1970

$$Zn \rightarrow Zn^{2+} + 2 e$$
-  
 $Cu \rightarrow Cu^{2+} + 2 e$ -  
 $E^{\circ} = 0.76 v$   
 $E^{\circ} = -0.34 v$ 

The solubility of H<sub>2</sub>S in water is approximately 0.1-molar.

$$Zn(OH)_{2(s)} + 2 OH^{-} \rightarrow Zn(OH)_{4^{2-}}$$
  $K = 4.5 \times 10^{-2}$   
 $Cu(OH)_{2(s)} + 2 OH^{-} \rightarrow Cu(OH)_{4^{2-}}$   $K = 1.6 \times 10^{-3}$ 

$$K_{sp}$$
 of ZnS = 10<sup>-23</sup>,  $K_{sp}$  of CuS = 10<sup>-44</sup>

A solution is approximately 1 molar in Cu<sup>2+</sup> and 1 molar in Zn<sup>2+</sup>. Based on the data above, outline three different methods for separating them discussing the theoretical bases for these separations.

# Answer:

- (1) Add a dilute solution of H<sub>2</sub>S, or any other soluble sulfide, dropwise to the solution to precipitate the less soluble CuS. Do not exceed a concentration of about 10<sup>-23</sup> M or ZnS will precipitate.
- (2) Copper(II) ions are more easily reduced than  $Zn^{2+}$  (it has a lower  $E^{\circ}$  than the zinc ion). Therefore, placing some iron ( $E^{\circ} = 0.44 \text{ v}$ ) in the solution will cause the Cu<sup>2+</sup> to reduce, the Fe to oxidize (to Fe<sup>2+</sup>), but the Zn<sup>2+</sup> will not reduce.
- (3) Precipitate the two with 4 moles of OH-, add a slight excess of hydroxide and the more soluble, Zn(OH)<sub>4</sub><sup>2-</sup>, will dissolve.

# 1972

A 10.00 milliliter sample of NH<sub>3</sub> solution is titrated with a standard HCl solution.

- 1) An unknown volume of water is added to the HCl solution.
- 2) An unknown volume of water is added to the 10.00 milliliter sample of NH<sub>3</sub> solution.
- 3) Phenolphthalein is used as the indicator.

For each of these three steps taken during the titration:

- (a) State whether it introduces an error into the titration results.
- (b) For any of the steps that introduce(s) an error, state whether the titration result will be raised or lowered compared to the result obtained if the error had not been made.
- (c) Explain why the result is high or low for each error that you detect.

Answer:

- (a) (1) error (2) no error (3) error
- (b) (1) raised (3) lowered
- (c) (1) a more dilute solution of HCl will require a greater volume of titrant. Therefore the apparent concentration of ammonia is stronger than the real concentration.
  - (3) The titration of a weak base by a strong acid has an equivalence point in the weak acid range while phenolphthalein changes color in the weak base range. Therefore, less acid would be added to see this change than is required and the apparent concentration of ammonia would be less than the real concentration.

### 1973 D

Briefly describe four different laboratory tests by which NaNO<sub>3</sub> can be distinguished from NH<sub>4</sub>Cl. Answer:

- (1) Warm both solids, ammonium chloride can be identified by the smell of ammonia.
- (2) Dissolve equal amounts in water, the ammonium chloride solution is slightly acidic while the sodium nitrate is neutral.
- (3) Dissolve each in water, add a few drops of copper (II) nitrate to each. The bluer solution is the ammonium chloride.
- (4) Dissolve each in water, add a solution of Pb<sup>2+</sup>, the one that gives the white precipitate of PbCl<sub>2</sub> is ammonium chloride.

[many other tests possible]

### 1973 D

What minimum data are needed to determine the molecular weight of each of the following substances in the laboratory? In each case, use a different method and give the mathematical formula(s) to be used for calculating the molecular weight from these minimal data.

- (a) A liquid that is insoluble in water and that boils at 65°C
- (b) A solid nonelectrolyte

## Answer:

- (a) Vaporize a sample of the liquid at a specific temperature, T, in a specific volume container, V, under a specific pressure, P. Condense the vapor and determine its mass, M. Using the universal gas law, PV = nRT, calculate n. The molecular weight = M/n.
- (b) Measure a known mass of a solvent,  $M_{solvent}$ . Look-up its freezing point depression constant, kf. Measure a known mass of solid non-electrolyte,  $M_{solute}$  and mix into the solvent. Measure the change in the freezing point between the solution and the pure solvent,  $\Delta T_{fp}$ . Calculate the moles of solute per kg of solvent =  $(\Delta T_{fp}/kf)$ . Calculate the grams solute/kg solvent =  $M_{solute}/M_{solvent}$  (in kg). The molecular weight is this mass/moles.

