ACIDS & BASES

Unit 8

Theories, Properties, pH, K_a, K_b, K_w, Buffers, Neutralizations, Titrations, Indicators

IN THE FUTURE...

- IAs are coming...things to remember

  - MUST be individual - NO shared work!

  - Follow the rubric and answer ALL questions associated with the lab

  - Explanations for what you are doing are helpful

  - When you take a measurement - write down every digit you know absolutely and ESTIMATE a final digit - the thermometers went to the nearest whole number - you should have measured to the nearest tenth (whatever the scale is broken down to plus one more number)

ARRHENIUS

- acid - substances that dissolves in water to form H^+

- base - substances that dissolves in water to form OH^-

- very limited theory - only discusses aqueous solutions

BRØNSTED - LOWRY

- Focuses on transfer of H^+ (a proton) ions during an acid-base reaction

- acids - donates a proton

- bases - accepts a proton

- $HCl + NH_3 \Leftrightarrow NH_4^+ + Cl^-$

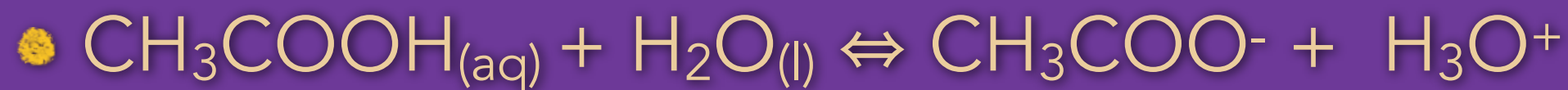- act of donating cannot happen in isolation - can't donate without an acceptor

CONJUGATE PAIRS

- Reaction between acid A and base B:

  - $HA + B \Leftrightarrow A^- + BH^+$

    - HA & A^- → conjugate acid-base pair

    - B & BH^+ → conjugate acid-base pair

CONJUGATE PAIRS

- $CH_3COOH_{(aq)} + H_2O_{(l)} \Leftrightarrow CH_3COO^- + H_3O^+$

  - Label the conjugate acid-base pairs in the reaction

- In a conjugate pair, the acid will always have one more proton than its conjugate base - makes it easy to predict formulas

PREDICTING FORMULAS

- Write the conjugate base for the following:

  - H_3O^+

  - NH_3

  - H_2CO_3

- Write the conjugate acid for the following

  - NO_2^-

  - OH^-

  - CO_3^{2-}

AMPHOTERIC / AMPHIPROTIC

being able to act as an acid or a base

- *what is water acting as in both reactions?*

- $CH_3COOH_{(aq)} + H_2O_{(l)} \Leftrightarrow CH_3COO^- + H_3O^+$

- $NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

- To act as a B-L acid - must be able to dissociate and release H^+ ions

- To act as a B-L base - must be able to accept H^+ - must have a lone pairs of electrons

PROPERTIES OF ACIDS/BASES

- How do we know if something is an acid or a base?

- indicators

indicator	color in acid	color in base
litmus	pink	blue
methyl orange	red	yellow
phenolphthalein	colorless	pink

ACID/BASE REACTIONS

- Acids react with metals, bases, carbonates to form salts

  - salt - when a hydrogen from an acid is replaced with a metal or another positive ion
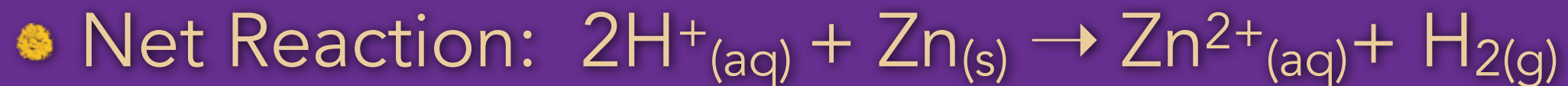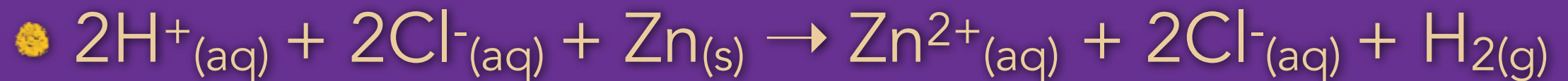
ACID/BASE REACTIONS

3 types of reactions

1. **Acid + metal → salt + hydrogen**

$$2HCl_{(aq)} + Zn_{(s)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

- Written as an ionic equation

- $2H^+_{(aq)} + 2Cl^-_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_{2(g)}$

- Net Reaction: $2H^+_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

- $Cl^- \rightarrow$ spectator ion because it does not change

ACID/BASE REACTIONS

2. **Acid + Base → Salt + Water**

$$HCl + NaOH \rightarrow NaCl + HOH$$

- This is the 'classic' neutralization

- $H^+ + OH^- \rightarrow HOH$

- This reaction can be studied quantitatively using a titration - later in chapter

- (acid soil, indigestion)

ACID/BASE REACTIONS

3. Acid + Carbonate → Salt + Water + CO$_2$

(An IB Favorite!)

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$

☀ will give off bubbles known as effervescence

STRONG AND WEAK: ACIDS AND BASES

- $HA_{(aq)} \Leftrightarrow H^+_{(aq)} + A^-_{(aq)}$

- The strength of the acid depends on where this equilibrium lies

- <u>strong acid</u> - equilibrium will lie to the right

  - Fully dissociated (i.e. HCl)

- <u>weak acid</u> - equilibrium will lie to the left

  - Partially dissociated (i.e. CH_3COOH)

STRENGTH...

