NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Laboratory Based Questions

2016 EDITION
PRESENTER

Periodic Table of the Elements

1 H 1.0079																		2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)						

§Not yet named

*Lanthanide Series:	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series:	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL	= liter(s), milliliter(s)		mm Hg	= millimeters of mercury
g	= gram(s)		J, kJ	= joule(s), kilojoule(s)
nm	= nanometer(s)		V	= volt(s)
atm	= atmosphere(s)		mol	= mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}

Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ where } a\,A + b\,B \rightleftarrows c\,C + d\,D$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

$$= K_a \times K_b$$

$$pH = -\log[H^+], \ pOH = -\log[OH^-]$$

$$14 = pH + pOH$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a, \ pK_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{total} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{total} = P_A + P_B + P_C + \ldots$$

$$n = \frac{m}{M}$$

$$K = {}^\circ C + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
M = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
a = molar absorptivity
b = path length
c = concentration

Gas constant, R = 8.314 J mol^{-1} K^{-1}
$\phantom{\text{Gas constant, } R}$ = 0.08206 L atm mol^{-1} K^{-1}
$\phantom{\text{Gas constant, } R}$ = 62.36 L torr mol^{-1} K^{-1}
1 atm = 760 mm Hg
$\phantom{\text{1 atm}}$ = 760 torr
STP = 0.00 $^\circ$C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -n F E^\circ$$

$$I = \frac{q}{t}$$

q = heat
m = mass
c = specific heat capacity
T = temperature
S° = standard entropy
H° = standard enthalpy
G° = standard free energy
n = number of moles
E° = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole
of electrons

$$1\,\text{volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

NATIONAL MATH + SCIENCE INITIATIVE

The Lab Based Questions
Writing for a "5"

What I Absolutely Have to Know to Survive the AP Exam

If asked to do the following, it might indicate the question deals with laboratory questions:
Design an experiment; list measurements needed; show setup of calculations needed, use sample data to do calculations; interpret or draw graphs; explain the affect of error on the calculated value; use qualitative observations…

Parts of a Lab Question

You may not have done that exact experiment but you can use the knowledge gained doing other experiments to help account for certain observations.

You may be asked to describe how to do an experiment or to design an experiment.
- Materials: If they give you a list of equipment, don't think you have to use all of it.
- Procedure: Be sure to include important techniques like rinsing the buret with the solution before a titration or heating to constant mass.
- Data needed: The data needed are values that can be measured like initial and final temperatures. Writing all the mathematical equations needed to do the calculations will help you determine what data is needed.
- Calculations: A calculation is using what was measured like temperature change. Show the set up of the mathematical equations required for the calculations. Use sample data when appropriate.
- Graphs: Be sure you label the axes and other important points on your graph.
- Error Analysis: State whether the quantity will be too high, too low, or no change. Use equations to help you determine what change will occur and to support your answer.

Common Lab Procedure: Calorimetry

Calorimetry is used to determine the heat released or absorbed in a chemical reaction. A calorimeter can determine the heat of a solution reaction at constant pressure.
Techniques:
- Use a double Styrofoam cup with a plastic top and hole for the thermometer
- Determine the change in temperature accurately
- Measure solution volumes precisely
- Start with a dry calorimeter
Information to know about calorimetry:
- Heat capacity (C) = the amount of heat needed to raise the temperature of an object by one degree Celsius or Kelvin, J/°C or J/K.
- The heat capacity of 1 mol of a substance is called its molar heat capacity (Joules per mole per degree) J/mol·°C or J/mol·K.
- Specific heat, c, also known as specific heat capacity, is defined as the amount of heat necessary to raise the temperature of 1.00 g of a substance by one degree. Units are (joules per gram per degree), J/g·°C or J/g·K. You often use the specific heat capacity in analyzing gathered data then convert to molar heat capacity.
Assumptions often made during calorimetry: (Be able to answer error analysis questions about each assumption below)
- The density of dilute solutions is the same for water. D = 1.0 g/mL
- The specific heat of the solutions is the same as that for water. $c = 4.184$ J/g°C
- The solutions react in their stochiometric amounts.
- There is no loss of heat to the surroundings.
Equations:
- $q = mc\Delta T$ (c = 4.184 J/g°C)
- $q = \Delta H = mc\Delta T$, at constant pressure
- Use the density of the solution to convert from volume to mass for $q = mc\Delta T$

**NATIONAL
MATH + SCIENCE
INITIATIVE**

Common Lab Procedure: Titration

A titration is a laboratory procedure for quantitative analysis. In a titration two reagents are mixed, one with a known concentration & known volume [or a solid with a known mass] and one with an unknown concentration. There is some way to indicate when the two reagents have reacted completely (typically an indicator), and at the end of the titration the unknown solution's concentration can be calculated since you have accurately determined the volume of that solution required to complete the reaction.

Terms to know:
- Titrant – A solution of known concentration; it is often standardized
- Standardized solution – A solution in which the exact concentration is known.
- Indicator - A weak acid or base used in a titration to indicate the endpoint has been reached.
- Equivalence point – moles of acid = moles of base; point at which enough titrant has been added to completely react with the solution being analyzed.
- End point – the point at which the indicator changes color; important to pick an indicator with a pKa very close to the pH at the equivalence point.

