EXAM 2 Review Session

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OUTLINE

- 1. Concentration & Dilutions
- 2. <u>Electrolytes</u>, <u>Salts</u>, <u>& Solubility Rules</u>
- 3. Precipitation Reactions & Acid-Base
- 4. Redox Reactions
- 5. Enthalpy, Heat, & Heating Curves
- 6. <u>Reaction Enthalpies & Hess's Law</u>
- 7. Ideal Gas Law
- 8. Partial Pressure
- 9. Gas: Speed, Diffusion, & Effusion

Different Units of Concentration

• Molarity:
$$\frac{\text{moles of solute (mol)}}{\text{Volume solution (L)}} = \frac{\text{mol}}{\text{L}} = M$$

• PPM: 1 ppm = $\frac{1 \text{ mg solute}}{1 \text{ kg solution}}$ CAN YOU CONVERT
BETWEEN THESE
UNITS?
• PPB: 1 ppm = $\frac{1 \mu \text{g solute}}{1 \text{ kg solution}}$

The solution is usually water (H₂O), so remember density is: $D_{H_2O} = \frac{1 \text{ g}}{1 \text{ mL}} = \frac{1 \text{ kg}}{1 \text{ L}}$

Determine the concentration of each solution in the correct units:

	INFORMATION	[CONCENTRATION]	Μ	PPM
A)	64.7 g LiCl in 250.0 mL water	[LiCI]		
B)	0.200 mol CaCl ₂ in 2.00 L water	[CI-]		
C)	6.42 × 10 ^{−2} mM KNO ₃	[KNO ₃]		
D)	0.200 mol Na ₂ CO ₃ in 200.0 g water	[Na ₂ CO ₃]		
		[Na ⁺]		
		[CO ₃ ^{2–}]		
		[ions]		n/a
E)	1.25 M HNO ³	[H+]		

I'll do parts of D for you: 0.200 mol Na₂CO₃ in 200.0 g water

To find the molarity (M) of $[Na_2CO_3]$, I need moles of Na_2CO_3 and the volume of water in liters:

$$[Na_{2}CO_{3}] = \frac{\# \text{ mol } Na_{2}CO_{3}}{Volume (L)}$$
$$= \frac{0.200 \text{ mol } Na_{2}CO_{3}}{200.0 \text{ g } \text{H}_{2}\text{O} \times \frac{1 \text{ mL } \text{H}_{2}\text{O}}{1 \text{ g } \text{H}_{2}\text{O}} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$
$$[Na_{2}CO_{3}] = 1.00 \text{ M}$$

<u>REMEMBER</u>

The solution is usually water (H₂O), and its density is: $D_{H_2O} = \frac{1 \text{ g}}{1 \text{ mL}} = \frac{1 \text{ kg}}{1 \text{ L}}$

To convert this concentration from M to PPM, I need the molar mass of $Na_2CO_3 = 105.99$ g/mol:

$$\frac{1.00 \text{ mol } \text{Na}_2\text{CO}_3}{1.00 \text{ L} \text{ H}_2\text{O}} \times \frac{105.99 \text{ g} \text{ Na}_2\text{CO}_3}{1 \text{ mol } \text{Na}_2\text{CO}_3} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mL } \text{H}_2\text{O}}{1 \text{ g} \text{ H}_2\text{O}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 106000 \text{ ppm } \text{Na}_2\text{CO}_3$$

To find the concentration of [Na⁺] in M and PPM:

 $\frac{1.00 \text{ mol } \text{Na}_2\text{CO}_3}{1.00 \text{ L} \text{ H}_2\text{O}} \times \frac{2 \text{ mol } \text{Na}^+}{1 \text{ mol } \text{Na}_2\text{CO}_3} = 2.00 \text{ M} \text{ Na}^+$

$$\frac{2.00 \text{ mol Na}^{+}}{1.00 \text{ L H}_{2}\text{O}} \times \frac{22.99 \text{ g Na}^{+}}{1 \text{ mol Na}^{+}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mL H}_{2}\text{O}}{1 \text{ g H}_{2}\text{O}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 4.60 \times 10^{4} \text{ ppm Na}^{+}$$

Determine the concentration of each solution in the correct units:

	INFORMATION	[CONCENTRATION]	Μ	РРМ
A)	64.7 g LiCl in 250.0 mL water	[LiCl]	6.11 M	259000 ppm
B)	0.200 mol CaCl ₂ in 2.00 L water	[C -]	0.200 M	7090 ppm
C)	6.42 × 10 ^{−2} mM KNO ₃	[KNO ₃]	6.42 × 10 ^{–5} M	6.49 ppm
D)	0.200 mol Na ₂ CO ₃ in 200.0 g water	[Na ₂ CO ₃]	1.00 M	106000 ppm
		[Na ⁺]	2.00 M	4.60 × 10 ⁴ ppm
		[CO ₃ ^{2–}]	1.00 M	6.00 × 10 ⁴ ppm
		[ions]	3.00 M	n/a
E)	1.25 M HNO ³	[H+]	1.25 M	1260 ppm

Dilutions: usually adding water/changing volume

$$Concentration = \frac{moles of solute}{Volume (L) of solution} ; M = \frac{mol}{L}$$

Think about what concentration means before getting into the math.



