CHEM 1A03: Intro. Chemistry I

McMaster University

Chemistry

Acid-Base Chemistry

Ch.16: Acids and Bases

http://en.wikipedia.org/wiki/File:Lemon.jpg

A World of Taste, Nutrition & Medicine

▪ Early qualitative tests to distinguish acids & bases by taste!

▪ Focus on fundamental acid-base chemistry to describe their reactivity in the context of energy, health & environment

Acidic: Sour

Phosphoric acid

Soft Drinks: Colas

http://www.freefoto.com/preview/09-14-60/Cola-Soft-Drink

Alkaline: Bitter
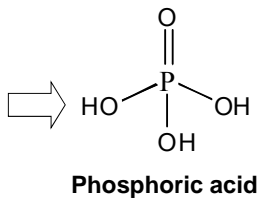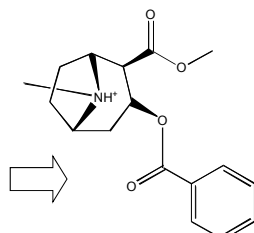
Coca Leaf

Cocaine (Alkaloid)

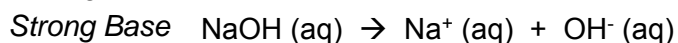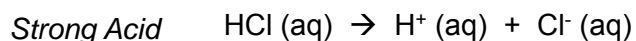http://en.wikipedia.org/wiki/File:Colcoca03.jpg

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Acid-Base Chemistry: Electrolyte Theory

**Arrhenius Theory**

- Electrolyte dissolution behaviour

- Acids ionize to generate proton → H^+ (aq), whereas bases ionize to produce hydroxide → OH^- (aq)

  Strong Acid HCl (aq) → H^+ (aq) + Cl^- (aq)

  Strong Base NaOH (aq) → Na^+ (aq) + OH^- (aq)

- Theory applicable to protic acids & metal hydroxides in water, however many exceptions → BF_3 and NH_3

- Neutralization reaction: Net Ionic Equation

$$H^+ \text{ (aq)} + OH^- \text{ (aq)} \rightarrow H_2O \text{ (l)}$$

http://en.wikipedia.org/wiki/Svante_Arrhenius
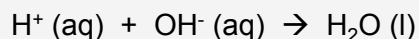
Refer to Ch. 16-1   **Nobel Prize 1903 → Electrolytic Theory**

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Acid-Base Chemistry: Focus on H^+

Brønsted-Lowry Theory

• acid = H^+ donor, base = H^+ acceptor

• acid/base reactants & conjugate acid/base products:

    Acid*   *Base* *Conjugate Base* *Conjugate Acid

   HCl (aq) + H_2O (l) → Cl^- (aq) + H_3O^+ (aq)

   Base*   *Acid* *Conjugate Acid* *Conjugate Base

  NH_3 (aq) + H_2O (l) ⇌ NH_4^+ (aq) + OH^- (aq)
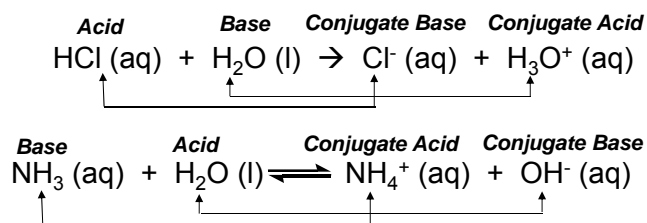
• H_2O is an amphoteric species (behaves as both an acid or a base)

Refer to Ch. 16-2 (note in 9th ed. arrows go in wrong direction in text)

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Acid-Base Chemistry: Electron Flow!

Lewis Theory

▪ Acid = e⁻ pair acceptor, base = e⁻ pair donor; an electron pair is shared.
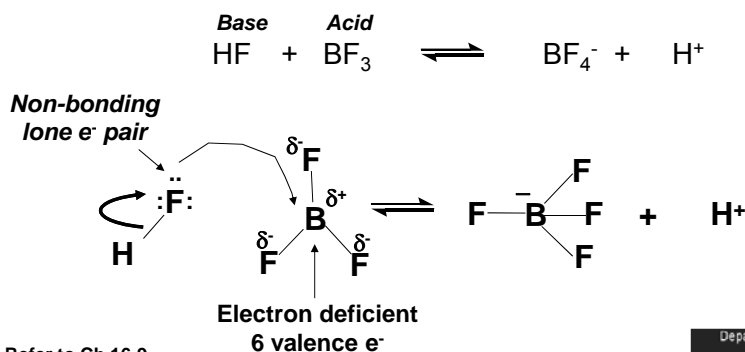
▪ Least restrictive definition that describes aqueous/non-aqueous solvents, as well as unusual non-protic acid systems.

Base   *Acid*

$HF \; + \; BF_3 \; \rightleftharpoons \; BF_4^- \; + \; H^+$

Non-bonding lone e⁻ pair
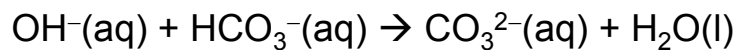
Electron deficient
6 valence e⁻

Refer to Ch 16-9

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iClicker Question #1

Identify the Brønsted-Lowry <u>acid</u> in the following reaction:

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

a. OH^-

b. CO_3^{2-}

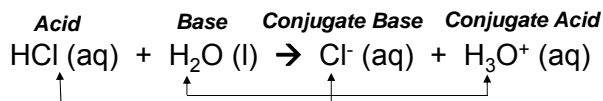c. HCO_3^-

d. This isn't a Brønsted-Lowry acid/base reaction

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Acid-Base Chemistry: Electron Flow!

