THERMODYNAMICS

Section A: Enthalpy and Enthalpy Diagrams

1. Thermodynamics is the study of changes in energy in chemical reaction and the influences of temperature on those changes, i.e it is the study of the transfer of energy in a chemical or physical change. All energy transferred is in the form of heat at constant pressure.
2. System: is the portion of the universe under study.
3. Surroundings: is everything in the universe that is not part of the system.
4. Heat content or enthalpy of a substance represents the total of all forms of energy within a substance.
   It is impossible to measure the total heat content of a substance: the heat content of a substance is constant as long as no energy enters or leaves the substance.
5. The capital letter H is the symbol used to represent the heat content (or **enthalpy**) of a substance, Enthalpy is measured in Joules (J) or kJ.
6. Molar Enthalpy: Heat content of one mole of the substance. This is a characteristic property of the substance. It is the energy stored in the substance during its formation. Heat stored, H, can not be measured directly, however, the changes in heat content that occur during a chemical reaction can be measured. It is impossible to estimate absolute enthalpies, only enthalpy changes may be determined.
7. **Elements in their standard state,** (i.e at 25 ^{O}C and 101.3 kPa), are regarded as having zero enthalpy, i.e. they are by convention assumed to have a heat content of zero.
8. ΔH (delta H) represents the changes in energy of a chemical reaction (the Heat of reaction) :

$$\Delta H = H_p - H_r$$

H_p = Enthalpy of the products
H_r = Enthalpy of the reactants

Since most laboratory work is carried out at constant pressure, it is usual to deal with the heat absorbed at constant pressure. This quantity is called the change in enthalpy, ΔH, and it is equal to the heat absorbed at constant pressure:

q = ΔH (at constant pressure) q = the quantity of heat (heat of the reaction)

9. An exothermic reaction has a negative, - ΔH. Heat is lost by the substance in a reaction, the temperature of the surrounding increases. The enthalpy of the products is lower than those of the reactants.
10. An endothermic reaction has a positive, + ΔH. Heat is gained by the substance in a reaction, the temperature of the surroundings decreases. The enthalpy of the products is higher than those of the reactants. *See Graphs ...*

11. The change in heat content, (enthalpy), of a reaction is related to:
    i) the change in the number of bonds breaking and forming, and
    ii) the strengths of these bond as the reactant form products.

12. The enthalpies of chemical substances depend upon temperature and pressure. By convention ΔH values are usually reported for reactions carried out at 25°C and the pressure is 100 kPa, (older convention for the standard pressure is 101.325 kPa). ΔH°, represents the standard enthalpy change at these conditions, the units are generally kJ or kcal unless otherwise stated. The reactants and products are in their usual or standard state at 25°C and the pressure is 100 kPa. If other conditions are employed they are noted.

13. Heat of reaction: when all transformations of energy produce heat energy. The sign of the ‘heat of reaction; indicates whether a reaction is endothermic or exothermic.
14. Energy is the ability to do work, it is measured in Joules, (J): 1 cal = 4.184 J

How is the energy stored in a molecule?

The total enthalpy, or heat content, of a molecule is the sum of all the kinetic energy, E_k, and potential energy, E_p, within the molecule.

Molecular Enthalpy, H, = sum of all $(E_k + E_p)$ + energy stored in the substance

Each substance has a characteristic enthalpy, measured per mole of the substance, referred to as the molar enthalpy:

Molar Enthalpy = $(E_k + E_p)$ for one mole of molecule (6×10^{23})

Kinetic Energy (E_k): is the energy of a moving object, temperature is a measure of E_K

$$E_k \text{ of translational is } \alpha \quad T \quad \alpha \quad \text{velocity} \quad = \frac{1}{2} mv^2$$

where T is the temperature, m is the mass in kg and v is the velocity in m s^{-1}, 1J = $1 kgm^2 / s^2$

There are three kinds of motion, (= total E_K), associated with a molecule:
1. Vibrational: the alternate movement of atoms towards and away from the centre of mass.
2. Rotational: energy associated with the end-over-end motion of a molecule as it twirls through space.
3. Translational: motion of the entire molecule through space

