Kinetics

Yellow - required   Green - bonus

2000 D Required

$$O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_{2(g)}$$

Consider the reaction represented above.

(a) Referring to the data in the table below, calculate the standard enthalpy change, for the reaction at 25°C. Be sure to show your work.

	$O_{3(g)}$	$NO_{(g)}$	$NO_{2(g)}$
Standard enthalpy of formation, ΔHeq \a(°,*f*) at 25°C (kJ mol^{-1})	143	90.	33

(b) Make a qualitative prediction about the magnitude of the standard entropy change, $\Delta S°$, for the reaction at 25°C. Justify your answer.

(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, for the reaction at 25°C. Explain your reasoning.

(d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[O_3]$ (mol L^{-1})	Initial [NO] (mol L^{-1})	Initial Rate of Formation of $[NO_2]$ (mol L^{-1} s^{-1})
1	0.0010	0.0010	x
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4x

(e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

Step I: $O_3 + NO \rightarrow O + NO_3$

Step II: $O + O_3 \rightarrow 2\ O_2$

Step III: $NO_3 + NO \rightarrow 2\ NO_2$

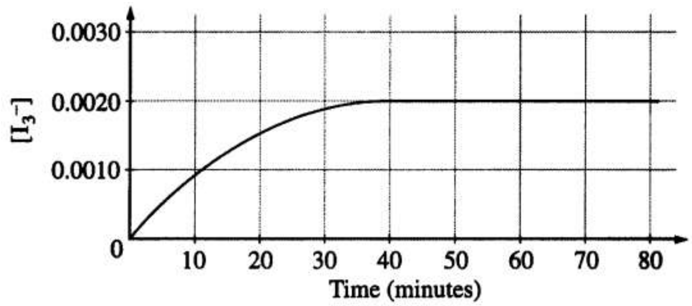
2001 D Required

$$3\ I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_3^-(aq) + 2\ SO_4^{2-}(aq)$$

Iodide ion, $I^-(aq)$, reacts with peroxydisulfate ion, $S_2O_8^{2-}(aq)$, according to the equation above. Assume that the reaction goes to completion.

(a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert $I^-(aq)$ to $I_3^-(aq)$.

(b) In an experiment, equal volumes of 0.0120 *M* $I^-(aq)$ and 0.0040 *M* $S_2O_8^{2-}(aq)$ are mixed at 25°C. The concentration of $I_3^-(aq)$ over the following 80 minutes is shown in the graph below.



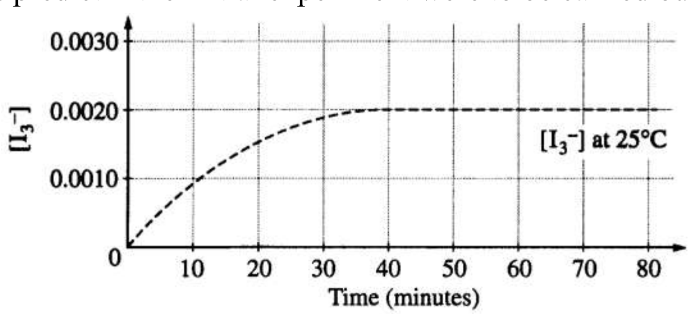
(i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning.

(ii) Explain how to determine the instantaneous rate of formation of $I_3^-(aq)$ at exactly 20 minutes. Draw on the graph above as part of your explanation.

(c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to $I^-(aq)$ and with respect to $S_2O_8^{2-}(aq)$.

(d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant, *k*, for the reaction.

(e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at 35°C rather than at 25°C.



2002 D

An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

Step I $O_3 + Cl \rightarrow O_2 + ClO$

Step II $ClO + O \rightarrow Cl + O_2$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

(d) If the rate law for the overall reaction is found to be rate = $k[O_3]$ [Cl], determine the following.

