CHEM 16.1 REVIEWER

A. **Experiment #6: Calorimetry**
B. **Experiment #7: Paper Chromatography**
C. **Experiment #8: Dynamic Equilibrium and Heats of Solution**
D. **Experiment #9: Distillation of Rubbing Alcohol**
E. **Experiment #10: Gases**
F. **Experiment #11: Colligative Properties**
G. **Experiment #12: pH, Conductivity, and Relative Strengths of Acids and Bases**

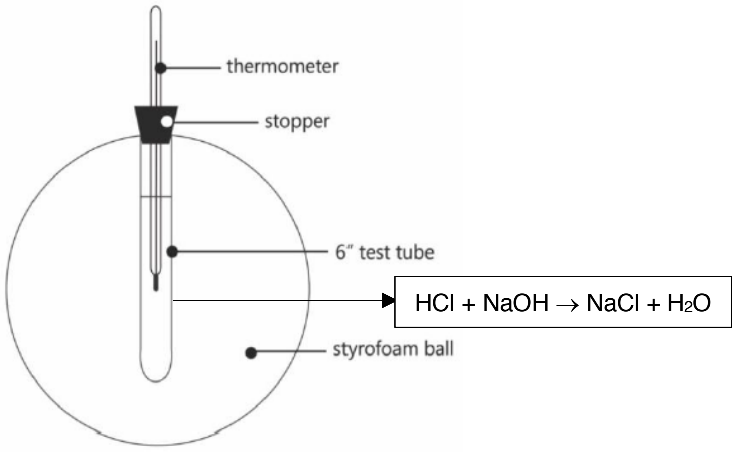
Calorimetry

- process of measuring the amount of heat released or absorbed during a chemical reaction
- 1st law of thermodynamics: the total internal energy of the universe is constant = energy can neither be created nor destroyed, it can only be converted from one form to another
    - Law of Conservation of Energy = universe is an isolated system

Types of Calorimetry

- Constant Pressure Calorimetry = Coffee Cup Calorimeter or Styroball Calorimeter
- Constant Volume Calorimetry = Bomb Calorimeter

Calorimetry set-up



Adiabatic system: no transfer of heat from the system to the surroundings

- Placed an insulator = Styrofoam ball
    - No easy absorbance/release of heat from the system
    - Very low heat capacity
        - Heat capacity = tendency to absorb/release heat

$q_{\text{isolated system}} = q_{rxn} + q_{cal}$
$q_{rxn} + q_{cal} = 0$
Thus, $q_{rxn} = -q_{cal}$

$q_{rxn} = (\Delta H_{rxn})(n_{LR})$
$q_{cal} = C\Delta T$; *where* $C = mc$ *or* nC_m
Thus, $(\Delta H_{rxn})(n_{LR}) = -C_{cal}\Delta T$

If (+) ΔH → absorbed heat → Endothermic; temperature decreases
If (-) ΔH → gives off heat → Exothermic; temperature increases

Procedure

Calibration (Determining heat capacity of calorimeter)

- C_{cal} is highly dependent on the amount of matter
- Need to calibrate because C_{cal} is not constant in all styrofoams; and in test tubes
- ΔH_{rxn} of $HCl + NaOH \rightarrow NaCl + H_2O$ = -55.85 kJ/mol
    - $C_{cal} = \frac{-\Delta H_{rxn} \cdot n_{LR}}{\Delta T}$

Determination of ΔH_{rxn}

- $\Delta H_{rxn} = \frac{-\mathrm{Ccal}\cdot\Delta T}{n_{LR}}$
- HCl + NaOH → NaCl + H_2O **and** HNO_3 + NaOH → $NaNO_3$ + H_2O should have the same ΔH_{rxn} given that they both have the same NIE ($H^+ + OH^- \rightarrow H_2O$)

Troubleshooting

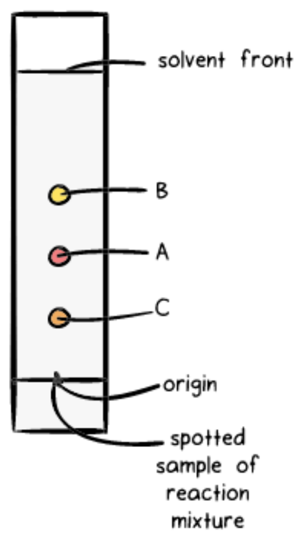
- There should be no space in between the test tube and the Styrofoam so the heat will not escape
- Don't change test tubes/styrofoams in the course of the experiment because the amount of matter calibration will change as well

Paper Chromatography

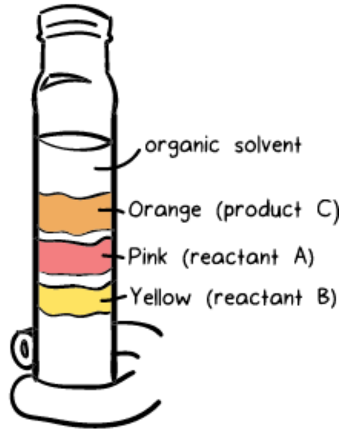
Chromatography

- "chroma" + "graphein" = to illustrate/write color
- A technique for separation of mixture
- Developed by Mikhail Tsvet
  - In his experiment, he added plant extracts (with color) on top of calcium carbonate powder. Then he added water to it and after all water has passed on the packed powder, separation of color is formed
  - Each color corresponds to a certain compound
- Types of Chromatography
  - Column Chromatography and Planar Chromatography

Thin Layer Chromatography (TLC)



Column Chromatography



Glass column packed with silica in an organic solvent, reaction mixture loaded on the silica bed with help of a glass pipette

Chromatographic Set-up

- Mobile Phase
  - Moving part (H_2O)
- Stationary phase
  - Staying part (paper)
- Sample mixture
  - To be separated

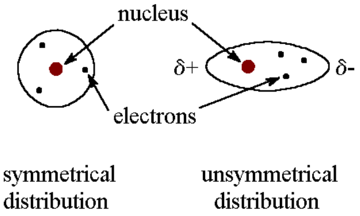
How does separation occur?