Each black dot represents a mole (the quantity/amount)

You have a 2.50 mL of a 0.559 M solution of Cl⁻. How much water do you need to add to make a solution that is 116 mM Cl⁻?

Concentration & Dilutions

You have a 2.50 mL of a 0.559 M solution of Cl⁻. How much water do you need to add to make a solution that is 116 mM Cl⁻?

First, find how many moles of Cl⁻ ions you have in 2.50 mL of the 0.559 M solution:

$$[Cl^{-}] = \frac{\# \text{ mol } Cl^{-}}{\text{Volume } (L)}$$

0.559 M =
$$\frac{\text{x mol } Cl^{-}}{2.50 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

x = 0.00139₈ mol Cl^{-}

Now, figure out the total volume of a 116 mM Cl⁻ solution containing this many moles of Cl⁻ ions:

$$[Cl^{-}] = \frac{\# \text{ mol } Cl^{-}}{\text{Volume } (L)}$$
116 mM× $\frac{1 \text{ M}}{1000 \text{ mM}} = \frac{0.00139_8 \text{ mol } Cl^{-}}{V}$

$$V = 0.0120_5 \text{ L}$$

ALTERNATIVE SOLUTION:

You can use the following equation:

 $M_1V_1 = M_2V_2$ (0.559 M)(2.50 mL) = (0.116 M)V_2 $V_2 = 12.0_5$ mL

But you still have to subtract at the end to find the volume of water added to the 2.50 mL of the original solution.

: This is total volume! So subtract to find the amount of water added: V_{added} = 12.05 mL – 2.50 mL = 9.55 mL water added.

Excentions

Dr. Huynh

Salts & Solubility Rules

A salt is an ionic compound: metal + nonmetal

Some salts are **soluble** in water (*aqueous*, *aq* = dissociates into ions in water). Some salts are **insoluble** in water (precipitate, solid, *s*).

MEMORIZE SOLUBILITY RULES:	Group 1 cations						
\rightarrow Table 4.4 or 4.5	H_4^+						
You should be able to quickly identify	CH ₃ COO-						
the ions that comprise a salt!	ΟΓ, Br⁻, I⁻ Ag⁺, Hg₂²⁺, Pb²⁺, Cu⁺						
	SO ₄ ²⁻ Hg ₂ ²⁺ , Pb ²⁺ , Ba ²⁺ , Ca ²⁺ , Sr ²⁺ ,						
	Group 1 cations, Ba ²⁺ , Ca ²⁺ , Sr ²⁺ , I	NH_4^+					
	S ^{2–} Group 1 cations, Ba ²⁺ , Ca ²⁺ , Sr ²⁺ , I	NH_4^+					
	$O_{3^{2-}}, PO_{4^{3-}}, F^-$ Group 1 cations, NH_4^+						

Electrolytes or Not?

Electrolytes are solutions that contain ions.



Which of the following has the greatest concentration of dissolved ions?

0.25 M NaBr 0.25 M Na₂SO₄ 0.25 M Na₃PO₄

Which of the following has the greatest concentration of dissolved ions?

0.25 M NaBr $0.25 \text{ M} \text{Na}_2 \text{SO}_4$

0.25 M Na₃PO₄

These are all soluble salts!

We can represent the dissociation of each salt into its ions:

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1 molecule NaBr = 1Na^+ + 1Br^-
1 mol NaBr = 1 mol Na<sup>+</sup> + 1 mol Br<sup>-</sup>
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1 molecule $Na_2SO_4 = 2Na^+ + 1SO_4^{2-}$ $1 \text{ mol } \text{Na}_2\text{SO}_4 = 2 \text{ mol } \text{Na}^+ + 1 \text{ mol } \text{SO}_4^{2-}$



Understand that the concentration of *ions* would be:

1 NaBr : 2 ions

 $1 \operatorname{Na}_2 \operatorname{SO}_4$: 3 ions $[ions] = 2 \times 0.25 \text{ M} = 0.50 \text{ M}$ $[ions] = 3 \times 0.25 \text{ M} = 0.75 \text{ M}$

1 molecule $Na_3PO_4 = 3Na^+ + 1PO_4^{3-}$ $1 \text{ mol Na}_{3}\text{PO}_{4} = 3 \text{ mol Na}^{+} + 1 \text{ mol PO}_{4}^{3-}$ Na⁺ PO43-Na⁺ Na⁺ $1 \text{ Na}_3 \text{PO}_4$: 4 ions $[ions] = 4 \times 0.25 \text{ M} = 1.00 \text{ M}$

Guided Introduction: Precipitation Reaction

Say we mix an aqueous solution of nickel(II) chloride with an aqueous solution of sodium sulfide.

