

# 2000 Advanced Placement Program® Free-Response Questions

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63	Eu	151.97	95	Am	(243)
62	Sm	150.4	94	Pu	
61	Pm	(145)	93	Np	S
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59	Pr	140.91	91	Pa	231.04
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	*Lanthanide Series			†Actinide Series	

Half-reactio	n		$E^{\circ}(V)$
$\operatorname{Li}^+ + e^-$	$\rightarrow$	Li(s)	-3.05
$Cs^+ + e^-$	$\rightarrow$	Cs(s)	-2.92
$K^{+} + e^{-}$	$\rightarrow$	K(s)	-2.92
$Rb^+ + e^-$	$\rightarrow$	Rb(s)	-2.92
$Ba^{2+} + 2e^{-}$	$\rightarrow$	Ba(s)	-2.90
$Sr^{2+} + 2e^{-}$	$\rightarrow$	Sr(s)	-2.89
$Ca^{2+} + 2e^{-}$	$\rightarrow$	Ca(s)	-2.87
$\mathrm{Na}^+ + e^-$	$\rightarrow$	Na(s)	-2.71
$Mg^{2+} + 2 e^{-}$	$\rightarrow$	Mg(s)	-2.37
$Be^{2+} + 2e^{-}$	$\rightarrow$	Be(s)	-1.70
$A1^{3+} + 3e^{-}$	$\rightarrow$	Al(s)	-1.66
$Mn^{2+} + 2 e^{-}$	$\rightarrow$	Mn(s)	-1.18
$Zn^{2+} + 2e^{-}$	$\rightarrow$	Zn(s)	-0.76
$Cr^{3+} + 3e^{-}$	$\rightarrow$	Cr(s)	-0.74
$Fe^{2+} + 2e^{-}$	$\rightarrow$	Fe(s)	-0.44
$Cr^{3+} + e^{-}$	$\rightarrow$	Cr <sup>2+</sup>	-0.41
$Cd^{2+} + 2e^{-}$	$\rightarrow$	Cd(s)	-0.40
$Tl^+ + e^-$	$\rightarrow$	Tl(s)	-0.34
$\text{Co}^{2+} + 2 e^{-}$	$\rightarrow$	Co(s)	-0.28
$Ni^{2+} + 2e^{-}$	$\rightarrow$	Ni(s)	-0.25
$\mathrm{Sn}^{2+} + 2 e^{-}$	$\rightarrow$	Sn(s)	-0.14
$Pb^{2+} + 2e^{-}$	$\rightarrow$	Pb(s)	-0.13
$2 \text{ H}^+ + 2 e^-$	$\rightarrow$	$H_2(g)$	0.00
$S(s) + 2 H^{+} + 2 e^{-}$	$\rightarrow$		0.14
$\operatorname{Sn}^{4+} + 2 e^{-}$	$\rightarrow$	Sn <sup>2+</sup>	0.15
$Cu^{2+} + e^{-}$	$\rightarrow$	Cu <sup>+</sup>	0.15
$Cu^{2+} + 2e^{-}$	$\rightarrow$	Cu(s)	0.34
$Cu^+ + e^-$		Cu(s)	0.52
$I_2(s) + 2e^{-s}$			0.53
$Fe^{3+} + e^{-}$		Fe <sup>2+</sup>	0.77
$Hg_2^{2+} + 2e^-$			
$Ag^+ + e^-$			
$Hg^{2+} + 2e^{-}$		_	
$2 \text{ Hg}^{2+} + 2 e^{-}$			
$\operatorname{Br}_2(l) + 2 e^-$		2 Br <sup>-</sup>	
$O_2(g) + 4 H^+ + 4 e^-$		_	1.23
2 (0)		2 Cl <sup>-</sup>	1.36
$Au^{3+} + 3e^{-}$			1.50
$\text{Co}^{3+} + e^{-}$	$\rightarrow$	Co <sup>2+</sup>	1.82
$F_2(g) + 2e^-$	$\rightarrow$	2 F <sup>-</sup>	2.87

