

AP[®] Chemistry 2010 Scoring Guidelines Form B

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Question 1 (10 points)

The compound butane, C_4H_{10} , occurs in two isomeric forms, *n*-butane and isobutane (2-methyl propane). Both compounds exist as gases at 25°C and 1.0 atm.

(a) Draw the structural formula of each of the isomers (include all atoms). Clearly label each structure.

Two points are earned for two correct structures with correct labels.

(Note: 1 point can be earned for either two correct structures that are mislabeled or one correct structure with or without correct label.)

OR

1 point can be earned for two skeletal structures (hydrogen atoms not shown) with proper labels.

(b) On the basis of molecular structure, identify the isomer that has the higher boiling point. Justify your answer.

The isomer *n*-butane has the higher boiling point. London (dispersion) forces are greater among molecules of *n*-butane than they are among molecules of isobutane because molecules of *n*-butane, with its linear structure, can approach one another more closely and can form a greater number of induced temporary dipoles than molecules of isobutane, with its more compact structure, can form.

One point is earned for the correct choice of isomer with justification.

The two isomers exist in equilibrium as represented by the equation below.

$$n$$
-butane $(g) \rightleftharpoons \text{isobutane}(g)$ $K_c = 2.5 \text{ at } 25^{\circ}\text{C}$

$$K_a = 2.5 \text{ at } 25^{\circ}\text{C}$$

Suppose that a 0.010 mol sample of pure *n*-butane is placed in an evacuated 1.0 L rigid container at 25°C.

(c) Write the expression for the equilibrium constant, K_c , for the reaction.

$$K_c = \frac{[\text{isobutane}]}{[n\text{-butane}]}$$

One point is earned for the correct equation.

Question 1 (continued)

(d) Calculate the initial pressure in the container when the *n*-butane is first introduced (before the reaction starts).

$$P = \frac{nRT}{V} = \frac{(0.010 \text{ mol})(0.0821 \frac{L \times atm}{\text{mol} \times K})(298 \text{ K})}{1.0 \text{ L}}$$

One point is earned for the correct substitution and numerical answer.

- = 0.24 atm
- (e) The *n*-butane reacts until equilibrium has been established at 25°C.
 - (i) Calculate the total pressure in the container at equilibrium. Justify your answer.

The total pressure in the container remains the same, 0.24 atm. As the reaction proceeds, the number of molecules in the container remains constant; one molecule of isobutane is produced for each molecule of n-butane consumed.

One point is earned for the correct answer with justification.

(ii) Calculate the molar concentration of each species at equilibrium.

$$K_c = \frac{\text{[isobutane]}}{\text{[}n\text{-butane]}} = \frac{x}{(0.010 - x)} = 2.5$$

$$x = 2.5(0.010 - x) = 0.025 - 2.5x$$

$$3.5x = 0.025 \implies x = 0.0071 M$$
 isobutane

$$(0.010 M - 0.0071 M) = 0.003 M n$$
-butane

One point is earned for the correct setup.

One point is earned for both correct numerical answers.

(iii) If the volume of the system is reduced to half of its original volume, what will be the new concentration of n-butane after equilibrium has been reestablished at 25°C? Justify your answer.

Halving the volume of the container at equilibrium doubles the pressure of both isobutane and n-butane, which has no effect on the equilibrium because the stoichiometry of the reaction is one mole of product produced for each mole of reactant consumed. Since the number of moles of each isomer is unchanged but the volume is reduced by half, concentrations of both isomers are doubled and the concentration of n-butane will be $2 \times 0.003 \, M = 0.006 \, M$.

One point is earned for the correct answer with justification.

Question 1 (continued)

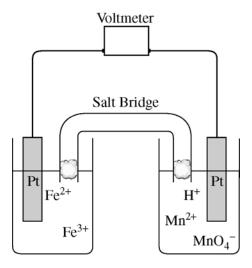
Suppose that in another experiment a 0.010 mol sample of pure isobutane is placed in an evacuated $1.0\,L$ rigid container and allowed to come to equilibrium at $25\,^{\circ}C$.

(f) Calculate the molar concentration of each species after equilibrium has been established.

