CHAPTER 7
THERMOCHEMISTRY

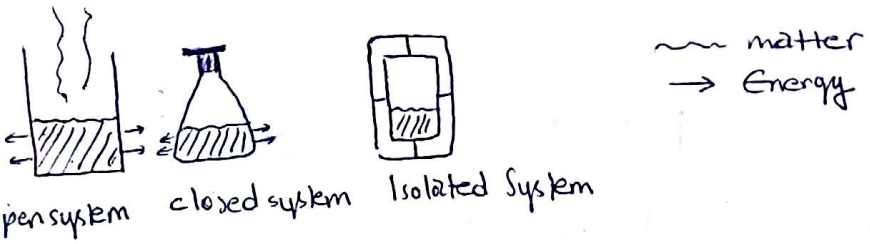
System: A system is the part of the universe chosen for study. And the surroundings are that part of the universe outside the system.

There are three types of systems

a) Open system: Freely exchanges energy and matter, with its surroundings.

b) Closed system: Can exchange energy, but not matter, with its surroundings.

c) Isolated system: No exchange of energy and matter occurs in an isolated system. It does not interact with its surroundings.



Energy: Energy is the capacity to do work. Work is done when a force acts through a distance.

Kinetic Energy: The energy of a moving object is called kinetic energy.

Kinetic energy $e_k = \frac{1}{2} m v^2$ $\quad kg\ m^2 s^{-2} = 1\ J = 1\ kg m^2 s^{-2}$

work $w = m \times a \times d$

a: acceleration

Potential Energy: is energy due to the condition, position or composition; it is an energy associated with forces of attraction or repulsion between objects.

Thermal Energy: A kinetic energy associated with random molecular motions is called thermal energy.

HEAT: Heat is energy transferred between a system and its surroundings as a result of temp. difference.

Energy that passes from a warmer body to a colder body is transferred as heat.

* A system does not contain heat, it contains energy and heat is simply a quantity of energy may be transferred between two objects.

The quantity of heat (q) depends on:

a) how much the temp. is to be changed (3)

b) the quantity of substance (1)

c) the nature of substance (2)

Calorie (cal): The quantity of heat to change the temp. of 1 g of water by 1 °C.

$$1\ cal = 4.184\ J$$

Heat capacity: Heat capacity is the amount of heat required to to change the temp. of a system by 1 °C.

* If the system is a 1 mole of substance, it is called molar heat capacity.
* If the system is 1 g of substance, it is called specific heat capacity. or specific heat.

→ At 25 °C, the specific heat of water:

$$4.18\ J/g\,^\circ C = 4.18\ J g^{-1} {}^\circ C^{-1}$$

$$\text{quantity of heat} = \underbrace{\text{mass of substance} \times \text{specific heat}}_{\text{heat capacity} = C} \times \text{temp. change}$$

$$q = m \times \text{specific heat} \times \Delta T = C \times \Delta T \qquad \Delta T = T_f - T_i$$

* If ΔT is (+), q will be (+) meaning that the system gains heat.
* If ΔT is (−), q will be (−) meaning that the system lost energy.

Law of conservation of energy : In interactions between a system and its surroundings, the total energy remains constant. Energy is neither created nor destroyed.

$$q_{system} + q_{surrounding} = 0$$

Example: How much heat is required to raise the temp. of 7.35 g water from 21 to 98 °C.

$$q = m \times s.heat \times \Delta T$$

$$q = 7.35\ g \times 4.18 \frac{J}{g\,°C} \times (98-21)\,°C = 2.36 \times 10^3\ J$$

Example: In a cup 150 g sample of lead is heated to 100°C. This lead added to a 50 g, 22°C water. The final temp. of lead-water mixture is 28.8 °C. What is the specific heat of lead.

$$q_{water} = 50\ g \times 4.18 \frac{J}{g\,°C} \times (28.8-22)\,°C = 1.4 \times 10^3\ J$$

$$q_{lead} = -q_{water} = -1.4 \times 10^3\ J$$

$$-1.4 \times 10^3\ J = 150\ g\ lead \times \text{specific heat} \times (28.8-100)\,°C$$

so, specific heat of lead = 0.13 $J/g\,°C$

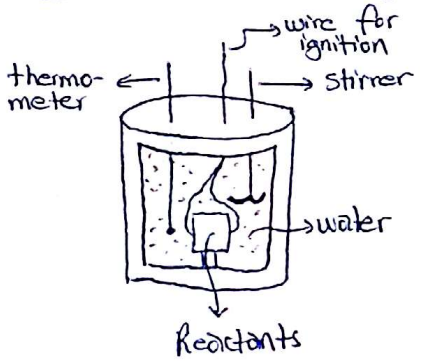
Heats of Rxn. and Calorimetry

A heat of rxn (q_{rxn}) is the quantity of heat exchanged between a system and its surroundings when a rxn. occurs within the system at a constant temp.

