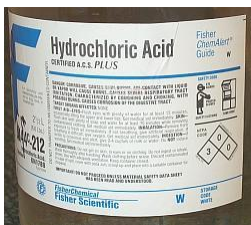# Acid - Base Equilibria 2

Reading: Ch 15 sections 8 – 12	Homework:	Chapter 15: 41, 57, 61*, 63, 65*, 67*, 73*, 85, 87*, 89, 91

* = 'important' homework question

Weak Acids

Review / Discussion: What is 'stronger' – HCl (aq) or vinegar (acetic acid)? What are the differences?

Strong (mineral) acids, such as HCl, *dissociate completely* in water:

Weak (organic) acids undergo *partial dissociation* in water (much more on this later):

> Because any weak acid and its respective dissociation products (H^+ and conjugate base) are in equilibrium, 'equilibrium math' can be used to define K

Task: Determine an equilibrium expression (K) for the generic weak acid equilibrium:

HA (aq) + H_2O (l) $\Leftrightarrow$ H_3O^+ (aq) + A^- (aq)
Weak   Water   Hydronium   Conjugate
Acid   ion   Base
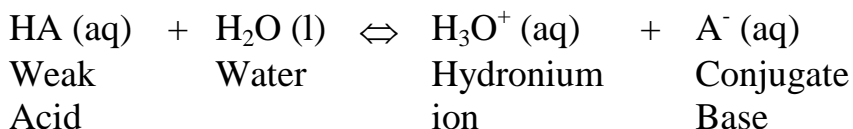
Note: Since, in this case, K pertains to the dissociation of a weak acid only, it is called the *acid dissociation constant* and assigned a suitable subscript:

$$K_a = \frac{[H^+]\ [A^-_{weak}]}{[HA_{weak}]}$$

Discussion: Will strong acids (like HCl) have large or small values for K_a? Will weak acids (like acetic acid) have large or small values for K_a?

Task: Complete the following table:

Acid	Type	Reaction with water	K_a
HCl	strong	$HCl\ (aq)\ \rightarrow\ H^+\ (aq)\ +\ Cl^-\ (aq)$	'∞'
HNO_3			
HF			$6.8\ x10^{-4}$
$HC_2H_3O_2$ (acetic)			$1.8\ x10^{-4}$
HCN			$4.9\ x10^{-10}$

Discussion: Of all the weak acids listed above, which is the 'strongest', weakest? Why?

The Relationship Between K_a and pH
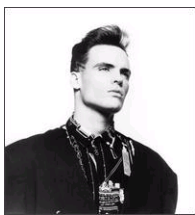
Overview: Since any weak acid is in equilibrium, a modified I.C.E. method can be used to determine *either* pH *or* K_a

Vanilla I.C.E., noted chemical philosopher

Worked Example: A sample of 0.10 M formic acid ($HCHO_2$) has a pH of 2.38. Determine K_a for formic acid and the % to which formic acid is dissociated.

Plan:

1. Find $[H^+]$

2. Set up and solve an I.C.E. table in order to find the equilibrium concentrations of HA, H^+, A^-. 'Insert and evaluate' to find K_a

3. Find % dissociation

Using K_a to find pH (the 'reverse' problem)

Question: What is the pH of 0.2 M HCN (aq) ($K_a = 4.9 \times 10^{-10}$)

Plan:

Execution:

IMPORTANT: The weak acid approximation: when $K_a \leq 10^{-3}$

$$[HA] - [H^+] \approx [HA]$$

This greatly simplifies the I.C.E. method, which is usually not undertaken unless the above is true (would otherwise require a quadratic equation to be solved)
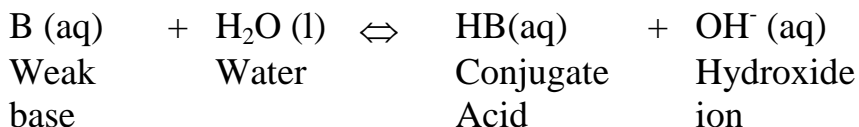
Group work: Skip ahead to the end of this handout and work through the first two practice exam problems
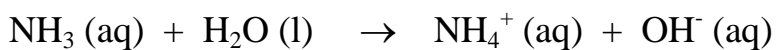
Weak Bases
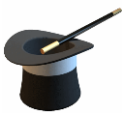
> Weak base problems are very similar to the I.C.E. weak acid examples, except that $[OH^-]$ and pOH (rather than $[H^+]$ and pH) are found initially

Generic Equilibrium:

B (aq)	+	H_2O (l)	$\Leftrightarrow$	HB(aq)	+	OH^- (aq)
Weak base		Water		Conjugate Acid		Hydroxide ion

For ammonia dissolved in water:

NH_3 (aq) + H_2O (l) $\rightarrow$ NH_4^+ (aq) + OH^- (aq)

Task: Determine K for the above ammonia equilibrium

Note: Since, in this case, K pertains to the dissociation of a weak base only, it is called the *base dissociation constant* and assigned a suitable subscript:

Task: Complete the following table:

Base	Type	Reaction with water	K_a
NaOH	strong	NaOH (aq) $\rightarrow$ Na$^+$ (aq) + OH$^-$ (aq)	'∞'
KOH			
NH$_3$			1.8 x10^{-5}
HS$^-$			1.8 x10^{-7}
CO$_3^{2-}$			1.8 x10^{-4}

Discussion: Of all the weak bases listed above, which is the 'strongest', weakest? Why?

