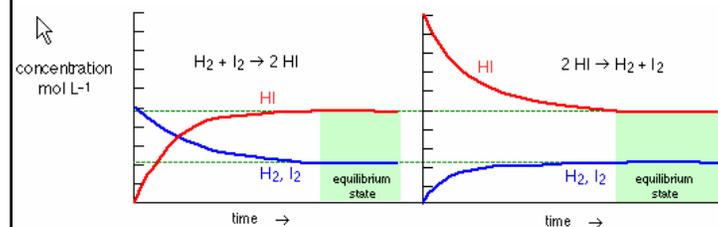


Daniel C. Harris
**Quantitative Chemical
 Analysis**
 Seventh Edition

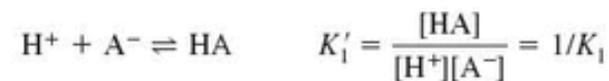
Chapter 6
 Chemical Equilibrium

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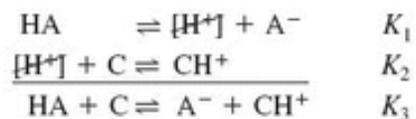


$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

REVERSE REACTION
 → reciprocal K



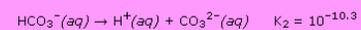
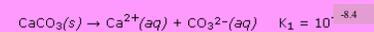
ADD REACTIONS
→ Multiply Ks



$$K_3 = K_1 K_2 = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{CH}^+]}{[\text{H}^+][\text{C}]} = \frac{[\text{A}^-][\text{CH}^+]}{[\text{HA}][\text{C}]}$$

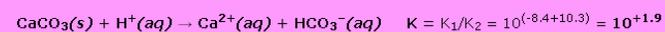
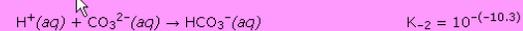
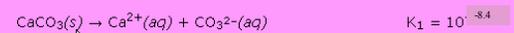
ADD REACTIONS
→ Multiply Ks

Given the following equilibrium constants:

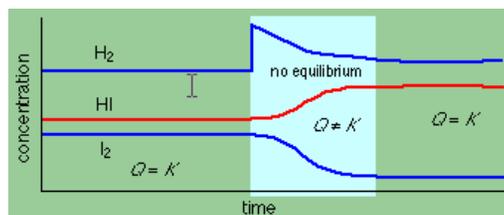
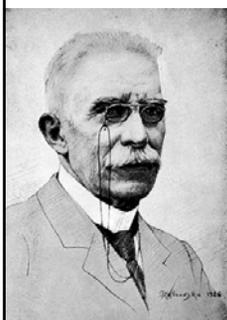


Calculate the value of K for the reaction $\text{CaCO}_3(s) + \text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq)$

Solution: The net reaction is the sum of reaction 1 and the reverse of reaction 2:



LE CHATELIER'S PRINCIPLE



LE CHATELIER'S PRINCIPLE

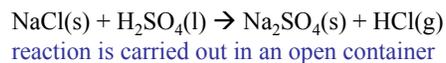


Shift to the right.
Continuous removal of a product will force any reaction to the right

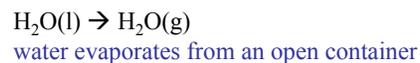


No change; N_2 is not a component of this reaction system.

LE CHATELIER'S PRINCIPLE

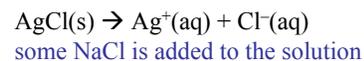


Because HCl is a gas that can escape from the system, the reaction is forced to the right.
This is the basis for the commercial production of hydrochloric acid.

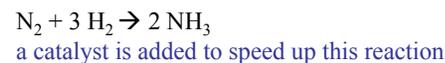


Continuous removal of water vapor forces the reaction to the right, so equilibrium is never achieved

LE CHATELIER'S PRINCIPLE

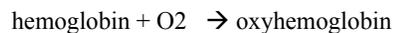


Shift to left due to increase in Cl⁻ concentration.
This is known as the common ion effect on solubility.