* Exothermic rxn. is one that produces temp. increase, gives off heat to the surroundings. ($q_{rxn} < 0$)
* Endothermic rxn. is one that gains of heat from the surroundings. ($q_{rxn} > 0$)

→ Heats of reaction are experimentally determined in a calorimeter; a device for measuring quantities of heat.

Bomb Calorimetry:



In bomb, the combustion rxn. is initiated by passing an electrical current through the wires. When wire becomes hot enough the sample start to burn and heat is released. when combustion occurs. This heat is absorbed by by calorimeter, causing a rise in the temp. of water.

To calculate the heat of combustion, total heat capacity of calorimeter (C_{cal}) must be known.

$$q_{calorimeter} = \text{heat capacity of calorimeter} \times \Delta T$$

$$\boxed{q_{cal} = C_{cal} \times \Delta T} \quad \text{and} \quad \boxed{q_{rxn} = -q_{cal}}$$

Example: The combustion of 1.010 g sucrose ($C_{12}H_{22}O_{11}$) in a bomb calorimeter causes the temp. to rise from 24.92 to 28.33 °C. Heat capacity of calorimeter is 4.90 kJ/°C.

$$q_{cal} = C_{cal} \times \Delta T = 4.90\ kJ\ °C^{-1} \times (28.33 - 24.92)°C = 16.7\ kJ$$

$$q_{rxn} = -q_{cal} = -16.7\ kJ \quad \text{(heat of combustion for 1.010 g sample)}$$

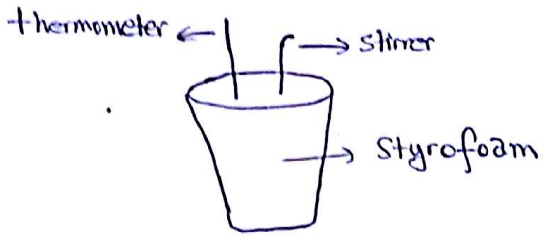
: for per gram $C_{12}H_{22}O_{11}$

$$q_{rxn} = \frac{-16.7\ kJ}{1.010\ g\ C_{12}H_{22}O_{11}} = -16.5\ kJ/g\ C_{12}H_{22}O_{11}$$

per mole $C_{12}H_{22}O_{11}$

$$q_{rxn} = \frac{-16.5\ kJ}{g\ C_{12}H_{22}O_{11}} \times \frac{342.3\ g\ C_{12}H_{22}O_{11}}{1\ mol\ C_{12}H_{22}O_{11}} = -5.65 \times 10^3\ kJ/mol\ sucrose$$

The "Coffe-Cup" Calorimeter



Example: $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

Two solutions, 25 mL of 2.5M HCl (aq) and 25 mL of 2.5 M NaOH(aq) both initially at 21.1°C are added to a coffe-cup calorimeter and allowed to react. The temp. became 37.8°C after the neutralization rxn. Determine the heat of the rxn. expressed per mol of H_2O formed.

$$q_{neutr.} = -q_{cal}$$

$$q_{cal} = 50\ mL \times \frac{1\ g}{mL} \times \frac{4.18\ J}{g\ °C} \times (37.8 - 21.1)\ °C = 3.5 \times 10^3\ J$$

$$q_{neutr} = -q_{cal} = -3.5\ kJ$$

In 25 mL of 2.50 M HCl, the amount of H^+ is

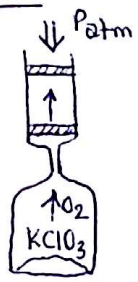
$$?\ mol\ H^+ = 25\ mL \times \frac{1\ L}{1000\ mL} \times \frac{2.50\ mol}{1\ L} \times \frac{1\ mol\ H^+}{1\ mol\ HCl} = 0.0625\ mol\ H^+$$

Similarly in 25 mL, 2.5 M NaOH there are 0.0625 mol OH^-

thus H^+ and OH^- combine to form 0.0625 mol H_2O

$$q_{neutr} = \frac{-3.5\ kJ}{0.0625\ mol\ H_2O} = -56\ kJ/mol\ H_2O$$

WORK



$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

In this system the O_2 gas pushes back the weight. It means the system does work on the surroindings.