Strong Acids/Bases

Brønsted-Lowry description:

$$\underset{Acid}{HCl\ (aq)}\ +\ \underset{Base}{H_2O\ (l)}\ \rightarrow\ \underset{Conjugate\ Base}{Cl^-\ (aq)}\ +\ \underset{Conjugate\ Acid}{H_3O^+\ (aq)}$$

Lewis description:
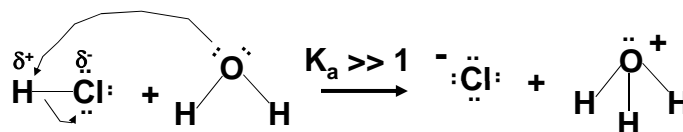
H₂O is a stronger base than Cl⁻/ HCl is a stronger acid than H₃O⁺

$$K_a > 1.0 \times 10^6 \ (25° \ C)$$

Refer to Ch 16-4

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Acid-Base Equilibrium: Weak acid & K_a

$$\underset{Acid}{CH_3COOH\ (aq)}\ +\ \underset{Base}{H_2O\ (l)}\ \underset{K_a}{\rightleftharpoons}\ \underset{Conjugate\ Base}{CH_3COO^-\ (aq)}\ +\ \underset{Conjugate\ Acid}{H_3O^+\ (aq)}$$
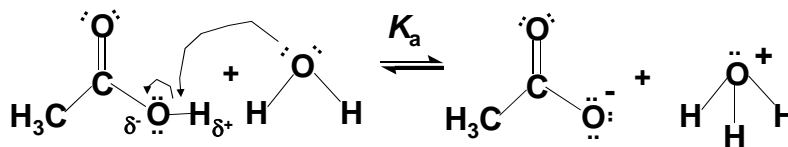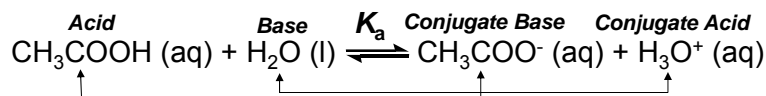
$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Equilibrium favours _reverse_ process:

Acidity of H₃O⁺ > CH₃COOH   **Basicity of CH₃COO⁻ > H₂O**

Refer to Ch 16-5

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Acid-Base Equilibrium: Weak base & K_b

Base   **Acid**   **Conjugate Acid**   **Conjugate Base**

NH_3 (aq) + H_2O (l) $\rightleftharpoons$ NH_4^+ (aq) + OH^- (aq)
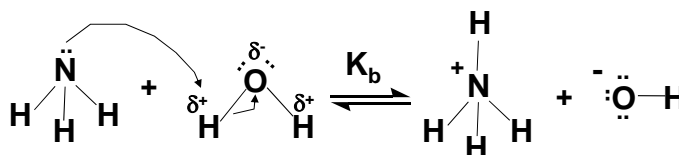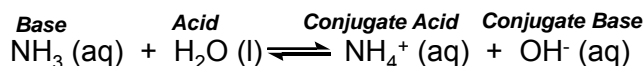
$$K_b = \frac{[NH_4^+][HO^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Equilibrium favours <u>reverse</u> process:

Basicity of OH^- > NH_3   **Acidity of NH_4^+ > H_2O**

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Auto-ionization of Water & pH Scale

▪ Water is amphoteric & undergoes acid-base reaction with itself

▪ Auto-ionization with defined equilibrium forms the basis of pH scale

$$H_2O \text{ (l)} + H_2O \text{ (l)} \xrightarrow{K_w} H_3O^+ \text{ (aq)} + OH^- \text{ (aq)}$$
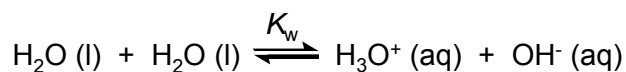
$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$
$$(25° \text{ C})$$

▪ Wide concentration range of H_3O^+/OH^- → Use $\log_{10}$ scale!

$$-\log \{K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\}$$

$$-\log K_w = -\log [H_3O^+] + (-\log [OH^-]) = 14.0$$

$$pK_w = pH + pOH = 14.0 \quad \textit{Aqueous solution}$$

Refer to Ch 16-3

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Concept Check: pH Scale

$$pH = -\log [H_3O^+]$$
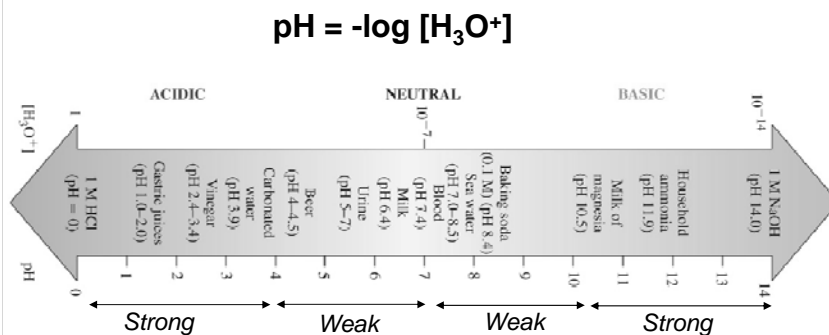
What is the pH of 10 M HCl?

