

SCH4U-C



Hess's Law

Introduction

In Lesson 11, you learned about alternative energy sources for heating and cooling your home. The focus of this lesson is again on alternative energy sources, but this time, you are going to consider alternative ways to power cars, including unconventional fuels. Most cars use gasoline (which is mostly octane, C_8H_{18}) as their fuel source. Other possible fossil fuels include natural gas (methane, CH_4) and propane (C_3H_8).

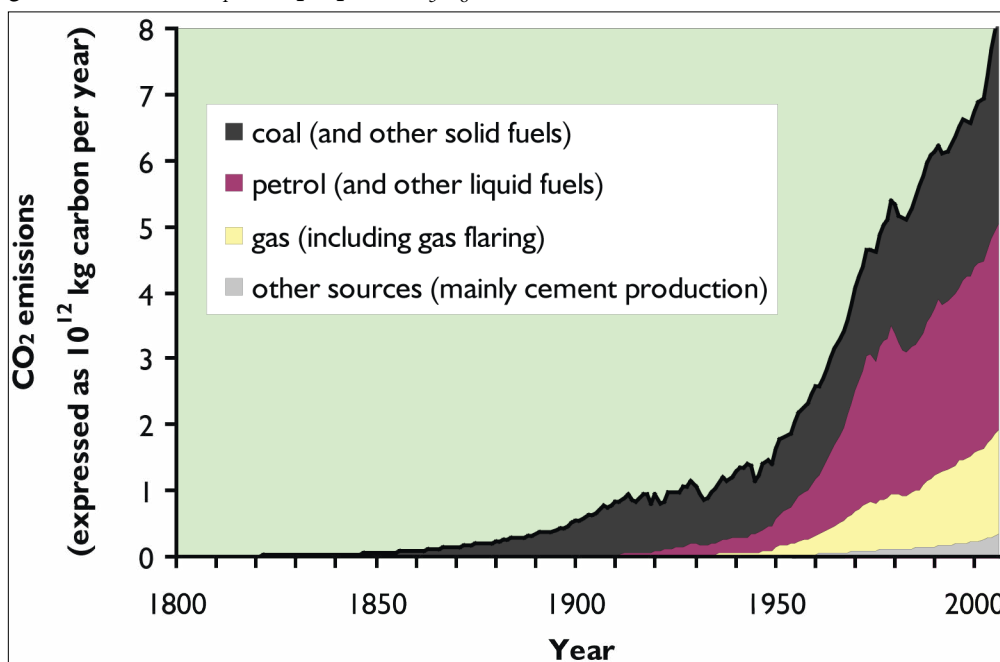


Figure 12.1: Annual global carbon dioxide emissions by source. The period covered is 1800 to 2006. Emissions are expressed in metric gigatonnes.

Source: <http://commons.wikimedia.org/wiki/File:CO2-src.png>

The combustion of fossil fuels results in the production of air pollutants because of impurities in the fuel and incomplete combustion of the fuel. However, only small quantities of these non-carbon pollutants are produced in comparison to the amount of carbon dioxide produced during combustion. Carbon dioxide is a greenhouse gas that traps heat within the earth's atmosphere, leading to global warming. Increased temperatures can cause the polar ice caps to melt. This raises global sea levels, causing the destruction of low-lying habitats. The increased atmospheric temperature also affects weather patterns. Storms become more intense, and parts of the earth may become wetter or drier, or they may become warmer or, surprisingly, colder. This is climate change.

Alternative means of powering cars, as well as other initiatives, are being developed in an effort to reduce the amount of carbon dioxide added to the atmosphere. You will learn about some of these proposals and initiatives in this lesson.

Planning Your Study

You may find this time grid helpful in planning when and how you will work through this lesson.