- Same is true for bases:

  - strong: $NaOH_{(aq)} \Leftrightarrow Na^+_{(aq)} + OH^-_{(aq)}$

  - weak: $NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+_{(aq)} + OH^-_{(aq)}$

STRONG VS. WEAK

- The number of weak acids/bases far outnumber the strong ones

  - Common strong acids: HCl, HNO$_3$, H$_2$SO$_4$

  - Common strong bases: LiOH, NaOH, KOH, Ba(OH)$_2$

    - remember these - all others will be weak

DISTINGUISHING BETWEEN STRONG AND WEAK

- Three properties that depend on the concentration of the ions:

  1. Electrical Conductivity

  2. Rate of reaction - faster rate with stronger acids

  3. pH - lower the pH, stronger the acid

The pH Scale

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

  - or

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

- features of the pH scale:

  - pH numbers are usually positive and have no units

  - pH is inversely related to $[H^+]$

  - The change of one pH unit = 10 fold change in $[H^+]$

pH

- Very wide range of concentration values into a 14 point scale

  - a change from 5.5 to 4.5 for the pH of rain can be fatal to some plant life

  - 7.4 - pH of our blood - 6.9 and 7.9 can be fatal (controlled by buffers [later])

  - Depends on relationship between $[H^+]$ and $[OH^-]$
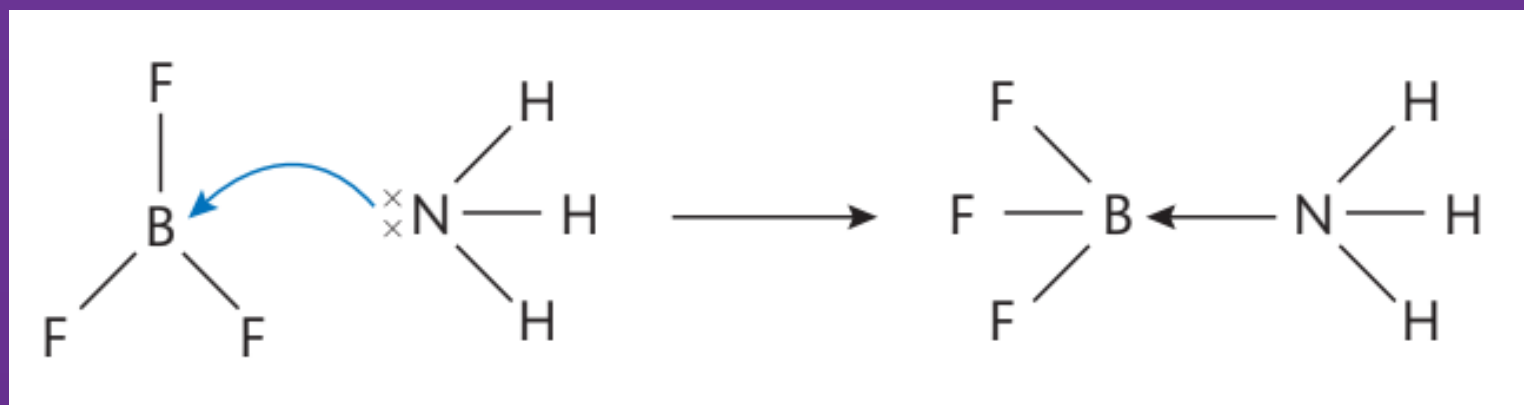
18.1 LEWIS ACID/BASE THEORY

- <u>Lewis</u> - discussed the transfer of electron <u>pairs</u>

- Lewis Acid - electron pair acceptor

- Lewis Base - electron pair donor

  - Lewis Bases & B-L Bases are same group of compounds

    - both must have a lone pair of electrons to donate

18.1 LEWIS ACID/BASE THEORY
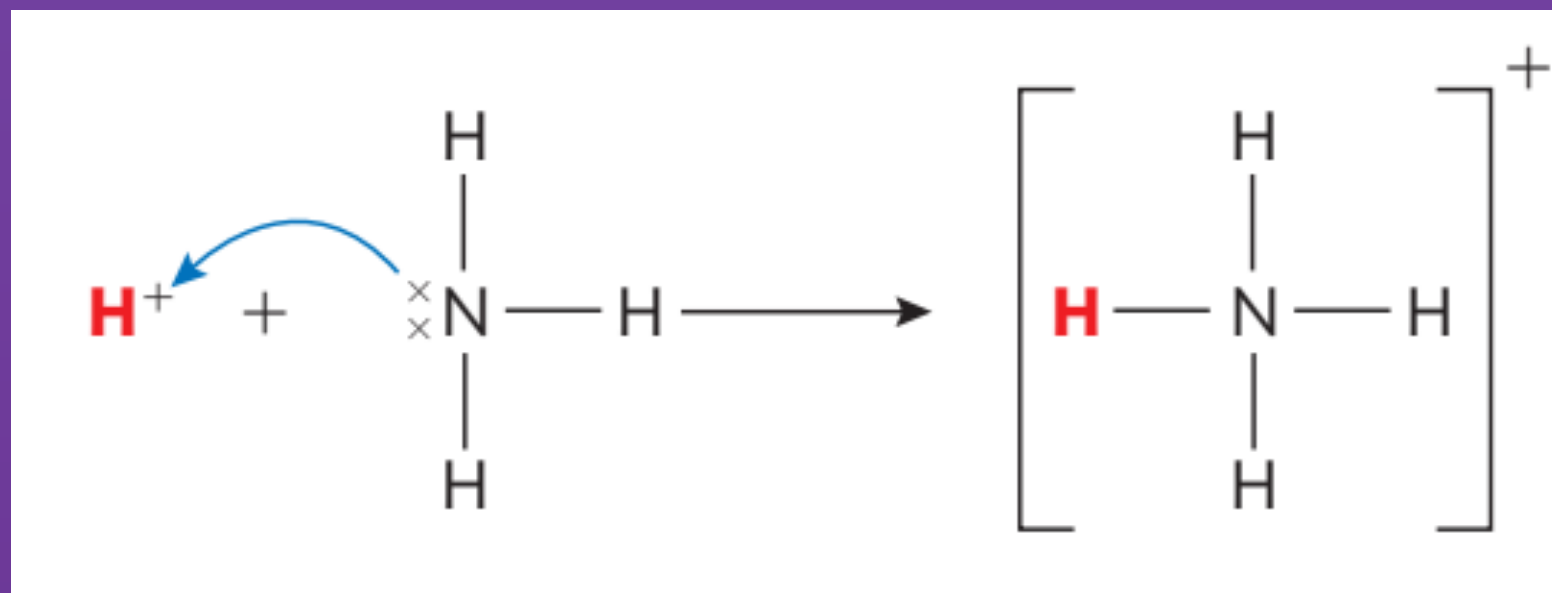
- The curly arrow is a convention used to show the donation of an electron pair.

- BF_3 has an incomplete octet, so it can act as a Lewis acid by accepting an electron pair from ammonia.
- A **coordinate bond** is formed.