- Two competing factors: There is a competition between the attraction of the sample to the solvent and to the paper.
  - Solubility to solvent (mobile phase)
  - Adsorption to paper (stationary phase)
- For paper chromatography
  - Higher solubility to solvent: moving faster
  - Higher adsorption to stationary phase: moving slowly
- Primary reason of solubility and adsorption: intermolecular forces of attraction (IMFA)

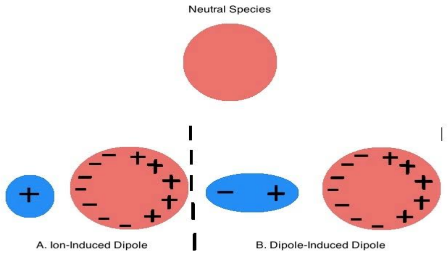
- Separation is based on polarity
    - Molecular polarity
        - Due to tendencies of some element to attract more electron (electronegativity), they tend to disrupt electron cloud molecule, which leads to partial charge formation
    - Polarity is dependent on:
        - Electronegativity of atoms
        - Geometry
    - General rule of polarity: Like dissolves like
    - Derivatives of Polarity: IMFA (arranged according to decreasing strength)
        - Ion-ion
        - Ion-dipole
        - H-bonding
        - Dipole-dipole
        - Ion-induced dipole
        - Dipole-induced dipole
        - London dispersion forces

Intermolecular Forces of Attraction

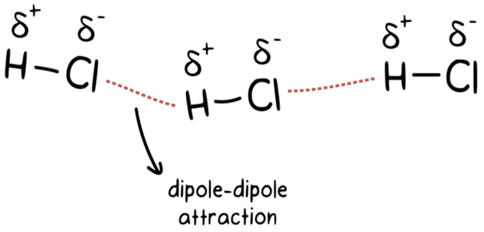
- London Dispersion Force
    - For all types of molecules



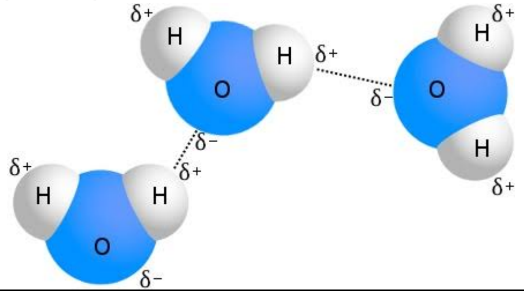
- Dipole-induced dipole and Ion-induced dipole

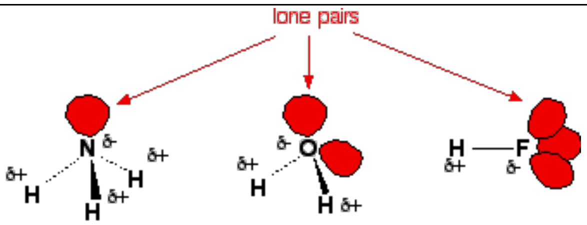


- Dipole-dipole
    - Polar + polar

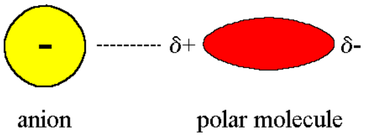


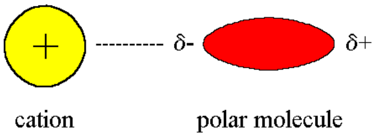
- Hydrogen bonding
    - Special type of dipole-dipole (H-O, H-N, H-F)



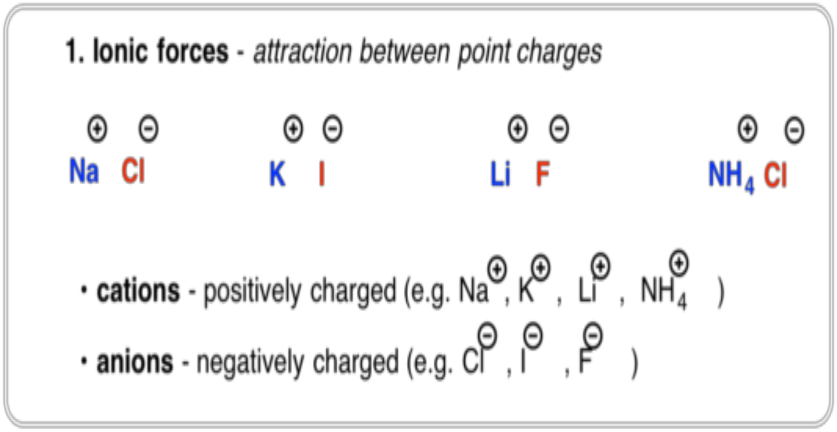


- Ion-dipole
  - Ion + polar molecules





- Ion-ion
  - Ion + ion (ionic)