(i) The overall order of the reaction

(ii) Appropriate units for the rate constant, k

(iii) The rate-determining step of the reaction, along with justification for your answer

2002 D

$$C_{(s)} + CO_{2(g)} \Leftrightarrow 2\ CO_{(g)}$$

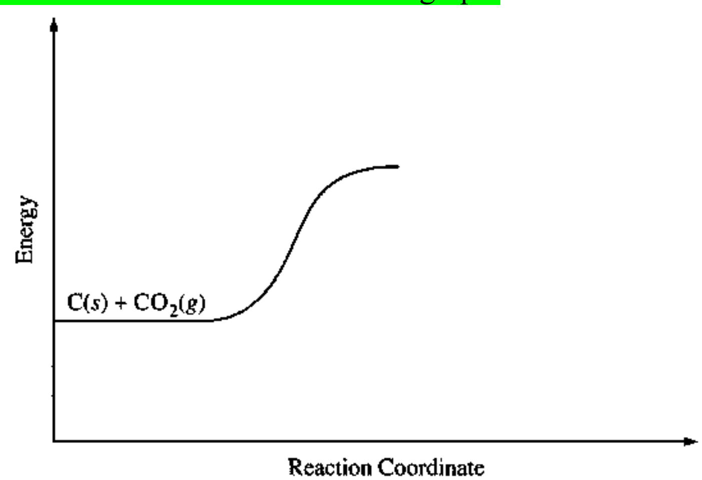
Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, ΔS, for the reaction. Justify your prediction.

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, ΔH, for the reaction. Justify your prediction.

Temperature	% CO
700˚C	60
850˚C	94

(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate ΔH for the reaction on the graph.



(d) If the initial amount of $C_{(s)}$ were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.

2003 B

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

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^-
   (ii) BrO_3^-
   (iii) H^+

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

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

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

Half-reaction	E˚ (V)
$Br_2(l) + 2e^- \rightarrow 2\ Br^-(aq)$	+1.065
$BrO_3^-(aq) + 6\ H^+(aq) + 5e^- \rightarrow \frac{1}{2}\ Br_2(l) + 3\ H_2O(l)$	+1.52

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

2004 B

The first-order decomposition of a colored chemical species, X, into colorless products is monitered 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 pathlength of the cuvetee 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 unknown species.

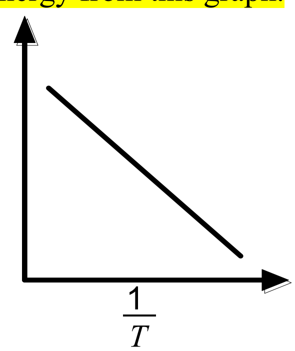
(b) Calculate the rate constant for the first order reaction using the values given for concentration and time. Include units with your answers.

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

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

(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 E_a, the activation energy.

- (i) Label the vertical axis of the graph
- (ii) Explain how to calculate the activation energy from this graph.



2005 B

Answer the following questions related to the kinetics of chemical reactions.

$$I^-(aq) + ClO^-(aq) \xrightarrow{OH} IO^-(aq) + Cl^-(aq)$$

Iodide ion, I^-, is oxidized to hypoiodite ion, IO^-, by hypochlorite, ClO^-, in basic solution according to the equation above. Three initial-rate experiments were conducted; the results shown in the following table.

Experiment	$[I^-]$ (mol L^{-1})	$[ClO^-]$ (mol L^{-1})	Initial Rate of Formation of IO^- (mol L^{-1} s^{-1})
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

(i) $I^-(aq)$

(ii) $ClO^-(aq)$

(b) For the reaction,

(i) write the rate law that is consistent with the calculations in part (a);

(ii) calculate the value of the specific rate constant, *k*, and specify units.

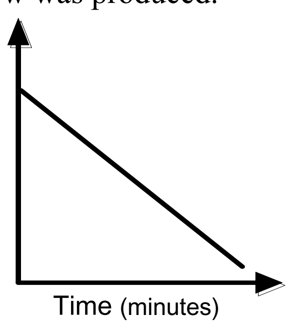
The catalyzed decomposition of hydrogen peroxide, $H_2O_2(aq)$, is represented by the following equation.

$$2\ H_2O_2(aq) \xrightarrow{catalyst} 2\ H_2O(l) + O_2(g)$$

The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below.

$[H_2O_2]$ (mol L^{-1})	Time (minutes)
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced.



