CollegeBoard
Advanced Placement Program

AP® Chemistry
2008 Scoring Guidelines
Form B

Question 1

Answer the following questions regarding the decomposition of arsenic pentafluoride, $AsF_5(g)$.

(a) A 55.8 g sample of $AsF_5(g)$ is introduced into an evacuated 10.5 L container at 105°C.

(i) What is the initial molar concentration of $AsF_5(g)$ in the container?

$\text{mol AsF}_5 = 55.8 \text{ g AsF}_5 \times \frac{1 \text{ mol AsF}_5}{169.9 \text{ g AsF}_5} = 0.328 \text{ mol}$ $[\text{AsF}_5]_i = \frac{0.328 \text{ mol AsF}_5}{10.5 \text{ L}} = 0.0313\ M$	One point is earned for the correct molar mass. One point is earned for the correct concentration.

(ii) What is the initial pressure, in atmospheres, of the $AsF_5(g)$ in the container?

$PV = nRT$ $P = \frac{0.328 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 378 \text{ K}}{10.5 \text{ L}} = 0.969 \text{ atm}$	One point is earned for the correct substitution. One point is earned for the correct pressure.

At 105°C, $AsF_5(g)$ decomposes into $AsF_3(g)$ and $F_2(g)$ according to the following chemical equation.

$$AsF_5(g) \rightleftarrows AsF_3(g) + F_2(g)$$

(b) In terms of molar concentrations, write the equilibrium-constant expression for the decomposition of $AsF_5(g)$.

$K = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]}$	One point is earned for the correct equation.

(c) When equilibrium is established, 27.7 percent of the original number of moles of $AsF_5(g)$ has decomposed.

(i) Calculate the molar concentration of $AsF_5(g)$ at equilibrium.

$100.0\% - 27.7\% = 72.3\%$ $[\text{AsF}_5] = 0.723 \times 0.0313\ M = 0.0226\ M$	One point is earned for the correct concentration.

Question 1 (continued)

(ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq}, at 105°C.

$[AsF_3] = [F_2] = 0.277 \times [AsF_5]_i$ $= 0.277 \times 0.0313\ M = 0.00867\ M$ $K_{eq} = \frac{[AsF_3]\,[F_2]}{[AsF_5]} = \frac{[0.00867]\,[0.00867]}{[0.0226]} = 0.00333$	One point is earned for setting $[AsF_3] = [F_2]$. Note: the point is not earned if the student indicates that $[AsF_3] = [F_2] = [AsF_5]$. One point is earned for the correct calculation of $[AsF_3]$ and $[F_2]$. One point is earned for the correct calculation of K_{eq}.

(d) Calculate the mole fraction of $F_2(g)$ in the container at equilibrium.

mol AsF_5 = $0.0226\ M \times 10.5$ L = 0.237 mol mol F_2 = mol AsF_3 = $0.00867\ M \times 10.5$ L = 0.0910 mol mol fraction F_2 = $\frac{\text{mol } F_2}{\text{mol } F_2 + \text{mol } AsF_3 + \text{mol } AsF_5}$ $= \frac{0.0910}{0.0910 + 0.0910 + 0.237} = 0.217$ OR mol fraction F_2 = $\frac{0.00864}{0.00864 + 0.00864 + 0.0226} = 0.217$	One point is earned for the correct calculation of the mole fraction of $F_2(g)$.

Question 2

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

For the gas-phase reaction represented above, the following experimental data were obtained.

Experiment	Initial [A] (mol L^{-1})	Initial [B] (mol L^{-1})	Initial Reaction Rate (mol L^{-1} s^{-1})
1	0.033	0.034	6.67×10^{-4}
2	0.034	0.137	1.08×10^{-2}
3	0.136	0.136	1.07×10^{-2}
4	0.202	0.233	?

(a) Determine the order of the reaction with respect to reactant A. Justify your answer.

Between experiments 2 and 3, [B] stays the same and [A] is quadrupled, but the initial reaction rate stays the same. This means that the initial reaction rate is not dependent on [A], so the reaction is zero order with respect to A. (May also justify using mathematics as shown in part (b).)	One point is earned for the correct order and for the justification.

(b) Determine the order of the reaction with respect to reactant B. Justify your answer.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\,[A]_2^x\,[B]_2^y}{k\,[A]_1^x\,[B]_1^y}$$

$$\frac{1.08 \times 10^{-2}}{6.67 \times 10^{-4}} = \frac{k\,(0.034)^x\,(0.137)^y}{k\,(0.033)^x\,(0.034)^y} \quad \text{where } x = 0$$

$16.2 = (4.03)^y$

$y = 2$, so the reaction is second order with respect to B

OR

Between experiments 1 and 2, [A] stays the same, [B] is multiplied by 4, and the initial reaction rate is multiplied by 16. This means that the reaction is second order with respect to B.