LEWIS ACIDS/BASES

- $Cu^{2+}_{(aq)} + 6H_2O_{(l)} \Leftrightarrow [Cu(H_2O)_6]^{2+}$

- in this situation, H_2O is a ligand, donating a pair of electrons to the copper
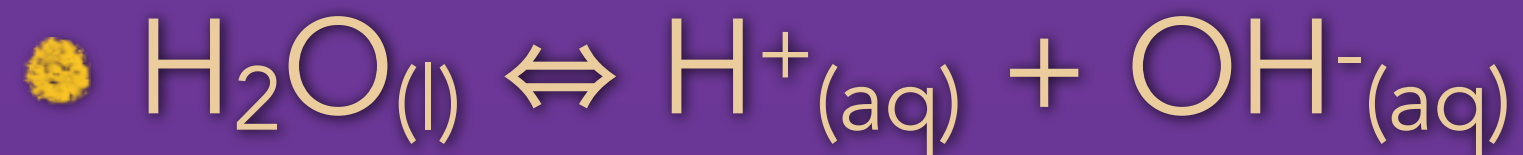
- $\therefore$ ligands will be the Lewis base

COMPARISON OF TWO THEORIES

Theory	Definition of acid	Definition of base
Brønsted-Lowry	Proton donor	Proton acceptor
Lewis	Electron pair acceptor	Electron pair donor

18.2 - Calculations involving acids and bases

- Ionization of water:

  - $H_2O_{(l)} \Leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$

  - Therefore K_c = ??

  - $K_c [H_2O] = [H^+][OH^-]$

  - $K_c[H_2O] = K_w = [H^+][OH^-]$

K$_W$

- K$_w$ has a fixed value @ 25°C = 1.00 x 10^{-14}

- In pure water [H$^+$] = [OH$^-$]

- So….[H$^+$] = 1.00 x 10^{-7} which gives pH = 7

- K$_w$ is temperature dependent…page 367!

H⁺ vs. OH⁻

- The relationship is inverse:

  - acidic solution $\rightarrow$ $[H^+] > [OH^-]$ pH < 7

  - neutral solution $\rightarrow$ $[H^+] = [OH^-]$ pH = 7

  - basic solution $\rightarrow$ $[H^+] < [OH^-]$ pH > 7

- If we know one, we can calculate the other…

EXAMPLE…

- A sample of blood at 25°C has [H^+] = 4.60 x 10^{-8} mol dm^{-3} (page 359)

  - Calculate the concentration of OH$^-$ and state whether the blood is acidic, basic or neutral.

  - How would you expect its pH to be altered at body temperature (37°C)?

pH & pOH

- $K_W = [H^+][OH^-] = 1.00 \times 10^{-14}$ @ 25°C

- $10^{-pH} \times 10^{-pOH} = 1.00 \times 10^{-14}$

  - take the negative log of both sides

- pH + pOH = 14

EXAMPLE

- Lemon juice has a pH of 2.90 @ 25°C. Calculate its [H$^+$], [OH$^-$], and pOH. (page 369)

EXAMPLE

- Calculate the pH of the following at 298K. (page 370)

  - 0.10 mol dm^{-3} NaOH$_{(aq)}$

  - 0.15 mol dm^{-3} H$_2$SO$_{4(aq)}$

- Why are some acids and bases considered weak?

- How do you think we can measure the amount that has dissociated?

- Generic weak acid HA dissociating in water

  - $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

  - what is K_c going to look like?

WEAK BASES

- Generic weak base B dissociating in water

  - $B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$

  - what is K_c going to look like?

K_A AND K_B

- K_a - acid dissociation constant

- K_b - base dissociation constant

- $[H_2O]$ is considered a constant so it is combined with K_c.

- Write the expressions for K_a and K_b for the following acid and base.

  - $CH_3COOH_{(aq)}$

  - $NH_{3(aq)}$

Calculations involving K_a and K_b

- Things to remember for K_a and K_b calculations

  - The given concentration is its **_initial_** concentration, before dissociation occurs

  - The pH (or pOH) refers to concentration of H^+ and OH^- at **_equilibrium_**

  - The values substituted into K_a and K_b expressions must be **_equilibrium_** values

  - when dissociation is small…use the approximations

    - $[acid]_{initial} = [acid]_{equilibrium}$ and $[base]_{initial} = [base]_{equilibrium}$

EXAMPLE

- Calculate K_a at 25°C for a 0.01 mol dm^{-3} solution of ethanoic acid, CH_3COOH. It has a pH of 3.4 at this temperature.

  - Use RICE!

ANOTHER

- Calculate K_b for a 0.100 mol dm^{-3} solution of methylamine, CH_3NH_2. Its pH is 11.80 at this temperature.

EXAMPLE...

- A 0.75 mol dm^{-3} solution of ethanoic acid has a value for $K_a = 1.8 \times 10^{-5}$ at a specified temperature. What is its pH at this temperature?

ONE MORE...

- A 0.20 mol dm^{-3} aqueous solution of ammonia has a K_b of 1.8 x 10^{-5} at 25°C. What is its pH?

pK$_a$ and pK$_b$

- Who enjoys using those very small numbers with negative exponents for K$_a$ and K$_b$?

  - You're in luck!!

- Just as we do with small concentrations → pH & pOH we will use the -log$_{10}$ to convert K$_x$ to pK$_x$

  - pK$_a$ = -log$_{10}$K$_a$ & pK$_b$ = -log$_{10}$K$_b$

  - K$_a$ = 10^{-pKa} & K$_b$ = 10^{-pKb}

INFORMATION ON K_A AND K_B

- pK$_a$ and pK$_b$ are usually positive and have no units - truly only useful for weak acids and bases

- The relationship between K$_a$ and pK$_a$ and between K$_b$ and pK$_b$ are inverse (stronger the acid/base, larger the K$_{a/b}$ lower the pK$_{a/b}$)