Suggested Timing For This Lesson (Hours)	
Hess's Law	$\frac{3}{4}$
Activity: Hess's Law	$\frac{3}{4}$
Heats of Formation	$\frac{1}{2}$
Case Study: Hybrid Cars	$\frac{1}{4}$
Key Questions	$1\frac{1}{4}$

What You Will Learn

After completing this lesson, you will be able to

- describe methods of reducing the production of greenhouse gases through policy initiatives and personal choices
- determine enthalpy changes for chemical reactions using Hess's law
- determine enthalpy changes for chemical reactions using heats of formation

Hess's Law

In Lesson 11, you learned about thermochemical equations and how ΔH is calculated using calorimetry techniques. In this lesson, you will learn about Hess's law, which is used to calculate ΔH values for reactions that are not measured directly through experiments and observations.

At times it may be necessary to alter a thermochemical equation. For example:



But if the equation is written without fractional coefficients, by doubling the whole equation, it would appear as:

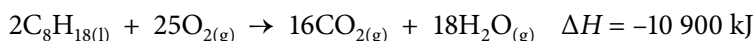
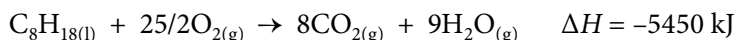


Notice that the value of ΔH has doubled because two moles of sodium chloride are produced.

This holds true for decomposition reactions, where a compound is broken down into elements or smaller compounds. Consider the pair of equations representing the decomposition of hydrogen peroxide:



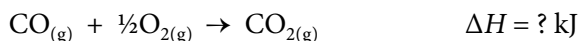
Combustion reactions work the same way. Check out the example for the combustion of octane, the key ingredient in gasoline:



Calorimetry is often used to determine ΔH values. However, it is not always possible to use this method. Some reactions happen too slowly or too quickly to measure all of the heat changes in the surroundings. Chemists had to come up with alternative means of determining ΔH .

Germain Hess, a chemist, proposed Hess's law to calculate ΔH values for reactions that could not be measured through calorimetry by using ΔH values from other related reactions.

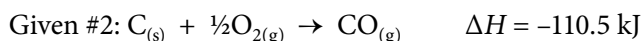
Consider the following example. A chemist wants to determine the ΔH value for the synthesis of carbon dioxide from carbon monoxide and an oxygen atom.



This is known as the *target equation*. In some reactions, the ΔH value cannot be determined directly through calorimetry. However, the chemist may know the ΔH values for some closely related reactions, such as:



and

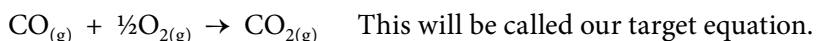


These are the *given* or *known equations* and they can be manipulated to yield the target equation.

Manipulations include reversing the equation so that the reactants become the products and the products become the reactants. If you reverse the equation, you must also reverse the sign of the ΔH value. It is also possible to multiply or divide the equation by a certain number to alter the coefficients. The ΔH value would then have to be multiplied or divided by the same number.

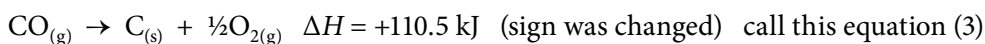
Recall from the lesson dealing with redox equations how half-reactions were added to produce the overall reaction. Hess's Law utilizes the same principle. We will find thermochemical equations, manipulate them as required, and add them together with the objective of producing the "target" equation (the desired equation).

In this situation, we wish to determine the ΔH for the equation



The target has two compounds in it; 1 mole of CO on the left side and 1 mole of CO_2 on the right side. Elements such as O_2 can be ignored because the process we follow will take care of elements for us. Let's now find equations that, when added, will give the target.

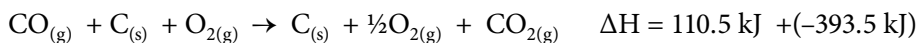
If we are to add equations to produce that target, then we need an equation that has 1 mole of CO on its left side. The given #2 equation will work for that if we reverse it.



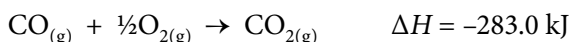
We also need an equation that has 1 mole of CO_2 on its right side (the target has that). The given #1 will work for that just the way it was written.



If we now add the two equations, (3) and (1), along with their associated ΔH values, we get



Simplifying this, the $\text{C}_{(s)}$ cancels and the O_2 is collected to one side.



We have produced our target by adding just two equations. Frequently, more than two equations are required, depending on the complexity of the target. It does not matter how many equations you use or which equations you find to use, as long as, when you add them, the desired equation (the target) is produced.

