Thermochemistry

Chapter 6

Thermodynamics

- The study of energy and its conversions
- Differentiates between a system and the surroundings

System

- That part of the universe that is being studied
- In chemistry this is the reactants and the products in a chemical reaction

Surroundings

- Everything else in the universe
- In chemistry, everything other than the reactants and the products in a chemical reaction

Reactions are either…

Exothermic Reaction

- The potential energy of the reactants, H_R, is greater that the potential energy of the products, H_P
- The excess potential energy is converted to random kinetic energy
- Heat flows out of the system

Endothermic Reaction

- The potential energy of the reactants, H_R, is less than the potential energy of the products, H_P
- Energy flows into the system to increase the potential energy of the system

The First Law of Thermodynamics- The change in a systems internal energy (ΔE) is equal to the heat gained by the system (q) plus the work done on the system (W).

$$\boxed{\Delta E = q + w}$$

- In thermodynamics, each changing property has a:
  1. number value: which is the magnitude of the change
  2. sign: which indicates the direction of the change
     a. + = into the system (the amount the system increases)
     b. - = out of the system (the amount the system decreases)

Ex. 6.1 (p244) Calculate the ΔE for a system undergoing an endothermic process in which 15.6kJ of heat flows & where 1.4kJ of work is done on the system.

How is…

Work Done By a Chemical Reaction

- Work is done by the system on the surroundings when a gas in the system expands against constant pressure
- The expanding gas pushes other gases out of the way
- The work is leaving the system so the sign on it is negative
- Work is done on the system by the surroundings, when a gas in the system is compressed at constant pressure
- The work is going into the system so it is positive
- To calculate work:

$$\boxed{w = -P\Delta V \text{ at constant pressure}}$$

Expansion: $w = -P\Delta V = -(+)(+)$
therefore w is negative
Compression: $w = -P\Delta V = -(+)(-)$
therefore w is positive

Ex. 6.2 (p245) Calculate the work associated with the expansion of a gas from 46L to 64L at a constant pressure of 15atm.

Enthalpy (H)

- A substances heat content
- This is the total of all forms of energy in a substance
- This cannot be measured
- Only changes in enthalpy (ΔH) can be measured
- At constant pressure, ΔH is the heat flow, q ($\Delta H=q$, derived on p247)
- For a chemical reaction, ΔH=the heat of reaction

$$\boxed{\Delta H=H_{products}-H_{reactants}}$$

-
- For exothermic reactions:
  - $H_R>H_P$
  - so $\Delta H= H_p$(smaller) – H_R (larger) = negative
  - exothermic = $-\Delta H$ (leaving the system)
- For endothermic reactions:
  - $H_R<H_P$
  - so $\Delta H= H_p$(larger) – H_R (smaller) = positive
  - exothermic = $+\Delta H$ (entering the system)

Ex. 6.4 (p247) for CH_4, ΔH= -890 kJ/mol
ΔH for burning 5.8g CH_4= ?

Calorimetry

- the science of measuring heat flow
- makes use of a calorimeter

Calorimeter

- a device used to determine heat flow
- the reaction occurs inside an insulated container
- the reaction transfers heat to or from the surrounding H_2O
- the system is not air tight so pressure is constant
- you must know the heat capacity (C) of the surroundings (usually H_2O)

Heat Capacity (C)

- also called "specific heat capacity"
- the amount of energy needed to raise the temperature of 1gram of a substance 1°C
- the units are J/g°C
- to calculate heat flow:

$$\boxed{q=mC\Delta T\ *}$$

*on formula sheets

q=heat flow
m=mass of substance whose temperature is changing
C=heat capacity ($\frac{J}{g^\circ C}$, sometimes $\frac{J}{mol^\circ C}$ for gases)
ΔT=the change in temperature, $T_f - T_i$

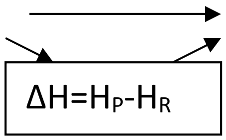
- if the surroundings is a dilute solution it is usually treated as being pure H_2O
- the density of dilute solutions is also considered to be the density of H_2O (1g/mL)

Ex. $\left.\begin{array}{l}\text{50.0mL of 1.0M HCl at 25°C}\\ \text{50.0mL of 1.0M NaOH at 25°C}\end{array}\right\}$ are mixed
T_{final}=31.9°C after the reaction ceases.
How much heat energy was released by this reaction?
(for H_2O: D=1g/mL, C=4.18 J/g°C)

Does how the change occurs make a difference in the resulting ΔH?