One point is earned for the correct order and for the justification.

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

rate = $k\,[B]^2$	One point is earned for the correct rate law (or a rate law consistent with the answers in part (a) and part (b)).

Question 2 (continued)

(d) Determine the value of the rate constant, k, for the reaction. Include units with your answer.

Using experiment 2: rate = $k\,[B]^2$ $k = \dfrac{\text{rate}}{[B]^2} = \dfrac{6.67\times10^{-4}\ \text{mol L}^{-1}\ \text{sec}^{-1}}{(0.034\ \text{mol L}^{-1})^2} = 0.577\ M^{-1}\ \text{sec}^{-1}$	One point is earned for the correct numerical value of the rate constant. One point is earned for the correct units.

(e) Calculate the initial reaction rate for experiment 4.

rate $= k\,[B]^2$ rate $= (0.577\ M^{-1}\ \text{sec}^{-1}) \times (0.233\ \text{mol L}^{-1})^2$ $= 3.13\times10^{-2}\ \text{mol L}^{-1}\ \text{sec}^{-1}$	One point is earned for the correct answer, including units.

(f) The following mechanism has been proposed for the reaction.

Step 1: $B + B \rightarrow E + D$ *slow*

Step 2: $E + A \rightleftarrows B + C$ *fast equilibrium*

Provide two reasons why the mechanism is acceptable.

(1) When steps 1 and 2 are added together, the overall reaction is $A + B \rightarrow C + D$. This is the stoichiometry that was given for the overall reaction. (2) The rate-determining step (slow step) is consistent with the rate law because only reactant B occurs in the rate law and it occurs to the power of 2, which is the number of B molecules colliding in the rate-determining step. (3) The rate-determining step is consistent with the rate law because A is absent from the rate-determining step and the reaction is zero order—i.e., reactant A does not appear in the rate law.	One point is earned for each correct reason, with a maximum of 2 points.

(g) In the mechanism in part (f), is species E a catalyst, or is it an intermediate? Justify your answer.

Species E is an intermediate; it is formed in step 1 and consumed in step 2. AND/OR Species E is not a catalyst because a catalyst occurs as a reactant in an earlier step and is then reproduced as a product in a later step.	One point is earned for the correct answer with justification.

Question 3

A 0.150 g sample of solid lead(II) nitrate is added to 125 mL of 0.100 *M* sodium iodide solution. Assume no change in volume of the solution. The chemical reaction that takes place is represented by the following equation.

$$Pb(NO_3)_2(s) + 2\ NaI(aq) \rightarrow PbI_2(s) + 2\ NaNO_3(aq)$$

(a) List an appropriate observation that provides evidence of a chemical reaction between the two compounds.

A precipitate forms with an appearance that is different from that of the dissolving solid.	One point is earned for stating that a precipitate is formed.

(b) Calculate the number of moles of each reactant.

$\text{mol } Pb(NO_3)_2 = 0.150 \text{ g } Pb(NO_3)_2 \times \frac{1 \text{ mol } Pb(NO_3)_2}{331 \text{ g } Pb(NO_3)_2}$ $= 4.53 \times 10^{-4} \text{ mol}$ $\text{mol NaI} = 0.100\ M \times 0.125 \text{ L} = 1.25 \times 10^{-2} \text{ mol}$	One point is earned for the correct number of moles of $Pb(NO_3)_2$. One point is earned for the correct number of moles of NaI.

(c) Identify the limiting reactant. Show calculations to support your identification.

