CHEM 230 SEMESTER 01-2015 HOMEWORK 3

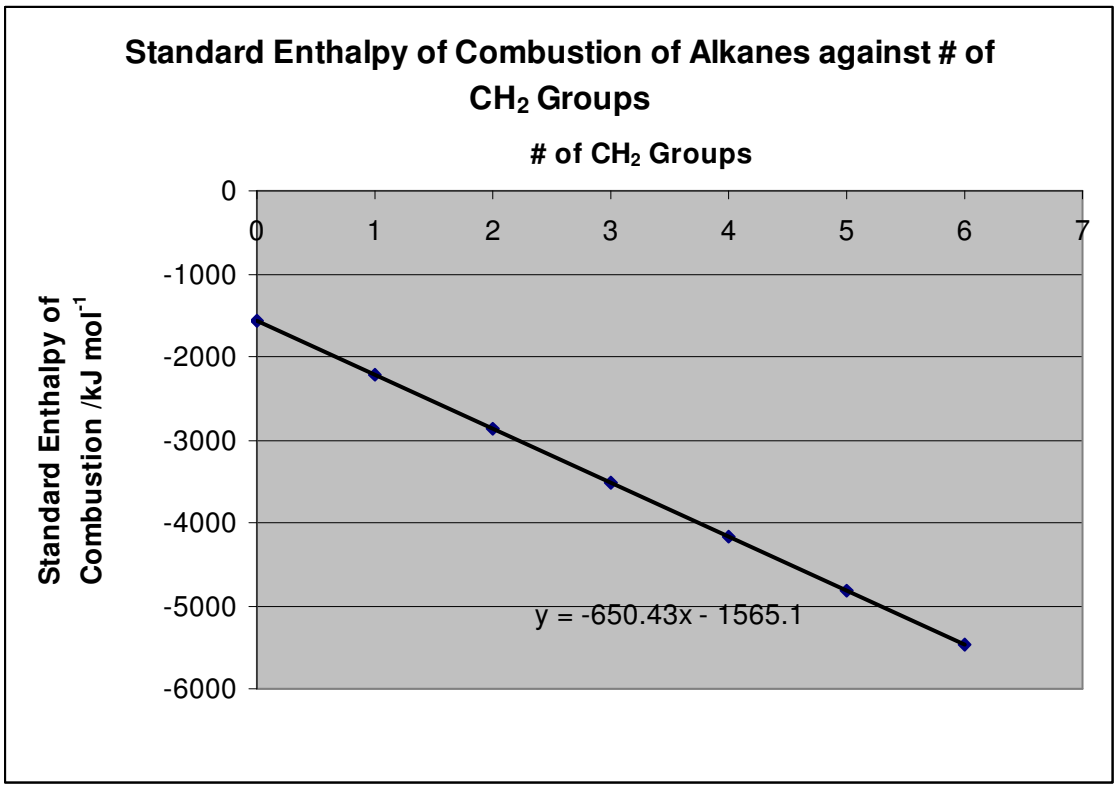
Print out this homework on letter sized paper. Answer the questions carefully (not on this sheet) and then submit your answers on Monday morning at the start of class. Note that if there is clear evidence of copying, the whole exercise may attract a zero mark, and the matter may be reported to the authorities.

1) The standard enthalpies of combustion of some *normal* (unbranched) alkanes at 25°C are given below:

Alkane	Molecular formula	$\Delta H_c^\ominus$ /kJ mol^{-1}
ethane	C_2H_6	-1560
propane	C_3H_8	-2219
butane	C_4H_{10}	-2877
pentane	C_5H_{12}	-3509
hexane	C_6H_{14}	-4163
heptane	C_7H_{16}	-4817
octane	C_8H_{18}	-5470

a) Using Excel, or otherwise, plot a graph of $\Delta H_c^\ominus$ against number of CH_2 (not CH_3) groups. (For help, see footnote[1] below.) From your graph determine the (average) value of $\Delta H_c^\ominus$ per CH_2 group. (The equation gives you the values you need.)