1. Ionic forces - *attraction between point charges*

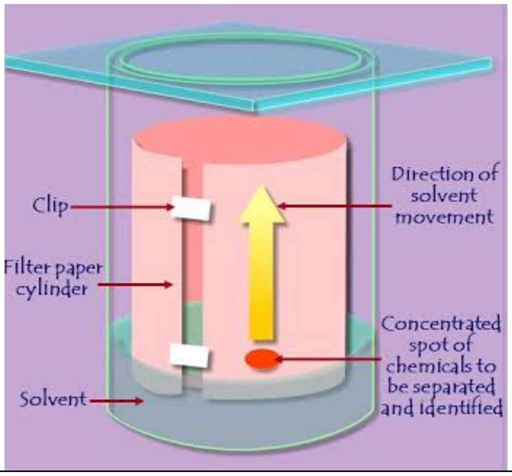
Na^{+} Cl^{-} K^{+} I^{-} Li^{+} F^{-} NH_4^{+} Cl^{-}

- **cations** - positively charged (e.g. Na^{+}, K^{+}, Li^{+}, NH_4^{+})
- **anions** - negatively charged (e.g. Cl^{-} , I^{-} , F^{-})

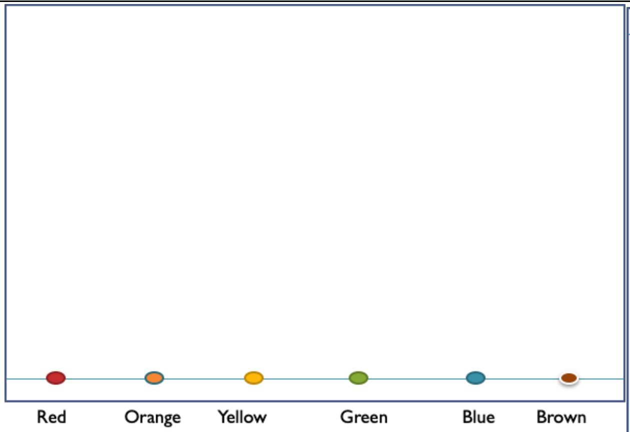
Types of Chromatography based on polarity of stationary phase

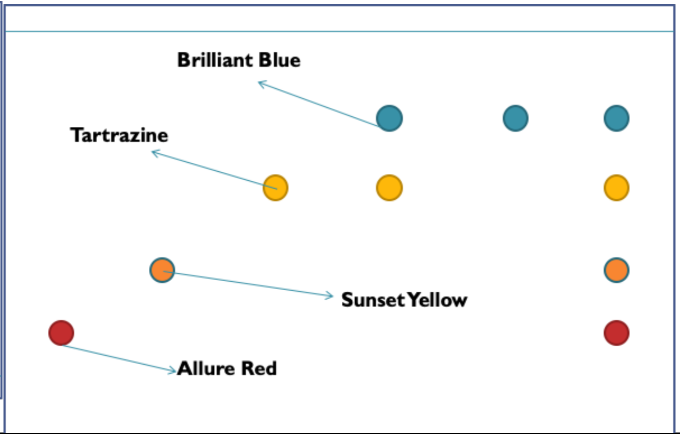
- Normal phase chromatography
  - Stationary phase is polar
- Reverse phase chromatography
  - Stationary phase is nonpolar
- Experiment made use of a Planar Normal Phase Chromatography (paper chromatography)
  - Stationary phase: water adsorbed in cellulose (cellulose is in paper)
  - Mobile phase: 1% NaCl solution in water

Paper Chromatography Set-up



- Chromatographic plate (chromatogram): filter paper with dye spots
    - Where the sample mixture to be separated is spotted
    - Stationary phase which is the filter paper
- Developing solvent: 1% NaCl solution
    - The mobile phase (1% NaCl solution)
    - Moves up the stationary phase via capillary actions
- Saturation Filter paper
    - Paper added besides the chromatographic plate
    - Used to ensure the system inside the chromatogram is saturated (prevent volatilization)
- Chromatographic Chamber: lid + beaker
    - Beaker + Lid = Where the chromatographic run is contained
    - Must be closed by lid to ensure no solvent would be volatilized

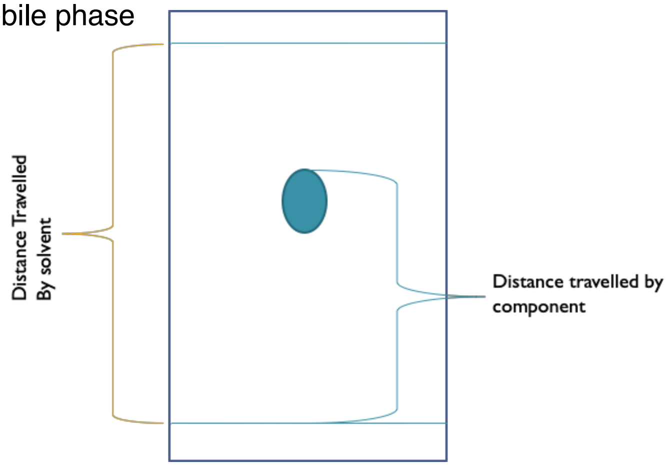




Retention Factor

- Degree of attraction of components to the mobile phase
- If the component is:
    - More polar = lower Rf
    - More nonpolar = higher Rf

$$Rf = \frac{\text{Distance travelled by component}}{\text{Distance travelled by solvent}}$$



- Rf values are qualitative (used for comparison)
- Based on Rf Values: Allure Red < Sunset Yellow <Tartrazine < Brilliant Blue
- Therefore based on Polarity: Brilliant Blue < Tartrazine< Sunset Yellow< Allure Red

Dynamic Equilibrium and Heats of Solution

Forward vs. Reverse Reaction

$H_2 + I_2 \rightarrow 2HI$

$2HI \rightarrow H_2 + I_2$

When will the forward-reverse reaction stop?

