## Bomb Calorimetry

- constant volume
- often used for combustion reactions
- heat released by reaction is absorbed by calorimeter contents
- need heat capacity of calorimeter
- $q_{cal} = -q_{rxn} = q_{bomb} + q_{water}$

Example 4

When 0.187 g of benzene, C_6H_6, is burned in a bomb calorimeter, the surrounding water bath rises in temperature by 7.48°C. Assuming that the bath contains 250.0 g of water and that the calorimeter has a heat capacity of 4.90 kJ/°C, calculate the energy change for the combustion of benzene in kJ/g.

$$C_6H_6 \ (\ell) + 15/2 \ O_2 \ (g) \rightarrow 6 \ CO_2 \ (g) + 3 \ H_2O \ (\ell)$$
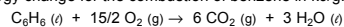
$q_{cal} = (4.90 \text{ kJ/°C})(7.48°C) = 36.7 \text{ kJ}$
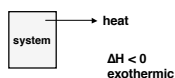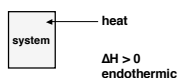
$q_{rxn} = -q_{cal} = -36.7 \text{ kJ} / 0.187 \text{ g } C_6H_6 = -196 \text{ kJ/g}$

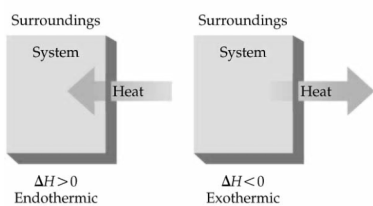$q_V = \Delta E = -196 \text{ kJ/g}$

Energy and Enthalpy

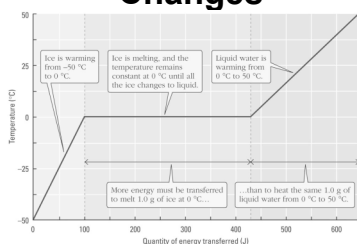Most physical and chemical changes take place at constant pressure

- Heat transferred at constant P - enthalpy (H)
  - Can only measure ΔH
  - $\Delta H = H_{final} - H_{initial} = q_P$
  - sign of ΔH indicates direction of heat transfer

Energy and Enthalpy

Surroundings — System ← Heat

$\Delta H > 0$
Endothermic

Surroundings — System → Heat

$\Delta H < 0$
Exothermic

Enthalpy and Phase Changes

Ice is warming from −50 °C to 0 °C.

Ice is melting, and the temperature remains constant at 0 °C until all the ice changes to liquid.

Liquid water is warming from 0 °C to 50 °C.

More energy must be transferred to melt 1.0 g of ice at 0 °C…

…than to heat the same 1.0 g of liquid water from 0 °C to 50 °C.

Temperature (°C)

Quantity of energy transferred (J)

© 2005 Brooks/Cole - Thomson
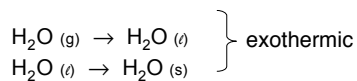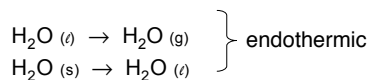

Enthalpy and Phase Changes

- Melting and freezing
  - Quantity of thermal energy that must be transferred *to* a solid to cause melting - heat of fusion (q_{fusion})
  - Quantity of thermal energy that must be transferred *from* a solid to cause freezing - heat of freezing ($q_{freezing}$)
  - $q_{fusion} = - q_{freezing}$
  - heat of fusion of ice = 333 J/g at 0°C

Enthalpy and Phase Changes

- Vaporization and condensation
  - Similarly: $q_{vaporization} = - q_{condensation}$
  - heat of vaporization of water = 2260 J/g at 100°C
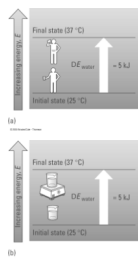 - 333 J of heat can melt 1.00 g ice at 0°C but it will boil only:

333 J x (1.00 g / 2260 J) = 0.147 g water

Enthalpy and Phase Changes

$H_2O_{(\ell)} \rightarrow H_2O_{(g)}$
$H_2O_{(s)} \rightarrow H_2O_{(\ell)}$ } endothermic

$H_2O_{(g)} \rightarrow H_2O_{(\ell)}$
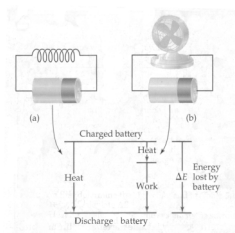$H_2O_{(\ell)} \rightarrow H_2O_{(s)}$ } exothermic

State Functions

- Value of a state function is independent of path taken to get to state - depends only on present state of system
- Internal energy is state function

State Functions

- q and w not state functions

Enthalpy and PV Work

H - state function
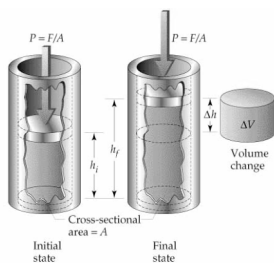q - not a state function $\Big\}$ so how can $\Delta H = q$??

