Name: _____
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Differential Rate Laws

(1) Consider the following reaction: $3I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_3^-(aq) + 2SO_4^{2-}(aq)$
Determine a rate law based on the experimental data collected.

Experiment	Initial $[I^-]$ (mol/L)	Initial $[S_2O_8^{2-}]$ (mol/L)	Initial Rate (mol/Ls)
1	0.200	0.200	2.2×10^{-3}
2	0.400	0.200	4.4×10^{-3}
3	0.400	0.400	8.8×10^{-3}

(2) Consider the following reaction: $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$
Determine a rate law based on the experimental data collected. What is the overall order of the reaction?

Experiment	Initial [NO] (mol/L)	Initial $[Cl_2]$ (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

(3) Consider the following reaction: $2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$
Determine a rate law based on the experimental data collected. What is the overall order of the reaction?

Experiment	Initial $[ClO_2]$ (mol/L)	Initial $[OH^-]$ (mol/L)	Initial Rate (mol/Ls)
1	0.050	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.050	1.15×10^{-1}

(4) Consider the following reaction: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$
Determine a rate law based on the experimental data collected.
What would the rate be if initially, [NO] = 0.350 M and $[H_2]$ = 0.155 M?

Experiment	Initial [NO] (mol/L)	Initial $[H_2]$ (mol/L)	Initial Rate (mol/Ls)
1	0.420	0.122	0.136
2	0.210	0.122	0.0340
3	0.210	0.244	0.0680

(5) In a study of the reaction of Pyridine (C_5H_5N) with methyl iodide (CH_3I), data was collected for a series of experiments.
Determine a rate law based on the results.
What would the rate be if initially, $[C_5H_5N] = 1.50\times10^{-4}$ M and $[CH_3I] = 2.20\times10^{-4}$ M?

Experiment	Initial $[C_5H_5N]$ (mol/L)	Initial $[CH_3I]$ (mol/L)	Initial Rate (mol/Ls)
1	1.00×10^{-4}	1.00×10^{-4}	7.5×10^{-7}
2	1.00×10^{-4}	2.00×10^{-4}	3.0×10^{-6}
3	2.00×10^{-4}	2.00×10^{-4}	6.0×10^{-6}

(6) Consider the following reaction: $2Br^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow Br_2(aq) + 2H_2O(l)$
Determine a rate law based on the experimental data collected. What is the overall order of the reaction?
What would the rate be if initially, $[Br^-]$ = 0.015 M, $[H_2O_2]$ = 0.018 M and $[H^+]$ = 0.016 M?

Experiment	Initial $[Br^-]$ (mol/L)	Initial $[H_2O_2]$ (mol/L)	Initial $[H^+]$ (mol/L)	Initial Rate (mol/Ls)
1	0.010	0.010	0.010	3.6×10^{-3}
2	0.020	0.010	0.010	7.2×10^{-3}
3	0.010	0.0050	0.010	1.8×10^{-3}
4	0.010	0.010	0.020	7.2×10^{-3}

Answers:

(1) $rate = 0.055\,L/mol\,s[I^-][S_2O_8^{2-}]$

(2) $rate = 180\,L^2/mol^2 s[NO]^2[Cl_2]$ overall order = 3

(3) $rate = 230\,L^2/mol^2 s[ClO_2]^2[OH^-]$ overall order = 3

(4) $rate = 6.32\,L^2/mol^2 s[NO_2]^2[H_2]$; rate = 0.120 mol/L s

(5) $rate = 7.5x10^5\,L^2/mol^2 s[C_5H_5N][CH_3I]^2$; rate = $5.45x10^{-6}$ mol/L s

