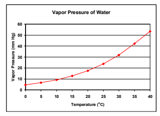
$s_i = k_H P_i$

Gasometric Determination of $NaHCO_3$ in a Mixture



$P = \Sigma P_i$

$(P+a/v^2)(v - b) = RT$

Virtual Lab 1 – Visible Spectroscopy is due on the day that you perform this exercise.

? QUESTIONS ?

Can we determine the composition of a mixture by measuring the amount of gas evolved when that mixture undergoes a chemical reaction?

What principles and concerns do we use in measuring the total amount of gas liberated?

What will limit the accuracy and precision of our determination?

Objective:
Determine the **percent of $NaHCO_3$** in a mixture by Gasometry

Concepts:

Stoichiometry, Limiting Reagents, Ideal Gas Law, Gas Non-ideality, Partial Pressure, Vapor Pressure, Henry's Law

Techniques:

Capture Gaseous Product, Determine System Volume, Determine Dissolved Gas

Apparatus:

Gas Syringe, Thermometer, Barometer, Balance, Cylinder

Gasometry: An analytical technique which depends on measuring an evolved gas.

The Exercise is Conceptually Simple

The unknowns, again, consist of a uniform solid mixture of $NaHCO_3$ and NaCl

1. Weigh Sample
2. Do Chemistry

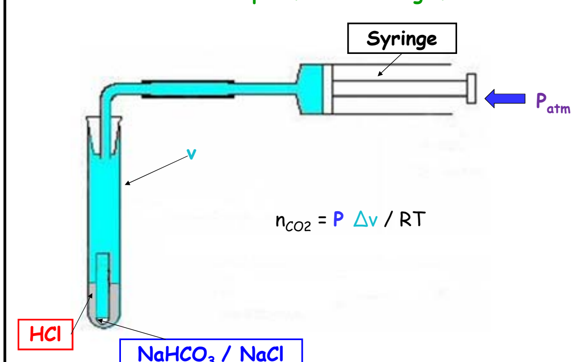
   $NaHCO_3$ reacts with HCl (aq) to liberate CO_2(g)

   NaCl does not react with HCl (aq)

   So, the moles of CO_2 should relate to $NaHCO_3$ moles
3. Determine volume of liberated gaseous CO_2

   Measure gas volume to get moles of CO_2

The Basic Experimental Arrangement



$n_{CO2} = P\ \Delta v / RT$

Our Tentative Model

1. Weigh unknown sample
2. React unknown with HCl (aq)

NaHCO$_3$ reacts with, HCl to liberate CO_2

a) $NaHCO_3$ (s) + H^+ (aq) → Na^+ (aq) + H_2O (l) + CO_2 (g)

b) NaCl(s) → Na^+ (aq) + Cl^- (aq)

NaCl dissolves, but does not react with, HCl

But, CO_2 (g) + H_2O (l) → CO_2 (aq)

Some CO_2 dissolves in water. (HCl is mostly water.)

3. Capture and measure the volume of liberated gaseous CO_2

Do we need to account for the dissolved amount?

5. Use Ideal Gas Law, $P_{atm}v = n_{CO2}RT$, to calculate moles of CO_2

But, the Ideal Gas Law as written applies to one pure gas. We have a mixture (there is air in our system).

$P_{CO2}v = n_{CO2}RT$

How do we measure P_{CO2}?

Some Questions

What could affect the accuracy & precision of our results?

1. Intrinsic limitations of apparatus
   a. Balance, syringe, thermometer, barometer – other apparatus?
2. Limitations due to our model
   a. Can CO_2 be treated as an ideal gas to adequate precision?
   b. Can we ignore the dissolved CO_2?
   c. Is $P_{CO2} = P_{atm}$?
3. Limitations due to procedure/techniques
   a. How do we insure that all of the $NaHCO_3$ has reacted?
   b. How accurately do we need to know the sample weight?
   c. How do we insure that all of the CO_2 has been captured?

Accuracy and Reproducibility 1

Syringe:
- **Maximum capacity is 60 mL**
- Syringe can be read to ± 0.5 mL

Balance:

Which balance shall we use?

Depends on how much unknown we will weigh.

- **Top Loading Balance** can be read to 0.01 g (10% at 0.1 g)
- **Analytical Balance** can be read to 0.0001 g (0.1% at 0.1 g)

Barometer:
- Can be read to 0.1 Torr (0.15% at 1 atm = 760 Torr)

Thermometer: (0.8% at 25 °C) (0.07% at 298 K)
- Can be read to 0.2 °C

Tube Volume:
- Assume ± 0.5 mL (0.6% at ~80 mL)

The Volume measurements have the least precision ~ 1%

Accuracy and Reproducibility 2

Capacity of syringe limits maximum weight of $NaHCO_3$/unknown

< 60 mL means < 2.5 mmol CO_2 max at Room Temp and 1 atm

That means 2.5 mmol $NaHCO_3$ max

max weight of unknown @ 100% $NaHCO_3$ = 2.5 X 84 = 168 mg

(can weigh up to 335 mg if unknown is 50% $NaHCO_3$)

For 50 mL of CO_2, the weight range of unknown is 140 – 280 mg

Everyone does a trial run (< 200 mg) to determine weight of unknown required to produce 40 ± 10 mL of CO_2

Procedure requires unknown to be the limiting reagent

Unknown weight of ~200 mg determines analytical balance must be used to weigh unknown if we want ~1 % accuracy.

