

13.5 Some Special Types of Equilibria

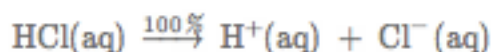
LEARNING OBJECTIVE

1. Identify several special chemical equilibria and construct their K_a expressions.

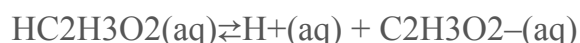
In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products or the form of the K_{eq} expression.

Weak Acids and Bases

In <http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch12>, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H_2O . $HCl(aq)$ is an example of a strong acid:



However, if an acid or base is weak, it may dissolve in H_2O but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. $HC_2H_3O_2$ is an example of a weak acid:



$HC_2H_3O_2$ is soluble in H_2O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An acid dissociation constant, K_a , is the equilibrium constant for the dissociation of a weak acid into ions. Note the a subscript on the K ; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid

is. http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch13_s05_s01_t01 lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

Table 13.1 Acid Dissociation Constants for Some Weak Acids

Acid	K_a
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
HClO_2	1.1×10^{-2}
H_2PO_4^-	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Note also that the acid dissociation constant refers to *one* H^+ ion coming off the initial reactant. Thus the acid dissociation constant for H_3PO_4 refers to this equilibrium:



The H_2PO_4^- ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:



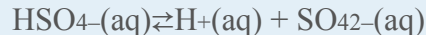
Thus for so-called *polyprotic* acids, each H^+ ion comes off in sequence, and each H^+ ion that ionizes does so with its own characteristic K_a .

EXAMPLE 10

Write the equilibrium equation and the K_a expression for HSO_4^- acting as a weak acid.

Solution

HSO_4^- acts as a weak acid by separating into an H^+ ion and an SO_4^{2-} ion:



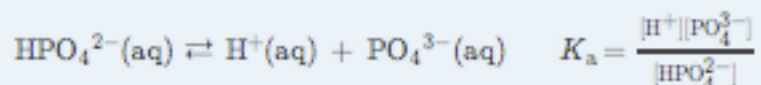
The K_a is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

Test Yourself

Write the equilibrium equation and the K_a expression for HPO_4^{2-} acting as a weak acid.

Answer



The K_a is used in equilibrium constant problems just like other equilibrium constants are. However, in some cases, we can simplify the mathematics if the numerical value of the K_a is small, much smaller than the concentration of the acid itself. Example 11 illustrates this.

EXAMPLE 11

What is the pH of a 1.00 M solution of $\text{HC}_2\text{H}_3\text{O}_2$? The K_a of $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} .

Solution

This is a two-part problem. We need to determine $[H^+]$ and then use the definition of pH to determine the pH of the solution. For the first part,

	$HC_2H_3O_2(aq)$	\rightleftharpoons	$H^+(g)$	+	$C_2H_3O_2^-(g)$
I	1.00		0		0
C	$-x$		$+x$		$+x$
E	$1.00 - x$		$+x$		$+x$

We now construct the K_a expression, substituting the concentrations from the equilibrium row in the ICE chart:

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{(1.00 - x)} = 1.8 \times 10^{-5}$$

Here is where a useful approximation comes in: at 1.8×10^{-5} , $HC_2H_3O_2$ will not ionize very much, so we expect that the value of x will be small. It should be so small that in the denominator of the fraction, the term $(1.00 - x)$ will likely be very close to 1.00. As such, we would introduce very little error if we simply neglect the x in that term, making it equal to 1.00:

$$(1.00 - x) \approx 1.00 \text{ for small values of } x$$

This simplifies the mathematical expression we need to solve:

$$\frac{(x)(x)}{1.00} = 1.8 \times 10^{-5}$$

This is much easier to solve than a more complete quadratic equation. The new equation to solve becomes

$$x^2 = 1.8 \times 10^{-5}$$

Taking the square root of both sides,

$$x = 4.2 \times 10^{-3}$$

Because x is the equilibrium concentrations of H^+ and $\text{C}_2\text{H}_3\text{O}_2^-$, we thus have

$$[\text{H}^+] = 4.2 \times 10^{-3} \text{ M}$$

Notice that we are justified by neglecting the x in the denominator; it truly is small compared to 1.00. Now we can determine the pH of the solution:

$$\text{pH} = -\log[\text{H}^+] = -\log(4.2 \times 10^{-3}) = 2.38$$

Test Yourself

What is the pH of a 0.500 M solution of HCN? The K_a of HCN is 6.2×10^{-10} .

