Energy Tutorial 1

1. Understand the meaning of "system". This is the chemical reaction in our case. The "surroundings" are everything outside the system. Heat and/or work can be transferred from one to the other

2. The internal energy of a system (E) is the sum of all kinetic and potential energies of the things in the system (usually the reactants and products of a reaction). The internal energy of the system increases if heat is added to the system or if work is done on the system. The internal energy of the system decreases if heat is lost to the surroundings or if the system does work on the surroundings.

1. Heat, q

Some substances can absorb more heat without their temperature increasing much. We say that these substances have a high heat capacity. The specific heat capacity, C, of any substance can be measured by measuring how much heat is required to raise the temperature of a certain mass of the substance by a certain amount. For instance, 4.18 J of heat are required to raise the temperature of 1 g of water by 1 Celcius degree, i.e. the specific heat capacity of water is $4.18\ \mathrm{J\ ^oC^{-1}\ g^{-1}}$ (= $75.3\ \mathrm{J\ ^oC^{-1}\ mol^{-1}}$). The amount of heat transferred can be calculated from $q = m\ C\ \Delta T$.

For example suppose you heat up a 2.00 kg block of iron metal from 25 ^{o}C to 500 ^{o}C. How much heat is required? For iron, $C = 25.10\ \mathrm{J\ mol^{-1}\ ^oC^{-1}}$.

$C = 25.10\ \mathrm{J\ mol^{-1}\ ^oC^{-1}} \times (1\ \mathrm{mol} / 55.85\ \mathrm{g}) = 0.449\ \mathrm{J\ g^{-1}\ ^oC^{-1}}$

$q = m\ C\ \Delta T$
$= 2{,}000\ \mathrm{g}\ (0.449\ \mathrm{J\ g^{-1}\ ^oC^{-1}})(500 - 25)^o\mathrm{C}$
$= 426{,}550\ \mathrm{J}$
$= 427\ \mathrm{kJ}$

What are q_{system} and $q_{surroundings}$ in this example?

Our system is the thing of interest, i.e. the block of iron in this case. Since it gained heat, $q_{system} > 0$, i.e. $q_{system} = +427$ kJ.
Thus, $q_{surroundings} = -q_{system} = -427$ kJ

For example suppose we do the reaction $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ in a calorimeter such that all the heat generated by the reaction is captured by the solution, i.e. the calorimeter absorbs a negligible amount of heat itself. Calculate the value of q for the reaction (i.e. q_{system}) if addition of 2 moles $HCl_{(aq)}$ to 2 moles $NaOH_{(aq)}$ in 5 L water causes a temperature rise of 5.33 ^{o}C. Assume that the heat capacity of the products is equal to that of pure water.

The total heat released will be q = m C ΔT, where m is the mass of the material absorbing the heat, C is the heat capacity of the absorber (4.18 J $^{o}C^{-1}$ g^{-1}) and ΔT = 5.33 ^{o}C. But note that the heat is lost from the system, so $q_{system} = -q_{surroundings} = -\, m\, C\, \Delta T$.

The mass of material absorbing the heat is the mass of the 5L of water (= 5,000 g), plus the products of reaction.

$$m = 5000\ g + 2\ mol\ NaCl \times (58.5) g\ mol^{-1} + 2\ mol\ H_2O \times (18.02) g\ mol^{-1} = 5153\ g$$

q = -5153 g x 4.18 J $^{o}C^{-1}$ g^{-1} x 5.33 ^{o}C
= -114,800 J
= -114.8 kJ

2. Work, w

Work is done when a force causes a mass to move. In the case of a chemical reaction, work is done when a gas expands or contracts. For instance as a balloon ascends through the atmosphere, it expands because the air pressure decreases. In effect, it pushes back the atmosphere, and we say the balloon "does work on the surroundings." The energy of the gas inside the balloon therefore decreases and so $w_{system} < 0$. In general, $w = -p\Delta V$, where ΔV is the change in volume of the system ($V_{final} - V_{initial}$).

For example suppose you inflate a balloon with helium gas from 10 mL to 1.5 L. Calculate the work done.

Here the work is done by the gas in the balloon, pushing back the atmosphere as the balloon expands.