## 1974 D

The heat liberated when 1.00 mole of acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, reacts with 1.00 mole of sodium hydroxide, NaOH, is 12.7 kilocalories. Describe how this value can be determined in a general chemistry laboratory.

Answer:

Use of calorimeter

Quantification of reactants

Measurement of temperature increase

Ouantification of total vol. (mass of solution)

Calculation described (inc. heat liberated per mole)

### 1975 D

Briefly outline a laboratory procedure that can be used to determine the composition of an alloy of copper and silver. The alloy dissolves completely in concentrated nitric acid.

### Answer:

One of many possible correct solutions:

Mass a sample of the alloy. Dissolve alloy in concentrated nitric acid. Precipitate the Ag<sup>+</sup> ions with any chloride (HCl as an example) as AgCl, the Cu<sup>2+</sup> remains in solution. Filter the precipitate, wash, dry, and weigh. The silver is 75.26% of the mass of the precipitate.

# 1979 D

In a laboratory determination of the atomic weight of tin, a sample of tin is weighed in a crucible. Nitric acid is added, and the reaction proceeds to give a hydrated tin(IV) oxide plus NO<sub>2</sub> and H<sub>2</sub>O. The hydrated tin(IV) oxide is then heated strongly and reacts as follows:

$$SnO_2.xH_2O(s) \rightarrow SnO_2(s) + xH_2O(g)$$

The SnO<sub>2</sub> is finally cooled and weighed in the crucible. Explain the effect on the calculated atomic weight of tin that would result from each of the following experimental errors:

- (a) Considerable spattering occurs when the nitric acid is added to the tin.
- (b) The hydrated tin(IV) oxide is not heated sufficiently to change it completely to tin oxide.

# Answer:

atomic wt. Sn = 
$$\frac{32(\text{wt}_{\text{Sn}})}{(\text{wt}_{\text{SnO}_2} - \text{wt}_{\text{Sn}})}$$
$$= \frac{32(\text{wt}_{\text{Sn}})}{\text{apparent wt of O}}$$

- (a) mass of residue will be too low, : the apparent at. wt. will be too high.
- (b) mass of residue will be too high, : the apparent at. wt. will be too low.

## 1982 D

Describe a laboratory procedure needed to carry out each of the following.

- (a) Separate a mixture of powdered solid CaCl<sub>2</sub> and CaCO<sub>3</sub>.
- (b) Determine the concentration of solute in an aqueous sodium chloride solution and give the concentration units that your method provides.
- (c) Separate a mixture of two volatile liquids.

### Answer:

- (a) Add water to the mixture. CaCO<sub>3</sub> doesn't dissolve, whereas, the CaCl<sub>2</sub> does dissolve. Filter the solution. The aqueous CaCl<sub>2</sub> solution passes through the filter paper and the CaCO<sub>3</sub> is collected on the paper.
- (b) Pipet an aliquot of known volume into a flask. Add excess AgNO<sub>3</sub> solution to precipitate AgCl. Filter, dry, and then weigh the AgCl.

$$\frac{\text{wt. AgCl}}{\text{mol.wt.AgCl}} = \# \text{ mol AgCl} = \# \text{ mol NaCl}$$

$$M = \frac{\text{mol AgCl (or NaCl)}}{\text{vol. aliquot in L}}$$

# OR

Take a known volume of solution. Evaporate solution to dryness and weigh the NaCl residue.

$$M = \frac{\text{wt. NaCl} / \text{mol. wt. NaCl}}{\text{vol. NaCl in L}}$$

[other procedures possible, such as the use of colligative properties, etc.]

(c) Fractional distillation.

# 1984 C

Given solid samples of KI and of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, briefly describe four simple laboratory tests by which these two compounds can be distinguished. For each test, report the expected result for each compound. Answer:

## Possibilities include:

- (1) Flame test: K<sup>+</sup> lavender; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, no lavender
- (2) Add Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>: KI, pink color in organic layer; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, no change
- (3) Add Pb<sup>2+</sup>: KI, yellow ppt of PbI<sub>2</sub>; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, white ppt of PbCO<sub>3</sub>.
- (4) Add Ag<sup>+</sup>: KI, pale yellow ppt of AgI; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, white ppt of Ag<sub>2</sub>CO<sub>3</sub>.
- (5) Add I<sub>2</sub>: KI, brown color of I<sub>3</sub>:; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, no change
- (6) Add good oxidizing agent: KI, brown color of I<sub>3</sub>; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, no change
- (7) Add strong base: KI, no change; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, odor of NH<sub>3</sub> or color change of red litmus
- (8) Add Ba<sup>2+</sup>, or Ca<sup>2+</sup> or Mg<sup>2+</sup>: KI, no change; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, with precipitate of carbonate
- (9) Dissolve in water and use litmus: KI, neutral; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, basic
- (10) Add nonoxidizing acid: KI, no change; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, bubbles of CO<sub>2</sub>
- (11) Test melting points: KI, high; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, decomposes before melting

### 1985 D

Describe a separate laboratory procedure for preparing each of the following.