We can write the reactants of this chemical reaction:

 $NiCl_2(aq) + Na_2S(aq) \rightarrow$

We can predict the products by exchanging the ions:

 $NiCl_2 (aq) + Na_2S (aq) \rightarrow NiS (s) + NaCl (aq)$

Determine the products first.

Then determine if each new product is soluble (aq) or insoluble (s)! Don't forget to balance the chemical reaction!

 $\underline{1}\text{NiCl}_2(aq) + \underline{1}\text{Na}_2S(aq) \rightarrow \underline{1}\text{NiS}(s) + \underline{2}\text{NaCl}(aq)$

Always go back to the microscopic picture of what's happening!

 \rightarrow NiS precipitate (solid) forms & other ions float in solution





Guided Introduction: Precipitation Reaction

This is called a molecular equation because we keep the salts as neutral "molecules":

 $\underline{1}\text{NiCl}_2(aq) + \underline{1}\text{Na}_2S(aq) \rightarrow \underline{1}\text{NiS}(s) + \underline{2}\text{NaCl}(aq)$

But we know that soluble salts (aqueous) exist as dissociated ions in solution! It would be more accurate to dissociate the *soluble* salts.

We can transform the molecular equation into an <u>complete ionic equation</u>:

 $\underline{1}Ni^{+}(aq) + \underline{2}Ci^{-}(aq) + \underline{2}Na^{+}(aq) + \underline{1}S^{2-}(aq) \rightarrow \underline{1}NiS(s) + \underline{2}Na^{+}(aq) + Ci^{-}(aq)$

SPECTACTOR IONS

Dr. Huynh

You may notice that some of these ions (Na⁺ and Cl⁻) don't actually chemically react.

We can ignore these!

We can write a <u>net ionic equation</u> by eliminating all the spectator ions:

<u>1Ni</u>⁺ (aq) + <u>1S</u>^{2–} (aq) \rightarrow <u>1NiS</u> (s)



For each reaction, write out the molecular, overall ionic, and net ionic equations:

1. An aqueous solution of potassium carbonate is added to a barium nitrate solution.

2. An iron(II) sulfate solution is mixed with a potassium hydroxide solution.

For each reaction, write out the molecular, overall ionic, and net ionic equations:

1. An aqueous solution of potassium carbonate is added to a barium nitrate solution. $K_2CO_3(aq) + Ba(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + BaCO_3(s)$ *molecular equation*

 $2K^{+}(aq) + CO_{3}^{2-}(aq) + Ba^{2+}(aq) + 2NO_{3}^{-}(aq) \rightarrow 2K^{+}(aq) + 2NO_{3}^{-}(aq) + BaCO_{3}(s)$ overall ionic equation

 $CO_3^{2-}(aq) + Ba^{2+}(aq) + \rightarrow BaCO_3(s)$

net ionic equation

2. An iron(II) sulfate solution is mixed with a potassium hydroxide solution. FeSO₄ (aq) + 2KOH (aq) → Fe(OH)₂ (s) + K₂SO₄ (aq) Fe²⁺ (aq) + SO₄²⁻ (aq) + 2K⁺ (aq) + 2OH⁻ (aq) → Fe(OH)₂ (s) + 2K⁺ (aq) + SO₄²⁻ (aq) overall ionic equation Fe²⁺ (aq) + 2OH⁻ (aq) → Fe(OH)₂ (s) net ionic equation

Precipitation Reaction Stoichiometry

A 250.0 mL solution of a 0.15 M potassium carbonate is added to 175 mL of a 0.200 M barium nitrate solution. What mass of precipitate is formed?

Precipitation Reaction Stoichiometry

A 250.0 mL solution of a 0.15 M potassium carbonate is added to 175 mL of a 0.200 M barium nitrate solution. What mass of precipitate is formed?

From previous slide, we know the following balanced chemical equations apply in this precipitation reaction:

K₂**CO**₃ (*aq*) + **Ba**(**NO**₃)₂ (*aq*) → 2**KNO**₃ (*aq*) + **BaCO**₃ (*s*) 2K⁺ (*aq*) + CO₃^{2−} (*aq*) + Ba²⁺ (*aq*) + 2NO₃[−] (*aq*) → 2K⁺ (*aq*) + 2NO₃[−] (*aq*) + BaCO₃ (*s*) CO₃^{2−} (*aq*) + Ba²⁺ (*aq*) + → BaCO₃ (*s*) molecular equation

overall ionic equation net ionic equation

It's easiest to apply the molecular equation in stoichiometry of precipitation reactions. First, determine the number of moles of the starting reactants and determine which is the limiting reactant:

$$0.15 \text{ M } \text{K}_2\text{CO}_3 = \frac{\text{x mol}}{0.2500 \text{ L}}$$

$$x = 0.037_5 \text{ mol } \text{K}_2\text{CO}_3$$

$$0.200 \text{ M } \text{Ba}(\text{NO}_3)_2 = \frac{\text{y mol}}{0.175 \text{ L}}$$

$$y = 0.0350 \text{ mol } \text{Ba}(\text{NO}_3)_2$$

: The limiting reactant is $Ba(NO_3)_2$. Why?