* The work involved in the expansion or compression of gases is called pressure-volume work

$$W = F \times \Delta h = (P \times A) \times \Delta h \Rightarrow \boxed{W = -P_{ext} \times \Delta V}$$

F = force, Δh = distance, $A \times \Delta h = \Delta V$, P_{ext} = external pressure

* When a gas expands, ΔV is (+) and W is (−). Energy leaves the system as work.
* When a gas is compressed, ΔV is (−) and W is (+). Energy enters the system as work.

$\rightarrow W = (atm) \times (liter) = atm \cdot L$; SI: $\frac{8.314\ J\ K^{-1}mol^{-1}}{0.08206\ atm.L.K^{-1}mol^{-1}} = 101.33\ \frac{J}{L.atm}$

The First Law of Thermodynamics

Internal energy (U) is the total energy (both kinetic and potential) in a system. A system contains only internal energy. A system does not contain energy in the form of heat or work. Heat and work exist only during a change in the system.

The relationship between heat, work and internal energy expressed as the first law of thermodynamics.

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

An isolated system is unable to exchange either heat or work with its surroundings so that

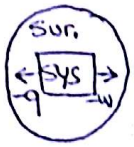
$$\boxed{\Delta U_{isolated\ system} = 0}$$

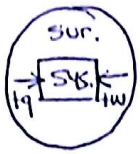
* The energy of an isolated system is constant (1st LAW)

: Using the equation $\Delta U = q + w$

Energy entering the system	Energy leaving the system
+ sign	− sign
$q > 0$, $w > 0$	$q < 0$, $w < 0$
heat is absorbed by the system	heat is given off by the sys.
work is done on the system	work is done by the sys.

* as a consequence $\Delta U_{system} = -\Delta U_{surroundings}$





Arrows represent the direction of heat and work.

Example : A gas, while expanding, absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

$$\Delta U = q + w = (+25\,J) + (-243\,J) = \underbrace{-218\,J}_{\text{lost energy.}}$$

$+25\,J$: heat absorbed (+) ; $-243\,J$: work done by the system (−)

Heats of Reactions : ΔU and ΔH

Think of the reactants in a chemical rxn. equation as the initial state and the products as the final state.

$$\underset{U_i}{\text{reactants}} \longrightarrow \underset{U_f}{\text{products}}$$

for this rxn. : $\Delta U = U_f - U_i$

* According to the 1st law of thermodynamics; we can say that $\Delta U = q + w$. We have previously identified a heat of rxn. as q_{rxn}.

Therefore we can write:

$$\Delta U = q_{rxn} + w$$

* If the rxn. carried out at constant volume (for instance, in a bomb calorimeter) we can say that. $\Delta V = 0$, and therefore no work is done. $w = -P\Delta V = 0$.

So we can write:

$$\Delta U = q_{rxn} + w = q_{rxn} + 0 = q_{rxn} = q_v$$

$$\boxed{\Delta U = q_v}$$

in this equation q_v: the heat of a rxn for constant volume.

* If the rxn carried out at constan pressure, a small amount of pressure-volume work is done. In this case the heat of rxn (q_p) is different than q_v.

So we can write:

$$\Delta U = q_p + w \quad \text{and}$$

$$\Delta U = q_p - P\Delta V \Rightarrow q_p = \Delta U + P\Delta V$$

and

$$\boxed{\Delta H = \Delta U + P\Delta V} \qquad \boxed{\Delta H = q_p}$$

U, P, and V are all state functions. We can derive another state function from the equation $\Delta U + P\Delta V$. This state function is called enthalpy (H), is the sum of the internal energy and the PV product of a system.

$$\Delta H = H_f - H_i = (U_f + P_f V_f) - (U_i + P_i V_i)$$

$$\Delta H = (U_f - U_i) + (P_f V_f - P_i V_i) \Rightarrow \Delta H = \Delta U + \Delta PV$$

* If the process is carried out at a constan temp. and pressure ($P_i = P_f$), the pressure-volume work can be written as follow.

$$P\Delta V = P(V_f - V_i)$$

and using the ideal gas equation

$$P\Delta V = RT(n_f - n_i)$$

finally

$$\Delta H = \Delta U + P\Delta V \quad \text{or} \quad \Delta U = \Delta H - P\Delta V \text{ or}$$

$$\boxed{\Delta H = \Delta H - RT(n_f - n_i)}$$

n_f: The number of moles of gases in products

n_i: " " " " " " in reactants

Example: How much heat is associated with the complete combustion of 1.00 kg of sucrose ($C_{12}H_{22}O_{11}$)? (-5.65×10^3 kJ/mol heat is associated with the combustion of 1 mol of sucrose)

First express the quantity in moles.

$$?\ \text{mol} = 1.00\ \text{kg sucrose} \times \frac{1000\ \text{gr suc}}{1\ \text{kg suc.}} \times \frac{1\ \text{mol suc.}}{342.3\ \text{g suc.}}$$

$$= 2.92\ \text{mol sucrose.}$$

Then,

$$?\ \text{kJ} = 2.92\ \text{mol suc.} \times \frac{-5.65 \times 10^3\ \text{kJ}}{1\ \text{mol suc.}} = -1.65 \times 10^4\ \text{kJ}$$

Example: Calculate ΔH for the process in which 50.0 g of water is converted from liquid at 10.0°C to vapor at 25.0 °C.