How do internal energy and enthalpy differ?

$\Delta E = q + w$

$\Delta H = q_P$

answer: work

Enthalpy and PV Work

Example 5

A gas is confined to a cylinder under constant atmospheric pressure. When the gas undergoes a particular chemical reaction, it releases 89 kJ of heat to its surroundings and does 36 kJ of PV work on its surroundings. What are the values of ΔH and ΔE for this process?

$q = -89$ kJ $w = -36$ kJ

@ constant pressure:

$\Delta H = q_P = -89$ kJ

$\Delta E = \Delta H + w = -89$ kJ $- 36$ kJ $= -125$ kJ

Thermochemical Equations

$\Delta H = H_{final} - H_{initial} = H_{(products)} - H_{(reactants)}$

ΔH_{rxn} - enthalpy or heat of reaction

$2 H_{2\ (g)} + O_{2\ (g)} \rightarrow 2 H_2O_{(\ell)}$ $\Delta H° = -571.66$ kJ
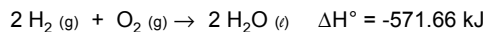
coefficients of equation represent # of moles of reactants and products producing this energy change
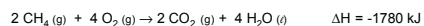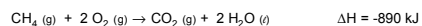
---

Thermochemical Equations

$\Delta H°$
- standard enthalpy change
- defined as enthalpy change at 1 bar pressure and 25°C

"Rules" of Enthalpy

- Enthalpy is an extensive property - magnitude of ΔH depends on amounts of reactants consumed

$$CH_4\ (g)\ +\ 2\ O_2\ (g) \rightarrow CO_2\ (g) +\ 2\ H_2O\ (\ell) \qquad \Delta H = -890\ kJ$$

$$2\ CH_4\ (g)\ +\ 4\ O_2\ (g) \rightarrow 2\ CO_2\ (g) +\ 4\ H_2O\ (\ell) \qquad \Delta H = -1780\ kJ$$

- Enthalpy change of a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction

$$CO_2\ (g)\ +\ 2\ H_2O\ (\ell) \rightarrow CH_4\ (g)\ +\ 2\ O_2\ (g) \qquad \Delta H = +890\ kJ$$
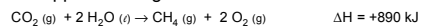
- Enthalpy change for a reaction depends on the states of the reactants and products

$$H_2O\ (\ell) \rightarrow H_2O\ (g) \qquad\qquad\qquad \Delta H = +44\ kJ$$
$$H_2O\ (s) \rightarrow H_2O\ (g) \qquad\qquad\qquad \Delta H = +50\ kJ$$

Example 6

Hydrogen peroxide can decompose to water and oxygen by the reaction:

$$2\ H_2O_2\ (\ell)\ \rightarrow\ 2\ H_2O\ (\ell) +\ O_2\ (g) \qquad \Delta H = -196\ kJ$$
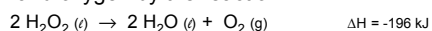
Calculate the value of q when 5.00 g of $H_2O_2\ (\ell)$ decomposes.

$$\text{mol } H_2O_2 = (5.00\ g)\left(\frac{1\ mol}{34.0146\ g}\right) = 0.147\ mol\ H_2O_2$$

$$\Delta H = q_p = (0.147\ mol\ H_2O_2)\left(\frac{-196\ kJ}{2\ mol\ H_2O_2}\right) = \boxed{-14.4\ kJ}$$

Example 7

Consider the following reaction, which occurs at room temperature and pressure:

$$2\ Cl\ (g) \rightarrow\ Cl_2\ (g) \qquad\qquad \Delta H = -243.4\ kJ$$

Which has the higher enthalpy under these conditions, 2 Cl or Cl_2?

$$2\ Cl\ (g)$$

Example 8

When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates:

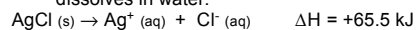$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ $\Delta H = -65.5$ kJ

(a) Calculate ΔH for the formation of 0.200 mol of AgCl by this reaction.

$$\Delta H = (0.200 \text{ mol AgCl})\left(\frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}}\right) = -13.1 \text{ kJ}$$

Example 8 (cont'd)

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ $\Delta H = -65.5$ kJ

(b) Calculate ΔH when 0.350 mmol AgCl dissolves in water.

