Essay Questions

1983

a) three points

Plot ln k or log k vs 1/T

Eact = - R (slope) or - 2,303 R (slope)

For partial credit, if the 2-point equation is given for the activation evergy, the student may receive a point. A student may also receive a point if it is stated that k is plotted vs 1/T or if ln K or log k is plotted vs T.

b) five points

Plot ln PA or log PA vs time.

Plot 1/PA vs time.

If ln PA vs time is linear, the reaction is first order. If 1/PA vs time is linear, the reaction is second order.

If first order, slope = - k1 or - k1 / 2.303.

If second order, slope = k2.

1985

Average score = 3.52

a) three points

Points on ordinate take into account the initial amounts of the three substances, and PCl_5 line rises while others fall.

Lines curved at start and flat after equilibrium.

Concentration changes should be consistant with the fact that all coefficients in the equation are unity.

b) two points - First order in both reactants, Inclusion of constant
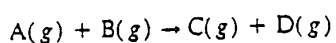
Rate = k $[PCl_3]$ $[Cl_2]$

c) one point

Reaction requires effective collisions between molecules of PCl_3 and Cl_2 As concentrations of these molecules increase, the number of effective collisions must increase and the rate of action increases.

d) two points

The fraction of colliding molecules with the required activation evergy increases as the temperature rises.

1990 $A(g) + B(g) \rightarrow C(g) + D(g)$ $\Delta H°$ reaction = −10 kilojoules

(a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.

(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.

(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.

$$A + B \rightleftharpoons [AB] \qquad \text{(fast)}$$

$$[AB] + B \rightarrow C + D \qquad \text{(slow)}$$
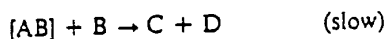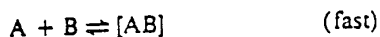
(d) Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

a) 1) The Kinetic energy of the molecules
(A certain minimum energy is required
for a reaction to occur (activation energy))(1)

2) The orientation of the molecules relative
to one another. Even very energetic collisions
may not lead to a reaction if the molecules (1)
are not oriented properly

b) 1) Decrease in temperature would decrease the rate (1)

2) Fewer molecules would have the energy necessary
to react. (Less effective collisions) (1)

c) Rate = K [A] [B]² (2)

d) 1) Catalyst increases the rate by providing
an alternate pathway which has a lower activation
energy. (1)

2) The value of the equilibrium constant does
not change as it does not affect the energies
of the reactants and products. (concentrations)(1)

Page 2

1992

$$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$$
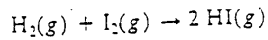
5.

For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows.
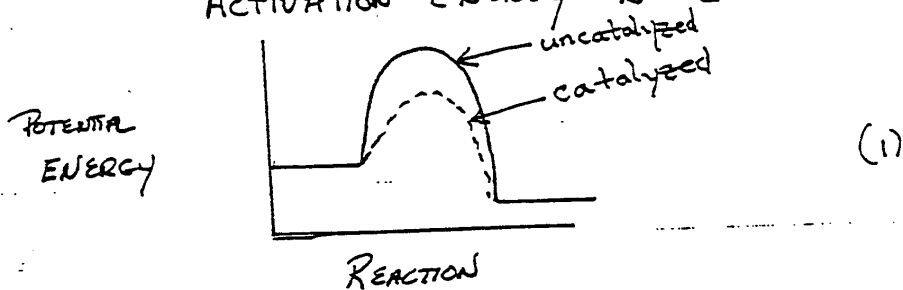
$$\text{Rate} = k[H_2][I_2]$$

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume
(b) Increase in volume of the reaction vessel at constant temperature
(c) Addition of a catalyst. In your explanation, include a diagram of potential energy *versus* reaction coordinate.
(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

a) EFFECT - INITIAL RATE WILL INCREASE (1)

EXPLANATION - RELATE INCREASE IN CONCENTRATION OF HYDROGEN TO AN INCREASE IN COLLISION RATE OR TO THE RATE LAW. (1)
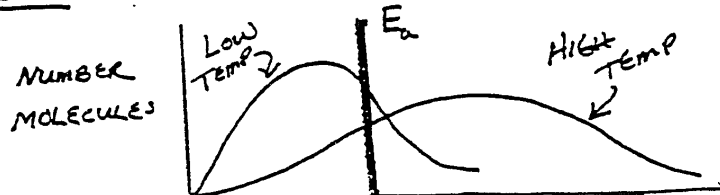
b) EFFECT - INITAL RATE WILL DECREASE

EXPLANATION - DECREASE IN THE CONCENTRATION OF REACTANTS } (1)

c) EFFECT - INITIAL RATE WILL INCREASE (1)

EXPLANATION -

ACTIVATION ENERGY IS LOWERED (1)

POTENTIAL ENERGY

uncatalyzed
catalyzed

REACTION

(1)

(d) EFFECT - INITIAL RATE WILL INCREASE (1)

EXPLANATION -

NUMBER MOLECULES

Low Temp

E_a

High Temp

(1) 27

QUESTION 9
(8 pts.)