Now, figure out how much barium carbonate you can make from this amount of limiting reactant:

$$0.0350 \text{ mol } Ba(NO_3)_2 \times \frac{1 \text{ mol } BaCO_3}{1 \text{ mol } Ba(NO_3)_2} \times \frac{137.3_1 \text{ g } BaCO_3}{1 \text{ mol } BaCO_3} = 6.91 \text{ g } BaCO_3$$

Guided Introduction: Acid-Base Titrations

Think of acid-base reactions special precipitation reactions called a <u>neutralization</u> reaction: $2NaOH(aq) + 1H_2SO_4(aq) \rightarrow 1Na_2SO_4(aq) + 2H_2O(l)$

But we know that soluble salts (aqueous) exist as dissociated ions in solution! It would be more accurate to dissociate the *soluble* salts.

OH-

H+

SO42-

H+

We can transform the molecular equation into an <u>complete ionic equation</u>:

 $2Na^{+}(aq) + \underline{2}OH^{-}(aq) + \underline{2}H^{+}(aq) + \underline{1}SO_{4}^{2-}(aq) \rightarrow \underline{2}Na^{+}(aq) + \underline{1}SO_{4}^{2-}(s) + \underline{2}H_{2}O(l)$

Na⁺

SO42-

H₂O (*I*)

Na+

SPECTACTOR IONS

Dr. Huynh

You may notice that some of these ions (Na⁺ and SO_4^{2-}) don't actually chemically react.

We can ignore these!

We can write a <u>net ionic equation</u> by eliminating all the spectator ions:

 $\underline{2}H^{+}(aq) + \underline{2}OH^{-}(aq) \rightarrow \underline{2}H_{2}O(I)$

Acid-Base Stoichiometry

What volume of a 0.50 M NaOH solution would be required to neutralize 40.0 mL of a 0.400 M H_2SO_4 solution?

Acid-Base Stoichiometry

What volume of a 0.50 M NaOH solution would be required to neutralize 40.0 mL of a 0.400 M H₂SO₄ solution?

From previous slide, we know the following balanced chemical equations apply in this <u>neutralization</u> reaction:

2NaOH (*aq*) + $1H_2SO_4(aq) \rightarrow 1Na_2SO_4(aq) + 2H_2O(l)$ **2Na⁺ (aq) + 2OH^-(aq) + 2H^+(aq) + 1SO_4^{2-}(aq) \rightarrow 2Na^+(aq) + 1SO_4^{2-}(s) + 2H_2O(l)** $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$ *molecular equation* **overall ionic equation** *net ionic equation*

It's easiest to apply the overall ionic equation in stoichiometry of neutralization reactions.

First, determine the number of moles of the H⁺:

To neutralize this many moles of H⁺, we need an equivalent number of moles of OH⁻:

 $n_{OH^{-}} = 0.0320 \text{ mol OH}^{-} = n_{NaOH}$

Now, figure out what volume of NaOH solution gives this many moles:

$$0.50 \text{ M NaOH} = \frac{0.0320 \text{ mol NaOH}}{V}$$
$$V = 0.0640 \text{ L}$$

Oxidation States/Numbers

The oxidation state is a hypothetical charge of an element <u>IF</u> it were 100% ionic.

Take-home message: Treat oxidation number/state like a charge.

Some general rules:

- 1. Pure elements have oxidation number = 0
- 2. Hydrogen usually has an oxidation number = +1
- 3. Oxygen usually has an oxidation number = -1
- 4. Everything else: follow the rules for ionic charges!

Ex) Br₂: each Br is 0 Ex) Mg: Mg is 0 Ex) H₂O; CH₄ Ex) H₂O; CO₂ Ex) NaCl: Na = +1; Cl = -1Ex) CF₄: C = +4; F = -1Ex) CO₂: C = +4; O = -2

Some reactions involve a change in the oxidation state of an atom/element!

For each flask, give the oxidation state of each element:



For each flask, give the oxidation state of each element:



What is a <u>redox</u> reaction?

A reaction in which the <u>oxidation states</u> of some elements change.

There are two types:

- 1. Reduction: Gain of an electron; becomes more negatively charged
- 2. Oxidation: Loss of an electron; becomes less negatively charged



How do I balance a redox reaction?

$$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$$

- 0. Assign the oxidation states of each element.
- 1. Separate into half-reactions.
- 2. Balance atoms (except O and H): already balanced
- 3. Balance O atoms with H_2O on opposite side.
- 4. Balance H atoms with H⁺ on opposite side.
- 5. Balance *total charge* with electrons (*e*–).
- 6. Balance the electrons by multiplying entire half-reactions.
- 7. Add the two half-reactions together. (Make sure overall equation is balanced and no extra electrons).

