AP® CHEMISTRY
2008 SCORING GUIDELINES (Form B)

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.

$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\,[A]_2^x\,[B]_2^y}{k\,[A]_1^x\,[B]_1^y}$ $\frac{1.08 \times 10^{-2}}{6.67 \times 10^{-4}} = \frac{k\,(0.034)^x\,(0.137)^y}{k\,(0.033)^x\,(0.034)^y}$ 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 = $k\,[\mathrm{B}]^2$ $k = \dfrac{\text{rate}}{[\mathrm{B}]^2} = \dfrac{6.67 \times 10^{-4}\ \text{mol L}^{-1}\ \text{sec}^{-1}}{(0.034\ \text{mol L}^{-1})^2} = 0.577\ M^{-1}\ \text{sec}^{-1}$	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 = $k\,[\mathrm{B}]^2$ rate = $(0.577\ M^{-1}\ \text{sec}^{-1}) \times (0.233\ \text{mol L}^{-1})^2$ = $3.13 \times 10^{-2}\ \text{mol L}^{-1}\ \text{sec}^{-1}$	One point is earned for the correct answer, including units.

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

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

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

Provide two reasons why the mechanism is acceptable.

(1) When steps 1 and 2 are added together, the overall reaction is $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$. 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.

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

2A,

2. 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}
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3	0.136	0.136	1.07×10^{-2}
4	0.202	0.233	?

×20 ×4 ×16

$\frac{mol}{Ls} = k\left(\frac{mol}{L}\right)^2$

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

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

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

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

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

(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.

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

2(a) Comparing Experiment 2 and 3,

$\because [B]_2 \approx [B]_3$

$[A]_2 \approx \frac{1}{4}[A]_3$

$R_2 \approx R_3$,

$\Rightarrow$ The reaction is <u>0</u> order with respect to A. //

2(b) Comparing Experiment 1 and 2,

$\because [A]_1 \approx [A]_2$

$[B]_1 \approx \frac{1}{4}[B]_2$

$R_1 \approx \frac{1}{16} R_2$

$\Rightarrow$ The reaction is <u>2nd</u> order with respect to B //

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

2(c) $R = K[A]^0[B]^2 = K[B]^2$ //

2(d) Looking at Experiment 3,

$1.07 \times 10^{-2} = K[0.136]^2$

$K = \frac{1.07 \times 10^{-2}}{[0.136]^2} = 0.579 \text{ L mol}^{-1}\text{s}^{-1}$ //

2(e) $R = K[B]^2 = 0.579(0.233)^2 = 3.14 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$ //

2(f) The slow reaction satisfies the rate equation ($R = K[B]^2$) found in part (c).
When step 1 and step 2 are added up, they give rise to the overall reaction, $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$

step 1: $B + B \rightarrow E + D$
step 2: $E + A \rightarrow B + C$
overall: $B + A \rightarrow C + D$

2(g) It is an intermediate. It can't be a catalyst because it is used as a reactant in step 2.
∵ It is produced in step 1 and used in step 2, it must be an intermediate.

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$A(g) + B(g) \rightarrow C(g) + D(g)$ 2B,

2. 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}
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3	0.136	0.136	1.07×10^{-2}
4	0.202	0.233	?

$R=k[B]^x$

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

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

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

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

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

(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.

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

(a) [A] [B] Rate

0.034 0.137 1.08×10^{-2}

0.136 0.136 1.07×10^{-2}

Although [A] changed by $\times 4$, the rate remained the same. Therefore [A] has no effect on the rate.

order = 0

(b) [A] [B] Rate

0.033 0.034 6.67×10^{-4}) 16

0.034 0.137 1.08×10^{-2})

When [B] was multiplied by 4, the rate was multiplied by 16. Therefore order = 2

$2B_2$

(c) $R = K[B]^2$

(d) $6.6\text{n} \times 10^{-4} \frac{\text{mol}}{\text{L·s}} = K\left(0.034 \frac{\text{mol}}{\text{L}}\right)^2$

$K = 6.6\text{n} \times 10^{-4} \frac{\text{mol}}{\text{L·s}} \times \frac{1}{0.034^2} \frac{\text{L}^2}{\text{mol}}$

$= 0.5\text{nn}\ \text{L/s}$

(e) $0.5\text{nn}\ (0.233)^2 = 0.0313\ \text{mol L}^{-1}\text{s}^{-1}$

(f). ① Because slow reaction determines the rate, it only contains B, just like how the rate equation only has [B].