1995

a) Sketch must show start at X_2+Y_2, rise to E_a that is less than that
for reaction I, then drop to 2 XY, which must be at
a higher PE than X_2+Y_2 to show an endothermic process.

(*1 pt.*)

(*1 pt.*)

b) The rate increases because more molecules have energy greater than E_a
at higher temperature and/or the higher speed of the molecules generates
a greater collision frequency

(*1 pt.*)

ΔH for the reaction is changed only slightly, or not at all with small changes
in temperature.

(*1 pt.*)

c) Hold one reactant concentration constant, vary the other, and measure initial <u>rate</u>
of reactant disappearance or product formation. Take ratios of rates equal to
$([\ ]_1 / [\ ]_2)^n$; repeat for the other reactant.

<u>or</u>

Follow concentrations of both reactants as functions of time, plot and
test for order of each (1st, 2nd, etc.) or do integral law calculations.

(*2 pts.*)

<u>or</u>

Add large concentrations of one reactant, follow the concentration of the other
as a function of time; repeat for the other reactant.

<u>Note:</u> 1 point awarded for less complete description

d) Reaction II proceeds faster

(*1 pt.*)

The reaction with the lower E_a, under same conditions of concentration and
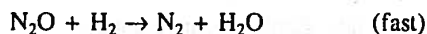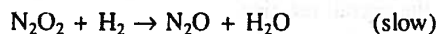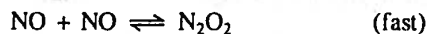temperature, will have a faster rate.

(*1 pt.*)

<u>OR</u>

It is not possible to determine which reaction has the faster rate without
knowledge of other (preexponential) factors. It cannot be assumed these
factors will be the same for X_2, Y_2, as for A_2, B_2, or that a similar mechanism
is involved.

(*2 pts.*)

QUESTION 8
(8 points)

8. The reaction between NO and H_2 is believed to occur in the following three-step process.

$$NO + NO \rightleftharpoons N_2O_2 \qquad \text{(fast)}$$
$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \qquad \text{(slow)}$$
$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad \text{(fast)}$$

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

(b) Identify the intermediates in the reaction. Explain your reasoning.

(c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is $rate = k[NO]^2[H_2]$. The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an H_2 molecule. Are conclusions (1) and (2) correct? Explain.

(d) Explain why an increase in temperature increases the rate constant, k, given the rate law in (c).

Scoring Guide

(a) $2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O$ — *1 point*

(b) N_2O_2 and N_2O are intermediates — *1 point*

   because they appear in the mechanism but not in the overall products (or reactants) — *1 point*

(c) Student indicates conclusion (1) is correct, — *1 point*
   because the sum of the exponents in rate law is $2 + 1 = 3$ — *1 point*

   Student indicates conclusion (2) is incorrect,
   because no step involves two NO molecules and a H_2 molecule — *1 point*

(d) $T\uparrow \Rightarrow k\uparrow$

   because increasing number of collisions between reactants — *1 point*
   are occuring with sufficient energy to form an activated complex — *1 point*

OR,

   $T\uparrow \Rightarrow rate\uparrow$ — *1 point*
   because no change in concentration of reactants, $\therefore k$ must increase — *1 point*

OR,

   from Arrhenius equation (not required in AP Chemistry curriculum, but noted in some attached student responses) — *1 point*
   as $T\uparrow$, $k\uparrow$ — *1 point*

OR,

   Graph as below with proper explanation — *2 points*
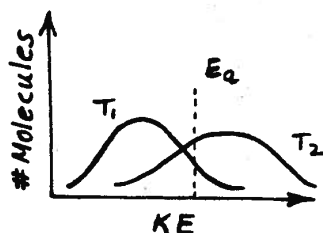
Question 8

Total Score 8 points

8. The decay of the radioisotope I-131 was studied in a laboratory. I-131 is known to decay by beta ($_{-1}^{0}e$) emission.

   (a) Write a balanced nuclear equation for the decay of I-131.

$_{53}^{131}\text{I} \rightarrow {}_{54}^{131}\text{Xe} + {}_{-1}^{0}e$	1 point for correct equation

Note: "β" for $_{-1}^{0}e$ is acceptable

   (b) What is the source of the beta particle emitted from the nucleus?