The process involves with two steps.

1) Raising the temp. from 10 – 25 °C
2) Vaporizing at 25°C

For a process at constant pressure, $\Delta H = q_p$. Therefore we need to calculate the absorbed heat in each step.

1) $?\ kJ = 50.0\ g\ H_2O \times \dfrac{4.18\ J}{g\ H_2O\ ^\circ C} \times (25-10)^\circ C \times \dfrac{1\ kJ}{1000\ J}$

$= 3.14\ kJ$

2) $?\ kJ = 50.0\ g\ H_2O \times \dfrac{1\ mol\ H_2O}{18.02\ g\ H_2O} \times \dfrac{44.0\ kJ}{1\ mol\ H_2O}$ (44.0 kJ: vaporization heat at 25°C)

$= 122\ kJ$

Total enthalpy change

$\Delta H = 3.14\ kJ + 122\ kJ = 125\ kJ$

HESS'S LAW

* ΔH is an extensive property: Enthalpy change is directly proportional to the amounts of substances in a system.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_a^\circ = 180.50\ kJ$$

so

$$\tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow NO(g) \quad \Delta H_b^\circ = \tfrac{1}{2} \Delta H_a^\circ$$

$= \frac{1}{2} \times 180.50\ kJ$

$= 90.25\ kJ$

* ΔH changes sign when a process is reversed:

$$NO(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \quad \Delta H_c^\circ = -\Delta H_b$$
$$= -90.25 \text{ kJ}$$

* Hess's Law of constant heat summation: If a process occurs in stages or steps, the enthalp change of the overall process is the sum of the enthalpy changes of the individual steps.

We can calculate the standart enthalpy change of the rxn.

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2 \quad \Delta H^\circ = ?$$

By using:

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow \cancel{NO(g)} + \cancel{\tfrac{1}{2} O_2} \quad \Delta H^\circ = +90.25 \text{ kJ}$$

$$+ \quad \cancel{NO(g)} + \cancel{\tfrac{1}{2} O_2}(g) \longrightarrow NO_2(g) \quad \Delta H^\circ = -57.07 \text{ kJ}$$

$$\tfrac{1}{2} N_2 + O_2(g) \longrightarrow NO_2 \quad \Delta H = +33.18 \text{ kJ}$$

Standart Enthalpies of Reaction

$$\Delta H^\circ = \sum \upsilon_p \Delta H_f^\circ (\text{products}) - \sum \upsilon_r \Delta H_f^\circ (\text{reactants})$$

where:

ΔH° : standart enthalpy of rxn.

ΔH_f° : " " of formation

υ : Stiochiometric coefficients

p : products

r : reactants

Example : What is the standart enthalpy of combustion of ethane (C_2H_6)?

$$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$$

$$\Delta H^\circ = \{ 2 \times \Delta H_f^\circ\ CO_2(g) + 3 \times \Delta H_f^\circ\ H_2O(\ell) \}$$

$$- \{ 1 \times \Delta H_f^\circ\ C_2H_6(g) + 7/2 \times \Delta H_f^\circ\ O_2(g) \}$$

$$= \{ 2 \times (-393.5\ kJ/mol\ CO_2) + 3 \times (-285.8\ kJ/mol\ H_2O) \}$$

$$- \{ 1 \times (-84.7\ kJ/mol\ C_2H_6) + 7/2 \times 0\ kJ/mol\ O_2 \}$$

(i) standart enthalpy of formation of an element is zero

$$= -1559.7\ kJ$$

Example : Given that $\Delta H_f^\circ\ BaSO_4(s) = -1473\ kJ/mol$. What is the standart enthalpy change for the following rxn.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) \quad \Delta H^\circ = ?$$

ΔH_f° (kJ/mol)	-537.6	-909.3	-1473

$$\Delta H^\circ = 1 \times \Delta H_f^\circ\ BaSO_4(s) - [1 \times \Delta H_f^\circ\ Ba^{2+} + 1 \times \Delta H_f^\circ\ SO_4^{2-}]$$

$$= -1473 - [-537.6 - 909.3]$$

$$= -26\ kJ$$