This also determines minimum amount of 1.0 M HCl required

To insure that $NaHCO_3$ is limiting for any unknown we must add at least 2.5 mmol of HCl. For 1.0 M HCl, this means 2.5 mL

$NaHCO_3$ (s) + H^+ (aq) → Na^+ (aq) + H_2O (l) + CO_2 (g)

How Much CO_2 Dissolves in the HCl (aq)?

Henry's Law: the ***partial pressure*** of a gas, P_x, in equilibrium with a solution of the gas at a given temperature, is proportional to the ***concentration*** of the gas in the solution, C_x.

Henry's Law $C_{CO2} = K_H P_{CO2}$ K_H is called the Henry's Law constant

And, $n_{CO2}{}^l = C_{CO2} v_l = K_H P_{CO2} v_l$

For CO_2 and water at room temperature, $K_H = 3.2 \times 10^{-2}$ mol/L-atm

In the typical lab setup, the total gas volume after the CO_2 is generated, v_f^{tot} is ~ 140 mL. If we generate 2.0 mmol of CO_2, the partial pressure of CO_2 at Room Temperature will be

$P_{CO2} = n_{CO2} RT/v_f^{tot} = 2.0 * 0.0821 * 298/140 \sim 0.35$ atm

From Henry's Law, the concentration of CO_2 in the water/HCl is

$C_{CO2} = 3.2 \times 10^{-2} * 0.35 = 0.011$ M

10 mL of solution contains 0.011 * 10 = 0.1 mmol of CO_2 which is

100 * 0.1 / 2 = 5% of the moles in the gas phase.

Accuracy and Reproducibility 3

Can CO_2 be treated as an Ideal Gas?

We can estimate the deviation from ideality by examining the van der Waals constants.

$$(P + n^2a / v^2) (v - nb) = nRT$$

For CO_2 at Room Temperature, the corrections to P and v are:

	a / v^2	b / v
CO_2	0.5%	0.2%

How does this compare with other corrections?

Accuracy and Reproducibility 4

$NaHCO_3$ (s) + H^+ (aq) → Na^+ (aq) + H_2O (l) + CO_2 (g)

Reaction produces water.

1 mol $NaHCO_3$ ⇔ 1 mol H_2O

Still, considering pure $NaHCO_3$,

(200 mg $NaHCO_3$ = 2.4 mmol)

We produce at most **2.4 mmol** of liquid H_2O

Is this volume significant compared to the ~ 10 mL of HCl?

1 drop = 0.05 mL

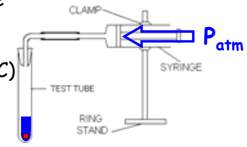
2.4 mmol X 18 mg/mmol = 43 mg; Volume = 0.043 mL

About 1 drop of water is produced (0.5%)

Gas Mixtures – Partial Pressure

Reaction is conducted in a ***closed*** system

- at constant external pressure
  - atmospheric (P ~ 1 atm)
- at constant temperature
  - room temperature (T ~ 25°C)



Initially:

System contains air & **water** (HCl)

Pressure in system is potentially due to:

- water (from HCl) — P_{H2O}
- the air in the system — P_{air}*

$P_{H2O} + P_{air} = P_{atm}$

After reaction, P_{H2O}, P_{air}*

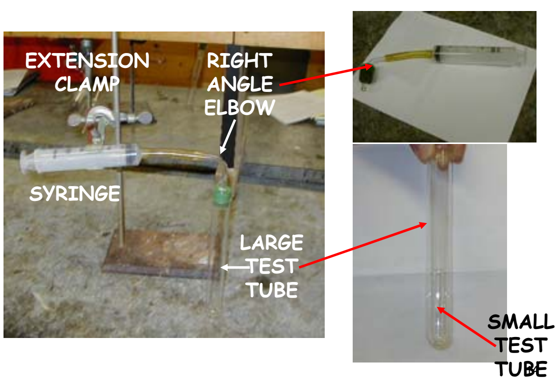
and

- the liberated CO_2 — P_{CO2}

$P_{H2O} + P_{air} + P_{CO2} = P_{atm}$

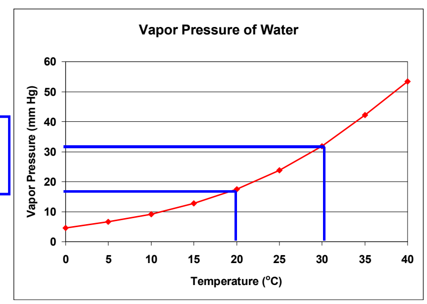
* P_{air} includes the partial pressure of any HCl in the gas phase

The Apparatus – More Detail



What is the Magnitude of P_{H2O} ?