Refer to Fig 16-6

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iClicker Question #2

What is the $[H_3O^+]$ in a solution with a pH of 3.25?

a. 10^{pH}

b. 10^{14-pH}

c. $10^{-(14-pH)}$

d. 10^{-pH}

e. 10^{pKw-pH}

pH Scale Demo: The pHrice Is Right

pH of household items and some salts

Trends observed:

Weak acids – edibles

Bases – cleaners

Salts: NaCl (neutral); NH_4Cl (acidic); $NaCH_3COO$ (basic)

Strong Acids/Bases

• Strong acids to know (6):
  HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4

• Strong bases to know:
  Grp I & Grp II hydroxides (many Grp II partially soluble)
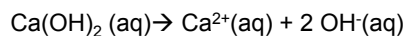 hydrides (H^-)
  oxides (O^{2-})

Refer to Ch 16-4

Take-Home Problem

Determine the pH of a 0.350M solution of $Ca(OH)_2$ (assume 100% dissociation)

a. 0.155

b. 11.636

c. 13.845

d. 12.112

e. 13.544

$Ca(OH)_2$ (aq)→ Ca^{2+}(aq) + 2 OH^-(aq)

0.350 M $Ca(OH)_2$ provides 2 (0.350 M) of OH^-(aq)

$[OH^-]$ = 0.700 M

$pOH = -\log_{10}[OH^-] = -\log_{10}[0.700]$

$pOH = 0.154_9$

$pH + pOH = 14$

$pH = 13.845$ (answer C)

Weak Acids/Bases

▪ Weak acids/bases undergo partial reversible ionization in H_2O

▪ Extent of equilibrium ionization described by magnitude of K_a or K_b

$$\underset{Acid}{CH_3COOH\ (aq)} + \underset{Base}{H_2O\ (l)} \overset{K_a}{\rightleftharpoons} \underset{Conjugate\ Base}{CH_3COO^-\ (aq)} + \underset{Conjugate\ Acid}{H_3O^+\ (aq)}$$
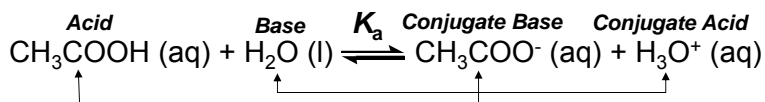
$$K_a = 1.8 \times 10^{-5} \text{ or } pK_a = -\log(K_a) = 4.74$$

For acid: Smaller pK_a = more acidic

For base: Smaller pK_b = more basic

Refer to Ch 16-5

Weak Acids/Bases

- Many organic molecules have weakly acidic carboxylic acid groups

Ibuprofen, pK_a 4.4

Carbonic acid

pK_{a1} 6.4; pK_{a2} 10.2

Pyruvic acid, pK_a 2.5

- Many weak bases are centered around N

NH_3	CH_3NH_2	$(CH_3CH_2)_2NH$
ammonia	methylamine	diethylamine
pK_b = 4.74	pK_b = 3.36	pK_b = 3.16

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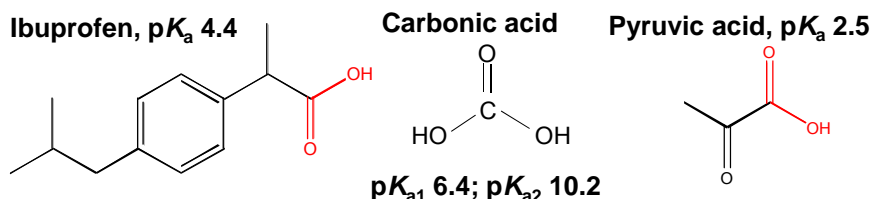
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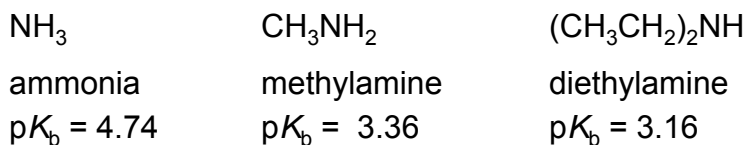
Weak Acids & Bases: K_a < 1 & K_b < 1

	Ionization Equilibrium	Ionization Constant K	pK
Acid		$K_a =$	p$K_a =$
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
* Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		$K_b =$	p$K_b =$
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
* Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

Refer to Table 16-3

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pK$_a$ & pK$_b$ Relationship for Conjugate Pairs

Acid   *Base*   **K$_a$**   *Conjugate Base*   *Conjugate Acid*

$$CH_3COOH \ (aq) + H_2O \ (l) \rightleftharpoons CH_3COO^- \ (aq) + H_3O^+ \ (aq)$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Base   *Acid*   **K$_b$**   *Conjugate Acid*   *Conjugate Base*

$$CH_3COO^- \ (aq) + H_2O \ (l) \rightleftharpoons CH_3COOH \ (aq) + OH^- \ (aq)$$
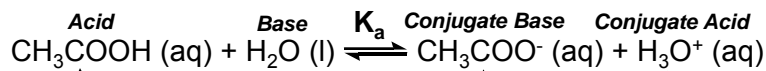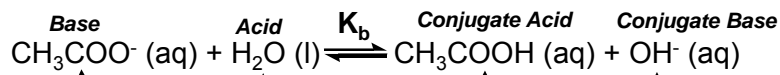
$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_a * K_b = \ [H_3O^+] \ [OH^-] = \ K_w \quad X - log$$

$$-\log_{10}(K_w) = - \log_{10}(K_a) \ + (-\log_{10}(K_b))$$

Refer to Ch 16-7

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pK$_a$ & pK$_b$ Relationship