Techniques:

Preparing the Buret:
1. Rinse a clean buret with distilled water and then the titrant (the solution that will be added to the flask).
2. Allow the titrant to drain through the buret so that the tip gets rinsed with titrant as well.
3. Discard the rinse solution. Fill it with the titrant. Remove air bubbles from the tip of the buret by draining several milliliters of titrant.

Preparing the Sample:
4. Pipet the desired volume of the solution to be analyzed into an Erlenmeyer flask. Record the exact volume. If the sample is a solid, weigh the desired mass, add the solid to an Erlenmeyer flask, and dissolve it in distilled water (the amount of water does matter since it doesn't change the moles of the solid). Be sure to record the exact mass of sample used.
5. Add the titrant to the flask until the equivalence point is reached. Calculate the volume of titrant added.
6. Change in color of a chemical indicator is usually used to signal the endpoint of the titration. The endpoint for this titration is reached when you reach a pale color that persists for several seconds.

Measured Data Required:
<u>**moles**</u> titrant = <u>**moles**</u> of substance analyzed @ equivalence point
- mass of DRY substance analyzed OR accurately measured volume of solution analyzed [measure with a pipet OR buret]
- *initial* volume of titrant (substance of known molarity) and *final* volume of titrant (required to reach end point)
- Molarity of titrant

Calculation Hints:
- Substance analyzed is solution/liquid:
  - $M_1V_1 = M_2V_2$ @ equivalence point
  - Volume of titrant used to reach end point [difference between final and initial volumes]
  - $M_{titrant}V_{of\ titrant\ added}$ = moles of titrant = moles of unknown
  - Molarity of unknown = Molarity of unknown $= \dfrac{\text{moles of unknown}}{\text{Liters of unknown}}$

NATIONAL
MATH + SCIENCE
INITIATIVE

- ▪ Substance analyzed is solid:
  - • Same as process as above
  - • $M_{titrant} V_{of\ titrant\ added}$ = moles of titrant = moles of unknown
  - • Molecular weight of the unknown $= \dfrac{\text{mass of solid dissolved}}{\text{moles of unknown}}$

Graphs:
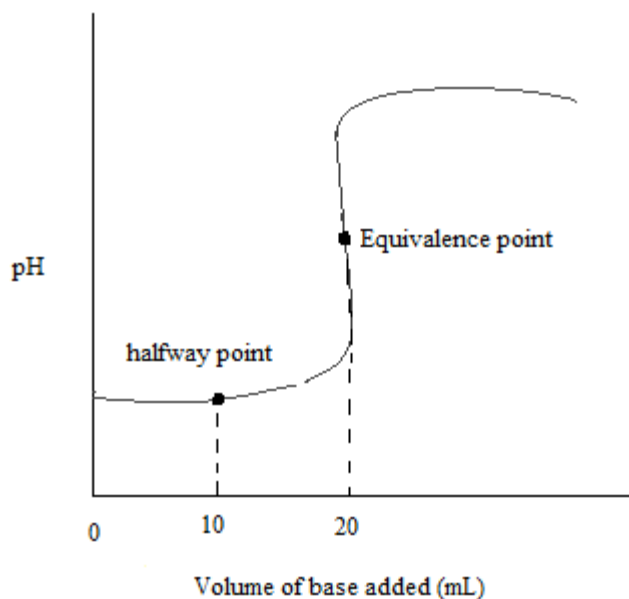
Common Lab Procedure: Gravimetric Analysis

One method for determining the amount of a given substance in solution is to form a precipitate that includes the substance. The precipitate is then filtered and dried. This process is called gravimetric analysis.

Techniques/Procedure:
1. Weigh sample
2. Form precipitate
3. Filter precipitate (A buchner funnel and aspirator can be used)
4. Dry precipitate (Be sure to dry to constant mass)
5. Weigh precipitate

For example if we wanted to determine the amount of chloride ions present in a given solid, we would weigh the solid sample, dissolve the sample in water, add an excess of silver nitrate solution to form the precipitate silver chloride. This precipitant would be filtered, and dried to constant mass. From the mass of silver chloride formed, we can determine the moles of silver chloride and the moles of chloride ion in the original sample.

NATIONAL
MATH + SCIENCE
INITIATIVE

Common Lab Procedure: Determining Molar Mass

Organize answer around calculations—paying special attention to what quantities are **measured** versus **calculated**!

$$\text{molar mass} = \frac{\text{mass of sample in grams}}{\text{moles of sample}}$$

Titration Data
- **moles** titrant = **moles** of substance analyzed @ equivalence point
- **Measured DATA** required:
  - mass of substance
  - *initial* volume of titrant (substance of known molarity) and *final* volume of titrant (required to reach end point)
  - Molarity of titrant
- **Calculations** required:
  - Molarity of titrant
  - Substance analyzed is solid:
  - $M_{titrant}V_{titrant}$ = moles titrant
  - $\text{molar mass} = \dfrac{\text{g of solid analzyed}}{\text{moles of titrant used}}$

Vaporization of a Volatile Liquid
- $PV = nRT$ used to determine moles
- **Measured DATA** Required:
  - Pressure = atmospheric pressure unless collected over water
  - *initial* mass of flask
  - *final* mass of flask
  - Temperature of boiling water—don't assume 100°C
  - Volume of gas = fill flask with water and measure the volume of water in a graduated cylinder
- **Constants** needed:
  - If collected over water, the water vapor pressure at the experimental temperature.
- **Calculations** Required:
  - If the gas was collected over water $P_{vapor} = P_{atmospheric/baraometric} - P_{water\ vapor\ at\ certain\ temperature}$
  - mass of sample = *final* mass of flask [includes vapors] – *initial* mass of flask

Common Lab Procedure: Colorimetric or Spectrophotometric Analysis

Colorimetric analysis is a quantitative analysis of a solution using color based on Beer's Law. Colorimetric analysis can be used to determine the concentration of an unknown solution, the rate constant of a reaction, the order of a reaction, etc.