This is known as the Hess's law method. This method uses given equations for related reactions to determine the ΔH for the target reaction. The following steps summarize the method:

Step 1: Write out the target equation and the known (given) equations, noting the identities and coefficients of reactants and products.

Step 2: Look at each of the given equations individually and compare them to the target equation. Concentrate on compounds in the target. Ignore elements such as $\text{O}_{(g)}$ or $\text{C}_{(s)}$

Step 3: If necessary, reverse a given equation so that a compound is on the same side as in the target equation. Reverse the sign of the ΔH value, if you reverse an equation.

Step 4: If necessary, multiply or divide a given equation by an appropriate number to have the same number of moles of the compound as the target equation. Multiply or divide the ΔH value by the same number.

Step 5: When you have finished all of your manipulations of the given equations and accounted for every compound in the target equation, add your equations and simplify.

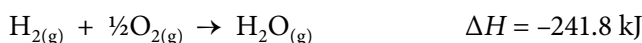
Step 6: Check to make sure that what you have left is the target equation.

Step 7: Add the individual ΔH values together to determine the ΔH value for the target equation.

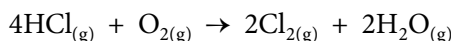
Now, notice how the above steps are used to solve the following examples.

Example

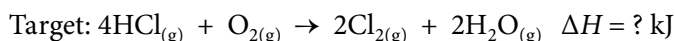
Given the following reactions,



determine the ΔH for this target equation:



Solution



Ignore elements $\text{O}_{2(g)}$ and $\text{Cl}_{2(g)}$. The procedure will take care of these when we add. Therefore, concentrate on the two compounds, 4HCl on the left side and $2\text{H}_2\text{O}$ on the right side. You could underline these in the target.

First, reverse the first given equation so that HCl is on the left side, as required in the target.



Then, double the reversed equation because there are four, not two, moles of HCl in the target:



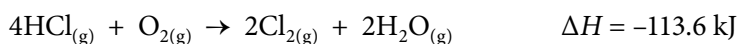
Finally, double the second equation (H_2O has a coefficient of 2):



Add the newly created equations together and cancel out the items that appear as both reactants and products. The newly created equations are shown below.



Check to make sure that you have reached the target equation. Add up the individual ΔH values to determine the ΔH value for the target:



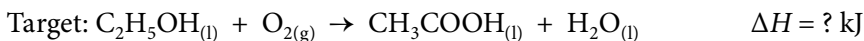
Notice how the elements, oxygen and chlorine, appeared when the addition was completed.

Example

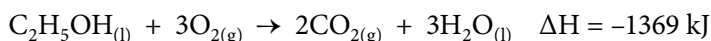
Ethanol reacts with oxygen to produce ethanoic acid and water. (This is the reaction that turns the alcohol in wine into vinegar.) What is the ΔH value for this reaction if the ΔH for the complete combustion of ethanol is $-1369 \text{ kJ}/(\text{mol of ethanol})$ and the ΔH value for the complete combustion of ethanoic acid is $-875 \text{ kJ}/(\text{mol of ethanoic acid})$?

Solution

In this example, you have to write and balance your own thermochemical equations from the information provided. You will have to refer back to earlier lessons on organic chemistry to come up with some of the formulas. Complete combustion means that the fuel reacts with sufficient oxygen to produce carbon dioxide and water.



Given #1: Combustion of ethanol



Given # 2: Combustion of ethanoic acid (acetic acid)

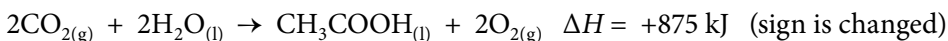
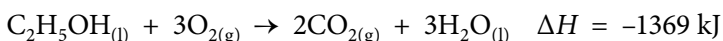


The element, $\text{O}_{2(\text{g})}$, in the target is ignored.

Given #1 has $1\text{C}_2\text{H}_5\text{OH}_{(\text{l})}$ on the left side (same as target), so that given will be used as is.

Given #2 will be reversed to have $1\text{CH}_3\text{COOH}_{(\text{l})}$ on the right side (like the target).