$pK_w = pK_a + pK_b = 14.0$ **For a conjugate acid-base pair**

NH$_3$ as Weak Base *vs.* NH$_4^+$ as Weak Acid

$K_b = 1.8 \times 10^{-5} \longrightarrow pK_b = 4.74 \longrightarrow pK_a = 14.0 - 4.74 = 9.26$

$K_a = 10^{-9.26} = 5.5 \times 10^{-10}$

CH$_3$COOH as Weak Acid *vs.* CH$_3$COO$^-$ as Weak Base

$K_a = 1.8 \times 10^{-5} \longrightarrow pK_a = 4.74 \longrightarrow pK_b = 14.0 - 4.74 = 9.26$

$K_b = 10^{-9.26} = 5.5 \times 10^{-10}$

CH$_3$COOH & NH$_4^+$ are both weak acids ($K_a < 1$)
NH$_3$ & CH$_3$COO$^-$ are both weak bases   ($K_b < 1$)

Refer to Ch 16-7

Relative Strength of Acid-Base Conjugate

The favoured direction of an acid-base reaction is from the stronger to the weaker member of the conjugate acid-base pair

$$HCl + OH^- \rightarrow Cl^- + H_2O \qquad H_2O + I^- \leftarrow OH^- + HI$$

Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
*Hydroiodic acid	HI	* Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
* Hydrochloric acid	HCl	* Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion^a	H_3O^+	Water^a	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	$HC_2H_3O_2$	Acetate ion	$C_2H_3O_2^-$
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
* Water	H_2O	* Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

Increasing acid strength → (left)   *Increasing base strength* → (right)

Stronger the acid (or base) → Weaker its conjugate base (or acid)
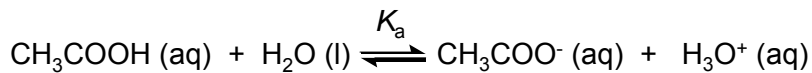
Refer to Table 16-1

Weak Acids/Bases: Calculations

Determine the pH and % ionization of a 0.100 M solution of acetic acid. K_a ($CH_3COOH = 1.8 \times 10^{-5}$)

→ *Write down the chemistry – correctly!*

$$CH_3COOH\ (aq)\ +\ H_2O\ (l)\ \underset{}{\overset{K_a}{\rightleftharpoons}}\ CH_3COO^-\ (aq)\ +\ H_3O^+\ (aq)$$

Initial	0.100 M	-	0 M	0 M
Change	-x M		+x M	+x M
Eqm	0.100-x M		x M	x M

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

Assume x << 0.100, then (0.100 – x) ≈ 0.100

Refer to Ex 16-6, pg 677

Weak Acids/Bases: Assumptions

Assuming x is small avoids a quadratic solution...
HOWEVER – we <u>must</u> check if the assumption is valid!

Check: If $\boxed{\dfrac{[HA]}{K_a} > 100}$ then assumption is valid (< 5% error):

$$\frac{0.100}{1.8 \times 10^{-5}} = 5.6 \times 10^{3}, \text{ which is } > 100$$

Then: $x^2 = (0.100)(1.8 \times 10^{-5})$; $x = [H_3O^+] = 1.3_4 \times 10^{-3}$

and: pH = -log (1.34×10^{-3}) **= 2.87**

% Ionization

$$\frac{[H_3O^+]}{[HA]_{initial}} \times 100 = \frac{1.3_4 \times 10^{-3} \, M}{0.100 \, M} \times 100 = \boxed{1.3\%}$$
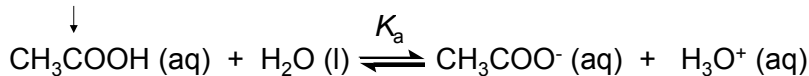
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Weak Acids/Bases: Quadratic Equation

Determine the pH and % ionization of 0.00050% by mass acetic acid.

Assume 1.0 L $\therefore$ [1000g/L x (5.0 x 10^{-4}/100)] / 60.022g/mol = 8.3_3 x 10^{-5} M

$$\downarrow$$

$$\overset{K_a}{CH_3COOH \, (aq) \; + \; H_2O \, (l) \; \rightleftharpoons \; CH_3COO^- \, (aq) \; + \; H_3O^+ \, (aq)}$$

Initial	8.3_3 x 10^{-5} M		
Change	-x	+x	+x
Eqm	8.3_3 x 10^{-5} M - x	x	x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{8.3_3 \text{ x } 10^{-5} - x} = 1.8 \text{ x } 10^{-5}$$

$$\boxed{\frac{8.3_3 \text{ x } 10^{-5}}{1.8 \text{ x } 10^{-5}} = 4.6}$$
< 100

Require use of quadratic equation because of the dilute conc. of weak acid!

