Acid-Base (Proton-Transfer) Reactions

Chapter 17

An example of equilibrium: Acid base chemistry

- What are acids and bases?
  - "Every day" descriptions
  - Chemical description of acidic and basic solutions by Arrhenius
  - Molecules as acids (proton donors) or bases (proton acceptors) - Brønsted–Lowry Acid–Base Theory
- How do they work?
  - Conjugate acid–base pairs
  - Strength and weakness
  - Acid base equilibrium reactions: predicting favored direction
- The water equilibrium
  - pH and pOH
  - Calculating the equilibrium constant from pH
- Buffer solutions

What are acids and bases?

- Historical Classifications:
- Acid: Something with a sour, biting taste (latin: acidus = sour)
  - lemon juice (citric acid)
  - vinegar (ethanoic acid or acetic acid)
- Base: Something that will neutralize an acid (arabic: alkali = “from the ashes”)
  - many medicines

What are acids and bases?

- Svante Arrhenius (1859–1927)
  - Nobel Prize, Chemistry, 1903
- The properties of an acidic solution are due to the presence of the $H^+(aq)$ ion
- An acid is therefore a solution with a relatively high $[H^+]$ (square brackets = “concentration of”)
- The properties of a basic solution are due to the presence of the $OH^-(aq)$ ion
- A base is therefore a solution with a relatively high $[OH^-]$

Arrhenius definition of acidic and basic solutions

- An Arrhenius acid
  - solution with a relatively high $[H^+]$

$$HCl(g) \xrightarrow{H_2O(l)} H^+(aq) + Cl^-(aq)$$

- An Arrhenius base
  - solution with a relatively high $[OH^-]$

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

Brønsted–Lowry Acid–Base Theory

- An acid–base reaction is a proton-transfer reaction
  - **Acid:** proton donor
  - **Base:** proton acceptor

$$B + HA \rightleftharpoons HB^+ + A^-$$

base proton acceptor

acid proton donor

Thomas Lowry
(1874 – 1936)
English chemist

Johannes Brønsted
(1879 – 1947)
Danish chemist

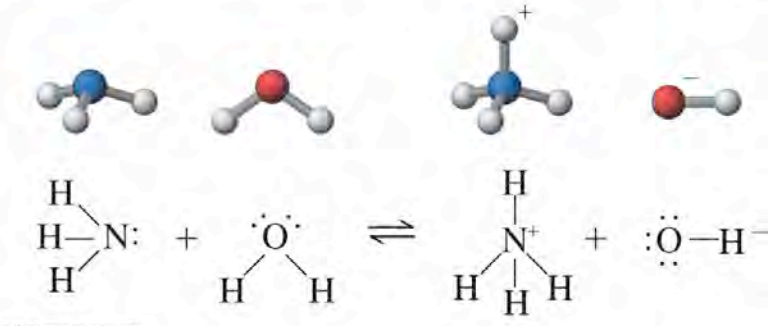
Proton-transfer reaction

Base: proton acceptor

Acid: proton donor

Reversible reaction!

$$NH_3(g) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



Acids and bases appear in pairs

- For every proton donor on the reactant side you need a proton acceptor on the product side!

Base: proton acceptor

Acid: proton donor

Acid: proton donor

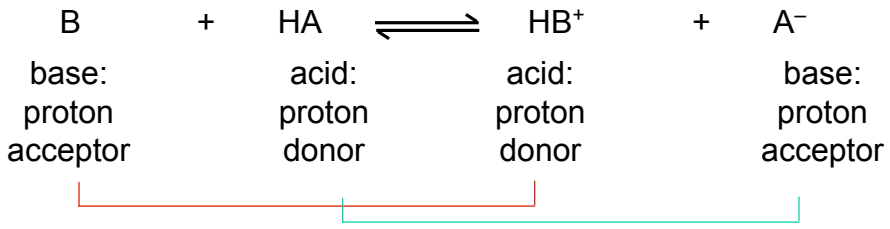
Base: proton acceptor

$$NH_3(g) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- Where does the equilibrium lie?
- In 1M NH_3(aq) less than 1% of the ammonia becomes ammonium ions
- NH_3 is the major species, the reverse reaction is favored

