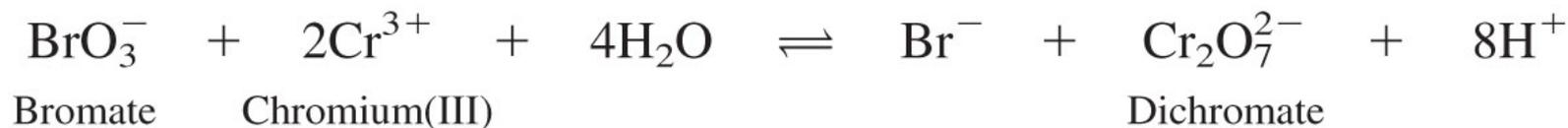


- Verify this behavior algebraically using the reaction quotient, Q

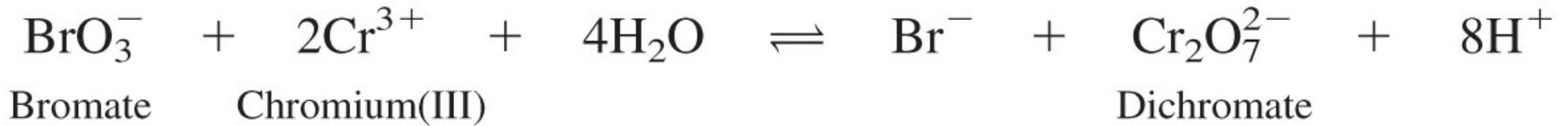


- In one particular equilibrium state of this system,
 → the following concentrations exist:

$$[\text{H}^+] = 5.0 \text{ M} \quad [\text{Cr}_2\text{O}_7^{2-}] = 0.10 \text{ M} \quad [\text{Cr}^{3+}] = 0.0030 \text{ M}$$

$$[\text{Br}^-] = 1.0 \text{ M} \quad [\text{BrO}_3^-] = 0.043 \text{ M}$$

$$K = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} = 1 \times 10^{11} \text{ at } 25^\circ\text{C}$$



$$K = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} = 1 \times 10^{11} \text{ at } 25^\circ\text{C}$$

- Suppose that the equilibrium is disturbed by adding dichromate to the solution to increase the concentration of $[\text{Cr}_2\text{O}_7^{2-}]$ from 0.10 to 0.20 M.
 → In what direction will the reaction proceed to reach equilibrium?

$$Q = \frac{(1.0)(0.20)(5.0)^8}{(0.043)(0.0030)^2} = 2 \times 10^{11} > K$$

- Because $Q > K$
 → the reaction must go to the left to decrease the numerator and increase the denominator, until $Q = K$



- If a reaction is at equilibrium and products are added (or reactants are removed),
→ the reaction goes to the left.
- If a reaction is at equilibrium and reactants are added (or products are removed),
→ the reaction goes to the right

- **The effect of temperature on K:**

$$\begin{aligned} K &= e^{-\Delta G^\circ/RT} = e^{-(\Delta H^\circ - T\Delta S^\circ)/RT} = e^{(-\Delta H^\circ/RT + \Delta S^\circ/R)} \\ &= e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R} \end{aligned}$$

- The term $e^{\Delta S^\circ/R}$ is independent of T
 - ΔS is constant at least over a limited temperature range
- If ΔH° is positive,
 - The term $e^{-\Delta H^\circ/RT}$ increases with increasing temperature
- If ΔH° is negative,
 - The term $e^{-\Delta H^\circ/RT}$ decreases with increasing temperature

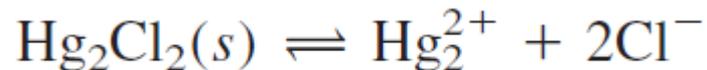
- **The effect of temperature on K:**

$$\begin{aligned} K &= e^{-\Delta G^\circ/RT} = e^{-(\Delta H^\circ - T\Delta S^\circ)/RT} = e^{(-\Delta H^\circ/RT + \Delta S^\circ/R)} \\ &= e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R} \end{aligned}$$

- If the temperature is raised,
 - The equilibrium constant of an endothermic reaction ($\Delta H^\circ > 0$) increases
 - The equilibrium constant of an exothermic reaction ($\Delta H^\circ < 0$) decreases
- If the temperature is raised,
 - an endothermic reaction is favored
- If the temperature is raised, then heat is added to the system.
 - The reaction proceeds to partially offset this heat
 - an endothermic reaction
 - Le Châtelier's principle

Solubility product

- The equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution.
→ Solid is omitted from the equilibrium constant because it is in its standard state.
- Consider the dissolution of mercury(I) chloride (Hg_2Cl_2 , also called mercurous chloride) in water.
→ The reaction is



→ for which the solubility product, K_{sp} , is

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 1.2 \times 10^{-18}$$

- The physical meaning of the solubility product is:
- If an aqueous solution is left in contact with excess solid Hg_2Cl_2 ,
→ the solid will dissolve until the condition $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$ is satisfied.
- Thereafter, the amount of undissolved solid remains constant.
- If Hg_2^{2+} and Cl^- are mixed together (with appropriate counterions) such that the product $[\text{Hg}_2^{2+}][\text{Cl}^-]^2$ exceeds K_{sp} ,
→ then Hg_2Cl_2 will precipitate

See Appendix F

- We most commonly use the solubility product to find the concentration of one ion when the concentration of the other is known or fixed by some means.