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Weak Acids/Bases: Quadratic Equation

Quadratic equation:

$$x^2 + 1.8 \times 10^{-5} x - 1.5 \times 10^{-9} \ldots \textit{Solve for x}$$
$$\;\;\;\; a \qquad\quad b \qquad\qquad c$$

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-1.8 \times 10^{-5} \pm 7.95 \times 10^{-5}}{2} = 3.0_8 \times 10^{-5} \text{ M}$$
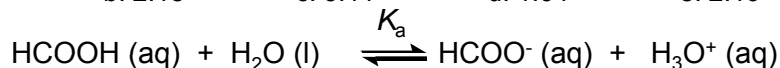
$$\boxed{\text{pH} = 4.51}$$

% Ionization

$$\frac{[H_3O^+]}{[HA]_{initial}} \; X\,100 = \frac{3.0_8 \times 10^{-5}\text{M}}{8.3_3 \times 10^{-5} \text{ M}} \; X\,100 \quad \boxed{= \textbf{37 \%}}$$

Dilution of vinegar results in lower acidity & higher % ionization!

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Take-Home Problem

Determine the pH of a 0.245 M solution of formic acid ($K_a = 1.8 \times 10^{-4}$)

a. 3.98   b. 2.18   c. 3.11   d. 1.64   e. 2.19

$$\text{HCOOH (aq)} + H_2O \text{ (l)} \;\; \overset{K_a}{\rightleftharpoons} \;\; \text{HCOO}^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$

	HCOOH	HCOO⁻	H₃O⁺
Initial	0.245 M		
Change	-x	+x	+x
Eqm	0.245 – x M	x	x

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = \frac{\textbf{x}^2}{\textbf{0.245 - x}} = \textbf{1.8 x 10}^{-4}$$

Assume x << 0.245, then (0.245 – x) ≈ 0.245

$$\frac{[HA]}{K_a} > 100 \qquad \text{Assumption is valid}$$

Then: $x^2 = (0.245)(1.8 \times 10^{-4})$; $x = [H_3O^+] = 6.64 \times 10^{-3}$

and: pH = -log (6.64×10^{-3}) = **2.18**

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pH & Percent Ionization of Weak Acid

Impact of Dilution

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pH of Salt Solutions

What is the pH of 0.1 M NaCl(aq)?

The salt is soluble, and dissociates in water:

$NaCl\ (aq) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$ • but what happens to the ions?

$Na^+\ (aq) + H_2O\ (l) \rightarrow$ *No Reaction* **Neither ion reacts with H_2O**

$Cl^-\ (aq) + H_2O\ (l) \rightarrow$ *No Reaction* **∴pH = 7 (Neutral)**
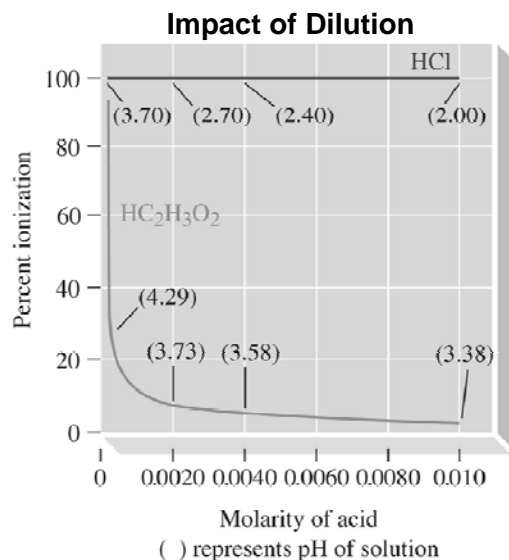
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pH of Salt Solutions

What is the pH of 0.1 M $NH_4Cl(aq)$?

NH_4Cl (aq) $\rightarrow$ NH_4^+ (aq) + Cl^- (aq)   • salt dissolves

what happens to the ions?

Cl^- (aq) + H_2O (l) $\rightarrow$ *No Reaction*
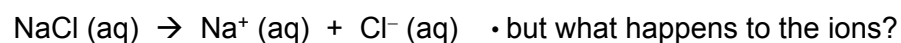
NH_4^+ (aq) + H_2O (l) $\rightleftharpoons$ NH_3 (aq) + H_3O^+ (aq)
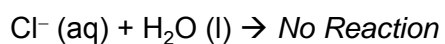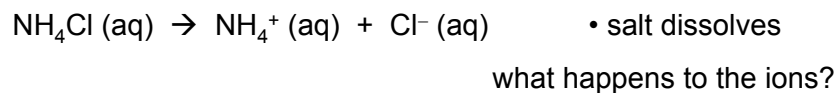
pH < 7 (acidic)

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pH of Salt Solutions

What is the pH of 0.1 M CH_3COONa (aq)?

CH_3COONa (aq) $\rightarrow$ Na^+ (aq) + CH_3COO^-(aq)   • salt dissolves

what happens to the ions?

Na^+ (aq) + H_2O (l) $\rightarrow$ *No Reaction*

CH_3COO^- (aq) + H_2O (l) $\rightleftharpoons$ OH^- (aq) + CH_3COOH (aq)
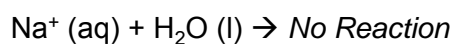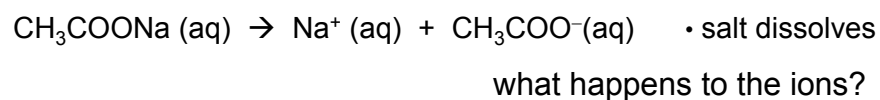
pH > 7 (alkaline)

pH of Salt Solutions: Practice Problem

What is the pH of 0.1 M NH_4CH_3COO dissolved in de-ionized water? K_a **(CH_3COOH) = 1.8 × 10^{-5},** K_b **(NH_3) = 1.8 × 10^{-5}**