- (a) Pure barium sulfate from an aqueous solution of barium chloride.
- (b) A pure aqueous solution of copper(II) nitrate from solid copper(II) carbonate.
- (c) A pure aqueous solution of calcium chloride from an aqueous solution of calcium bromide.

- (a) Precipitation of insoluble BaSO<sub>4</sub> by adding a solution of a soluble sulfate, e.g., Na<sub>2</sub>SO<sub>4</sub>. Isolate BaSO<sub>4</sub> by filtration. Purify BaSO<sub>4</sub> by washing and drying it.
- (b) Dissolve CuCO<sub>3</sub> with HNO<sub>3</sub> to form Cu(NO<sub>3</sub>)<sub>2</sub> solution. Isolate by avoiding the addition of excess acid. Purify by heating to drive off CO<sub>2</sub>.
- (c) Form CaCl<sub>2</sub> solution by treating CaBr<sub>2</sub> solution with Cl<sub>2</sub>. **OR** Add a soluble carbonate. Separate the precipitated CaCO<sub>3</sub>, wash, and dissolve in HCl. Purify CaCl<sub>2</sub> solution by extracting the Br<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub> or equivalent. **OR** Heat the solution.

## 1988 D

An experiment is to be performed to determine the standard molar enthalpy of neutralization of a strong acid by a strong base. Standard school laboratory equipment and a supply of standardized 1.00-molar HCl and standardized 1.00-molar NaOH are available.

- (a) What equipment would be needed?
- (b) What measurements should be taken?
- (c) Without performing calculations, describe how the resulting data should be used to obtain the standard molar enthalpy of neutralization.
- (d) When a class of students performed this experiment, the average of the results was -55.0 kilojoules per mole. The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base -57.7 kilojoules per mole. Propose two likely sources of experimental error that could account for the result obtained by the class.

## Answer:

- (a) Equipment needed includes a thermometer, and a container for the reaction, preferably a container that serves as a calorimeter, and volumetric glassware (graduated cylinder, pipet, etc.).
- (b) Measurements include the difference in temperatures between just before the start of the reaction and the completion of the reaction, and amounts (volumes, moles) of the acid and the base.
- (c) Determination of heat (evolved or absorbed): The sum of the volumes (or masses) of the two solutions, the change in temperature and the specific heat of water are multiplied together to determine the heat of solution for the sample used. ( $q = m c_p \Delta T$ ). Division of the calculated heat of neutralization by moles of water produced, or moles of H<sup>+</sup>, or moles of OH<sup>-</sup>, or moles of limiting reagent.
- (d) Experimental errors: heat loss to the calorimeter wall, to air, to the thermometer; incomplete transfer of acid or base from graduated cylinder; spattering of some of the acid or base so that incomplete mixing occurred... Experimenter error: dirty glassware, spilled solution, misread volume or temperature...

### 1990 D

An experiment is performed to determine the empirical formula of a copper iodide formed by direct combination of elements. A clean strip of copper metal is weighed accurately. It is suspended in a test tube containing iodine vapor generated by heating solid iodine. A white compound forms on the strip of copper, coating it uniformly. The strip with the adhering compound is weighed. Finally, the compound is washed completely from the surface of the metal and the clean strip is dried and reweighed.

DATA TABLE	
Mass of clean copper strip	1.2789 grams
Mass of copper strip and compound	1.2874 grams

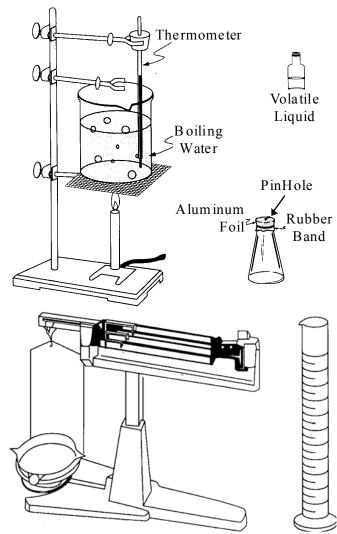
Mass of copper strip after washing 1.2748 grams

- (a) State how you would use the data above to determine each of the following. (Calculations not required.)
  - (1) The number of moles of iodine that reacted
  - (2) The number of moles of copper that reacted
- (b) Explain how you would determine the empirical formula for the copper iodide.
- (c) Explain how each of the following would affect the empirical formula that could be calculated.

- (1) Some unreacted iodine condensed on the strip.
- (2) A small amount of the white compound flaked off before weighing.