For example,

- What is the concentration of Hg_2^{2+} in equilibrium with 0.10 M Cl^- in a solution of KCl containing excess, undissolved $\text{Hg}_2\text{Cl}_2(\text{s})$?

→ To answer this question,

$$[\text{Hg}_2^{2+}] = \frac{K_{\text{sp}}}{[\text{Cl}^-]^2} = \frac{1.2 \times 10^{-18}}{0.10^2} = 1.2 \times 10^{-16} \text{ M}$$

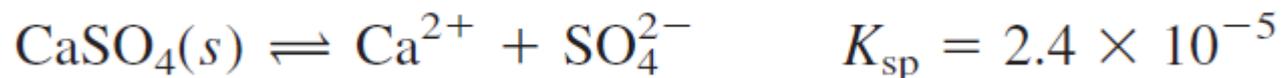
- Because Hg_2Cl_2 is so slightly soluble,
→ additional Cl^- obtained from Hg_2Cl_2 is negligible compared with 0.10 M Cl^- .

- Most salts form soluble **ion pairs** to some extent.
 - That is, MX(s) can give MX(aq) as well as $\text{M}^+(\text{aq})$ and $\text{X}^-(\text{aq})$.
 - MX(aq) : ion pair
 - the ion pair is a closely associated pair of ions that behaves as one species in solution

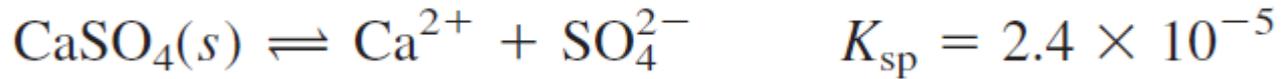
- In a saturated solution of CaSO_4 ,
 - two-thirds of the dissolved calcium is Ca^{2+}
 - one third is $\text{CaSO}_4(\text{aq})$.

Common Ion Effect

- For the ionic solubility reaction



- In the presence of excess solid CaSO_4 ,
 - the product $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ is constant at equilibrium
- If the concentration of $[\text{Ca}^{2+}]$ were increased by adding another source of Ca^{2+} , such as CaCl_2 ,
 - then the concentration of $[\text{SO}_4^{2-}]$ must decrease so that the product remains constant.
 - In other words, less $\text{CaSO}_4(s)$ will dissolve if $[\text{Ca}^{2+}]$ or $[\text{SO}_4^{2-}]$ is already present from some other source.



- Figure 6-1 shows how the solubility of CaSO_4 decreases in the presence of dissolved CaCl_2 .
- Le Châtelier's principle
 - A salt will be less soluble if one of its constituent ions is already present in the solution.
 - called the **common ion effect**.

See Fig 6-1

- **PbI₂(s) in 0.030 M NaI (complete dissociate to Na⁺ & I⁻), [Pb²⁺]?**

| | PbI ₂ (s) | ⇌ | Pb ²⁺ | + 2I ⁻ |
|--------------|----------------------|---|------------------|-------------------|
| initial conc | solid | | 0 | 0.030 |
| final conc | solid | | x | 2x+0.030 |

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 7.9 \times 10^{-9}$$

i) Without NaI

$$[\text{Pb}^{2+}][\text{I}^{-}]^2 = (x) \cdot (2x)^2 = 7.9 \times 10^{-9}$$

$$x = [\text{Pb}^{2+}] = \underline{1.3 \times 10^{-3} \text{ M}}$$

ii) With NaI

$$[\text{Pb}^{2+}][\text{I}^{-}]^2 = (x) \cdot (2x+0.030)^2 = 7.9 \times 10^{-9}$$

$$\text{expect } 2x \ll 0.030 \rightarrow (x) \cdot (0.030)^2 = 7.9 \times 10^{-9}$$