- pK$_a$ and pK$_b$ must be quoted at a specific temperature

- More data booklet!! - **Table 21** - common pK$_a$ and pK$_b$ values

K_A, K_B, AND K_W

- $K_a \times K_b = [H^+][OH^-] = K_w$

  - take negative log of both sides

- $pK_a + pK_b = pK_w$

- at 25°C $K_w = 1.00 \times 10^{-14}$

- $pK_w = 14.00$

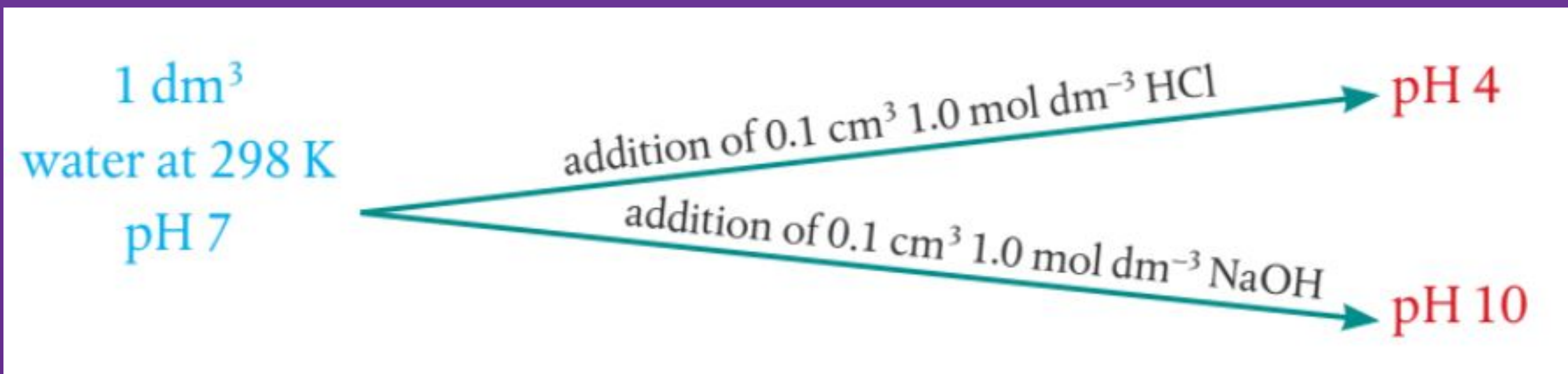- $\therefore pK_a + pK_b = 14.00$ (at 25°C)

CONJUGATE PAIRS

- $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

  - $K_a = 1.8 \times 10^{-5}$

  - what do you know about the dissociation in this reaction?

  - Is this a strong acid?

  - What about its conjugate base (CH_3COO^-)?

    - Chart on page 377

EXAMPLE

- The pK_a of ethanoic acid, CH_3COOH, at 25°C is 4.76. What is the pK_b of its conjugate base, CH_3COO^-?

- The pK_a of methanoic acid, $HCOOH$ at 25°C is 3.75. Is its conjugate base weaker or stronger than that of ethanoic acid?

BUFFER SOLUTIONS

- something that acts to reduce the impact of one thing on another (a shock absorber)

- A *buffer solution* is resistant to changes in pH with the addition of **small amounts** of acid or alkali

$1\ dm^3$
water at 298 K
pH 7

addition of $0.1\ cm^3\ 1.0\ mol\ dm^{-3}\ HCl$ → pH 4

addition of $0.1\ cm^3\ 1.0\ mol\ dm^{-3}\ NaOH$ → pH 10

HOW BUFFERS WORK

- **2 main types of buffers**

  - acidic - maintain the pH at a value less than 7

  - basic - maintain the pH at a value more than 7

- Mixture of 2 solutions

  - each contain a conjugate acid-base pair

ACIDIC BUFFERS

- Made by mixing a weak acid with a solution of its salt of a strong alkali

  - ie. $CH_3COOH_{(aq)}$ with $NaCH_3COO$

    - weak acid   salt of weak acid with strong alkali

  - Two equilibria exist in this buffer

    - $CH_3COOH \Leftrightarrow CH_3COO^- + H^+$

    - $NaCH_3COO \Leftrightarrow Na^+ + CH_3COO^-$

Has high concentrations of both acid and base - ready to react with either H^+ or OH^-

RESPONSE TO ADDED ACIDS AND BASES

- Adding acid -

  - $CH_3COO^- + H^+ \Leftrightarrow CH_3COOH$

- Adding base

  - $CH_3COOH + OH^- \Leftrightarrow CH_3COO^- + H_2O$

BASIC BUFFERS

- Made by mixing a weak base with a solution of its salt of a strong acid

  - ie. NH_3 with NH_4Cl

    - $NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

    - $NH_4Cl \rightarrow NH_4^+ + Cl^-$

Has high concentrations of both acid and base - ready to react with either H^+ or OH^-

Response to added acids and bases

- Addition of acid

  - H^+ combines with the base NH_3 to form NH_4^+

- Addition of base

  - OH^- combines with the acid NH_4^+ to form NH_3 and water - removing most of OH^-

What can influence buffers?

- <u>Dilution</u>

  - does not change the pH of the buffer, but it does lower the buffering capacity (the amount of acid or base a buffer can absorb without significant changes in pH) - dependent on Molar concentrations

- <u>Temperature</u>

  - Temperature affects the values of K_a and K_b therefore affects the pH (must be held constant)

    - What's another process that temperature must be constant?

SALT HYDROLYSIS

- Tell me what you know about neutralization reactions

- acid + base → salt + water

- Is this solution neutral? Will it always be?

- What do you think the pH will depend on?

ANION HYDROLYSIS

- HA - acid A^- - conjugate base

- When the acid is weak, this conjugate base, A^-, is strong enough to hydrolyse water:

  - $A^-_{(aq)} + H_2O \rightarrow HA + OH^-$

  - This release of OH^- will cause an increase in pH

CATION HYDROLYSIS

- MOH - base M^+ - conjugate

- When the base is weak, and the conjugate is a non-metal, (ie. NH_4^+), it is able to hydrolyse water:

  - $M^+ + H_2O \rightarrow MOH + H^+$ (decrease in pH)

CATION HYDROLYSIS

- When the cation is a metal, there is a little complexity involved - depends on charge density as well

- For ions with a +2 or +3 charge and are small, they hydrolyse water to form a complex

  - The charge center attracts the water and forms OH bonds - H^+ are then released into the solution - (acidic)

CATION HYDROLYSIS

- The ions that can do this:

  - Be^{+2}, Al^{+3}, and transition metals – most notably - Fe^{+3}

- Group 1 & other group 2 metals do not have sufficient charge density to be acidic in water

ACID/BASE BEHAVIOR

- What happens when:

  - Strong Acid - Strong Base

  - Weak Acid - Strong Base

  - Strong Acid - Weak Base

  - Weak Acid - Weak Base

TITRATION

- Quick Vocabulary:

  - Burette - long graduated cylinder with stopcock

  - Pipette - small glass measuring tube

  - Equivalence Point - point at which the acid and base exactly neutralize each other

TITRATION CURVES

- pH vs. Volume added

- Four types of Curves:

  - Strong Acid/Strong Base

  - Weak Acid/Strong Base

  - Strong Acid/ Weak Base

  - Weak Acid/Weak Base

- What you need to find out (put in your notes):

  - An example of each

  - Short description

  - Drawing of the titration curve

 - Add any extra relevant information

STRONG ACID & STRONG BASE

- Initial pH = 1 (pH of strong acid)

- pH changes only gradually until equivalence

- Very sharp jump in pH at equivalence: from pH 3 to pH 11

- after equivalence the curve flattens out at a high value (pH of strong base)

- The pH at equivalence = 7.
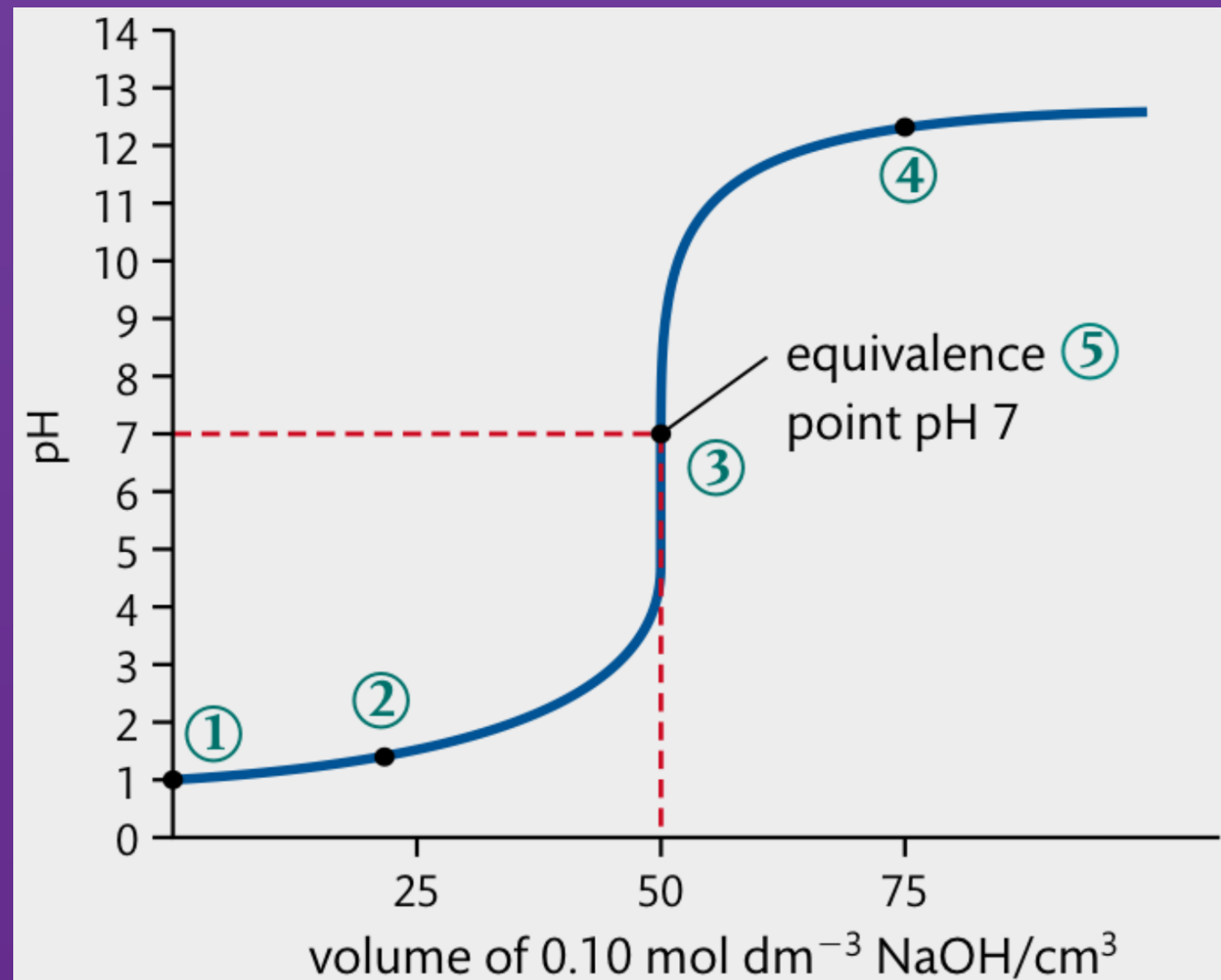
WEAK ACID & STRONG BASE

- Initial pH fairly high (pH of weak acid)

- The pH stays relatively constant until equivalence - labeled as buffer region

- Jump in pH at equivalence from about pH 7.0-11.0, which is not as much of a jump as for a strong acid-strong base titration