- (a) (1) (mass of Cu Strip + compound) (mass of original clean Cu strip) = mass of iodine (mass of iodine)/(atomic mass of iodine) = moles of iodine in the sample of compound (2) (mass of original clean Cu strip) (mass of strip after washing and drying) = mass of Cu (mass of Cu) / (atomic mass of Cu) = moles of Cu in sample of compound
- (b) The empirical formula is the ratio (moles iodine) / (moles Cu). **OR** (moles Cu) / (moles iodine).
- (c) (1) Unreacted I<sub>2</sub> would make the apparent mass of compound and the iodine too high. Thus, the I:Cu ratio in the empirical formula would be too high.
  - (2) If some compound flaked off, the mass of compound (and the I<sub>2</sub>) would be too low. Thus the I:Cu ratio in the empirical formula would be too low.

1991 D



An experiment is to be performed to determine the molecular mass of a volatile liquid by the vapor density method. The equipment shown above is to be used for the experiment. A barometer is also available.

- (a) What data are needed to calculate the molecular mass of the liquid?
- (b) What procedures are needed to obtain these data?
- (c) List the calculations necessary to determine the molecular mass.
- (d) If the volatile liquid contains non-volatile impurities, how would the calculated value of the molecular mass be affected? Explain your reasoning.

- (a) 1. mass of flask + cap (foil)
  - 2. mass of flask + cap + liquid
  - 3. temp. of boiling water
  - 4. barometric pressure
  - 5. volume of flask
- (b) 1. Measure mass of empty flask w/cap
  - 2. Pour about 3 mL of volatile liquid into flask.
  - 3. Replace cap and place flask into boiling water.
  - 4. Record temperature and barometric pressure.
  - 5. When all the liquid has evaporated remove flask and allow to cool, wipe if necessary.
  - 6. Weigh flask w/cap and condensed liquid.
  - 7. Fill the flask completely with water and measure the volume by pouring the water into a graduated cylinder.
- (c) 1. calculated mass of condensed liquid (i.e. the mass of the vapor)
  - 2. volume of vapor at STP
  - 3. moles of vapor (from PV=nRT)
  - 4. molecular weight of vapor = mass/mol
- (d) If non-volatile impurities were present it would make the calculated mass of condensed liquid larger than expected but not change the volume significantly. Therefore, the calculated molecular weight (in grams/mol) would be too large.

#### 1992 D

Four bottles, each containing about 5 grams of finely powdered white substance, are found in a laboratory. Near the bottles are four labels specifying high purity and indicating that the substances are glucose ( $C_6H_{12}O_6$ ), sodium chloride (NaCl), aluminum oxide ( $Al_2O_3$ ), and zinc sulfate ( $ZnSO_4$ ).

Assume that these labels belong to the bottles and that each bottle contains a single substance. Describe the tests that you could conduct to determine which label belongs to which bottle. Give the results you would expect for each test.

#### Answer:

[A <u>series</u> of chemical and/or physical tests must be performed which lead to distinct and unambiguous identification of these unknowns <u>relative to each other</u>. Tasting is explicitly excluded as a test technique.]

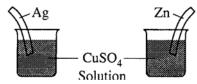
<u>One</u> of many possible solutions:

- (1) Add water to a small sample of each. The one that does NOT easily dissolve is Al<sub>2</sub>O<sub>3</sub>, the remaining will form clear, colorless solutions.
- (2) Test each of the remainders for electrical conductivity, the lowest will be C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.
- (3) To the remaining two solutions add a small amount of barium nitrate, Ba(NO<sub>3</sub>)<sub>2</sub> solution. The one that gives a white ppt. of BaSO<sub>4</sub> is the ZnSO<sub>4</sub>.
- (4) By exclusion, the remaining solution is NaCl.

## 1994 D (Required)

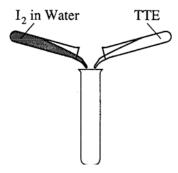
Discuss the following phenomena in terms of the chemical and physical properties of the substances involved and general principles of chemical and physical change.

[(a) & (b) in solid-liquid-solution section]



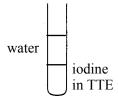
(c) What will be observed on the surfaces of zinc and silver strips shortly after they are placed in separate solutions of CuSO<sub>4</sub>, as shown on the right? Account for these observations.

(d) A water solution of I<sub>2</sub> is shaken with an equal volume of a nonpolar solvent such as TTE (trichlorotrifluoroethane). Describe the appearance of this system after shaking. (A diagram may be helpful.) Account for this observation.



### Answer:

- (c) No reaction in the Ag | Cu<sup>2+</sup> beaker because Ag<sup>+</sup> is easier to reduce than Cu<sup>2+</sup>. The zinc will go into solution as Zn<sup>2+</sup> while the Cu<sup>2+</sup> will reduce to Cu, forming on the surface of the zinc.  $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$   $E_{cell}^{\circ} = +1.10 \text{ v}$
- (d) (i) Water and TTE will form separate layers becasue the polar water is not miscible with the non-polar TTE.



