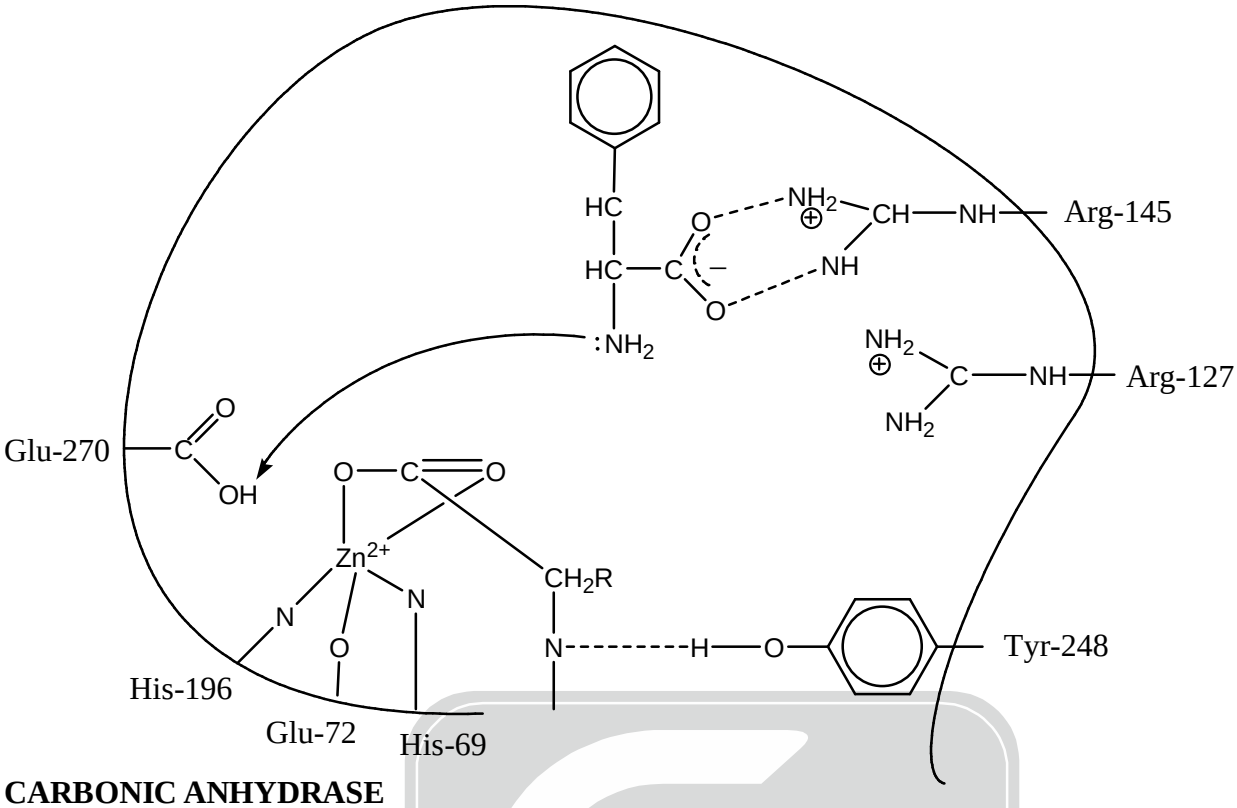


CARBONIC ANHYDRASE

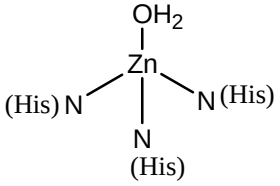
The uncatalysed following equilibrium is relatively very slow.

