



AP[®] Chemistry 2003 Scoring Guidelines

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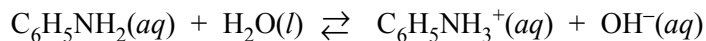
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Question 1



1. Aniline, a weak base, reacts with water according to the reaction represented above.

(a) Write the equilibrium expression, K_b , for the reaction represented above.

$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$	1 point for correct expression
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(b) A sample of aniline is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant, K_b , for this reaction.

<p>pH = 8.82</p> <p>pOH = 14 – 8.82 = 5.18</p> <p>$[\text{OH}^-] = 10^{-5.18} = 6.61 \times 10^{-6} \text{ M}$</p> <p>$[\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{OH}^-] = 6.6 \times 10^{-6} \text{ M}$</p> <p>$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(6.6 \times 10^{-6})^2}{0.10}$</p> <p>$K_b = 4.4 \times 10^{-10}$</p>	<p style="text-align: center;">1 point for calculation of $[\text{OH}^-]$</p> <p style="text-align: center;">1 point for $[\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{OH}^-]$</p> <p style="text-align: center;">1 point for calculation of K_b</p>
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Note: Following this point, any value of K_b obtained must be carried through.

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Question 1 (cont'd.)

- (c) The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.

$n_{\text{C}_6\text{H}_5\text{NH}_2} = 0.025 \text{ L} \left(\frac{0.10 \text{ mol}}{1 \text{ L}} \right) = 0.0025 \text{ mol C}_6\text{H}_5\text{NH}_2$ $n_{\text{HCl}} = 0.0050 \text{ L} \left(\frac{0.10 \text{ mol}}{1 \text{ L}} \right) = 0.00050 \text{ mol HCl (or H}^+\text{)}$ $\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq})$ <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 20px;">0.0025 mol</td> <td style="padding-right: 20px;">0.00050 mol</td> <td>0 mol</td> </tr> <tr> <td>C</td> <td>-0.00050</td> <td>-0.00050</td> <td>+0.00050</td> </tr> <tr> <td>E</td> <td>0.0020</td> <td>0</td> <td>0.00050</td> </tr> </table> $\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$ <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;">I</td> <td style="padding-right: 20px;">$\frac{0.0020 \text{ mol}}{0.030 \text{ L}} = 0.0667 \text{ M}$</td> <td style="padding-right: 20px;">$\frac{0.00050 \text{ mol}}{0.030 \text{ L}} = 0.0167 \text{ M}$</td> <td></td> </tr> <tr> <td>C</td> <td>-x</td> <td>+x</td> <td>+x</td> </tr> <tr> <td>E</td> <td>0.0667 - x</td> <td>0.0167 + x</td> <td>x</td> </tr> </table> $K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 4.37 \times 10^{-10}$ $4.37 \times 10^{-10} = \frac{(0.0167 + x)(x)}{(0.0667 - x)}$ <p>assume that $x \ll 0.0667 \text{ M}$: $4.37 \times 10^{-10} = \frac{(0.0167)(x)}{0.0667}$</p> $x = [\text{OH}^-] = 1.75 \times 10^{-9} \text{ M}$ $\text{pOH} = -\log(1.75 \times 10^{-9}) = 8.76$ $\text{pH} = 14 - 8.76 = 5.24$ <p>OR</p> $\text{pOH} = \text{p}K_b + \log \frac{[\text{C}_6\text{H}_5\text{NH}_3^+]}{[\text{C}_6\text{H}_5\text{NH}_2]}$ $\text{pOH} = -\log(4.37 \times 10^{-10}) + \log \frac{0.0167}{0.0667}$ $\text{pOH} = 9.36 + \log 0.25$ $\text{pOH} = 9.36 + (-0.60) = 8.76$ $\text{pH} = 14 - 8.76 = 5.24$	I	0.0025 mol	0.00050 mol	0 mol	C	-0.00050	-0.00050	+0.00050	E	0.0020	0	0.00050	I	$\frac{0.0020 \text{ mol}}{0.030 \text{ L}} = 0.0667 \text{ M}$	$\frac{0.00050 \text{ mol}}{0.030 \text{ L}} = 0.0167 \text{ M}$		C	-x	+x	+x	E	0.0667 - x	0.0167 + x	x	<p>1 point for <u>initial</u> number of moles or molarities of $\text{C}_6\text{H}_5\text{NH}_2$ and HCl/H^+</p> <p>1 point for <u>final</u> number of moles or molarities of $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NH}_3^+$ after mixing</p> <p style="text-align: center; margin-top: 100px;">1 point for pH</p>
I	0.0025 mol	0.00050 mol	0 mol																						
C	-0.00050	-0.00050	+0.00050																						
E	0.0020	0	0.00050																						
I	$\frac{0.0020 \text{ mol}}{0.030 \text{ L}} = 0.0667 \text{ M}$	$\frac{0.00050 \text{ mol}}{0.030 \text{ L}} = 0.0167 \text{ M}$																							
C	-x	+x	+x																						
E	0.0667 - x	0.0167 + x	x																						

