

- 3 factors determine the pressure of a gas in a container: mass of each molecule, speed of the molecules, and the frequency of collisions (which is related to the # of molecules,  $N$  and the volume of the container)
- Basic equation of the kinetic theory of gases:  $P = \frac{1}{3} \frac{N}{V} m \overline{u^2}$ , which leads to  $\overline{u^2} = \frac{3RT}{MM}$
- At any given moment, some molecules are moving faster and some are moving slower
- **Root-Mean-Square Speed of Gas Molecules:**  $u_{rms} = \sqrt{\frac{3RT}{MM}}$ , where molar mass is in kg
- The  $u_{rms}$  for 2 gases is inversely proportional to the square root ratio of their molar masses:
  - $\frac{u_{rms(A)}}{u_{rms(B)}} = \sqrt{\frac{MM_B}{MM_A}}$

### Effusion and Graham's Law

- **Effusion** – flow of gas molecules at low pressures through tiny pores or pinholes
- The rate of effusion of a gas is inversely proportional to the square root of its molar mass
  - Therefore lighter molecules effuse more rapidly than heavier ones
- When 2 gases effuse through a small hole, Graham's Law can be written as:
  - $\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{N_A}{N_B} \sqrt{\frac{MM_B}{MM_A}}$
- The gas that emerges from a container is *enriched* in the lighter component
- The  $\sqrt{\frac{MM_B}{MM_A}}$  proportion of Graham's Law is called the enrichment factor, where the heavier MM is the numerator of the fraction
- If a mixture of 2 gases has the same # of moles of each gas, after the mixture effusing for a certain length of time, the mixture that effused would have a proportionally higher ratio of the lighter gas

## Chapter 2.1 – Heat, Work and Energy

### Thermodynamics

- The study of the energy changes involved in physical and chemical processes
  - *Physical process* → heating and cooling of substances, phase changes, and V/P changes
  - *Chemical process* → chemical reactions
- **Thermochemistry** – investigates the heat flow that occurs during these reactions
  - Rates of most chemical reactions increases as temperature increases

### Systems and Surroundings

- **Heat flow** – the transfer of thermal energy in the process being studied
  - Heat always flows from the warmer object to the cooler object
- **System** – the part of the universe that one wants to study
- **Surroundings** – the remaining parts of the universe that can interact (e.g. exchange energy) with a system under study
- In a chemical reaction, the system is the reactants and the surroundings is the vessel (flask) in which the reaction takes place, including the air and any other material making thermal contact with the vessel, such as the solution in which the reaction occurs

- Types of Systems
  - **Open system** – exchanges both matter and energy with its surroundings
  - **Closed system** – exchanges energy, not matter with its surroundings
  - **Isolated system** – exchanges neither matter nor energy with its surroundings

## Energy

- **Energy** – the capacity to do work
  - *Heat (thermal energy)* – energy transferred between the system and the surroundings, or from one object to another, as a result of a temperature difference
  - *Kinetic energy* – energy associated with motion
  - *Potential energy* – stored energy or the energy a body possesses due to its position
  - *Chemical energy* – a form of potential energy
- **Work** – the product of a force, acting on an object, and the distance the object moves in response to the force; measured in joules ( $w = F \times d$ )
- **Pressure-volume (PV)** – the work involved in the expansion or compression of gases; measured in kPa L ( $w = -P \times \Delta V$ )

## Heat Capacity and its Uses

- **Heat capacity ( $C$ )** – a measure of how many joules are required to change the temperature of an OBJECT by one degree; measured in J/°C
  - $q = C\Delta T$
- **Specific heat capacity ( $c$ )** – a measure of how many joules are required to change the temperature of one mass unit of a SUBSTANCE by one degree; measured in J/kg°C
  - $q = mc\Delta T$
- **Molar heat capacity** – same as above, except moles are used instead of grams (J/mol°C)
- **NOTE:**  $\Delta T = T_f - T_i$ , and the temperature difference is the same in K and °C
- **Endothermic (+ $q$ )** – when a system absorbs energy from the surrounding (warms up)
- **Exothermic (– $q$ )** – when a system releases energy to the surroundings (cools down)
- **Thermal equilibrium** – the number of joules lost by the warmer object must equal the number of joules gained by the cooler object (both objects therefore reach the same temperature)
  - $-q_{lost} = q_{gained}$