A neutron spontaneously decays to an electron and a proton.	1 point for identifying a neutron as the source of the beta emission

The radioactivity of a sample of I-131 was measured. The data collected are plotted on the graph below.
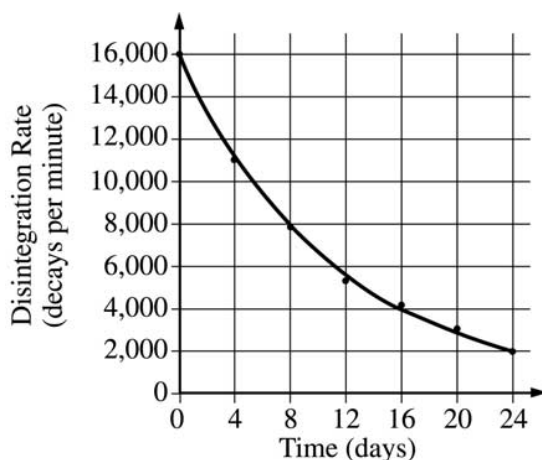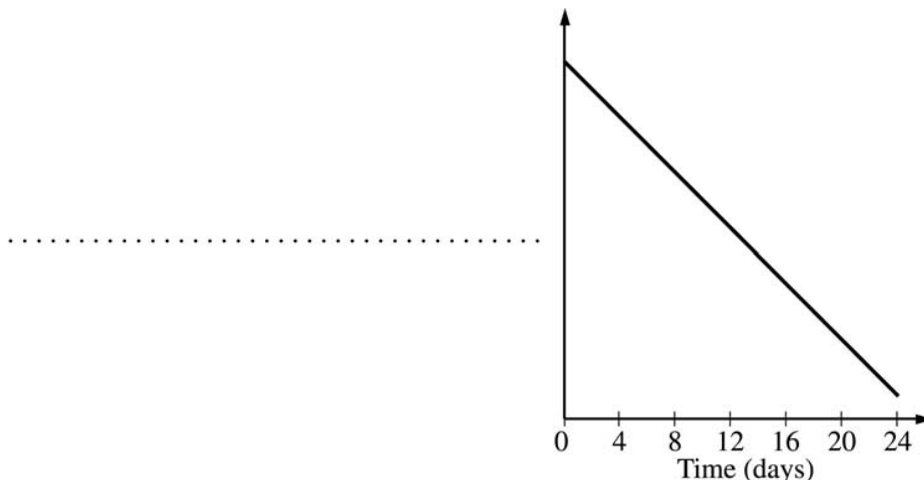

   (c) Determine the half-life, $t_{1/2}$, of I-131 using the graph above.

The half-life is 8 days. That is the time required for the disintegration rate to fall from 16,000 to one-half its initial value, 8,000.	1 point for half-life

Question 8 (cont'd.)

(d) The data can be used to show that the decay of I-131 is a first-order reaction, as indicated on the graph below.

(i) Label the vertical axis of the graph above.

The label on the y-axis should be ln or log one of the following: disintegrations or moles or atoms or [I-131] or disintegration rate.	1 point for correct label on y-axis

(ii) What are the units of the rate constant, k, for the decay reaction?

From the graph, the units on the rate constant are days^{-1} (Units of time^{-1} is acceptable)	1 point for correct units

(iii) Explain how the half-life of I-131 can be calculated using the slope of the line plotted on the graph.

The slope of the line is $-k$. The slope is negative, so k is a positive number. The half-life can then be calculated using the relationship $t_{1/2} = \dfrac{0.693}{k}$.	1 point for indicating slope is k 1 point for half-life equation

(d) Compare the value of the half-life of I-131 at 25°C to its value at 50°C.

The half-life will be the same at the different temperatures. The half-life of a nuclear decay process is independent of temperature.	1 point

Problems

1981

a) 6 points

rate = k $[A]^m [B]^n$

m = 2

n = 1

b) 3 points

Substitution of any one set of data from experiments 1-5 into the rate equation.

For example, experiment #1:

$8.00 \text{ mol L}^{-1} \text{ hr}^{-1} = k [0.240 \text{ mol / L}]^2 [0.480 \text{ mol / L}]$

$k = 289 \text{ L}^2 \text{ mol}^{-2} \text{ hr}^{-1}$

c) 2 points

rate = $289 \text{ L}^2 \text{ mol}^{-2} \text{ hr}^{-1} (0.0140 \text{ mol / L})^2 (1.35 \text{ mol / L})$

rate = $0.0766 \text{ mol L}^{-1} \text{ hr}^{-1}$

d) 4 points

acknowledgement of a limiting reagent

identification of B as the limiting reagent

correct mole ratio

[C] = (3C / 2B) x 0.120 mol / L of B

1984

Average score 4.81

a) three points; one point for correct form of law and two points for correct methodology without an
error; one point for correct methodology with an error

Rate = k[Y]

b) two points

$7.0 \times 10^{-4} \text{ mole / L sec} = k (0.10 \text{ mole / L})$

$k = 7.0 \times 10^{-3} \text{ sec}^{-1}$

c) two points

$2.3 \log c_o / c = k t$

$2.3 \log 0.60 / 0.40 = (7.0 \times 10^{-3}) (t)$

t = 58 s

d) two point

Mechanism 3 is correct.