Ox
 5

$$Fe^{2+}(aq)$$
 \rightarrow
 5
 $Fe^{3+}(aq)$
 +
 5
 e^{-1}

 Red
 5
 e^{-1}
 +
 8
 $H^+(aq)$
 +
 1
 $MnO_4^-(aq)$
 \rightarrow
 1
 $Mn^{2+}(aq)$
 +
 4
 $H_2O(l)$

 Overall
 8
 $H^+(aq)$
 +
 1
 $MnO_4^-(aq)$
 \rightarrow
 5
 $Fe^{3+}(aq)$
 +
 1
 $Mn^{2+}(aq)$
 +
 4
 $H_2O(l)$

Fe²⁺ = +2 Mn in MnO₄⁻: +7 O in MnO₄⁻: -2 Fe³⁺ = +3 Mn²⁺: +2

Assign the oxidation states for each element in the redox reaction below:

	$Mn^{2+}(aq) + BiO_3^-(aq) \rightarrow MnO_4^-(aq) + Bi^{3+}(aq)$
Mn ²⁺ :	Mn in MnO ₄ - :
Bi in BiO ₃ - :	Bi ³⁺ :
O in BiO_3^- :	O in MnO ₄ - :

Assign the oxidation states for each element in the redox reaction below:

$$Mn^{2+} (aq) + BiO_{3}^{-} (aq) \rightarrow MnO_{4}^{-} (aq) + Bi^{3+} (aq)$$

$$Mn^{2+} : +2 \qquad Mn \text{ in } MnO_{4}^{-} : +7$$

$$Bi \text{ in } BiO_{3}^{-} : +5 \qquad Bi^{3+} : +3$$

$$O \text{ in } BiO_{3}^{-} : -2 \qquad O \text{ in } MnO_{4}^{-} : -2$$

Balance the following reaction using the half-reactions method in acidic solution:

$$Mn^{2+} (aq) + BiO_{3}^{-} (aq) \rightarrow MnO_{4}^{-} (aq) + Bi^{3+} (aq)$$

$$Mn^{2+} : +2 \qquad Mn \text{ in } MnO_{4}^{-} : +7$$

$$Bi \text{ in } BiO_{3}^{-} : +5 \qquad Bi^{3+} : +3$$

$$O \text{ in } BiO_{3}^{-} : -2 \qquad O \text{ in } MnO_{4}^{-} : -2$$

Balance the following reaction using the half-reactions method in acidic solution:

	$Mn^{2+}(aq) + BiO_3^-(aq) \rightarrow MnO_4^-(aq) + Bi^{3+}(aq)$						
Mn ²⁺ : +2	2		Mn in MnO_4^- : +7				
Bi in BiO ₃ -: +5	5		Bi ³⁺ : +3				
O in BiO ₃ −: −2	2		O in MnO_4^- : -2				
1. Separate half-reactions:	red: 1	$BiO_{3}^{-}(aq) \rightarrow 1$	Bi ³⁺ (<i>aq</i>)				

2. Balance heavy atoms:					OX:		1	Mn²+ (<i>aq</i>)	\rightarrow	1	MnO ₄ - (<i>aq</i>)					
3. Balance O with H ₂ O:							1	$\operatorname{BiO}_3^-(aq)$	\rightarrow	1	Bi ³⁺ (<i>aq</i>)	+	3	H ₂ O (<i>I</i>)		
				4	H ₂ O (<i>I</i>)	+	1	Mn ²⁺ (<i>aq</i>)	\rightarrow	1	MnO ₄ - (<i>aq</i>)					
4. Balance H with H⁺:				6	H+ (<i>aq</i>)	+	1	BiO ₃ - (aq)	\rightarrow	1	Bi ³⁺ (<i>aq</i>)	+	3	H ₂ O (<i>I</i>)		
				4	H ₂ O (<i>I</i>)	+	1	Mn²+ (<i>aq</i>)	\rightarrow	1	MnO ₄ - (<i>aq</i>)	+	8	H⁺ (<i>aq</i>)		
5. Balance charge with e⁻:		5 × [2 e-	+	6	H⁺ (<i>aq</i>)	+	1	$\operatorname{BiO}_3^-(aq)$	\rightarrow	1	Bi ³⁺ (<i>aq</i>)	+	3	H ₂ O (/)]	
		2 ×	[4	H ₂ O (<i>I</i>)	+	1	Mn ²⁺ (<i>aq</i>)	\rightarrow	1	MnO ₄ - (<i>aq</i>)	+	8	H⁺ (<i>aq</i>)	+	5 e⁻]
6: Add the reactions:	5	$BiO_3^-(aq)$	+	14	H⁺ (<i>aq</i>)	+	2	Mn ²⁺ (<i>aq</i>)	\rightarrow	5	Bi ³⁺ (aq)	+	7	H ₂ O (/)	+	2 MnO ₄ - (<i>aq</i>)

Exothermic vs. Endothermic

Because of the law of conservation of energy (energy cannot be created or destroyed), any energy *lost* from the <u>system</u> is energy *gained* by the <u>surroundings</u>. $q_{surr} = -q_{sys}$

Because of the law of conservation of energy (energy cannot be created or destroyed), any energy gained by the system is energy *lost* from the surroundings. $q_{surr} = -q_{sys}$

Q1: Is this endothermic or exothermic relative to the system? A1: Exothermic.

