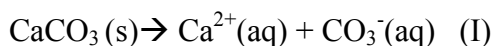
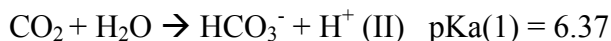


1. The presence of carbon dioxide in the atmosphere is a concern because of the role it plays in absorbing blackbody emission by the earth. The atmosphere is 0.036% carbon dioxide.
  - A. Calculate the mole fraction of CO<sub>2</sub> and the total number of metric tons of CO<sub>2</sub> in the atmosphere. For this calculation use 6400 km for the radius of the earth.
  - B. If an average of 10 billion tons of CO<sub>2</sub> is emitted into the atmosphere each year, calculate the partial pressure of CO<sub>2</sub> that one can expect in 2105 (100 years from now) assuming that no CO<sub>2</sub> is absorbed by the oceans.
2. CO<sub>2</sub> sequestration has occurred on a geologic time scale by the formation of limestone (CaCO<sub>3</sub>) in the oceans. However the process is slow and there is a significant calcium carbonate and bicarbonate concentration in seawater and brackish water. The calcium content of seawater is about 410 mg/L. The solubility product of calcium carbonate is  $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9}$  at 298 K.

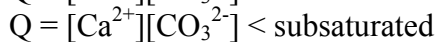
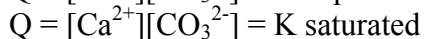
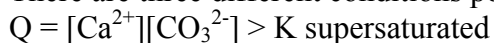


Eqn. I is an example of a heterogeneous equilibrium. One does not consider the concentration of CaCO<sub>3</sub> in the equilibrium constant. This expression can also apply to a particle of CaCO<sub>3</sub> as it settles to the bottom of the ocean.

The concentration of CO<sub>3</sub><sup>2-</sup> depends on pH because of the two acid equilibria.



There are three different conditions possible:

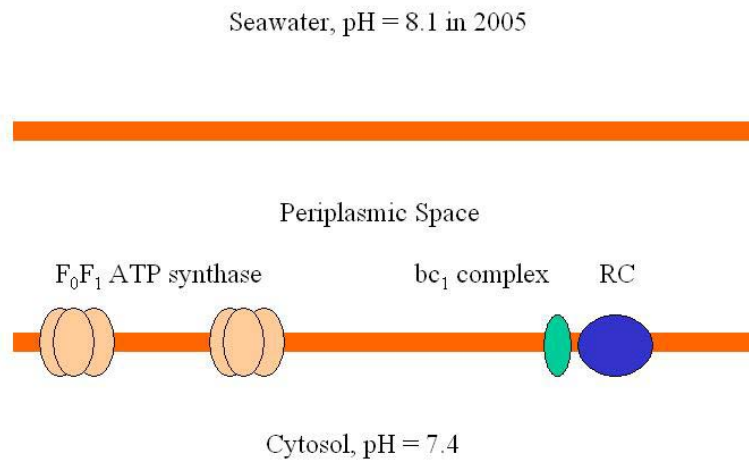


- A. Calculate the concentration of CO<sub>2</sub> in seawater assuming 360 ppm CO<sub>2</sub> in the atmosphere. The Henry's law constant for CO<sub>2</sub> is 29.76 atm/(mol/L).
- B. Calculate the concentration of bicarbonate and carbonate in seawater at pH = 8.1 using the equilibria above and assuming that there is not other source of carbonate or hydrogen carbonate other than from the atmosphere.

- C. Based on the calculation of  $\text{CO}_3^{2-}$  from part B. find  $\Delta G$  for formation of calcium carbonate in the ocean. Predict whether  $\text{CaCO}_3$  would precipitate or dissolve under the conditions that all of the carbon came from the atmosphere. In other words predict the degree of saturation.
- D. In reality there is much more carbonate in the ocean than one would predict based on Henry's law and the above equilibria. The reason is that the ocean absorbs  $\text{CO}_2$ . By Le Chatelier's principle the  $\text{CO}_2$  gets converted to  $\text{HCO}_3^-$  and then to  $\text{CO}_3^{2-}$  so that the ocean can absorb much more  $\text{CO}_2$  than Henry's law would indicate. This is a complicated equilibrium and we will not attempt to calculate this from first principles. Current estimates are that the actual carbonate concentration is  $200 \mu\text{M}$ . Calculate the degree of saturation when this concentration is present and the calcium ion concentration is  $410 \text{ mg/L}$  as above. Assume  $T = 298 \text{ K}$ .
- E. Apparently the oceans are absorbing a lot of the  $\text{CO}_2$  that is emitted by human activity (by the equilibrium you calculated above using Henry's law). As  $\text{CO}_2$  is absorbed it can react with the  $\text{CO}_3^{2-}$  in the ocean according to the equilibrium:  

$$\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^-$$
Using the data above calculate the equilibrium constant for this reaction. Assuming that the concentration of  $[\text{CO}_3^{2-}]$  is  $200 \mu\text{M}$  and the concentration of  $\text{CO}_2$  is given by Henry's law (calculated in part A. above) calculate the concentration of hydrogen carbonate in the ocean.
- F. If all of the carbonate were to sediment the ocean would keep absorbing  $\text{CO}_2$  (following the Henry's law equilibrium). Calculate the change in pH according to the data you have calculated above, if all of the atmospheric  $\text{CO}_2$  were absorbed by the ocean. The volume of the oceans is  $1.347 \times 10^{18} \text{ m}^3$ .
- G. Calcium carbonate dissolves at high pressure. If one examines the bottom of the earth's oceans, one finds that calcite and aragonite deposits (the two major forms of calcium carbonate) only occur in water that has depth less than about  $5000 \text{ m}$ . The depth of  $5000 \text{ m}$  is called the Carbonate Compensation Depth (CCD). It is also called the "snow line". In water that is shallower than  $5000 \text{ m}$  calcium carbonate can precipitate (snow) and cover the ocean floor. In ocean water deeper than  $5000 \text{ m}$  there is no calcium carbonate and the ocean bottom is a clay flat known as the abyssal plain.  
It turns out the main driving force for the dissolution of calcium carbonate in deep water is the change in the density of water from its bulk density ( $1.0 \text{ g/ml}$ .) to a high local density in the inner coordination sphere of calcium and carbonate ions. Calculate this local density assuming that the free energy for the dissolution of the crystal is  $46.8 \text{ kJ/mol}$ . In other words  $\Delta G$  is  $46.8 \text{ kJ/mol}$  for the reaction  $\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$ .

3. A photosynthetic bacterium that lives in the ocean creates a transmembrane potential of  $-150\text{ mV}$  for the purpose of driving  $F_0F_1$  ATP synthase. It does so by pumping protons into intracellular space known as the periplasm by pumping protons. The photosynthetic reaction center (RC) and  $bc_1$  complex pump protons. This is illustrated below.



- A. What pH must be maintained in the periplasmic space in order to keep the transmembrane potential at  $150\text{ mV}$  with respect to the cytosol?
- B. There are no proton channels in the outer membrane. How much work must be done to charge up the periplasmic space assuming it is initially in equilibrium with seawater (i.e. at pH of 8.1)? Please account for both the inner and outer membranes. You can simply calculate the two membranes separately and add them together.