pH, Equilibrium and Ocean Buffering

Introduction

Discussion of acids, bases, pH and buffering can include consideration of the equilibrium between dissolved inorganic carbon species:

$CO_2\ (g) \rightarrow CO_2\ (aq)$

$CO_2(aq) + H_2O(1) \rightarrow H_2CO_3(aq)$

$H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H^+(aq)$

$HCO_3^-(aq) \rightarrow CO_3^{2-}(aq) + H^+(aq)$

These equations provide a good illustration of acids, pH and buffering. The inorganic carbon species constitutes an important mechanism for buffering the pH of the ocean. Understanding the behavior of inorganic carbon in the ocean is important. It plays a role in the dissolution or preservation of the carbonate hard parts of many marine organisms that ultimately become limestone or other carbonate minerals. Recent attention to inorganic carbon in the ocean is related to the greenhouse effect. Scientists want to know how the increase in atmospheric CO_2 concentrations (from burning fossil fuels) affects oceanic pH or vice versa.

Oceans represent one of the most visible features on our planet. Covering approximately 71 percent of the earth's surface area, the oceans play an important role in the distribution of elements on the earth. Many reactions and processes that involve these elements take place in the oceans. Table 1 presents a brief description of the oceans' features.

Table 1.
General Features of the Oceans

The average ocean depth is approximately 3,800 meters (12,200 feet or 2.3 miles).

The deepest point is about 11,000 meters below sea level (the Philippine Trench and Marianas Trench in the Pacific).

The volume of all the oceans is approximately 317 million cubic miles or 1.33 billion cubic kilometers.

The average ocean temperature is 38.3°F (3.5°C). Temperatures range from 32°F (0°C) or less in the polar regions to 98.6°F (37°C) in the Persian Gulf.

Only about 0.33 percent of all the earth's water is fresh water for drinking and irrigation.

Table 2 lists the most abundant elements in seawater. Given the range in depths (that result in a range of pressure conditions) and temperatures, the quantities and types of elements present and its large surface area, it is not surprising that chemical processes occurring in the ocean have a significant influence upon living conditions on our planet.

Table 2.
Major Elements in Seawater

Element	metric tons/cubic kilometer
chlorine (Cl^-)	19,600,000
sodium (Na^+)	10,900,000
magnesium (Mg^{2+})	1,400,000
sulfur (S^{2-}, SO_4^{2-})	920,000
calcium (Ca^{2+})	420,000
potassium (K^+)	390,000
bromine (Br^-)	67,000
carbon (HCO_3^-,CO_3^{2-})	29,000
strontium (Sr^{2+})	8,300

Carbon, an important element to all living things, interacts in major processes that affect living conditions and the oceans' chemistry. The ocean is a natural, complex example of how acids and bases interact and of how certain compounds behave to buffer the pH level of the ocean. The main agents involved in these processes are carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). The main reactions involving these compounds and ions are depicted in Figure 1a below.

Figure 1a Carbon cycle

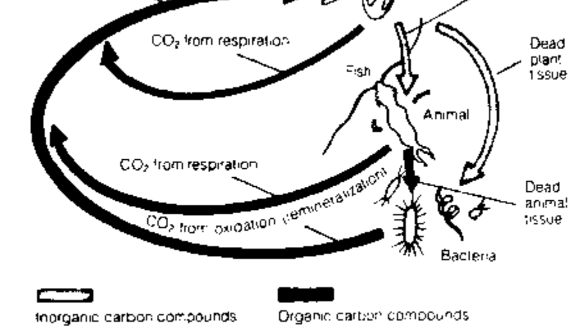

Figure 1b Inorganic carbon compound reactions in seawater

(1) $CO_2(g) \rightarrow CO_2(aq)$

(2a) $CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$

(2b) $H_2O(l) + H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H_3O^+(aq)$

(2) $CO_2(aq) + 2H_2O(l) \rightarrow HCO_3^-(aq) + H_3O^+(aq)$
(sum of 2a and 2b)

(3) $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$

ACTIVITY 1

Acids and Bases in the Ocean

Purpose

To identify acids and bases in the ocean environment and to interpret acid/base equations.