(6); $rate = 3.6x10^3\,L^2/mol^2 s[Br^-][H_2O_2][H^+]$; rate = 0.016 mol/L s

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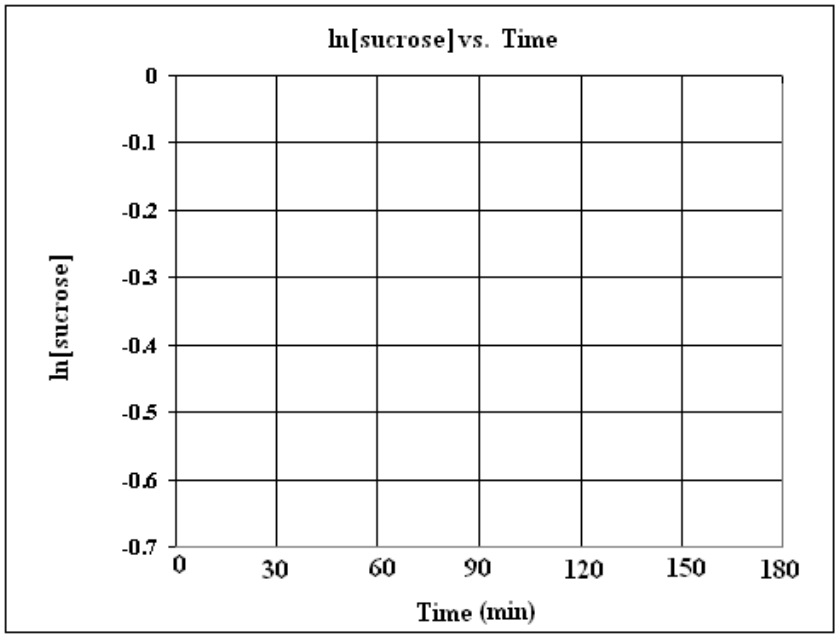
Integrated Rate Laws

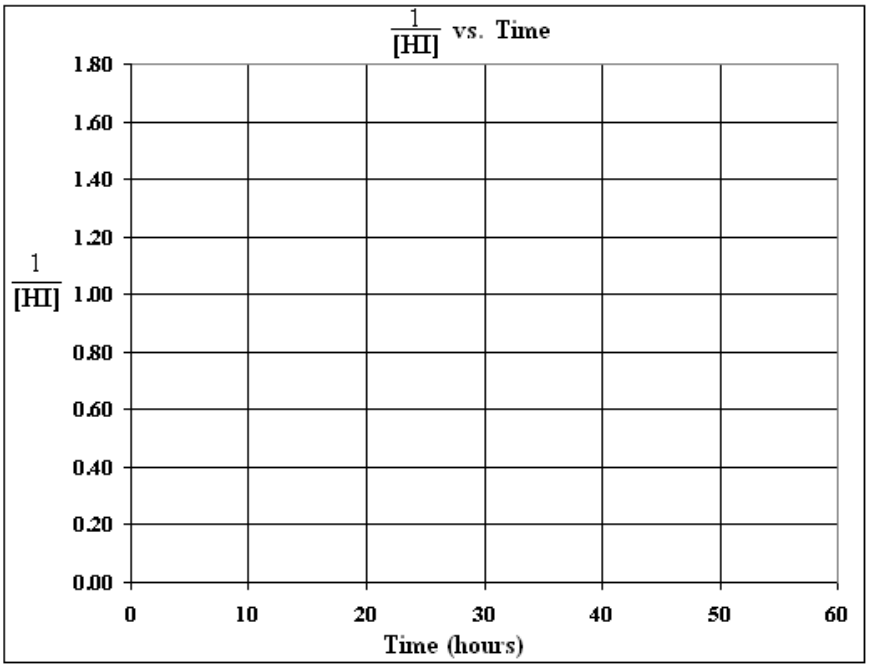
(1) Sucrose undergoes a hydrolysis reaction in an acidic solution to form glucose and fructose. Using the data collected for an experiment, show that the hydrolysis of sucrose is a first order process. Determine the specific rate constant and give the integrated rate law. What is the half-life for this process? What would be the concentration of Sucrose after 200 minutes? At what time would the concentration of sucrose be 0.20 mol/L?

Time (min)	[sucrose] (mol/L)	ln[sucrose]
0	1.00	
30	0.90	
60	0.81	
90	0.73	
130	0.64	
180	0.53	



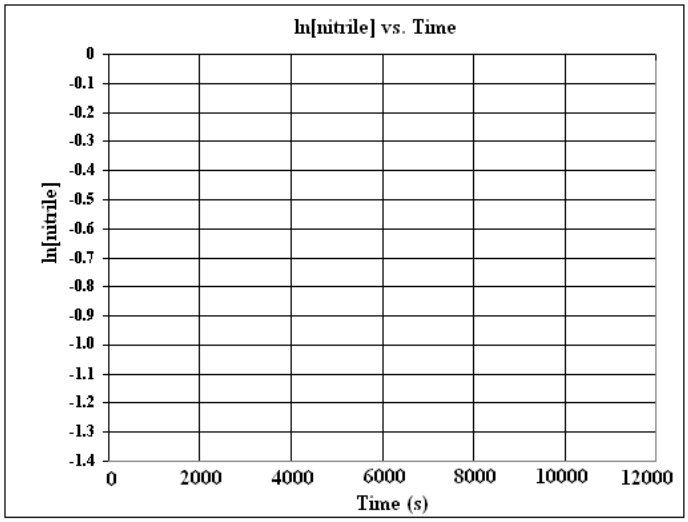
(2) The compound HI decomposes according to the following reaction: $2HI \rightarrow H_2 + I_2$.
Using the data collected for an experiment, show that the decomposition of HI is a second order reaction. Determine the specific rate constant and give the integrated rate law. What is the half-life for this process? What would be the concentration of HI after 75 hours? At what time would the concentration of HI be 0.40 mol/L?