- After equivalence the curve flattens out at a high value (pH of strong base)
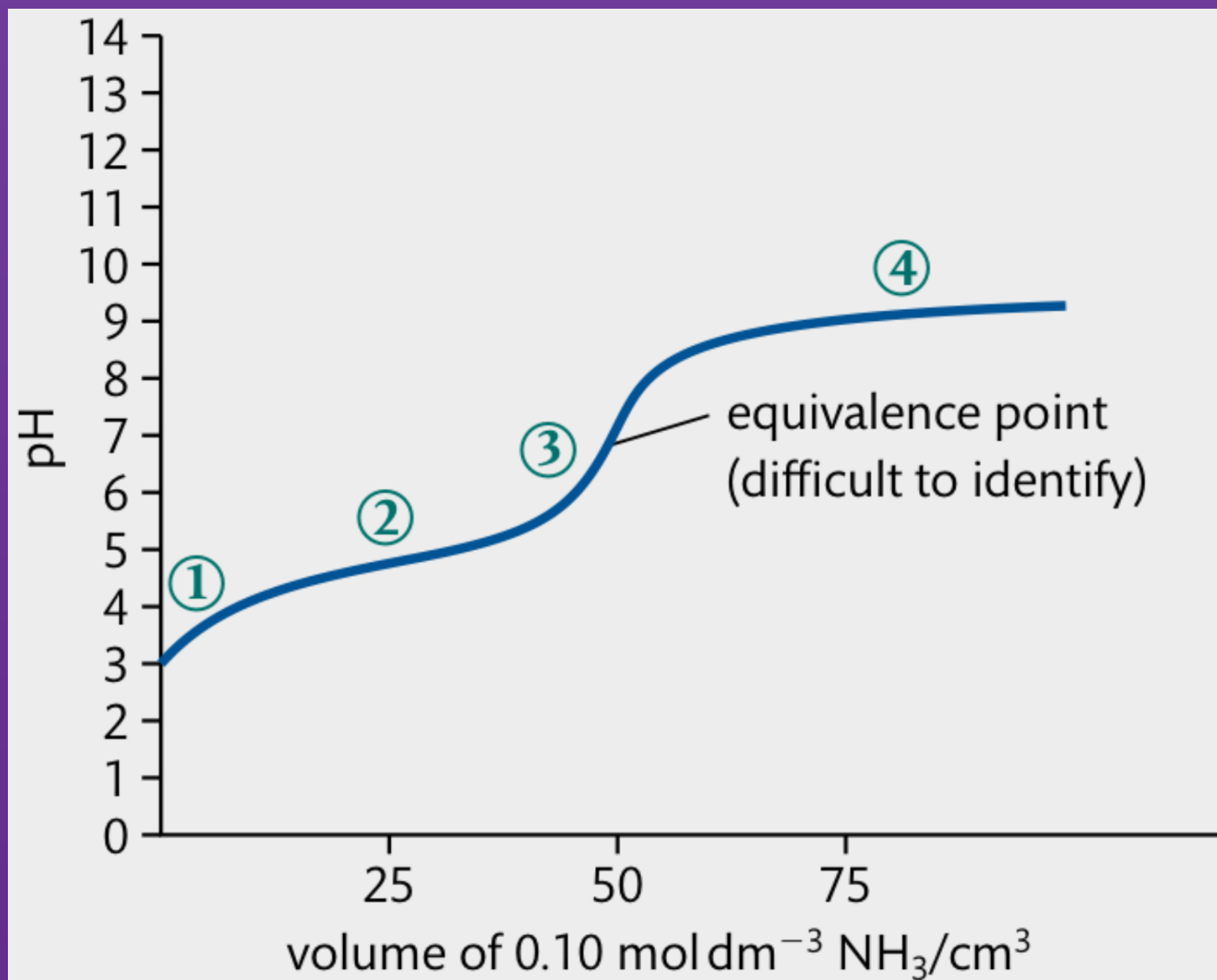
- The pH at equivalence is > 7
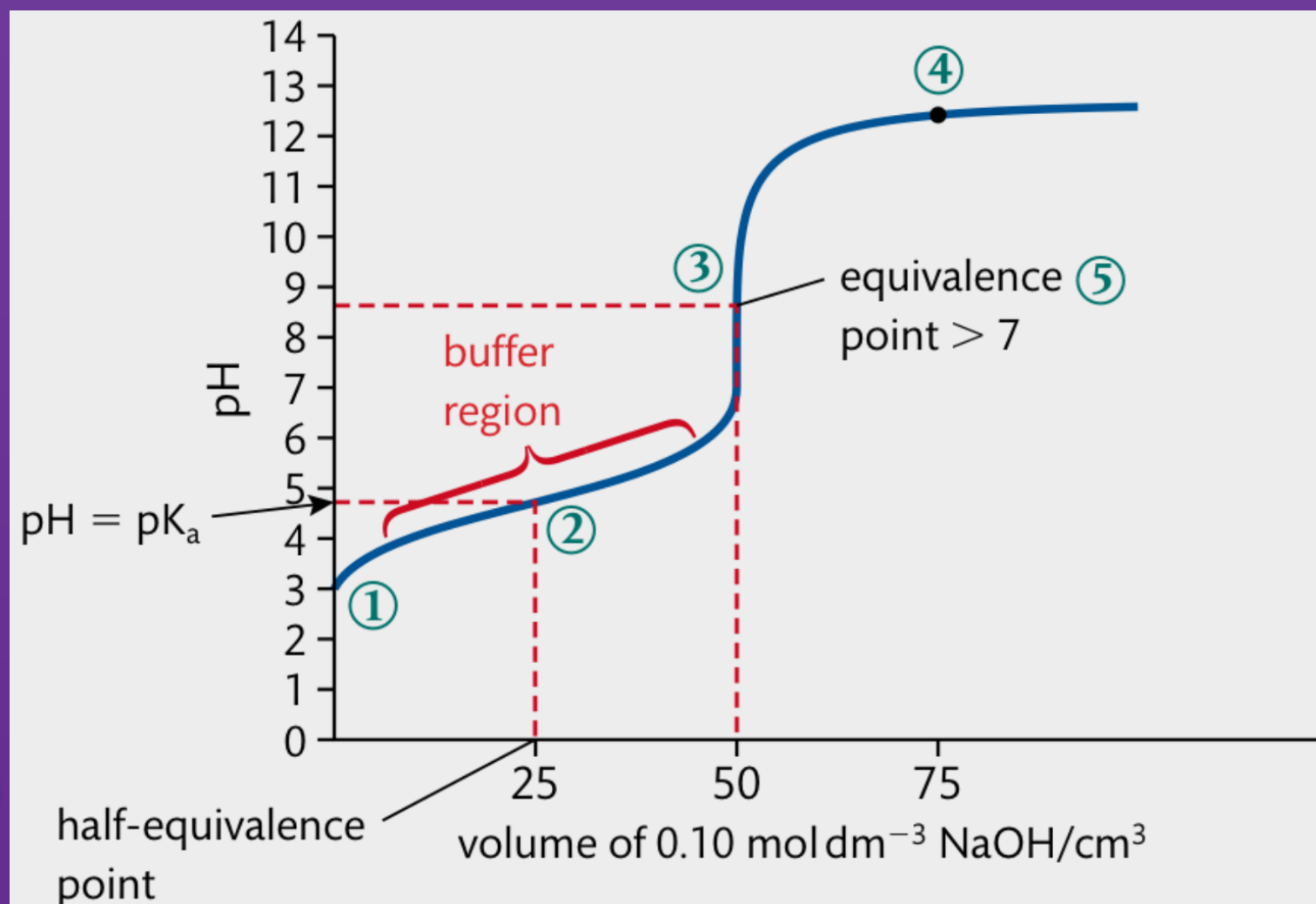
STRONG ACID & WEAK BASE

- Initial pH = 1 (pH of strong acid)

- The pH stays relatively constant through the buffer region to equivalence.