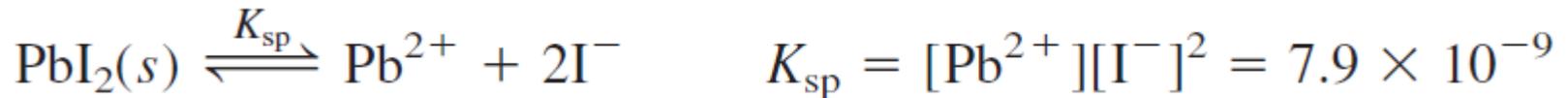
$$x = [\text{Pb}^{2+}] = \underline{8.8 \times 10^{-6} \text{ M}}$$

Complex formation

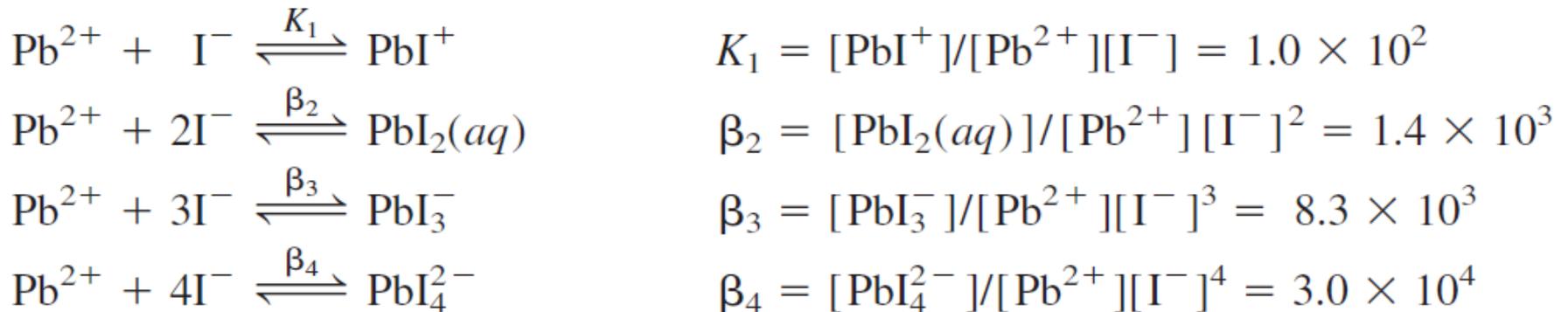
- If anion X^- precipitates metal M^+ ,
→ it is often observed that a high concentration of X^- causes solid MX to redissolve.
- The increased solubility arises from formation of complex ions, such as MX_2^- , which consist of two or more simple ions bonded to one another.

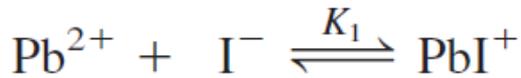
Effect of Complex Ion Formation on Solubility

- If Pb^{2+} and I^- only reacted to form solid PbI_2 ,
→ then the solubility of Pb^{2+} would always be very low in the presence of excess I^-

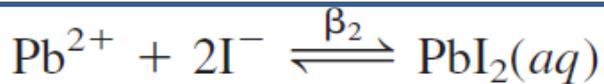


- However, we observe that high concentrations of I^- cause solid PbI_2 to dissolve.
→ We explain this by the formation of a series of complex ions:

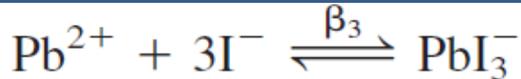




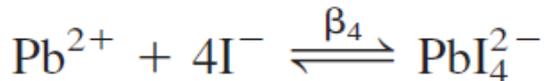
$$K_1 = [\text{PbI}^{+}]/[\text{Pb}^{2+}][\text{I}^{-}] = 1.0 \times 10^2$$



$$\beta_2 = [\text{PbI}_2(aq)]/[\text{Pb}^{2+}][\text{I}^{-}]^2 = 1.4 \times 10^3$$



$$\beta_3 = [\text{PbI}_3^{-}]/[\text{Pb}^{2+}][\text{I}^{-}]^3 = 8.3 \times 10^3$$

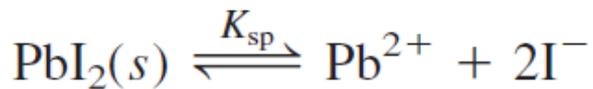


$$\beta_4 = [\text{PbI}_4^{2-}]/[\text{Pb}^{2+}][\text{I}^{-}]^4 = 3.0 \times 10^4$$

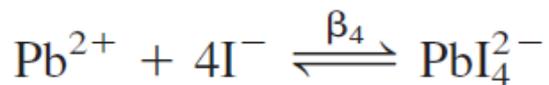
- The species $\text{PbI}_2(aq)$ is dissolved PbI_2 , containing two iodine atoms bound to a lead atom.
- At low I^{-} concentrations,
→ the solubility of lead is governed by precipitation of $\text{PbI}_2(s)$.
- At high I^{-} concentrations,
→ the above reactions are driven to the right (Le Chatelier's principle)
→ the total concentration of dissolved lead is considerably greater than that of Pb^{2+} alone

See Fig 6-3

- As $[I^-]$ increases,
→ $[Pb]_{\text{total}}$ decreases because of the common ion effect.
- At high values of $[I^-]$,
→ $PbI_2(s)$ redissolves because it reacts with I^- to form soluble complex ions, such as PbI_4^{2-} .