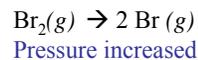


No change.
Catalysts affect only the rate of a reaction;
they have no effect at all on the composition of the equilibrium state

LE CHATELIER'S PRINCIPLE



Take up in lungs at high O₂ pressure
Release in cells at low O₂ concentration



shift to left
To reduce number of molecules or atoms

REACTION QUOTIENT, Q

K is thus the special value that *Q* has when the reaction is at equilibrium

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

REACTION QUOTIENT, Q

K is thus the special value that Q has when the reaction is at equilibrium

Q/K	
> 1	Product concentration too high for equilibrium; net reaction proceeds to left.
= 1	System is at equilibrium; no net change will occur.
< 1	Product concentration too low for equilibrium; net reaction proceeds to right.

REACTION QUOTIENT, Q

Problem Example 3

Phosgene (COCl_2) is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant $K_p = 0.0041$ at 600°K . Find the equilibrium composition of the system after 0.124 atm of COCl_2 is allowed to reach equilibrium at this temperature.

Solution: Start by drawing up a table showing the relationships between the components:

	$\text{COCl}_2 \rightarrow$	CO	Cl_2
initial pressures:	0.124 atm	0	0
change:	$-x$	$+x$	$+x$
equilibrium pressures:	$0.124 - x$	x	x

Substitution of the equilibrium pressures into the equilibrium expression gives

$$\frac{x^2}{0.124 - x} = 0.0041$$

THERMODYNAMICS and equilibrium

$$\Delta G = \Delta H - T\Delta S$$

$$K = e^{-\Delta G^\circ/RT}$$

THERMODYNAMICS and equilibrium

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

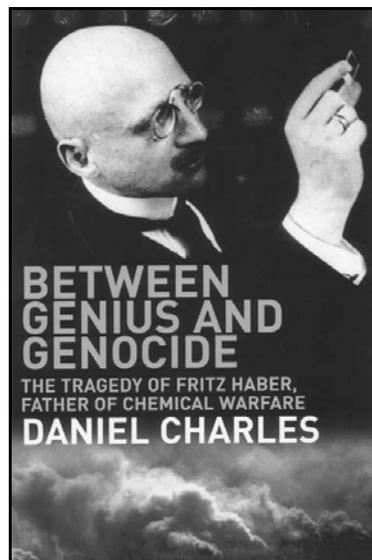
1. The equilibrium constant of an endothermic reaction

$(\Delta H^\circ = +)$ **increases** if the temperature is raised.

2. The equilibrium constant of an exothermic reaction

$(\Delta H^\circ = -)$ **decreases** if the temperature is raised.

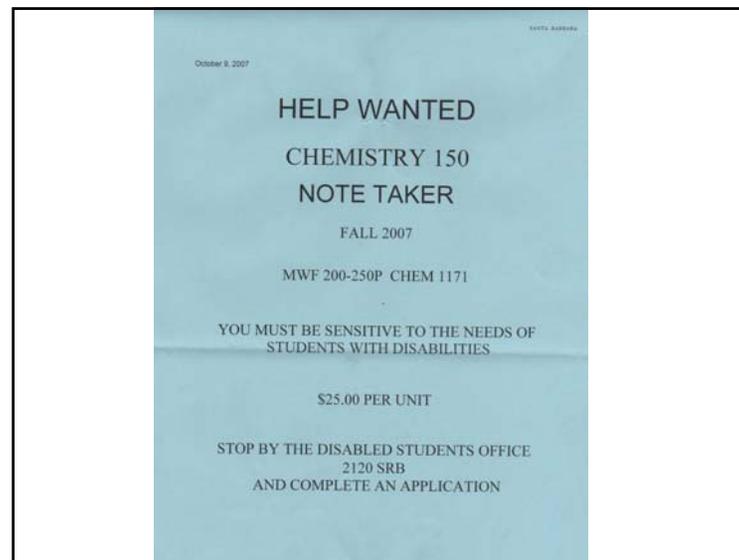
NB: understand this from *Le Chatelier's principle*!



HABER-BOSCH:



$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



K IS DIMENSIONLESS!

- Concentrations in mol/liter (M)
- pressures in atmospheres (atm)
- ignore solids
- ignore solvents

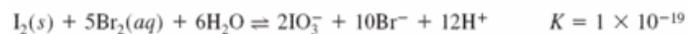
Equilibrium calculation EXAMPLE



0.001 mol Br_2
 0.005 mol IO_3^-
 0.02 mol Br^-
 1.00 mol H^+
 Solid I_2

What will be the concentrations at equilibrium?