The concentrations of isobutane and <i>n</i> -butane would
be the same as they were calculated in part (e)(ii),
0.0071 <i>M</i> and 0.003 <i>M</i> , respectively.

One point is earned for correct numerical answers or a correct statement regarding their equivalence to values obtained in part (e)(ii).

Question 2 (10 points)



$$5 \text{ Fe}^{2+}(aq) + \text{MnO}_4^-(aq) + 8 \text{ H}^+(aq) \rightarrow 5 \text{ Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4 \text{ H}_2\text{O}(l)$$

A galvanic cell and the balanced equation for the spontaneous cell reaction are shown above. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

Half-Reaction	<i>E</i> ° (V) at 298 K
$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$	+ 0.77
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$	+1.49

(a) On the diagram, clearly label the cathode.

The electrode in the beaker on the right should be labeled.	One point is earned for correct identification of the cathode.
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(b) Calculate the value of the standard potential, E° , for the spontaneous cell reaction.

$E_{cell} = 1.49 - 0.77 = 0.72 \text{ V}$	One point is earned for the correct numerical answer.

(c) How many moles of electrons are transferred when 1.0 mol of $MnO_4^-(aq)$ is consumed in the overall cell reaction?

5.0 moles of electrons are transferred.	One point is earned for the correct numerical answer.
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Question 2 (continued)

(d) Calculate the value of the equilibrium constant, K_{eq} , for the cell reaction at 25°C. Explain what the magnitude of K_{eq} tells you about the extent of the reaction.

$$\log K_{eq} = \frac{nE}{0.0592} = \frac{5 \times 0.72}{0.0592} = 61$$

$$K_{eq} = 6.5 \times 10^{60}$$

Because the magnitude of K_{eq} is very large, the extent of the cell reaction is also very large and the reaction goes essentially to completion.

One point is earned for the correct substitution.

One point is earned for the correct numerical answer.

One point is earned for an explanation.

Three solutions, one containing $\mathrm{Fe^{2+}}(aq)$, one containing $\mathrm{MnO_4^-}(aq)$, and one containing $\mathrm{H^+}(aq)$, are mixed in a beaker and allowed to react. The initial concentrations of the species in the mixture are $0.60~M~\mathrm{Fe^{2+}}(aq)$, $0.10~M~\mathrm{MnO_4^-}(aq)$, and $1.0~M~\mathrm{H^+}(aq)$.

(e) When the reaction mixture has come to equilibrium, which species has the higher concentration, $\text{Mn}^{2+}(aq)$ or $\text{MnO}_4^-(aq)$? Explain.

 $[Mn^{2+}(aq)]$ will be greater than $[MnO_4^-(aq)]$ because:

- (1) as indicated in part (d), the reaction essentially goes to completion, and
- (2) there is more than sufficient Fe^{2+} and H^+ to react completely with the MnO_4^- .

 $[MnO_4^-(aq)]$ at equilibrium is essentially zero.

One point is earned for the choice of Mn^{2+} with the explanation including only item (1).

One point is earned for including item (2) in the explanation.

(f) When the reaction mixture has come to equilibrium, what are the molar concentrations of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$?

At equilibrium,

$$[Fe^{2+}(aq)] = [Fe^{2+}(aq)]_{initial} - 5[MnO_4^{-}(aq)]_{reacted}$$

$$= 0.60 - 5(0.10) = 0.10 M$$

$$[Fe^{3+}(aq)] = 5 \times [MnO_4^{-}(aq)]_{reacted}$$

$$= 5(0.10) = 0.50 M$$

One point is earned for a correct setup (including a correct setup for an equilibrium calculation).

One point is earned for correct numerical answers.

Question 3 (10 points)

A sample of ore containing the mineral tellurite, TeO_2 , was dissolved in acid. The resulting solution was then reacted with a solution of $K_2Cr_2O_7$ to form telluric acid, H_2TeO_4 . The unbalanced chemical equation for the reaction is given below.

