How Do O_2 and CO_2 Partition Between the Atmosphere and the Hydrosphere?

Equilibrium Calculations

Chemists often need to know whether a reaction is spontaneous by a quantitative measure. They do this by developing an expression called the **equilibrium constant**. A reaction is at **equilibrium** when the ratio of the products and reactants is constant with time. Though it can appear that the reaction between reactants has ceased at equilibrium, the product and reactant molecules continue to react. At equilibrium, the **rate** of formation of the products is equal to the rate of formation of reactants. Thus, we write the reaction with a two-way arrow to indicate that a forward and a reverse reaction are simultaneously occurring at equal rates. In this exploration, you will learn about the relation between Gibbs energy and the equilibrium constant. This relation, one of the most important applications of Gibbs energy, will allow you to quantitatively predict how many moles of products and reactants exist in a system at equilibrium.

In this exploration, we start with an interesting reaction as a simple example, the hydration of carbon dioxide:

$$CO_2(g) \Leftrightarrow CO_2(aq)$$

Using the calculated Gibbs energy one can predict the concentration of gaseous CO_2 that dissolves in water at equilibrium with the gas phase. A more negative Gibbs energy indicates greater CO_2 solubility in water. A more positive Gibbs energy indicates lower CO_2 solubility in water. The ratio of the amount of product ($CO_2(aq)$) to the amount reactant ($CO_2(g)$) is called the reaction quotient (Q). All gas concentrations are expressed as pressures (in bar) and all aqueous solutes are expressed in molar concentration (M). If the system is at equilibrium, then the ratio Q equals K, where K is called the equilibrium constant. Though Q and K are identical in form, they have the same numerical value only when the system is at equilibrium. It is understood that all concentrations and pressures in the reaction quotient and the equilibrium constant are actually ratios of the actual pressure or concentration to the standard pressure (1 bar.) or the standard concentration (1 M). Thus, the equilibrium constant has no units associated with it.

$$Q = [CO_2(aq)] / P_{CO2}$$

$$K = [CO_2(aq)]_{eq} / P_{CO2\ eq}$$

The subscript "eq" represents the concentration or pressure of each molecule at equilibrium.

We determine the spontaneous direction of the reaction by comparing the ratio of Q/K.

Q > K: reaction goes spontaneously to the left (forms more reactants)

Q < K: reaction goes spontaneously to the right (forms more products)

Q = K: reaction is at equilibrium

To reiterate, a constant ratio of products and reactants does not mean that molecules are not reacting. Rather, it means the rate of the forward and reverse reactions are equal. The concept of a forward and reverse reaction occurring at equal rates is called dynamic equilibrium. Molecules constantly react, but the concentration ratios do not change. If the ratio (Q) is not constant over time, the mixture is not at equilibrium. At equilibrium, the specific CO_2 molecules in the gas and liquid phase are always changing, but the ratio (K) of the concentration of aqueous CO_2 and the pressure of gaseous CO_2 remains constant.

The thermodynamic variable that relates to the reaction quotient (Q) is the Gibbs energy (ΔG). Negative ΔG values indicate the reaction is spontaneous in the forward direction; positive ΔG values indicate the reaction is spontaneous in the reverse direction. It is easy to confuse thermodynamic variables as they are subtly differentiated by superscripts and subscripts. Thus, you must make sure you do not mistake ΔG (Gibbs energy) for the standard Gibbs energy ($\Delta G°$). The relation between the two is:

$$\Delta G = \Delta G° + RT \ln Q$$

Since the standard state conditions are at one atmosphere pressure and one molar concentration, Q must equal one at standard conditions. Thus, if all reactants and products are at their standard states, $\Delta G = \Delta G°$.

$$\Delta G = \Delta G° + RT \ln 1 = \Delta G°$$

Similarly, if (and only if) the system is at equilibrium, then Q equals K and $\Delta G = 0$. Thus,

$$\Delta G = \Delta G° + RT \ln Q$$

$$0 = \Delta G° + RT \ln K$$

$$\Delta G° = - RT \ln K$$

To summarize, the following relations always hold:

$$\Delta G° = - RT \ln K \qquad \Delta G = \Delta G° + RT \ln Q$$

The following hold only when the system is at standard state:

$$\Delta G = \Delta G° \qquad Q = 1$$

The following hold only when the system is at equilibrium:

$$\Delta G = 0 \qquad Q = K$$

Real World Applications

What happens when you open up a new bottle of pop (soda)?