Equilibrium calculation EXAMPLE



0.001 mol Br₂
 0.005 mol IO₃⁻
 0.02 mol Br⁻
 1.00 mol H⁺
 Solid I₂

First calculate Q to know the direction

$$Q = \frac{[\text{IO}_3^-]^2 [\text{Br}^-]^{10} [\text{H}^+]^{12}}{[\text{Br}_2(aq)]^5} = \frac{[0.005 \text{ } 0]^2 [0.020]^{10} [1.00]^{12}}{[0.001 \text{ } 0]^5} = 2.5_6 \times 10^{-7} > K$$

So which way does it go?

Equilibrium calculation EXAMPLE



0.001 mol Br₂
 0.005 mol IO₃⁻
 0.02 mol Br⁻
 1.00 mol H⁺
 Solid I₂

Make an ICE table

Solve for x

	I ₂ (s)	+	5Br ₂ (aq)	+	6H ₂ O	⇌	2IO ₃ ⁻	+	10Br ⁻	+	12H ⁺
Initial concentration	excess		0.001	0			0.005	0	0.020		1.00
Final concentration	excess		0.001	0 + 2.5x			0.005	0 - x	0.020 - 5x		1.00 - 6x

$$K = \frac{[\text{IO}_3^-]^2 [\text{Br}^-]^{10} [\text{H}^+]^{12}}{[\text{Br}_2(aq)]^5} = \frac{[0.005 \text{ } 0 - x]^{12} [0.020 - 5x]^{10} [1.00 - 6x]^{12}}{[0.001 \text{ } 0 + 2.5x]^5} = 1 \times 10^{-19}$$

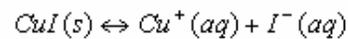
SOLUBILITY PRODUCT K_{sp}

K_{sp} = equilibrium constant of a reaction that forms a precipitate



Figure 6-2
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SOLUBILITY PRODUCT K_{sp}



I	-----	0	0
C	-----	+S	+S
E	-----	S	S

$$K_{sp} = 5.1 \times 10^{-12} = [\text{Cu}^+][\text{I}^-]$$

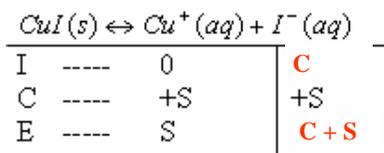
$$5.1 \times 10^{-12} = (S)(S)$$

$$5.1 \times 10^{-12} = S^2$$

$$2.3 \times 10^{-6} = S$$

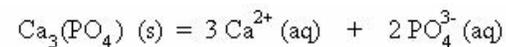
SOLUBILITY PRODUCT K_{sp}

COMMON ION EFFECT



$$K_{sp} = 5.1 \times 10^{-12} = [Cu^+][I^-]$$

SOLUBILITY PRODUCT K_{sp}



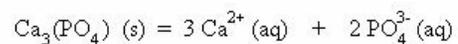
Initial	0	0
Change	3x	2x
Equilibrium	3x	2x