P_{H2O} is a function of Temperature



Over the range 20°C – 30°C, P_{H2O} increases from:

17.5 to 31.8 mm Hg (0.023 to 0.042 atm)

2.3% to 4.2% for P ~1 atm

What Substances are in the System?

Species	Initial (mmol)	Final (mmol)
Air (g)	w mmol	w mmol
H_2O (l)	556 mmol	556 + x mmol
HCl (aq)	10 mmol	10 – x mmol
$NaHCO_3$ (s)	x mmol	0 mmol
NaCl (s)	y mmol	0 mmol
NaCl (aq)	0 mmol	x + y mmol
CO_2 (g)	0 mmol	x - z mmol
CO_2 (aq)	0 mmol	z mmol

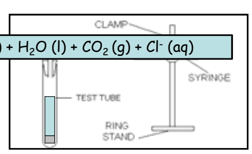
10 mL of 1.0 M HCl contains:

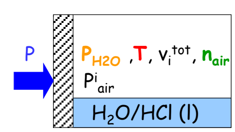
$NaHCO_3$ (s) + H^+ (aq) + Cl^- (aq) → Na^+ (aq) + H_2O (l) + CO_2 (g) + Cl^- (aq)

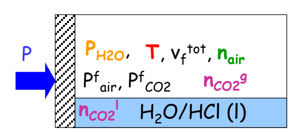
10 mL H_2O = 10 g H_2O

10 g = 10,000 mg / 18.0 mg/mmol

= 556 mmol H_2O







Initially, we have

$P = P^i_{air} + P_{H2O}$

Finally, we have

$P = P^f_{air} + P_{H2O} + P^f_{CO2}$

$P^i_{air} + \cancel{P_{H2O}} = P^f_{air} + \cancel{P_{H2O}} + P^f_{CO2}$

$P^f_{CO2} = P^i_{air} - P^f_{air} = n_{air} RT (1/v_i^{tot} - 1v_f^{tot})$

But, $P^i_{air} = n_{air} RT/v_i^{tot} = P - P_{H2O}$

So, $n_{air} = (P - P_{H2O}) v_i^{tot} / RT$

$P^f_{CO2^g} = [(P - P_{H2O}) v_i^{tot} / \cancel{RT}] (1/v_i^{tot} - 1/v_f^{tot}) \cancel{RT}$

$P^f_{CO2^g} = (P - P_{H2O}) (1 - v_i^{tot}/v_f^{tot})$

$$P^f_{CO_2}{}^g = (P - P_{H_2O})(1 - v_i^{tot}/v_f^{tot})$$

$$n_{CO_2}{}^g = P^f_{CO_2}\, v_f^{tot}/RT = (P - P_{H_2O})(1 - v_i^{tot}/v_f^{tot})\, v_f^{tot}/RT$$

$$= (P - P_{H_2O})(v_f^{tot} - v_i^{tot})/RT$$

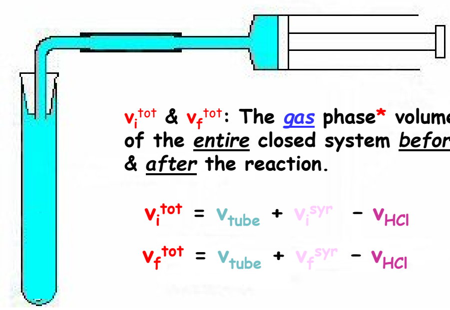
$$n_{CO_2}{}^g = (P - P_{H_2O})(v_f^{syr} - v_i^{syr}) / RT \quad \textbf{Equation 3}$$

We have determined $n_{CO_2}{}^g$ We need $n_{CO_2}{}^l$

From the partial pressure of CO_2, we can calculate $n_{CO_2}{}^l$ using Henry's Law

$$n_{CO_2}{}^l = K_H\, P^f_{CO_2}\, v_l$$

What are the various volumes in the exercise?



v_i^{tot} & v_f^{tot}: **The *gas* phase* volumes of the *entire* closed system *before* & *after* the reaction.**

$$v_i^{tot} = v_{tube} + v_i^{syr} - v_{HCl}$$

$$v_f^{tot} = v_{tube} + v_f^{syr} - v_{HCl}$$

*We must exclude the volume of the liquid HCl (10 mL)
but we can ignore the initial solid unknown (~ 0.1 mL)