When equilibrium is achieved = stable state.

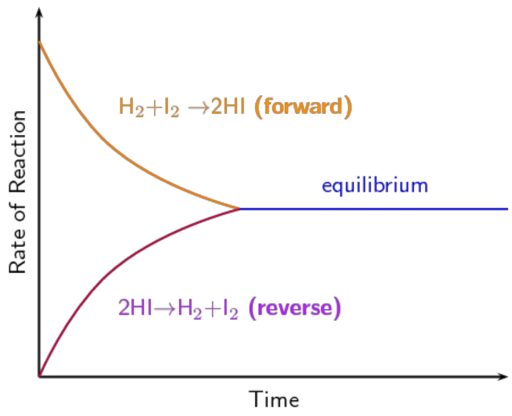
Dynamic Equilibrium: a state in which the rate of the forward reaction is the same as the rate of the backward reaction

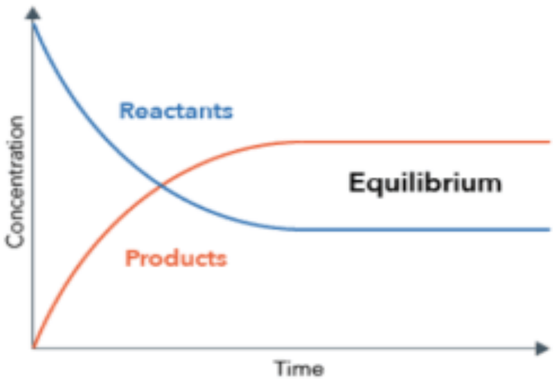
Chemical equilibrium is achieved when

- Rate of Forward Reaction = Rate of Reverse Reaction
- $\frac{-d[Reactants]}{dt} = \frac{-d[Products]}{dt}$

Rate of reactions

- Indicates how fast a reaction occur
- Given by rate of change of concentration over time (derivatives)





Le Chatelier's Principle

- If a dynamic equilibrium is disturbed, the system would react with the change to attain equilibrium again (counteract with the change)
- Aims to restore balance
- Proposed by Henry-Louis Le Chatelier

Two types of equilibria

- Acid-base equilibria
  - Effect of pH
    - ↑pH = ↓H^+
    - ↓pH = ↑H^+
  - Color changes are observed
  - We collected colored pigments (dyes) which contain anthocyanins that serve as natural indicators (have similar properties as phenolphthalein)
- Solubility equilibria
  - Effect of the nature of solute and solvent (miscible and immiscible)
    - Solubility occurs when the IMFA of the solute-solvent > solute-solute & solvent-solvent IMFA
    - Ex. Water & oil
      - Water-water's dominant IMFA is H-bonding
      - Oil-oil's dominant IMFA is LDF
      - Water-oil's dominant IMFA is dipole-induced dipole
      - H-bonding > Dipole-induced dipole > LDF
      - Thus, they would not interact with each other and form an immiscible liquid
    - Ex. Water & alcohol
      - Water-water's dominant IMFA is H-bonding
      - Alcohol-alcohol's dominant IMFA is H-bonding
      - Water-alcohol's dominant IMFA is H-bonding
      - Thus, they would interact with each other and form a miscible liquid
  - Change in strength of the IMFA leads to change in the volume of solvent mixture
  - System wants to attain highest IMFA possible because it is most stable, and its harder to break

Acid-base equilibria example

Reaction: $H^+ + In \leftrightarrow HIn^+$

$\uparrow pH = \downarrow H^+$ = reverse reaction

$\downarrow pH = \uparrow H^+$ = forward reaction

$$pH = -\log [H^+]$$

When added HCl = forward reaction = $\downarrow pH$

$H^+ + In \rightarrow HIn^+$

In = color A

HIn^+ = color B

When added NaOH = reverse reaction = $\uparrow pH$

$H^+ + OH^- + In \rightarrow HIn^+$

$H^+ + OH^-$ would form water and thus, would lessen H^+

$HIn^+ \rightarrow H^+ + In$

Bougainvillea Extract

Extract	pH	Color	Condition
Original	5	Red	Slightly acidic
+ 1M HCl	1	Reddish pink	Acidic
+ 1M NaOH	9	Reddish brown	Basic

Gumamela Extract

Extract	pH	Color	Condition
Original	5	Dull pink	Slightly acidic
+ 1M HCl	3	Bright red	Acidic
+ 1M NaOH	9	Dark green	Basic

Camote Tops Extract

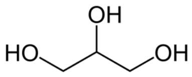
Extract	pH	Color	Condition
Own	6	Violet	Slightly acidic
+ 1M HCl	1	Magenta	Acidic
+ 1M NaOH	8	Dark green	Basic

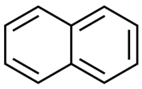
Solubility Equilibria

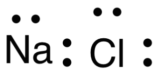
Effect of Nature of Solvent and Solute

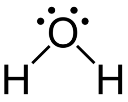
Solute	Solvent		
	Water (P)	Ethanol (P)	Toluene (NP)
NaCl (ionic)	soluble	soluble/insoluble*	insoluble
Napthalene (NP)	immiscible	soluble/insoluble*	miscible
Glycerol (P)	miscible	misicible	immiscible

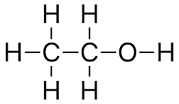
Solute and Solvent

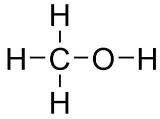
Glycerol:  (polar; H-bonding)

Naphthalene:  (non-polar; LDF)

