2.81 INVESTIGATE THIS

Are CO_2 solutions affected by added acids and bases?

Do this as a class investigation and work in small groups to discuss and analyze the results.

(a) Use a 125-mL Erlenmeyer flask, a three-hole rubber stopper to fit the flask, 75 mL of a saturated solution of $CO_2(g)$ in water (seltzer water), 0.6 g of solid sodium hydrogen carbonate, $NaHOCO_2$, and a few drops of universal acid–base indicator solution. Fit the three holes of the stopper with a plastic pipet about half full (3 mL) of 6 *M* hydrochloric acid, HCl, solution, a second plastic pipet filled completely (6 mL) with 6 *M* aqueous sodium hydroxide, NaOH, solution, and a glass or plastic tube to which a small balloon is tightly sealed. Place the sodium hydrogen carbonate and indicator in the flask, add the seltzer water, and insert the rubber stopper to seal the flask, as shown in this photograph. Swirl the flask gently to mix the contents. Record the color of the solution, the state of inflation of the balloon, and any other observations on the system. As a control solution, add a few drops of universal indicator to 75 mL of seltzer water in another flask and record its color.

(b) Add the hydrochloric acid to the mixture in the flask by squeezing out the contents of its pipet. Again swirl the flask gently to mix the contents and record the color of the solution, the state of inflation of the balloon, and any other observations on the system.

(c) Add the sodium hydroxide to the mixture by squeezing out the contents of its pipet. Again swirl the flask gently to mix the contents and record the color of the solution, the state of inflation of the balloon, and any other observations on the system.

2.82 CONSIDER THIS

How are CO_2 solutions affected by added acids and bases?

(a) Is there evidence for reaction(s) when the acid and the base are added to the mixture in Investigate This 2.81? What is the evidence in each case? *Note:* Universal indicator is red in acidic solutions, yellow to green in pH 5–8 solutions, and blue in basic solutions.

(b) Under what, if any, conditions was gas evolved by the mixture? Under what, if any, conditions was gas absorbed by the mixture? How might you explain your observations?

In Investigate This 2.81, addition of hydrogen carbonate ion, $HOCO_2^-(aq)$, to a solution of carbon dioxide dissolved in water (carbonic acid) gives a solution with a pH of about 5–6 (a little higher than carbonic acid alone) and produces no bubbles of gas. If the $(HO)_2CO(aq)$ solution equilibrium is described by equation (2.23) and very little of the $(HO)_2CO(aq)$ transfers a proton to water, as we discussed above, these are the results we expect. The added $HOCO_2^-(aq)$ reacts with some of the $H_3O^+(aq)$ to produce a tiny bit of $(HO)_2CO(aq)$. The result is a solution with a slightly higher pH (lower $[H_3O^+(aq)]$) than for carbonic acid alone. We might expect the additional $(HO)_2CO$*(aq)* to disturb the equation (2.27) equilibrium and produce some CO_2*(g)* by the reverse of the reaction. However, the amount of extra $(HO)_2CO$*(aq)* that can be formed is so tiny that reaction (2.27) is barely disturbed and no detectable gas is produced.

Le Chatelier's principle The situation we have just described is an example of Le Chatelier's principle in action. Henry Louis Le Chatelier (French chemist, 1850–1936) worked on many industrial processes and was interested in ways to assure that reactions would proceed in the directions that produced desired products. Since many such processes involve reversible reactions, he looked for and found patterns in the behavior of equilibrium systems when they were disturbed or changed. **Le Chatelier's principle** states that *a system at equilibrium responds to a disturbance in a way that minimizes the effect of the disturbance.* The only disturbances that affect equilibria are changes in the *concentrations* of the reactants and/or products and changes in the *temperature* of the system. For example, increasing the concentration of a reactant or product causes the reacting system to respond in such a way as to use up some of the added molecules.

Sometimes factors other than concentration and temperature are mentioned as disturbances, but you will find that they all really boil down to concentration or temperature effects.

Returning to our $(HO)_2CO$*(aq)* equilibrium system to which $HOCO_2^-$*(aq)* is added, we note that the disturbance to the equilibrium, reaction (2.23), is the addition of one of the reaction products, $HOCO_2^-$*(aq)*. Le Chatelier's principle says that the system will respond by trying to use up some of the added product. Reaction (2.23) will proceed in reverse until equilibrium is reattained with less of the products, H_3O^+*(aq)* and $HOCO_2^-$*(aq)*, and more of the reactant, $(HO)_2CO$*(aq)*, than were present in the instant after the addition. We can represent the change this way:

$$(HO)_2CO(aq) + H_2O(l) \leftarrow H_3O^+(aq) + HOCO_2^-(aq) \qquad \textbf{(2.29)}$$

Equation (2.29) symbolizes the chemistry we discussed above when we said that $[H_3O^+(aq)]$ would be decreased a bit by addition of $HOCO_2^-$*(aq)*. Formation of more $(HO)_2CO$*(aq)* will disturb equilibrium reaction (2.27) as well:

$$CO_2(g) + H_2O(l) \leftarrow (HO)_2CO(aq) \qquad \textbf{(2.30)}$$

As we said, the response to the minor disturbance was too small to be detectable.