(g). intermediate.
Because the species does not appear either on the reactant or product side.
Catalyst appears in the reactant side and re-appears in the product.

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2C 1

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

2. 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.

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

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

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

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

(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.

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

a) For Exp 3: $R_3 = k[A_3]^n[B_3]^m$

For Exp 2: $R_2 = k[A_2]^n[B_2]^m$

$\Rightarrow \frac{R_3}{R_2} = \frac{[A_3]^n[B_3]^m}{[A_2]^n[B_2]^m}$

$\Rightarrow \frac{1.07 \times 10^{-2}}{1.08 \times 10^{-2}} = \left[\frac{0.136}{0.034}\right]^n \left[\frac{0.136}{0.137}\right]^m \Rightarrow 0.99 = \left(\frac{0.136}{0.034}\right)^n (0.99)^m$

$\simeq 1 = \left(\frac{0.136}{0.034}\right)^n (1)^m \Rightarrow \left(\frac{0.136}{0.034}\right)^n = 1 \Rightarrow 4^n = 1$

$\Rightarrow n \ln 4 = \ln 1 \Rightarrow n = \frac{\ln 1}{\ln 4} \Rightarrow n = 0$

$\Rightarrow$ The order of rxn for reactant A is of zero order.

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b) From part (a) ⇒

$\frac{R_3}{R_2} = \frac{[A_3]^n[B_3]^m}{[A_2]^n[B_2]^m} \Rightarrow n=0 \Rightarrow$

$\frac{1.07\times10^{-2}}{1.08\times10^{-2}} = \left(\frac{0.136}{0.137}\right)^m \Rightarrow 0.99 = (0.99)^m$

$\Rightarrow m=1$

⇒ The order of the rxn for reactant B is of the 1st order.

c) Rate Law $= [A][B]^1 \Rightarrow$ Rate Law $= [B]$

d) $\Rightarrow K = \frac{R_3}{[A_3]^n[B_3]^m} \Rightarrow \frac{1.07\times10^{-2}}{(0.136)^0(0.136)^1} \Rightarrow K = 0.07868$

$\Rightarrow K = 7.87\times10^{-2}$

e) $R_4 = K[A_4]^0[B_4]^1 \Rightarrow 7.87\times10^{-2}(0.233)$

$\Rightarrow R_4 = 0.0183371 \Rightarrow R_4 = 1.83\times10^{-2}$ Mol/Ls

f) The mechanism is accepted because the last equilibrium rxn takes place when, A, the reactant with the zero order of rxn is used and the slow reaction ($B+B \rightarrow E+D$) is a non-reversible rxn which gives a new product.

g) It is a catalyst, because it speeds up the rxn of A to make products, knowing that A is a reactant of zero order.

AP® CHEMISTRY
2008 SCORING COMMENTARY (Form B)

Question 2

Sample: 2A
Score: 9

This response earned all 9 points: 1 for part (a), 1 for part (b), 1 for part (c), 2 for part (d), 1 for part (e), 2 for part (f), and 1 for part (g).

Sample: 2B
Score: 7

All of the points were earned in parts (a), (b), and (c). Only 1 point was earned in part (d) because of incorrect units. The point was earned in part (e). In part (f) 1 point was earned for one reason (justifying the lack of reactant A in the rate law based on its absence in the slow step). The point was earned in part (g) because the student makes the correct choice and correctly states the distinction between an intermediate and a catalyst.

Sample: 2C
Score: 4

The point was earned in part (a), but the point was not earned in part (b). The rate law in part (c) is consistent with the incorrect order given in part (b). The point was earned in part (c), even though the rate constant is omitted, because subsequently in part (d) the student does correctly insert *k* into the rate law. In part (d) 1 point was earned for a calculation based on consistent substitutions, but the second point was not earned because of lack of units. The point was earned in part (e) for a calculation with consistent substitution and correct units. The points were not earned in parts (f) or (g).