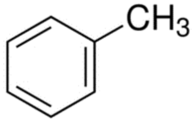
Sodium Chloride:  (ionic; ion-ion)

Water:  H_2O (polar; H-bonding)

Ethanol:  CH_3CH_2OH (polar; H-bonding)

Methanol:  CH_3OH (polar; H-bonding)

Methanol is more polar than ethanol because the presence of C atoms also affects the polarity of the molecule. Less C = more polar; More C = more nonpolar

Toluene: 

Thus,

- Glycerol + Water = Miscible (both polar)
- Glycerol + Naphthalene = Insoluble (polar and nonpolar)
- Ethanol + Naphthalene = Slightly Soluble (even if ethanol is polar, it still has an ethyl (C_2H_5) group that is nonpolar, thus attracting nonpolar solutes)

Effect of Solubility examples

- $I_2 + H_2O$ will not dissolve completely because I – I interaction is stronger (ion-ion) but will still dissolve because of $I + I \Leftrightarrow I_2$
- $I_2 + KI$ in H_2O will dissolve because $KI + I_2 \Leftrightarrow I_3^-$ (represented by the change in color)

Effect of temperature examples

NH_4Cl + water = endothermic (lumamig)
$NH_4Cl + \Delta H \Leftrightarrow NH_4^+ + Cl^-$
↑ temperature = more dissolved = forward reaction

$Ca(OH)_2$ in H_2O = exothermic (uminit)
$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^- + \Delta H$
↓ temperature = more dissolved = forward reaction

Changes in Volume and Heat

H_2O + MeOH (methanol)

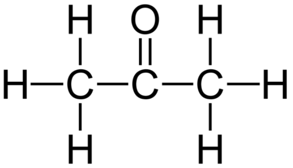
$$\Delta H_{solution} = \sum \Delta H_{solute-solute} + \sum \Delta H_{solvent-solute} + \sum \Delta H_{solvent-solvent}$$

$$\Delta H_{solution} = \sum [+BB] + \sum [-BF] + \sum [+BB]$$

$$\text{IMFA}_{\text{solute-solvent}} > \text{IMFA}_{\text{solute-solute}} + \text{IMFA}_{\text{solvent-solvent}}$$

Thus, it is an exothermic reaction, ↑T, ↓V

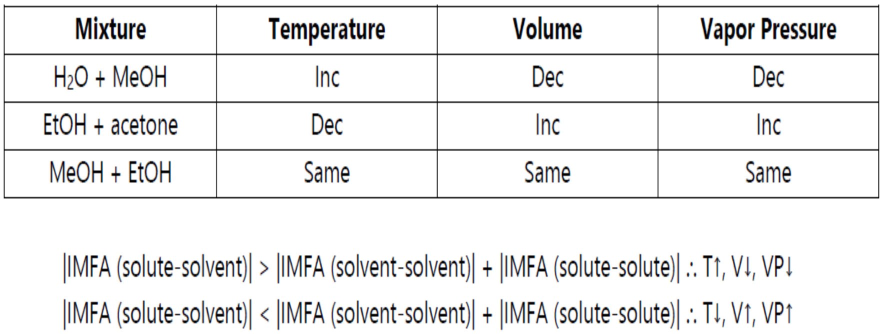
Acetone + EtOH



Acetone

$$\text{IMFA}_{\text{solute-solvent}} < \text{IMFA}_{\text{solute-solute}} + \text{IMFA}_{\text{solvent-solvent}}$$

Thus, it is an endothermic reaction, ↓T, ↑V because the substances do not want to interact



Mixture	Temperature	Volume	Vapor Pressure
H_2O + MeOH	Inc	Dec	Dec
EtOH + acetone	Dec	Inc	Inc
MeOH + EtOH	Same	Same	Same

|IMFA (solute-solvent)| > |IMFA (solvent-solvent)| + |IMFA (solute-solute)| ∴ T↑, V↓, VP↓

|IMFA (solute-solvent)| < |IMFA (solvent-solvent)| + |IMFA (solute-solute)| ∴ T↓, V↑, VP↑

Response to IMFA

- ↑IMFA = ↓V
- ↓IMFA = ↑V

Response to Concentration

- A + B ←→ C + D
- More A: forward reaction
  - To reduce A, increase C
- More C: reverse reaction
  - To reduce C, increase A

Response to Temperature

- Exothermic: A + B → C + heat
  - Decrease temperature to form heat
- Endothermic: A + B + heat → C
  - Increase temperature to absorb heat, to compensate with high temperature

Response to Pressure

- ↓V, ↑P = forward reaction (less gass molecules)
- ↑V, ↓P = reverse reaction (more gas molecules)

Distillation of Rubbing Alcohol

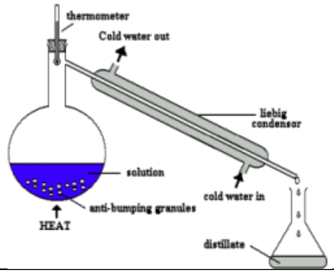
Distillation

- Separation of miscible solutions
  - Miscible: unsure of the components
- Separation can be done by using the differences in the boiling points of the components

Types of Distillation Set-up

- Simple distillation
  - used for separating liquids boiling below 150 °C at 1 atm from either nonvolatile impurities or another liquid with boiling point that is at least 25 °C from the first
- Vacuum distillation
  - used for separating liquids boiling above 150 °C at 1 atm from either non-volatile impurities or another liquid with boiling point that is at least 25 °C from the first
- Fractional distillation
  - used for separating liquids whose boiling points differ by less than 25 °C
- Steam distillation
  - used for separating liquids that are insoluble or slightly soluble in water

Simple Distillation set-up



Distilling flask: contains the mixture or solution

How does Distillation occur?

