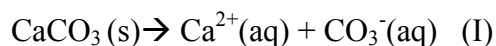
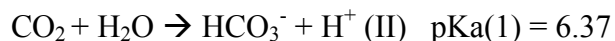


1. The presence of carbon dioxide in the atmosphere is a concern because of the role it plays in absorbing blackbody emission by the earth. The atmosphere is 0.036% carbon dioxide.
 - A. Calculate the mole fraction of CO₂ and the total number of metric tons of CO₂ in the atmosphere. For this calculation use 6400 km for the radius of the earth.
 - B. If an average of 10 billion tons of CO₂ is emitted into the atmosphere each year, calculate the partial pressure of CO₂ that one can expect in 2105 (100 years from now) assuming that no CO₂ is absorbed by the oceans.
2. CO₂ sequestration has occurred on a geologic time scale by the formation of limestone (CaCO₃) 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.

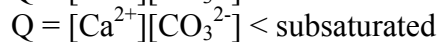
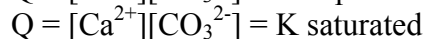
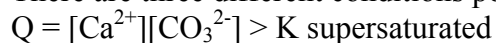


Eqn. I is an example of a heterogeneous equilibrium. One does not consider the concentration of CaCO₃ in the equilibrium constant. This expression can also apply to a particle of CaCO₃ as it settles to the bottom of the ocean.

The concentration of CO₃²⁻ depends on pH because of the two acid equilibria.



There are three different conditions possible:

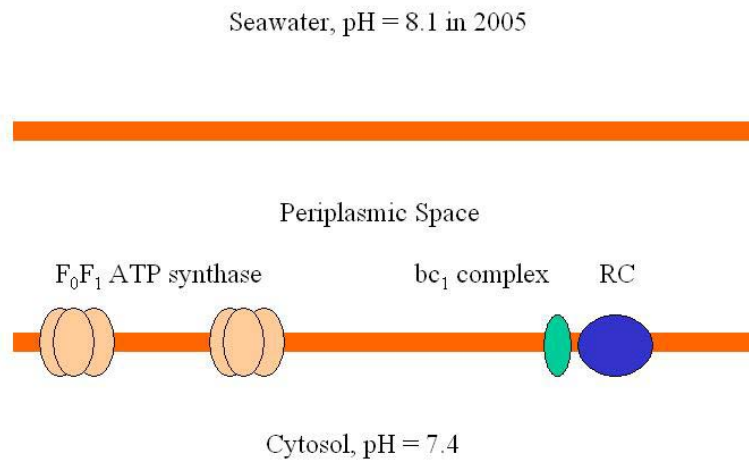


- A. Calculate the concentration of CO₂ in seawater assuming 360 ppm CO₂ in the atmosphere. The Henry's law constant for CO₂ is 29.76 atm/(mol/L).
- B. Calculate the concentration of bicarbonate and carbonate in seawater at pH = 8.1 using the equilibria above and assuming that there is not other source of carbonate or hydrogen carbonate other than from the atmosphere.

- C. Based on this calculation find ΔG for formation of calcium carbonate in the ocean. Predict whether 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 CO_2 . By Le Chatelier's principle the CO_2 gets converted to HCO_3^- and then to CO_3^{2-} so that the ocean can absorb much more 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 mg/L as above. Assume $T = 298 \text{ K}$.
- E. Apparently the oceans are absorbing a lot of the CO_2 that is emitted by human activity (by the equilibrium you calculated above using Henry's law). As CO_2 is absorbed it can react with the 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 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 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 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 m . The depth of 5000 m is called the Carbonate Compensation Depth (CCD). It is also called the "snow line". In water that is shallower than 5000 m calcium carbonate can precipitate (snow) and cover the ocean floor. In ocean water deeper than 5000 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 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 kJ/mol . In other words ΔG is 46.8 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 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 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.