$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.9 \times 10^{-9}$$



$$\beta_4 = [PbI_4^{2-}]/[Pb^{2+}][I^-]^4 = 3.0 \times 10^4$$

- A most useful characteristic of chemical equilibrium is that all equilibria are satisfied simultaneously.
- If we know $[I^-]$,
 - we can calculate $[Pb^{2+}]$ by substituting the value of $[I^-]$ into the equilibrium constant expression for the reaction below, regardless of whether there are other reactions involving Pb^{2+}
- The concentration of Pb^{2+} that satisfies any one equilibrium must satisfy all equilibria.
 - There can be only one concentration of Pb^{2+} in the solution

EXAMPLE Effect of I^- on the Solubility of Pb^{2+}

Find the concentrations of PbI^+ , $PbI_2(aq)$, PbI_3^- , and PbI_4^{2-} in a solution saturated with $PbI_2(s)$ and containing dissolved I^- with a concentration of (a) 0.001 0 M and (b) 1.0 M.

Solution (a) From K_{sp} for Reaction 6-12, we calculate

$$[Pb^{2+}] = K_{sp}/[I^-]^2 = (7.9 \times 10^{-9})/(0.001\ 0)^2 = 7.9 \times 10^{-3}\ M$$

From Reactions 6-13 through 6-16, we then calculate the concentrations of the other Pb[II] species:

$$\begin{aligned} [PbI^+] &= K_1[Pb^{2+}][I^-] = (1.0 \times 10^2)(7.9 \times 10^{-3})(1.0 \times 10^{-3}) \\ &= 7.9 \times 10^{-4}\ M \end{aligned}$$

$$[PbI_2(aq)] = \beta_2[Pb^{2+}][I^-]^2 = 1.1 \times 10^{-5}\ M$$

$$[PbI_3^-] = \beta_3[Pb^{2+}][I^-]^3 = 6.6 \times 10^{-8}\ M$$

$$[PbI_4^{2-}] = \beta_4[Pb^{2+}][I^-]^4 = 2.4 \times 10^{-10}\ M$$

(b) If, instead, we take $[I^-] = 1.0\ M$, then analogous computations show that

$$[Pb^{2+}] = 7.9 \times 10^{-9}\ M \quad [PbI_3^-] = 6.6 \times 10^{-5}\ M$$

$$[PbI^+] = 7.9 \times 10^{-7}\ M \quad [PbI_4^{2-}] = 2.4 \times 10^{-4}\ M$$

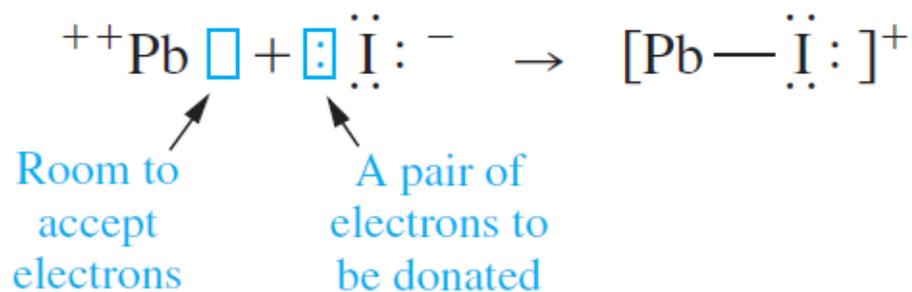
$$[PbI_2(aq)] = 1.1 \times 10^{-5}\ M$$

TEST YOURSELF Find $[Pb^{2+}]$, $PbI_2(aq)$, and $[PbI_3^-]$, in a saturated solution of $PbI_2(s)$ with $[I^-] = 0.10\ M$. (Answer: 7.9×10^{-7} , 1.1×10^{-5} , $6.6 \times 10^{-6}\ M$)

Lewis Acids and Bases

- In complex ions such as PbI^+ , PbI_3^- , and PbI_4^{2-} ,
→ iodide is said to be the **ligand** of Pb^{2+} .
- A ligand is any atom or group of atoms attached to the species of interest.
- Pb^{2+} acts as a Lewis acid and I^- acts as a Lewis base in these complexes.
→ A Lewis acid accepts a pair of electrons from a Lewis base when the two

form a bond:



→ The product of the reaction between a Lewis acid and a Lewis base is called an **adduct**.

