Chemistry (Tuesday)

Fuels

- Calorific Value
  - High: HCV (Grates) - includes latent heat of vap
  - Low: LCV (Net) = HCV

\[ LCV = HCV - \frac{9 \times H \times 587 \text{ cal/g}}{100} \] (latent heat of vap)

- Properties of fuel - moderate ignition temp
  - Cheap - easily available - high CV - low CV

- Determination of C.V. of a fuel
  - Bomb Calorimeter - heat is measured

\[ \text{Heat gained} = \text{Heat lost} \]

\[ C \times \Delta T = (W + C_0) (T_2 - T_1) \]

- Corrections:
  1. Mg oxide correction (heat generated when MgO reacts with H_2O)
  2. Acid correction (cuten acid made by HCl and excess)
  3. Cooling effect (error in temp due to simultaneity)
So, \( C_x = (W + w)(T_2 - T_1 + \theta) - (\theta + 0) \)

Boyle's Calorimeter

- Combustion chamber
- Condensed water
- Heat gained: \( W = (T_2 - T_1) \)
- \( \text{mass of condensed H}_2\text{O} \)

Dulong's Formula - to measure theoretical \( CV \)

\[
HCV = \frac{1}{100} \left[ 8080C + 634500 \left( \frac{H - O}{8} \right) + 2240S \right] \text{cal/g}
\]

\( C = \) molality of \( H_2O \) as not all \( H \) and \( O \) contains \( H \) of \( H_2O \) so we subtract it.

In \( H_2O \):
- 16 g of O = 2 g H
- 18 g of O = \( \frac{18}{16} \) H
- 9 g of O = \( \frac{9}{16} \) H
Number of 3 phases in one complex (P, M) and each phase has its own phase, i.e.,

\[ \beta_x = \beta_p \rightarrow \text{dem. total} = \beta_p \]
\[ \beta_x = \beta_r \]

New no of eq. is possible at equilibrium:
\[ C(P-1) \]

\[ F = \frac{(P(C-1)+2)}{C-1} - (C-1) \]
\[ F = C - P + 2 \]

Add. - simple method to classify eq. states
- explains behaviour of \( x \)

One Component System (Homogeneous system):

\[ \uparrow \text{boiling curve} \]

\[ P \text{ (atm)} \quad 1 \text{atm} \quad 4 \text{ atm} \quad 4 \text{ atm} \]

\[ T \text{ (°C)} \quad 0 \quad 100 \quad 374 \]

\[ F = 2, P = 1 \]

\[ 0.07 \text{ °C} \]

\[ T \rightarrow \text{subsolidus} \quad \text{curve} \]

\[ \text{Solid} \quad \text{Liquid} \quad \text{Vapour} \quad \text{Pressure} \quad \text{curve} \]

\[ AOB = \text{vapour} \]
\[ AOC = \text{vapour} \]
\[ BOC = 1 \text{ mol} \]

\[ O = \text{Triple point} \ (F = 0, P = 3) \]
\[ AO = \text{vapour-liquid} \]
\[ OB = \text{Ice-water} \]
- Poison - Negative Catalyst
  - Characteristics of a good catalyst -
  - retain back after re-use - at optimum temp
  - specific in their act* - selective in nature

- Homogeneous Catalyst -
  - Acid Base - Enzymes - Wilkinson's

- Acid - Base Catalyst -
  - They are of two types - specific & general
  - a. Acid - catalysed by H+ ions only
    - (Acetic acid)
    - Eg - Inversion of carbohy.
  - b. Base - catalysed by OH- ions only
    - (Ammonia & water)
    - Eg - Hydrogenation

- g. Acid- catalysed by all types of acid
  - Eg -
    - \( \text{CH}_3 - \text{C} - \text{CH}_3 + I_2 \xrightarrow{\text{catalyst}} \text{CH}_3 - \text{C} - \text{CH}_3 I \)
  - (iodoacetic acid)

- g. Base - catalysed by all types of base
  - Eg -
    - \( \text{NH}_2 \text{NO}_2 + \text{CH}_3\text{COOH} \rightarrow \text{N}_2 \text{O} + \text{H}_2 \text{O} \)
  - (decomp. of nitramide cat. by acetate ion)
Rate = \frac{-d[S]}{dt} = R_3 [S H^+] [A^-]

Applying SSA,

\[ [S H^+] [A^-] = \frac{R_1 [S][A H^+]}{R_1 + R_3} \]

Rate = \frac{R_1 R_3 [S][A H^+]}{R_2 + R_3}, general acid

Enzyme Catalysis:
- Highly biological processes
- Specific in nature: work at optimum temp.
- Work only at optimum pH (7.4)
- Inhibitors
- Co-enzymes: metal ions (Na^+\textsuperscript{+}, Cu^2\textsuperscript{+}, Mg^2\textsuperscript{+})

Temperature vs. rate of reaction:
- Optimum temp.
- H+parent pH. - IF temp. denature, enzyme destroys

Mechanism of Enzyme Reaction:
- Lock & key Model
- Intermediate formed: decrease energy of activation
- Unstable, so breaks down fast

\[ \text{Reactant} \rightarrow \text{enzyme} \rightarrow \text{complex} \rightarrow \text{product} \rightarrow \text{ready type enzyme} \]
Kinetics of Enzyme Catalysis (Michaelis-Menten)

\[
\frac{S + E}{R_1} \xrightarrow{R_2} [ES] \quad \text{(fast)}
\]

\[
[ES] \xrightarrow{R_3} P + E \quad \text{(slow)}
\]

So, Rate = \( R_3[ES] \)

By SSA,

\[
R_1[ES][E] - R_2[ES] - R_3[ES] = 0
\]

\[
[ES] = \frac{R_1[ES][E]}{R_2 + R_3}
\]

\[ [E] \text{ can be determined, so,} \]

\[
\frac{[E]}{[S] + R_3 + R_2}
\]

\[ \frac{[S]}{R_1} \text{ (Michaelis-Menten constant)} \]

For initial rate,

\[
\frac{r_0}{R_3} = \frac{[S_0][E_0]}{[S_0] + R_m}
\]

I. \( [S_0] \gg R_m, \) \( \frac{r_0}{R_3} = \frac{[E_0]}{[S_0] + R_m} = V_{\text{max}} = \frac{V_{\text{max}}}{[S_0]} \quad \text{generation}
\]

II. \( R_m \gg [S_0], \) \( \frac{r_0}{R_3} = \frac{[E_0][S_0]}{R_m} \quad \text{Lancaster}\)

\[ \frac{r}{R_m} = \frac{V_{\text{max}}}{[S]} \]

If \( R_m = 5, \) \( r = \frac{V_{\text{max}}}{5} \)
Catalysis by Metal Salts
- Wilkinson's catalyst

Mechanism:
- Solvent

Equation:
\[ \text{Cl} + \text{R} \rightarrow \text{Rh} \rightarrow \text{Rh}^{(II)} \rightarrow \text{Rh}^{(III)} \]

Reactions:
- \[ \text{R} - \text{Cl} \]
- \[ \text{H} - \text{H} \]