Answer

4.75

Weak bases also have dissociation constants, labeled K_b (the b subscript stands for base). However, values of K_b are rarely tabulated because there is a simple relationship between the K_b of a base and the K_a of its conjugate acid:

$$K_a \times K_b = 1.0 \times 10^{-14}$$


Thus it is simple to calculate the K_b of a base from the K_a of its conjugate acid.

EXAMPLE 12

What is the value of K_b for $C_2H_3O_2^-$, which can accept a proton and act as a base?

Solution

To determine the K_b for $C_2H_3O_2^-$, we need to know the K_a of its conjugate acid. The conjugate acid of $C_2H_3O_2^-$ is $HC_2H_3O_2$. The K_a for $HC_2H_3O_2$ is in [http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch13_s05_s01_t01](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch13_s05_s01_t01) and is 1.8×10^{-5} . Using the mathematical relationship between K_a and K_b :

$$(1.8 \times 10^{-5})K_b = 1.0 \times 10^{-14}$$

Solving,

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Test Yourself

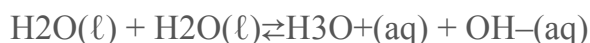
What is the value of K_b for PO_4^{3-} , which can accept a proton and act as a base? The K_a for HPO_4^{2-} is 2.2×10^{-13} .

Answer

$$4.5 \times 10^{-2}$$

Autoionization of Water

In [http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch12](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch12), we introduced the autoionization of water—the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid ([http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch12_s04_t01](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch12_s04_t01)), it must be a weak acid, which means that its behavior as an acid must be described as an equilibrium. That equilibrium is as follows:



The equilibrium constant includes $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ but not $[\text{H}_2\text{O}(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:
 $K = [\text{H}_3\text{O}^+][\text{OH}^-] \equiv K_w = 1.0 \times 10^{-14}$

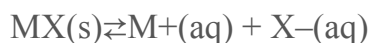
This is the same K_w that was introduced in [http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch12](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch12) and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:
 $K_a \times K_b = K_w$

Insoluble Compounds

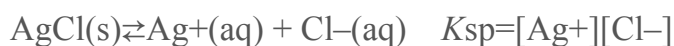
In [http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch04](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch04), [http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch04_s02](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch04_s02), on chemical reactions, the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:





The equilibrium constant for a compound normally considered insoluble is called a solubility product constant and is labeled K_{sp} (with the subscript *sp*, meaning “solubility product”). Because the reactant is a solid, its concentration does not appear in the K_{sp} expression, so like K_{w} , expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:



[http://catalog.flatworldknowledge.com/bookhub/reader/2273 - ball-ch13_s05_s03_t01](http://catalog.flatworldknowledge.com/bookhub/reader/2273-ball-ch13_s05_s03_t01) lists some values of the K_{sp} for slightly soluble ionic compounds.

Table 13.2 Solubility Product Constants for Slightly Soluble Ionic Compounds

Compound	K_{sp}
BaSO ₄	1.1×10^{-10}
Ca(OH) ₂	5.0×10^{-6}
Ca ₃ (PO ₄) ₂	2.1×10^{-33}
Mg(OH) ₂	5.6×10^{-12}
HgI ₂	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag ₂ SO ₄	1.5×10^{-5}

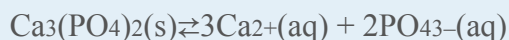
EXAMPLE 13

Write the K_{sp} expression for Ca₃(PO₄)₂.

Solution



Recall that when an ionic compound dissolves, it separates into its individual ions. For $\text{Ca}_3(\text{PO}_4)_2$, the ionization reaction is as follows:



Hence the K_{sp} expression is

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

Test Yourself

Write the K_{sp} expression Ag_2SO_4 .

Answer

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

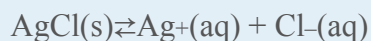
Equilibrium problems involving the K_{sp} can also be done, and they are usually more straightforward than other equilibrium problems because there is no denominator in the K_{sp} expression. Care must be taken, however, in completing the ICE chart and evaluating exponential expressions.