→ The bond between a Lewis acid and a Lewis base is called a **coordinate covalent bond**.

Protic Acids and Bases

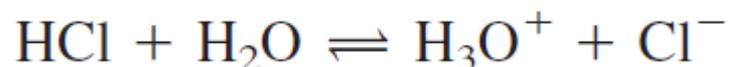
- The word protic refers to chemistry involving transfer of H^+ from one molecule to another.

Arrhenius acids

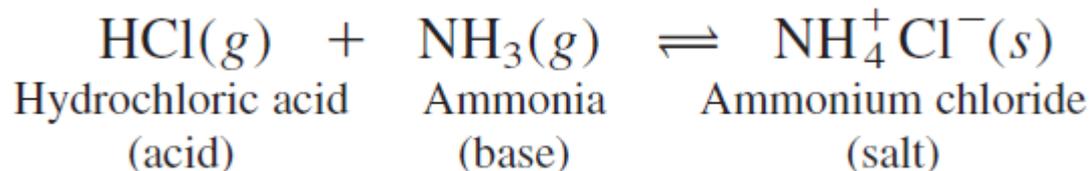
- In aqueous chemistry, an acid is a substance that increases the concentration of H_3O^+ (hydronium ion) when added to water.
- Conversely, a base decreases the concentration of H_3O^+ .
 - a decrease in H_3O^+ concentration necessarily requires an increase in OH^- concentration.
 - Therefore, a base increases the concentration of OH^- in aqueous solution.

Brønsted-Lowry Acids and Bases

- Brønsted and Lowry classified
 - acids as proton donors
 - bases as proton acceptors.
- HCl is an acid (a proton donor), and it increases the concentration of H_3O^+ in water:



- The Brønsted-Lowry definition does not require that H_3O^+ be formed.
 - This definition can therefore be extended to nonaqueous solvents and to the gas phase:



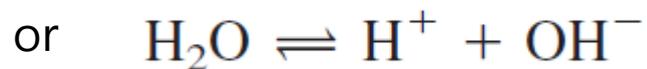
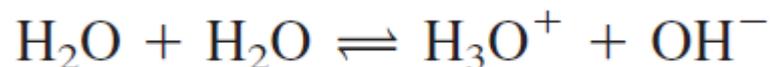
Salts

- Any ionic solid, such as ammonium chloride, is called a salt.
- In a formal sense, a salt can be thought of as the product of an acid-base reaction.
 - When an acid and a base react, they are said to neutralize each other.
- Most salts containing cations and anions with single positive and negative charges are strong electrolytes
 - they dissociate nearly completely into ions in dilute aqueous solution.

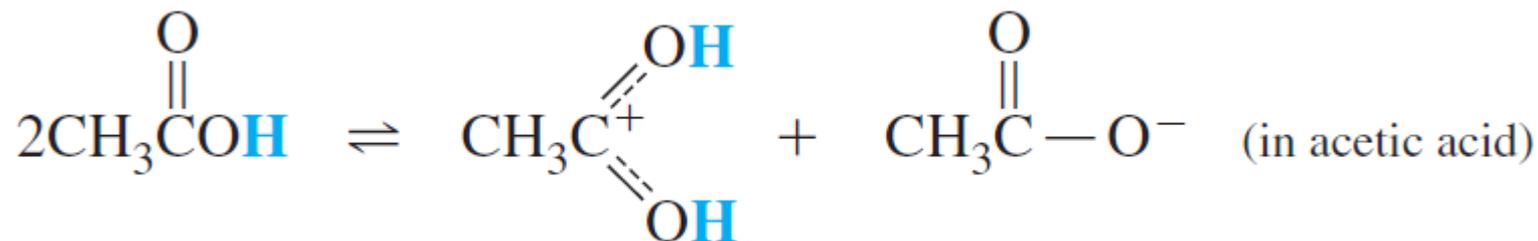


Autoprotolysis

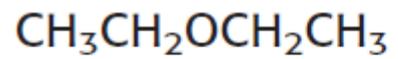
- Water undergoes self-ionization, called autoprotolysis,
→ it acts as both an acid and a base:



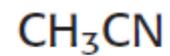
- Protic solvents** have a reactive H^+
→ all protic solvents undergo autoprotolysis.
→ An example is acetic acid:



- Examples of **aprotic solvents** (no acidic protons):



Diethyl ether



Acetonitrile

pH

- The autoprotolysis constant for H₂O has the special symbol K_w , where “w” stands for water:

*Autoprotolysis
of water:*



→ H₂O (the solvent) is omitted from the equilibrium constant

EXAMPLE Concentration of OH⁻ When [H⁺] Is Known

What is the concentration of OH⁻ if [H⁺] = 1.0 × 10⁻³ M? (From now on, assume that the temperature is 25°C unless otherwise stated.)