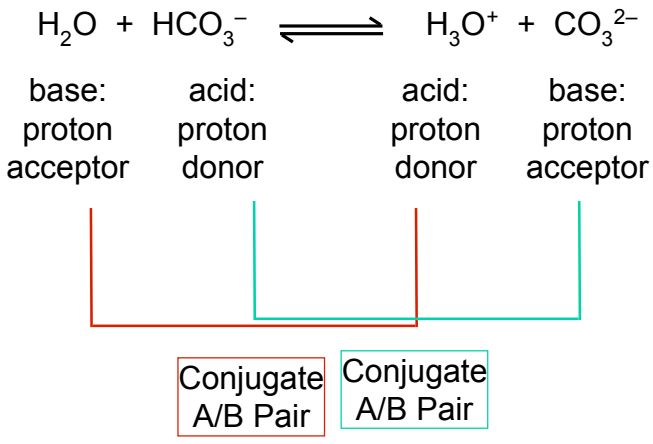
Acids and bases appear in pairs

- For every proton donor you need a proton acceptor!



- B and HB^+ differ by a proton:
- They form a **conjugate acid–base pair**
- Similarly, HA and A^- are a conjugate acid–base pair

Example



Water is (again) remarkable

$HNO_3(aq) + H_2O(l) \rightleftharpoons NO_3^-(aq) + H_3O^+(aq)$

Base = Proton Acceptor: $H_2O(l)$

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

Acid = Proton Donor: $H_2O(l)$

Water is an acid in one case
and a base in another

Amphoteric: A species that can behave as either an acid or a base

Strong and weak acids

Question: What determines the position of the equilibrium?

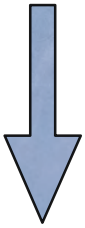
Answer: The *strengths* of the acid and base

- Strong acids are (almost) completely ionized:
- $HSt(aq) \rightleftharpoons H^+(aq) + St^-(aq)$
- They are better proton donors

- Weak acids are not ionized:
- $HWk(aq) \rightleftharpoons H^+(aq) + Wk^-(aq)$
- They do not as readily donate protons

Strong and weak acids

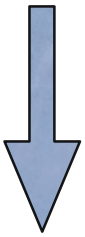
Stronger acids



Weaker acids

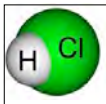
HI	$H^+ + I^-$
HCl	$H^+ + Cl^-$
H_2SO_4	$H^+ + HSO_4^-$
$C_2H_3O_2H$	$H^+ + C_2H_3O_2^-$
$H_2PO_4^-$	$H^+ + HPO_4^-$
HCN	$H^+ + HCN^-$
H_2O	$H^+ + HO^-$
OH^-	$H^+ + O^{2-}$

More ionized



Less ionized

Strong acid = better proton donor



HCl(aq), hydrochloric acid, is a stronger acid:
It is a good proton donor

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

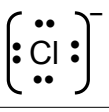
Now consider the reaction in the reverse direction:

How good is $Cl^-(aq)$ as a base?

$HCl(aq) \leftarrow H^+(aq) + Cl^-(aq)$

Chloride ion is a relatively poor proton acceptor
Therefore it is a weaker base

Recall: Cl^- is relatively stable because it has noble gas electron configuration



$C_2H_3O_2H(aq)$, acetic acid, is a weaker acid:
It is a poor proton donor

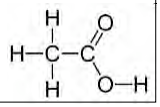
$$C_2H_3O_2H(aq) \Rightarrow H^+(aq) + C_2H_3O_2^-(aq)$$

Now consider the reaction in the reverse direction:

How good is $C_2H_3O_2^-(aq)$ as a base?

$$C_2H_3O_2H(aq) \Leftarrow H^+(aq) + C_2H_3O_2^-(aq)$$

The $C_2H_3O_2^-(aq)$ ion has a strong attraction for protons
It is a strong base