- Jump in pH at equivalence from about pH 3.0-7.0

- After equivalence the curve flattens out at a fairly low pH (pH of weak base)

- The pH at equivalence < 7.
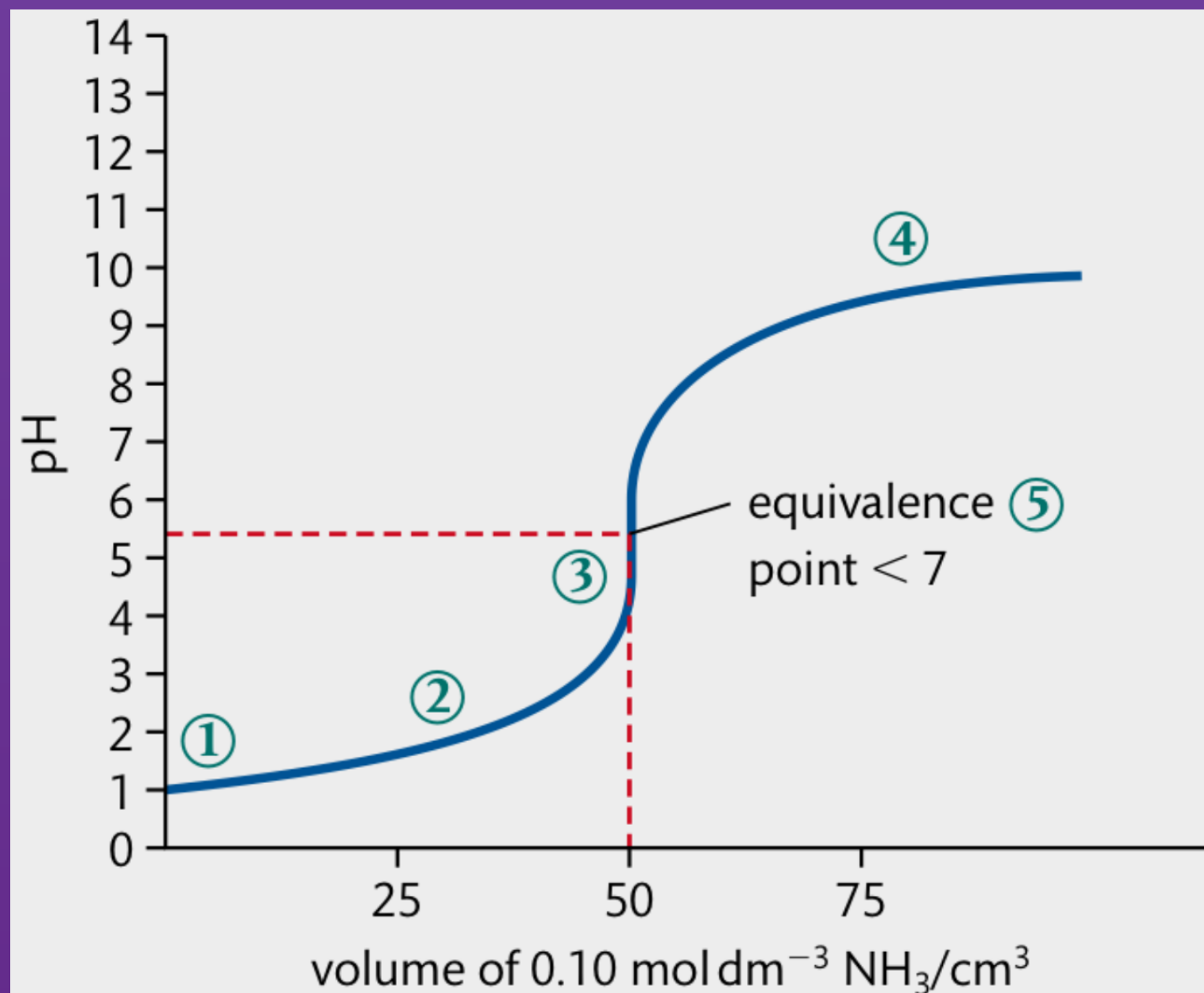
WEAK ACID & WEAK BASE

- Initial pH is fairly high (pH of weak acid)

- Addition of base causes the pH to rise steadily

- Change in pH at the equivalence point is much less sharp than in the other titration

- After equivalence the curve flattens out at a fairly low pH (pH of weak base

INDICATORS

- Either weak acids or bases in which the dissociated and the undissociated forms are different colors

- $HIn \Leftrightarrow H^+ + In^-$

- color A   color B

- Using Le Chatelier's, a shift in H^+ will cause a change in color

WHEN DO INDICATORS CHANGE?

- When the pH = pK_a : known as the change point

- Change points and pK_a are listed on Table 22 ! Yay!