## Intensive and Extensive Properties

- **Intensive (intrinsic) property** – physical property that does not depend on the amount of material in the system (e.g. temperature, density, etc.)
  - *Temperature* – the speed of the molecules in a sample (avg. kinetic energy)
- **Extensive (extrinsic) property** – physical property or quantity whose value is proportional to the size of the system it describes (e.g. mass, length, volume, enthalpy, entropy, energy, etc.)
  - *Thermal energy* – the number of molecules in a sample (total kinetic energy)

## State Functions

- **State function** – a property whose value depends only on the current state of the system; it does not matter how the state of the system was reached
- Examples → internal energy and enthalpy
- Heat and work are NOT state functions since the work done on or heat transferred to a system by following different paths is different, although the initial and final states of the two paths are identical

## First Law of Thermodynamics

- *The total energy of a system and surroundings is conserved*
- **Internal energy (E)** – the sum of all the kinetic and potential energies of all the atoms, ions and molecules in the system
  - Although the absolute internal energy of a system cannot be determined, internal energy changes,  $\Delta E$ , can be determined
- EXPANSION → the expanding gas (system) is doing work on the surroundings and the value of  $w$  is negative (work energy has been used, so it has been removed from the system)
- COMPRESSION → the surroundings are doing work on the system, and the value of  $w$  is positive (the system has gained work energy)
- If a process does NOT involve a compression or expansion, there is no volume change ( $\Delta V = 0$ ) and the value of  $w$  is zero
- $\Delta E = q + w$ 
  - If the surroundings do work on, or supply heat to the system, internal energy of the system increases ( $\Delta E > 0$ )
  - If the system does work on, or supplies heat to the surroundings, internal energy of the system decreases ( $\Delta E < 0$ )
  - If the system is at a constant volume (zero work), then  $\Delta E = q_v$

## Chapter 2.2 – Enthalpy

### Enthalpy

- **Enthalpy (H)** – the energy content of a system at constant pressure
  - $H = E + PV$ , but absolute enthalpy cannot be measured so:  $\Delta H = \Delta E + P\Delta V$
  - At constant pressure, the  $\Delta H$  of a system is equal to the heat ( $q_p$ ) flowing into or out of a system →  $\Delta H = q_p$
- NOTE: The standard conditions used at 1 atm (101.33 kPa) and 25°C (298.15 K)
  - Enthalpy changes under standard conditions are reported as  $\Delta H^0$
- Physical Processes and Latent Heat
  - **Latent heat** – the energy change associated with physical processes that involve a change of state (phase)
    - Melting, boiling, and sublimation are endothermic processes
    - Condensation, freezing and deposition are exothermic processes
    - Temperature of the substance remains CONSTANT for any of these processes
  - If the phase changes are carried out at constant pressure, the latent heat values are also  $\Delta H$  values
  - If the processes are occurring under standard conditions, the  $\Delta H^0$  values are slightly different due to the different temperatures

### $\Delta H$ For Chemical Reactions

- $\Delta H_{rxn}^0 = \sum H^0(\text{products}) - \sum H^0(\text{reactants})$
- Exothermic reactions have  $\Delta H < 0$  and endothermic reactions have  $\Delta H > 0$
- $\Delta H$  for a reaction may be found experimentally by measuring the heat lost or gained when a process is carried out at a constant pressure