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Question 1 (cont'd.)

- (d) Calculate the pH at the equivalence point of the titration in part (c).

<p>At the equivalence point, moles of $C_6H_5NH_2 = \text{moles of } H^+$</p> $C_6H_5NH_2(aq) + H^+(aq) \rightleftharpoons C_6H_5NH_3^+(aq)$ <table border="0"><tr><td>I</td><td>0.0025 mol</td><td>0.0025 mol</td><td>0 mol</td></tr><tr><td>C</td><td>-0.0025</td><td>-0.0025</td><td>+0.0025</td></tr><tr><td>E</td><td>0</td><td>0</td><td>0.0025</td></tr></table> <p>Need 25 mL of 0.1 M HCl to reach the equivalence point of this titration. The total volume of the solution is 50.0 mL</p> $[C_6H_5NH_3^+] = \frac{0.0025 \text{ mol}}{0.050 \text{ L}} = 0.050 M$ $C_6H_5NH_3^+(aq) \rightleftharpoons C_6H_5NH_2(aq) + H^+(aq)$ <table border="0"><tr><td>I</td><td>0.050 M</td><td>0</td><td>0</td></tr><tr><td>C</td><td>-x</td><td>+x</td><td>+x</td></tr><tr><td>E</td><td>0.050 - x</td><td>x</td><td>x</td></tr></table> $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-10}} = 2.3 \times 10^{-5}$ $\frac{[C_6H_5NH_2][H^+]}{[C_6H_5NH_3^+]} = 2.3 \times 10^{-5} = \frac{(x)(x)}{(0.050 - x)}$ <p>assume that $x \ll 0.050 M$: $2.3 \times 10^{-5} = \frac{(x)(x)}{0.050}$</p> $x = [H^+] = 1.1 \times 10^{-3} M$ <p>pH = 2.96</p>	I	0.0025 mol	0.0025 mol	0 mol	C	-0.0025	-0.0025	+0.0025	E	0	0	0.0025	I	0.050 M	0	0	C	-x	+x	+x	E	0.050 - x	x	x	<p>1 point for number of moles or molarity of $C_6H_5NH_3^+$</p> <p>1 point for pH</p>
I	0.0025 mol	0.0025 mol	0 mol																						
C	-0.0025	-0.0025	+0.0025																						
E	0	0	0.0025																						
I	0.050 M	0	0																						
C	-x	+x	+x																						
E	0.050 - x	x	x																						

- (e) The pK_a values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	pK_a
Erythrosine	3
Litmus	7
Thymolphthalein	10

<p>The pH at the equivalence point is acidic. The best indicator is erythrosine, for which the value of pK_a is closest to the pH at the equivalence point.</p>	<p>1 point for correct indicator and justification</p>
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Question 2

2. A rigid 5.00 L cylinder contains 24.5 g of N₂(g) and 28.0 g of O₂(g).

(a) Calculate the total pressure, in atm, of the gas mixture in the cylinder at 298 K.