What happens when you heat an open can of pop (soda)?

Discuss your answers in terms of their thermodynamic rationale with your classmates.

Working with Information

1. Write a reaction that describes the dissolution of gaseous CO_2 in water.

2. Write the equilibrium constant expression for the dissolution of CO_2 in terms of pressures and concentration of the two different species of CO_2.

3. Using the appropriate values from the table below predict whether CO_2 should be more or less soluble at higher temperatures. What thermodynamic variable seems to control the solubility as a function of temperature?

4. Calculate $\Delta G°$ for the dissolution of CO_2 at your assigned temperature: 2°C, 5°C or 15°C using the appropriate values from the table below.

Species	$\Delta H°$ (kJ/mole)	$S°$ (J/mole-K)
$CO_2(g)$	-393.5	213.8
$CO_2(aq)$	-412.9	121

5. Calculate the equilibrium constant at your assigned temperature.

6. Do the values of the equilibrium constants as a function of temperature make sense based upon every day experience? What implication might these values have for feedback in a warming climate?

7. The solubility of O_2 in water can be explained by the following reaction:

$$O_2(g) \Leftrightarrow O_2(aq)$$

Which species represents dissolved oxygen? Write the equilibrium constant expression for the reaction.

8. The data from the NIST website for the dissolution of oxygen indicates the following temperature dependence for the Henry's constant:

$$K_H = 0.0013e^{1700\left(\frac{1}{T}-\frac{1}{298}\right)}$$
Equation 1

The units for the constant are in M/bar. Without using a calculator, determine the solubility of oxygen at 298 K in molar units. What is the solubility in ppm (mg/L) units?

9. Explain the behavior of dissolved oxygen vs. temperature as a function of depth in the following figure taken from a small lake in Maine. Start by labeling the appropriate line for temperature and dissolved oxygen.
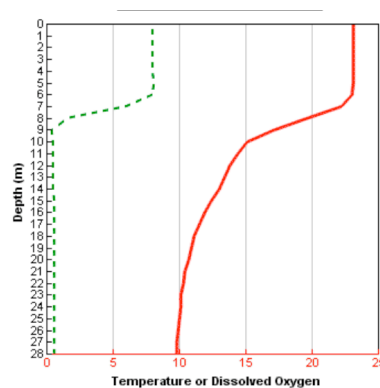
10. You are serving as a research scientist with the Environmental Protection Agency. You are monitoring the health of rivers in an area by examining the amount of oxygen dissolved in the water. In an effort to work with the local industries, you ask companies along these rivers to collect samples and determine the amount of oxygen dissolved in the samples. You receive the following results.

| River	Company	Dissolved oxygen
Apple River	Apple Sewage Treatment Plant	6 mg/L
Big River	Big River Golf Course	9 mg/L
Chattanooga River	Chattanooga Dam and Electric Plant	14 mg/L
Durham River	Durham Fertilizer Plant	10 mg/L
East River	East River Sawmill	4 mg/L

You note one value that causes you some alarm, and you immediately alert your boss and tell her that you suspect one company is causing problems. Who do you suspect and why?

A.   Apple Sewage Treatment; the levels of dissolved oxygen are too low considering the sewage that is probably getting in the water.

B.   Big River Golf Course; the levels of dissolved oxygen are too high for the amount fertilizer that is probably entering the water.

C.   Chattanooga Dam and Electric Plant; the levels of dissolved oxygen are impossible to obtain under normal circumstances.

D.   Durham Fertilizer Plant; the levels of dissolved oxygen are too high for the amount of waste that is probably entering the water.