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.0 \times 10^{-26}$$

$$= (3x)^3 (2x)^2 = 1.0 \times 10^{-26}$$

SOLUBILITY PRODUCT K_{sp}

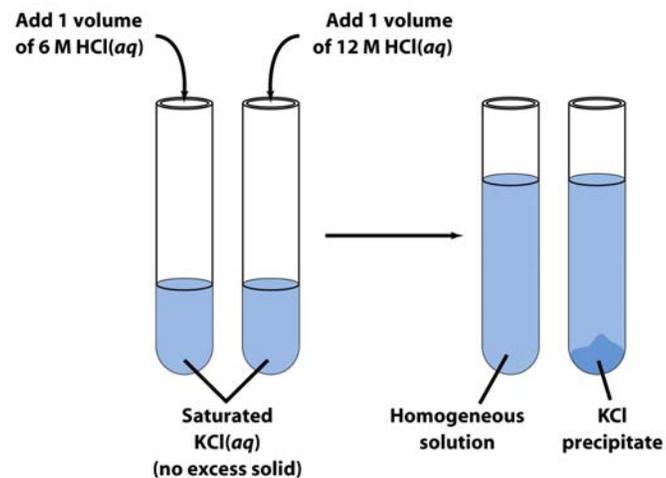
COMMON ION EFFECT



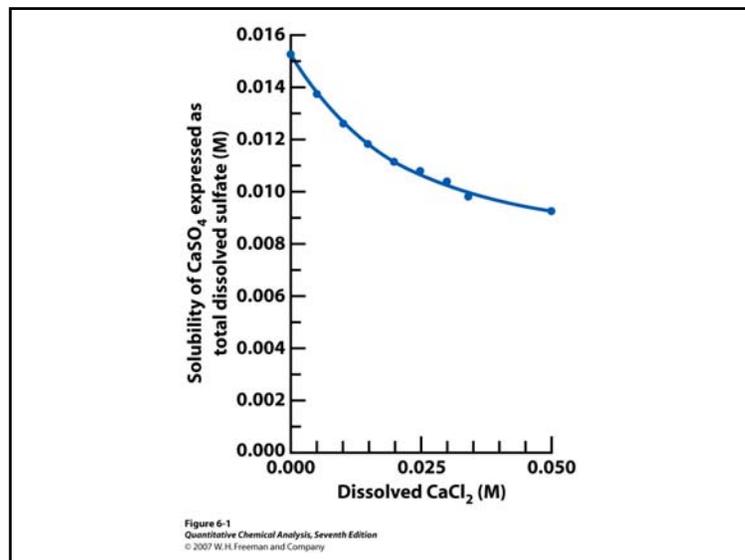
Initial	0	0.10 M
Change	3x	2x
Equilibrium	3x	0.10 M + 2x

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.0 \times 10^{-26}$$

$$= (3x)^3 (0.10 + 2x)^2 = 1.0 \times 10^{-26}$$



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SOLUBILITY PRODUCT K_{sp}
SEPARATION BY PRECIPITATION

Which will form a precipitate first?
Higher or lower K_{sp} ?

$$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^- \quad K_{sp} = 7.9 \times 10^{-9}$$

$$\text{Hg}_2\text{I}_2(s) \rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^- \quad K_{sp} = 4.6 \times 10^{-29}$$

SOLUBILITY PRODUCT K_{sp}
SEPARATION BY PRECIPITATION

Starting with 0.01 M of each, can you precipitate 99.99% of Hg_2^{2+} without losing any Pb^{2+} ?

$$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^- \quad K_{sp} = 7.9 \times 10^{-9}$$

$$\text{Hg}_2\text{I}_2(s) \rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^- \quad K_{sp} = 4.6 \times 10^{-29}$$

SOLUBILITY PRODUCT K_{sp}
SEPARATION BY PRECIPITATION

When (BrO_3^-) is added to a solution containing equal concentrations of Ag^+ and Pb^{2+} , which will precipitate first and why?

$$K_{sp} = 5.49 \times 10^{-5} \text{ for } \text{AgBrO}_3$$

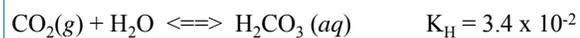
$$K_{sp} = 3.23 \times 10^{-5} \text{ for } \text{Pb}(\text{BrO}_3)_2$$

Stoichiometry!

Gas – solution equilibrium K_H

Henry's Law

CO_2 dissolves in water:



at a CO_2 pressure of 3×10^{-4} atmospheres,
what is the concentration of the carbonic acid in the water?

10^{-5} M

WATER EQUILIBRIUM K_w

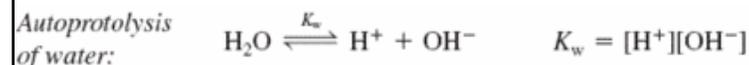


Table 6-1 Temperature dependence of K_w^a

Temperature (°C)	K_w	$\text{p}K_w = -\log K_w$	Temperature (°C)	K_w	$\text{p}K_w = -\log K_w$
0	1.15×10^{-15}	14.938	40	2.88×10^{-14}	13.541
5	1.88×10^{-15}	14.726	45	3.94×10^{-14}	13.405
10	2.97×10^{-15}	14.527	50	5.31×10^{-14}	13.275
15	4.57×10^{-15}	14.340	100	5.43×10^{-13}	12.265
20	6.88×10^{-15}	14.163	150	2.30×10^{-12}	11.638
25	1.01×10^{-14}	13.995	200	5.14×10^{-12}	11.289
30	1.46×10^{-14}	13.836	250	6.44×10^{-12}	11.191
35	2.07×10^{-14}	13.685	300	3.93×10^{-12}	11.406

a. Concentrations in the product $[\text{H}^+][\text{OH}^-]$ in this table are expressed in molality rather than in molarity. Accuracy of $\log K_w$ is ± 0.01 . To convert molality (mol/kg) into molarity (mol/L), multiply by the density of H_2O at each temperature. At 25°C, $K_w = 10^{-14.00} \text{ (mol/kg)}^2 / (0.99705 \text{ kg/L})^2 = 10^{-14.00} \text{ (mol/L)}^2$.