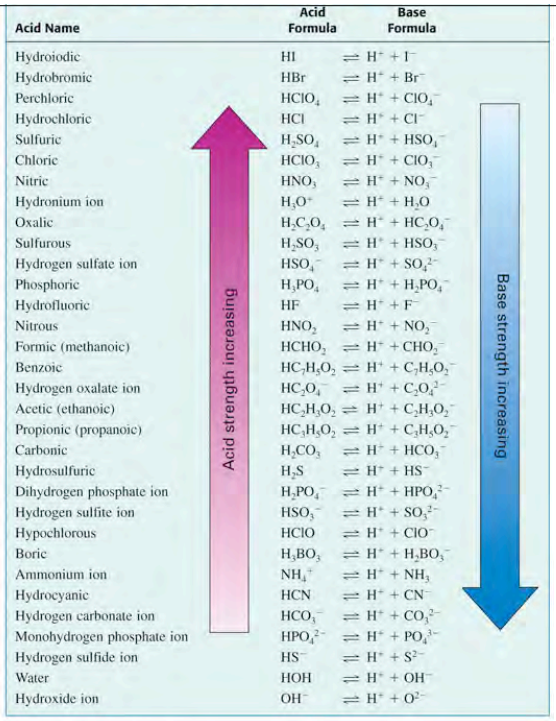
Strong and weak: summary

- Stronger acid = weaker conjugate base
  - The conjugate base is poor at accepting a proton
  - The acid is good at donating a proton
  - The species prefers to be de-protonated!

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

- Weak acid = stronger conjugate base
  - The conjugate base is good at accepting a proton
  - The acid is poor at donating a proton
  - The species prefers to be protonated!

$$C_2H_3O_2H(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$



Reactivity of acids

- Most acid-base reactions are reversible. Can we predict which will be present in greater concentration at equilibrium : reactants or products?

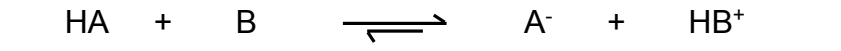
- A stronger acid is good at donating protons: It is relatively reactive
- A stronger base is good at accepting protons: It is relatively reactive
- A weaker acid is a poor proton donor: It is relatively inert
- A weaker base is a poor proton acceptor: It is relatively inert

Reactivity of acids

- It's all about the conjugate base!
- If the CB has available electrons (-) it will hold a proton (+) tightly - strong conjugate base, weak acid (eg acetic acid)
- If the CB has a noble gas configuration, electrons are not available for bonding and the proton is not held tightly - weak conjugate base, strong acid (eg HCl)

Proton-transfer reactions at equilibrium:

- The stronger acid will transfer a proton to the stronger base, yielding the weaker acid and weaker base as favored species at equilibrium



Strong acid: good proton donor	Strong base: good proton acceptor	Weak base: poor proton acceptor	Weak acid: poor proton donor

Example

- Write the equation for the reaction between hydrogen sulfate ion and hydroxide ion.
- Predict which side will be favored at equilibrium.

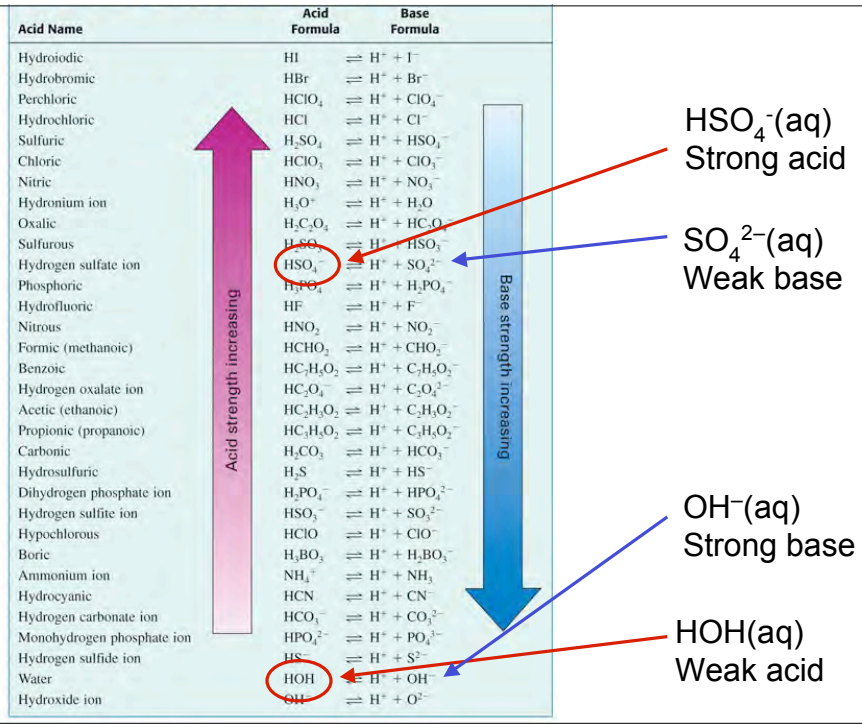
Step 1: Write the equation for the proton transfer