Hess's Law- The change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

- Enthalpy is a "state function"
- It depends on what "state" the substances are in
- Change is dependent on the enthalpies of the initial and final states but not the path of change



$$\boxed{\Delta H=H_P-H_R}$$

H_R H_P

$X \rightarrow Y \rightarrow Z$

- If a series of steps yields a desired overall equation, the sum of the ΔH's for the steps is the ΔH for the overall reaction

Ex. Given:

$N_{2\,(g)} + O_{2\,(g)} \rightarrow 2NO_{(g)}$ $\Delta H = 180kJ$

$2NO_{(g)} + O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$ $\Delta H = -112kJ$

What is the ΔH for the reaction: $N_{2\,(g)} + 2O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$?

Q: What happens to the ΔH if you use a step in the reverse direction?
A: Change the sign on the ΔH!

Ex. 6.7 (p255) For graphite: (C_g)

$C_{g\,(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H = -394kJ$

For diamond: (C_d)

$C_{d\,(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H = -396kJ$

What is the ΔH for the reaction: $C_{g\,(s)} \rightarrow C_{d\,(s)}$?

Ex. 6.8 (p256) Given:

Given:	ΔH:
a) $2B_{(s)} + 3/2\ O_{2\,(g)} \rightarrow B_2O_{3\,(s)}$	-1273kJ
b) $B_2H_{6\,(g)} + 3O_{2\,(g)} \rightarrow B_2O_{3\,(s)} + 3H_2O_{(g)}$	-2035kJ
c) $H_{2\,(g)} + \frac{1}{2}\ O_{2\,(g)} \rightarrow H_2O_{(l)}$	-286kJ
d) $H_2O_{(l)} \rightarrow H_2O_{(g)}$	44kJ

What is the ΔH for the reaction: $2B_{(s)} + 3H_{2\,(g)} \rightarrow B_2H_{6\,(g)}$?

Standard Enthalpy of Formation

- The change in the enthalpy when 1 mole of a compound is formed from its elements in the standard state

$$\Delta H_f^o$$

←standard state (o)

←a formation reaction (f)

Standard State:

- For a gas, pressure = 1atm
- For a solution, concentration = 1M
- For a pure solid or liquid, the solid or liquid state
- ΔH_f^o is a state function
- The ΔH of many reactions can be calculated by using ΔH_f^o of the reactants and products.
- For a chemical reaction:

$$\Delta H^o = \sum \Delta H_f^o{}_{\text{products}} - \sum \Delta H_f^o{}_{\text{reactants}} \ *$$

*on formula sheet

- The enthalpy change for a given reaction can be calculated by substacting the enthalpies of formation of the reactants from the enthalpies of formation of the products
- ΔH_f^o are found in Appendix 4
- ΔH_f^o for an element is zero

Why does this work?

- Remember Hess's Law:
  ΔH is the same no matter what path a reaction takes

$$\begin{tikzcd}
\text{Reactants} \arrow[rr] \arrow[dr, "\Delta H_f^o \text{ reactants}"'] & & \text{Products} \\
& \text{Elements} \arrow[ur, "\Delta H_f^o \text{ products}"'] &
\end{tikzcd}$$

($\Delta H = H_P - H_R$
so it's the same)

Ex. $CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(g)}$

1. Break the reactants up to form elements:

$CH_{4\,(g)} \rightarrow C_{(s)} + 2H_{2\,(g)}$ $\quad \Delta H_1 = -\Delta H_f^o\ CH_4$ (reverse reaction so -)

$2O_{2\,(g)} \rightarrow 2O_{2\,(g)}$ $\quad \Delta H_2 = 0\ (-\Delta H_f^o\ O_2)$ (no change)

2. Use the elements to form the products:

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\quad \Delta H_3 = \Delta H_f^o\ CO_2$

$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$ $\quad \Delta H_4 = 2\Delta H_f^o\ H_2O$

Total: $CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(g)}$

- Since the four reactions add up to yield the desired equation, the sum of the four ΔH's will be the ΔH of the desired equation.
- $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$ or
  $\Delta H = (\Delta H_3 + \Delta H_4) + (\Delta H_1 + \Delta H_2)$

But: ΔH_f^o $_{\text{products}}=\Delta H_3+\Delta H_4$ and

$-\Delta H_f^o$ $_{\text{reactants}}=\Delta H_1+\Delta H_2$

$\therefore \boxed{\Delta H=\Delta H_f^o{}_{\text{products}}-\Delta H_f^o{}_{\text{reactants}}}$

<u>Ex. 6.9</u> (p261) $4NH_{3\,(g)} + 7O_{2\,(g)} \rightarrow 4NO_{2\,(g)} + 6H_2O_{(l)}$

<u>Ex. 6.10</u> (p264) $2Al_{(s)} + Fe_2O_{3\,(s)} \rightarrow Al_2O_{3\,(s)} + 2Fe_{(s)}$

$\Delta H=?$