## Measurement of $\Delta H$

- **Calorimetry** – studies the heat flow of physical and chemical processes
- In an exothermic process, the heat released ( $q_{sys}$ ) is absorbed by the surroundings ( $q_{surr}$ ), which causes the calorimeter and its contents to rise in temperature, and vice versa
  - $q_{sys} = -q_{surr}$  a.k.a.  $q_{rxn} = -q_{surr}$  where  $q_{rxn} = \Delta H_{rxn}$
- In a simple calorimeter, the surroundings consist of both the calorimeter assembly (vessel, thermometer, stirrer) and the solution contained within the vessel
  - The system consists of just the reactants used
- **Molar enthalpy of reaction** – expressing  $\Delta H$  in terms of the amount of a key reactant (or product) in the reaction; expressed as some amount of energy in KJ/mol of that reactant
- $q_{rxn} = -(q_{cal} + q_{solution}) = -(C_{cal}\Delta T + m_s c_s \Delta T)$
- To determine  $C_{cal}$ , you have to do a calorimeter calibration, using one of 2 methods:
  - Add a known amount of hot water with a known initial temperature to the calorimeter and then measure the temperature at equilibrium ( $q_{hot\ water} = -q_{cal}$ )
    - No chemical reaction is taking place
  - Carry out a reaction with a known  $\Delta H_{rxn}$ , inside a bomb calorimeter, where no solution is present ( $q_{rxn} = -q_{cal}$ )
- **Bomb calorimeter** – usually involved in measuring the heat liberated from gaseous or combustion reactions
  - Unlike a simple calorimeter (which takes place at constant pressure), reactions in a bomb calorimeter take place under constant volume
  - However, for combustion reactions, we can assume constant pressure as well

## Standard Enthalpy of Formation ( $\Delta H_f^\circ$ )

- This is the enthalpy change that occurs when one mole of a substance is formed from its constituent elements in their standard states
- $\Delta H_f^\circ$  (element in standard state) = 0
- **Formation reaction:** *elements (standard state)  $\rightarrow$  1 mole of a substance*

## Hess's Law of Thermochemistry

- **Hess's Law** – the enthalpy change for a reaction is the sum of the enthalpy changes for the individual steps of the reaction
- $\Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$ 
  - Note that the stoichiometric coefficients are essential in the equation
- Any set of  $\Delta H^\circ$  values can be combined, not just  $\Delta H_f^\circ$
- **Heat of combustion ( $\Delta H_c^\circ$ )** – the energy released when one mole of a fuel in its standard state undergoes complete combustion with oxygen to form  $H_2O_{(l)}$  and  $CO_{2(g)}$

## Bond Enthalpy

- **Bond Enthalpy (BE)** – the energy required to break one mole of a specific type of bond (single, double or triple) between two atoms, providing the reactants and products are both gases
- Bonds broken = energy absorbed (endothermic), therefore BE is always positive
- **Total Bond Enthalpy (TBE)** – the energy required to break all of the bonds in one mole of a gaseous compound
  1.  $TBE = \Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$
  2. TBE = sum of all the enthalpies of all the bonds in the mole, using avg. bond enthalpies

- Both of these methods give slightly different values for the TBE because molecular structure has an impact on bond enthalpy (since avg. bond enthalpies are used)
- **Average bond enthalpy** – may be determined from the TBE found using method 1]
  - E.g. TBE of  $\text{CH}_4(\text{g}) = 1661.8 \text{ kJ/mol}$ ,  $\therefore$  avg. bond enthalpy of C-H bond =  $415.5 \text{ kJ/mol}$
- Bond strength increases with bond order (triple bond is the strongest)
- $\Delta H$  of gas phase reactions
  - If a reaction has all its reactants and products in the gas phase, it is possible to estimate the enthalpy change of the gas-phase reaction using average bond enthalpies
  - $\Delta H_{\text{rxn}} = \sum \text{enthalpies of bonds broken} - \sum \text{enthalpies of bonds formed}$

## Chapter 23 – Entropy and Spontaneous Change

### Spontaneous Processes

- A spontaneous process is one that occurs in the absence of any ongoing outside intervention
- Processes spontaneous in one direction are non-spontaneous in the reverse direction
- A negative  $\Delta E$  or  $\Delta H$  are not the only criterion needed for a reaction to occur spontaneously
  - You need to consider **entropy** ( $S$ ) – measure of the randomness/disorder of a system
  - The higher the # of possible arrangements for a system, the greater the entropy
  - $\Delta S = S_f - S_i$
  - $\Delta S > 0$  is an increase in disorder, and  $\Delta S < 0$  is a decrease in disorder
  - States that are highly disordered are generally more probable in nature
- Spontaneity and reaction rate are unrelated
  - Therefore, spontaneous processes don't have to be necessarily fast
- **Standard molar enthalpies** – always greater than zero since entropy increases with temperature
  - Reported in J/molK and refer to standard conditions
  - $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$
  - $S^\circ = 0$  at 0 K