Example: Find [OH$^-$] and pH for 0.15 M NH$_3$ solution (K$_b$ = 1.8 x10^{-5})

Plan:

Recall that [OH-] and pOH can be found initially, then pH can be determined via:

$$\text{pH} + \text{pOH} = 14$$

Execution:

Group Task: An NH$_3$ (aq) solution has a pH of 10.50. What is [NH$_3$] in this solution?

The Relationship between K_a and K_b

Recall: All weak acids and bases are in equilibrium with their respective conjugates. Each will also have an equilibrium (K) expression, e.g.:

NH_4^+ (aq) $\rightarrow$ H^+ (aq) + NH_3 (aq); $K_a =$

NH_3 (aq) + H_2O (l) $\rightarrow$ NH_4^+ (aq) + OH^- (aq); $K_b =$
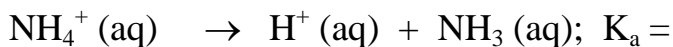
	'Equilibrium constant math' can be applied to the above pair of equations.

Task: Add the above equations and find an expression for K in terms of K_a and K_b. Do you notice something familiar?

	For any weak acid or weak base:
	$$K_a K_b = K_w = 1 \times 10^{-14} = [H^+][OH^-]$$
	Also, since $K_a K_b = K_w$:
	$$pK_a + pK_b = pK_w$$

Quick Question: What is K_a for NH_3 (aq)?

Group work: Skip ahead to the last page of this handout and work through the practice exam problem 'Weak Base'

"What's the pH?"

<u>Question 2</u> (25 points): Calculate the pH of each of the following solutions:

1. 0.015 M HCl (aq) (assume complete dissociation)

2. 0.015 M H_2SO_4 (aq) (assume complete dissociation)

3. 0.015 M NaOH (aq) (assume complete dissociation)

4. 0.015 M $HC_2H_3O_2$ (aq), $K_a = 1.8 \times 10^{-5}$

"Weak Acid"

Question 3 (25 points): A 0.200 M solution of a weak acid HA (aq) is 9.4 % ionized (dissociated) at equilibrium. Use this information to calculate $[H^+]$, $[HA]$ and K_a for HA.

"Weak Base"

Codeine ($C_{18}H_{21}NO_3$) is a weak organic base. A 5.0 x 10^{-3} M solution of codeine has a pH of 9.95.

Question 4a (20 points): Calculate K_b for codeine.

Question 4b (5 points): Calculate pK_a for codeine.

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.

HF

HF   HF

F⁻

HF

HF

H_3O^+ F⁻

HF H_3O^+

H_3O^+

HF

F⁻

(a)

CHO_2^-

H_3O^+

$HCHO_2$

(c)