The rate law shows that the slow reaction must involve one Y, consistent with mechanism 3.

Mechanisms 1 and 2 would involve both [X] and [Y] in the rate law, not consistent with the rate law.

1987

a) three points; one each for form of rate law, $HgCl_2$ exponent, $C_2O_4^{2-}$ exponent

Rate = k $[HgCl_2][C_2O_4^{2-}]^2$

b) three points; two for correct substitution and arithmetic, one for units

0.52×10^{-4} M/min = k $[0.0836][0.202]^2$

k = 1.52×10^{-2} M^{-2} min^{-1}

(note: sometimes this unit is written as L^2 mol^{-2} min^{-1})

c) one point

+ $d[Cl^-] / dt = 0.52 \times 10^{-4} \times (1\ C_2O_4^{2-} / 2\ Cl^-) = 2.6 \times 10^{-5}$ M/min
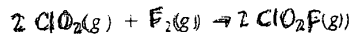
no credit for inverting ratio

d) two points

1.27×10^{-4} M/min = $(1.52 \times 10^{-2}\ M^{-2}\ min^{-1}) (0.0316)[C_2O_4^{2-}]^2$

$[C_2O_4^{2-}]^2 = 0.264\ M^2$

$[C_2O_4^{2-}] = 0.514$ M

3.

$$2\ ClO_2(g) + F_2(g) \rightarrow 2\ ClO_2F(g)$$

The following results were obtained when the reaction represented above was studied at 25° C.

Experiment	Initial [ClO$_2$], (mol L^{-1})	Initial [F$_2$], (mol L^{-1})	Initial Rate of Increase of [ClO$_2$F], (mol L^{-1} sec^{-1})
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.20	9.6×10^{-3}

(a) Write the rate law expression for the reaction above.

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of [F$_2$]?

(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a)? Justify your choice.

I. $ClO_2 + F_2 \leftrightarrows ClO_2F_2$ (fast)
    $ClO_2F_2 \rightarrow ClO_2F + F$ (slow)
    $ClO_2 + F \rightarrow ClO_2F$ (fast)

II. $F_2 \rightarrow 2F$ (slow)
    $2(ClO_2 + F \rightarrow ClO_2F)$ (fast)

*They go out of their way to find an equation when rate law ≠ data order.

a) Rate = k [ClO$_2$][F$_2$]

[1] - rate eqn. form, k
[1] - F$_2$ order
[1] - ClO$_2$ order

b) k = Rate/[ClO$_2$][F$_2$]

$= \dfrac{2.4 \times 10^{-3}\ mol\ L^{-1}\ sec^{-1}}{(0.010\ mol/L)(0.10\ mol/L)}$

$= 2.4\ L\ mol^{-1}\ sec^{-1}$

[1] value consistent with equation in (a)

[1] units consistent with equation in (a)

*People who made 8 instead of 9 - missed their point here. - Must look at stoichiometry of the equation

c) $2ClO_2 + F_2 \longrightarrow 2ClO_2F$

(at example on the next page) - must explain if you don't show the work.
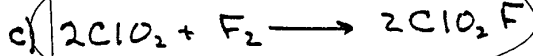
$-\dfrac{d[F_2]}{dt} = \frac{1}{2}\left(\dfrac{d[ClO_2F]}{dt}\right)$

$= \frac{1}{2}(9.6 \times 10^{-3})$

$= 4.8 \times 10^{-3}\ mol\ L^{-1}\ sec^{-1}$

[1]

d) Mechanism I *   [1]

$ClO_2F + F_2 \rightleftharpoons ClO_2F_2$ (fast)
$ClO_2F_2 \longrightarrow ClO_2F + F$ (slow)
$ClO_2 + F \longrightarrow ClO_2F$ (fast)
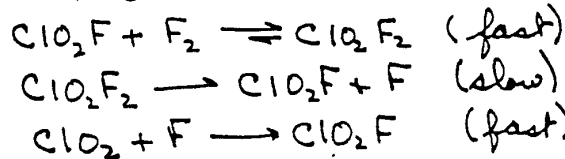
defense [1]
slow step is first order
3 eqns add to proper stoichiometry

*If ClO$_2$ order in rate eqn of part (a) is 0, mechanism II must be chosen to obtain credit.