Solution Putting [H⁺] = 1.0 × 10⁻³ M into the K_w expression gives

$$K_w = 1.0 \times 10^{-14} = (1.0 \times 10^{-3})[\text{OH}^-] \Rightarrow [\text{OH}^-] = 1.0 \times 10^{-11} \text{ M}$$

A concentration of [H⁺] = 1.0 × 10⁻³ M gives [OH⁻] = 1.0 × 10⁻¹¹ M. *As the concentration of H⁺ increases, the concentration of OH⁻ necessarily decreases, and vice versa.* A concentration of [OH⁻] = 1.0 × 10⁻³ M gives [H⁺] = 1.0 × 10⁻¹¹ M.

TEST YOURSELF Find [OH⁻] if [H⁺] = 1.0 × 10⁻⁴ M. (*Answer:* 1.0 × 10⁻¹⁰ M)

- An approximate definition of pH is the negative logarithm of the H^+ concentration.

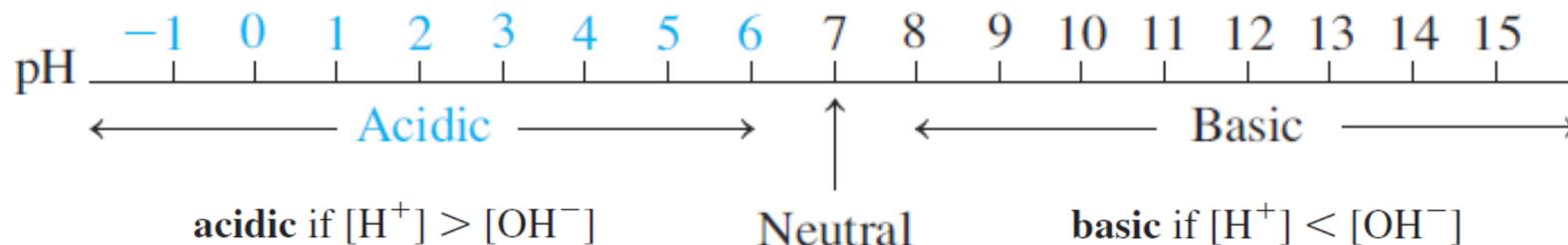
Approximate definition of pH: $pH \approx -\log[H^+]$

$$pH + pOH = -\log(K_w) = 14.00 \text{ at } 25^\circ\text{C}$$

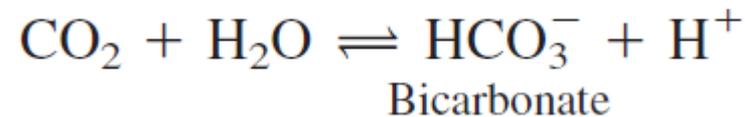
$$pOH = -\log[OH^-]$$

→ if $pH = 3.58$, then $pOH = 14.00 - 3.58 = 10.42$,

→ $[OH^-] = 10^{-10.42} = 3.8 \times 10^{-11} \text{ M}$.