Q2: Will the system be warmer or cooler than it was?A2: Cooler, lost energy.



Q1: Is this endothermic or exothermic relative to the system?A1: Endothermic.

Q2: Will the system be warmer or cooler than it was?A2: Warmer, gained energy.

How do we measure enthalpy of a reaction (ΔH_{rxn})? Calorimetry.

Typically, we don't measure the energy of a system directly (it's hard to do so).

Usually, we measure the change in the energy (or heat) as the system undergoes a change, like a chemical reaction. This is called the change in enthalpy or heat of a reaction, denoted ΔH .

Also, we usually measure the surroundings and not the system itself.

Remember, that $q_{surr} = -q_{sys}$.

More specifically, we use a <u>calorimeter</u> as the surroundings. And our <u>system</u> is a particular reaction taking place.

A <u>calorimeter</u> is a well-insulated water bath, such that: $\Delta H_{\rm rxn} = -q_{\rm calorimeter}$



In a calorimeter at constant pressure and 25.2 °C, you mix solutions of potassium carbonate and barium nitrate, which releases $\Delta H_{rxn} = -196$ kJ. If the total volume of the solution is 1.2 L, what is the final temperature of the solution after the reaction is complete?

The molar heat capacity of liquid water is 75.3 $\frac{J}{\text{mol} \cdot ^{\circ}\text{C}}$.

In a calorimeter at constant pressure and 25.2 °C, you mix solutions of potassium carbonate and barium nitrate, which releases $\Delta H_{rxn} = -196$ kJ. If the total volume of the solution is 1.2 L, what is the final temperature of the solution after the reaction is complete?

The molar heat capacity of liquid water is 75.3 $\frac{J}{mol^{\circ}C}$.

Understand the heat of the reaction occurring is <u>absorbed</u> by the solution (the water), so

 $q_{water} = -\Delta H_{rxn} = 196 \text{ kJ}$

Now, figure out what happens to the water if we were to heat it with 196 kJ of heat:

$$q = nc_{P}\Delta T$$

$$196 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \left(1.2 \text{ L} \text{ H}_{2}\text{O} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol } \text{H}_{2}\text{O}}{18.02 \text{ g} \text{ H}_{2}\text{O}}\right) \left(75.3 \frac{\text{J}}{\text{mol} \cdot ^{\circ}\text{C}}\right) (\text{T}_{f} - 25.2 \text{ °C})$$

$$T_{f} = 64 \text{ °C}$$

Hess's Law: Guided Example

Let's say you want to calculate the heat of reaction for the following reaction:

 $C(s) + O_2(g) \rightarrow CO_2(g)$

You don't want to carry out the actual reaction, but you have access to the heats of reactions of some related reactions:

- (1) $C(s) + \frac{1}{2}O_2(g) \to CO(g)$ $\Delta H = -111 \text{ kJ}$
- (2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283 \text{ kJ}$

Since enthalpy is a state function, if you add up (in some manner) these two reactions to get the reaction you are interested in, then you can also get the heat of reaction.

Let's simply add reactions (1) and (2) to get reaction (3) below:

(1)	$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	∆ <i>H</i> = –111 kJ
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- (2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283 \text{ kJ}$
- (3) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{rxn} = -111 \text{ kJ} + (-283 \text{ kJ}) = -394 \text{ kJ}$

Reaction (3) is exactly the reaction we are interested in. Now let's add the numbers in!

Another Example

Let's say you want to calculate the heat of reaction for the following reaction:

 $\mathsf{CIF}(g) + \mathsf{F}_2(g) \to \mathsf{CIF}_3(g)$

You have access to the heats of reactions of some related reactions:

(1)	$2OF_2(g) \rightarrow O_2(g) + 2F_2(g)$	∆ <i>H</i> = –49.4 kJ
(2)	$2CIF(g) + O_2(g) \rightarrow CI_2O(g) + OF_2(g)$	∆ <i>H</i> = +205.6 kJ

(3)
$$CIF_3(g) + O_2(g) \rightarrow 1/2 CI_2O(g) + 3/2 OF_2(g)$$
 $\Delta H = +266.7 \text{ kJ}$

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(3)	$CIF_3\left(g ight)$ + $O_2\left(g ight)$ $ ightarrow$ 1/2 $Cl_2O\left(g ight)$ + 3/2 $OF_2\left(g ight)$	∆ <i>H</i> = +266.7 kJ

Add up reactions (2), reverse of (1), and reverse of (3):

(2)
$$CIF(g) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CI_2O(g) + \frac{1}{2}OF_2(g)$$

(1)
$$F_2(g) + \frac{1}{2}O_2(g) \to OF_2(g)$$

(3)
$$1/2 \operatorname{Cl}_2 O(g) + 3/2 \operatorname{OF}_2(g) \to \operatorname{ClF}_3(g) + O_2(g)$$

 $\operatorname{ClF}(g) + \operatorname{F}_2(g) \to \operatorname{ClF}_3(g)$

 $\Delta H = \frac{1}{2} (+205.6 \text{ kJ})$ $\Delta H = \frac{1}{2} (+49.4 \text{ kJ})$ $\Delta H = -266.7 \text{ kJ}$ $\Delta H_{rxn} = -139.2 \text{ kJ}$

Note: Flip sign when you invert reaction!