Beer's Law is an expression than can be used to determine how much light passes through the solution. It also shows that concentration and absorbance are directly related.

$A = \varepsilon bc$

- A = absorbance (measured with a colorimeter)
- ε = molar absorptivity (how much light will be absorbed by 1 cm of a 1 M solution of the chemical)
- b = path length of the cuvette in cm
- c = concentration in molarity

NATIONAL
MATH + SCIENCE
INITIATIVE

The Lab Based Question – Writing for a "5"

Lab Based Questions Cheat Sheet

Relationships

Calorimetry $q = \Delta H = mc\Delta T$ at constant pressure

- c = specific heat
- ΔT = change is temperature
- m = mass
- q = heat

Beer's Law $A = \varepsilon bc$

- A = absorbance
- ε = molar absorptivity
- b = path length of the cuvette in cm
- c = concentration in molarity

Ideal Gas Law $PV = nRT$

- V = volume in liters
- n = moles
- T = temperature in Kelvin
- P = pressure

If collected using water displacement:

$P_{vapor} = P_{atmospheric/baraometric} - P_{water\ vapor\ at\ certain\ temperature}$

Other important relationships:

@ Equivalence point $M_1V_1 = M_2V_2$

$$molar\ mass = \frac{mass\ of\ sample\ in\ grams}{moles\ of\ sample}$$

$$\%error = \frac{accepted - experimental}{accepted} \times 100$$

Connections

Electrochemistry: draw diagram of galvanic or electrolytic cell, qualitative observations that can be made at the cathode and anode, etc.	Stoichiometry: empirical formula of a compound, percent of an element in a compound, etc.
Thermodynamics: heat of reaction, molar heat capacity, etc.	Acids and Bases: standardizing a solution, drawing a titration curve, etc.
Qualitative Analysis: identifying a compound based on observations and tests	

Potential Pitfalls

Be aware there are quantities you **measure** [such an initial temperature and final temperature or initial pressure and final pressure, etc.] and terms you **calculate** *using what you measured* such as ΔT or ΔP

Be sure to include important steps in the procedure like "heat to constant mass," "rinse the buret with distilled water and then the ***solution*** before titrating", "dissolve the solid in about 100 mL of water and then add water to the 500 mL mark on the volumetric flask," etc.

Writing the mathematical equations may help determine how an error affects the results. Use the equations to justify your error analysis.

If given a laboratory situation you have not specifically done, use the observations and the concepts you learned in your labs throughout the year to reason your way through the lab question.

NATIONAL
MATH + SCIENCE
INITIATIVE

NMSI SUPER PROBLEM

A sample of 6 *M* hydrochloric acid (about 5 mL) is placed at the bottom of the test tube and then carefully filled with distilled water so not to disturb the HCl. A piece of magnesium is placed on top of the distilled water and then the test tube is inverted into a beaker with distilled water. The magnesium is allowed to react completely. The gas is collected in the test tube at room temperature. Before the test tube with the gas is removed, the water levels inside and outside the test tube are the same. The chemicals and lab equipment used are listed below.

6 *M* hydrochloric acid	Barometer	Strip of magnesium metal	600 mL beaker
Distilled water	Balance	Test tube	
Table of water vapor pressures	Graduated cylinder	Thermometer	

(a) Write the balanced net ionic reaction that occurs when hydrochloric acid reacts with magnesium.

$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$	**1 point** for the correct balanced net ionic equation

(b) List the *measurements* needed to calculate the molar volume of the gas produced?

Mass of the magnesium Temperature of water Barometric pressure Volume of water after the reaction Total volume of test tube	**2 points** for all correct measurements. **1 point** for any three measurements

(c) Show the setup for the calculations needed to determine:

 (i) the moles of gas produced

$\text{moles of Mg} = \dfrac{\text{mass Mg}}{\text{molar mass of Mg}}$ $\text{moles of H}_2 = \text{moles of Mg} \times \dfrac{1 \text{ mol of H}_2}{1 \text{ mol Mg}}$	**1 point** for the correct calculation for the number of moles of Mg **1 point** for the correct calculation for the number of moles of H$_2$

 (ii) the volume of the gas produced

$\text{Volume of H}_2 = \dfrac{\text{total volume of test tube(mL) - volume of liquid after reaction(mL)}}{1000}$	**1point** for the correct calculation of volume.

(iii) the molar volume of the gas (at STP)

First you must find the pressure of the gas subtracting the vapor pressure of water: $P_{H_2} = P_{barometric} - P_{water\ vapor}$ Then solve for the volume of the gas at STP using the volume of gas collected at the experimental temperature and pressure $V_{STP} = \dfrac{P_{H_2}V_{H_2}T_{STP}}{T_{H_2}P_{STP}}$ Once you know the volume at STP, you can divide by the number of moles to get the molar volume: molar volume of H_2 $=$ $\dfrac{\text{volume of } H_2 \text{ at STP}}{\text{moles of } H_2 \text{ produced}}$	**1 point** for calculating the pressure of gas subtracting the vapor pressure of water **1 point** for calculating the correct volume of gas at STP **1 point** for calculating the molar volume of the gas

(d) What test can be done to prove which gas is produced?