- (ii) The TTE will be the bottom layer because its density is greater than the water.
- (iii) The non-polar iodine will dissolve better in the non-polar TTE and form a pinkish-purple tint.

### 1996 D

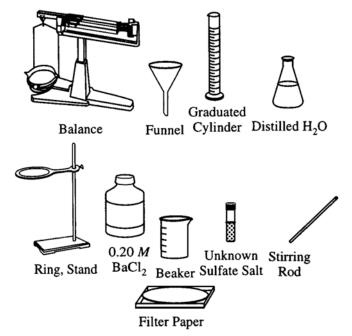
A 0.500-gram sample of a weak, nonvolatile acid, HA, was dissolved in sufficient water to make 50.0 milliliters of solution. The solution was then titrated with a standard NaOH solution. Predict how the calculated molar mass of HA would be affected (too high, too low, or not affected) by the following laboratory procedures. Explain each of your answers.

- (a) After rinsing the buret with distilled water, the buret is filled with the standard NaOH solution; the weak acid HA is titrated to its equivalence point.
- (b) Extra water is added to the 0.500-gram sample of HA.
- (c) An indicator that changes color at pH 5 is used to signal the equivalence point.
- (d) An air bubble passes unnoticed through the tip of the buret during the titration.

# Answer:

- (a) too low; molarity NaOH is lower concentration (through dilution with the drops of distilled water remaining in the buret) than standard leading to a higher volume used in titration, since M<sub>B</sub>V<sub>B</sub> = mol<sub>A</sub> and 0.500 g/mol<sub>A</sub> = molar mass, then a larger denominator gives a result that is too small.
- (b) not affected; extra water changes neither the moles of acid originally measured nor the volume of base required to reach the end point.
- (c) too high; the equivalence point is reached with too little volume of base, since M<sub>B</sub>V<sub>B</sub> = mol<sub>A</sub> and 0.500 g/mol<sub>A</sub> = molar mass, then a smaller denominator gives a result that is too large.

  (N.B., there would be no effect if the NaOH were standardized with the same indicator)
- (d) too low; the volume of NaOH would be higher than expected, since  $M_BV_B = mol_A$  and 0.500 g/mol\_A = molar mass, then a larger denominator gives a result that is too small.



An experiment is to be performed to determine the mass percent of sulfate in an unknown soluble sulfate salt. The equipment shown above is available for the experiment. A drying oven is also available.

- (a) Briefly list the steps needed to carry out this experiment.
- (b) What experimental data need to be collected to calculate the mass percent of sulfate in the unknown?
- (c) List the calculations necessary to determine the mass percent of sulfate in the unknown.
- (d) Would 0.20-molar MgCl<sub>2</sub> be an acceptable substitute for the BaCl<sub>2</sub> solution provided for this experiment? Explain.

### Answer:

- (a) mass container of unknown sulfate salt
  - pour some salt into beaker
  - mass container of unknown sulfate salt
  - add some distilled water to dissolve salt
  - add enough barium chloride solution to salt solution to precipitate all the barium sulfate
  - mass filter paper
  - fold filter paper, place into funnel and place into ring on stand
  - filter precipitate, use distilled water to wash out beaker and pass through filter paper.
  - wash ppt with distilled water
  - remove filter paper and ppt from funnel and dry in oven
  - mass filter paper and ppt, replace in oven and re-mass to constant weight
- (b) mass of unknown salt container before removal
  - mass of unknown salt container after removal
  - mass of filter paper
  - mass of dried filter paper + ppt
- (c) mass of unknown sulfate container, start
  - mass of unknown sulfate container, end
  - = mass of unknown sulfate

mass of dried filter paper + ppt

- mass of filter paper
- = mass of dried ppt

molar mass of BaSO<sub>4</sub>

sulfate is 41.16% (by mass) of BaSO<sub>4</sub>

mass of ppt  $\times$  0.4116 = mass of sulfate

f(mass of sulfate, mass of unknown sulfate)  $\times 100 = \%$  sulfate

(d) MgCl<sub>2</sub> would not be an acceptable substitute because magnesium sulfate is much more soluble than barium sulfate and would produce little or no ppt.

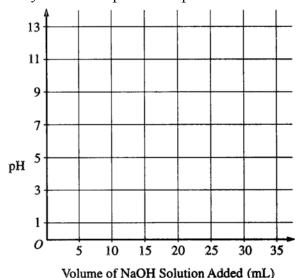
# 1998 D (Required)

[repeated in acid-base section]

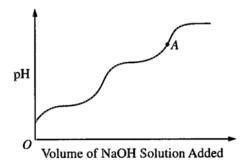
- An approximately 0.1-molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.
  - Clean, dry 50 mL buret
  - 250 mL Erlenmeyer flask

the titration curve in part (c).

