

Chem 315, Fall 2001

Answers to Problem Set #10

19.1.

- not exactly calcium carbonate, but rather hydroxyapatite (a calcium-containing mineral) seems to be the main constituent of bones;
- entropy considerations are important. In addition, there is some strain release in the coils of Hb which works as well.
- Correct statement: both the Lewis acid and hydroxo- mechanisms are applicable.

19.4. The main difference in binding to oxygen at different partial oxygen pressures is caused by number of heme units: in Hb (four heme units) we deal with both tertiary and quaternary structures, whereas in Mb case (single heme unit) - with tertiary structure. This leads to different affinities to O₂, which is reflected by difference in oxygen binding curves.

19.5. The pockets present in carbonic anhydrase are hydrophobic (favorable for non-polar CO₂ molecules) and adjacent to the proposed site of CO₂ association. Coordination is to OH⁻ ions. In contrast, Zn²⁺ ions in carboxypaptidases are coordinated to water, so the pocket near Zn-sites would be hydrophilic.

See pp. 656-657 of your textbook for more detailed.

Ex. 19.3. As the number of valence electros increases from 12 (O₂) to 14 (O₂⁻), the antibonding 2_g orbital becomes more populated, which leads to decreasing the bond order and elongating the bonds. The net spins of the given species are 1, ½, and 0, respectively.

Ex.19.5 Since O₂ and CO are similar electronically as well as sterically, they can both bind to the same sites in metalloproteins such as hemoglobin. If CO is present and binds it can then block the binding of Oxygen, thus preventing oxygen from being distributed to various parts of the body.

Ex.19.8 Mn, Fe, Co and Cu have a least two stable oxidation states readily available. Zn, Ga, and Ca only have one stable oxidation state.

Ex19.20 Hemoglobin contains four subunits, each consisting of a polypeptide and an Iron(II) porphyrin, while myoglobin only contains one subunit. Cooperative binding occurs in Hemoglobin but not in myoglobin. Hemoglobin binding in pH dependent while myoglobin is not.