$24.5 \text{ g N}_2 \left(\frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} \right) = 0.875 \text{ mol N}_2$ $28.0 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.875 \text{ mol O}_2$	1 point for moles of N ₂ (g) and O ₂ (g) (Must show ratio of mass/molar mass for both elements in calculations)
$PV = nRT: \quad P = \frac{nRT}{V} = \frac{(n_{\text{N}_2} + n_{\text{O}_2})RT}{V}$ $P = \frac{(0.875 + 0.875) \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{5.00 \text{ L}} = 8.56 \text{ atm}$	1 point for correct pressure setup and value

- Note:
- Only 1 point earned if calculation of moles is incorrect, but then wrong values used correctly in $P = nRT/V$
 - Only 1 point earned if no calculations shown for moles, but work and correct answer from $P = nRT/V$ are shown
 - Only 1 point earned if wrong R value used and/or wrong unit of P is shown – no deduction for same mistake in subsequent parts

(b) The temperature of the gas mixture in the cylinder is decreased to 280 K. Calculate each of the following.

(i) The mole fraction of N₂(g) in the cylinder

$X_{\text{N}_2} = \left(\frac{0.875 \text{ mol N}_2}{0.875 \text{ mol N}_2 + 0.875 \text{ mol O}_2} \right) = 0.500$	1 point for mol fraction of N ₂ (g)
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Note:

- Ratio must be consistent with part (a)

- 1 point earned for $\frac{P_{\text{N}_2}}{P_{\text{Total}}}$

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Question 2 (cont'd.)

(ii) The partial pressure, in atm, of N₂(g) in the cylinder

$P_T = \frac{n_T RT}{V} = \frac{(0.875 + 0.875) \text{ mol} \times 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 280 \text{ K}}{5.00 \text{ L}}$ $= 8.0 \text{ atm}$ $P_{\text{N}_2} = X_{\text{N}_2} \times P_T = 0.500 \times 8.0 \text{ atm} = 4.0 \text{ atm}$	1 point for partial pressure of N ₂ (g)
<p>OR</p> $P_{\text{N}_2} = \frac{n_{\text{N}_2} RT}{V} = \frac{(0.875) \text{ mol} \times 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 280 \text{ K}}{5.00 \text{ L}} = 4.0 \text{ atm}$	
<p>OR</p> $\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \frac{8.56 \text{ atm}}{298 \text{ K}} = \frac{P}{280 \text{ K}} \quad P_T = 8.0 \text{ atm}$ $P_{\text{N}_2} = X_{\text{N}_2} \times P_T = 0.500 \times 8.0 \text{ atm} = 4.0 \text{ atm}$	

Note: No point earned if 298 K is used instead of 280 K

(c) If the cylinder develops a pinhole-sized leak and some of the gaseous mixture escapes, would the ratio $\frac{\text{moles of N}_2(\text{g})}{\text{moles of O}_2(\text{g})}$ in the cylinder increase, decrease, or remain the same? Justify your answer.

<p>The ratio $\frac{\text{moles of N}_2(\text{g})}{\text{moles of O}_2(\text{g})}$ will decrease.</p> <p>N₂(g) will effuse faster than O₂(g) because N₂(g) has a lower molar mass. Thus, in the cylinder, the moles of N₂(g) will <u>decrease</u> faster than the moles of O₂(g).</p>	1 point for <u>both</u> correct direction and explanation.
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Question 2 (cont'd.)

A different rigid 5.00 L cylinder contains 0.176 mol of NO(g) at 298 K. A 0.176 mol sample of O₂(g) is added to the cylinder, where a reaction occurs to produce NO₂(g).

(d) Write the balanced equation for the reaction.

$2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$	1 point for correct balanced equation
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(e) Calculate the total pressure, in atm, in the cylinder at 298 K after the reaction is complete.