E.   East River Sawmill; the levels of dissolved oxygen are impossible to obtain under normal circumstances.

11. Indicate any potential problems you see with the following diagram that relates temperature and dissolved oxygen:
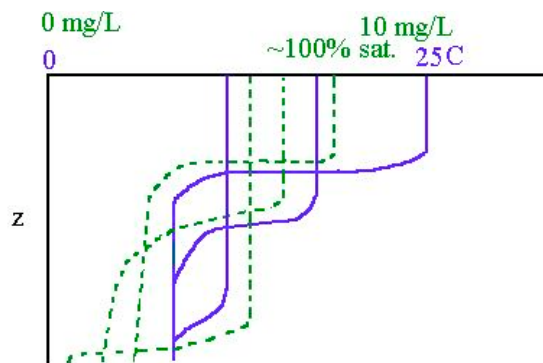
12. The figure below is meant to help you calculate dissolved oxygen at any temperature. Water at 10°C has an observed concentration of dissolved oxygen of 10 ppm. Is it saturated? Check to see if Equation 1 gives the same answers at 10°C as the diagram below.   What would need to be done in Colorado Springs to make this chart more useful? How might the correction relate to Equation 1?
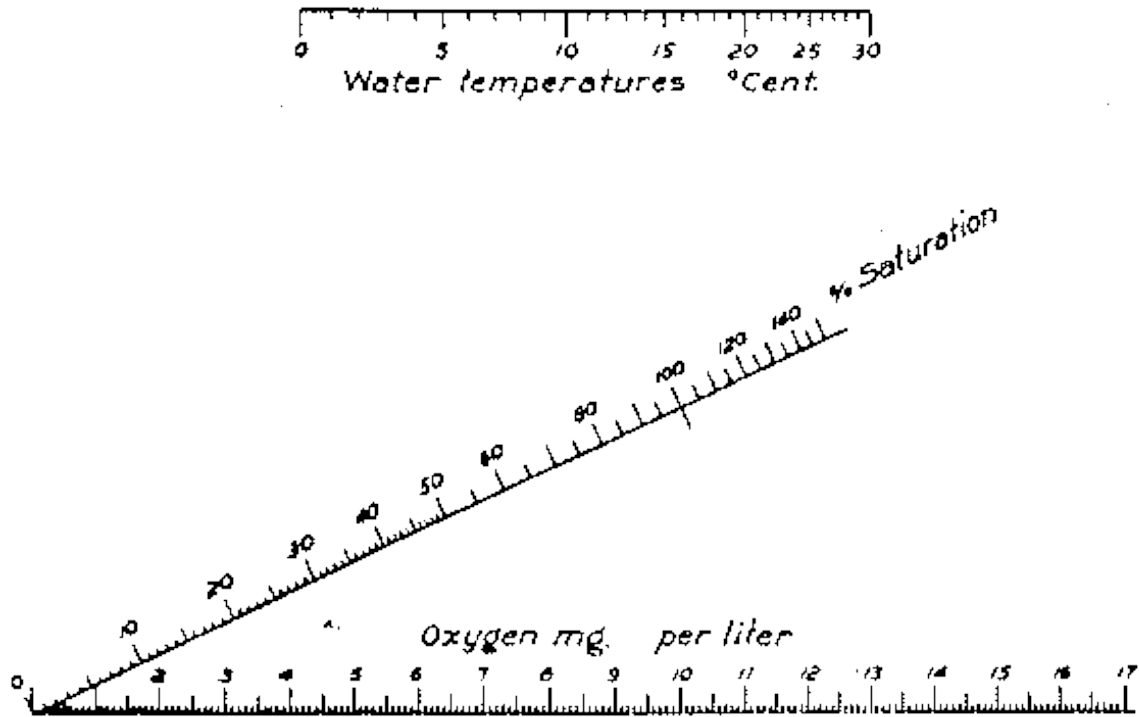
13. The maximum percentage of dissolved oxygen in water at 4°C and 0.21 bar pressure is about _____.

    A.   21%
    B.   5%
    C.   1%
    D.   0.5%
    E.   0.001%