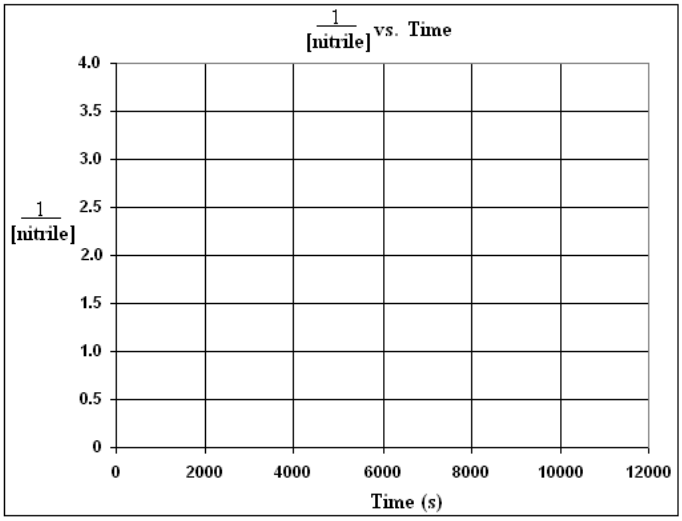
Time (hours)	[HI] (mol/L)	$\frac{1}{[HI]}$
0	1.00	
10	0.905	
20	0.827	
30	0.761	
40	0.705	
50	0.656	
60	0.614	



(3) Data was collected for the decomposition of an organic nitrile. Is the decomposition a first order or second order reaction? Determine the specific rate constant and give the integrated rate law. What is the half-life for this process?

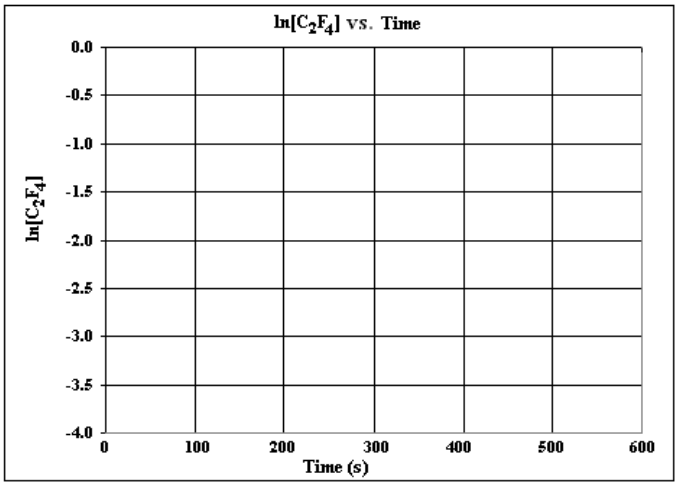
Time (s)	[nitrile] (mol/L)	ln[nitrile]	$\frac{1}{[\text{nitrile}]}$
0	1.10		
2000	0.86		
4000	0.67		
6000	0.52		
8000	0.41		
10000	0.32		
12000	0.25		

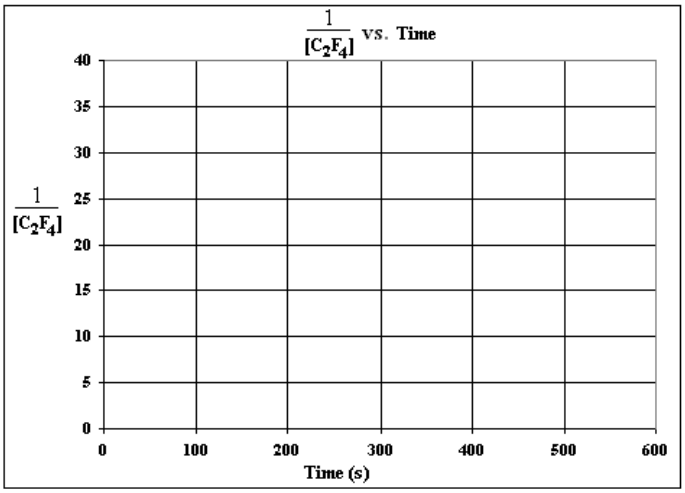




(4) The compound C_2F_4 dimerizes according to the following reaction: $2C_2F_4 \rightarrow C_4F_8$. Is the dimerization a first order or second order process? Determine the specific rate constant and give the integrated rate law. What is the half-life for this process?