$2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px 5px;">initial</td> <td style="padding: 2px 5px;">0.176</td> <td style="padding: 2px 5px;">0.176</td> <td style="padding: 2px 5px;">0</td> </tr> <tr> <td style="padding: 2px 5px;">change</td> <td style="padding: 2px 5px;">-0.176</td> <td style="padding: 2px 5px;">-0.088</td> <td style="padding: 2px 5px;">0.176</td> </tr> <tr> <td style="padding: 2px 5px;">final</td> <td style="padding: 2px 5px;">0</td> <td style="padding: 2px 5px;">0.088</td> <td style="padding: 2px 5px;">0.176</td> </tr> </table> $0.176 \text{ mol NO} \times \left(\frac{1 \text{ mol O}_2}{2 \text{ mol NO}} \right) = 0.088 \text{ mol O}_2 \text{ reacted}$ $0.176 \text{ mol NO} \times \left(\frac{2 \text{ mol NO}_2}{2 \text{ mol NO}} \right) = 0.176 \text{ mol NO}_2 \text{ formed}$	initial	0.176	0.176	0	change	-0.176	-0.088	0.176	final	0	0.088	0.176	1 point for <u>both</u> moles of O ₂ and NO ₂ after reaction is complete
initial	0.176	0.176	0										
change	-0.176	-0.088	0.176										
final	0	0.088	0.176										
$P = \frac{nRT}{V} = \frac{(n_{\text{O}_2} + n_{\text{NO}_2})RT}{V}$ $P = \frac{(0.088 + 0.176) \text{ mol} \times 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 298 \text{ K}}{5.00 \text{ L}} = 1.29 \text{ atm}$	1 point for total pressure in the cylinder												

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Question 3



3. In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial [Br ⁻] (mol L ⁻¹)	Initial [BrO ₃ ⁻] (mol L ⁻¹)	Initial [H ⁺] (mol L ⁻¹)	Rate of Disappearance of BrO ₃ ⁻ (mol L ⁻¹ s ⁻¹)
1	0.00100	0.00500	0.100	2.50 × 10 ⁻⁴
2	0.00200	0.00500	0.100	5.00 × 10 ⁻⁴
3	0.00100	0.00750	0.100	3.75 × 10 ⁻⁴
4	0.00100	0.01500	0.200	3.00 × 10 ⁻³

- (a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br⁻

<p>Experiments 1 and 2:</p> $\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[\text{Br}^-]_2^x[\text{BrO}_3^-]_2^y[\text{H}^+]_2^z}{k_1[\text{Br}^-]_1^x[\text{BrO}_3^-]_1^y[\text{H}^+]_1^z}$ $\frac{5.00 \times 10^{-4}}{2.50 \times 10^{-4}} = \frac{k_2(0.00200)^x(0.00500)^y(0.100)^z}{k_1(0.00100)^x(0.00500)^y(0.100)^z}$ $2 = \frac{(0.00200)^x}{(0.00100)^x} = 2^x$ $x = 1 \Rightarrow \text{first order}$	<p>1 point for correct order of the reaction with respect to Br⁻</p>
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(ii) BrO₃⁻

<p>Experiments 1 and 3:</p> $\frac{\text{rate}_3}{\text{rate}_1} = \frac{k_3[\text{Br}^-]_3^1[\text{BrO}_3^-]_3^y[\text{H}^+]_3^z}{k_1[\text{Br}^-]_1^1[\text{BrO}_3^-]_1^y[\text{H}^+]_1^z}$ $\frac{3.75 \times 10^{-4}}{2.50 \times 10^{-4}} = \frac{k_3(0.00100)^1(0.00750)^y(0.100)^z}{k_1(0.00100)^1(0.00500)^y(0.100)^z}$ $1.5 = \frac{(0.00750)^y}{(0.00500)^y} = 1.5^y$ $y = 1 \Rightarrow \text{first order}$	<p>1 point for correct order of the reaction with respect to BrO₃⁻</p>
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Question 3 (cont'd.)

(iii) H^+

<p>Experiments 3 and 4:</p> $\frac{\text{rate}_4}{\text{rate}_3} = \frac{k_4[\text{Br}^-]_4^1[\text{BrO}_3^-]_4^1[\text{H}^+]_4^z}{k_3[\text{Br}^-]_3^1[\text{BrO}_3^-]_3^1[\text{H}^+]_3^z}$ $\frac{3.00 \times 10^{-3}}{3.75 \times 10^{-4}} = \frac{k_4(0.00100)^1(0.01500)^1(0.200)^z}{k_3(0.00100)^1(0.00750)^1(0.100)^z}$ $8 = \frac{(0.01500)^1(0.200)^z}{(0.00750)^1(0.100)^z}$ $8 = 2 \frac{(0.200)^z}{(0.100)^z}$ $4 = \frac{(0.200)^z}{(0.100)^z} = 2^z$ $z = 2 \Rightarrow \text{second order}$	<p>1 point for correct order of the reaction with respect to H^+</p>
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Note: Word explanations can also be used for part (a). The rate order can also be calculated from Experiment 4 and Experiment 1 or 2 or 3 after the orders of $[\text{Br}^-]$ and $[\text{BrO}_3^-]$ are determined.