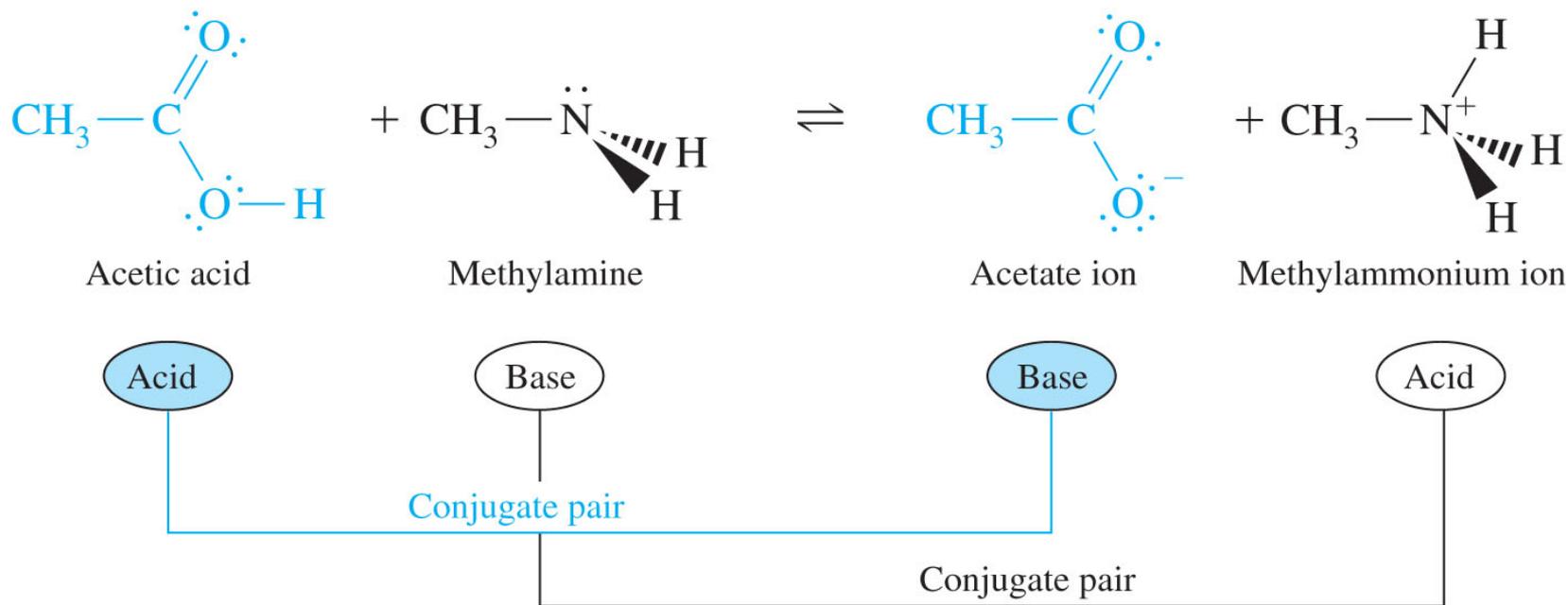


- Pure water at 25°C should have a pH of 7.00.
- Distilled water from the tap in most labs is acidic
 - because it contains CO₂ from the atmosphere.
 - CO₂ is an acid by virtue of the reaction

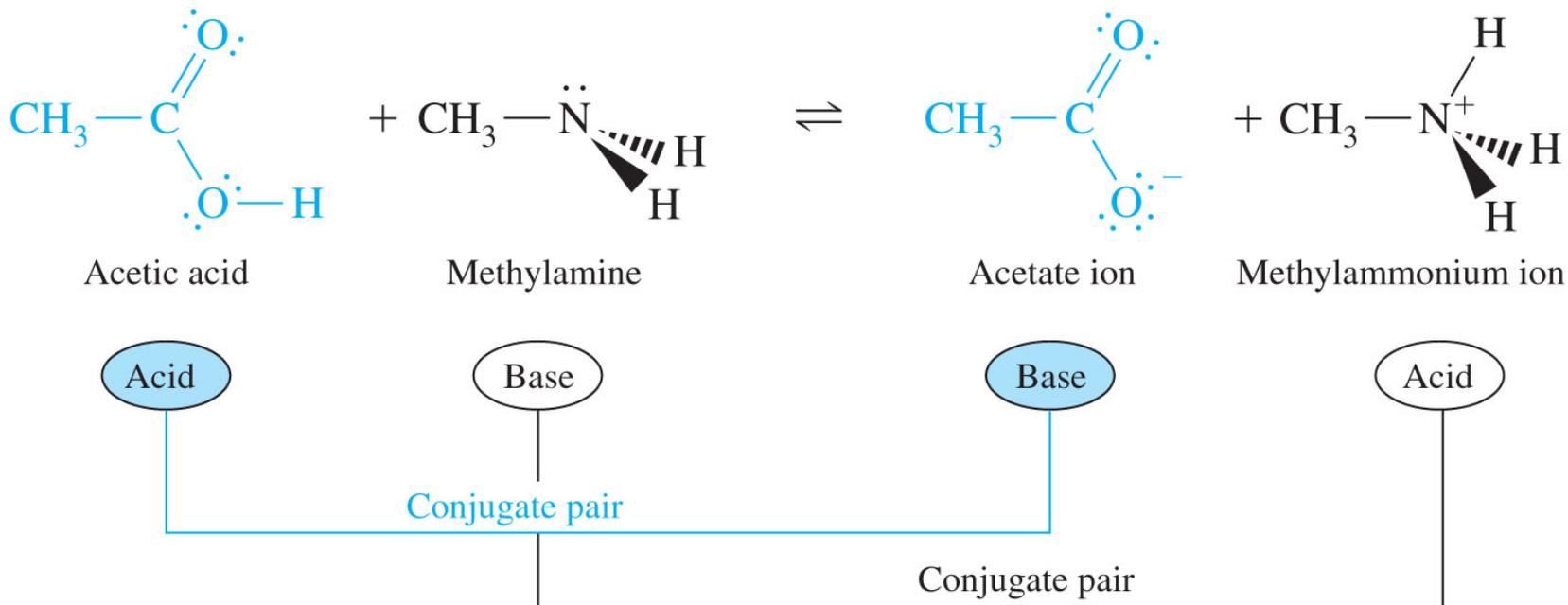


Conjugate Acids and Bases

- The products of a reaction between an acid and a base are also classified as acids and bases



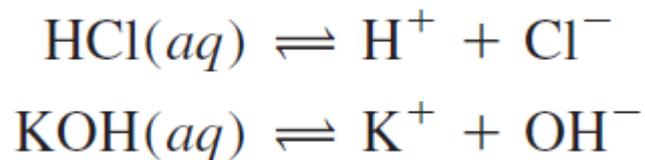
- Acetate is a **base** because it can accept a proton to make acetic acid.
- Methylammonium ion is an **acid** because it can donate a proton and become methylamine.