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AP® CHEMISTRY
2003 SCORING GUIDELINES

Question 3

$$5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2(l) + 3\ H_2O(l)$$

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

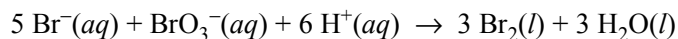| Experiment	Initial $[Br^-]$ (mol L^{-1})	Initial $[BrO_3^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Rate of Disappearance of BrO_3^- (mol L^{-1} s^{-1})
1	0.00100	0.00500	0.100	2.50×10^{-4}
2	0.00200	0.00500	0.100	5.00×10^{-4}
3	0.00100	0.00750	0.100	3.75×10^{-4}
4	0.00100	0.01500	0.200	3.00×10^{-3}

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

   (i) Br^-

Experiments 1 and 2: $$\frac{rate_2}{rate_1} = \frac{k_2[Br^-]_2^x[BrO_3^-]_2^y[H^+]_2^z}{k_1[Br^-]_1^x[BrO_3^-]_1^y[H^+]_1^z}$$ $$\frac{5.00 \times 10^{-4}}{2.50 \times 10^{-4}} = \frac{k_2(0.00200)^x(0.00500)^y(0.100)^z}{k_1(0.00100)^x(0.00500)^y(0.100)^z}$$ $$2 = \frac{(0.00200)^x}{(0.00100)^x} = 2^x$$ $x = 1 \implies$ first order	1 point for correct order of the reaction with respect to Br^-

   (ii) BrO^{3-}

Experiments 1 and 3: $$\frac{rate_3}{rate_1} = \frac{k_3[Br^-]_3^1[BrO_3^-]_3^y[H^+]_3^z}{k_1[Br^-]_1^1[BrO_3^-]_1^y[H^+]_1^z}$$ $$\frac{3.75 \times 10^{-4}}{2.50 \times 10^{-4}} = \frac{k_3(0.00100)^1(0.00750)^y(0.100)^z}{k_1(0.00100)^1(0.00500)^y(0.100)^z}$$ $$1.5 = \frac{(0.00750)^y}{(0.00500)^y} = 1.5^y$$ $y = 1 \implies$ first order	1 point for correct order of the reaction with respect to BrO_3^-

8

(iii) H^+

Experiments 3 and 4: $\dfrac{rate_4}{rate_3} = \dfrac{k_4[Br^-]_4{}^1[BrO_3{}^-]_4{}^1[H^+]_4{}^z}{k_3[Br^-]_3{}^1[BrO_3{}^-]_3{}^1[H^+]_3{}^z}$ $\dfrac{3.00 \times 10^{-3}}{3.75 \times 10^{-4}} = \dfrac{k_4(0.00100)^1(0.01500)^1(0.200)^z}{k_3(0.00100)^1(0.00750)^1(0.100)^z}$ $8 = \dfrac{(0.01500)^1(0.200)^z}{(0.00750)^1(0.100)^z}$ $8 = 2\dfrac{(0.200)^z}{(0.100)^z}$ $4 = \dfrac{(0.200)^z}{(0.100)^z} = 2^z$ $z = 2 \implies$ second order	1 point for correct order of the reaction with respect to H^+

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 $[Br^-]$ and $[BrO_3{}^-]$ are determined.

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

$rate = k[Br^-]^1\,[BrO_3{}^-]^1\,[H^+]^2$	1 point for correct rate law based on exponents determined in part (a)

(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

$rate = k[Br^-]^1\,[BrO_3{}^-]^1\,[H^+]^2$ $k = \dfrac{rate}{[Br^-]^1[BrO_3{}^-]^1[H^+]^2}$ Use data from any Experiment – using Experiment #1: $k = \dfrac{2.50 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}{(0.00100\ mol\ L^{-1})^1(0.00500\ mol\ L^{-1})^1(0.100\ mol\ L^{-1})^2}$ $k = 5.00 \times 10^3\ L^3\ mol^{-3}\ s^{-1}$ (units $M^{-3}\ s^{-1}$ also acceptable)	1 point for value of rate constant 1 point for correct units

9

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)
$Br_2(l) + 2\ e^- \rightarrow 2\ Br^-(aq)$	+1.065
$BrO_3^-(aq) + 6\ H^+(aq) \rightarrow Br_2(l) + 3\ H_2O(l)$	+1.52

$E° = +1.52\ V - 1.065\ V = +0.46\ V$	1 point for correct standard cell potential

(e) Determine the total number of electrons transferred in the overall reaction.

$5 \times (2\ Br^-(aq) \rightarrow Br_2(l) + 2\ e^-)$ $2 \times (BrO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightarrow \frac{1}{2} Br_2(l) + 3\ H_2O(l))$ $10\ Br^-(aq) + 2\ BrO_3^-(aq) + 12\ H^+(aq) + 10\ e^- \rightarrow 6\ Br_2(l) + 6\ H_2O(l) + 10\ e^-$ Divide by 2 to get the equation at the beginning of the problem: $5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2(l) + 3\ H_2O(l)$ Total number of electrons transferred is $5\ e^-$	1 point for correct number of electrons transferred

Question 3

The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of 5.00×10^3 cm^{-1} M^{-1} and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

(a) Calculate the initial concentration of the colored species.