(i) Label the vertical axis of the graph

(ii) What are the units of the rate constant, k, for the decomposition of $H_2O_2(aq)$?

(iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of $1.00\ M\ H_2O_2(aq)$.

2007 *part B*, question #6 *(repeated in bonding section)*

Answer the following questions, which pertain to binary compounds.

(a) In the box provided below, draw a complete Lewis electron-dot diagram for the IF_3 molecule.

(b) On the basis of the Lewis electron-dot diagram that you drew in part (a), predict the molecular geometry of the IF_3 molecule.

(c) In the SO_2 molecule, both of the bonds between sulfur and oxygen have the same length. Explain this observation, supporting your explanation by drawing in the box below a Lewis electron-dot diagram (or diagrams) for the SO_2 molecule.

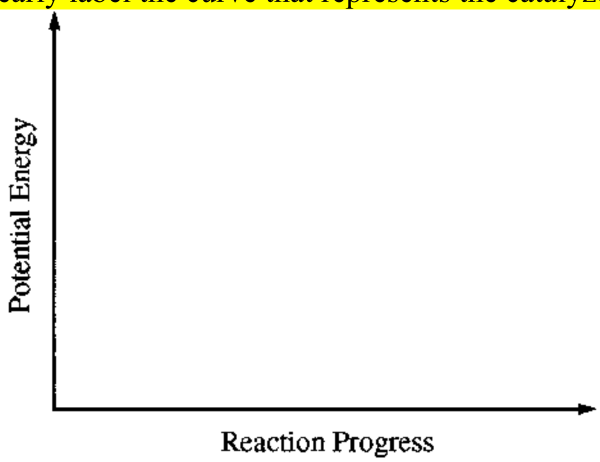
(d) On the basis of your Lewis electron-dot diagram(s) in part (c), identify the hybridization of the sulfur atom in the SO_2 molecule.

The reaction between $SO_{2(g)}$ and $O_{2(g)}$ to form $SO_{3(g)}$ is represented below.

$$2\ SO_{2(g)} + O_{2(g)} \leftrightarrow 2\ SO_{3(g)}$$

The reaction is exothermic. The reaction is slow at 25˚C; however, a catalyst will cause the reaction to proceed faster.

(e) Using the axes provided, draw the complete potential-energy diagram for both the catalyzed and uncatalyzed reactions. Clearly label the curve that represents the catalyzed reaction.



(f) Predict how the ratio of the equilibrium pressures, $\frac{P_{SO_2}}{P_{SO_3}}$, would change when the temperature of the uncatalyzed reaction mixture is increased. Justify your prediction.

(g) How would the presence of a catalyst affect the change in the ratio described in part (f)? Explain.

Kinetics

2008 part A, form A, question #3

Answer the following questions related to chemical reactions involving nitrogen monoxide, $NO_{(g)}$.

The reaction between solid copper and nitric acid to form copper(II) ion, nitrogen monoxide gas, and water is represented by the following equation.

$$3\ Cu_{(s)} + 2\ NO_3^-{}_{(aq)} + 8\ H^+{}_{(aq)} \rightarrow 3\ Cu^{2+}{}_{(aq)} + 2\ NO_{(g)} + 4\ H_2O_{(l)} \qquad E^\circ = +0.62\ V$$

(a) Using the information above and in the table below, calculate the standard reduction potential, E°, for the reduction of NO_3^- in acidic solution.

Half-Reaction	*Standard Reduction Potential, E^0*
$Cu^{2+}{}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$	+0.34 V
$NO_3^-{}_{(aq)} + 4\ H^+{}_{(aq)} + 3\ e^- \rightarrow NO_{(g)} + 2\ H_2O_{(l)}$	?

(b) Calculate the value of the standard free energy change, ΔG°, for the overall reaction between solid copper and nitric acid.

(c) Predict whether the value of the standard entropy change, ΔS°, for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.

Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.

$$2\ NO_{(g)} + O_{2(g)} \rightarrow\ 2\ NO_{2(g)}$$

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

(i) NO

(ii) O_2

(e) Write the expression for the rate law for the reaction as determined from the experimental data.

(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

2008 part A 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.
(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: $E + A \quad B + C$ *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.