- · Wash bottle filled with distilled water
- Analytical balance
- Phenolphthalein indicator solution
- Potassium hydrogen phthalate, KHP, a pure solid monoprotic acid (to be used as the primary standard)
- (a) Briefly describe the steps you would take, using the materials listed above, to standardize the NaOH solution.
- (b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.
- (c) After the NaOH solution has been standardized, it is used to titrate a weak monoprotic acid, HX. The equivalence point is reached when 25.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0 to 35.0 mL. Clearly label the equivalence point on the curve.

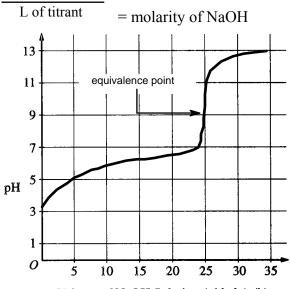


- (d) Describe how the value of the acid-dissociation constant,  $K_a$ , for the weak acid HX could be determined from
- (e) The graph below shows the results obtained by titrating a different weak acid, H<sub>2</sub>Y, with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter A on the curve.



- (a) exactly mass a sample of KHP in the Erlenmeyer flask and add distilled water to dissolve the solid.
  - add a few drops of phenolphthalein to the flask.
  - · rinse the buret with the NaOH solution and fill.
  - record starting volume of base in buret.
  - with mixing, titrate the KHP with the NaOH solution until it just turns slightly pink.
  - · record end volume of buret.
  - repeat to check your results. mass of KHP
- (b)  $\frac{\text{molar mass KHP}}{\text{moles of KHP}}$  = moles of KHP

since KHP is monoprotic, this is the number of moles of NaOH moles of NaOH



- (c) Volume of NaOH Solution Added (mL)
- (d) from the titration curve, at the 12.5 mL volume point, the acid is half-neutralized and the pH =  $pK_a$ .  $K_a = 10^{pK}a$
- (e)  $Y^{2-}$  (could it be OH-?)

# 2000 D Required

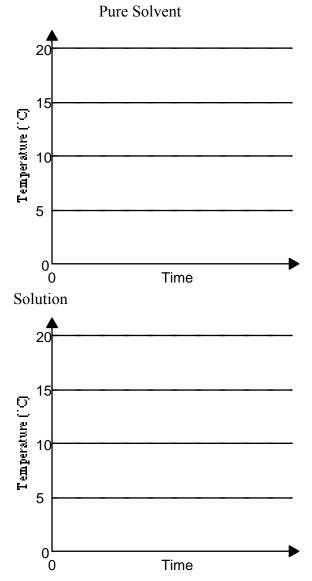
The molar mass of an unknown solid, which is nonvolatile and a nonelectrolyte, is to be determined by the freezing-point depression method. The pure solvent used in the experiment freezes at  $10^{\circ}$ C and has a known molal freezing-point depression constant,  $K_f$ . Assume that the following materials are also available.

- test tubes
- stirrer
- pipet

- stopwatch
- graph paper
- thermometer balance
- beaker

- ice
- hot-water bath

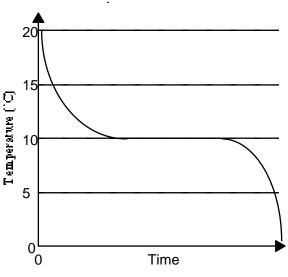
(a) Using the two sets of axes provided below, sketch cooling curves for (i) the pure solvent and for (ii) the solution as each is cooled from  $20^{\circ}$ C to  $0.0^{\circ}$ C



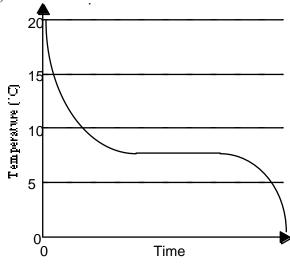
- (b) Information from these graphs may be used to determine the molar mass of the unknown solid.
  - (i) Describe the measurements that must be made to determine the molar mass of the unknown solid by this method.
  - (ii) Show the setup(s) for the calculation(s) that must be performed to determine the molar mass of the unknown solid from the experimental data.
  - (iii) Explain how the difference(s) between the two graphs in part (a) can be used to obtain information needed to calculate the molar mass of the unknown solid.
- (c) Suppose that during the experiment a significant but unknown amount of solvent evaporates from the test tube. What effect would this have on (he calculated value of the molar mass of the solid (*i.e.*, too large, too small, or no effect)? Justify your answer.
- (d) Show the setup for the calculation of the percentage error in a student's result if the student obtains a value of 126 g mol<sup>-1</sup> for the molar mass of the solid when the actual value is 120. g mol<sup>-1</sup>.

