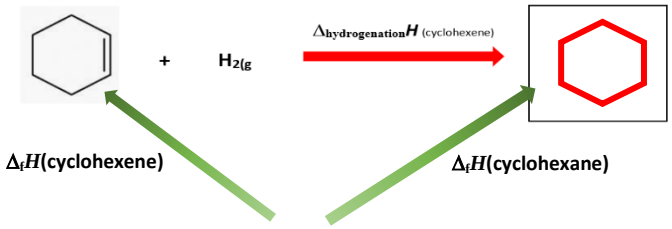
We now need to calculate the value for this **enthalpy change**, $\Delta_{hydrogenation}H$ (cyclohexene).

We can do it in **two possible ways** thanks to Hess's Law.

Here is some relevant data.

Chemical	Enthalpy of **formation**, $\Delta_f H$ /kJ mol^{-1}	Enthalpy of **combustion**, $\Delta_c H$ /kJ mol^{-1}
hydrogen	**…….**	**-286**
cyclohexane	**-156.4**	**-3920**
cyclohexene	**-38.2**	**-3752**
cyclohex-1,3-diene	**+71.41**	**-3576**
benzene	**+48.7**	**-3273**

6. Fill in the blank cell in the table!
7. Draw a Hess Cycle that uses the **enthalpies of formation** to calculate the enthalpy change for the hydrogenation of cyclohexene**.** It has been started for you. Then calculate the value**.**



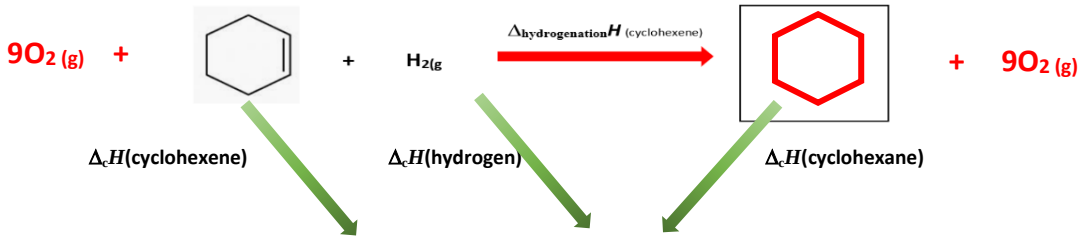
6 C$_{(s)}$ + 6H$_{2(g)}$

$\Delta_{hydrogenation}H$(cyclohexene) = $(-\Delta_f H$(cyclohexene)$)$ + $(\Delta_f H$(cyclohexane)$)$

= (- -38.2) + (-156.4) = -118.2 kJ mol^{-1}

$\Delta_{hydrogenation}H$(cyclohexene) **-118 kJ mol-1**

8. Draw a Hess Cycle that uses the **enthalpies of combustion** to calculate the enthalpy change for the hydrogenation of cyclohexene**.** Then calculate the value**.**



6CO$_{2\,(g)}$ + 6H$_2$O$_{(l)}$

$\Delta_{hydrogenation}H$(cyclohexene) = (Δ_cH(cyclohexene)) + (Δ_cH(hydrogen)) + (- Δ_cH(cyclohexane))

= (-3752) + (-286) + (- -3920) = -118 kJ mol^{-1}

$\Delta_{hydrogenation}H$(cyclohexene) **-118 kJ mol^{-1}**

The answers for $\Delta_{hydrogenation}H$(cyclohexene) should be **pretty close!**

9. Now, using Δ_fH data, **repeat** this exercise to calculate the $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene)

The Hess cycle using combustion data must include **2 x $\Delta_cH_{(H_2)}$**

enthalpy of hydrogenation using formation data $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene)… **-227 kJ mol^{-1}**

enthalpy of hydrogenation using combustion data $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene)… **-228 kJ mol^{-1}**

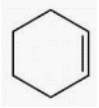
10. Finally, **repeat** this exercise to calculate the $\Delta_{hydrogenation}H$(benzene)

The Hess cycle using combustion data must include **3 x $\Delta_cH_{(H_2)}$**

enthalpy of hydrogenation using formation data $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene)… **-205 kJ mol^{-1}**

enthalpy of hydrogenation using combustion data $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene)… **-211 kJ mol^{-1}**

So, you now have calculated three **enthalpies of hydrogenation for cyclohexene, cyclohexa-1,3-diene and benzene** using experimental data. Write the values below.