We will write down these two manipulations of the given equations and add them, even though we have not considered the $\text{H}_2\text{O}_{(\text{l})}$ in the target. Notice that both given equations have water in them. Hopefully the water will work out for us.



Adding...

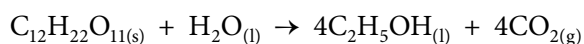


Notice that the water *did* work out for us. If it had not, we would look for a third given equation dealing with water.

Support Question

Be sure to try the Support Questions on your own before looking at the suggested answers provided.

37. Sucrose ferments, producing ethanol, according to the following equation:



Calculate the ΔH for this reaction, given that the ΔH value for the complete combustion of sucrose is -5645 kJ/mol , and the ΔH value for the complete combustion of ethanol is -1369 kJ/mol .

Heats of Formation

Another method of determining the enthalpy change for reactions is by using the heats of formation, ΔH_f values, for the reactants and products. A formation reaction is a very specific type of reaction. It involves the formation of one mole of a compound from its elements in their natural state only. Their “natural state” means their molecular and physical state (a solid, liquid, or gas), as found in the laboratory or in the real world.

A few elements will never be found as lone atoms—they always exist as diatomic molecules: hydrogen (H_2), oxygen (O_2), fluorine (F_2), bromine (Br_2), iodine (I_2), nitrogen (N_2) and chlorine (Cl_2). All the rest of the elements exist naturally as single atoms. When these elements are included in formation reactions, they must be written in their natural, diatomic state. In other words, you should write H_2 rather than H .

The following are potential formation reactions for sodium hydroxide. Only one is written correctly as a formation reaction. Can you pick out the correct one? What is wrong with the other four?

1. $\text{H}_{2(g)} + \text{O}_{2(g)} + 2\text{Na}_{(s)} \rightarrow 2\text{NaOH}_{(s)}$
2. $\text{H}_{(g)} + \text{O}_{(g)} + \text{Na}_{(s)} \rightarrow \text{NaOH}_{(s)}$
3. $\frac{1}{2}\text{Na}_2\text{O}_{(s)} + \frac{1}{2}\text{H}_2\text{O}_{(l)} \rightarrow \text{NaOH}_{(s)}$
4. $\frac{1}{2}\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} + \text{Na}_{(s)} \rightarrow \text{NaOH}_{(s)}$
5. $\text{Na}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow 2\text{NaOH}_{(s)}$

The fourth one is the only correct one. It shows hydrogen and oxygen as diatomic gases (their natural state), and has one mole of sodium hydroxide as the product. The first is close: the elements are in their natural state, but the equation has been balanced so that there are two moles of product instead of one. In the second one, hydrogen and oxygen should be diatomic (their natural state). The third and the fifth use compounds, not elements, to form sodium

hydroxide. The fifth also has two moles of compound instead of one, and NaOH is not forming from its basic elements.

Over the years, chemists have determined the ΔH_f° values for many formation reactions. These are listed in the table provided on the next page. They were determined under standard conditions, which is why the “o” appears with the ΔH_f° . The ΔH_f° value is not known for every compound. The following table shows some common ΔH_f° values—the ones you will be using in this part of the lesson, and in the Support Questions, Key Questions, and Final Test. You do not have to memorize these values.

Table 12.1: The heats of formation (ΔH_f°) values for selected compounds

Compound	ΔH_f° (kJ/mol)
$\text{CH}_4(\text{g})$	-74.4
$\text{C}_2\text{H}_6(\text{g})$	-83.8
$\text{C}_3\text{H}_8(\text{g})$	-104.7
$\text{C}_4\text{H}_{10}(\text{l})$	-125.6
$\text{Na}_2\text{CO}_3(\text{s})$	-1130.8
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{H}_2\text{O}(\text{g})$	-241.8
$\text{C}_6\text{H}_6(\text{l})$	+49.0

How are these values used to calculate the ΔH for a chemical reaction? The equation that you use is:

$$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

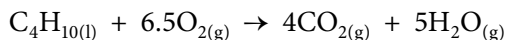
In other words, this means that the enthalpy change for a reaction is equal to the sum (Σ) of the ΔH_f° values of the products minus the sum (Σ) of the ΔH_f° values of the reactants. You look up the values on the table, substitute them into the equation, and solve the equation. Note that this method will give you the same result as the previous method that you learned.