EXAMPLE 14

What are $[\text{Ag}^+]$ and $[\text{Cl}^-]$ in a saturated solution of AgCl ? The K_{sp} of AgCl is 1.8×10^{-10} .

Solution

The chemical equation for the dissolving of AgCl is



The K_{sp} expression is as follows:

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

So the ICE chart for the equilibrium is as follows:

	AgCl(s)	\rightleftharpoons	Ag⁺(aq)	+	Cl⁻(aq)
I			0		0
C	-x		+x		+x
E			+x		+x

Notice that we have little in the column under AgCl except the stoichiometry of the change; we do not need to know its initial or equilibrium concentrations because its concentration does not appear in the K_{sp} expression. Substituting the equilibrium values into the expression:

$$(x)(x) = 1.8 \times 10^{-10}$$

Solving,

$$x^2 = 1.8 \times 10^{-10} \quad x = 1.3 \times 10^{-5}$$

Thus $[\text{Ag}^+]$ and $[\text{Cl}^-]$ are both $1.3 \times 10^{-5} \text{ M}$.

Test Yourself

What are $[\text{Ba}^{2+}]$ and $[\text{SO}_4^{2-}]$ in a saturated solution of BaSO_4 ? The K_{sp} of BaSO_4 is 1.1×10^{-10} .

Answer

$$1.0 \times 10^{-5} \text{ M}$$

EXAMPLE 15

What are $[\text{Ca}^{2+}]$ and $[\text{PO}_4^{3-}]$ in a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$? The K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$ is 2.1×10^{-33} .

Solution

This is similar to Example 14, but the ICE chart is much different because of the number of ions formed.

	$\text{Ca}_3(\text{PO}_4)_2(s)$	\rightleftharpoons	$3\text{Ca}^{2+}(aq)$	+	$2\text{PO}_4^{3-}(aq)$
I			0		0
C	$-x$		$+3x$		$+2x$
E			$+3x$		$+2x$

For every unit of $\text{Ca}_3(\text{PO}_4)_2$ that dissolves, three Ca^{2+} ions and two PO_4^{3-} ions are formed. The expression for the K_{sp} is also different:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = 2.1 \times 10^{-33}$$

Now when we substitute the unknown concentrations into the expression, we get

$$(3x)^3(2x)^2 = 2.1 \times 10^{-33}$$

When we raise each expression inside parentheses to the proper power, remember that the power affects everything inside the parentheses, including the number. So

$$(27x^3)(4x^2) = 2.1 \times 10^{-33}$$

Simplifying,

$$108x^5 = 2.1 \times 10^{-33}$$

Dividing both sides of the equation by 108, we get

$$x^5 = 1.9 \times 10^{-35}$$

Now we take the fifth root of both sides of the equation (be sure you know how to do this on your calculator):

$$x = 1.1 \times 10^{-7}$$

We are not done yet. We still need to determine the concentrations of the ions. According to the ICE chart, $[\text{Ca}^{2+}]$ is $3x$, not x . So

$$[\text{Ca}^{2+}] = 3x = 3 \times 1.1 \times 10^{-7} = 3.3 \times 10^{-7} \text{ M}$$

$[\text{PO}_4^{3-}]$ is $2x$, so

$$[\text{PO}_4^{3-}] = 2x = 2 \times 1.1 \times 10^{-7} = 2.2 \times 10^{-7} \text{ M}$$

Test Yourself

What are $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ in a saturated solution of $\text{Mg}(\text{OH})_2$?

The K_{sp} of $\text{Mg}(\text{OH})_2$ is 5.6×10^{-12} .

Answer

$$[\text{Mg}^{2+}] = 1.1 \times 10^{-4} \text{ M}; [\text{OH}^-] = 2.2 \times 10^{-4} \text{ M}$$

Food and Drink App: Solids in Your Wine Bottle

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine, either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with colored crystals. What are these crystals?



The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine.

Source: Photo courtesy of Paul A.

Hernandez, http://www.flickr.com/photos/paul_a_hernandez/2940862302/.

One of the acids in wine is tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H_2O , dissolving over 130 g of the acid in only 100 g of H_2O . However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H_2O . Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The color of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers don't like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

KEY TAKEAWAY

- Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.