$V_{initial}$ = 0.010 L
V_{final} = 1.5 L
p = 1.00 bar (room pressure – the gas is expanding against this constant pressure)

$w = -p\Delta V$
$= -\, p(V_{final} - V_{initial})$
= - 1.00 bar (1.5 L – 0.010 L)
= - 1.49 L bar
= - 149 J (1 L bar = 100 J)

3. Internal Energy, E

In a chemical reaction, heat and work may be transferred between the system and the surroundings. The internal energy (E) of the system may increase or decrease as a consequence.

For example the reaction to make ammonia is $N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$. One mole of this reaction releases 92.2 kJ of heat. If the pressure is constant at 40 bar and the volume change is -1.12 L, calculate ΔE.

$\Delta E = q + w$
$= q - p\Delta V$
$= - 92{,}200 \text{ J} - 40 \text{ bar}(-1.12 \text{ L}) \times (100 \text{ L bar / J})$
$= - 87{,}720 \text{ J}$
$= - 87.7 \text{ kJ}$

Note that $\Delta E < q$. This is because the system contracted and a small amount of energy in the form of $p\Delta V$ work is obtained by the system.

4. Enthalpy

Enthalpy (H) is a measure of the heat in a system. When a change takes place in the system (e.g. a reaction occurs), there is likely a change in enthalpy (ΔH^o). Heat is then either absorbed from the surroundings or given off by the system to the surroundings. ΔH^o is thus a measure of the difference in heats in the products and the reactants. Note that we use the superscript ^{o} to indicate that the reaction is taking place at standard conditions, i.e. 1 atm pressure, 25°C, with all reactants and products in their standard states under these conditions. Although not all reactions actually take place under these conditions, the value of ΔH^o is not very different from the value of ΔH under the actual conditions used.

Using Hess' law, it is not difficult to show that the value of ΔH^o is the sum of the ΔH_f^o values (standard heats of formation) of the products minus those of the reactants.

Example 1. For instance, take the reaction:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

For this reaction, $\Delta H^o = + 131.3 \text{ kJ mol}^{-1}$ (i.e. endothermic; heat must be supplied by the surroundings to the system to make the reaction go.)

Find ΔH^o for the reaction involving 10.0 g $C_{(s)}$ and excess $H_2O_{(g)}$.

$$10.0\ g\ C \times \frac{1\ mol\ C}{12.01\ g\ C} \times \frac{1\ mol\ reaction}{1\ mol\ C} \times \frac{131.3\ kJ}{1\ mol\ reaction} = 109.3\ kJ$$

Example 2. $\Delta H^o = -890.3 \text{ kJ mol}^{-1}$ for the reaction:

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

How many litres of $CH_{4(g)}$ at 2 bar, 25°C must be burned to heat 3.00 L of water from 20°C to 100°C. Assume half of the heat is lost, i.e. is not absorbed by the water.

1. Heat required = $m\ C\ \Delta T = 3{,}000 \text{ g } (4.18 \text{ J } ^oC \text{ g}^{-1})(100 - 20)^oC = 1.00 \times 10^6 \text{ J}$ (= 1 MJ)

2. Moles of reaction required = 1.00 x 10^6 J / (890.3 x 10^3 J / mol) = 1.12 moles
3. Moles $CH_{4(g)}$ = moles reaction = 1.12 moles $CH_{4(g)}$ required (x 2 = 2.24 moles, accounting for lost heat!)

4. $V = \frac{nRT}{p} = \frac{2.24\,mol(0.08314\ \frac{\text{L bar}}{\text{mol K}})(25+273)K}{2.00\,bar} = 27.6\,L$

5. Reaction Enthalpy

Using Hess' law, it is not difficult to show that the value of ΔH^o is the sum of the ΔH_f^o values (standard enthalpies of formation) of the products minus those of the reactants.

Example 1. For instance, take the reaction:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

For this reaction, $\Delta H^o = (\Delta H_f^o\ (CO_{(g)}) + \Delta H_f^o\ (H_{2(g)})) - (\Delta H_f^o\ (C_{(s)}) + \Delta H_f^o\ (H_2O_{(g)}))$ (i.e. products minus reactants). Note that two of these quantities are zero, because the enthalpy of formation of elements in their standard states are zero. Thus, this simplifies to $\Delta H^o = \Delta H_f^o\ (CO_{(g)}) - \Delta H_f^o\ (H_2O_{(g)}) = -110.5 - (-241.8) = +131.3$ kJ mol^{-1} (i.e. endothermic; heat must be supplied by the surroundings to the system to make the reaction go.)