$$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$

Step 2: Label acids and bases

$$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$

Acid Base Base Acid



Example

Acids: $HSO_4^-(aq) > H_2O(l)$

Bases: $SO_4^{2-}(aq) < OH^-(aq)$

$$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$

Stronger acid	Stronger base	Weaker base	Weaker acid

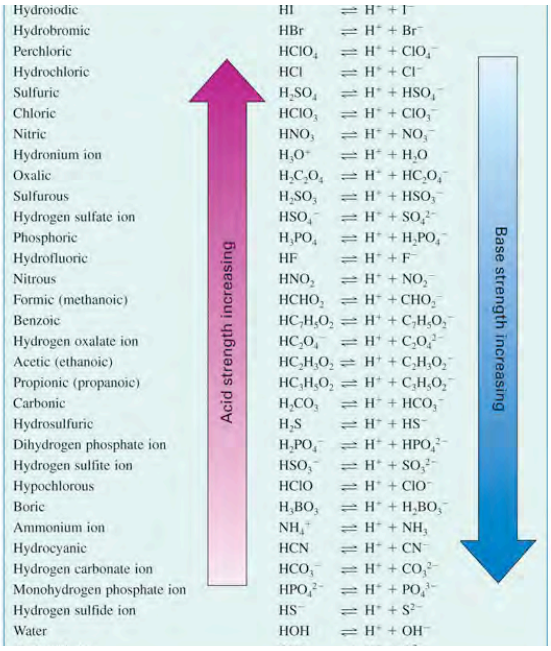
Reaction is favored in the forward direction

Chalkboard example

- For the following acids and bases complete the proton transfer equation and predict the direction in which the resulting equilibrium will be favored

$NH_4^+(aq) + H_2BO_3^-(aq)$

$NO_2^-(aq) + H_3O^+(aq)$



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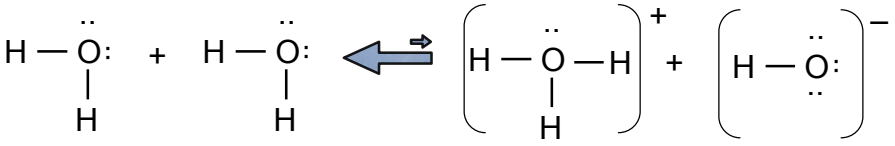
The water equilibrium

- Autoionization of water



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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The water equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

- For pure water at 25°C, $[H^+] = 1.0 \times 10^{-7}$ M (this is a measured quantity)
- Every H_2O that breaks apart creates one OH^- and one H^+
- So $[OH^-] = [H^+]$ in pure water
- $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

- Thinking like a chemist: one in ten million H-bonded water molecules give their proton to another H_2O

The water equilibrium

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

- In pure water, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

Equilibrium constant = $K_w = [H^+][OH^-]$

$= (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$

What are acids and bases?

- An aqueous solution is said to be **neutral** if $[H^+] = [OH^-]$

For pure water at 25°C,
$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

- If $[H^+] > [OH^-]$, a solution is **acidic**

$[H^+] > 1.0 \times 10^{-7}$ M and
$[OH^-] < 1.0 \times 10^{-7}$ M

- If $[OH^-] > [H^+]$, a solution is **basic**

$[OH^-] > 1.0 \times 10^{-7}$ M and
$[H^+] < 1.0 \times 10^{-7}$ M

Example

- What is the hydrogen ion concentration in a solution in which the hydroxide ion concentration is 10^{-4} M?
- Is the solution acidic or basic?