Potential Energy (E_p): is the energy a motionless body has by virtue of its position.
The total potential energy of a substance depends upon a number of factors. Some of them are:

1. The attractive forces between the molecules (intermolecular E_p). These forces are small in gases , relatively large in liquids and even greater in solids.
2. The type and the number of chemical bonds in a molecule (i.e intramolecular E_p). This could be the energy of a covalent bond or that of an ionic bond as in NaCl. When forces acting between particles in a substance are strong , the E_p of the substance is low; and the system is stable.
3. The temperature
4. The state of the substance. i.e gas, liquid or solid.

E_p is due to attractive forces in a substance and is associated with change of state.

The tendency of matter towards **maximum stability** can be viewed as the tendency towards **minimum enthalpy** that is lowest E_p.

Therefore chemical reactions tend towards products with lower E_p.

Section B: Specific Heat and Heat Capacity

The energy required to raise one gram of water by 1 ^{O}C is called the calorie, this is from the Latin word calor meaning ...

The heat flow associated with a chemical reaction is measured experimentally using a device called a ***calorimeter.*** ***Calorimetry***, the science of measuring heat flow, is observing the temperature change when a body absorbs or releases heat, Substance differ in their responses to being heated. One substance might require a great deal of heat to raise its temperature by one degree, while another will exhibit the same temperature change after absorbing relatively little heat. The magnitude of the heat flow that accompanies an increase in temperature depends upon the mass and the identity of the substance involved. To determine the amount of heat associated with a known ΔT for a given amount of a substance, it is necessary to know the ***heat capacity, C,*** of that substance. Every object has a heat capacity.

Definition: **Heat Capacity**: the amount of heat energy required to raise the temperature of a given amount of a substance by one degree:

$$\text{Heat Capacity, C} = \frac{\text{Heat Absorbed, or released by an object, Q}}{\text{Increase in Temperature, } \Delta \text{ T}}$$

Also, since the heat required will depend on the amount of substance being heated, that quantity must be specified. Thus the units for heat capacity are usually given as J/g or J/ mol °C .

Heat Capacity is an extensive property because it depends directly on the amount of substance. In contrast, an intensive property is not related to the amount of substance, ex. temperature. Heat capacity values are sometimes tabulated as **specific heat capacity**, commonly referred to as **specific heat, c.**

Specific Heat, c: is the amount of heat required to raise the temperature of one gram of material by one degree (J/g K)

$$\text{Specific Heat, c} = \frac{\text{Heat Capacity, C}}{\text{Mass, m}}$$

$$\text{Specific Heat, c} = \frac{\text{Heat Absorbed, Q}}{\text{(Mass, m) x (Change in Temperature, } \Delta \text{ T)}}$$

Therefore,

Heat Energy, Q = (Mass, m) x (Specific Heat, c) x (Change in Temperature, ΔT)

In symbols: $\mathbf{Q = m\,c\,\Delta T}$

Sometimes it is more useful to express specific heats in terms of the molar heat capacity. Simply defined the molar heat capacity is the energy required to heat one mole of material one degree Celsius.

Molar Heat capacity = specific heat capacity x molar mass (J/mol ^{O}C)

Water is an excellent liquid for use in hot water bottles because of its high specific heat capacity, (4.18 $\text{Jg}^{-1}\text{K}^{-1}$). For a given temperature rise above room temperature, it stores almost twice as much heat as, for example, ethanol, whose specific heat capacity is only 2.4 $\text{Jg}^{-1}\text{ K}^{-1}$

Examples:

1. When 2.71 x 10^{2} J of energy is absorbed by a cup of tea, its temperature rises by 8.30 ^{O}C What is the heat capacity of the cup of tea?
2. A gold ring with a mass of 5.5 g changes temperature form 25.0 to 28.0^{O}C, how much energy in Joules has it absorbed. (c = 0.129 J/g^{O}C for gold)
3. If 25.6 g of aluminium absorbs 0.5571 kJ of heat, its temperature rises by 42.6^{O}C. What was the original temperature of the aluminium? (c = 0.902 J/g^{O}C for Al)

Now Complete:

1. Heat Capacity and Specific Heat Problems: I
2. Heat Capacity and Specific Heat Problems: **II**

Section C: Labelling Enthalpy Changes

In order to tabulate numerical values of standard enthalpy change, certain types of reaction and their enthalpy changes are labelled.