Answer: (1a) (5)



The value of the standard enthalpy of combustion per CH_2 group is given by the slope of the line, -650.5 kJ mol^{-1}. (1)

b) The difference between $\Delta H_c^\ominus$(pentane) and $\Delta H_c^\ominus$(butane) is 632 kJ mol^{-1}, somewhat different from your

[1] On older versions of Excel it is a little tricky to choose the values to put on the *x*-axis. Choose *scatter plot* as the type of chart. Select the $\Delta H_c^\ominus$ values to plot. Insert the chart in the spread sheet and then right-click on one of the data points. Select *source date*, select *series*, and, with the cursor in the box for *x-values* (which should be empty), select the required values. Click on OK. Right-click on one of the data points again, select *add trendline* and *linear*. Now click on *options* and check *display equation on chart*.

average value. Explain this difference by considering the states of the reactants.

Answer: (1b) (2)

Butane is a gas under standard conditions, whereas pentane, and subsequent alkanes are liquids. Some of the heat given out by the combustion of pentane is used to vaporize the liquid and so its enthalpy of combustion is a bit less exothermic. This gives a smaller difference between pentane and butane than in the other cases.

2) The catalytic hydrogenation of alkenes is exothermic and its value depends to some extent on how the alkene is substituted, as shown below:

Situation of double bond	Description of alkene	$\Delta H_H^\ominus$ / (average over many different molecules)[2]
	unsubstituted	-32.5
	monosubstituted	-30.0
	*cis*-disubstituted	-28.2
	*gem*-disubstituted	-27.9
	*trans*-disubstituted	-27.4
	trisubstituted	-26.8
	fully substituted	-26.3

a) Which are the least and most stable types of alkene? Explain your choice and calculate the percentage difference, in terms of energy, between the least and most stable forms.

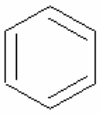
Answer: (2a) (4)

The unsubstituted alkene is the least stable and the fully substituted alkenes are the most stable. This is shown by standard enthalpies of hydrogenation. The most stable one has lowest energy, and therefore least energy (26.3 kcal mol^{-1}) is released when it is hydrogenated. The least stable one has highest energy, so the most energy (32.5 kcal mol^{-1}) is released when it is hydrogenated.

The difference between the least and most stable forms is given by 32.5 - 26.3 = 6.2 kcal mol^{-1} (differences are not signed). One may express this as a percentage of the largest value, the smallest value, or best, the average of the two, (32.5+26.3)/2 = 29.4. Thus the percentage works out to 6.2/29.4= 21.4% (2)

b) Calculate the $\Delta H_H^\ominus$ value for the hypothetical molecule, 1,3,5-cyclohexatriene. (Like benzene, but with alternate double and single bonds.) Explain the difference between your calculated value and the observed $\Delta H_H^\ominus$ value for benzene of -49.8 kcal mol^{-1}.

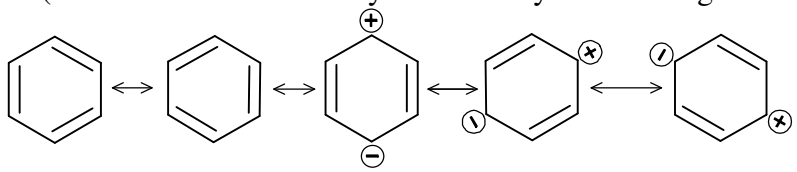
Answer: (2b) (5)

1,3,5-cyclohexatriene has structure  ,which appears to be the same as that of benzene, but has 3 discrete *cis*-disubstituted double bonds, whose standard enthalpy of hydrogenation (from the table) is -28.2 kcal mol^{-1} each. Hence the predicted standard enthalpy of combustion of 1,3,5-cyclohexatriene is

[2] These are common, but obsolete, units. One may multiply by 4.18 to convert to kJ mol^{-1}.