GIVEN: $[OH^-] = 10^{-4}$ M *WANTED:* $[H^+]$

EQUATION: $K_w = [H^+]\,[OH^-] = 1.0 \times 10^{-14}$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

Since $[H^+] = 10^{-10} < [OH^-] = 10^{-4}$,
the solution is basic

A touch of math here:

- Multiplying numbers in exponential notation: add the powers

$(1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$

- simple demonstration:

$2^3 \times 2^5 = (2 \times 2 \times 2) \times (2 \times 2 \times 2 \times 2 \times 2) = 2^8$

- Division: subtract the powers

$(1.0 \times 10^{-28}) \times (1.0 \times 10^{-21}) = 1.0 \times 10^{-7}$

- simple demonstration:

$$2^5 / 2^3 = \frac{(2 \times 2 \times \cancel{2 \times 2 \times 2})}{\cancel{(2 \times 2 \times 2)}} = 2^2$$

Logarithms or logs

- The logarithms of a number to a given base is the power or exponent to which the base must be raised in order to produce the number
- if $x = b^y$ then $y = \log_b(x)$
- $\log_{10}(1 \times 10^7)$ is 7
- $\log_{10}(1 \times 10^8)$ is 8
- $\log_{10}(6.2 \times 10^7)$ is 7.79



John Napier conceived the idea of logarithms in 1594 and spent the next 20 years doing seven million calculations by hand before he perfected the system.

Logarithms or logs

$\log_{10}(1 \times 10^{-7})$ is -7
$\log_{10}(0.0001)$ is -4
$\log_{10}(0.00001)$ is -5
$\log_{10}(0.00002)$ is -4.699

Play with the log button on your calculator until this starts to make sense

Why use logarithms ?

- Multiplying very large or very small numbers was extremely difficult before the advent of calculators
- It is much more convenient for numbers that have large powers of 10
- For example: concentrations of $[H^+]$ and $[OH^-]$!

The p function

- p is math short-hand for ' -1 x $\log_{10}$ '

Applied to $[H^+]$ and $[OH^-]$,

$pH = -\log_{10}[H^+]$

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

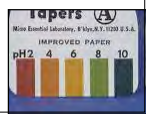
In pure water, $[H^+] = [OH^-] = 10^{-7}$ M

$pH = pOH = -\log_{10}(10^{-7}) = 7$

pH and pOH

- An aqueous solution is **neutral** if $[H^+] = 10^{-7}$ M
- A solution is **acidic** if $[H^+] > 10^{-7}$ M
- A solution is **basic** if $[H^+] < 10^{-7}$ M

- Translating concentrations to pH's:
  - Neutral: pH = 7
  - Acidic: pH < 7
  - Basic: pH > 7



Example

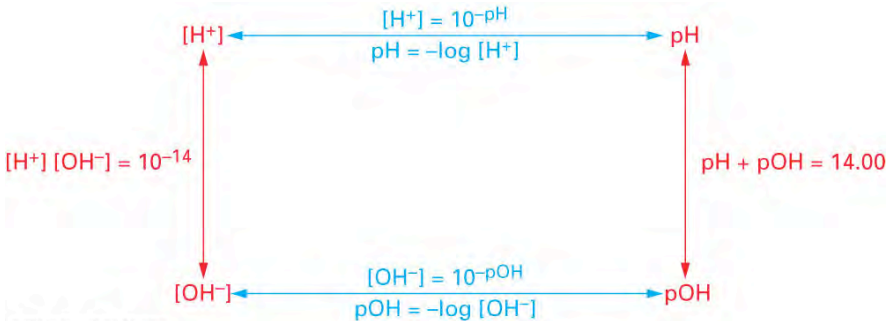
- The hydrogen ion concentration of a solution is 2.7×10^{-6} M.
- What are the pH, pOH, and hydroxide ion concentration?

$$pH = -\log_{10}[H^+] = -\log_{10}(2.7 \times 10^{-6}) = 5.57$$

$$pH + pOH = 14$$
$$pOH = 14.00 - pH = 14.00 - 5.57 = 8.43$$

$$[OH^-] = 10^{(-pOH)} =$$
$$10^{(-8.43)} = 3.7 \times 10^{-9} \text{ M}$$

Working with pH and pOH



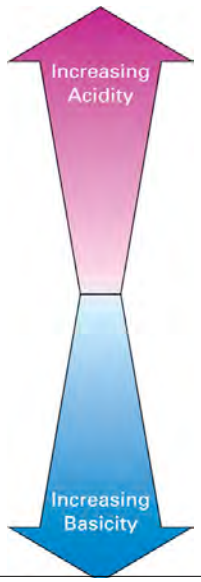
The pH Loop

Given the value for any corner of the loop, all other values may be calculated by progressing round the loop (in either direction)