Energy Changes during Changes of State:

The particles of a solid are arranged in a regular three-dimensional structure. When a solid is heated the particles gain energy and vibrate more vigorously. Eventually they are able to leave their positions in the structure and move past one another, they flow as a liquid; the solid melts.

ΔH increasing (+), Endothermic
\-->
solid $\rightleftharpoons$ liquid $\rightleftharpoons$ Vapour
<--
ΔH decreasing (-), Exothermic

Molar Heat of Fusion, ΔH^0 : the heat absorbed by one mole of solid when it melts to a liquid at constant temperature and pressure.

Molar Heat of Solidification: the heat released by one mole of liquid when it solidifies to a solid at constant temperature and pressure.
(The enthalpy of solidification is the negative of the enthalpy of fusion.)
Molar Heat of Condensation:
Molar Heat of Vaporisation:
Molar Heat of Sublimation:

For a given substance $\Delta H_{vapourisation} > \Delta H_{fusion}$ because in the change from liquid to vapour there are much greater changes in intermolecular distances and a much larger increase in $E_{p.}$

Calculating Enthalpy Changes for Warming Substances and for Changes of State

Liquid → Vapour

This requires energy (heat); this is the reason (a) you cool down after swimming.
(b) you use water to put out a fire.

Heating/Cooling Curve for Water

Example 1

What quantity of heat is required to melt 500.0 g of ice and heat the water to steam at 100˚C?
(specific heat of water = 4.2 J/g K, Heat of Fusion of ice = 333 J/g.
Heat of vapourization = 2260 J/g)

Solution

1. To melt ice…
2. To raise water from 0˚C to 100˚C …
3. To evaporate water at 100˚C …
4. Total heat energy…

Example 2

50.0 cm^3 of liquid at 25°C is lowered to -4°C to form ice.

a) Calculate ΔH for this change
b) Calculate the ΔH for one mole of water changing from 25°C to -4°C.

Now Do Assignment Sheet:

Enthalpy Changes for Warming Substances and for Changes of State

Section D: Standard Heats of Reaction, ΔH^0

Thermo-chemical data may be given by writing a chemical reaction and listing the ΔH^0 value as it is written , i.e.

$$H_{2\,(g)} + 1/2\ O_{2(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H^0 = -242\ kJ$$

Note:

1. Fractional coefficients are now acceptable.
2. ΔH^0 is used to represent an enthalpy change per mole measured at 298 K and 100 kPa pressure, and the state of the substance is in which they appear in the equation.
3. The state symbol of each substance must be specified, occasionally allotropes (different forms of the same element, such as diamond and graphite, which are allotropes of carbon), will be encountered. the most stable of these, (graphite for carbon), is the standard state.
4. The units of ΔH^0 are kJ mol^{-1}
5. When a **reaction is reversed the sign of the ΔH^0 is also reversed** ...

$$H_2O_{(g)} \longrightarrow H_{2\,(g)} + 1/2\ O_{2(g)} \qquad \Delta H^0 = +242\ kJ$$

6. If the coefficients of the substances in a chemical reaction are multiplied by a factor, then the ΔH^0 value must be multiplied by the **same** factor ...

$$2\ H_2O_{(g)} \longrightarrow 2\ H_{2\,(g)} + O_{2(g)} \qquad \Delta H^0 = +484\ kJ$$

Example: The thermite reaction is highly exothermic:

$$\_\_\ Al_{(s)} + \_Fe_2O_{3\,(s)} \longrightarrow \_\ Fe_{(s)} + \_\ Al_2O_{3(s)} \qquad \Delta H^0 = -848\ kJ$$

How much heat is liberated when 36.0 g of Al react with an excess of $Fe_2O_{3(s)}$? (First: Balance the equation.)