#### ATOMIC STRUCTURE

$$\Delta E = hv$$

$$c = \lambda v$$

$$\lambda = \frac{h}{mv}$$

$$p = mv$$

$$E_n = \frac{-2.178 \times 10^{-18}}{r^2} \text{ joule}$$

# **EQUILIBRIUM**

$$K_{a} = \frac{[\mathrm{H}^{+}][\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

$$K_{b} = \frac{[\mathrm{OH}^{-}][\mathrm{HB}^{+}]}{[\mathrm{B}]}$$

$$K_{w} = [\mathrm{OH}^{-}][\mathrm{H}^{+}] = 1.0 \times 10^{-14} @ 25^{\circ}\mathrm{C}$$

$$= K_{a} \times K_{b}$$

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

$$14 = \mathrm{pH} + \mathrm{pOH}$$

$$\mathrm{pH} = \mathrm{p}K_{a} + \log\frac{[\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

$$\mathrm{pOH} = \mathrm{p}K_{b} + \log\frac{[\mathrm{HB}^{+}]}{[\mathrm{B}]}$$

$$\mathrm{p}K_{a} = -\log K_{a}, \ \mathrm{p}K_{b} = -\log K_{b}$$

$$K_{p} = K_{c}(RT)^{\Delta n},$$
where  $\Delta n$  = moles product gas – moles reactant gas

#### **THERMOCHEMISTRY**

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

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

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

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

$$= -RT \ln K = -2.303 RT \log K$$

$$= -n \mathcal{F} E^{\circ}$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q = \Delta G^{\circ} + 2.303 RT \log Q$$

$$q = mc\Delta T$$

$$C_{p} = \frac{\Delta H}{\Delta T}$$

$$E = \text{energy}$$
 $v = \text{frequency}$ 
 $\lambda = \text{wavelength}$ 
 $p = \text{momentum}$ 
 $v = \text{velocity}$ 
 $v = \text{principal quantum number}$ 
 $v = \text{mass}$ 

Speed of light, 
$$c = 3.0 \times 10^8 \,\mathrm{m\ s^{-1}}$$
  
Planck's constant,  $h = 6.63 \times 10^{-34} \,\mathrm{J\ s}$   
Boltzmann's constant,  $k = 1.38 \times 10^{-23} \,\mathrm{J\ K^{-1}}$   
Avogadro's number  $= 6.022 \times 10^{23} \,\mathrm{molecules\ mol^{-1}}$   
Electron charge,  $e = -1.602 \times 10^{-19} \,\mathrm{coulomb}$   
1 electron volt per atom  $= 96.5 \,\mathrm{kJ\ mol^{-1}}$ 

# **Equilibrium Constants**

$K_a$	(weak acid)
$K_b$	(weak base)
$K_{w}$	(water)
$K_p$	(gas pressure)
$K_c$	(molar concentrations)

$$S^{\circ} = \text{standard entropy}$$
 $H^{\circ} = \text{standard enthalpy}$ 
 $G^{\circ} = \text{standard free energy}$ 
 $E^{\circ} = \text{standard reduction potential}$ 
 $T = \text{temperature}$ 
 $n = \text{moles}$ 
 $m = \text{mass}$ 
 $q = \text{heat}$ 
 $c = \text{specific heat capacity}$ 
 $C_p = \text{molar heat capacity at constants}$ 

$$C_p$$
 = molar heat capacity at constant pressure  
1 faraday  $\mathcal{F}$  = 96,500 coulombs

#### GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

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

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

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

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

$$KE \text{ per mole} = \frac{3}{2}RT$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{molarity, } M = \text{moles solute per liter solution}$$

$$\text{molarity, } M = \text{moles solute per kilogram solvent}$$

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = \frac{nRT}{V}i$$

#### OXIDATION-REDUCTION; ELECTROCHEMISTRY

$$Q = \frac{\left[C\right]^{c} \left[D\right]^{d}}{\left[A\right]^{a} \left[B\right]^{b}}, \text{ where } a A + b B \rightarrow c C + d D$$