A glowing splint will "pop" when placed at the mouth of the test tube since hydrogen gas is produced.	**1 point** for a correct test

(e) What is the purpose of making the water level inside the test tube equal to the water level in the beaker?

To ensure that the total pressure in the test tube is equal to the barometric pressure.	**1 point** for the correct answer.

(f) If the vapor pressure of water is not used in the calculation, how will the molar volume of the gas at STP be affected? (higher, lower or the same) Explain.

If the water vapor pressure is not accounted for, the pressure of the hydrogen gas will seem higher than it really is. This makes the volume of H_2 at STP higher. Therefore, the calculated molar volume of H_2 gas will be larger than it actaully is. molar volume of H_2 $=$ $\dfrac{\text{volume of } H_2 \text{ at STP}}{\text{moles of } H_2 \text{ produced}}$	**1 point** for correct justification **1 point** for stating the molar volume will be smaller

Another sample of hydrochloric acid was used to titrate a solution of calcium hydroxide.

(g) Describe the steps needed to make 50.0 mL of a 0.50 M solution from the 6 M solution of hydrochloric acid, using a dropper, 5.0 mL pipet, 50.0 mL volumetric flask, and distilled water. Be sure to mathematically justify your process.
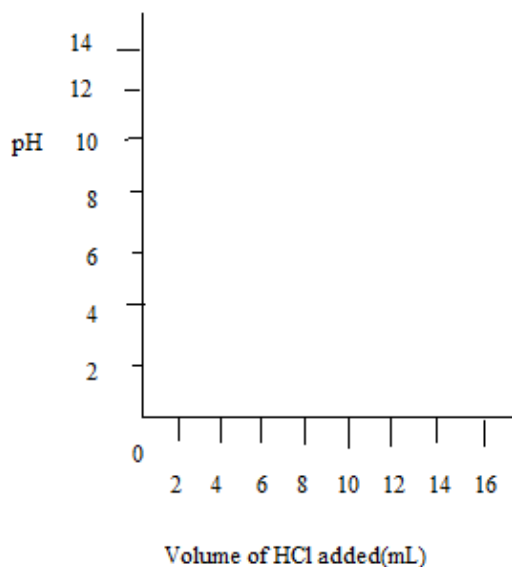
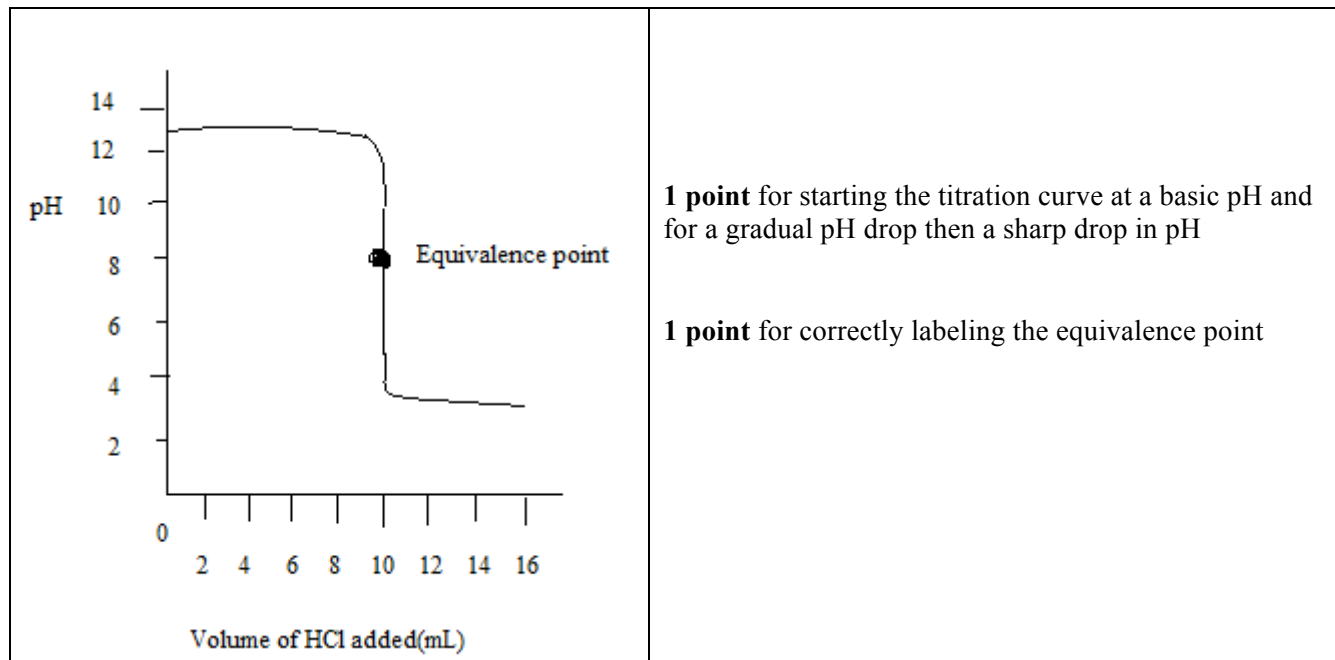|	
$M_1V_1 = M_2V_2$ $(50.0 \text{ mL}) \times (0.50 \, M) = (6 \, M) \times (V_2)$ $V_2 = \dfrac{(50.0 \text{ mL}) \times (0.50 \, M)}{(6.00 \, M)} = 4.17 \text{ mL}$ Put about 20 mL of distilled water into a 50.0 mL volumetric flask. Measure out 4.17 mL of 2.00 M HCl using the pipet. While swirling, add the HCl to the volumetric flask. Mix the solution. Using the dropper, add enough distilled water to fill the volumetric flask to the 50.0 mL mark and mix.	**1 point** for determining the correct volume of 6 M hydrochloric acid needed **1 point** for identifying the correct procedural steps for the dilution **1 point** for the correct equation and calculations