Example 2. Find ΔH^o for the reaction $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

Note that the Na^+ and Cl^- are spectator ions, and the net ionic reaction is just:

$$H^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow H_2O_{(l)}$$

$$\Delta H^o = \Delta H_f^o\ (H_2O_{(l)}) - \Delta H_f^o\ (H^+{}_{(aq)}) - \Delta H_f^o\ (OH^-{}_{(aq)}) = -285.8 - 0 - (-230.0) = -55.8 \text{ kJ mol}^{-1}$$

(exothermic, as observed when adding an acid to a base).

Example 3. Find ΔH^o for the reaction $3\ H_{2(g)} + N_{2(g)} \rightarrow 2\ NH_{3(g)}$. Note that not all of the stoichiometric coefficients are equal to one in this example. Thus,

$$\Delta H^o = 2\ \Delta H_f^o\ (NH_{3(g)}) - 3\ \Delta H_f^o\ (H_{2(g)}) - \Delta H_f^o\ (N_{2(g)}) = 2(-46.1) - 2(0) - 3(0) = -92.2 \text{ kJ mol}^{-1}$$

Example 4. The combustion of thiophene: $C_4H_4S_{(l)} + 6\ O_{2(g)} \rightarrow 4\ CO_{2(g)} + 2\ H_2O_{(l)} + SO_{2(g)}$

ΔH_{comb} for this reaction = -2523 kJ mol^{-1}. Find the standard enthalpy of formation of thiophene.

$\Delta H_{comb} = [4\ \Delta H_f^o(CO_{2(g)}) + 2\ \Delta H_f^o(H_2O_{(g)}) + \Delta H_f^o(SO_{2(g)})] - [\Delta H_f^o(C_4H_4S_{(l)}) + 6\ \Delta H_f^o(O_{2(g)})]$

$-2523 = [4(-393.5) + 2(-285.8) + (-296.8)] - [\Delta H_f^o(C_4H_4S_{(l)}) + 6\ (0)]$

solving, $\Delta H_f^o(C_4H_4S_{(l)}) = +80.6$ kJ mol^{-1}

Example 5: find the enthalpy of reaction for $2\ C_{(graphite)} + 2\ H_{2(g)} \rightarrow C_2H_{4(g)}$

(Note that we are really finding the enthalpy of formation of ethylene ($C_2H_{4(g)}$) here!)

using the following information:

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}\ \Delta H = -393.5\ \text{kJ mol}^{-1}$ **(reaction 1)**

$C_2H_{4(g)} + 3\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 2\ H_2O_{(g)}\ \Delta H = -1410.9\ \text{kJ mol}^{-1}$ **(reaction 2)**

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}\ \Delta H = -571.6\ \text{kJ mol}^{-1}$ **(reaction 3)**

first, we note that we need $2\ C_{(graphite)}$ on the LHS. Thus, use twice reaction 1:

$2\ C_{(graphite)} + 2\ O_{2(g)} \rightarrow 2\ CO_{2(g)}\ \Delta H = 2(-393.5\ \text{kJ mol}^{-1})$

we also need $2\ H_2$ on the LHS, thus use reaction 3:

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}\ \Delta H = -571.6\ \text{kJ mol}^{-1}$

and we need C_2H_4 on the RHS, thus use the reverse of reaction 1. Note the reversal of the sign on ΔH:

$2\ CO_{2(g)} + 2\ H_2O_{(l)} \rightarrow C_2H_{4(g)} + 3\ O_{2(g)}\ \Delta H = +1410.9\ \text{kJ mol}^{-1}$

Adding the above three reactions gives the desired reaction, and the ΔH is the sum of the ΔH’s of the three reactions:

$2\ C_{(graphite)} + 2\ H_{2(g)} \rightarrow C_2H_{4(g)}\ \Delta H = +52.3\ \text{kJ mol}^{-1}$