NH_4CH_3COO (aq) → NH_4^+ (aq) + CH_3COO^- (aq)   and the ions:

CH_3COO^- (aq) + H_2O (l) $\xrightleftharpoons{K_b}$ CH_3COOH (aq) + OH^- (aq)

NH_4^+ (aq) + H_2O (l) $\xrightleftharpoons{K_a}$ NH_3 (aq) + H_3O^+ (aq)
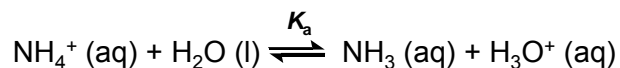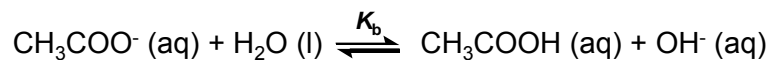
Acidic or Alkaline Solution?

K_b **= 5.5 x 10^{-10} and** K_a **= 5.5 x 10^{-10}**

pH = 7 (Neutral) because of equal magnitudes of K_a **&** K_b
(larger magnitude K **prevails)**

Refer to Ch 16-7

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iClicker Question #3

What is the pH of 0.1 M NaF (aq)? (no calculations required)

a. Acidic
b. Basic
c. Neutral

Take-Home Problem

What is the pH of a 0.350 M solution of NaF? (K_a HF = 6.6 x 10^{-4})

a. 5.54   b. 10.11   c. 8.36   d. 6.22   e. 9.73

$$F^- \text{ (aq)} + H_2O \text{ (l)} \xrightleftharpoons{K_b} HF \text{ (aq)} + OH^- \text{(aq)}$$
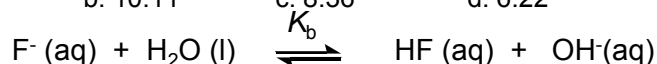
Initial	0.350 M		
Change	-x	+x	+x
Eqm	0.350 – x M	x	x

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{0.350 - x} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-4}} = 1.5_2 \times 10^{-11}$$

Assume x << 0.350, then (0.350 – x) $\approx$ 0.350

$$\frac{[base]}{K_b} > 100 \qquad \text{Assumption is valid}$$

Then: $x^2 = (0.350)(1.5_2 \times 10^{-11}); x = [OH^-] = 2.31 \times 10^{-6}$

And: pOH = -log (2.31×10^{-6}) = 5.636; pH = 14.00 – 5.636 = 8.36

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Molecular Structure & Acid-Base Behavior

▪ **Relative strength of acid & bases**

1) **Can be deduced by Lewis molecular structure and chemical bonding principles**

2) **Anion/conjugate base (X$^-$) stability predicts acid strength. The more stable X$^-$ the stronger the acid (and vice versa for bases).**

$$HX \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons X^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$

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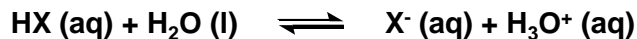
Molecular Structure & Acid-Base Behavior

- **Binary Acids: Trends Down a Group!**

$$HI \quad > \quad HBr \quad > \quad HCl \quad > \quad HF$$

pK_a -9.0   <   -8.0   <   -6.1   <   3.2 ← **Less acidic!**
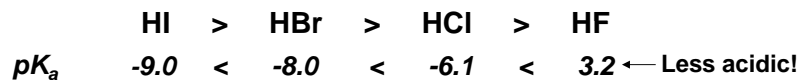
HF is actually a weak acid in water!

Anion Stability
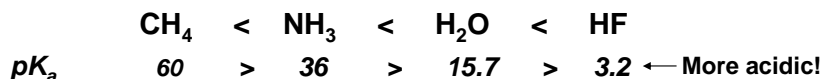
$$I^- \quad > \quad Br^- \quad > \quad Cl^- \quad > \quad F^-$$

In water, the larger anion disperses the negative charge most effectively, causing I^- to be the most stable anion in this series.

Refer to Ch 16-8

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Molecular Structure & Acid-Base Behaviour: Binary Acids

- **Trends Across a Period:**

$$HA\ (aq)\ +\ H_2O\ (l) \rightleftharpoons A^-\ (aq)\ +\ H_3O^+\ (aq)$$

$$CH_4 \quad < \quad NH_3 \quad < \quad H_2O \quad < \quad HF$$

pK_a 60   >   36   >   15.7   >   3.2 ← **More acidic!**

Electronegativity (ΔEN) of H–X bond is very important. All anions are close to equal in size. The anion bearing the most electronegative atom will be most stable.