(h) Write the balanced net ionic equation for the dissociation of $Ca(OH)_2(s)$ in aqueous solution, and write the equilibrium-constant expression for the dissolving $Ca(OH)_2$.

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2 \text{ OH}^-$ $K_{sp} = [Ca^{2+}][OH^-]^2$	**1 point** for correct chemical equation **1 point** for correct K_{sp} expression

A 15.0 mL unknown solution of $Ca(OH)_2$ is titrated with a standardized 0.50 M solution of hydrochloric acid. It takes exactly 10.5 mL of hydrochloric acid to reach the equivalence point where the pH is 8.50.

(i) Sketch the titration curve that shows the pH change as the volume of hydrochloric acid added increases from 0 to 16.0 mL. Be sure to label the equivalence point of the titration.


Volume of HCl added(mL)

	1 point for starting the titration curve at a basic pH and for a gradual pH drop then a sharp drop in pH

1 point for correctly labeling the equivalence point |

(j)   Calculate the concentration of $[OH]^-$ from the titration.

mol H^+ = $(0.500\,M) \times (10.50\text{ mL})$ =

mol H^+ = 5.25 mmol H^+ = 5.25 mmol OH^-

$[OH^-] = \dfrac{5.25\text{ mmol}}{15.0\text{ mL}} = 0.35\,M$ | **1 point** for the correct number of moles of hydroxide ions

1 point for the correct concentration of hydroxide ions |

AP® CHEMISTRY
2013 SCORING GUIDELINES

Question 3
(9 points)

$$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$$
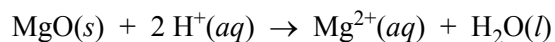
A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
3	100.0	0.25	26.0	28.1
4	100.0	0.50	24.1	28.1

(a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.

$0.100 \text{ L} \times \dfrac{1.0 \text{ mol HCl}}{1.0 \text{ L}} = 0.10 \text{ mol HCl}$ $0.50 \text{ g MgO} \times \dfrac{1 \text{ mol MgO}}{40.30 \text{ g MgO}} = 0.0124 \text{ mol MgO}$ By the stoichiometry of the equation, only $2 \times (0.0124 \text{ mol}) = 0.025 \text{ mol HCl}$ is needed to react with the MgO, thus HCl is in excess and MgO is limiting. OR The temperature change depended on the amount of MgO added, indicating that MgO was the limiting reactant.	1 point is earned for the correct choice with justification.

(b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

Trial 1 is inconsistent. The temperature change should be directly proportional (approximately) to the amount of the limiting reactant present. The ratio $\Delta T/(\text{mass MgO})$ should be constant. In trial 1, the ratio is one-half of trials 2, 3, and 4. Therefore, trial 1 is inconsistent with the other trials.	1 point is earned for identifying trial 1 with a valid justification.

AP® CHEMISTRY
2013 SCORING GUIDELINES

Question 3 (continued)

For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is 4.18 J/(g·C°). Assume that the density of the HCl(*aq*) is 1.0 g/mL.

(c) Calculate the magnitude of q, the thermal energy change, when the MgO was added to the 1.0 *M* HCl(*aq*). Include units with your answer.

$q_{calorimeter} = q_{cal} = mc\Delta T$ In trial 2, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.50 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot °\text{C}}\right)\left(4.1°\text{C}\right) = 1700 \text{ J or } 1.7 \text{ kJ}$ OR In trial 3, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.25 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot °\text{C}}\right)\left(2.1°\text{C}\right) = 880 \text{ J or } 0.88 \text{ kJ}$ OR In trial 4, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.50 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot °\text{C}}\right)\left(4.0°\text{C}\right) = 1700 \text{ J or } 1.7 \text{ kJ}$	1 point is earned for the correct mass of the solution. 1 point is earned for the correct calculation of q for any trial with a valid ΔT and correct units.

(d) Determine the student's experimental value of $\Delta H°$ for the reaction between MgO and HCl in units of kJ/mol$_{rxn}$.

Assuming that no heat was lost to the surroundings, $q_{rxn} = -q_{cal}$. In trials 2 and 4, $\Delta H° = \dfrac{q_{rxn}}{n_{MgO}} = \dfrac{-1,700 \text{ J}}{0.50 \text{ g MgO} \times \dfrac{1 \text{ mol MgO}}{40.30 \text{ g MgO}}} = -140,000 \text{ J/mol}_{rxn} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}}$ $= -140 \text{ kJ/mol}_{rxn}$ In trial 3, $\Delta H° = \dfrac{-880 \text{ J}}{0.25 \text{ g MgO} \times \dfrac{1 \text{ mol MgO}}{40.30 \text{ g MgO}}} = -140,000 \text{ J/mol}_{rxn} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}}$ $= -140 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct calculation of moles of MgO or setup of equation. 1 point is earned for the value of $\Delta H°$ and sign consistent with the setup.