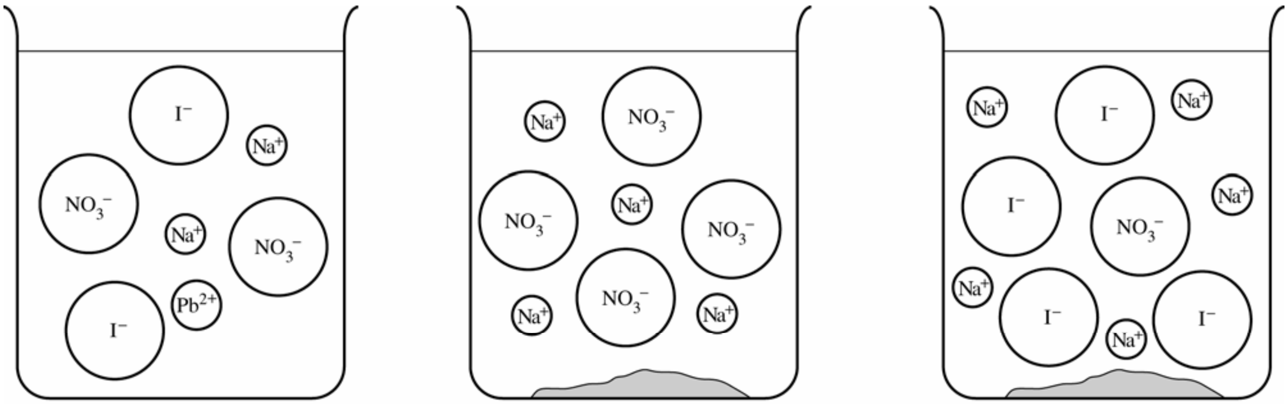
$\text{mol NaI reacting} = 4.53 \times 10^{-4} \text{ mol } Pb(NO_3)_2 \times \frac{2 \text{ mol NaI}}{1 \text{ mol } Pb(NO_3)_2}$ $= 9.06 \times 10^{-4} \text{ mol}$ There is 1.25×10^{-2} mol of NaI initially, thus $Pb(NO_3)_2$ is the limiting reactant.	One point is earned for the identification of $Pb(NO_3)_2$. One point is earned for a justification in terms of the relative numbers of moles.

(d) Calculate the molar concentration of $NO_3^-(aq)$ in the mixture after the reaction is complete.

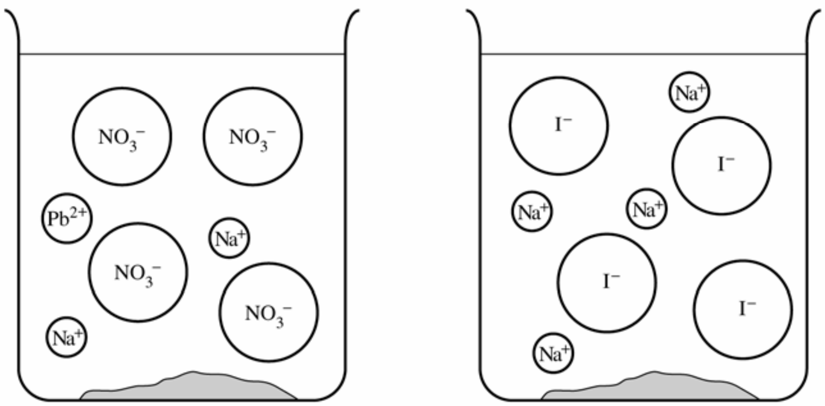
$[NO_3^-]_f = \frac{2 \times (4.53 \times 10^{-4} \text{ mol})}{0.125 \text{ L}} = 7.25 \times 10^{-3}\ M$	One point is earned for the correct NO_3^-/Pb^{2+} stoichiometry. One point is earned for the correct molarity.

Question 3 (continued)

(e) Circle the diagram below that best represents the results after the mixture reacts as completely as possible. Explain the reasoning used in making your choice.



No Precipitate — Solid PbI_2 — Solid PbI_2



Solid PbI_2 — Solid $Pb(NO_3)_2$

The rightmost diagram in the top row should be circled. PbI_2 precipitates and $Pb(NO_3)_2$ is the limiting reactant, so there is essentially no Pb^{2+} in solution. Because there was so much NaI in excess, some of the I^- remains in solution, along with the Na^+ and NO_3^-.	One point is earned for the selection of the correct diagram. One point is earned for the correct rationale.

Question 4

For each of the following three reactions, in part (i) write a balanced equation for the reaction and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

(a) Chlorine gas, an oxidizing agent, is bubbled into a solution of potassium bromide at 25°C.

(i) Balanced equation: $Cl_2 + 2\,Br^- \rightarrow 2\,Cl^- + Br_2$	One point is earned for the correct reactants. Two points are earned for the correct products. One point is earned for balancing the equation for mass and charge.

(ii) Predict the sign of $\Delta S°$ for the reaction at 25°C. Justify your prediction.

The sign of $\Delta S°$ is negative. One of the reactants, Cl_2, is a gas at 25°C, but there are no gaseous products. Gases have high entropies, so the entropy of the reactants is greater than the entropy of the products, making $\Delta S°$ negative.	One point is earned for a correct answer involving entropy of a gas.

(b) Solid strontium hydroxide is added to a solution of nitric acid.