A Weak Base

NH$_3$

NH$_3$ OH$^-$
NH$_4$$^+$
NH$_3$
NH$_3$
NH$_3$
OH$^-$ NH$_4$$^+$

OH$^-$ —

NH$_3$ —

NH$_4$$^+$ —

(a)
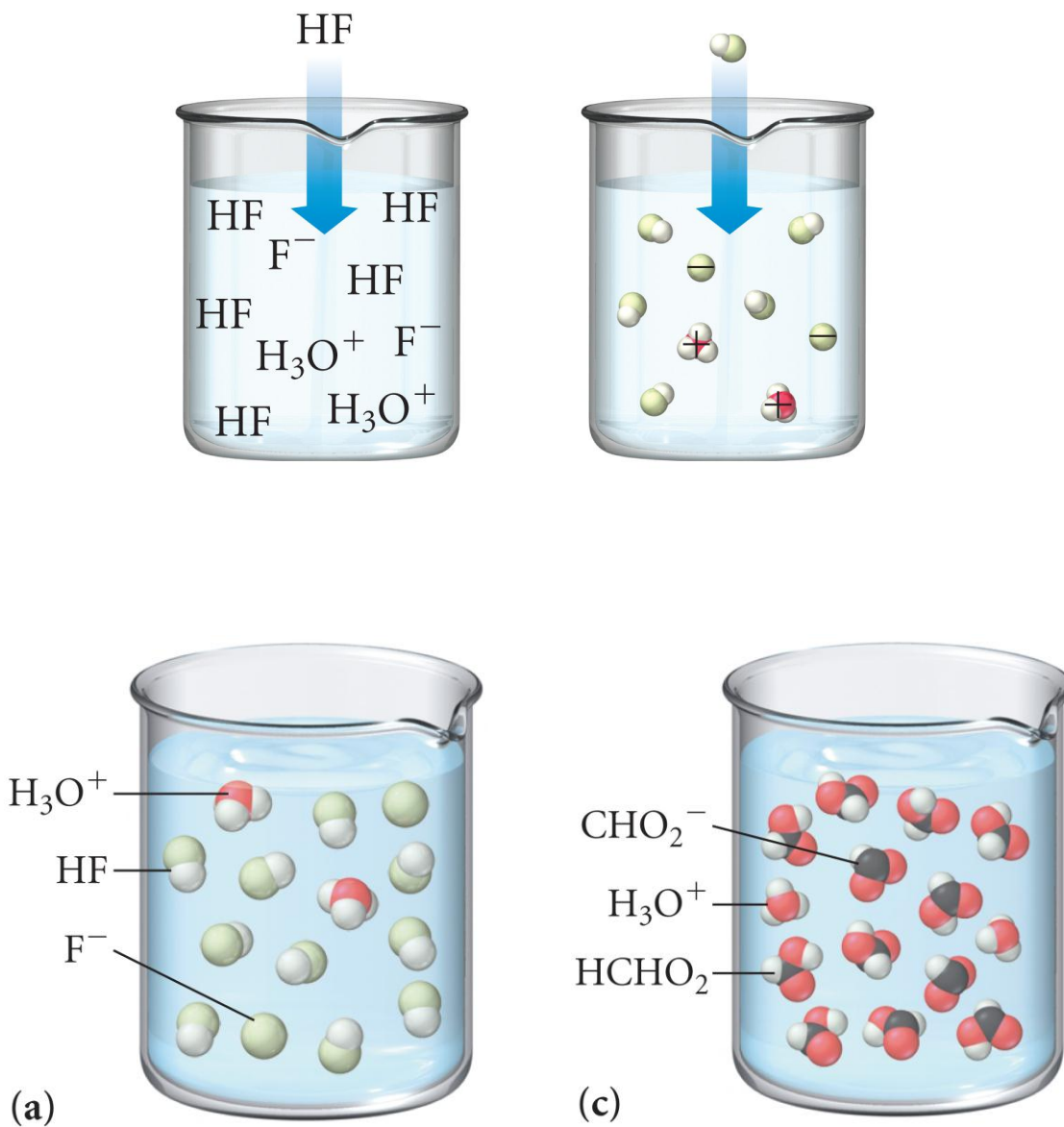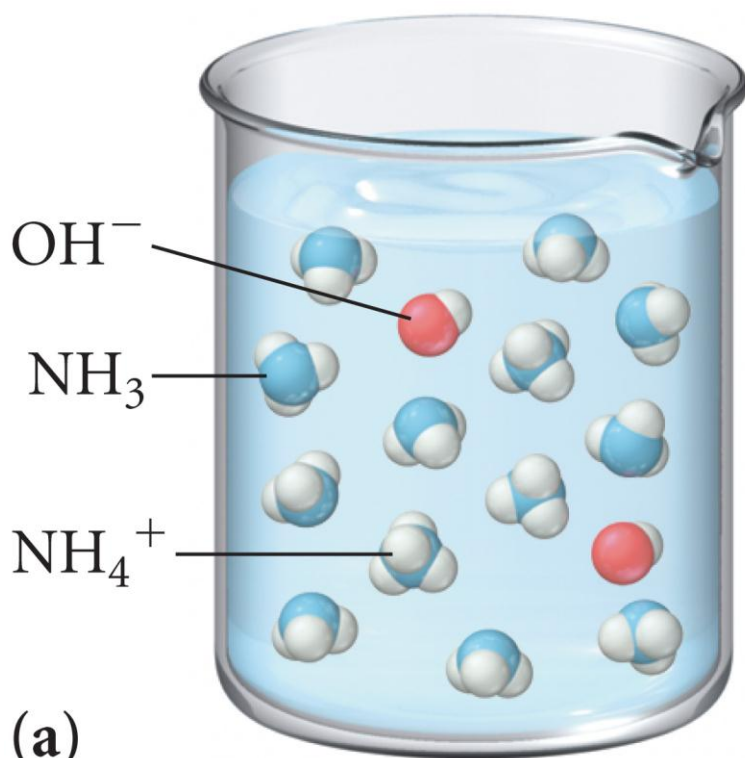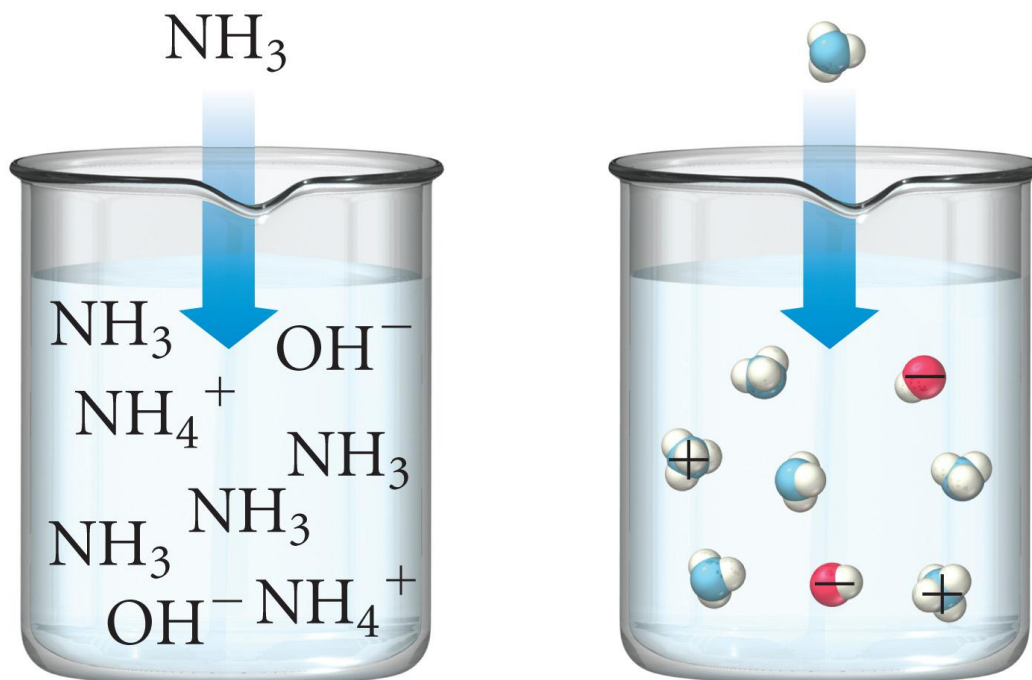
	Acid	Base	
Strong	HCl	Cl^-	**Neutral**
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
Weak	HSO_4^-	SO_4^{2-}	**Weak**
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	**Strong**
Negligible	HS^-	S^{2-}	
	OH^-	O^{2-}	