AP® CHEMISTRY
2013 SCORING GUIDELINES

Question 3 (continued)

(e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of $\Delta H°$ for the reaction between MgO(s) and HCl(aq).

Substance	$\Delta H_f°$ (kJ/mol)
MgO(s)	−602
$H_2O(l)$	−286
$H^+(aq)$	0
$Mg^{2+}(aq)$	−467

$\Delta H° = \sum n_p \Delta H_f° \text{ products} - \sum n_r \Delta H_f° \text{ reactants}$ $= \left[\Delta H_f° \, Mg^{2+}(aq) + \Delta H_f° \, H_2O(l) \right] - \left[\Delta H_f° \, MgO(s) + 2\,\Delta H_f° \, H^+(aq) \right]$ $= \left[-467 \text{ kJ/mol} + (-286 \text{ kJ/mol}) \right] - \left[-602 \text{ kJ/mol} + 2(0) \text{ kJ/mol} \right]$ $= -151 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct setup using the $\Delta H_f°$ values. 1 point is earned for the correct value and sign consistent with the setup.

(f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

Yes. The experimentally determined value for $\Delta H°$ was less negative than the accepted value. If heat had leaked out of the calorimeter, then the ΔT of the contents would be less than expected, leading to a smaller calculated value for q and a less negative value for $\Delta H°$.	1 point is earned for the correct response with a valid explanation.

AP® CHEMISTRY
2011 SCORING GUIDELINES (Form B)

Question 5
(9 points)

A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

(a) Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH solution.

$M_1V_1 = M_2V_2$ $V_1 = \dfrac{M_2V_2}{M_1} = \dfrac{(1.250\ M)(100.0\ \text{mL})}{5.000\ M} = 25.00\ \text{mL}$	1 point is earned for the correct volume.

(b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH solution using 5.000 M NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H_2O	Crucible

Pipet 25.00 mL of 5.000 M NaOH solution into the 100 mL volumetric flask. Fill the volumetric flask to the calibration line with distilled water; using an eyedropper for the last few drops is advised. Cap the volumetric flask and invert several times to ensure homogeneity.	1 point is earned for descriptions of any <u>two</u> of the three steps. An additional point is earned if all <u>three</u> steps are described.

(c) The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

   (i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

When a weak acid is titrated with a strong base, the reaction forms water and the A^- ion. $\text{HA} + \text{OH}^- \rightleftarrows \text{A}^- + \text{H}_2\text{O}$ The A^- ion formed in the titration reacts with the solvent water to release OH^- ions, making the solution basic at the equivalence point. $\text{A}^- + \text{H}_2\text{O} \rightleftarrows \text{HA} + \text{OH}^-$	1 point is earned for either the correct equation or a clear statement that the conjugate base, A^-, is a (weak) base. 1 point is earned for indicating that the solution is basic because of the formation of OH^-.

AP® CHEMISTRY
2011 SCORING GUIDELINES (Form B)

Question 5 (continued)

(ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pK_a
Methyl red	5
Bromothymol blue	7
Phenolphthalein	9

Because the pH is basic at the equivalence point, it is best to use an indicator that changes color in basic solution. Therefore, phenolphthalein would be the best indicator for the titration.	1 point is earned for an answer consistent with the answer to part (c)(i) with justification.

(d) The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.

(i) What is the value of the acid-dissociation constant, K_a, for the weak acid? Explain your reasoning.

The resulting solution is at the half-equivalence-point, where [HA] = [A$^-$], thus pH = pK_a = 5.0 $\Rightarrow$ K_a = 1 × 10^{-5}.	1 point is earned for showing that the system is at the half-equivalence point. 1 point is earned for the correct value of K_a.

(ii) Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

The resulting solution is a buffer; therefore adding a few drops of acid or base does not appreciably change the pH.	1 point is earned for indicating that the solution is a buffer.

AP® CHEMISTRY
2011 SCORING GUIDELINES

Question 2

A student is assigned the task of determining the mass percent of silver in an alloy of copper and silver by dissolving a sample of the alloy in excess nitric acid and then precipitating the silver as $AgCl$.

First the student prepares 50. mL of 6 M HNO_3.

(a) The student is provided with a stock solution of 16 M HNO_3, two 100 mL graduated cylinders that can be read to ± 1 mL, a 100 mL beaker that can be read to ± 10 mL, safety goggles, rubber gloves, a glass stirring rod, a dropper, and distilled H_2O.

   (i) Calculate the volume, in mL, of 16 M HNO_3 that the student should use for preparing 50. mL of 6 M HNO_3.

moles before dilution $=$ moles after dilution $$M_i V_i = M_f V_f$$ $$(16\ M)(V_i) = (6\ M)(50.\ \text{mL})$$ $V_i = 19$ mL or 20 mL (to one significant figure)	1 point is earned for the correct volume.

   (ii) Briefly list the steps of an appropriate and safe procedure for preparing the 50. mL of 6 M HNO_3. Only materials selected from those provided to the student (listed above) may be used.

Wear safety goggles and rubber gloves. Then measure 19 mL of 16 $M$$HNO_3$ using a 100 mL graduated cylinder. Measure 31 mL of distilled H_2O using a 100 mL graduated cylinder. Transfer the water to a 100 mL beaker. Add the acid to the water with stirring.	1 point is earned for properly measuring the volume of 16 $M$$HNO_3$ and preparing a 6 $M$$HNO_3$ acid solution. 1 point is earned for wearing protective gear and for adding acid to water.