Example

What is the ΔH for the complete combustion of butane to water vapour and carbon dioxide?

Solution

Step 1: Start off by writing down the balanced equation:



Step 2: Then, substitute heats of formation values into the equation from the table, remembering to multiply by any coefficients:

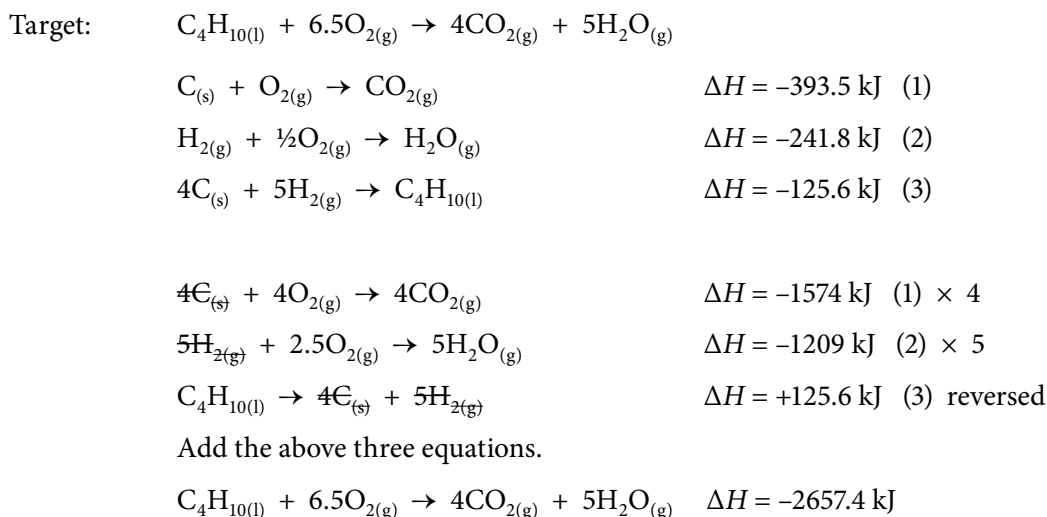
$$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\begin{aligned}\Delta H &= [4 \text{ mol } \Delta H_f^\circ(\text{CO}_2) + 5 \text{ mol } \Delta H_f^\circ(\text{H}_2\text{O})] - [1 \text{ mol } \Delta H_f^\circ(\text{C}_4\text{H}_{10})] \\ &= [4 \text{ mol } (-393.5 \text{ kJ/mol}) + 5 \text{ mol } (-241.8 \text{ kJ/mol})] - [1 \text{ mol } (-125.6 \text{ kJ/mol})] \\ &= -2657.4 \text{ kJ}\end{aligned}$$

The enthalpy change for the given reaction for the combustion of butane is -2657.4 kJ .

Note that oxygen did not appear in the substitution and is not listed in the table. That is because oxygen is already in its natural state and does not have to be “formed.” As well, check the state of water carefully. It can exist as both a vapour and a liquid, and each has a different ΔH_f° value.

This method of determining ΔH is related to Hess’s law. If the combustion of butane is the target equation and the various formation reactions are known or given, you can see the connection.



Notice how the units (mol and kJ/mol) were included within the calculations. Units are critical to all problem solutions and must always be included. Note also that the answer would contain one decimal place because all of the heats of formation being used had one decimal. We are just adding and subtracting values in this problem so decimal places are considered, not sig-figs.

Support Questions

- 38.** Write formation equations for the following compounds:
- a) $\text{NaHCO}_{3(s)}$
 - b) $\text{Ca(OH)}_{2(s)}$
 - c) $\text{NH}_4\text{Cl}_{(s)}$
- 39.** Benzene ($\text{C}_6\text{H}_{6(l)}$) undergoes complete combustion. Assume that liquid water is produced.
- a) Write a balanced equation for the complete combustion of 1 mole of liquid benzene.
 - b) Using heats of formation values from Table 12.1, determine the enthalpy change for the reaction written in a). Write the thermochemical equation two ways.