Time (s)	[C_2F_4] (mol/L)	ln[C_2F_4]	$\frac{1}{[C_2F_4]}$
0	0.100		
100	0.0691		
200	0.0527		
300	0.0427		
400	0.0358		
500	0.0309		
600	0.0271		





Answers:

(1) k = 0.0035 min^{-1}; integrated rate law: $\ln[sucrose] = -0.0035\,\text{min}^{-1}\,t$; $t_{½}$ = 198 minutes;
at 220 minutes, [sucrose] = 0.46 mol/L; [sucrose] = 0.20 mol/L at 460 minutes

(2) k = 0.0105 L/mol hour; integrated rate law: $\frac{1}{[HI]} = 0.0105\,L/mol\,hour\;t + 1$; $t_{½}$ = 95 hours;
at 75 hours, [HI] = 0.56 mol/L; [HI] = 0.40 mol/L at 143 hours

(3) First Order, k = 1.23×10^{-4} s^{-1}; integrated rate law: $\ln[nitrile] = 1.23\text{x}10^{-4}\text{s}^{-1}\,t + \ln[1.10]$; $t_{½}$ = 5635 seconds

(2) Second Order, k = 0.0448 L/mol s; integrated rate law: $\frac{1}{[C_2F_4]} = 0.0448\,L/mol\,s\;t + 10$; $t_{½}$ = 223 seconds

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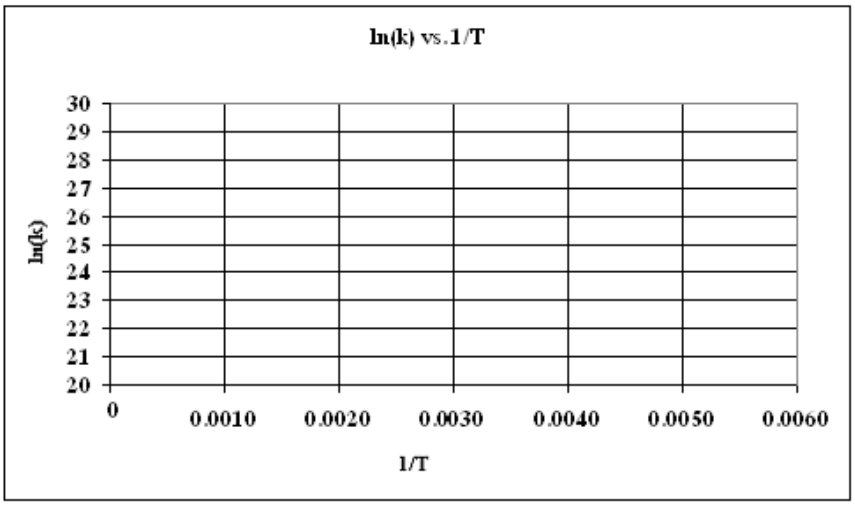
Reaction Rate and Temperature

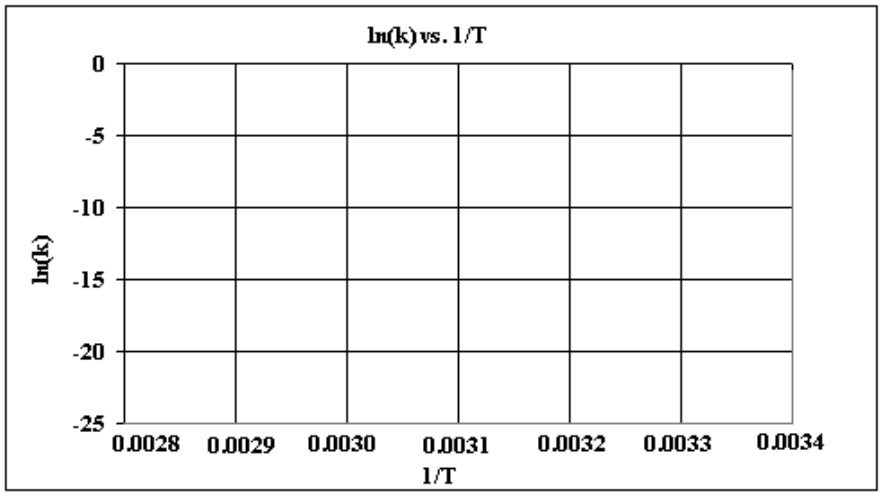
(1) The reaction $NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$ was studied at different temperatures and the experimental values of k were obtained. Determine E_a and A.

