

## Constant-Pressure Calorimetry III

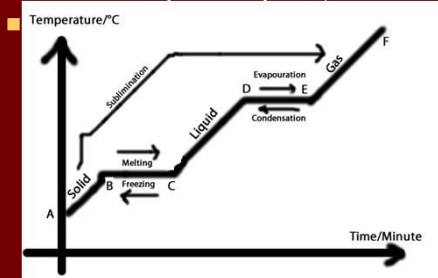
- A 0.5269 g of octane is placed in a bomb calorimeter known to have a heat capacity of 11.3 kJ/°C. The octane, a component of gasoline, is ignited in the presence of excess oxygen. The temperature is increased by 2.25° C. What is the energy released per mole?

## Enthalpy for phase changes

- There are constant values for the enthalpy of a phase change.
- The energy required to go from solid to liquid is called the heat of fusion ( $H_{fus}$ ).
- The energy required to go from liquid to gas is called heat of vaporization ( $H_{vap}$ ).
- $q = H n$
- For heating a substance,  $q = nC\Delta T$  or  $q = mc \Delta T$

## Quantitative Aspects of Changes of State

- The Heating-Cooling Curve.



## Problem

- How much heat is required to heat 3.65 mol of ice at  $-15^{\circ}\text{C}$  to steam at  $115^{\circ}\text{C}$ ?
- $H_{fus} = 6010 \text{ J/mol}$   $H_{vap} = 40,700 \text{ J/mol}$
- $C_{ice} = 38.09$   $C_{water} = 75.3$   $C_{steam} = 36.8$
- (heat to melting -15 to 0) (heat to melt) (heat to boiling 0 to 100) (heat to boil off) (heat to 100 to 115)
- $q = 3.65(38.09)15 + 3.65(6010) + 3.65(75.3)100 + 3.65(40700) + 3.65(36.8)15$
- $q = 202 \text{ kJ}$

It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of 11.3 kJ/°C. When 1.50 g sample of methane gas burned with excess oxygen in the calorimeter, the temperature increased by 7.3 °C. When a 1.15g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3 °C. Calculate the energy of combustion (per gram and per mole) for hydrogen and methane.

## Hess's Law

- Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway.
- In going from one particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or a series of steps.
- This is known as **Hess's Law**

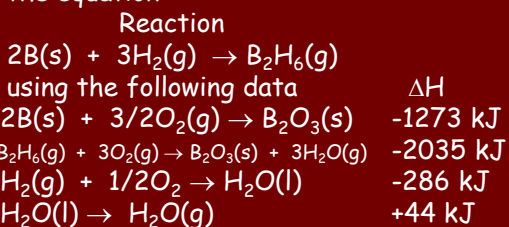
## Characteristics of Enthalpy Changes

- Two important characteristics of  $\Delta H$  for a reaction.
- If a reaction is reversed, the sign of  $\Delta H$  is also reversed
- The magnitude of  $\Delta H$  is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of  $\Delta H$  is multiplied by the same integer.

## Hess's Law I.

- Two forms of carbon are graphite, the soft, black, slippery material used in "lead" pencils and as a lubricant for locks, and diamond, the brilliant, hard gemstone. Using the enthalpies of combustion for graphite (-394 kJ/mol) and diamond (-396 kJ/mol), calculate  $\Delta H$  for the conversion of graphite to diamond:
- $C_{\text{graphite}}(s) \rightarrow C_{\text{diamond}}(s)$

Diborane ( $B_2H_6$ ) is a highly reactive boron hydride, which was once considered as a possible rocket fuel for the US space program. Calculate  $\Delta H$  for the synthesis of diborane from its elements, according to the equation



## Using Hess's Law

- Work backwards from the required reaction, using the reactant and products to decide how to manipulate the other given reactions at your disposal.
- Reverse any reactions as needed to give the required reactants and products, and then multiply reactions to give the correct number of reactants and products.

## More Practice

- Calculate the enthalpy change for the following
- $ClF_{(g)} + F_{2(g)} \rightarrow ClF_{3(g)}$
- Given the following reactions
- $2ClF_{(g)} + O_{2(g)} \rightarrow Cl_2O_{(g)} + F_2O_{(g)} \quad \Delta H = 167.4 \text{ kJ}$
- $2ClF_{3(g)} + 2O_{2(g)} \rightarrow Cl_2O_{(g)} + 3F_2O_{(g)} \quad \Delta H = 341.4 \text{ kJ}$
- $2F_{2(g)} + O_{2(g)} \rightarrow 2F_2O_{(g)} \quad \Delta H = -43.4 \text{ kJ}$

## Standard Enthalpy of Formation and Standard States

- Because enthalpy is a state function,  $\Delta H$  may be calculated more than one way.
- The **standard enthalpy of formation** ( $\Delta H_f^\circ$ ) of a compound is defined as the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.
- Standard state is indicated by symbol,  $^\circ$ .
- A **standard state** is a reference state for a specific substance defined according to a set of conventional definitions

## Standard state of a compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For a substance present in a solution, the standard state is a concentration of exactly 1 M.

## Standard State of an Element

- The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25 °C. (The standard state for oxygen is O<sub>2</sub>(g) at a pressure of 1 atmosphere; the standard state for sodium is Na(s); the standard state for mercury is Hg(l), and so on.)
- For an element in its standard state,  $\Delta H_f^\circ = 0$ , always!
- Values may be found in Appendix 4 of your book

## Standard Enthalpy of Reaction.

- The standard heat of reaction ( $\Delta H_{rxn}^\circ$ ) is the sum of the standard heats (enthalpies) of formation of the products minus the sum of the standard heats of formation of the reactants.

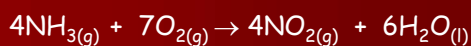
$$\Delta H_{rxn}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

- Elements are not included in the calculations because their value is equal to zero

## AP Equation Sheet

THERMODYNAMICS/ELECTROCHEMISTRY	
$q = mc\Delta T$	$q = \text{heat}$
$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$	$n = \text{mass}$
$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$	$c = \text{specific heat capacity}$
$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$	$T = \text{temperature}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	$S^\circ = \text{standard entropy}$
$= -RT \ln K$	$H^\circ = \text{standard enthalpy}$
$= -nFE^\circ$	$G^\circ = \text{standard Gibbs free energy}$
$I = \frac{q}{t}$	$n = \text{number of moles}$
$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$	$E^\circ = \text{standard reduction potential}$
	$I = \text{current (amperes)}$
	$q = \text{charge (coulombs)}$
	$t = \text{time (seconds)}$
	$Q = \text{reaction quotient}$
	Faraday's constant, $F = 96,485 \text{ coulombs per mole of electrons}$
	$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$

## Standard enthalpy of formation



Using the standard enthalpies of formation listed in Table, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.

Standard Enthalpy of Formation $\Delta H_f^\circ$ (kJ/mol)	
NH <sub>3</sub> (g)	-46
NO <sub>2</sub> (g)	34
H <sub>2</sub> O(l)	-286
Al <sub>2</sub> O <sub>3</sub> (s)	-1676
Fe <sub>2</sub> O <sub>3</sub> (s)	-826
CO <sub>2</sub>	-394
CH <sub>3</sub> OH(l)	-239
C <sub>6</sub> H <sub>18</sub> (l)	-269