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

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{n\mathcal{F}} \ln Q = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q @ 25^{\circ}C$$

$$\log K = \frac{nE^{\circ}}{0.0592}$$

P = pressure

V = volume

T = temperature

n = number of moles

D = density

m = mass

v = velocity

 $u_{rms}$  = root-mean-square speed

KE = kinetic energy

r =rate of effusion

M = molar mass

 $\pi$  = osmotic pressure

i = van't Hoff factor

 $K_f$  = molal freezing-point depression constant

 $K_b$  = molal boiling-point elevation constant

Q = reaction quotient

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

 $E^{\circ}$  = standard reduction potential

K = equilibrium constant

Gas constant, 
$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$
  
=  $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$   
=  $8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$ 

Boltzmann's constant,  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ 

$$K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$$

$$K_b \text{ for H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$$

$$STP = 0.000^{\circ}C \text{ and } 1.000 \text{ atm}$$

Faraday's constant, 
$$\mathcal{F} = 96,500$$
 coulombs per mole of electrons

#### CHEMISTRY—SECTION II

(Total time—90 minutes)

# Part A Time—40 minutes

#### YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in this booklet.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

$$2 \operatorname{H}_2 S(g) \rightleftharpoons 2 \operatorname{H}_2(g) + S_2(g)$$

- 1. When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of  $H_2S(g)$  is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and  $3.72 \times 10^{-2}$  mol of  $S_2(g)$  is present at equilibrium.
  - (a) Write the expression for the equilibrium constant,  $K_c$ , for the decomposition reaction represented above.
  - (b) Calculate the equilibrium concentration, in mol  $L^{-1}$ , of the following gases in the container at 483 K.
    - (i)  $H_2(g)$
    - (ii)  $H_2S(g)$
  - (c) Calculate the value of the equilibrium constant,  $K_c$ , for the decomposition reaction at 483 K.
  - (d) Calculate the partial pressure of  $S_2(g)$  in the container at equilibrium at 483 K.
  - (e) For the reaction  $H_2(g) + \frac{1}{2} S_2(g) \rightleftharpoons H_2S(g)$  at 483 K, calculate the value of the equilibrium constant,  $K_c$ .

Answer EITHER Question 2 below OR Question 3 printed on page 8. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.

- 2. Answer the following questions that relate to electrochemical reactions.
  - (a) Under standard conditions at 25°C, Zn(s) reacts with  $Co^{2+}(aq)$  to produce Co(s).
    - (i) Write the balanced equation for the oxidation half reaction.
    - (ii) Write the balanced net-ionic equation for the overall reaction.
    - (iii) Calculate the standard potential,  $E^{\circ}$ , for the overall reaction at 25°C.
  - (b) At 25°C, H<sub>2</sub>O<sub>2</sub> decomposes according to the following equation.

$$2 \text{ H}_2\text{O}_2(aq) \rightarrow 2 \text{ H}_2\text{O}(l) + \text{O}_2(g)$$
  $E^\circ = 0.55 \text{ V}$ 

- (i) Determine the value of the standard free energy change,  $\Delta G^{\circ}$ , for the reaction at 25°C.
- (ii) Determine the value of the equilibrium constant,  $K_{eq}$ , for the reaction at 25°C.
- (iii) The standard reduction potential,  $E^{\circ}$ , for the half reaction  $O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$  has a value of 1.23 V. Using this information in addition to the information given above, determine the value of the standard reduction potential,  $E^{\circ}$ , for the half reaction below.

$$O_2(g) + 2 H^+(aq) + 2 e^- \rightarrow H_2O_2(aq)$$

(c) In an electrolytic cell, Cu(s) is produced by the electrolysis of  $CuSO_4(aq)$ . Calculate the maximum mass of Cu(s) that can be deposited by a direct current of 100. amperes passed through 5.00 L of 2.00 M  $CuSO_4(aq)$  for a period of 1.00 hour.