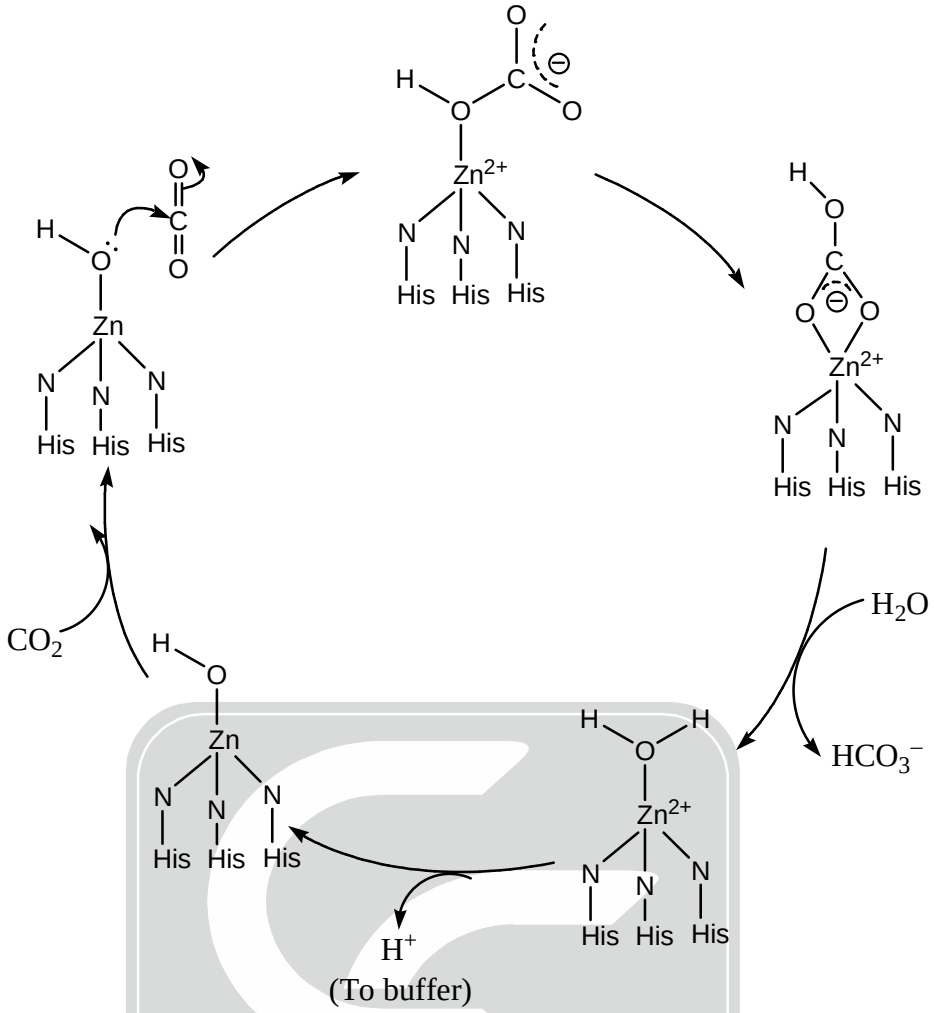
$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

In the erythrocytes (red blood cells) the forward (hydration) reaction occurs during the uptake of CO_2 by blood in tissue whereas the backward (dehydration) reaction occurs when CO_2 is released in the lungs. The carbonic anhydrase enzyme increases the rate of this equilibrium by about one million times.

The molar mass of this enzyme is about 30, 000 and it contains a single protein unit of 260 amino acids and the active site contains a Zn^{2+} ion coordinated tetrahedrally to three histidine imidazole nitrogen atoms (His-94, His-96 and His-119), and water molecule or hydroxide ion. It contains other amino acids that may functions through hydrogen bonding, proton transfer etc.

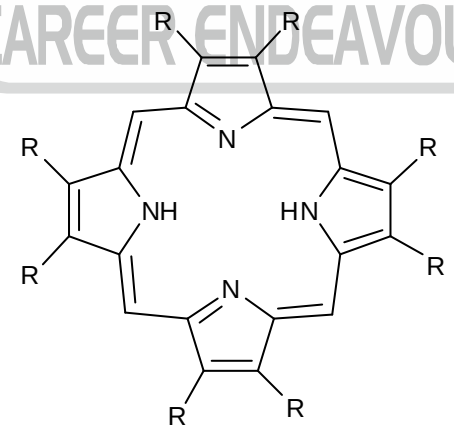
The rates of forward and backward reactions in the CO_2 hydration equilibrium increase as the pH is raised. The Zn^{2+} ion is less acidic in carbonic anhydrase than in carboxy peptidase. The presence of a neutral or less basic histidine residue instead of the glutanmate residue contribute to the greater acidity of Zn^{2+} ion. Also, the three histidine residues are pulled back, therefore, Zn^{2+} ion becomes more electronegative and more acidic toward the fourth position. Thus, the coordinated water becomes more polarized and losses H^+ ion to give $Zn–OH^-$. The nucleophilic OH^- then attacks on the carbon atom of CO_2 captured in the hydrophobic pocket near the Zn^{2+} ion, and a transient five coordinate Zn^{2+} ion is formed in which a carbonato oxygen from HCO_3^- coordinates to the Zn^{2+} ion. After rearrangement, the HCO_3^- ligand is replaced by H_2O. The protonation of H_2O ligand coordinated to Zn^{2+} ion then regenerate $Zn–OH^-$ which then attacks another CO_2 with the continuation of the catalytic cycle.





15.2. PORPHYRINS

Porphyrins are tetrapyrrole macrocycles with conjugated double bonds and various groups attached to the perimeter. The porphyrins can accept two hydrogen ions to form +2 diacids or donate two protons to form –2 dianions.



(Porphyrin)

variation of substituents facilitates the tuning of electron donating and electron withdrawing ability of the ligand.

The porphyrin and corrin ring systems are of great biological importance. Four pyrrole units are linked by —CH═ bridges as shown in figure but in corrin ring one —CH═ group is less.