This was not the case when you added a good deal of H_3O^+*(aq)* (in the form of hydrochloric acid solution) to the reaction mixture. The disturbance to the system is again the addition of one of the reaction products. Equation (2.29) again represents the change that will occur as the system responds to minimize the effect of the disturbance by using up some of the added product. In this case, a large amount of $(HO)_2CO$*(aq)* can be formed by the added acid; equilibrium (2.27) is greatly disturbed; and reaction (2.30) represents the system's response, which you observed as a copious formation of bubbles and inflation of the balloon.

2.83 WORKED EXAMPLE

Stoichiometry of addition of acid in Investigate This 2.79

Approximately what volume of CO_2*(g)* can be produced by reaction (2.30) in Investigate This 2.81(b), if all the newly formed $(HO)_2CO$*(aq)* reacts? Assume that a mole of gas at room temperature and one atmosphere pressure occupies 25 L.

continued

Necessary information: We need the mass of sodium hydrogen carbonate added, 0.6 g, the volume of 6 *M* hydrochloric acid added, 3 mL, the stoichiometry of the reactions, and the molar volume of a gas from the problem statement.

Strategy: Calculate the volume of gas, $CO_2(g)$, produced from the moles of gas produced. Assume all the extra $(HO)_2CO(aq)$ produced by reaction (2.29) reacts by reaction (2.30) to give $CO_2(g)$. This is a reasonable assumption because the original solution is saturated with $CO_2(g)$, which is in equilibrium with the original amount of $(HO)_2CO(aq)$. No more $CO_2(g)$ can be accommodated in the solution, so any formed by reaction (2.29) will escape and the reaction will proceed until only the original amount of $(HO)_2CO(aq)$ is left. Calculate the moles of $H_3O^+(aq)$ and $HOCO_2^-(aq)$ in the mixture to determine which is the limiting reactant and then calculate the moles of $(HO)_2CO(aq)$ formed and, hence, moles of $CO_2(g)$ produced.

Implementation: The moles of $H_3O^+(aq)$ and $HOCO_2^-(aq)$ in the mixture are

$$\text{mol } H_3O^+(aq) = \text{mol HCl}(aq) = (6\ M)(0.003\ \text{L}) = 18 \times 10^{-3}\ \text{mol}$$

$$1\ \text{mol NaHOCO}_2 = 84\ \text{g}$$

$$\text{mol HOCO}_2^-(aq) = \text{mol NaHOCO}_2 = \frac{0.6\ \text{g NaHOCO}_2}{84\ \text{g·mol}^{-1}\ \text{NaHOCO}_2}$$

$$= 7 \times 10^{-3}\ \text{mol}$$

The hydronium and hydrogen carbonate ions react in a one-to-one ratio. Hydronium ion is in great excess, so $HOCO_2^-(aq)$ is the limiting reactant and can produce 7×10^{-3} mol $(HO)_2CO(aq)$ by reaction (2.29), which can in turn produce 7×10^{-3} mol $CO_2(g)$ by reaction (2.30).

$$\text{volume } CO_2(g) = [7 \times 10^{-3}\ \text{mol } CO_2(g)](25\ \text{L·mol}^{-1})$$

$$= 0.175\ \text{L} \approx 180\ \text{mL } CO_2(g)$$

Does the answer make sense? When the hydrochloric acid was added in Investigate This 2.81(b), gas bubbles were produced in the mixture and the small balloon inflated somewhat. A 7-cm-diameter sphere has a volume of about 180 mL and your inflated balloon probably had a diameter close to this, so the answer makes sense.

2.84 Consider This

What is the stoichiometry of addition of base in Investigate This 2.81?

(a) In Investigate This 2.81(c), how many moles of hydroxide ion (as a 6 *M* solution of NaOH) were added to the reaction mixture? Explain.

(b) What did you observe when the hydroxide ion was added to the mixture? What can you conclude about the direction of reaction (2.27) in this system with added hydroxide ion? Explain your reasoning.

continued

(c) Hydroxide ion reacts with acids in aqueous solution to form water by proton transfer from the acid. There are two acids for hydroxide ion to react with in the mixture from Investigate This 2.81(b); the stoichiometries of the reactions are

$$2OH^-(aq) + (HO)_2CO(aq) \rightarrow 2H_2O(l) + CO_3^{2-}(aq) \quad \textbf{(2.31)}$$

$$OH^-(aq) + H_3O^+(aq)\,[\text{from added excess of HCl}(aq)] \rightarrow 2H_2O(l) \quad \textbf{(2.32)}$$

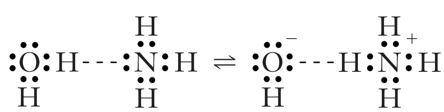
How many moles of $(HO)_2CO(aq)$ are available for the hydroxide to react with? Remember to account for both the original solution and your answer in part (b). Explain your reasoning. How many moles of $H_3O^+(aq)$ from the excess added in Investigate This 2.81(b) are present for the hydroxide to react with? Explain.