$A = abc$ $c = \dfrac{A}{ab} = \dfrac{0.600}{\left(5.00 \times 10^3 \text{ cm}^{-1} M^{-1}\right)(1.00 \text{ cm})}$ $\quad = 1.20 \times 10^{-4}\ M$ <u>OR</u> $A_0 = abc_0 \qquad A_1 = abc_1$ $\dfrac{A_0}{c_0} = \dfrac{A_1}{c_1} \qquad \dfrac{0.600}{c_0} = \dfrac{0.200}{4.00 \times 10^{-5}}$ $c_0 = 1.20 \times 10^{-4}\ M$	1 point for concentration of X

(b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.

Using the first two readings, $\ln[X]_t - \ln[X]_0 = -kt \quad$ <u>OR</u> $\quad \ln \dfrac{[X]_t}{[X]_0} = -kt$ $\ln \dfrac{4.00 \times 10^{-5}}{1.20 \times 10^{-4}} = -k\,(35.0 \text{ min})$ $\ln(0.333) = -k\,(35.0 \text{ min})$ $-1.10 = -k\,(35.0 \text{ min})$ $k = 3.14 \times 10^{-2} \text{ min}^{-1}$	1 point for magnitude and correct sign of rate constant 1 point for correct units

Question 3 (cont'd.)

(c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.

$\ln \dfrac{[X]_t}{[X]_0} = -kt$ $\ln \dfrac{1.50 \times 10^{-5}}{1.20 \times 10^{-4}} = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t$ $\ln (0.125) = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t$ $-2.08 = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t$ $t = 66.2 \text{ min}$	1 point for correct substitution 1 point for correct answer <u>Note</u>: students may use half-lives to answer this question.

(d) Calculate the half-life of the reaction. Include units with your answer.

$\ln \dfrac{[X]_t}{[X]_0} = -kt$ $\ln \dfrac{0.5\,[X]_0}{[X]_0} = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t_{1/2}$ $\ln (0.5) = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t_{1/2}$ $-0.693 = (-3.14 \times 10^{-2} \text{ min}^{-1})\, t_{1/2}$ $22.1 \text{ min} = t_{1/2}$ <u>OR</u> $t_{1/2} = \dfrac{0.693}{k}$ $t_{1/2} = \dfrac{0.693}{3.14 \times 10^{-2} \text{ min}^{-1}} = 22.1 \text{ min}$	1 point for correct magnitude 1 point for the correct units (1 point for the half-life equation if no k is given)

(e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy, E_a, of the reaction.

    (i) Label the vertical axis of the graph.

|	
The vertical axis should be labeled $\ln k$.	1 point

Question 3 (cont'd.)

(ii) Explain how to calculate the activation energy from this graph.

The slope of the line is related to the activation energy: $$\text{slope} = -\frac{E_a}{R}$$ To determine the activation energy for the reaction, multiply the slope by $-8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.	1 point for recognizing that the slope must be measured 1 point for the correct explanation of how to obtain the activation energy

Question 3

$$2 \text{ H}_2\text{O}_2(aq) \rightarrow 2 \text{ H}_2\text{O}(l) + \text{O}_2(g)$$
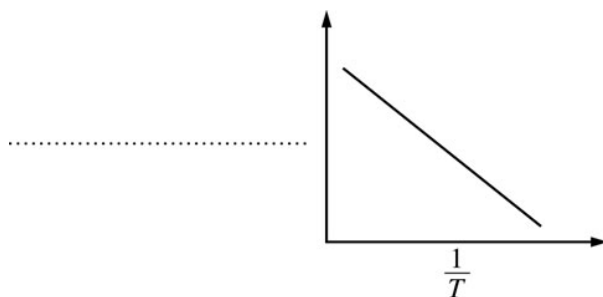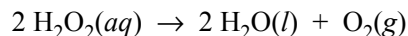
3. Hydrogen peroxide decomposes according to the equation above.

   (a) An aqueous solution of H_2O_2 that is 6.00 percent H_2O_2 by mass has a density of 1.03 g mL^{-1}. Calculate each of the following.

      (i) The original number of moles of H_2O_2 in a 125 mL sample of the 6.00 percent H_2O_2 solution

$n_{\text{H}_2\text{O}_2} = 125 \text{ mL H}_2\text{O}_2(aq) \times \dfrac{1.03 \text{ g H}_2\text{O}_2(aq)}{1.00 \text{ mL H}_2\text{O}_2(aq)} \times$ $\dfrac{6.00 \text{ g H}_2\text{O}_2}{100 \text{ g H}_2\text{O}_2(aq)} \times \dfrac{1 \text{ mol H}_2\text{O}_2}{34.0 \text{ g H}_2\text{O}_2} = 0.227 \text{ mol H}_2\text{O}_2$	1 point for determining mass of $\text{H}_2\text{O}_2(aq)$ 1 point for mass of H_2O_2 1 point for moles of H_2O_2

      (ii) The number of moles of $\text{O}_2(g)$ that are produced when all of the H_2O_2 in the 125 mL sample decomposes