SOURCE: W. L. Marshall and E. U. Franck, "Ion Product of Water Substance, 0–1 000°C, 1–10,000 Bars," J. Phys. Chem. Ref. Data 1981, 10, 295.

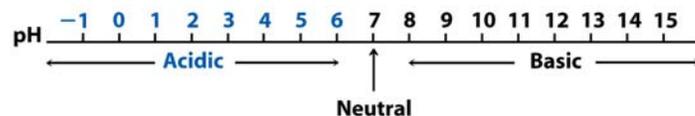
Table 6-1
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WATER EQUILIBRIUM K_w

pH

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

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



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ACIDS & BASES

Svante Arrhenius (1859-1927)



Swedish chemist who explained the electrical conductivity of ionic solutions by presuming that **compounds dissociated into oppositely charged ions** whose motions constituted a current.

This conclusion was supported by observing that the freezing point depression of ionic solids were integer multiples larger than their concentrations would indicate according to Raoult's Law.

ACIDS & BASES

Svante Arrhenius (1859-1927)



He described his theory in his 1884 thesis, which passed the defense with the lowest passing grade.

However, it won him the Nobel Prize in chemistry in 1903.

He also discovered the Arrhenius Rate Law, which describes the rate at which chemical reactions occur.

ACIDS & BASES

Brønsted-Lowry

Acids donate H⁺ ions to other ions or molecules, which act as a base.

In an operational sense:

- an **acid** is any substance that **increases the concentration of the H⁺ ion** when it dissolves in water.
- a **base** is any substance that **increases the concentration of the OH⁻ ion** when it dissolves in water.

Table 6-2 Common strong acids and bases

Formula	Name
Acids	
HCl	Hydrochloric acid (hydrogen chloride)
HBr	Hydrogen bromide
HI	Hydrogen iodide
H ₂ SO ₄ ^a	Sulfuric acid
HNO ₃	Nitric acid
HClO ₄	Perchloric acid
Bases	
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
R ₄ NOH ^b	Quaternary ammonium hydroxide

a. For H₂SO₄, only the first proton ionization is complete. Dissociation of the second proton has an equilibrium constant of 10 × 10⁻².

b. This is a general formula for any hydroxide salt of an ammonium cation containing four organic groups. An example is tetrabutylammonium hydroxide: (C₄H₉)₄N⁺OH⁻.

Table 6-2
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ACIDS & BASES

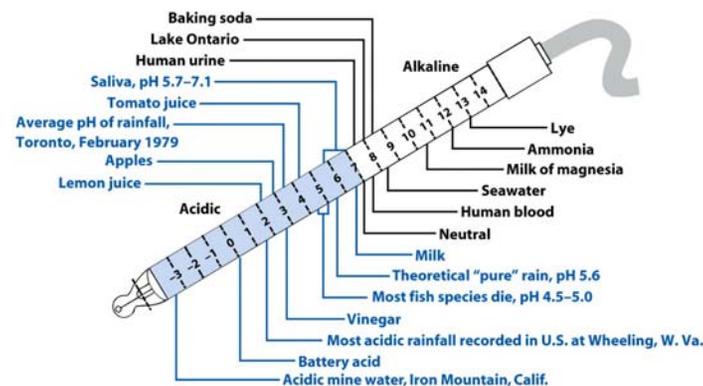
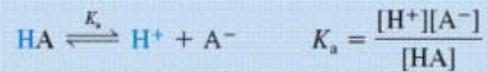
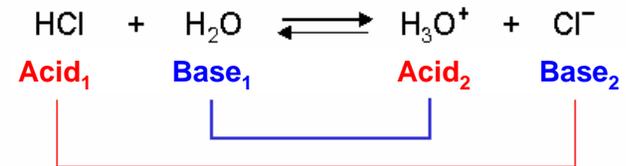
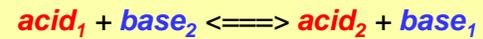


Figure 6-7
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Dissociation of weak acid:



Conjugated Acids and Bases



- Cl^- : Conjugated **base** to **acid HCl**
- H_3O^+ : Conjugated **acid** to **base H_2O**

Gas – solution equilibrium K_H

Henry's Law

CO_2 dissolves in water:

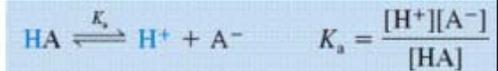


at a CO_2 pressure of 3×10^{-4} atmospheres,
what is the concentration of the carbonic acid in the water?