Questions

Identifying acids and bases (use equations in Figure 1b)

1. Which chemical equation(s) contains a Bronsted-Lowry acid? A Bronsted-Lowry base?

2. Identify the Bronsted-Lowry acid(s) and base(s) in each equation listed in answer 1 above.

3. Which of the following is an Arrhenius acid?

(a) HCO_3^- (b) CO_3^{2-} (c) CO_2

4. Why did you select your answer to number 3?

Identifying conjugate acids and bases

5. What are the conjugate acid-base pairs in each chemical equation you listed in number 1 above?

6. Which of the following represents a conjugate acid-base pair in chemical equation 3?

(a) CO_3^{2-} and H_2O (b) HCO_3^- and CO_3^{2-}
(c) H_2O and HCO_3^- (d) CO_3^{2-} and H_3O^+

Identifying the symbols in the chemical equations

7. What does $H_2O(l)$ symbolize?

8. How is $CO_2(g)$ different from $CO_2(aq)$?

Translating the symbolism of chemical equations

You have learned the meaning of the components of the chemical equation and certain acid-base expressions and how to identify them. Now test your understanding of what is represented or symbolized by a chemical equation as a whole.

9. What is happening to CO_2 in Figure 1b?

10. What is happening to the other compounds in Figure 1b?

11. What is H_3O^+ called?

12. Is bicarbonate ion (HCO_3) a Bronsted-Lowry acid, base, both or neither? Explain why, and include definition(s) of a Bronsted-Lowry acid and a Bronsted-Lowry base in your answer.

13. What are the reactants of equation 3 in Figure 1b as it is written? The products?

ACTIVITY 2

Inorganic Carbon Compound Reactions and Their Equilibrium Constants

Purpose

To identify the products and reactants in chemical equations, construct equilibrium constant expressions for given reactions, use tables to determine the value for equilibrium constants of inorganic carbon reactions, and calculate the concentrations of a product or reactant in a reaction. Students will use the equilibrium constant expressions and their values as determined from the given tables and other concentrations.

Background

For a given temperature and pressure, there is a definite relationship between the concentrations of the reactants and the products in a reaction when equilibrium is reached. This relationship is expressed by the equilibrium constant, represented by the letter K. Hence for the general reaction:

(1) aA + bB = cC + dD

where A and B are reactants and C and D are products, the equilibrium constant expression is:

(2) $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Students need to be reminded that pure liquids and solids are omitted from the right side of an equilibrium expression.

Questions

1. For reactions involving inorganic carbon compounds, fill in the blanks.

$CO_2(g) \rightarrow CO_2(aq)$

Reactants ______ Products ______ Equilibrium Constant Expression K_1 = ____________

$CO_2(aq) + 2H_2O(l) \rightarrow HCO_3^-(aq) + H_3O^+(aq)$

Reactants ______ Products ______ Equilibrium Constant Expression K_2 = ____________

$HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$

Reactants ______ Products ______ Equilibrium Constant Expression K_3 = ____________

Tables 3 and 4 provide values for K_2 and K_3, respectively, under different conditions of chlorinity and temperature. Chlorinity is a measure of the amount of salt dissolved in water. It is measured in parts per thousand, symbolized by ‰. (Similarly, percentages, which are parts per hundred, are represented by %).

Table 3.
Values for K_2* at Different Cl ‰ and Temperatures°(C)

Cl ‰	0	5	10	15	20	25	30	35
0	2.63	3.01	3.38	3.80	4.16	4.46	4.67	4.89
1	3.38	3.80	4.26	4.67	5.12	5.49	5.75	5.88
4	4.36	4.78	5.24	5.75	6.16	6.60	6.91	7.07
9	5.37	5.88	6.45	7.07	7.41	7.94	8.31	8.51
16	6.60	7.24	7.76	8.51	8.91	9.33	9.77	10.2
17	6.76	7.41	7.94	8.70	9.12	9.54	10.0	10.5
18	6.91	7.58	8.12	8.70	9.33	9.77	10.2	10.7
19	7.07	7.76	8.31	8.91	9.54	10.0	10.5	10.7
20	7.24	7.94	8.51	9.12	9.77	10.2	10.7	11.0
21	7.41	8.12	8.70	9.33	10.0	10.5	11.0	11.2
25	8.12	8.91	9.54	10.0	10.7	11.2	11.7	12.0
49	12.0	13.2	13.8	14.5	15.1	15.8	16.6	17.0

*These values should be multiplied by 1×10^{-7}.