   (iii) Explain why it is <u>not</u> necessary to use a volumetric flask (calibrated to 50.00 mL ± 0.05 mL) to perform the dilution.

The graduated cylinders provide sufficient precision in volume measurement to provide two significant figures, making the use of the volumetric flask unnecessary.	1 point is earned for an acceptable explanation.

   (iv) During the preparation of the solution, the student accidentally spills about 1 mL of 16 M HNO_3 on the bench top. The student finds three bottles containing liquids sitting near the spill: a bottle of distilled water, a bottle of 5 percent $NaHCO_3(aq)$, and a bottle of saturated $NaCl(aq)$. Which of the liquids is best to use in cleaning up the spill? Justify your choice.

AP® CHEMISTRY
2011 SCORING GUIDELINES

Question 2 (continued)

$NaHCO_3(aq)$ should be used. The HCO_3^- ion will react as a base to neutralize the HNO_3.	1 point is earned for the correct choice with explanation.

Then the student pours 25 mL of the 6 M HNO_3 into a beaker and adds a 0.6489 g sample of the alloy. After the sample completely reacts with the acid, some saturated $NaCl(aq)$ is added to the beaker, resulting in the formation of an AgCl precipitate. Additional $NaCl(aq)$ is added until no more precipitate is observed to form. The precipitate is filtered, washed, dried, and weighed to constant mass in a filter crucible. The data are shown in the table below.

Mass of sample of copper-silver alloy	0.6489 g
Mass of dry filter crucible	28.7210 g
Mass of filter crucible and precipitate (first weighing)	29.3587 g
Mass of filter crucible and precipitate (second weighing)	29.2599 g
Mass of filter crucible and precipitate (third weighing)	29.2598 g

(b) Calculate the number of moles of AgCl precipitate collected.

mass of AgCl collected $= (29.2598 - 28.7210)$ g $= 0.5388$ g $$\frac{0.5388 \text{ g}}{(107.87 + 35.45) \text{ g mol}^{-1}} = 3.759 \times 10^{-3} \text{ mol AgCl}$$	1 point is earned for the correct mass of AgCl. 1 point is earned for the correct number of moles of AgCl given with the correct number of significant figures.

(c) Calculate the mass percent of silver in the alloy of copper and silver.

3.759×10^{-3} mol Ag $\times \dfrac{107.87 \text{ g Ag}}{1 \text{ mol Ag}} = 0.4055$ g Ag $$\frac{0.4055 \text{ g}}{0.6489 \text{ g}} \times 100\% = 62.49\% \text{ Ag}$$	1 point is earned for the correct setup and the correct calculation of the mass of Ag. 1 point is earned for the correct percent of Ag.

AP® CHEMISTRY
2008 SCORING GUIDELINES (Form B)

Question 5

The identity of an unknown solid is to be determined. The compound is one of the seven salts in the following table.

$Al(NO_3)_3 \cdot 9H_2O$	$BaCl_2 \cdot 2H_2O$	$CaCO_3$	$CuSO_4 \cdot 5H_2O$
NaCl	$BaSO_4$	$Ni(NO_3)_2 \cdot 6H_2O$	

Use the results of the following observations or laboratory tests to explain how each compound in the table may be eliminated or confirmed. The tests are done in sequence from (a) through (e).

(a) The unknown compound is white. In the table below, cross out the two compounds that can be eliminated using this observation. Be sure to cross out these same two compounds in the tables in parts (b), (c), and (d).

$Al(NO_3)_3 \cdot 9H_2O$	$BaCl_2 \cdot 2H_2O$	$CaCO_3$	~~$CuSO_4 \cdot 5H_2O$~~
NaCl	$BaSO_4$	~~$Ni(NO_3)_2 \cdot 6H_2O$~~	

> One point is earned for each correctly crossed-out compound.

(b) When the unknown compound is added to water, it dissolves readily. In the table below, cross out the two compounds that can be eliminated using this test. Be sure to cross out these same two compounds in the tables in parts (c) and (d).

$Al(NO_3)_3 \cdot 9H_2O$	$BaCl_2 \cdot 2H_2O$	~~$CaCO_3$~~	~~$CuSO_4 \cdot 5H_2O$~~
NaCl	~~$BaSO_4$~~	~~$Ni(NO_3)_2 \cdot 6H_2O$~~	

> One point is earned for each additional correctly crossed-out compound.

(c) When $AgNO_3(aq)$ is added to an aqueous solution of the unknown compound, a white precipitate forms. In the table below, cross out each compound that can be eliminated using this test. Be sure to cross out the same compound(s) in the table in part (d).

~~$Al(NO_3)_3 \cdot 9H_2O$~~	$BaCl_2 \cdot 2H_2O$	~~$CaCO_3$~~	~~$CuSO_4 \cdot 5H_2O$~~
NaCl	~~$BaSO_4$~~	~~$Ni(NO_3)_2 \cdot 6H_2O$~~	

> One point is earned for crossing out $Al(NO_3)_3 \cdot 9H_2O$ or for crossing out $Ni(NO_3)_2 \cdot 6H_2O$ if it had not been crossed out earlier.

AP® CHEMISTRY
2008 SCORING GUIDELINES (Form B)

Question 5 (continued)

(d) When the unknown compound is carefully heated, it loses mass. In the table below, cross out each compound that can be eliminated using this test.