Dr. Huynh

Heats of Formation ($\Delta H_{\rm f}$)

Let's say we want to calculate the standard heat of reaction for the following reaction: $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

Instead of Hess's Law, you could also use the standard heats of formations (ΔH_{f}°) to calculate ΔH_{rxn} .

Q: What is a heat of formation anyway?

A: It's the amount of heat required to form 1 mole of a substance from its elements in standard states.

Q: What is a standard state?

A: 1 bar (~1 atm) of pressure and 25 °C. (This is NOT STP for gases!)



How to use heats of formation ($\Delta H_{\rm f}$)

A <u>heat of combustion</u> (ΔH_{comb}) is the same thing as the heat of reaction but pertains to a combustion reaction, such as:

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2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)
```

PAY ATTENTION TO THE STOICHIOMETRIC AMOUNTS WHEN GIVEN HEATS OF REACTION!

Calculate the heat of this reaction (combustion):

 $\Delta H_{rxn}^{o} = \sum_{\text{products}} n_{\text{products}} \Delta H_{f,\text{products}}^{o} - \sum_{\text{reactants}} n_{\text{reactants}} \Delta H_{f,\text{reactants}}^{o}$ $\Delta H_{rxn}^{o} = n_{\text{CO}_{2}} \Delta H_{\text{CO}_{2}}^{o} + n_{\text{H}_{2}\text{O}} \Delta H_{\text{H}_{2}\text{O}}^{o} - n_{\text{CH}_{3}\text{OH}} \Delta H_{\text{CH}_{3}\text{OH}}^{o} - n_{\text{O}_{2}} \Delta H_{\text{O}_{2}}^{o}$ $\Delta H_{rxn}^{o} = 2 \text{ mol} \left(-393.5 \frac{\text{kJ}}{\text{mol}}\right) + 4 \text{ mol} \left(-241.8 \frac{\text{kJ}}{\text{mol}}\right) - 2 \text{ mol} \left(-200.7 \frac{\text{kJ}}{\text{mol}}\right) - 3 \left(0 \frac{\text{kJ}}{\text{mol}}\right)$ $\Delta H_{rxn}^{o} = -1353 \text{ kJ}$ THIS IS HOW MUCH HEAT RELEASED IF 2 MOLES OF CH₃OH ARE BURNED!

When are gases ideal? When are they not ideal?

Gases behave ideally when:

- Pressure is low
- Temperature is high
- Volume of container is much larger than volume of actual gas particles

Gases behave non-ideally when:

- Pressure is high
- Temperature extremely low
- Volume of the gas becomes important
- Intermolecular or van der Waals interactions between the gas particles cannot be ignored

The Ideal Gas Law

PV = nRT

 $\begin{array}{l} \mathsf{P} = \mathsf{absolute \ pressure \ (units: atm)} \\ \mathsf{V} = \mathsf{volume \ of \ container \ (units: L)} \\ \mathsf{n} = \mathsf{number \ of \ moles \ of \ gas \ (units: mol)} \\ \mathsf{T} = \mathsf{absolute \ temperature \ (units: K)} \\ \mathsf{R} = \mathsf{universal \ gas \ constant \ } \left(0.08206 \ \frac{\mathsf{L} \cdot \mathsf{atm}}{\mathsf{mol} \cdot \mathsf{K}} \right) \end{array}$

Reference Points for Gases

Standard Temperature and Pressure (STP)

- P = 1 atm
- T = 0 °C = 273 K

Molar Volume: volume occupied by one mole of any ideal gas at STP = 22.4 L

ALWAYS WORK IN ABSOLUTE TEMPERATURE SCALE (K) ALWAYS WORK IN ABSOLUTE PRESSURE SCALE (ATM)

A bulb with a volume of 500.0 mL is filled with a gas at STP. How many moles of gas are in the bulb?

A bulb with a volume of 500.0 mL is filled with a gas at STP. How many moles of gas are in the bulb?

Start by recognizing that the contents of the bulb are at STP (1 atm and 0 °C).

This means that 1 mole of the gas will occupy 22.4 L of volume.

We can use the following dimensional analysis to find the total number of moles:

$$500.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.02232 \text{ mol gas}$$

Alternatively, use the Ideal Gas Law: PV = nRT $n = \frac{PV}{RT}$ $= \frac{(1.0 \text{ atm}) (500.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}})}{(0.08206 \frac{\text{L} \cdot \text{ atm}}{\text{mol} \cdot \text{K}}) (273.15 \text{ K})}$ n = 0.02232 mol gas

Consider the following four identical 1.0 L flasks:



A) Which flask has the largest number of atoms?

B) Which flask has the highest pressure?