CH_4 & NH_3 **(non-acidic)**, H_2O **(amphoteric)** & HF **(acidic)**

$$NH_3\ (aq)\ +\ H_2O\ (l) \not\rightleftharpoons NH_2^-\ (aq)\ +\ H_3O^+\ (aq)$$

$$HF\ (aq)\ +\ H_2O\ (l) \rightleftharpoons F^-\ (aq)\ +\ H_3O^+\ (aq)$$

Refer to Ch 16-8

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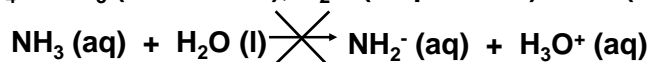
**Molecular Structure & Acid-Base Behavior: Oxyacids**

- Oxyacids: Substituent "inductive" effects & resonance stabilization

$$HA\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ A^-\ (aq)\ +\ H_3O^+\ (aq)$$

Sulfurous Acid

Sulfuric Acid   *More EN O atoms!*

$pK_{a1} = 1.89$

$pK_{a1} = -3.00$

Stronger acid: conjugate base is stabilized

Conjugate base: 2 resonance stabilized species

Conjugate base: 3 resonance stabilized species

Refer to Ch 16-8

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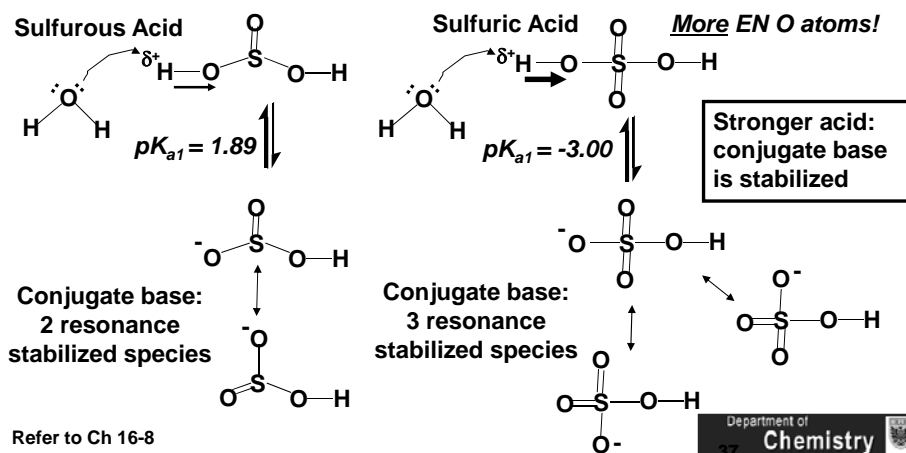
Molecular Structure & Acid-Base Behaviour: Oxyacids

- For systems with same number of O atoms, the electronegativity of the central atom differentiates strength (underline negative charge is always on oxygen):

  H-O-Cl   H-O-Br
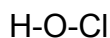
  $K_a = 2.9 \times 10^{-8}$ $K_a = 2.1 \times 10^{-9}$
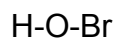
  EN (Cl) = 3.0   EN (Br) = 2.8

  Inductive effect:
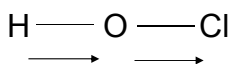
  H —— O —— Cl   **Higher EN of Cl (*vs.* Br) attracts electron density away from the H-O bond**

  H-O bond is weakened in HOCl

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iClicker Question #4

Which of the following is the MOST acidic:

a
$$O$$
$$\|$$
$$C$$
H_3C — O-H

b
$$O$$
$$\|$$
$$C$$
Cl_3C — O-H
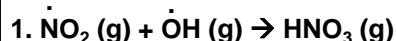
c
$$O$$
$$\|$$
$$C$$
I_3C — O-H

d H_3C—CH_2—O-H
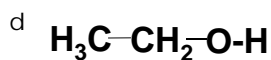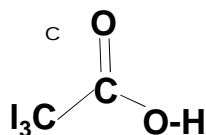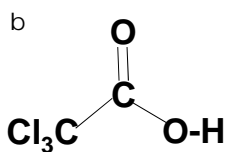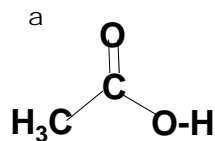
Refer to Ch 16-8

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Take-Home Problem

Which of the following is the LEAST basic:

a
$$H$$
$$|$$
H — N:
$$|$$
$$H$$
2nd most basic

b
$$I$$
$$|$$
I — N:
$$|$$
$$I$$
3rd most basic

c
$$H$$
$$|$$
H — N:
$$..$$
most basic
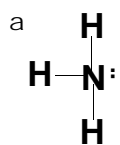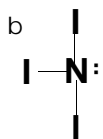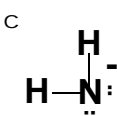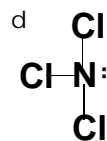
d
$$Cl$$
$$|$$
Cl — N:
$$|$$
$$Cl$$
least basic

(Inductive effect of Cl)

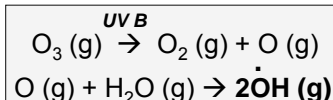Refer to Ch 16-8

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Acid Rain: Primary VS Secondary Pollutants

▪ Most natural water is weakly acidic (pH ≈ 5.6) due to dissolution of carbon dioxide → CO_2 is a minor trace gas > 380 ppm

▪ Other acidic gases are SO_2 & NO_x → Natural sources (< 0.01 ppm) include volcanic eruptions, microbe/algae populations, lightning etc.
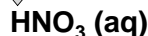
Homogenous Gas-Phase Oxidation

$$UV\,B$$
$$O_3\,(g) \rightarrow O_2\,(g) + O\,(g)$$
$$O\,(g) + H_2O\,(g) \rightarrow 2\dot{O}H\,(g)$$

Hydroxyl Radical: Oxidizing Agent!