Acid Strength (increasing upward)

Base Strength (increasing downward)

TABLE 15.5 Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25°C

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Chlorous acid	$HClO_2$	H—O—Cl=O	$HClO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO_2^-(aq)$	1.1×10^{-2}
Nitrous acid	HNO_2	H—O—N=O	$HNO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + NO_2^-(aq)$	4.6×10^{-4}
Hydrofluoric acid	HF	H—F	$HF(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + F^-(aq)$	3.5×10^{-4}
Formic acid	$HCHO_2$	H—O—C(=O)—H	$HCHO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CHO_2^-(aq)$	1.8×10^{-4}
Benzoic acid	$HC_7H_5O_2$	H—O—C(=O)—C(benzene ring)	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.5×10^{-5}
Acetic acid	$HC_2H_3O_2$	H—O—C(=O)—CH$_3$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous acid	$HClO$	H—O—Cl	$HClO(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO^-(aq)$	2.9×10^{-8}
Hydrocyanic acid	HCN	H—C≡N	$HCN(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol	HC_6H_5O	HO—C(benzene ring)	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

TABLE 15.10 Common Polyprotic Acids and Ionization Constants

Name (Formula)	Structure	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric Acid (H_2SO_4)		Strong	1.2×10^{-2}	
Oxalic Acid ($H_2C_2O_4$)		6.0×10^{-2}	6.1×10^{-5}	
Sulfurous Acid (H_2SO_3)		1.6×10^{-2}	6.4×10^{-8}	
Phosphoric Acid (H_3PO_4)		7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric Acid ($H_3C_6H_5O_3$)		7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Ascorbic Acid ($H_2C_6H_6O_6$)		8.0×10^{-5}	1.6×10^{-12}	
Carbonic Acid (H_2CO_3)		4.3×10^{-7}	5.6×10^{-11}	

TABLE 15.8 Some Common Weak Bases

Weak Base	Ionization Reaction	K_b
Carbonate ion (CO_3^{2-})*	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	4.4×10^{-4}
Ethylamine ($C_2H_5NH_2$)	$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$	5.6×10^{-4}
Ammonia (NH_3)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	1.76×10^{-5}
Pyridine (C_5H_5N)	$C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$	1.7×10^{-9}
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	1.7×10^{-9}
Aniline ($C_6H_5NH_2$)	$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$	3.9×10^{-10}

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ($NaHCO_3$) basic. We look more closely at ionic bases in Section 15.8.