...
$$\operatorname{TeO}_2(s) + \ldots \operatorname{Cr}_2 \operatorname{O}_7^{2-}(aq) + \ldots \operatorname{H}^+(aq) \rightarrow \ldots \operatorname{H}_2 \operatorname{TeO}_4(aq) + \ldots \operatorname{Cr}^{3+}(aq) + \ldots \operatorname{H}_2 \operatorname{O}(l)$$

(a) Identify the molecule or ion that is being oxidized in the reaction.

Т	CeO ₂ or Te ⁴⁺	One point is earned for correct identification of molecule or ion.
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(b) Give the oxidation number of Cr in the $Cr_2O_7^{2-}(aq)$ ion.

+6	One point is earned for the correct answer.	Ì

(c) Balance the chemical equation given above by writing the correct lowest whole-number coefficients on the dotted lines.

$$3 \text{ TeO}_2(s) + 1 \text{ Cr}_2\text{O}_7^{2-}(aq) + 8 \text{ H}^+(aq) \rightarrow 3 \text{ H}_2\text{TeO}_4(aq) + 2 \text{ Cr}^{3+}(aq) + 1 \text{ H}_2\text{O}(l)$$

One point is earned for either

(1) two correct balances among Cr, H, O, charge, and Te vs. $\text{Cr}_2\text{O}_7^{2-}$ (for balancing by inspection or oxidation number method)

OR

(2) one correct half reaction or use of the correct multiplier to balance the charge (for balancing by half-reaction method).

One additional point is earned for a correctly balanced equation.

In the procedure described above, 46.00 mL of 0.03109 M K₂Cr₂O₇ was added to the ore sample after it was dissolved in acid. When the chemical reaction had progressed as completely as possible, the amount of unreacted (excess) Cr₂O₇²⁻(aq) was determined by titrating the solution with 0.110 M Fe(NO₃)₂. The reaction that occurred during the titration is represented by the following balanced equation.

$$6 \, \mathrm{Fe^{2+}}(aq) + \mathrm{Cr_2O_7^{2-}}(aq) + 14 \, \mathrm{H^+}(aq) \, \rightarrow \, 2 \, \mathrm{Cr^{3+}}(aq) + 6 \, \mathrm{Fe^{3+}}(aq) + 7 \, \mathrm{H_2O}(l)$$

A volume of 9.85 mL of $0.110 M \text{ Fe}(\text{NO}_3)_2$ was required to reach the equivalence point.

Question 3 (continued)

(d) Calculate the number of moles of excess $Cr_2O_7^{2-}(aq)$ that was titrated.

By the stoichiometry of the titration reaction, moles of excess $Cr_2O_7^{2-}$ titrated

$$=$$
 $\left(\frac{1}{6}\right)$ mol Fe²⁺ in 9.85 mL of 0.110 M Fe(NO₃)₂

$$= \left(\frac{1}{6}\right) (0.00985 \text{ L})(0.110 \text{ mol Fe}(\text{NO}_3)_2 \text{ L}^{-1})$$

= 0.000181 mol

One point is earned for either the correct stoichiometric factor OR correct use of (0.00985)(0.110) factor.

One point is earned for the correct numerical answer with the correct number of significant figures.

(e) Calculate the number of moles of $\operatorname{Cr_2O_7}^{2-}(aq)$ that reacted with the tellurite.

moles Cr₂O₇²⁻ that reacted with TeO₂

- = total mol $Cr_2O_7^{2-}$ added excess mol $Cr_2O_7^{2-}$ titrated
- = $(0.04600 \text{ L})(0.03109 \text{ mol } \text{Cr}_2\text{O}_7^{2-} \text{L}^{-1})$ excess mol $\text{Cr}_2\text{O}_7^{2-}$ titrated
- $= 0.001430 \text{ mol} 0.000181 \text{ mol} = 0.001249 \text{ mol } \text{Cr}_2\text{O}_7^{2-}$

One point is earned for correct calculation of initial moles of dichromate ion.

One point is earned for correct numerical answer with correct number of significant figures.

(f) Calculate the mass, in grams, of tellurite that was in the ore sample.

mass of TeO₂ in sample

= 0.001249 mol
$$\operatorname{Cr_2O_7^{2-}} \times \frac{3 \text{ mol } \operatorname{TeO_2}}{1 \text{ mol } \operatorname{Cr_2O_7^{2-}}} \times \frac{159.6 \text{ g } \operatorname{TeO_2}}{1 \text{ mol } \operatorname{TeO_2}}$$

 $= 0.5980 \,\mathrm{g}$

One point is earned for appropriate use of the stoichiometric factor *OR*

for correct calculation of molar mass of TeO₂.