- 3. Answer the following questions about  $BeC_2O_4(s)$  and its hydrate.
  - (a) Calculate the mass percent of carbon in the hydrated form of the solid that has the formula  $BeC_2O_4 \cdot 3H_2O$
  - (b) When heated to 220.°C, BeC<sub>2</sub>O<sub>4</sub> · 3 H<sub>2</sub>O(s) dehydrates completely as represented below.

$$BeC_2O_4 \cdot 3 H_2O(s) \rightarrow BeC_2O_4(s) + 3 H_2O(g)$$

If 3.21 g of  $BeC_2O_4 \cdot 3 H_2O(s)$  is heated to 220.°C, calculate

- (i) the mass of  $BeC_2O_4(s)$  formed, and,
- (ii) the volume of the  $H_2O(g)$  released, measured at 220.°C and 735 mm Hg.
- (c) A 0.345 g sample of anhydrous  $BeC_2O_4$ , which contains an inert impurity, was dissolved in sufficient water to produce 100. mL of solution. A 20.0 mL portion of the solution was titrated with  $KMnO_4(aq)$ . The balanced equation for the reaction that occurred is as follows.

$$16 \text{ H}^{+}(aq) + 2 \text{ MnO}_{4}^{-}(aq) + 5 \text{ C}_{2}\text{O}_{4}^{2-}(aq) \rightarrow 2 \text{ Mn}^{2+}(aq) + 10 \text{ CO}_{2}(g) + 8 \text{ H}_{2}\text{O}(l).$$

The volume of  $0.0150 \, M$  KMnO<sub>4</sub>(aq) required to reach the equivalence point was 17.80 mL.

- (i) Identify the reducing agent in the titration reaction.
- (ii) For the titration at the equivalence point, calculate the number of moles of each of the following that reacted.
  - $MnO_4^-(aq)$
  - $C_2O_4^{2-}(aq)$
- (iii) Calculate the total number of moles of  $C_2O_4^{2-}(aq)$  that were present in the 100. mL of prepared solution.
- (iv) Calculate the mass percent of  $BeC_2O_4(s)$  in the impure 0.345 g sample.

#### **CHEMISTRY**

# Part B Time—50 minutes

#### NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 15 percent.

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases, a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

Example: A strip of magnesium is added to a solution of silver nitrate.

$$Ex.$$
  $Mg + Ag^+ \rightarrow Mg^{2+} + Ag$ 

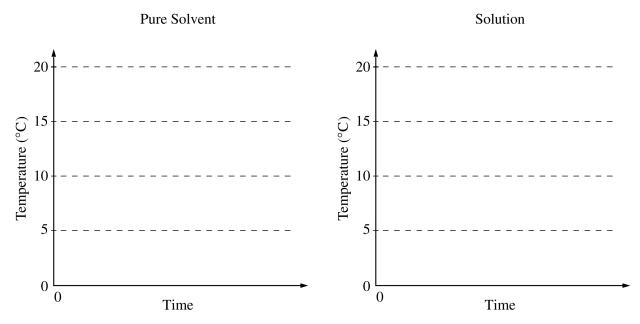
- (a) A small piece of calcium metal is added to hot distilled water.
- (b) Butanol is burned in air.
- (c) Excess concentrated ammonia solution is added to a solution of nickel(II) sulfate.
- (d) A solution of copper(II) chloride is added to a solution of sodium sulfide.
- (e) A solution of tin(II) nitrate is added to a solution of silver nitrate.
- (f) Excess hydrobromic acid solution is added to a solution of potassium hydrogen carbonate.
- (g) Powdered strontium oxide is added to distilled water.
- (h) Carbon monoxide gas is passed over hot iron(III) oxide.

Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

Answer BOTH Question 5 below AND Question 6 printed on page 11. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

- 5. 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
- thermometer
- balance

- beaker
- stopwatch
- graph paper
- hot-water bath
- ice
- (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°C to 0.0°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 the 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>.

$$O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$$

- 6. Consider the reaction represented above.
  - (a) Referring to the data in the table below, calculate the standard enthalpy change,  $\Delta H^{\circ}$ , for the reaction at 25°C. Be sure to show your work.

	$O_3(g)$	NO(g)	$NO_2(g)$
Standard enthalpy of formation, $\Delta H_f^{\circ}$ , at 25°C	143	90.	33
$(kJ \text{ mol}^{-1})$			

- (b) Make a qualitative prediction about the magnitude of the standard entropy change,  $\Delta S^{\circ}$ , for the reaction at 25°C. Justify your answer.
- (c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change,  $\Delta G^{\circ}$ , for the reaction at 25°C. Explain your reasoning.
- (d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[O_3]$ (mol $L^{-1}$ )	Initial [NO] (mol L <sup>-1</sup> )	Initial Rate of Formation of NO <sub>2</sub> (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.0010	0.0010	x
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4 <i>x</i>

(e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

Step I: 
$$O_3 + NO \rightarrow O + NO_3$$

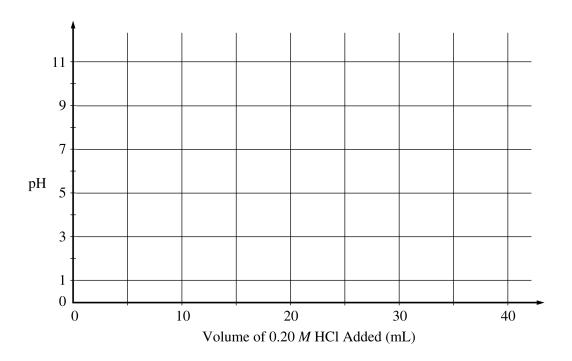
Step II: 
$$O + O_3 \rightarrow 2 O_2$$

Step III: 
$$NO_3 + NO \rightarrow 2 NO_2$$

Answer EITHER Question 7 below OR Question 8 printed on page 13. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

- 7. Answer the following questions about the element selenium, Se (atomic number 34).
  - (a) Samples of natural selenium contain six stable isotopes. In terms of atomic structure, explain what these isotopes have in common, and how they differ.
  - (b) Write the complete electron configuration (e.g.,  $1s^2 2s^2$ ... etc.) for a selenium atom in the ground state. Indicate the number of unpaired electrons in the ground-state atom, and explain your reasoning.
  - (c) In terms of atomic structure, explain why the first ionization energy of selenium is
    - (i) less than that of bromine (atomic number 35), and
    - (ii) greater than that of tellurium (atomic number 52).
  - (d) Selenium reacts with fluorine to form SeF<sub>4</sub>. Draw the complete Lewis electron-dot structure for SeF<sub>4</sub> and sketch the molecular structure. Indicate whether the molecule is polar or nonpolar, and justify your answer.

- 8. A volume of 30.0 mL of 0.10 M NH<sub>3</sub>(aq) is titrated with 0.20 M HCl(aq). The value of the base-dissociation constant,  $K_b$ , for NH<sub>3</sub> in water is  $1.8 \times 10^{-5}$  at 25°C.
  - (a) Write the net-ionic equation for the reaction of  $NH_3(aq)$  with HCl(aq).
  - (b) Using the axes provided below, sketch the titration curve that results when a total of 40.0 mL of 0.20 M HCl(aq) is added dropwise to the 30.0 mL volume of  $0.10 M \text{ NH}_3(aq)$ .



(c) From the table below, select the most appropriate indicator for the titration. Justify your choice.

Indicator	pK <sub>a</sub>
Methyl Red	5.5
Bromothymol Blue	7.1
Phenolphthalein	8.7

(d) If equal volumes of  $0.10 \, M \, \text{NH}_3(aq)$  and  $0.10 \, M \, \text{NH}_4\text{Cl}(aq)$  are mixed, is the resulting solution acidic, neutral, or basic? Explain.

#### **END OF EXAMINATION**