EXERCISES

1. Explain the difference between the K_{eq} and the K_{sp} .
2. Explain the difference between the K_{a} and the K_{b} .
3. Write the balanced chemical equation that represents the equilibrium between $\text{HF}(\text{aq})$ as reactants and $\text{H}^+(\text{aq})$ and $\text{F}^-(\text{aq})$ as products.
4. Write the balanced chemical equation that represents the equilibrium between $\text{CaF}_2(\text{s})$ as reactants and $\text{Ca}^{2+}(\text{aq})$ and $\text{F}^-(\text{aq})$ as products.
5. Assuming that all species are dissolved in solution, write the K_{eq} expression for the chemical equation in Exercise 3.
6. Noting the phase labels, write the K_{sp} expression for the chemical equation in Exercise 4.
7. Determine the concentrations of all species in the ionization of 0.100 M HClO_2 in H_2O . The K_{a} for HClO_2 is 1.1×10^{-2} .
8. Determine the concentrations of all species in the ionization of 0.0800 M HCN in H_2O . The K_{a} for HCN is 6.2×10^{-10} .
9. Determine the pH of a 1.00 M solution of HNO_2 . The K_{a} for HNO_2 is 5.6×10^{-4} .
10. Determine the pH of a 3.35 M solution of $\text{HC}_2\text{H}_3\text{O}_2$. The K_{a} for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} .



11. Write the chemical equations and K_a expressions for the stepwise dissociation of H_3PO_4 .
12. Write the chemical equations and K_a expressions for the stepwise dissociation of $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.
13. If the K_a for HNO_2 is 5.6×10^{-4} , what is the K_b for $\text{NO}_2^-(\text{aq})$?
14. If the K_a for HCN is 6.2×10^{-10} , what is the K_b for $\text{CN}^-(\text{aq})$?
15. What is $[\text{OH}^-]$ in a solution whose $[\text{H}^+]$ is $3.23 \times 10^{-6} \text{ M}$?
16. What is $[\text{OH}^-]$ in a solution whose $[\text{H}^+]$ is $9.44 \times 10^{-11} \text{ M}$?
17. What is $[\text{H}^+]$ in a solution whose $[\text{OH}^-]$ is $2.09 \times 10^{-2} \text{ M}$?
18. What is $[\text{H}^+]$ in a solution whose $[\text{OH}^-]$ is $4.07 \times 10^{-7} \text{ M}$?
19. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $\text{Mg}(\text{OH})_2(\text{s})$.
20. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $\text{Fe}_2(\text{SO}_4)_3(\text{s})$.
21. What are $[\text{Sr}^{2+}]$ and $[\text{SO}_4^{2-}]$ in a saturated solution of $\text{SrSO}_4(\text{s})$? The K_{sp} of $\text{SrSO}_4(\text{s})$ is 3.8×10^{-4} .
22. What are $[\text{Ba}^{2+}]$ and $[\text{F}^-]$ in a saturated solution of $\text{BaF}_2(\text{s})$? The K_{sp} of $\text{BaF}_2(\text{s})$ is 1.8×10^{-7} .



23. What are $[\text{Ca}^{2+}]$ and $[\text{OH}^-]$ in a saturated solution of $\text{Ca}(\text{OH})_2(\text{s})$? The K_{sp} of $\text{Ca}(\text{OH})_2(\text{s})$ is 5.0×10^{-6} .

24. What are $[\text{Pb}^{2+}]$ and $[\text{I}^-]$ in a saturated solution of PbI_2 ? The K_{sp} for PbI_2 is 9.8×10^{-9} .

ANSWERS

1. The K_{sp} is a special type of the K_{eq} and applies to compounds that are only slightly soluble.

3. $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$

5. $K_{\text{eq}} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$

7. $[\text{HClO}_2] = 0.0719 \text{ M}$; $[\text{H}^+] = [\text{ClO}_2^-] = 0.0281 \text{ M}$

9. 1.63

11. $\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}); K_{\text{a}} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$

$\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}); K_{\text{a}} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$

$\text{HPO}_4^{2-}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}); K_{\text{a}} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$

13. 1.8×10^{-11}

15. $3.10 \times 10^{-9} \text{ M}$

$$17.4.78 \times 10^{-13} \text{ M}$$



$$21. [\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 1.9 \times 10^{-2} \text{ M}$$

$$23. [\text{Ca}^{2+}] = 0.011 \text{ M}; [\text{OH}^{-}] = 0.022 \text{ M}$$