One point is earned for the correct numerical answer.

Question 4 (15 points)

(a) Solid copper(II) sulfate pentahydrate is gently heated.

(i)	Balance	d equation	ι:

 $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5 H_2O$

One point is earned for the reactant.

Two points are earned for products.

One point is earned for balancing the equation.

(ii) How many grams of water are present in 1.00 mol of copper(II) sulfate pentahydrate?

1.00 mol CuSO ₄ $5H_2O \times \frac{1}{1.00}$	$\frac{5 \text{ mol H}_2\text{O}}{00 \text{ mol CuSO}_4 5\text{H}_2\text{O}} >$	$< \frac{18.0 \text{ g H}_2\text{O}}{1.00 \text{ mol H}_2\text{O}}$
=	$90.0~\mathrm{g~H_2O}$	

One point is earned for the correct numerical answer.

- (b) Excess concentrated aqueous ammonia is added to a solution of nickel(II) nitrate, leading to the formation of a complex ion.
 - (i) Balanced equation:

 $Ni^{2+} + 6 NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$

Two points are earned for reactants.

One point is earned for the product.

One point is earned for balancing (mass and charge) the equation.

(ii) Which of the reactants acts as a Lewis acid?

One point is earned for correct identification of the Lewis acid.

- (c) Methylamine (CH₃NH₂) is added to a solution of hydrochloric acid.
 - (i) Balanced equation:

$$CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$$
OR

 $CH_3NH_2 \ + \ H_3O^+ \ \rightarrow \ CH_3NH_3^+ + H_2O$

Two points are earned for reactants.

One point is earned for the product.

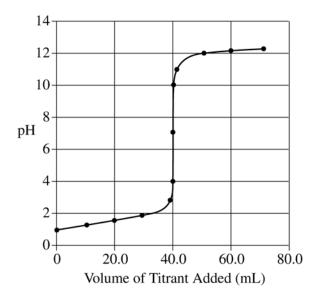
One point is earned for balancing (mass and charge) the equation.

(ii) Methylamine dissolves in water to form a solution. Indicate whether this solution is acidic, basic, or neutral.

The solution would be basic (because it would react with water to form $CH_3NH_3^+$ ions and OH^- ions).

One point is earned for the correct choice.





A solution of 0.100 *M* HCl and a solution of 0.100 *M* NaOH are prepared. A 40.0 mL sample of one of the solutions is added to a beaker and then titrated with the other solution. A pH electrode is used to obtain the data that are plotted in the titration curve shown above.

(a) Identify the solution that was initially added to the beaker. Explain your reasoning.

The solution in the beaker was the 0.100 *M* HCl because the initial pH was 1 (the pH of 0.100 *M* HCl).

One point is earned for the correct identification with rationale.

(b) On the titration curve above, circle the point that corresponds to the equivalence point.

The point with coordinates (40.0, 7) is circled.

One point is earned for the correct choice of point.

(c) At the equivalence point, how many moles of titrant have been added?

 $0.0400 \text{ L} \times \frac{0.100 \text{ mol NaOH}}{1.00 \text{ L}} = 0.00400 \text{ mol NaOH}$

One point is earned for the correct numerical answer.

(d) The same titration is to be performed again, this time using an indicator. Use the information in the table below to select the best indicator for the titration. Explain your choice.

Methyl red would be best because its color change will occur closest to the equivalence point (when the pH changes from about 4 to 10).

One point is earned for the correct selection of indicator.

One point is earned for the explanation.

Question 5 (continued)

Indicator	pH Range of Color Change
Methyl violet	0 – 1.6
Methyl red	4 – 6
Alizarin yellow	10 – 12

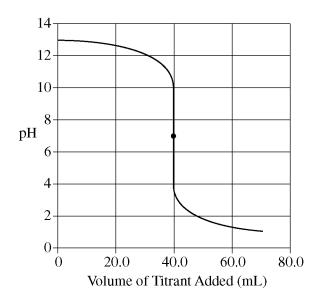
(e) What is the difference between the <u>equivalence point</u> of a titration and the <u>end point</u> of a titration?