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

$\text{rate} = k[\text{Br}^-]^1[\text{BrO}_3^-]^1[\text{H}^+]^2$	<p>1 point for correct rate law based on exponents determined in part (a)</p>
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(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

$\text{rate} = k[\text{Br}^-]^1[\text{BrO}_3^-]^1[\text{H}^+]^2$ $k = \frac{\text{rate}}{[\text{Br}^-]^1[\text{BrO}_3^-]^1[\text{H}^+]^2}$ <p>Use data from any Experiment – using Experiment #1:</p> $k = \frac{2.50 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.00100 \text{ mol L}^{-1})^1(0.00500 \text{ mol L}^{-1})^1(0.100 \text{ mol L}^{-1})^2}$ $k = 5.00 \times 10^3 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1} \text{ (units } M^{-3} \text{ s}^{-1} \text{ also acceptable)}$	<p>1 point for value of rate constant</p> <p>1 point for correct units</p>
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Question 3 (cont'd.)

- (d) Calculate the value of the standard cell potential, E° , for the reaction using the information in the table below.

Half-reaction	E° (V)
$\text{Br}_2(l) + 2 e^- \rightarrow 2 \text{Br}^-(aq)$	+1.065
$\text{BrO}_3^-(aq) + 6 \text{H}^+(aq) \rightarrow \text{Br}_2(l) + 3 \text{H}_2\text{O}(l)$	+1.52

$E^\circ = +1.52 \text{ V} - 1.065 \text{ V} = +0.46 \text{ V}$	1 point for correct standard cell potential
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- (e) Determine the total number of electrons transferred in the overall reaction.

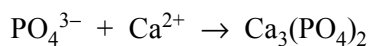
$5 \times (2 \text{Br}^-(aq) \rightarrow \text{Br}_2(l) + 2 e^-)$ $2 \times (\text{BrO}_3^-(aq) + 6 \text{H}^+(aq) + 5 e^- \rightarrow \frac{1}{2} \text{Br}_2(l) + 3 \text{H}_2\text{O}(l))$ $10 \text{Br}^-(aq) + 2 \text{BrO}_3^-(aq) + 12 \text{H}^+(aq) + 10 e^- \rightarrow 6 \text{Br}_2(l) + 6 \text{H}_2\text{O}(l) + 10 e^-$ <p>Divide by 2 to get the equation at the beginning of the problem:</p> $5 \text{Br}^-(aq) + \text{BrO}_3^-(aq) + 6 \text{H}^+(aq) \rightarrow 3 \text{Br}_2(l) + 3 \text{H}_2\text{O}(l)$ <p>Total number of electrons transferred is $5 e^-$</p>	1 point for correct number of electrons transferred
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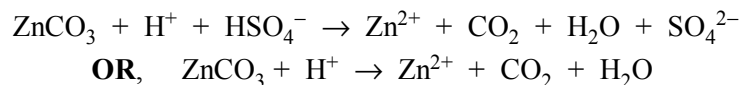
4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases, a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution 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.

General Scoring: 3 points each: 1 point for correct reactant(s) and 2 points for correct product(s)

- (a) A solution of potassium phosphate is mixed with a solution of calcium acetate.

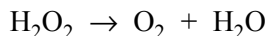


- (b) Solid zinc carbonate is added to 1.0 M sulfuric acid.



Note: 1 product point earned for any 2 of 4 (or 2 of 3) products

- (c) A solution of hydrogen peroxide is exposed to strong sunlight.

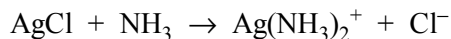


- (d) A 0.02 M hydrochloric acid solution is mixed with an equal volume of 0.01 M calcium hydroxide solution.