# Answer:

(a) (i) pure solvent



(ii) solution

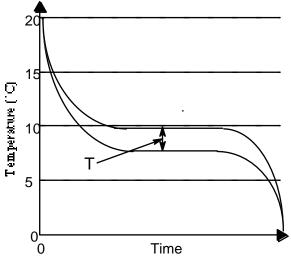


- (b) (i) mass of pure solvent; freezing point of pure solvent; mass of unknown solid solute added to pure solvent; freezing point of resulting solution
  - (ii) determine the change in freezing point,  $\Delta T$

 $\Delta T = K_f \cdot m$ , where m = and moles solute =

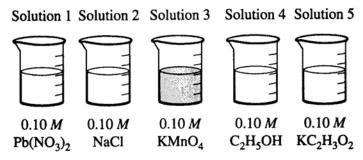
therefore, molar mass =

(iii) the change in temperature is the difference in the flat portions of the graph.



- (c) Too small. If solvent evaporates then its mass decreases and the recorded denominator in the equation in (b)(i) is larger than the expt. value and the resulting answer decreases.
- (d) % error =  $\times 100\%$

# 2001 D Required



Answer the questions below that relate to the five aqueous solutions at 25°C shown above.

- (a) Which solution has the highest boiling point? Explain.
- (b) Which solution has the highest pH? Explain.
- (c) Identify a pair of the solutions that would produce a precipitate when mixed together. Write the formula of the precipitate.
- (d) Which solution could be used to oxidize the  $Cl^{-}(aq)$  ion? Identify the product of the oxidation.
- (e) Which solution would be the <u>least</u> effective conductor of electricity? Explain.

### Answer:

- (a) solution 1, Pb(NO<sub>3</sub>)<sub>2</sub>. This compound will dissociate into three ions with the highest total particle molality. The greater the molality, the higher the boiling point. Solutions 2, 3, and 5 will produce two ions while solution 4 is molecular.
- (b) solution 5, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. The salt of a weak acid (in this case, acetic acid) produces a basic solution, and, a higher pH.
- (c) solution 1, Pb(NO<sub>3</sub>)<sub>2</sub>, and solution 2, NaCl. PbCl<sub>2</sub>
- (d) solution 3, KMnO<sub>4</sub>, ClO<sub>3</sub><sup>-</sup>
- (e) solution 4, C<sub>2</sub>H<sub>5</sub>OH. Ethyl alcohol is covalently bonded and does not form ions in water. Therefore, the solution is not a better conductor of electricity than water, which is also covalently bonded.

# 2002 D Required (repeated in thermodynamics)

A student is asked to determine the molar enthalpy of neutralization,  $\Delta H_{neut}$ , for the reaction represented above. The student combines equal volumes of 1.0 M HCl and 1.0 M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation  $q = mc\Delta T$ .

Assume the following.

- Both solutions are at the same temperature before they are combined.
- The densities of all the solutions are the same as that of water.
- Any heat lost to the calorimeter or to the air is negligible.
- The specific heat capacity of the combined solutions is the same as that of water.
- (a) Give appropriate units for each of the terms in the equation  $q = mc\Delta T$ .
- (b) List the measurements that must be made in order to obtain the value of q.
- (c) Explain how to calculate each of the following.
  - (i) The number of moles of water formed during the experiment
  - (ii) The value of the molar enthalpy of neutralization,  $\Delta H_{neut}$ , for the reaction between HCl(aq) and NaOH(aq)
- (d) The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 *M* HCl and 2.0 *M* NaOH.

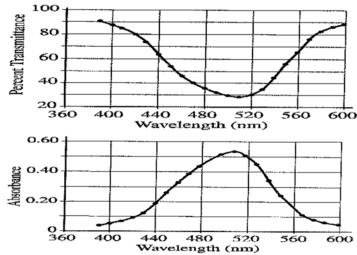
- (i) Indicate whether the value of q increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.
- (ii) Indicate whether the value of the molar enthalpy of neutralization,  $\Delta H_{neut}$ , increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.
- (e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization,  $\Delta H_{neu}$ ? Justify your answer.