- Due to difference of IMFA of the mixture's components
    - For instance, in Rubbing alcohol, it is composed of H_2O and Ethanol/Isopropyl Alcohol
    - However, Ethanol/isopropyl alcohol has weaker IMFA compared to water
    - Therefore, easier energy is needed to induce evaporation to it
    - Thus, it evaporates at lower temp compared to water

Important Notes

- Temperature should not be greater than 100 C because by then, water would also evaporate
- You remove the first mL in the distillate because you assume they're impurities
- There's a hole in the condenser for air circulation, to avoid too high pressure that would lead to the breakage of the glassware
    - Because of this, there is an assumed loss of heat (energy is not fully conserved)

Gases

- have weak IMFA, they are loosely connected
- no definite shape/volume; compressible
- have their own
    - pressure
    - volume
    - temperature
    - moles

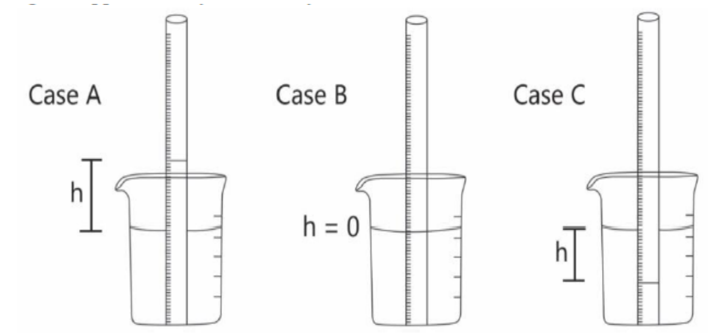
Gas Law	Formula	Description
Boyle's Law	$P_1V_1 = P_2V_2$	At constant T, as ↑P, ↓V
Charles' Law	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	At constant P, as ↑V, ↑T
Gay-Lussac's Law	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	At constant V, as ↑P, ↑T
Combined Law	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	Obtained by combining Boyle's, Charles', and Gay-Lussac's Law
Ideal Gas Law	$PV = nRT$	$R = 0.0821\frac{Latm}{molK}$

Objectives of the experiment

- The presence of gas law: the effect of presence of moles of gas molecules to pressure and volume and response to temperature
- How to use a eudiometer
    - Eudiometer is a classical instrument used to collect gas particles from a reaction to determine the volume of the gas

Eudiometer

- Same as a barometer
- Solvent: water
- Three cases = three different formulas



$$Case\ A = P_{trapped\ air} = P_{bar} - \frac{h}{13.6}$$

$$Case\ B = P_{trapped\ air} = P_{bar}$$
$$Case\ C = P_{trapped\ air} = P_{bar} + \frac{h}{13.6}$$

* The discrepancy in level of water (represented by h) is due to difference in pressure of the outside (atmospheric pressure) and inside (pressure of trapped air)

Determining pressure in eudiometer

In the experiment, we were interested in the pressure of captured H2 gas in the reaction of Mg and HCl

$$Mg + 2HCl \rightarrow H_2 + MgCl_2$$

We are interested in the pressure of H2 only but water has a contribution to pressure due to vapor pressure

Therefore,

$$P_{dry\ air} = P_{trapped\ air} - P_{water\ vapor}$$

Determining Moles (n) of H_2 gas

$$PV = nRT$$

Colligative Properties

Colligative properties

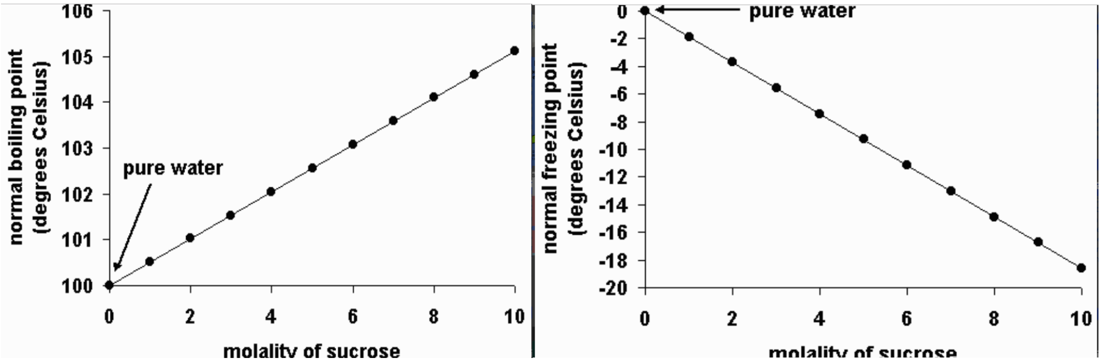
- Properties of solutions which are dependent on the concentration of solute molecules/ions
- independent from identity of solute

Types of colligative properties

- Boiling Point Elevation (BPE)
- Freezing Point Depression (FPD)
- Vapor Pressure Lowering (VPL)
- Osmotic Pressure (OP)

Relationship of BPE and FPD to Concentration

$$\Delta T = iKm$$
$$\Delta T_b = iK_b m$$
$$\Delta T_f = -iK_f m$$



Where:

- T = change in temperature compared to original solution
- K = proportionality constant (different for BP and FP)
  - K_f of water= 1.86 C/m
  - K_b of water = 0.512 C/m
  - Dependent to solvent, not solute
  - Determined empirically
- m = molality
  - $m = \frac{moles\ solute}{kg\ solvent}$
- i = Van't Hoff factor
  - Ratio between the actual concentration of particles produced when the substance is dissolved and the concentration of a substance as calculated from its mass
  - Van't Hoff Factor is dependent on the type of electrolyte the solute is
    - For Strong Electrolytes, i = total ions it produces upon dissolution
    - For Weak Electrolytes, i = less than the total ions it produces upon dissolution

        - For Non-electrolytes, i = 1
        - Example: $(NH_4)_3PO_4$, i = 4
- (-) sign for FPD designates its decrease

Thus:

- Boiling Point Elevation
    - ΔT is (+) “elevation” → harder to boil
- Freezing Point Depression
    - ΔT is (-) “depression” → harder to freeze

Determination of i

- $i = \frac{\Delta T_{solution}}{\Delta T_{nonelectrolyte}}$
- $i = 2$ theoretically in the experiment
- $i > 2$, due to instrumental errors
- $i < 2$, due to high molality concentration; oversaturated solutions (this is why we’d rather have diluted/unsaturated solutions)

Addition of salt to the ice bath

- Salt decreases the freezing point of ice
- Induces melting of ice
- Melting of ice is endothermic
- More ice melting = more endothermic reaction
- Would lower the temperature of the solution
- Lowered temperature = achieve freezing point

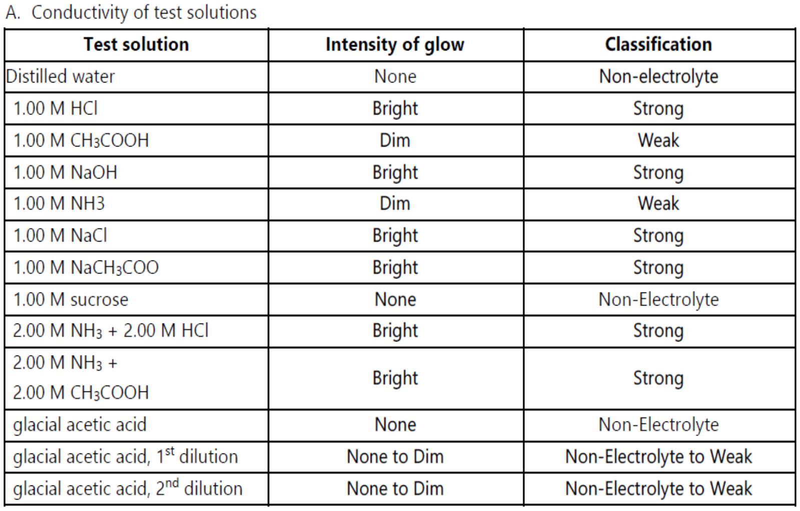
pH, Conductivity, and Relative Strengths of Acids and Bases

Definitions of Acids and Bases

- Arrhenius Definition
    - Acid: gives off H^+
        - Ex: HCl, HNO_3
    - Base: gives off OH^-
        - Ex: NaOH, NH_4OH
    - However, there are compounds that are similar to properties of acids and bases that do not have OH^-
- Bronsted Lowry Definition
    - Acid: proton donor
        - Ex: HCl, HNO_3
    - Base: proton acceptor
        - Ex: NaOH, NH_3
    - However, these definitions cannot explain acids and bases in inorganic compounds
- Lewis Definition
    - Acid: electron acceptor
    - Base: electron donor

Properties of acids and bases

Conductivity Test



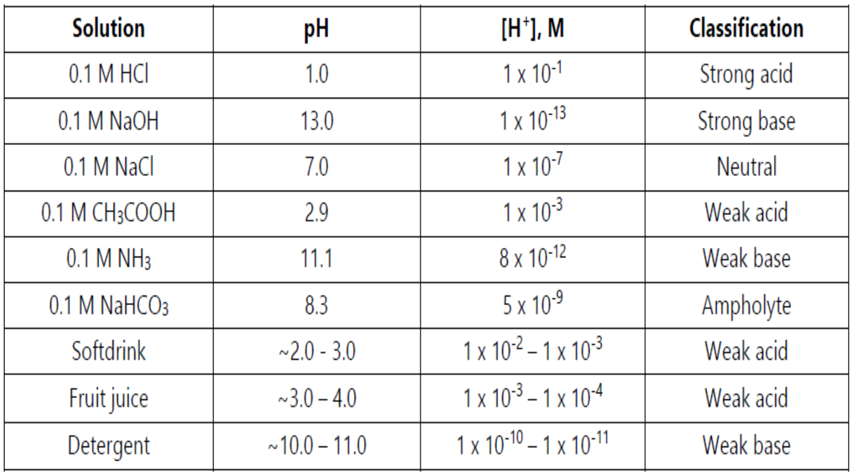
A. Conductivity of test solutions

Test solution	Intensity of glow	Classification
Distilled water	None	Non-electrolyte
1.00 M HCl	Bright	Strong
1.00 M CH_3COOH	Dim	Weak
1.00 M NaOH	Bright	Strong
1.00 M NH3	Dim	Weak
1.00 M NaCl	Bright	Strong
1.00 M $NaCH_3COO$	Bright	Strong
1.00 M sucrose	None	Non-Electrolyte
2.00 M NH_3 + 2.00 M HCl	Bright	Strong
2.00 M NH_3 + 2.00 M CH_3COOH	Bright	Strong
glacial acetic acid	None	Non-Electrolyte
glacial acetic acid, 1st dilution	None to Dim	Non-Electrolyte to Weak
glacial acetic acid, 2nd dilution	None to Dim	Non-Electrolyte to Weak