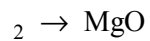


Note: No reactant point earned for undissociated $\text{Ca}(\text{OH})_2$

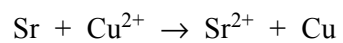
- (e) Excess concentrated aqueous ammonia is added to solid silver chloride.



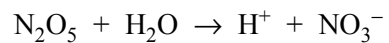
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(g) A bar of strontium metal is immersed in a 1.0 M copper(II) nitrate solution.



(h) Solid dinitrogen pentoxide is added to water.



Note: *Undissociated HNO₃ as product earns only 1 point*

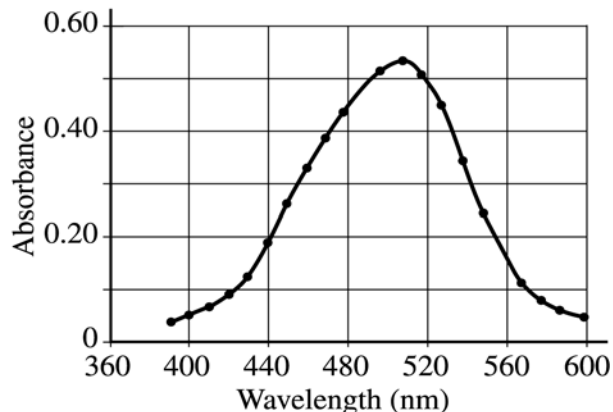
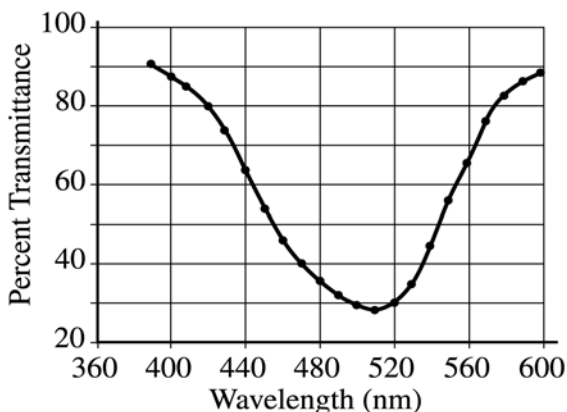
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based on absorption of light (spectrometric/colorimetric method). The student is provided with a 0.10 *M* solution of CoCl₂ with which to prepare standard solutions with concentrations of 0.020 *M*, 0.040 *M*, 0.060 *M* and 0.080 *M*.

- (a) Describe the procedure for diluting the 0.10 *M* solution 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.

$M_1V_1 = M_2V_2 : \quad V_1 = \frac{M_2V_2}{M_1}$ $V_1 = \frac{(0.020\ M)(100\ \text{mL})}{0.10\ M} = 20.\ \text{mL}$ <p>Pipet 20 mL of 0.10 <i>M</i> CoCl₂ into the 100 mL volumetric flask, then add enough water to reach the 100 mL mark on the neck of the volumetric flask. Stopper the flask and mix.</p>	<p>1 point for 20 mL of 0.10 <i>M</i> CoCl₂ (unit required)</p> <p>1 point for adding enough water to reach final volume of 100 mL</p>
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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.

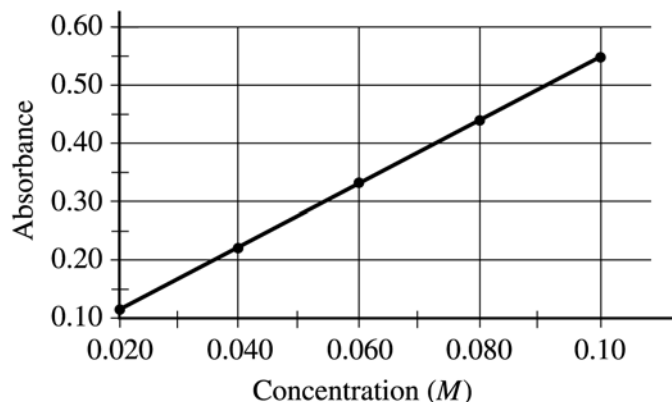


- (b) Identify the optimum wavelength for the analysis.

510 nm (acceptable range 490-520 nm)	1 point for wavelength ~510 nm (unit not required)
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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.