- (a) q in J, m in grams, C in J/g°C, T in °C
- (b) mass or volume of each solution starting temperature of each reagent ending temperature of mixture
- (c) (i) both are 1 M acid and base and react on a 1:1 basis volume  $\times \times = \text{mol of H}^+$   $H^+ + OH^- \longrightarrow H_2O$ 
  - (ii)
- (d) (i) increases. Twice as much water is produced so it is twice the energy released in the same volume of solution
  - (ii) same. = same result
- (e) smaller, heat lost to the air gives a smaller amount of temperature change in the solution, which leads to a smaller measured heat release

# 2003 D Required

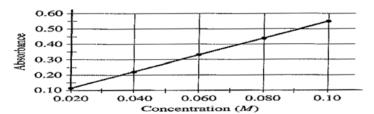
- 5. A student is instructed to determine the concentration of a solution of CoCl<sub>2</sub> based on absorption of light (spectrometric/colorimetric method). The student is provided with a 0.10 *M* solution of CoCl<sub>2</sub> with which to prepare standard solutions with concentrations of 0.020 *M*, 0.040 *M*, 0.060 *M* and 0.080 *M*.
- (a) Describe the procedure for diluting the 0.10 *M* solutions to a concentration of 0.020 *M* using distilled water, a 100 mL volumetric flask, and a pipet or buret. Include specific amounts where appropriate.

The student takes the 0.10 M solution and determines the percent transmittance and the absorbance at various wavelengths. The two graphs below represent the data.



(b) Identify the optimum wavelength for the analysis.

The student measures the absorbance of the  $0.020\,M$ ,  $0.040\,M$ ,  $0.060\,M$ ,  $0.080\,M$  and  $0.10\,M$  solutions. The data are plotted below.

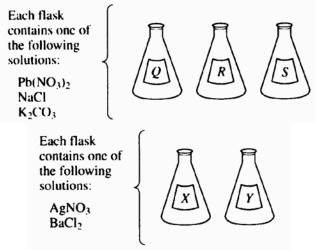


- (c) The absorbance of the unknown solution is 0.275. What is the concentration of the solution?
- (d) Beer's Law is an expression that includes three factors that determine the amount of light that passes through a solution. Identify two of these factors.
- (e) The student handles the sample container (*e.g.*, test tube or cuvette) that holds the unknown solution and leaves fingerprints in the path of the light beam. How will this affect the calculated concentration of the unknown? Explain your answer.
- (f) Why is this method of determining the concentration of CoCl<sub>2</sub> solution appropriate, whereas using the same method for measuring the concentration of NaCl solution would not be appropriate?

- (a)  $M_1V_1 = M_2V_2$ ;  $(0.10M)(V_1) = (0.020M)(100. mL)$  $V_1 = 20.0 mL$ 
  - a 20.0 mL aliquot of 0.10 M solution is measured by buret or pipet. this aliquot is added to the 100-mL volumetric flask and filled, with mixing, to the line on the neck with distilled water
- (b) approx. 510 nm
- (c) approx. 0.05 M
- (d) extinction coefficient path length of light concentration of absorbing species
- (e) fingerprints scatter light and the detector gets less light, the reading of absorbance is higher, indicating a higher than expected concentration
- (f) the Na<sup>+</sup> ion does not absorb energy in the visible spectrum, whereas the Co<sup>2+</sup> is a rose color

# 2004 D Required

In a laboratory class, a student is given three flasks that are labeled Q, R, and S. Each flask contains one of the following solutions:  $1.0 M \text{ Pb}(\text{NO}_3)_2$ , 1.0 M NaCl, or  $1.0 M \text{ K}_2\text{CO}_3$ . The student is also given two flasks that are labeled X and Y. One of these flasks contains  $1.0 M \text{ AgNO}_3$ , and the other contains  $1.0 M \text{ BaCl}_2$ . This information is summarized in the diagram below.



(a) When the student combined a sample of the solution Q with a sample of X, a precipitate formed. A precipitate also formed when samples of solutions Q and Y are combined.

- (i) Identify solution Q.
- (ii) Write the chemical formulas for each of the two precipitates.
- (b) When solution Q is mixed with solution R, a precipitate forms. However, no precipitate forms when solution Q is mixed with solution S.
  - (i) Identify solution *R* and solution *S*.
  - (ii) Write the chemical formula of the precipitate that forms when solution Q is mixed with solution R.
- (c) The identity of solution X and solution Y are to be determined using the following solutions:  $1.0 M \, \text{Pb}(\text{NO}_3)_2$ ,  $1.0 M \, \text{NaCl}$ , and  $1.0 M \, \text{K}_2 \, \text{CO}_3$ .
  - (i) Describe a procedure to identify solution X and solution Y.
  - (ii) Describe the observations that would allow you to distinguish between solution X and solution Y.
  - (iii) Explain how the observations would enable you to distinguish between solution X and solution Y.

- (a) (i)  $K_2CO_3$ 
  - (ii) Ag<sub>2</sub>CO<sub>3</sub>, BaCO<sub>3</sub>
- (b) (i)  $R = Pb(NO_3)_2$ , S = NaC1
  - (ii) PbCO<sub>3</sub>
- (c) (i) mix solution X with 1.0 M NaCl, mix solution Y with 1.0 M NaCl
  - (ii) whether a white ppt forms or not
  - (iii) X with NaCl will produce a white ppt, Y with NaCl will not produce a ppt