$n_{\text{O}_2} = 0.227 \text{ mol H}_2\text{O}_2 \times \dfrac{1 \text{ mol O}_2(g)}{2 \text{ mol H}_2\text{O}_2(aq)} = 0.114 \text{ mol O}_2(g)$	1 point for moles of $\text{O}_2(g)$

   (b) The graphs below show results from a study of the decomposition of H_2O_2.
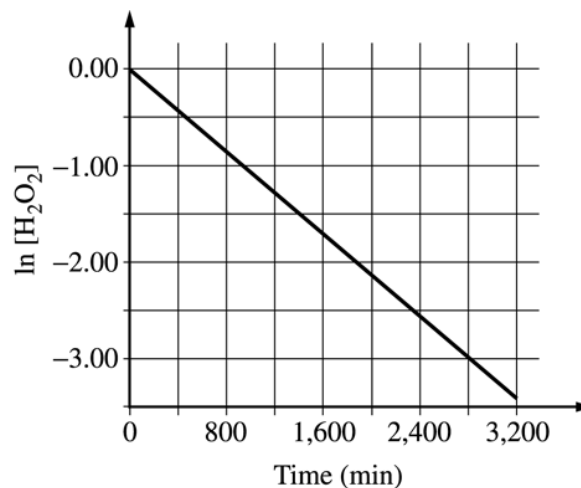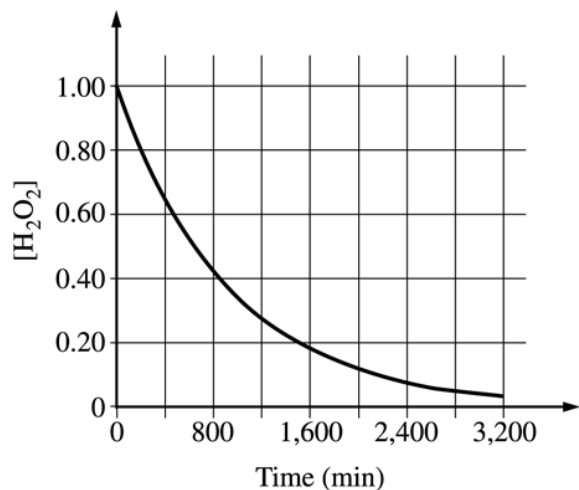
(i) Write the rate law for the reaction. Justify your answer.

rate $= k[H_2O_2]^1$ A plot of $\ln[H_2O_2]$ versus time is a straight line, so the reaction follows simple first-order kinetics.	1 point for correct rate law 1 point for explanation

(ii) Determine the half-life of the reaction.

Using the graph showing $[H_2O_2]$ versus time, the half-life is about 650 minutes. *OR* Calculate from $t_{1/2} = \dfrac{0.693}{k}$ after determining k from the slope in part (b)(iii)	1 point for a half-life between 600 and 700 minutes

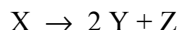(iii) Calculate the value of the rate constant, k. Include appropriate units in your answer.

$t_{1/2} = \dfrac{0.693}{k}$ $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{650 \text{ min}} = 1.1 \times 10^{-3} \text{ min}^{-1}$ *OR* k can be obtained from the determination of the slope of the line in the $\ln k$ versus time plot	1 point for the magnitude of the rate constant 1 point for the units

(iv) Determine $[H_2O_2]$ after 2,000 minutes elapse from the time the reaction began.

From the graph of $[H_2O_2]$ versus time, $[H_2O_2]$ is approximately 0.12 M. *OR* From the graph of $\ln[H_2O_2]$ versus time, $\ln[H_2O_2]$ is approximately –2.2, so $[H_2O_2] = e^{-2.2} = 0.11$ M	1 point for $0.09 < [H_2O_2] < 0.13$ M

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Question 3

$$X \rightarrow 2\,Y + Z$$

The decomposition of gas X to produce gases Y and Z is represented by the equation above. In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from this experiment were used to produce the information in the table below, which is plotted in the graphs that follow.