$AgCl_{(s)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$ $\Delta H = +65.5$ kJ

$$\Delta H = (0.350 \times 10^{-3} \text{ mol AgCl})\left(\frac{+65.5 \text{ kJ}}{1 \text{ mol AgCl}}\right) = 0.0229 \text{ kJ} = 22.9 \text{ J}$$
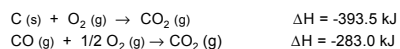
Bond Enthalpies

- during chemical reaction bonds are broken and made
- breaking bonds requires energy input (endothermic)
- formation of bonds releases energy (exothermic)
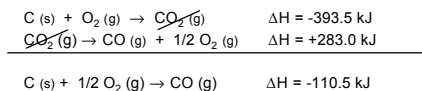- weaker bonds broken and stronger bonds formed

Hess's Law

- we can calculate ΔH for a reaction using ΔHs for other known reactions
- ΔH is a state function - result is same no matter how we arrive at the final state
- Hess's Law - if a reaction is carried out in a series of steps, ΔH for overall reaction is equal to sum of ΔHs for steps
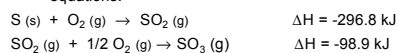
Hess's Law

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H = -393.5$ kJ
$CO_{(g)} + 1/2\,O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H = -283.0$ kJ

What is ΔH for $C_{(s)} + 1/2\,O_{2\,(g)} \rightarrow CO_{(g)}$???

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H = -393.5$ kJ
$CO_{2\,(g)} \rightarrow CO_{(g)} + 1/2\,O_{2\,(g)}$ $\Delta H = +283.0$ kJ

$C_{(s)} + 1/2\,O_{2\,(g)} \rightarrow CO_{(g)}$ $\Delta H = -110.5$ kJ

Example 9

Calculate ΔH for the conversion of S to SO_3 given the following equations:

$S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$ $\Delta H = -296.8$ kJ
$SO_{2\,(g)} + 1/2\,O_{2\,(g)} \rightarrow SO_{3\,(g)}$ $\Delta H = -98.9$ kJ

want $S_{(s)} \rightarrow SO_{3\,(g)}$

$S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$ $\Delta H = -296.8$ kJ
$SO_{2\,(g)} + 1/2\,O_{2\,(g)} \rightarrow SO_{3\,(g)}$ $\Delta H = -98.9$ kJ

$S_{(s)} + 3/2\,O_{2\,(g)} \rightarrow SO_{3\,(g)}$ $\Delta H = -395.7$ kJ
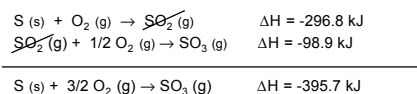
Enthalpies of Formation

- tables of enthalpies (ΔH_{vap}, ΔH_{fus}, etc.)
- ΔH_f - enthalpy of formation of a compound from its constituent elements.
- magnitude of ΔH - condition dependent
- standard state - state of substance in pure form at 1 bar and 25°C
- $\Delta H_f°$ - change in enthalpy for reaction that forms 1 mol of compound from its elements (all in standard state)
- $\Delta H_f°$ of most stable form of any element is 0

CO_2:

$$C_{(graphite)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} \qquad \Delta H_f° = -393.5 \text{ kJ/mol}$$
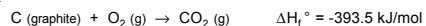
Calculating $\Delta H_{rxn}°$ from $\Delta H_f°$

- we can use $\Delta H_f°$ values to calculate $\Delta H_{rxn}°$ for any reaction
- $\Delta H_{rxn}° = \sum [n\ \Delta H_f°\ (products)] - \sum [n\ \Delta H_f°\ (reactants)]$

$$C_6H_{6\,(\ell)} + 15/2\ O_{2\,(g)} \rightarrow 6\ CO_{2\,(g)} + 3\ H_2O_{(\ell)}$$
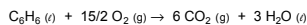
$\Delta H_{rxn}° = [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-285.83 \text{ kJ/mol})]$
$\qquad\qquad - [(1 \text{ mol})(49.0 \text{ kJ /mol}) + (15/2 \text{ mol})(0 \text{ kJ/mol})]$
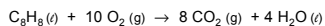
$\Delta H_{rxn}° = -3267 \text{ kJ/mol}$

Example 10

Styrene (C_8H_8), the precursor of polystyrene polymers, has a standard heat of combustion of -4395.2 kJ/mol. Write a balanced equation for the combustion reaction and calculate $\Delta H_f°$ for styrene (in kJ/mol).

$\Delta H_f°\ (CO_2) = -393.5 \text{ kJ/mol}$
$\Delta H_f°\ (H_2O) = -285.8 \text{ kJ/mol}$

$$C_8H_{8\,(\ell)} + 10\ O_{2\,(g)} \rightarrow 8\ CO_{2\,(g)} + 4\ H_2O_{(\ell)}$$

$\Delta H_{rxn}° = -4395.2 \text{ kJ/mol} = [(8 \text{ mol})(-393.5 \text{ kJ/mol}) + (4)(-285.8)]$
$\qquad\qquad\qquad\qquad\qquad\qquad - [(1)\ \Delta H_f°\ (C_8H_8) + (10)(0)]$

$\Delta H_f°\ (C_8H_8) = 104.0 \text{ kJ/mol}$