Enthalpy of hydrogenation of **cyclohexene,**  $\Delta_{hydrogenation}H$(cyclohexene) **-118** kJ mol^{-1}

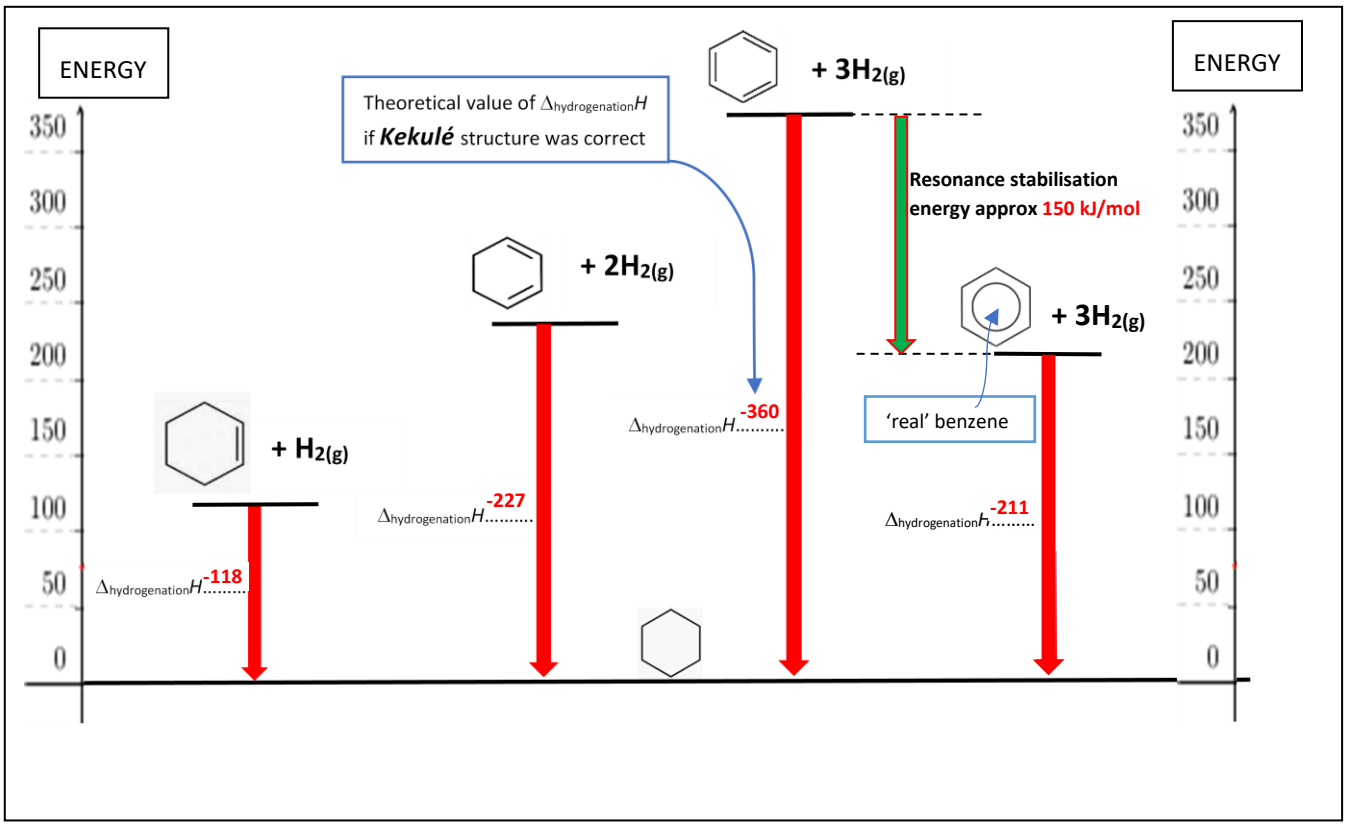
Enthalpy of hydrogenation of **cyclohexa-1,3-diene,**  $\Delta_{hydrogenation}H$(cyclohexa-1,3-diene) **-227** kJ mol^{-1}

Enthalpy of hydrogenation of **benzene,**  $\Delta_{hydrogenation}H$(benzene) **-211** kJ mol^{-1}

11. If you had only calculated the values for **enthalpies of hydrogenation for cyclohexene** and **cyclohexa-1,3-diene,** what would you **predict** the value of **enthalpy of hydrogenation for benzene** to be if the ***Kekulé benzene* structure** was correct, i.e. cyclohexa-1,3,5-diene?

3 x value for cyclohexene = appro **-360** kJ mol^{-1}

Now we are going to draw a diagram that clearly illustrates that 'real benzene' must be significantly more chemically stable than the structure that ***Kekulé*** proposed.



12. On the diagram above, draw a fourth **arrow** that would represent the true **enthalpy of hydrogenation for benzene** that you calculated in question 10. It is 'true' because it was obtained experimentally. Think about where the level would be on the diagram. The arrow has been started for you. Represent 'real benzene' using the following structure. 

13. Calculate the difference between the predicted value for $\Delta_{hydrogenation}H$(Kekulé benzene) and the actual value for $\Delta_{hydrogenation}H$('real' benzene) obtained from **experimental data**.

149 kJ mol^{-1} Depending on which enthalpy of hydrogenation use choose!

The conclusion is that 'real' benzene is around 150 kJ mol^{-1} **more stable** that the Kekulé benzene.

Next LESSON, we will consider a structure of benzene that is consistent with these 3 pieces of evidence that have been discussed. To do this we will introduce a modification to the standard covalent bond.