- Acids and bases have electrolytic properties = conduct electricity
- Strong acid/base = strong electrolytes = all ions dissolve
- Weak acid/base = weak electrolyte = partial dissociation
- $CH_3COOH_{(l)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$
    - Glacial acetic acid does not conduct electricity alone, but when diluted, it conducts electricity

H^+ and OH^- concentration

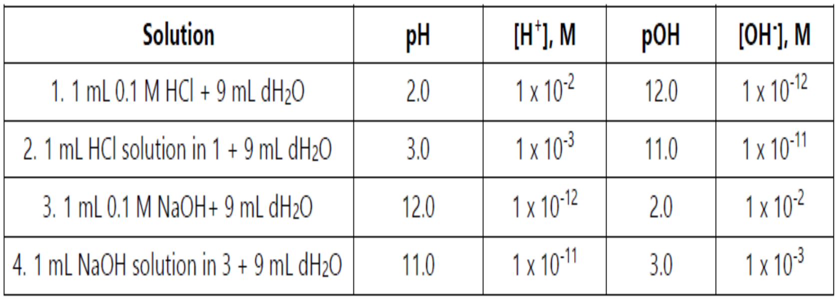
- pH paper = pH solution
    - pH < 7; acidic
        - Strong acids: 0-1
    - pH = 7; neutral
    - pH > 7; basic
        - strong bases: 13-14
- $pH = -\log [H^+]$
- $pOH = -\log [OH^-]$
- pH + pOH = 14



Solution	pH	$[H^+]$, M	Classification
0.1 M HCl	1.0	1×10^{-1}	Strong acid
0.1 M NaOH	13.0	1×10^{-13}	Strong base
0.1 M NaCl	7.0	1×10^{-7}	Neutral
0.1 M CH_3COOH	2.9	1×10^{-3}	Weak acid
0.1 M NH_3	11.1	8×10^{-12}	Weak base
0.1 M $NaHCO_3$	8.3	5×10^{-9}	Ampholyte
Softdrink	~2.0 - 3.0	$1 \times 10^{-2} - 1 \times 10^{-3}$	Weak acid
Fruit juice	~3.0 – 4.0	$1 \times 10^{-3} - 1 \times 10^{-4}$	Weak acid
Detergent	~10.0 – 11.0	$1 \times 10^{-10} - 1 \times 10^{-11}$	Weak base

- Ampholyte: can act as both an acid and a base

pH as a function of concentration

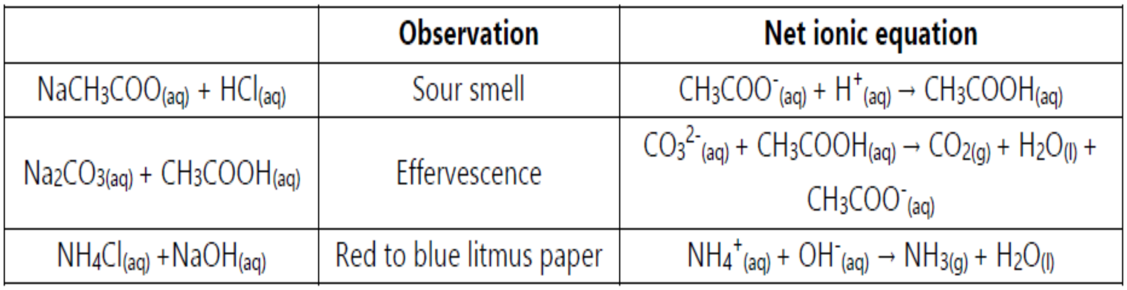


Solution	pH	$[H^+]$, M	pOH	$[OH^-]$, M
1. 1 mL 0.1 M HCl + 9 mL dH_2O	2.0	1×10^{-2}	12.0	1×10^{-12}
2. 1 mL HCl solution in 1 + 9 mL dH_2O	3.0	1×10^{-3}	11.0	1×10^{-11}
3. 1 mL 0.1 M NaOH+ 9 mL dH_2O	12.0	1×10^{-12}	2.0	1×10^{-2}
4. 1 mL NaOH solution in 3 + 9 mL dH_2O	11.0	1×10^{-11}	3.0	1×10^{-3}

Actual pH vs Theoretical pH

- based from pH paper
- based from concentration of H^+ in the solution prepared

Relative Strengths of Acids and Bases

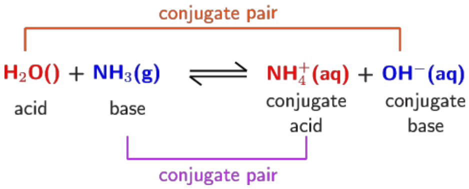


	Observation	Net ionic equation
$NaCH_3COO_{(aq)} + HCl_{(aq)}$	Sour smell	$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightarrow CH_3COOH_{(aq)}$
$Na_2CO_{3(aq)} + CH_3COOH_{(aq)}$	Effervescence	$CO_3^{2-}{}_{(aq)} + CH_3COOH_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CH_3COO^-_{(aq)}$
$NH_4Cl_{(aq)} + NaOH_{(aq)}$	Red to blue litmus paper	$NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightarrow NH_{3(g)} + H_2O_{(l)}$

Relative Acidity: $HCl > CH_3COOH > H_2CO_3$

Relative Basicity: $NaOH > NH_3$

Direction of the Reaction



- Direction of reaction is determined by the relative strengths of the acids and bases.
- The more acidic/basic the reactants, the more the reaction would proceed to react the reactants
- The reaction would proceed forward