4. $SO_3\,(g) + H_2O\,(g) \rightarrow H_2SO_4\,(g)$

3. $H\dot{S}O_3\,(g) + O_2\,(g) \rightarrow SO_3\,(g) + H\dot{O}_2\,(g)$

2. $SO_2\,(g) + \dot{O}H\,(g) \rightarrow H\dot{S}O_3\,(g)$

1. $\dot{N}O_2\,(g) + \dot{O}H\,(g) \rightarrow HNO_3\,(g)$

H_2SO_4 (aq)
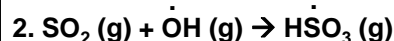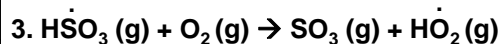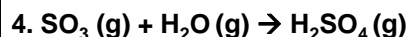
SO₂/NOₓ emissions
Combustion of fossil fuels
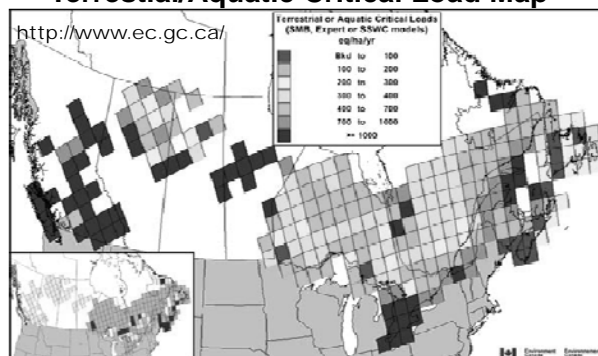
HNO_3 (aq)

Acid Rain, pH < 5

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Acid Rain: Areas of Concern & Impact

▪ Environmental Impact: Acidification of soil/water, high $[H_3O^+]$ & leached Al^{3+} metals toxic to aquatic organisms & plants/trees

▪ Health Issues: Primary & secondary pollutants are irritants (asthma/CVD), components of photochemical smog/acid mist

Terrestial/Aquatic Critical Load Map

http://www.ec.gc.ca/

Terrestrial or Aquatic Critical Loads
(SMB, Expert or SSWC models)
eq/ha/yr

Bkd to	100
100 to	200
200 to	300
300 to	400
400 to	700
700 to	1000
>= 1000	

High-loading capacity

Mid-loading capacity

Low-loading capacity
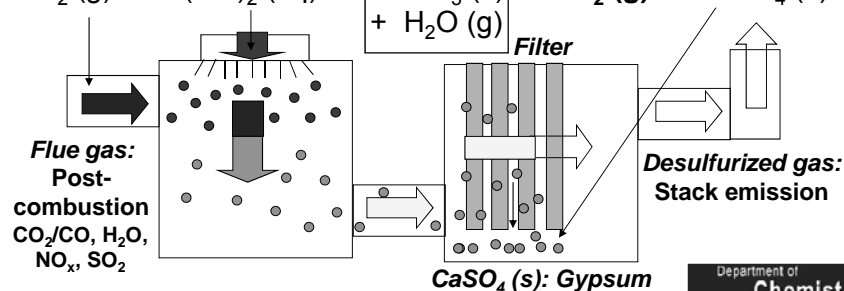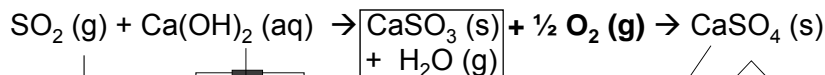
Refer to Ch 16, Focus On pg 698-699

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Remediation & Flue Gas Desulfurization

- Certain lakes can resist acidification by neutralization reaction:

$$CaCO_3 \ (s) + 2H^+ \ (aq) \rightarrow Ca^{2+} \ (aq) + H_2O \ (l) + CO_2 \ (g)$$

- Acidified lakes can also be remediated through CaO addition!

- Best policy is to reduce SO_2 gas emissions from sources via "slaked lime" slurry, $Ca(OH)_2$ → Flue gas desulfurization!

$$SO_2 \ (g) + Ca(OH)_2 \ (aq) \rightarrow \boxed{CaSO_3 \ (s) + H_2O \ (g)} + \tfrac{1}{2} \ O_2 \ (g) \rightarrow CaSO_4 \ (s)$$

Filter

Flue gas:
Post-combustion
CO_2/CO, H_2O,
NO_x, SO_2

Desulfurized gas:
Stack emission

CaSO$_4$ (s): Gypsum
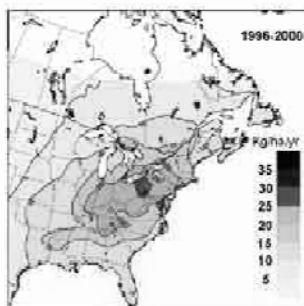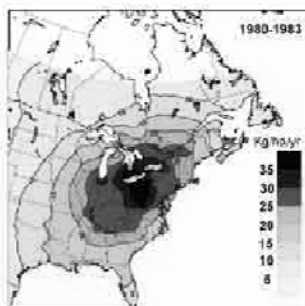
Refer to Ch 5-3, pg 152

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Acid Rain Remediation: A Success Story?

Reduction in H_2SO_4 fraction of acid rain with flue gas desulfurization practices in industry → Clean Air Act (1990)

Wet sulphate deposition down since 1980s
Wet sulphate deposition four-years mean (kilograms/hectare per year)

http://www.ec.gc.ca/

1980-1983

1996-2000

Source: Canadian National Atmospheric Chemistry Database, Meteorological Service of Canada, Environment Canada.

No significant change in HNO_3 fraction of acid rain because of increasing automobile usage → Acidification still a problem!

Refer to Ch 16, Focus On pg 698-699

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