Case Study: Hybrid Cars

The car that you choose to drive, or whether you drive at all, has a great impact on the environment. Two alternative means of powering cars are the fuel cell (which was described in Lesson 10) and the gasoline-electric hybrid.

Much of the fuel-cell technology that is used today resulted from the inventions of Geoffrey Ballard, a Canadian scientist. The fuel cell uses hydrogen as its fuel and produces only water vapour as a waste product—there are no greenhouse gases or other pollutants. Ballard's fuel cells are used in urban transit buses in Vancouver and in a number of European cities. Ballard's fuel cells are also used in forklifts in warehouses, where the production of poisonous carbon monoxide is a concern, as well as for generating electricity in remote locations that have a ready source of hydrogen-rich compounds (such as methane). Ballard believed that personal cars would not be powered by fuel cells until there was some kind of incentive to persuade people to give up fossil-fuel-powered cars. Fuel-cell technology is expensive initially, but pays for itself when fuel and environmental savings are factored in. Because hydrogen is difficult to handle, store, and transport, there are no mass-produced fuel-cell-powered cars for sale in Canada.

The other alternative to fossil-fuel-powered cars is the hybrid car. These are becoming increasingly common on Canada's roads. Currently, there are 12 different models from 8 different car manufacturers available for sale in Canada. As of 2010, the federal and provincial governments have offered tax rebates of up to \$4000 to people who purchase hybrid cars. Insurance companies have provided a discount on premiums for owners of hybrid cars, and manufacturers have included extended warranties in the price of these cars.

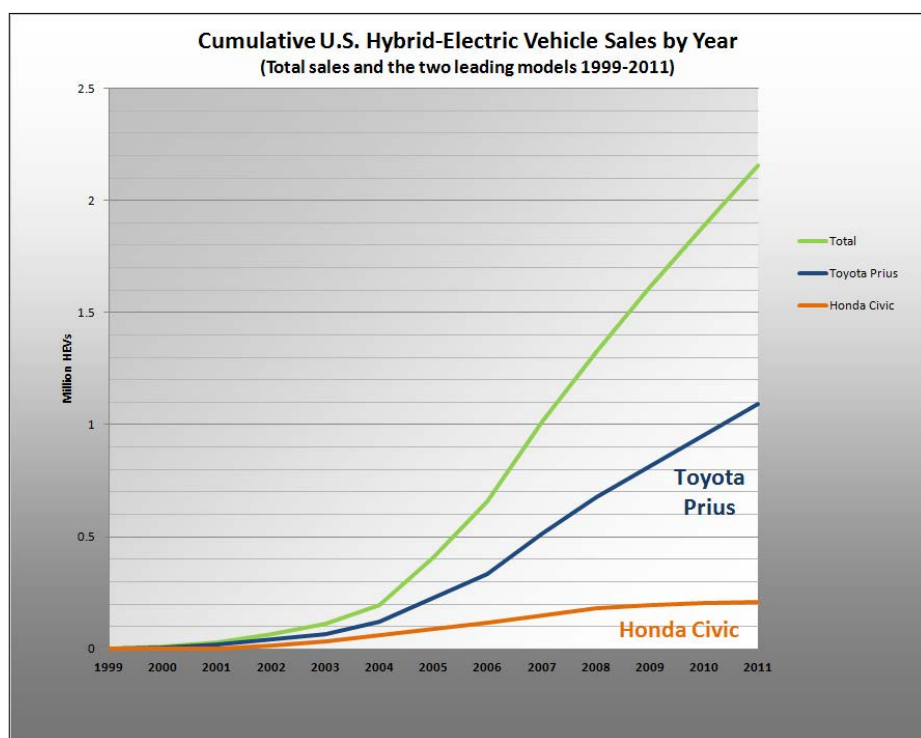


Figure 12.2: Graph showing historical trend of cumulative sales of US hybrids series 1999–2009. Data series taken from Alternative Fuels and Advanced Vehicles Data Center (US DoE).