Now work through the Assignment: Equations using Heats of Reactions

Section E: Enthalpy Changes

The word 'standard' is sometimes omitted but is always implied by the symbol $^{\varnothing}$, the word 'change' is also often omitted in the following enthalpy changes…

Enthalpy of formation, ΔH^0_f: the enthalpy change when one mole of compound is formed from its elements under standard condition.

Enthalpy of combustion, ΔH^0_c

Enthalpy of solution, ΔH^0_{soln}

Enthalpy of neutralisation, $\Delta H^0_{neutralisation}$
(Note: All neutralisation reactions involving a strong acid and a strong base have the same standard molar enthalpy change, WHY??? Write the net ionic equations for each of the following reactions to enable you to answer the question:
(1) $HCl_{(aq)} + NaOH_{(aq)}$ **------>** (2) $H_2SO_4 + KOH$ ----> **)**

See: Table of Definitions of Types of Enthalpy Changes

Section F: Experimental Determination of Enthalpy Change

Enthalpy change of a reaction may be measured using a calorimeter in which the system is insulated from the surroundings. If the maximum temperature of the system is recorded and if the heat capacity of the system is known, it is east to calculate the quantity of heat, which would have to be taken from the system in order to restore it to its initial temperature. This quantity of heat is the enthalpy change.

There are several types of insulated calorimeter one can use for simple experiments (see your textbook). These calorimeters insulate the system from the surroundings so that all energy changes occur within the system. The energy exchanged with the surroundings is usually small enough to be ignored. Bomb Calorimeters give the best results.

Example: How the enthalpy change of reaction can be calculated from experimental data.
An excess of zinc powder was added to 50.0 cm^3 of 0.100 mol dm^{-3} $AgNO_3$ in a polystyrene cup. Initially, the temperature was 21.10 ˚C and it rose to 25.40 ˚C. Calculate the enthalpy change for the reaction:

$$Zn_{(s)} + 2\,Ag^{+1}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + 2\,Ag_{(s)}$$

Assume that the density of the solution is the same as that of water, 1.00 g cm^{-3} and its specific heat capacity is the same as that of water, 4.18 kJ kg^{-1} K^{-1}. Ignore the heat capacity of the metals.

Solution

1.Since the polystyrene cup is an insulator and its heat capacity is almost zero, you can assume that no energy is exchanged between system and surroundings. All the chemical energy released in the chemical reaction is transformed into heat energy, which raised the temperature of the solution: $\Delta H = m\,c\,\Delta T$

2. Calculate the enthalpy change for 2 mole of Ag^{+1}:
3. Now, write the complete thermochemical equation:

Assignment

1. Calculate the enthalpy change for one mole of Zn and $CuSO_{4\,(aq)}$:

   $$Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

   when 25.0 cm^3 of 1.00 mol dm^{-3} of $CuSO_{4(aq)}$ initially at 27.0˚C is placed in a polystyrene cup, 6.00 g of $Zn_{(s)}$ is added, the temperature rose to 77.8 ˚C

2. A calorimeter has a heat capacity of 6.00 kJ K^{-1}. The combustion of 2.00 g of magnesium raised the temperature from 20.20 ^{O}C to 22.32 ^{O}C. Calculate the enthalpy change of combustion.
3. A pellet of potassium hydroxide weighing 0.166 g is added to 50.0 g of water in a styrofoam cup. The temperature of the water rises from 19.4 ^{O}C to 20.2 ^{O}C. Find the standard enthalpy of solution of KOH.
4. A bomb calorimeter was calibrated by burning a pellet of benzenecarboxylic acid, $C_7H_6O_2$, of mass 0.7934 g. The temperature rise was 2.037 ^{O}C. ΔH_c^0 for benzenecarboxylic acid is - 3227.0 kJ mol^{-1}

a) What fraction of a mole of benzenecarboxylic acid was used?
b) Calculate the heat capacity of the calorimeter using the relationship:
heat given out = heat capacity x temperature rise.