Table 4.
Values for K_3 at Different Cl ‰ and Temperatures°(C)

Cl ‰	0	5	10	15	20	25	30	35
0	.240	.282	.324	.372	.417	.468	.513	.562
1	.871	1.02	1.17	1.35	1.55	1.74	1.95	.562
2	1.66	1.91	2.14	2.45	2.88	3.24	3.72	4.17
9	2.29	2.63	3.02	3.47	3.98	4.57	5.37	6.17
16	3.47	3.98	4.47	5.13	5.89	6.76	7.94	9.55
17	3.63	4.17	4.79	5.37	6.17	7.08	8.32	10.0
18	3.80	4.37	5.01	5.62	6.46	7.59	8.71	10.5
19	3.98	4.57	5.25	5.89	6.76	7.94	9.55	11.2
20	4.17	4.79	5.50	6.17	7.08	8.32	9.77	12.0
21	4.37	5.01	5.62	6.46	7.41	8.71	10.5	12.9
25	5.13	5.89	6.76	7.76	8.91	10.5	12.3	15.1
49	11.2	12.9	15.1	17.8	20.9	24.5	29.5	37.2

*These values should be multiplied by 1×10^{-10}.

2. Using Tables 3 and 4, find the expected values of K_2 and K_3 for the following oceanic conditions and fill in the blanks below.

Oceanic Conditions	K_2	K_3
Cl ‰ = 17 ‰, T = 5°C	______	______
Cl ‰ = 49 ‰, T = 35°C	______	______
Cl ‰ = 21 ‰, T = 20°C	______	______

You are ready to use the equilibrium constant expressions and the equilibrium constant values from Tables 3 and 4.

3. You collected samples of ocean water at different depths while on the research submarine *Alvin* (the vessel that explored the *Titanic* in 1986). You measured Cl ‰ and temperatures from the submarine; lab technicians measured $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H_3O^+]$ from the *Atlantic II*, which transports *Alvin* to its dive sites. The technicians made several mistakes, so some of their data was not used. The collected data is represented in Table 5. Fill in the blanks.

Table 5.
Cruise Data

dpth(m)	Cl ‰	T(°C)	*a K_2	*b K_3	*1 HCO_3^-]	*2 $[CO_3^{2-}]$	*3 $[H_3O^+]$	*4 $[CO_2]$
0	21	30	______	______	2.04	3.98	3.98	______
100	20	25	______	______	3.40	______	5.01	1.67
200	18	20	______	______	5.72	5.86	6.31	______
300	17	20	______	______	8.51	5.25	10.0	______
400	16	10	______	______	13.5	______	______	21.6
500	16	10	______	______	13.3	______	______	21.9
750	16	10	______	______	14.0	6.53	12.6	______
1000	16	5	______	______	36.0	7.16	20.0	______

*1 Values are to be multiplied by 1×10^{-6}
*2 Values are to be multiplied by 1×10^{-7}
*3 Values are to be multiplied by 1×10^{-9}
*4 Values are to be multiplied by 1×10^{-8}
*a Values are to be multiplied by 1×10^{-7}
*b Values are to be multiplied by 1×10^{-10}

ACTIVITY 3

What is the pH?

Purpose

To work pH problems and to determine the pH of various aqueous solutions.

Background

The pH concept originated in 1909 with a Danish biochemist named Sorensen. The "p" in pH comes from "potenz," a German word for power. The "H" stands for hydrogen ions. The pH is a measure of the concentration of hydrogen (hydronium) ions in an aqueous solution. The formula, $pH = -\log [H^+]$, is used to calculate pH.

The pH scale, which generally ranges from 0 to 14, is used to indicate the acidity or basicity of a dilute (1 molar or less) water solution. Acidic solutions have a pH less than 7. Basic solutions have a pH greater than 7, and neutral solutions, a pH equal to 7. Citrus juices are acidic; pure water, neutral; and seawater, basic (Table 6).

The concentration of hydronium ion (H_3O^+) in aqueous solutions, often referred to as a hydrated proton, is important. These ions react with and affect many other elements, compounds and/or ions. The measure of $[H_3O^+]$ is so important that scientists have selected a convenient way to express it—pH. The pH is related to $[H_3O^+]$ by the following expression:

(1) $pH = -\log [H_3O^+]$

The pH of pure water is 7 ($[H_3O^+] = 1 \times 10^{-7}$ M).