Choosing an Appropriate indicator

- determine what combination of weak and strong acid and base are reacting

- find the pH of the salt solution at the equivalence point

- Choose an indicator with an endpoint in the range of the equivalence point

ACID DEPOSITION

- rain is naturally acidic (dissolved CO_2), pH = 5.6

- Acid Rain: solutions with pH below 5.6

- <u>Primary Pollutants</u>: oxides of sulfur and nitrogen

- <u>Secondary Pollutant</u>: acid rain after the acidic gases dissolve in water.
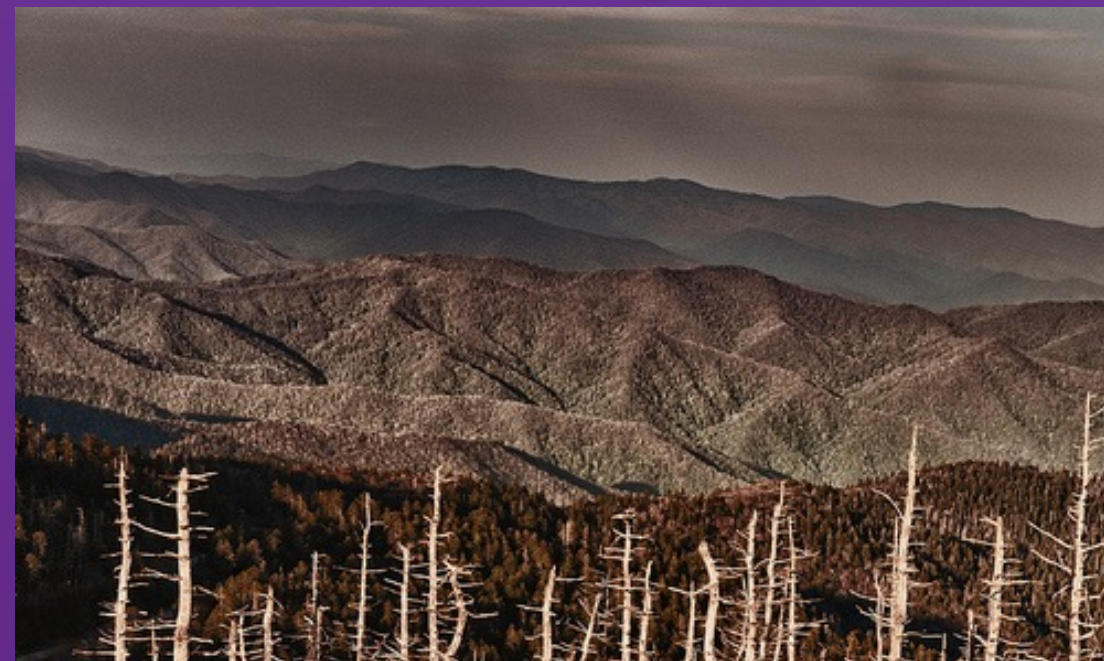
ACID DEPOSITION

- <u>Wet acid deposition</u>: rain, snow, sleet, hail, fog, mist, dew falling to the ground.

- <u>Dry acid deposition</u>: acidifying particles, gases fall to ground as dust/smoke, later dissolving in water to form acids.
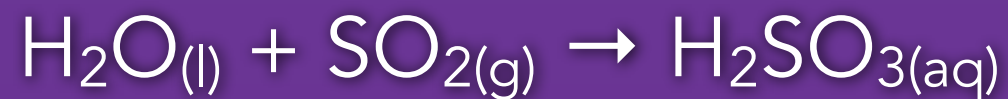
SULFUR OXIDES

- Produced from burning of fossil fuels (coal / heavy oil) in power plants used to generate electricity

- Smelting - extracting metal from ore

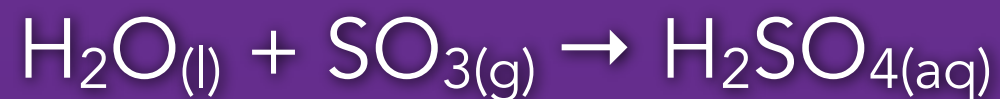- ESTIMATE: 50% of sulfur dioxide comes from burning coal.

SULFUR DIOXIDE

$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$

Colorless gas with a sharp smell (rotten eggs). Dissolves in water to form $H_2SO_{3(aq)}$

$H_2O_{(l)} + SO_{2(g)} \rightarrow H_2SO_{3(aq)}$

Sulfuric acid can also result:

$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)}$
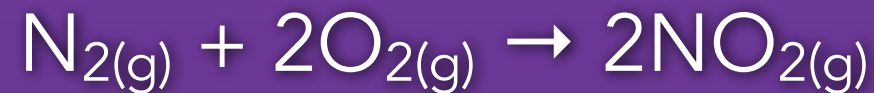
OTHER OXIDATIONS

- Photo-oxidation - during sunlight hours

- Catalyzed by tiny particles of metal (Fe, Mn)

- O_3 or H_2O_2 present as pollutants

- Hydroxyl free radicals:

$$\bullet HO + SO_2 \rightarrow \bullet HOSO_2$$

$$\bullet HOSO_2 + O_2 \rightarrow \bullet HO_2 + SO_3$$

NITROGEN OXIDES

- NO produced from internal combustion engines

- NO_2 also produced (brown gas)

$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Further reaction with water:

$H_2O_{(l)} + 2NO_{2(g)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$

Alternatively:

$2H_2O_{(l)} + 4NO_{2(g)} + O_{2(g)} \rightarrow 4HNO_{3(aq)}$

HYDROXYL FREE RADICALS

- $HO + NO \rightarrow NHO_2$

- $HO + NO_2 \rightarrow HNO_3$

In summary: main components of acid rain are H_2SO_3, H_2SO_4, HNO_2, and HNO_3

EFFECTS OF ACID DEPOSITION

- Materials (stone and metal)

  - marble and limestone are $CaCO_3$ and react with acid to form $CaSO_4$ (with sulfuric acid) and $Ca(NO_3)_2$ (with nitric acid).

  - both are more soluble than the carbonate and so dissolve or cause expansion (cracking the structure)

  - Metals (Fe) also form soluble salts ($FeSO_4$) with sulfuric acid.

  - Aluminum will also react with nitric acid to form soluble $Al(NO_3)_3$ damaging bridges, vehicles and railroad tracks.

EFFECT ON PLANT LIFE

- LEACHING:

- important minerals like Mg^{2+}, Ca^{2+}, and K^+ become soluble and wash away.

- Mg: impedes chlorophyll synthesis

- Al: increased release of this ion damages plant roots

EFFECT ON WATER

- Al^{3+} ions leaching into the water interfere with fish gill function, limiting oxygen intake.

- Results in bodies of water becoming 'dead' - unable to support life.

- Fish can't survive below a pH of 5.

- ***Eutrophication:*** over fertilization of bodies of water, resulting in algal blooms, leading to oxygen depletion.

IMPACT ON HUMAN HEALTH

- Not direct, but increased particulates in atmosphere are linked to asthma, bronchitis and emphysema.

- Irritants to eyes

- Reaction of acid rain with metals could increase heavy metal ion concentration in water supplies (Pb, Al, Cu)

RESPONSES TO ACID RAIN

Reduction of SO$_2$ emissions

1. Pre-combustion

   Hydrodesulfurization - catalytic process to remove sulfur from refined petroleum products

2. Post-combustion

   Flue-gas desulfurization (remove 90% of SO$_2$) by forming CaSO$_4$ which has an industrial use in making plasterboard.

REDUCTION OF NO$_X$

1. Catalytic converters in vehicles

   - hot gases mixed over Pt or Pd based catalysts converting them back to CO$_2$ and N$_2$

2. Lower temperature combustion

   - Recirculating exhaust gases back into the engine lowers temperature to reduce nitrogen oxide emissions.