Review

Assuming P and T do not change during a run

Issue	Affected Variable	Effect %	
Volume of H_2O Produced	v_l	~ 0.5	X
Volume Change of Unknown	$v_{CO_2}{}^g$	~ 0.1	X
Non -Ideality of CO_2	P_{CO_2}	~ 0.5	X
Vapor Pressure of Water	P_{CO_2}	~ 3.0	√
Solubility of CO_2	$n_{CO_2}{}^{tot}$	~ 5.0	√

If we seek accuracy to within 1%
in the % $NaHCO_3$

Our Final Procedure

1. Measure volume of tube assembly, v_{tube}
2. Weigh unknown sample, w_{sample} (By difference!)
3. Measure Temperature and convert to Absolute, T
4. Look up Vapor Pressure of water, P_{H_2O}
5. Record Atmospheric Pressure, P
6. Measure Initial Syringe Reading, v_i^{syr}
7. React Unknown with 10.0 mL 1 M HCl (aq), v_l
8. Measure Final Syringe Reading, v_f^{syr}

Our Final Model

1. Use ideal gas law to calculate moles of CO_2 in gas phase

   $n_{CO_2}{}^g = (P - P_{H_2O}) (v_f^{syr} - v_i^{syr}) / RT$
2. From ideal gas law, Calculate P_{CO_2}

   $P_{CO_2} = n_{CO_2}{}^g\, RT / (v_f^{syr} + v_{tube} - v_l)$
3. Use Henry's Law to calculate moles of CO_2 in liquid phase

   $n_{CO_2}{}^l = P_{CO_2}\, K_H\, v_l$
4. Calculate weight of $NaHCO_3$ in sample

   $w_{NaHCO_3} = (n_{CO_2}{}^g + n_{CO_2}{}^l)\ 84.01$
5. Calculate % $NaHCO_3$ in unknown

   $\% NaHCO_3 = 100 * w_{NaHCO_3} / w_{sample}$

Calculations

Final Small Test Tube	*15.7488 g*
Initial Small Test Tube	*15.5341 g*
Weight of Sample	0.2147 g
Volume of HCl	10.0 mL
Tube Volume, V_{tube}	100.0 mL
Initial Syringe	*5.0 mL*
Final Syringe	*50.7 mL*
Volume of gaseous CO_2, v	45.7 mL
Pressure, P = 752 mm Hg =	**0.989 atm**
Temperature, T = 23.3 °C =	**296.4 K**
P_{H_2O}@ 23.3°C (from Table) 21.9 mm Hg	**0.028 atm**

mmol CO_2 (gas) $= (P - P_{H_2O})\, v / RT$ 1.81 mmol

mmol CO_2 (liquid) (Henry's Law) ???

To calculate the Henry's Law correction, we need the partial pressure of CO_2 & the final total gas volume, v_f^{tot}

The final gas volume is,

$$v_f^{tot} = 100.0 - 10.0 + 50.7$$
$$= 140.7 \text{ mL}$$

$$P_{CO2} = n_{CO2}^{g} R T / v_f^{tot}$$
$$= (1.81 * 0.0821 * 296) / 140.7$$
$$= 0.312 \text{ atm}$$

Henry's Law gives us the CO_2 concentration:

$$c_{CO2} = 3.2 \times 10^{-2} \text{ mol/L-atm} * 0.312 \text{ atm} = 0.010 \text{ M}$$

which in 10.0 mL of water/HCl contains

$$n_{CO2}^{l} = 10.0 \text{ mL} * 0.010 \text{ mmol/mL} = 0.10 \text{ mmol}$$

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Calculations

Weight of Sample	**0.2147 g**
Volume of gaseous CO_2 v	**45.7 mL**
Pressure, P = 752 mm Hg =	**0.989 atm**
Temperature, T = 23°C =	**296 K**
P_{H2O}@ 23°C (from Table) 21 mm Hg	**0.028 atm**

mmol CO_2 (gas) = $(P - P_{H2O})\, v / RT$	1.81 mmol
mmol CO_2 (liquid) (Henry's Law)	0.10 mmol
Total CO_2	1.91 mmol
mmol $NaHCO_3$ (from stoichiometry)	1.91 mmol
Weight of $NaHCO_3$ 1.91 X 84.0	0.160 g

% $NaHCO_3$ = 100 X 0.160 / **0.2147** = **74.5 %**

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Procedure - Notes

Everyone should weigh **~ 200 mg** = **0.2 g**
– ACCURATELY – for their trial run

Depending on your sample, you must **adjust the weight** in subsequent runs to insure that you get between 35 and 50 mL of CO_2, but not more than 50 mL. (Check before doing the run!)

Test that system is **air-tight** before using

Set syringe at 5.0 mL initially – read to ± 0.5 mL
– remember to subtract initial from final volume

Do test run - then up to 4 which you report.

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