Table 6.
The pH of Some Common Substances

Substance	pH
hydrochloric adic, HCl (0.1 M)	1.0
digestive juices in the stomach	2.0
lemon juice	2.3
vinegar	2.8
acetic acid, $HC_2H_3O_2$ (0.1 M)	2.9
carbonated drinks	3.0
grapefruit juice	3.1
orange juice	3.5
tomato juice	4.2
rainwater	6.2
milk	6.5
pure water	7.0
blood	7.4
seawater	8.1–8.3
sodium bicarbonate, $NaHCO_3$ (0.1 M)	8.4
milk of magnesia	11.1
ammonia water, NH_4OH (0.1 M)	11.1
sodium hydroxide, NaOH (0.1 M)	13.0

1. Using equation 1, calculate pH if:

a. $[H_3O^+] = 1.0 \times 10^{-4}$

b. $[H_3O^+] = 1.0 \times 10^{-14}$

c. $[H_3O^+] = 1.0 \times 10^{-7.1}$

d. $[H_3O^+] = 1.0 \times 10^{1.6}$

e. $[H_3O^+] = 3.56 \times 10^{-5}$

f. $[H_3O^+] = 2.91 \times 10^{-8}$

2. Using equation 1, calculate $[H_3O^+]$ if:

a. pH = 5

b. pH = 1

c. pH = 3.6

d. pH = 9.3

e. pH = 7.46

f. pH = 13.8

Equipment/Materials

stirring rod
drinking straw
wire
gauze
Bunsen burner
ring stand
2 rings
small test tube
100-ml beaker
two vials of pH paper*
  one with even-numbered chart on the label
  one with odd-numbered chart on the label
1 M lead (II) nitrate
1 M hydrochloric acid
0.8 M sodium bicarbonate
1 M acetic acid
0.1 M sodium carbonate
vinegar
shampoo
lemon juice
seawater**
household solutions

* The pH paper is identical in both vials. With two vials you will have access to both the even- and odd-numbered pH charts.

**Seawater (from the Pacific, Atlantic and the Gulf of Mexico) can be purchased. Seawater can also be simulated. There are two methods of achieving a solution with a pH near that of seawater (8.5). Prepare a 1.0 M solution of sodium bicarbonate (pH = 8.4). Or purchase powdered buffer formulations with a specific pH conveniently packaged in capsules. Dissolve the powder in distilled water. The seawater could be used to introduce the lab and show the correct use of pH paper. This would especially be desirable if you have to purchase seawater.

CAUTION: Do not begin this lab until your teacher has given you lab instructions and cautions for each chemical. Wear eye and clothing protection.

Procedure

When using pH paper to determine the pH of a solution, put one or two drops of the solution on the paper. This is easily done if the solutions are in dropper bottles. If they are not, dip a clean stirring rod in the solution to be tested and touch the rod to the pH paper. In either case, immediately compare the moistened pH paper to the odd- and even-numbered charts on the pH vials. Use a separate piece of pH paper for each solution. Discard the paper after use.

Step 1. The teacher will provide a list of solutions. Use pH paper to determine the pH of each of these solutions. Record the results in a data table. Remember that a data table must have a number and a title.

Step 2. Determine the pH of tap water and distilled water. Record this data in your data table.

Carbon dioxide can enter the ocean from the atmosphere. Water can hold higher concentrations of carbon dioxide than air, volume for volume. Dissolved carbon dioxide affects the pH of seawater. The saltier and colder the water, the more carbon dioxide it can dissolve.

Step 3. Put approximately 25 ml of distilled water (room temperature or colder) in a 100-ml beaker. Make sure the beaker is clean. Use a drinking straw to blow into the water for two minutes. Determine the pH of this water. Record it in your data table. (Instead of distilled water, students could use simulated seawater.)

Step 4. Set up the ring stand and rings so that heating can be done. One ring is to support the wire gauze and the other ring is situated so that it surrounds the beaker to prevent tipping. Gently boil the 25 ml of water from the step above for two minutes. Determine the pH of the boiled water. Record it in your data table. Do not let the water cool before taking the pH. Remember that the rings, beaker and water are very hot. Be careful.