Interpreting pH Values

Table 17.3 pH and Hydrogen Ion Concentration

$[H^+]$	$[H^+]$	pH	Acidity or Basicity*
1.0	10^0	0	Strongly acid pH < 4
0.1	10^{-1}	1	
0.01	10^{-2}	2	
0.001	10^{-3}	3	
0.0001	10^{-4}	4	
0.0001	10^{-4}	4	Weakly acid 4 ≤ pH < 6
0.00001	10^{-5}	5	
0.000001	10^{-6}	6	
0.000001	10^{-6}	6	Neutral (or near neutral) 6 ≤ pH < 8
0.0000001	10^{-7}	7	
0.00000001	10^{-8}	8	
0.00000001	10^{-8}	8	Weakly basic 8 ≤ pH < 10
0.000000001	10^{-9}	9	
0.0000000001	10^{-10}	10	
0.0000000001	10^{-10}	10	Strongly basic 10 ≤ pH
0.00000000001	10^{-11}	11	
0.000000000001	10^{-12}	12	
0.0000000000001	10^{-13}	13	
0.00000000000001	10^{-14}	14	



Calculating K_a, the equilibrium constant, for weak acids

- Strong acids can be assumed to be completely dissociated
- For weak acids (K_a between 1 x 10^{-3} and 1 x 10^{-13}) the equilibrium constant can be estimated from the pH of a known concentration

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$pH = -\log [H^+], \quad \text{so } [H^+] = 10^{-pH}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

Example

Calculate the K_a for benzoic acid ($C_6H_5CO_2H$).
When 4.2g of benzoic acid are dissolved in 1 L of water the pH is 2.84

1) Write the equation and the equilibrium constant expression

$$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$$

$$Ka = \frac{[C_6H_5CO_2^-]\,[H^+]}{[C_6H_5CO_2H]}$$

2) Determine the relative concentrations of the species

The total concentration of benzoic acid is:

$$[C_6H_5CO_2H] = \frac{4.2g\ C_6H_5CO_2H}{122g\ C_6H_5CO_2H} = 0.034\ M$$

The concentration of dissociated benzoic acid is:

$$[\ C_6H_5CO_2^-\ ] = [\ H^+\ ] = 10^{-pH} = 10^{-2.84} = 1.45 \times 10^{-3}\ M$$

Less than 5% of the benzoic acid is deprotonated = weak acid

3) Plug these numbers back into the K_a expression

$$K_a = \frac{[C_6H_5CO_2^-\ ]\ [\ H^+\ ]}{[\ C_6H_5CO_2H\ ]} = \frac{(1.45 \times 10^{-3})\ (1.45 \times 10^{-3})}{0.034}$$

$$K_a = 6.2 \times 10^{-5}$$

Notice that we have assumed that all the acid is undissociated.
If we solve correctly it doesn't make much difference for weak acids:

$$K_a = \frac{[C_6H_5CO_2^-\ ]\ [\ H^+\ ]}{[\ C_6H_5CO_2H\ ]} = \frac{(1.45 \times 10^{-3})\ (1.45 \times 10^{-3})}{(0.034 - 1.45 \times 10^{-3})}$$

$$K_a = 6.5 \times 10^{-5}$$

Buffer solutions

- A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.
- It has the property that the pH of the solution changes very little when a small amount of acid or base is added to it.
  - Add base: it is neutralized by (reacts with) the acid
  - Add acid: it is neutralized by (reacts with) the base
- Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications.

Buffer solutions

- In a buffer solution there is an equilibrium between a weak acid, HA, and its conjugate base, A-

$$HA \rightleftharpoons H^+ + A^-$$

- When hydrogen ions are added to the solution the equilibrium moves to the left, in accordance with Le Chatelier's principle
- When hydroxide ions are added the equilibrium moves to the right as hydrogen ions are removed in the reaction

$$H^+ + OH^- \rightleftharpoons H_2O$$

- Some of the added material is consumed in shifting the equilibrium and the pH changes by less than it would do if the solution were not buffered.

Example: the $H_2PO_4^-/HPO_4^{2-}$ system

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

$$K_a = \frac{[H^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]}$$

Add acid:

$$H^+(aq) + HPO_4^{2-}(aq) \longrightarrow H_2PO_4^-(aq)$$

Add base:

$$OH^-(aq) + H_2PO_4^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(l)$$