(i) Balanced equation: $Sr(OH)_2 + 2\,H^+ \rightarrow Sr^{2+} + 2\,H_2O$	One point is earned for the correct reactants. Two points are earned for the correct products. One point is earned for balancing the equation for mass and charge.

(ii) How many moles of strontium hydroxide would react completely with 500. mL of 0.40 *M* nitric acid?

There is 0.20 mol of H^+ in 500. mL of 0.40 *M* nitric acid. Because there are two moles of OH^- in each mole of $Sr(OH)_2$, 0.10 mol of $Sr(OH)_2$ is needed to react completely.	One point is earned for the correct answer.

Question 4 (continued)

(c) A solution of barium chloride is added drop by drop to a solution of sodium carbonate, causing a precipitate to form.

(i) Balanced equation: $Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3$	One point is earned for the correct reactants. Two points are earned for the correct product. One point is earned for balancing the equation for mass and charge.

(ii) What happens to the pH of the sodium carbonate solution as the barium chloride is added to it?

A solution of sodium carbonate is basic. When carbonate precipitates out, this decreases the pH.	One point is earned for the correct answer (no explanation is required).

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2008 SCORING GUIDELINES (Form B)

Question 5

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

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

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

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

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

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

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

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

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

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

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

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

Question 5 (continued)

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

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

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

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

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

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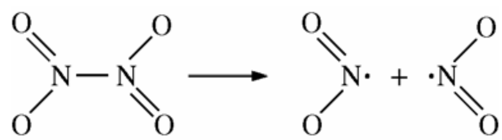
2008 SCORING GUIDELINES (Form B)

Question 6

Use principles of thermodynamics to answer the following questions.

(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



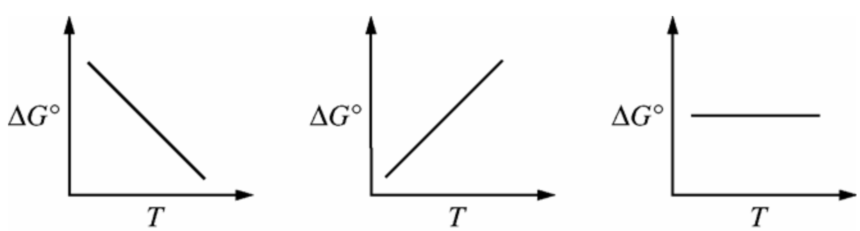
(i) Predict the sign of $\Delta H°$ for the reaction. Justify your answer.

Bonds are broken when NO_2 molecules form from N_2O_4 molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of $\Delta H°$ is positive.	One point is earned for the correct sign <u>and</u> a correct explanation.

(ii) Predict the sign of $\Delta S°$ for the reaction. Justify your answer.

There are two gaseous product molecules for each gaseous reactant molecule, so the product has more entropy than the reactant. The entropy increases as the reaction proceeds, so the sign of $\Delta S°$ is positive.	One point is earned for the correct sign <u>and</u> a correct explanation.

(b) One of the diagrams below best represents the relationship between $\Delta G°$ and temperature for the reaction given in part (a). Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.



Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G° = \Delta H° - T\Delta S°$.

The leftmost graph should be circled. $\Delta S°$ is positive, so as T increases, $T\Delta S°$ becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from $\Delta H°$ to get $\Delta G°$, so $\Delta G°$ decreases with increasing temperature.	One point is earned for the correct graph selection. One point is earned for the explanation.

Question 6 (continued)

(c) A reaction mixture of N_2O_4 and NO_2 is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of N_2O_4 decreases.

The reaction is endothermic. For endothermic reactions, increasing the temperature drives the reaction to the right. This increases the equilibrium concentration of NO_2 and decreases the equilibrium concentration of N_2O_4.	One point is earned for the correct explanation.

(ii) The value of K_{eq} at 25°C is 5.0×10^{-3}. Will the value of K_{eq} at 100°C be greater than, less than, or equal to this value?

Because the reaction is endothermic, at higher temperatures the reaction goes further to the right. This means that the value of K_{eq} at 100°C will be greater than the value of K_{eq} at 25°C.	One point is earned for the correct choice. (No explanation required.)

(d) Using the value of K_{eq} at 25°C given in part (c)(ii), predict whether the value of $\Delta H°$ is expected to be greater than, less than, or equal to the value of $T\Delta S°$. Explain.

K_{eq} at 25°C is less than 1, hence $\Delta G°$ must be positive. And in order for $\Delta G°$ to be positive, $\Delta H°$ must be greater than $T\Delta S°$.	One point is earned for the correct prediction. One point is earned for the explanation.