Step 5. Determine the pH of the following solutions: lead (II) nitrate, vinegar, sodium carbonate, sodium bicarbonate, 1 M acetic acid, 1 M hydrochloric acid, shampoo, lemon juice and seawater. Record the results in your data table.

Step 6. In a small clean test tube, combine two drops of baking soda (sodium bicarbonate) and two drops of vinegar. Use data you have already collected to predict the pH of this combination of solutions. Write your prediction in the data table.

Step 7. Use a clean stirring rod to determine the actual pH of the combination of solutions above. Record this in your data table.

Questions

1. In step 3, what gas did you put into the water that could affect its pH?

2. In step 4, what gas (besides oxygen) was given off during the boiling process?

3. Mention one way that carbon dioxide enters the ocean.

4. Write the balanced equation for the reaction between carbon dioxide and water.

5. Why are the pHs different in steps 3 and 4?

6. What reasoning did you use to make a prediction in step 6?

7. Did your prediction in step 6 match the actual pH measured in step 7?

8. An acid reacts with a base to produce a ______ and water. This reaction is called ______.

9. What acid and base should be reacted to produce the salt, lead (II) nitrate?

10. What acid and base should be reacted to produce the salt, sodium carbonate?

11. Judging from the name of an acid-base reaction you would expect a salt solution to be neutral and have a pH of ______. However, not all salt solutions are neutral.

12. The ions of some salts undergo hydrolysis, and thus their water solutions are not neutral. Define hydrolysis.

13. What was the pH of the lead (II) nitrate solution? Does lead (II) nitrate hydrolyze?

14. What was the pH of the sodium carbonate solution? Does sodium carbonate hydrolyze?

15. Acetic acid is a (weak, strong) acid/electrolyte and does not completely ionize in water solution.

16. Hydrochloric acid is a (weak, strong) acid/electrolyte and ionizes 100 percent in water solution.

17. What was the pH of the 1 M acetic acid solution?

18. What was the pH of the 1 M hydrochloric acid?

19. Explain why acetic acid and hydrochloric acid have different pHs even though they are both 1 molar solutions.

20. Sodium bicarbonate (baking soda) forms a(n) (acidic, basic) solution.

21. Medicinally, how is a sodium bicarbonate solution used?

22. Hair can be damaged by combing or brushing immediately after it is washed. Wet hair is strongest and least vulnerable if it has a pH range of 4.0 to 5.0. Would the shampoo tested in this experiment be a good one to use to give your hair maximum wet strength?

23. If a shampoo has a pH that is too high, which household items from the list below could be used as a rinse after shampooing to reduce the pH nearer the acceptable level? You may choose more than one item.

Vinegar
Lemon juice
Sodium bicarbonate solution (baking soda)

24. Vinegar is used to preserve foods such as pickles because the (acidic, basic) nature of the vinegar inhibits the decomposition of tissues. Some lakes are as acidic as vinegar because of pollution and acid rain. Plants and animals have difficulty surviving in this type of environment.

25. What is the pH of seawater?

26. Use your answer above to explain why acid rain does not appreciably affect the ocean and its life forms.

27. The ocean is a buffer solution relative to acids because it has a large carbon dioxide content. Define buffer.

Competency Factors/References

Competency Indicators

Chemistry-academic—

7.3 know physical characteristics and chemical properties of solutions of acids, bases and salts; and

7.6 have a knowledge of acid-base equilibria and pH.

Chemistry-applied technical—

7.3 know physical characteristics and chemical properties of solutions.

Chemistry—

7.6 know about acids, bases and pH.

Competency Measures

Chemistry-academic—

7.3.2 determine experimentally the pH, the effect on litmus paper and other physical characteristics of acids, bases and salts;

7.3.3 explain the characteristics of solutions of acids, bases and salts in terms of interaction with water;

7.6.1 develop an understanding of pH and pOH as logarithmic expressions of concentrations of H_3O^+ and OH^- ions; and

7.6.2 calculate the pH of an acidic or basic solution given its concentration.

Chemistry-applied/technical—

7.3.1 (see 7.3.2 above);

7.3.2 (see 7.3.3 above);

7.6.1 draw a diagram of pH and pOH scales and give examples of everyday materials in the corresponding ranges; and

7.6.2 determine the pH of an acidic or basic solution given a pH meter or test kit.