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(c) The absorbance of the unknown solution is 0.275. What is the concentration of the solution?

0.050 M (acceptable range 0.045 to 0.055 M)	1 point for concentration ~ 0.050 M (unit not required)
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(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.

$A = a b c$ a = molar absorptivity (<u>not</u> absorbance) b = path length of cuvette/test tube c = concentration	1 point for each factor
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Note: Symbols alone not sufficient; for a , accept molar absorbance, absorptivity, & absorbance coefficient

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Question 5 (cont'd.)

- (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.

The presence of the fingerprints will scatter or absorb light. Since less light reaches the detector, the solution will have a higher apparent absorbance, and therefore a higher reported concentration.	1 point for increase in reported concentration of CoCl_2 1 point for “apparent” increase in absorbance or decrease in light
---	---

- (f) Why is this method of determining the concentration of CoCl_2 solution appropriate, whereas using the same method for measuring the concentration of NaCl solution would not be appropriate?

A CoCl_2 solution absorbs visible light. A NaCl solution is colorless (or does not absorb visible light). OR CoCl_2 solution has an appreciable molar absorptivity in the visible region and NaCl does not.	1 point for indicating that NaCl does not absorb visible light or is colorless
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Question 6

6. For each of the following, use appropriate chemical principles to explain the observation. Include chemical equations as appropriate.

(a) In areas affected by acid rain, statues and structures made of limestone (calcium carbonate) often show signs of considerable deterioration.

Acid rain has a low pH, which means $[H^+]$ is relatively large. The acid reacts with the calcium carbonate solid in the statue according to the following: $H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$ The result is the erosion of the statue as the solid calcium carbonate reacts, forming a salt (partially soluble), a liquid, and a gas.	1 point for indicating acid rain has a high $[H^+]$ 1 point for indicating calcium carbonate solid forms gaseous carbon dioxide
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(b) When table salt (NaCl) and sugar ($C_{12}H_{22}O_{11}$) are dissolved in water, it is observed that

(i) both solutions have higher boiling points than pure water, and

The higher boiling point is due to the change in vapor pressure above the solution compared to the vapor pressure above pure water. The presence of a nonvolatile solute lowers the vapor pressure above the solution and results in a higher boiling point.	1 point for indicating the lower vapor pressure above the solution
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(ii) the boiling point of $0.10\ M\ NaCl(aq)$ is higher than that of $0.10\ M\ C_{12}H_{22}O_{11}(aq)$.

NaCl has a higher boiling point because the change in boiling point, ΔT_{bp} , is directly dependent on the <u>number</u> of solute particles in solution. NaCl is an ionic compound which dissociates into two particles, whereas $C_{12}H_{22}O_{11}$ is a covalent compound and does not dissociate.	1 point for indicating NaCl forms two moles of particles and $C_{12}H_{22}O_{11}$ forms one mole of particles.
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Question 6 (cont'd.)

(c) Methane gas does not behave as an ideal gas at low temperature and high pressures.

<p>Two factors contribute to nonideal gas behavior: attractive forces and excluded volume. At low temperature, the molecules are moving slower and are closer together. The attractive forces between the molecules are more important relative to their kinetic energy. At high pressure, the molecules of methane are closer together and the volume occupied by the molecules is a greater percentage of the volume of the container. Since the molecules take up some volume, there is less volume available to the methane molecules.</p>	<p>1 point for identifying and discussing attractive forces</p> <p>1 point for identifying and discussing excluded volume</p>
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(d) Water droplets form on the outside of a beaker containing an ice bath.

<p>Water vapor in the air in contact with the lower temperature on the surface of the glass condenses because the equilibrium vapor pressure for water at the lower temperature is lower than the pressure exerted by the water in the vapor phase in the room.</p>	<p>1 point for indicating that the water droplets on the glass surface comes from water in the vapor phase (in the room)</p> <p>1 point for indicating that condensation occurs because the equilibrium vapor pressure at the temperature on the glass surface is lower than the pressure due to water vapor in the air in the room</p> <p style="text-align: center;">OR</p> <p>1 point for clearly indicating that moisture is forming from the air and that there is sufficient energy transfer (loss) to cause a change of state (condensation)</p>
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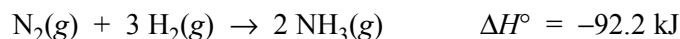


Using the table of average bond energies below, determine the enthalpy change, ΔH , for the reaction.