The equivalence point in a titration occurs when the number of moles of titrant added is exactly sufficient to react completely with the number of moles of the titrated species present in the sample being titrated.

The end point of a titration is the point in a titration at which the indicator undergoes its color change.

One point is earned for each correct definition.

(f) On the grid provided below, sketch the titration curve that would result if the solutions in the beaker and buret were reversed (i.e., if 40.0 mL of the solution used in the buret in the previous titration were titrated with the solution that was in the beaker).



One point is earned for starting between pH 12 and 14 and for finishing below pH 2.

One point is earned for locating the equivalence point at pH 7 and volume 40.0 mL.

One point is earned for the overall shape of the curve.

Question 6 (8 points)

$$H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$$

The table below gives data for a reaction rate study of the reaction represented above.

Experiment	Initial $[H_2]$ $(\text{mol } L^{-1})$	Initial [Cl ₂] (mol L ⁻¹)	Initial Rate of Formation of HCl (mol L ⁻¹ s ⁻¹)
1	0.00100	0.000500	1.82×10^{-12}
2	0.00200	0.000500	3.64×10^{-12}
3	0.00200	0.000250	1.82×10^{-12}

(a) Determine the order of the reaction with respect to H_2 and justify your answer.

The order of the reaction with respect to $\rm H_2$ is 1. Comparing experiments 1 and 2, doubling the initial concentration of $\rm H_2$ while keeping the initial concentration of $\rm Cl_2$ constant results in a doubling of the reaction rate.

One point is earned for the correct order with justification.

(b) Determine the order of the reaction with respect to Cl₂ and justify your answer.

The order of the reaction with respect to Cl_2 is 1. Comparing experiments 2 and 3, halving the initial concentration of Cl_2 while keeping the initial concentration of H_2 constant results in a halving of the reaction rate.

One point is earned for the correct order with justification.

(c) Write the overall rate law for the reaction.

rate = $k [H_2][Cl_2]$	One point is earned for a rate law consistent with part (a) and part (b).
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(d) Write the units of the rate constant.

$$k = \frac{rate}{[H_2][Cl_2]} = \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol } L^{-1} \text{ mol } L^{-1}}$$
$$= \frac{\text{s}^{-1}}{\text{mol } L^{-1}} = L \text{ mol}^{-1} \text{ s}^{-1}$$

One point is earned for units consistent with part (c).

Question 6 (continued)

(e) Predict the initial rate of the reaction if the initial concentration of H_2 is 0.00300 mol L^{-1} and the initial concentration of Cl_2 is 0.000500 mol L^{-1} .

For this reaction, the initial concentration of Cl_2 is the same as in Experiment 1 but the initial concentration of H_2 is three times as large. And because the reaction is first order with respect to each reactant, the initial rate of the reaction would be $5.46 \times 10^{-12} \, \text{mol L}^{-1} \, \text{s}^{-1}$, which is three times the rate of the initial rate of the reaction in Experiment 1.

One point is earned for the correct numerical answer or correct multiplier consistent with the rate law from part (c).

The gas-phase decomposition of nitrous oxide has the following two-step mechanism.

Step 1:
$$N_2O \rightarrow N_2 + O$$

Step 2:
$$O + N_2O \rightarrow N_2 + O_2$$

(f) Write the balanced equation for the overall reaction.

 $2~N_2O~\rightarrow~2~N_2+O_2$

One point is earned for the correct balanced equation.

(g) Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.

The O atom is an intermediate because it is formed and then consumed during the course of the reaction. (Had it been a catalyst, it would have been present both at the beginning and the end of the reaction.)

One point is earned for the correct choice with explanation.

(h) Identify the slower step in the mechanism if the rate law for the reaction was determined to be $rate = k [N_2O]$. Justify your answer.

Step 1 is slower because N_2O appears in Step 1 as the single reactant, which is consistent with the given rate law.

One point is earned for the correct choice with justification.