### Effect of Heat and Chemical Reactions on Entropy

- The addition of heat, particularly when associated with a phase change, greatly affects entropy
- Vaporization, melting and sublimation all increase the entropy ( $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ )
- **3rd law of thermodynamics** – the entropy of a perfectly ordered crystalline solid is defined to be zero at a temperature of absolute zero (0 K)
  - At absolute zero, a substance has no translational or rotational motion, but the atoms are still vibrating due to a quantum effect known as *zero-point energy*
  - Increasing temperature of a solid increases only the particles' *vibrational* motion, hence an increase in entropy
  - $\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$
- Chemical reactions can affect entropy if they involve reactants/products in the gas phase
  - Increasing the # of molecules in the gas phase also increases the entropy
- **2nd law of thermodynamics** – every spontaneous process increases the entropy of the universe
  - Therefore,  $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$
  - Nature tolerates the creation of order in one part of the universe, as long as this is compensated by the formation of chaos somewhere else

# Chapter 2.4 – Free Energy

## Gibbs Free Energy

- **Gibbs free energy** – amount of energy available (“free”) to enable spontaneous change to occur
- Every chemical reaction is associated with a free energy change given by:
  - $\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$
- **Gibb’s equation:**  $\Delta G = \Delta H - T\Delta S$ 
  - $\Delta G < 0$             Reaction will proceed spontaneously (*favours* formation of products)
  - $\Delta G = 0$             System is at equilibrium; # of moles of reactant/product don’t change
  - $\Delta G > 0$             Reaction will not occur spontaneously (*favours* the reactants)
- **NOTE:** thermodynamics ( $\Delta G, \Delta H, \Delta S$ ) does not determine the rate of a reaction
- According to the Gibb’s equation, all systems tend towards the lowest possible enthalpy and the highest possible entropy

## What Drives a Process?

- **The Impact of Temperature and Signs on Gibbs Free Energy:**
  - $+\Delta S$  and  $-\Delta H \rightarrow$  enthalpically and entropically driven ( $-\Delta G$ )
  - $-\Delta S$  and  $+\Delta H \rightarrow$  never spontaneous ( $+\Delta G$ )
  - $-\Delta S$  and  $-\Delta H \rightarrow$  enthalpically driven, if spontaneous ( $\pm\Delta G$ , depending on temp.)
  - $+\Delta S$  and  $+\Delta H \rightarrow$  entropically driven, if spontaneous ( $\pm\Delta G$ , depending on temp.)
- Enthalpically Driven Processes
  - These are exothermic spontaneous processes with  $\Delta H \ll 0$  and  $\Delta S < 0$
  - The negative entropy is unfavourable
- Entropically Driven Processes
  - Endothermic reactions ( $\Delta H > 0$ ) can only be spontaneous if they are associated with a large entropy increase ( $\Delta S \gg 0$ )
  - Temperature must be high enough to give a negative Gibbs free energy
  - There is a point where the temperature gives a  $\Delta G$  of zero
    - This is the melting point temperature ( $T_m$ ), where  $\Delta H = T\Delta S$ , since  $\Delta G = 0$
- Enthalpically and Entropically Driven Processes
  - These processes are spontaneous because they are associated with favourable enthalpy ( $\Delta H \ll 0$ ) and entropy changes ( $\Delta S \gg 0$ )

## Standard Free Energy Change

- The free energy change under standard conditions is denoted as  $\Delta G^\circ$ 
  - Thus,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- As with enthalpy, the absolute free energy of a substance cannot be determined
- **Standard free energy of formation ( $\Delta G_f^\circ$ )** – the standard free energy change that occurs when 1 mol of a compound is made from elements in their standard states
  - The  $\Delta G_f^\circ$  of any element in its standard state is defined as zero
  - $\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$