Bond	Average Bond Energy (kJ mol ⁻¹)
N — N	160
N = N	420
N ≡ N	950

$\Delta H = -950 \text{ kJ}$ The reaction is exothermic because the chemical equation shows the formation of the N ≡ N bond.	1 point for correct sign 1 point for magnitude
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(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.



Predict the sign of the standard entropy change, ΔS° , for the reaction. Justify your answer.

ΔS° is negative. There are fewer moles of product gas (2 mol) compared to reactant gases (4 mol), so the reaction is becoming more ordered.	1 point for correct sign 1 point for indicating fewer moles of products compared to reactants (in the gas phase)
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(c) The value of ΔG° for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ΔH° and ΔS° are negative. At low temperatures, the $T\Delta S^\circ$ term is smaller than ΔH° , and ΔG° is negative. At high temperatures, the $T\Delta S^\circ$ term is higher than ΔH° , and ΔG° is positive.	1 point each for using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to explain the sign of ΔG° at high and low temperatures.
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$\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ are placed in a sealed container at a low temperature, no measurable amount of NH_3 is produced. Explain.

<p>Even though the reaction is spontaneous at low temperature, the reaction is very slow. The speed of a reaction depends on the fraction of colliding molecules with energy that exceeds the activation energy for the reaction. At low temperature, few reactant particles collide with an energy greater than the activation energy.</p>	<p>1 point for indicating that the frequency of collision (or kinetic energy) of molecules is low at low temperature (thus the rate is slow)</p> <p>1 point for indicating that at low temperature the kinetic energy will likely be too small to exceed the activation energy</p>
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Question 8

Compound Name	Compound Formula	ΔH_{vap}° (kJ mol ⁻¹)
Propane	CH ₃ CH ₂ CH ₃	19.0
Propanone	CH ₃ COCH ₃	32.0
1-propanol	CH ₃ CH ₂ CH ₂ OH	47.3

8. Using the information in the table above, answer the following questions about organic compounds.

(a) For propanone,

(i) draw the complete structural formula (showing all atoms and bonds);

$ \begin{array}{ccccc} & \text{H} & & \text{O} & & \text{H} \\ & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & \\ & \text{H} & & & & \text{H} \end{array} $	1 point for complete and correct structural formula
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(ii) predict the approximate carbon-to-carbon-to-carbon bond angle.

The C–C–C bond angle is 120°	1 point for bond angle
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(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization, ΔH_{vap}° . (You must include specific information about both compounds in each pair.)

(i) Propane and propanone

The intermolecular attractive forces in propane are dispersion forces only. The IMFs in propanone are dispersion and dipole-dipole. Since the intermolecular attractive forces differ in the two substances, the enthalpy of vaporization will differ.	1 point for correctly identifying the IMFs for each substance
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Question 8 (cont'd.)

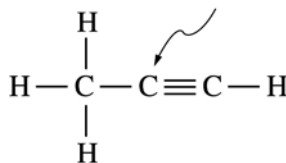
(ii) Propanone and 1-propanol

The intermolecular attractive forces in 1-propanol are dispersion forces and hydrogen-bonding. The IMFs in propanone are dispersion and dipole-dipole. Since the intermolecular attractive forces differ in the two substances, the enthalpy of vaporization will differ.	1 point for correctly identifying the IMFs for each substance
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(c) Draw the complete structural formula for an isomer of the molecule you drew in part (a) (i).

$ \begin{array}{ccccc} & \text{H} & & \text{H} & & \text{O} \\ & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & & \text{H} & & & \end{array} $	1 point for correct, complete structural formula
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(d) Given the structural formula for propyne below,



(i) indicate the hybridization of the carbon atom indicated by the arrow in the structure above;

<i>sp</i> hybridization	1 point for correct hybridization
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(ii) indicate the total number of sigma (σ) bonds and the total number of pi (π) bonds in the molecule.

6 sigma bonds 2 pi bonds	1 point for correct number of sigma bonds 1 point for correct number of pi bonds
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