Temperature (K)	k (s^{-1})	$\frac{1}{T}$	ln(k)
195	1.08×10^{9}		
230	2.95×10^{9}		
260	5.42×10^{9}		
298	1.20×10^{10}		
369	3.55×10^{10}		



(2) The reaction $2NO_2\ (g) \rightarrow 2NO\ (g) + O_2\ (g)$ was studied at different temperatures and the experimental values of k were obtained. Determine E_a and A.

Temperature (K)	k (s^{-1})	$\frac{1}{T}$	ln(k)
300	1.0×10^{-10}		
310	4.2×10^{-10}		
320	1.6×10^{-9}		
330	5.6×10^{-9}		
340	1.9×10^{-8}		
350	5.7×10^{-8}		



(3) The reaction for the decomposition of hydroxylamine (NH_2OH) in the presence of oxygen was found to have a rate constant of 2.37×10^{-5} L/mol s at 273 K and 2.64×10^{-4} L/mol s at 298 K. Calculate E_a and A for this reaction.

(4) The reaction BH_4^- (aq) + NH_4^+ (aq) → BH_3NH_3 (aq) + H_2 (g) was found to have a rate constant of 1.94×10^{-4} L/ mol s at 30 ºC and 1.49×10^{-3} L/mol s at 40 ºC. Calculate E_a and A for this reaction.

Answers:
(1) $E_a = 1.19 \times 10^4$ J/mol A = 1.55×10^{12}

(2) $E_a = 1.1 \times 10^5$ J/mol A = 2.0×10^9

(3) $E_a = 6.52 \times 10^4$ J/mol A = 7.11×10^7

(4) $E_a = 1.61 \times 10^5$ J/mol A = 1.00×10^{24}

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Reaction Mechanisms

(1) Determine the overall reaction given the following steps:

Step 1: $H_2 + ICl \rightarrow HI + HCl$
Step 2: $HI + ICl \rightarrow HCl + I_2$

Identify any reaction intermediates.

(2) Determine the overall reaction given the following steps:

Step 1: $NO + NO \rightarrow N_2O_2$
Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

Identify any reaction intermediates.

(3) Determine the overall reaction given the following steps:

Step 1: $ClO_2 + ClO_2 \rightarrow Cl_2O_4$
Step 2: $Cl_2O_4 + OH^- \rightarrow ClO_3^- + HClO_2$
Step 3: $HClO_2 + OH^- \rightarrow ClO_2^- + H_2O$

Identify any reaction intermediates.

(4) The following reaction occurs in two steps: $2NO_2 + F_2 \rightarrow 2NO_2F$

Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$

Determine step 2 of this reaction mechanism.
Identify any reaction intermediates..

(5) The following reaction occurs in three steps: $2Ce^{4+} + Tl^+ \rightarrow 2Ce^{3+} + Tl^{3+}$

Step 1: $Ce^{4+} + Mn^{2+} \rightarrow Mn^{3+} + Ce^{3+}$

Step 3: $Mn^{4+} + Tl^+ \rightarrow Mn^{2+} + Tl^{3+}$

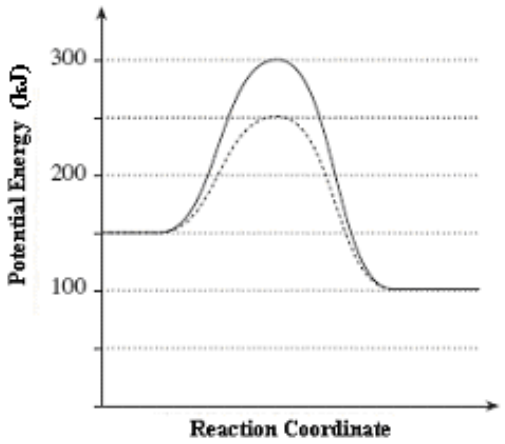
Determine step 2 of this reaction mechanism.
Identify any reaction intermediates.