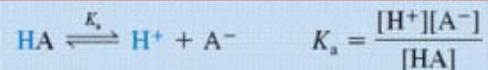


What is $[\text{H}^+]$? - What is pH?

Dissociation of weak acid:



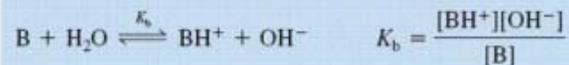
Dissociation of weak acid:



Dissociation of weak acid: $\text{HA} + \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{H}_3\text{O}^+ + \text{A}^-$

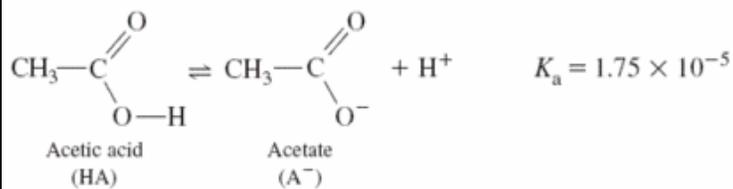
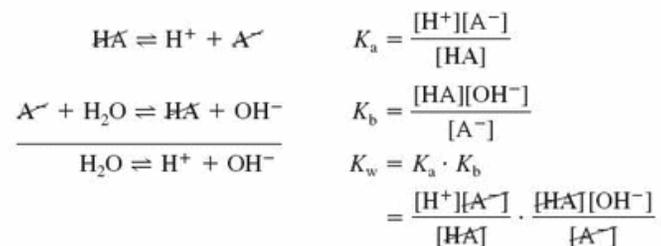


Base hydrolysis:

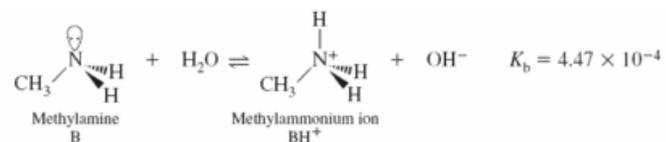
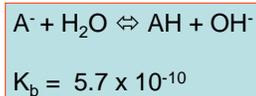


Relation between K_a and K_b for a conjugate pair:

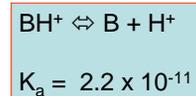
$$K_a \cdot K_b = K_w$$



What is K_b for the acetate ion?



What is K_a for the methylammonium ion?



The Role of H^+ and OH^- Ions in Aqueous Solutions

To what extent does H_2O dissociate to form ions?

At 25°C, the density of water is 0.9971 g/cm³,
or 0.9971 g/mL.

$$\frac{0.9971 \text{ g } H_2O}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 55.35 \text{ mol } H_2O/L$$

The concentration of H_2O is 55.35 molar.

The Role of H^+ and OH^- Ions in Aqueous Solutions

To what extent does H_2O dissociate to form ions?

The **concentration** of the H^+ and OH^- ions formed
by the dissociation of neutral H_2O molecules at this
temperature is only 1.0×10^{-7} mol/L.

The Role of H^+ and OH^- Ions in Aqueous Solutions

To what extent does H_2O dissociate to form ions?

The **concentration** of the H^+ and OH^- ions formed
by the dissociation of neutral H_2O molecules at this
temperature is only 1.0×10^{-7} mol/L.

$$\frac{1.0 \times 10^{-7} \text{ M } H^+}{55.35 \text{ M } H_2O} = 1.8 \times 10^{-9}$$

Accordingly, the ratio of the concentration of
the H^+ (or OH^-) ion to that of the neutral H_2O
molecules is 1.8×10^{-9} .

The Role of H^+ and OH^- Ions in Aqueous Solutions

To what extent does H_2O
dissociate to form ions?

At 25°C only about **2 parts per
billion (ppb)** of the H_2O
molecules **dissociate** into ions.