(d) Was enough hydroxide ion added to react with all the acid present? What are the major ions present in the mixture at the end of Investigate This 2.81? Explain your reasoning.

(e) Show how reaction (2.31) and Le Chatelier's principle explain your observations and support the conclusion you reached in part (b).

A Brønsted–Lowry base: Ammonia We have discussed the results of Investigate This 2.67 for the gases that dissolve to produce acidic solutions ($pH < 7$) and have shown how water accepts a proton from these molecules to give solutions with higher concentrations of hydronium ions than are present in pure water. To complete our discussion, we need to consider ammonia, $NH_3(g)$, which dissolves to give a basic solution ($pH > 7$) with a higher concentration of hydroxide ions than in pure water. Ammonia is a small polar molecule that can form hydrogen bonds with four water molecules, so its high solubility is not surprising. The solution conducts electricity, but poorly, so not many ions are present. The only source of hydroxide ion in this basic solution is water itself, so water molecules must transfer protons to ammonia, which acts as a Brønsted–Lowry base:

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq) \quad \textbf{(2.33)}$$



(2.34)

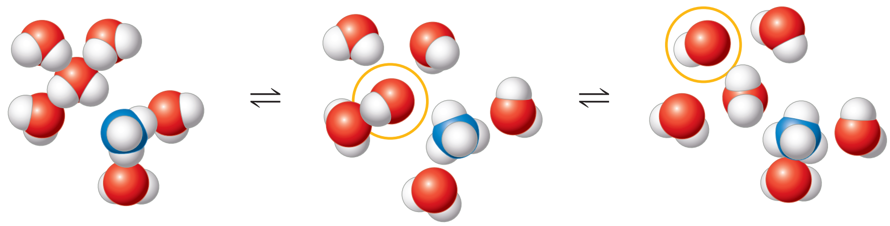
Web Companion

Chapter 2, Section 2.13.4

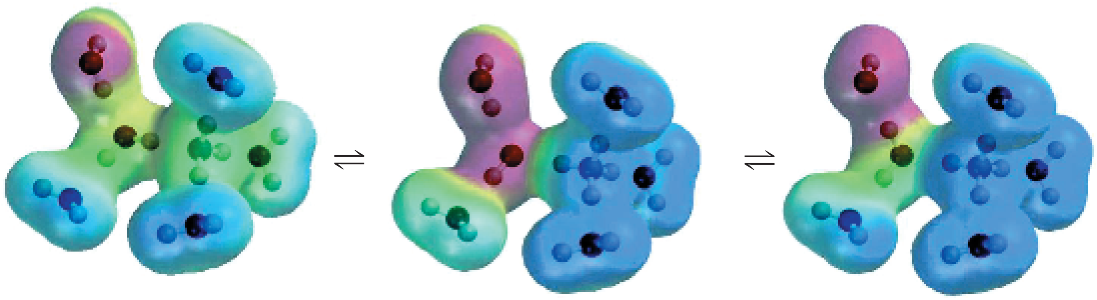
Study and analyze molecular-level animations of NH_3 reacting with H_2O.

1
2
3
4

Reaction (2.33) produces a Brønsted–Lowry acid, ammonium ion, $NH_4^+(aq)$, and a Brønsted–Lowry base, hydroxide ion, as illustrated in Figure 2.29(a) with space-filling models and in Figure 2.29(b) with charge density models. The formation of ions explains why the solution conducts an electrical current and the formation of hydroxide ion makes the solution basic. The double arrows remind us that the reaction is reversible; hydroxide and ammonium ions can react to form water and ammonia. The rather poor electrical conductivity and only moderately basic solution (pH about 11) are indicators that reaction (2.33) does not go to completion, so produces low concentrations of $OH^-(aq)$ and $NH_4^+(aq)$ ions.



(a) The hydroxide ion is circled to make it easier to find as it is formed and "migrates" by further proton transfer.



(b) Charge density model of the reactions shown in (a). The water molecules are shown in different orientations.

Figure 2.29.

Formation and migration of an ammonium and hydroxide ion by proton transfers.

2.85 INVESTIGATE THIS

What happens when ammonium and hydroxide ions mix?

(a) Add a few drops of water to about 0.25 g of solid ammonium chloride, $NH_4Cl(s)$, in a small test tube. Carefully determine whether this mixture produces any odor.
(b) Repeat part (a), but use a mixture of 0.25 g $NH_4Cl(s)$ and 0.25 g $NaOH(s)$.

2.86 CONSIDER THIS

How do ammonium and hydroxide ions react?

(a) What were the similarities and differences between the observations you made in parts (a) and (b) in Investigate This 2.85? What can you conclude about any reactions occurring in either case? Explain your reasoning.
(b) Show how Le Chatelier's principle and what you know about reaction (2.33) support your conclusion in part (a).

Review the properties of solutions of gases We have now interpreted all of the results from Investigate This 2.67, based on whether molecules can react with water to produce ions in solution and, if so, how they react:

- Distilled water (with dissolved N_2 and O_2 and a tiny bit of CO_2) does not conduct an electrical current because so few ions are present.