3×-28.2 kcal mol^{-1} = <u>-84.6 kcal mol^{-1}</u>.

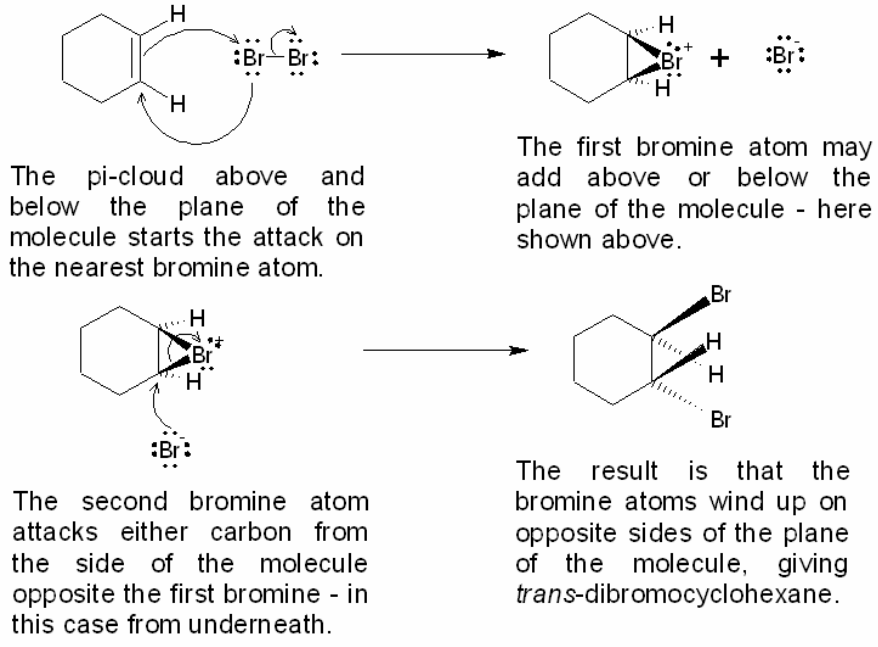
This value shows that the hydrogenation of benzene releases much less heat than expected on the basis that benzene is 1,3,5-cyclohexatriene, with 3 discrete double bonds. This difference may be explained on the basis of resonance (benzene is a resonance hybrid of many contributing structures, such as



as well as others. The more contributing structures, the lower the energy.

Alternatively one may use the molecular orbital description, which shows that the electrons in the 2p atomic orbitals of the carbon atoms are delocalised in π molecular orbitals. Delocalised electrons have lower energy. Resonance (as above) also gives delocalisation of the electrons.

3) Show, by means of stereochemical formulae and mechanisms, why the reaction of cyclohexene with bromine leads to the formation of *trans*-1,2-dibromocyclohexane, and not *cis*-1,2-dibromocyclohexane.



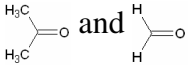
The diagrams themselves are not quite enough because one cannot easily show from which side the bromide ion attacks. Description is also required.

4) In each of the following cases, suggest a formula for the alkene which would give rise to the product (or products) of reductive ozonolysis. Give also the name of the alkene in each case.

a) 

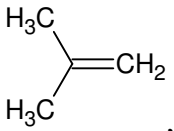
Answer: (4a)

$H_2C{=}CH_2$, ethene

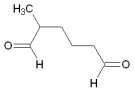
b)  in equimolar quantities

Answer: (4b)

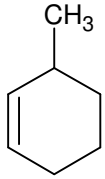
Just join the molecules back to back and leave out the oxygens:



, 2-methyl-1-propene.
(A mixture of ethene and 2,3-dimethylbut-2-ene would not give an equimolar mixture in general. Besides the questions asks for *the alkene*.)

c)  only.

Answer: (4c)
The best answer is produced by connecting the oxygen bearing atoms in one molecule together to give a ring:



This is 3-methyl-1-cyclohexene.