$Al(NO_3)_3 \cdot 9H_2O$	$BaCl_2 \cdot 2H_2O$	~~$CaCO_3$~~	~~$CuSO_4 \cdot 5H_2O$~~
~~$NaCl$~~	~~$BaSO_4$~~	~~$Ni(NO_3)_2 \cdot 6H_2O$~~	

One point is earned for crossing out NaCl or for crossing out either $CaCO_3$ or $BaSO_4$ if they had not been crossed out earlier.

(e) Describe a test that can be used to confirm the identity of the unknown compound identified in part (d). Limit your confirmation test to a reaction between an aqueous solution of the unknown compound and an aqueous solution of one of the other soluble salts listed in the tables above. Describe the expected results of the test; include the formula(s) of any product(s).

Mix an aqueous solution of $BaCl_2 \cdot 2H_2O$ with an aqueous solution of $CuSO_4 \cdot 5H_2O$. The $BaSO_4$ will precipitate.	One point is earned for describing a precipitation reaction between the compound left in part (d) and another compound given in the problem. One point is earned for a correct identification of a precipitate that would form upon the mixing of the chosen solutions.

AP® CHEMISTRY
2008 SCORING GUIDELINES

Question 2

Answer the following questions relating to gravimetric analysis.

In the first of two experiments, a student is assigned the task of determining the number of moles of water in one mole of $MgCl_2 \cdot n\,H_2O$. The student collects the data shown in the following table.

Mass of empty container	22.347 g
Initial mass of sample and container	25.825 g
Mass of sample and container after first heating	23.982 g
Mass of sample and container after second heating	23.976 g
Mass of sample and container after third heating	23.977 g

(a) Explain why the student can correctly conclude that the hydrate was heated a sufficient number of times in the experiment.

No additional mass was lost during the third heating, indicating that all the water of hydration had been driven off.	One point is earned for the correct explanation.

(b) Use the data above to

(i) calculate the total number of moles of water lost when the sample was heated, and

mass of H_2O lost $= 25.825 - 23.977 = 1.848$ g *OR* $25.825 - 23.976 = 1.849$ g $1.848 \text{ g } H_2O \times \dfrac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.1026 \text{ mol } H_2O$	One point is earned for calculating the correct number of moles of water.

(ii) determine the formula of the hydrated compound.

mass of anhydrous $MgCl_2 = 23.977 - 22.347 = 1.630$ g $1.630 \text{ g } MgCl_2 \times \dfrac{1 \text{ mol } MgCl_2}{95.20 \text{ g } MgCl_2} = 0.01712 \text{ mol } MgCl_2$ $\dfrac{0.1026 \text{ mol } H_2O}{0.01712 \text{ mol } MgCl_2} = 5.993 \approx 6 \text{ mol } H_2O \text{ per mol } MgCl_2$ $\Rightarrow$ formula is $MgCl_2 \cdot 6\,H_2O$	One point is earned for calculating the correct number of moles of anhydrous $MgCl_2$. One point is earned for writing the correct formula (with supporting calculations).

AP® CHEMISTRY
2008 SCORING GUIDELINES

Question 2 (continued)

(c) A different student heats the hydrate in an uncovered crucible, and some of the solid spatters out of the crucible. This spattering will have what effect on the calculated mass of the water lost by the hydrate? Justify your answer.

The calculated mass (or moles) of water lost by the hydrate will be too large because the mass of the solid that was lost will be assumed to be water when it actually included some $MgCl_2$ as well.	One point is earned for the correct answer with justification.

In the second experiment, a student is given 2.94 g of a mixture containing anhydrous $MgCl_2$ and KNO_3. To determine the percentage by mass of $MgCl_2$ in the mixture, the student uses excess $AgNO_3(aq)$ to precipitate the chloride ion as $AgCl(s)$.

(d) Starting with the 2.94 g sample of the mixture dissolved in water, briefly describe the steps necessary to quantitatively determine the mass of the $AgCl$ precipitate.

Add excess $AgNO_3$. - Separate the AgCl precipitate (by filtration). - Wash the precipitate and dry the precipitate completely. - Determine the mass of AgCl by difference.	Two points are earned for <u>all three major steps</u>: filtering the mixture, drying the precipitate, and determining the mass by difference. One point is earned for any two steps.

(e) The student determines the mass of the $AgCl$ precipitate to be 5.48 g. On the basis of this information, calculate each of the following.

   (i) The number of moles of $MgCl_2$ in the original mixture

$5.48 \text{ g AgCl} \times \dfrac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} = 0.0382 \text{ mol AgCl}$ $0.0382 \text{ mol AgCl} \times \dfrac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} \times \dfrac{1 \text{ mol MgCl}_2}{2 \text{ mol Cl}} = 0.0191 \text{ mol MgCl}_2$	One point is earned for calculating the number of moles of AgCl. One point is earned for conversion to moles of $MgCl_2$.

   (ii) The percent by mass of $MgCl_2$ in the original mixture

$0.0191 \text{ mol MgCl}_2 \times \dfrac{95.20 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} = 1.82 \text{ g MgCl}_2$ $\dfrac{1.82 \text{ g MgCl}_2}{2.94 \text{ g sample}} \times 100\% = 61.9\% \text{ MgCl}_2 \text{ by mass}$	One point is earned for calculating the correct percentage.