Time (minutes)	[X] (mol L^{-1})	ln [X]	[X]$^{-1}$ (L mol^{-1})
0	0.00633	−5.062	158
10.	0.00520	−5.259	192
20.	0.00427	−5.456	234
30.	0.00349	−5.658	287
50.	0.00236	−6.049	424
70.	0.00160	−6.438	625
100.	0.000900	−7.013	1,110
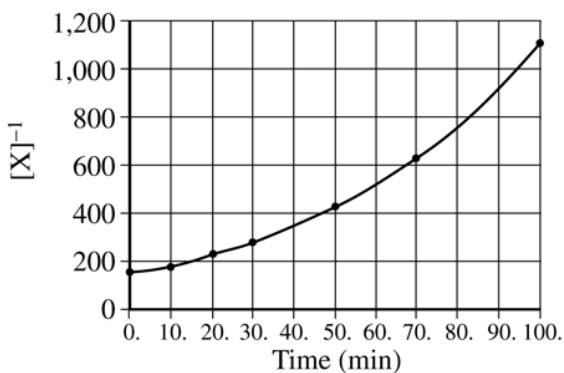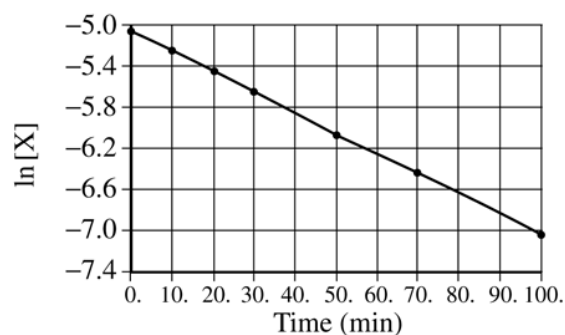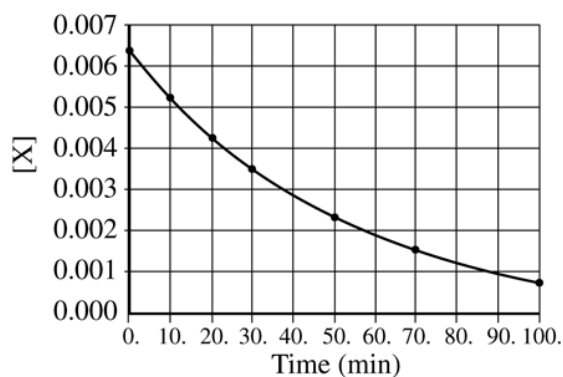
(a) How many moles of X were initially in the flask?

[X] at 0 minutes = 0.00633, so $5.00 \text{ L} \times 0.00633\ \dfrac{\text{mol X}}{\text{L}} = 3.17 \times 10^{-2} \text{ mol X}$	One point is earned for correct number of moles of X.

(b) How many molecules of Y were produced in the first 20. minutes of the reaction?

After 20. minutes of reaction, the number of moles of X remaining in the flask is $(5.00 \text{ L}) \times (0.00427 \, \frac{\text{mol X}}{\text{L}}) = 2.14 \times 10^{-2}$ mol X . Then the number of moles of X that reacted in the first 20 minutes is $(3.17 \times 10^{-2} \text{ mol X}) - (2.14 \times 10^{-2} \text{ mol X}) = 1.03 \times 10^{-2}$ mol X.	One point is earned for the number of moles of X that react or for the correct stoichiometry between X and Y.
Thus the number of molecules of Y produced in the first 20. minutes is $(1.03 \times 10^{-2} \text{ mol X}) \times \left(\frac{2 \text{ mol Y produced}}{1 \text{ mol X reacted}} \right) \times \left(\frac{6.02 \times 10^{23} \text{ molecules Y}}{1 \text{ mol Y}} \right)$ $= 1.24 \times 10^{22}$ molecules Y produced	One point is earned for the number of molecules of Y produced.

(c) What is the order of this reaction with respect to X ? Justify your answer.

The reaction is first order with respect to X because a plot of ln [X] versus time produces a straight line with a negative slope.	One point is earned for the correct order and an explanation.

(d) Write the rate law for this reaction.

rate $= k[\text{X}]^1$	One point is earned for the rate law consistent with part (c).

(e) Calculate the specific rate constant for this reaction. Specify units.

$\ln \dfrac{[\text{X}]_t}{[\text{X}]_0} = -kt$ From the first two data points, $\ln \left(\dfrac{0.00520}{0.00633} \right) = -k \, (10 \text{ min})$ $k = -\left(\dfrac{\ln 0.821}{10 \text{ min}} \right) = 0.0197 \text{ min}^{-1}$	One point is earned for the magnitude of the rate constant. One point is earned for the units.

Question 3 (continued

(f) Calculate the concentration of X in the flask after a total of 150. minutes of reaction.

$\ln \dfrac{[X]_t}{[X]_0} = -kt$ means the same thing as $\ln [X]_t - \ln[X]_0 = -kt$ $\ln [X]_{150} - \ln (0.00633) = -(0.0197 \text{ min}^{-1})(150 \text{ minutes})$ $\ln [X]_{150} = -(0.0197 \text{ min}^{-1})(150 \text{ minutes}) + \ln (0.00633)$ $\ln [X]_{150} = -(0.0197 \text{ min}^{-1})(150 \text{ minutes}) + (-5.062)$ $\ln [X]_{150} = -2.955 + (-5.062) = -8.017$ $e^{\ln[X]_{150}} = e^{-8.017} = 3.30 \times 10^{-4}$ $[X]$ at 150. minutes $= 3.30 \times 10^{-4} \, M$	One point is earned for substituting into the integrated rate law. One point is earned for the correct concentration of X.