Consider the following four identical 1.0 L flasks:



Given 6.0 L of nitrogen gas at –25 °C, what volume will the nitrogen gas occupy at 72 °C? Assume constant pressure.

Ideal Gas Law

P and n are constant.

Given 6.0 L of nitrogen gas at –25 °C, what volume will the nitrogen gas occupy at 72 °C? Assume constant pressure.

Start by collecting the information we know:

$$V_1 = 6.0 L$$
 $V_2 = ?$
 $T_1 = -25 \ ^{\circ}C = 284_{.15} K$ $T_2 = 72 \ ^{\circ}C = 345_{.15} K$

Set up the gas law and solve for final volume (V_2) :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$= \frac{(6.0 \text{ L})(345_{\cdot 15} \text{ K})}{248_{\cdot 15} \text{ K}}$$

$$V_2 = 8.3 \text{ L}$$

How to calculate partial pressures of a mixture of gases?

If you have a mixture of gases, and each gas behaves ideally, then the gases do not interact with each other and you can apply the ideal gas law to each gas independently.

This means that you can simply add the partial pressure of each gas together to find the total pressure:

 $P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} \dots$ $n_{\text{total}} = n_{\text{A}} + n_{\text{B}} + n_{\text{C}} \dots$

How to calculate partial pressure of gas A in a mixture:

- Determine moles of the gas n_A
 Determine the mole ratio X_A
- Multiply mole ratio by total pressure
- Ptotal can be found by using the ideal gas law

 N_A $X_A = n_A/n_{total}$ $P_A = X_A P_{total}$ $P_{total} = n_{total} RT/V$

• Or apply the ideal gas law on gas A only to find P_A

Partial Pressure



Imagine that both stopcocks were opened so that the gases mix at 298 K.

What is the partial pressure of each gas after opening?

Partial Pressure



Imagine that both stopcocks were opened so that the gases mix at 298 K.

What is the partial pressure of each gas after opening?

Solve for the number of moles using the pressures of each gas using the ideal gas law:

$$n_{CO_{2}} = \frac{PV}{RT} \qquad n_{H_{2}} = \frac{PV}{RT} \qquad n_{H_{2}} = \frac{PV}{RT} \qquad n_{Ar} = \frac{PV}{RT}$$

If we open the stopcocks, the total volume changes to 4.50 L. Now solve for new pressures:



The root-mean-square speed $(u_{\rm rms})$

ROOT-MEAN-SQUARE (RMS) SPEEDS

$$u_{\rm rms} = \sqrt{\frac{3RT}{MM}}$$
; $\frac{u_{\rm rms,A}}{u_{\rm rms,B}} = \sqrt{\frac{MM_{\rm B}}{MM_{\rm A}}}$; $R = 8.314 \frac{\rm kg \cdot m^2}{\rm mol \cdot K \cdot s^2}$

At a given temperature, gases with larger molar masses (MM) move more slowly.

<u>EFFUSION RATE (r_{eff}) </u> $\frac{r_{eff,A}}{r_{eff,B}} = \frac{u_{rms,A}}{u_{rms,B}} = \sqrt{\frac{MM_B}{MM_A}}$

Consider the following four identical 1.0 L flasks:



A) In which flask will the diffusion of the gas be the slowest?

B) Which flask contains the gas with the smallest average velocity?

Consider the following four identical 1.0 L flasks:



A) In which flask will the diffusion of the gas be the slowest?

$$u_{\rm rms} = \sqrt{\frac{3RT}{MM}} \Rightarrow u_{\rm rms} \propto \frac{T}{MM} \qquad \qquad \frac{T_{\rm A}}{MM_{\rm A}} = \frac{300}{146.1} = 2.1 \quad \frac{T_{\rm C}}{MM_{\rm C}} = \frac{273}{38.0} = 7.2 \\ \frac{T_{\rm B}}{MM_{\rm B}} = \frac{600}{44.0} = 13.6 \quad \frac{T_{\rm D}}{MM_{\rm D}} = \frac{200}{30.0} = 6.7$$

The larger the $u_{\rm rms}$, the slower the rate of diffusion. So, Flask A has the slowest rate of diffusion.

B) Which flask contains the gas with the smallest average velocity?

$$u_{\text{avg}} = \sqrt{\frac{8\text{RT}}{\pi \cdot \text{MM}}} \Rightarrow u_{\text{avg}} \propto \frac{T}{\text{MM}} \qquad \frac{T_{\text{A}}}{\text{MM}_{\text{A}}} = \frac{300}{146.1} = 2.1 \quad \frac{T_{\text{C}}}{\text{MM}_{\text{C}}} = \frac{273}{38.0} = 7.2$$
$$\frac{T_{\text{B}}}{\text{MM}_{\text{B}}} = \frac{600}{44.0} = 13.6 \quad \frac{T_{\text{D}}}{\text{MM}_{\text{D}}} = \frac{200}{30.0} = 6.7$$

Flask A has the smallest average velocity.