Source: http://commons.wikimedia.org/wiki/File:Cumulative_US_HEV_Sales_by_year_1999_2009.png

Careers in Chemistry

Margaret-Ann Armour

Birthplace: Scotland; Canadian citizen and named to the Order of Canada 2006



Photo of Dr. Armour

***In Focus*—Margaret-Ann Armour (Department of Chemistry: University of Alberta)**

“We are pleased to present to you one of our distinguished colleagues, Margaret-Ann Armour, who has been actively engaged in various aspects of science education and research. An invaluable member of our department, she is internationally recognized for her commitment to advancing the role of women in science and engineering, and is the recipient of numerous national and international awards.”

Biographical Sketch

Margaret-Ann Armour was born in Scotland and educated at Edinburgh University, where she obtained Bachelor and Master of Science degrees. She worked as a research chemist in the paper-making industry for five years before coming to the University of Alberta in Edmonton where, in 1970, she graduated with a Ph.D. in physical organic chemistry. From 1979–1989 she was supervisor of the undergraduate organic chemistry laboratories in the Chemistry Department and since 1989, has served as Assistant Chair.

Her research has been into the development and testing of methods for recycling or disposing of small quantities of waste and surplus chemicals. The results are described in “Hazardous Laboratory Chemicals Disposal Guide” published by CRC Press (third edition, 2003). Dr. Armour has presented talks on the work to many groups of small quantity generators of hazardous waste in North America and throughout Asia. Dr. Armour is the author or co-author of over 100 proceedings and papers on chemical education, hazardous waste disposal and women in science. She serves on the Board of SHAD International and of the Pacific Basin Consortium for Hazardous Waste Research and Management. She has been a Scientific Advisor to the Asian Association for Academic Activity on Waste Management.

Since 1984, Dr. Armour has been Vice-Chair and Convenor of WISEST, a committee of the Vice-President, Research, at the University of Alberta on Women in Scholarship, Engineering, Science and Technology with a mandate to take action to increase the proportion of women in decision-making roles in the sciences and engineering.

Source: Text and photo, Department of Chemistry, University of Alberta.

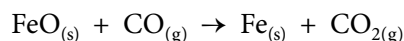
Key Questions

Now work on your Key Questions in the [online submission tool](#). You may continue to work at this task over several sessions, but be sure to save your work each time. When you have answered all the unit's Key Questions, submit your work to the ILC.

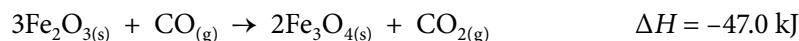
- 45.** You have been asked to write an opinion for an environmental magazine about the benefits of purchasing a hybrid vehicle for day-to-day driving. You can use some of the information in the lesson to help get you started, but you will have to do some additional research at a library or at home, on the Internet. You should use at least two sources, which you must list in a properly formatted bibliography. Your answer to this Key Question should be about 500 words long.

Your writing should include the following:

- An explanation of the operation of a hybrid car, including how it reduces greenhouse-gas emissions (**3 marks**)
 - The benefits of hybrid cars (**3 marks**)
 - The concerns about hybrid cars (**2 marks**)
 - At least three detailed explanations to support your opinion on whether you believe that the benefits outweigh the concerns (**3 marks**)
 - At least two sources, which you must list in a properly formatted “references” section (**2 marks**)
 - Communication skills, such as proper spelling and full sentences, which will add to your marks (**2 marks**)
- 46.** Using Hess's law, calculate the ΔH value for the following reaction: (**8 marks**)



Use these three reactions:



- 47.** Sodium bicarbonate (NaHCO_3) is often used in the kitchen to extinguish fires. When heated, it decomposes into sodium carbonate, water vapour, and carbon dioxide. The ΔH for the reaction of 1 mole of sodium bicarbonate is +64.6 kJ.
- Write a balanced thermochemical equation for this reaction. (**2 marks**)
 - Using the enthalpies of formation, calculate the enthalpy of formation of sodium bicarbonate. (**5 marks**)

This is the last lesson in Unit 3. When you have completed all the Key Questions, submit your work to the ILC. A teacher will mark it and you will receive your results online.