- Acetic acid and the acetate ion are said to be **a conjugate acid-base pair**.
- Methylamine and methylammonium ion are likewise conjugate.
 - Conjugate acids and bases are **related to each other by the gain or loss of one H⁺**

Strengths of Acids and Bases

- Acids and bases are commonly classified as **strong** or **weak**, depending on whether they react nearly “completely” or only “partially” to produce H^+ or OH^- .
- Although there is no sharp distinction between weak and strong,
 - a strong acid or base is completely dissociated in aqueous solution.
 - that is, the equilibrium constants for the strong acids and bases are large

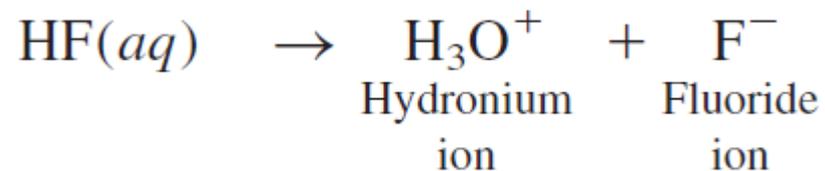


- by convention, everything else is termed weak.

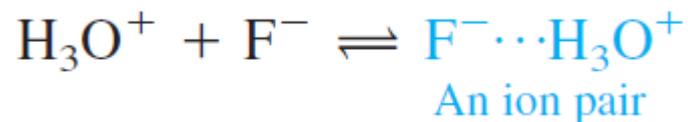
Strong Acids and Bases

- Common strong acids and bases are listed in Table 6-2
 - Even though the hydrogen halides HCl, HBr, and HI are strong acids,
→ HF is not a strong acid
 - HF does completely give up its proton to H₂O:

See Table 6-2



- Fluoride forms the strongest hydrogen bond of any ion.
- The hydronium ion remains tightly associated with F through a hydrogen bond.
→ We call such an association an ion pair.



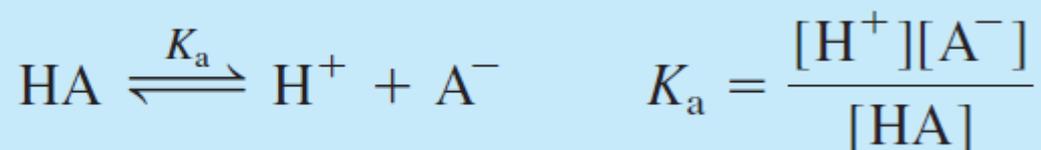
- HF does not behave as a strong acid
→ because F⁻ and H₃O⁺ remain associated with each other.
- Dissolving one mole of the strong acid HCl in water creates one mole of free H₃O⁺.
→ Dissolving one mole of the “weak” acid HF in water creates little free H₃O⁺.

Weak Acids and Bases

- All weak acids, denoted HA, react with water by donating a proton to H₂O:



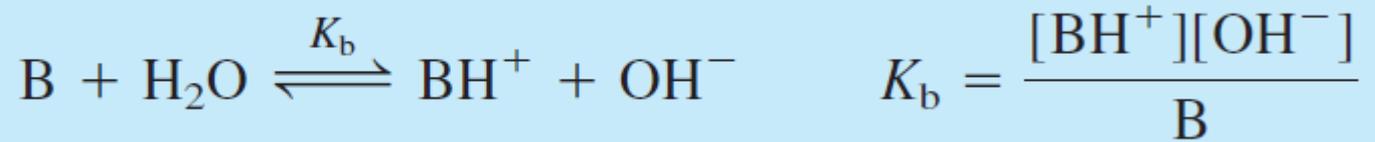
*Dissociation of
weak acid:*



- The equilibrium constant is called K_a , the acid dissociation constant.
- By definition, a weak acid is one that is only **partially dissociated** in water,
→ so K_a is "small".

- Weak bases, B, react with water by abstracting a proton from H₂O:

*Base
hydrolysis:*



- The equilibrium constant K_b is the base hydrolysis constant,
→ which is “small” for a weak base.