5. Describe how you would measure the molar enthalpy of combustion of ethanol in the laboratory. Say what precautions you would take to minimise error. Explain how you would calculate ΔH_c from the results.

Measuring an Enthalpy Change of Solution

When substances dissolve, the enthalpy change depends on the relative amounts of solute and solvent.

Example 1
When 0.85 g of anhydrous LiCl was added to 36.0 g of H_20 at 25.0˚C in a polystyrene cup, the final temperature of the solution was 29.7˚C. Calculate the enthalpy change of solution for one mole of LiCl.

Example 2
25.0 cm^3 of 1.00 mol dm^{-3} $HCl_{(aq)}$ at 21.5 ^OC were placed in a polystyrene cup.
25.0 cm^3 of 1.00 mol dm^{-3} $NaOH_{(aq)}$ at 21.5 ^OC were added. The mixture was stirred, and the temperature rose to 28.2 ^OC.
The density of each solution = 1.00 gcm^3, and the specific heat capacity of each solution = 4.18 JK^{-1} g^{-1}. Calculate the standard molar enthalpy of neutralisation.
(Answer = 56.0 kJ mol^{-1})

Example 3
You want to boil a kettle. The kettle contains 2.00 kg of water at 20 ^OC. What mass of natural gas, (FYI: methane, CH_4), must be burned to raise this quantity of water to 100 ^OC ? (assume no heat is lost. Specific heat capacity of water = 4.18 Jg^{-1} K^{-1}, ΔH^0_c (CH_4) = - 890 kJ mol^{-1}.)

Example 4
When 6.16 g of $MgSO_4 . 7\ H_20$ was dissolved in 50.0 cm^3 of water. The temperature change was 15.75˚C. Calculate the enthalpy change of solution $MgSO_4 . 7\ H_20$.
Now, you can use this method of calculation to plan a lab for determination an enthalpy change of solution.
Now Do Assignment: Enthalpy Review Questions

Reading: MREs Are Heated in the FRH

If you have been in the Army or Marine Corps. You know about MREs- meal ready to ear- and FRHs- Flameless Ration Heaters. Soldiers need to ear when in the fields, and so, until recently, they carried the canned C-rations made famous in World War II. Beginning with Operation Desert Storm, however, the 1990-1991 war to push Iraq out of Kuwait, and in the recent effort to feed starving people in Somalia, soldiers carried MREs with an FRH.

The main course of a MREs is a meal, such as chicken stew or spaghetti and meatballs. In a pouch made of plastic and aluminium foil. The food can be heated by dropping the pouch unto a pot of boiling water or leaning it on the exhaust manifold of an engine. But there may not be time to boil water or wait for dinner to hear on an engine.

The alternative is the FRH, To hear an MRE a soldier drops the food pouch into a bag-like sleeve, slides in the FRH which is enclosed in a thin plastic sleeve of its own, and them adds a small amount of water to the sleeve. The FRH contains magnesium metal, which combines with water to form magnesium hydroxide in a very exothermic, oxidation-reduction reaction.

$$Mg_{(s)} + 2\ H_2O_{(l)} \rightarrow Mg(OH)_{2(aq)} + H_{2(g)} + \text{heat}$$

The reaction generates enough hear to cook the meal without flame or smoke. If you have never seen an MRE with its FRH, you might find a hand warmer in a camping store that world on the same principle. One type of hand warmer contains iron powder and other chemicals. It also works by an oxidation-reduction reaction, but in this case it is the reaction of iron with the oxygen gas of air.

$$4Fe_{(s)} + 3\ O_{2\ (g)} \rightarrow 2\ Fe_2O_{3(s)} + \text{heat}$$

This reaction is also very exothermic and can allow the hand warmer to maintain a temperature of 57˚C to 69˚C for several hours if the oxygen flow is somewhat restricted, as by keeping the warmer in one of your gloves.