Periodic Table

Group 1
IA

1
H
Hydrogen
1.00794

2
He
Helium
4.002602

3
Li
Lithium
6.941

4
Be
Beryllium
9.012182

5
B
Boron
10.811

6
C
Carbon
12.011

7
N
Nitrogen
14.00674

8
O
Oxygen
15.9994

9
F
Fluorine
18.9984032

10
Ne
Neon
20.1797

11
Na
Sodium
22.98976928

12
Mg
Magnesium
24.3050

13
Al
Aluminum
26.9815385

14
Si
Silicon
28.0855

15
P
Phosphorus
30.973762

16
S
Sulfur
32.066

17
Cl
Chlorine
35.4527

18
Ar
Argon
39.948

19
K
Potassium
39.0983

20
Ca
Calcium
40.078

21
Sc
Scandium
44.955910

22
Ti
Titanium
47.88

23
V
Vanadium
50.9415

24
Cr
Chromium
51.9961

25
Mn
Manganese
54.93805

26
Fe
Iron
55.847

27
Co
Cobalt
58.93320

28
Ni
Nickel
58.6934

29
Cu
Copper
63.546

30
Zn
Zinc
65.39

31
Ga
Gallium
69.723

32
Ge
Germanium
72.61

33
As
Arsenic
74.92159

34
Se
Selenium
78.96

35
Br
Bromine
79.904

36
Kr
Krypton
83.80

37
Rb
Rubidium
85.4678

38
Sr
Strontium
87.62

39
Y
Yttrium
88.90585

40
Zr
Zirconium
91.224

41
Nb
Niobium
92.90638

42
Mo
Molybdenum
95.94

43
Tc
Technetium
(97.9072)

44
Ru
Ruthenium
101.07

45
Rh
Rhodium
102.90550

46
Pd
Palladium
106.42

47
Ag
Silver
107.8652

48
Cd
Cadmium
112.411

49
In
Indium
114.818

50
Sn
Tin
118.710

51
Sb
Antimony
121.757

52
Te
Tellurium
127.60

53
I
Iodine
126.90447

54
Xe
Xenon
131.29

55
Cs
Cesium
132.90543

56
Ba
Barium
137.327

57
La
Lanthanum
138.9055

72
Hf
Hafnium
178.49

73
Ta
Tantalum
180.9479

74
W
Tungsten
183.84

75
Re
Rhenium
186.207

76
Os
Osmium
190.23

77
Ir
Iridium
192.22

78
Pt
Platinum
195.08

79
Au
Gold
196.96654

80
Hg
Mercury
200.59

81
Tl
Thallium
204.3833

82
Pb
Lead
207.2

83
Bi
Bismuth
208.98037

84
Po
Polonium
(209.9824)

85
At
Astatine
(209.9871)

86
Rn
Radon
(222.0176)

87
Fr
Francium
(223.0197)

88
Ra
Radium
(226.0254)

89
Ac
Actinium
(227.0278)

104
Rf
Rutherfordium
(261.11)

105
Db
Dubnium
(262.114)

106
Sg
Seaborgium
(263.118)

107
Bh
Bohrium
(262.12)

108
Hs
Hassium
(269)

109
Mt
Meitnerium
(266)

110
Ds
Darmstadtium
(269)

111
Rg
Roentgenium
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112
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113
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Ununtrium
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114
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115
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Ununpentium
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116
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Ununhexium
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117
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Ununseptium
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118
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Ununoctium
(292)

119
Pa
Protactinium
231.03688

120
Th
Thorium
232.03758

121
U
Uranium
238.02891

122
Np
Neptunium
237.04817

123
Pu
Plutonium
244.06422

124
Am
Americium
243.06114

125
Cm
Curium
247.07030

126
Bk
Berkelium
247.07030

127
Cf
Californium
251.07958

128
Es
Einsteinium
252.08329

129
Fm
Fermium
257.09511

130
Md
Mendelevium
(258.10)

131
No
Nobelium
(259.1009)

132
Lr
Lawrencium
(262.111)

133
Rf
Rutherfordium
(261.103)

134
Db
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(262.114)

135
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(263.118)

136
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(262.117)

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