(6) Determine the overall reaction given the following steps:

Step 1: $H_2O_2 \rightarrow H_2O + O$
Step 2: $O + CF_2Cl_2 \rightarrow ClO + CF_2Cl$
Step 3: $ClO + O_3 \rightarrow Cl + 2O_2$
Step 4: $Cl + CF_2Cl \rightarrow CF_2Cl_2$

Identify any reaction intermediates/catalysts.

(7) The potential energy diagram for a reaction is shown below.



(a) What is E_a for the forward, uncatalyzed reaction?

(b) What is E_a for the forward, catalyzed reaction?

(c) What is E_a for the reverse, uncatalyzed reaction?

(d) What is E_a for the reverse, catalyzed reaction?

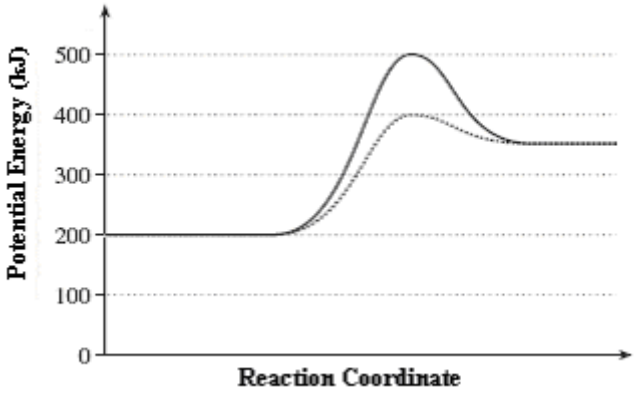
(e) What is ΔH for the forward, uncatalyzed reaction?

(f) What is ΔH for the forward, catalyzed reaction?

(g) What is ΔH for the reverse, uncatalyzed reaction?

(h) What is ΔH for the reverse, catalyzed reaction?

(8) The potential energy diagram for a reaction is shown below.



(a) What is E_a for the forward, uncatalyzed reaction?

(b) What is E_a for the forward, catalyzed reaction?

(c) What is E_a for the reverse, uncatalyzed reaction?

(d) What is E_a for the reverse, catalyzed reaction?

(e) What is ΔH for the forward, uncatalyzed reaction?

(f) What is ΔH for the forward, catalyzed reaction?

(g) What is ΔH for the reverse, uncatalyzed reaction?

(h) What is ΔH for the reverse, catalyzed reaction?

(9) Determine the overall reaction given the following steps.

Step 1: $NO + NO \rightarrow N_2O_2$ (fast)
Step 2: $N_2O_2 + Br_2 \rightarrow 2NOBr$ (slow)

Sketch a potential energy diagram (given that the overall reaction is exothermic) and label the rate determining step.
Identify any reaction intermediates.
Suggest a rate law for the overall reaction based on the reaction mechanism.

(10) The following reaction occurs in three steps: $2H_2O_2 \rightarrow 2O_2 + 2H_2O$ + heat

Step 1: $H_2O_2 \rightarrow 2OH$ (slow)
Step 2: $H_2O_2 + OH \rightarrow H_2O + HO_2$ (fast)

Determine step 3 of this reaction mechanism (fast).
Sketch a potential energy diagram and label the rate determining step.
Identify any reaction intermediates.
Suggest a rate law for the overall reaction based on the reaction mechanism.

Answers:
(1) overall: $H_2 + 2ICl \rightarrow 2HCl + I_2$
reaction intermediate: HI

(2) overall: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
reaction intermediates: N_2O_2, N_2O

(3) overall: $2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$
reaction intermediate: Cl_2O_4, $HClO_2$

(4) Step 2: $F + NO_2 \rightarrow NO_2F$
reaction intermediate: F

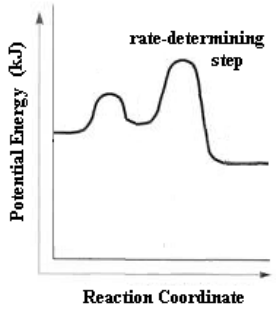
(5) Step 2: $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$
reaction intermediate: Mn^{3+}, Mn^{4+}

(6) overall: $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$
reaction intermediate: O, CF_2Cl, ClO, Cl
catalyst: CF_2Cl_2

(7) (a) 150 kJ (b) 100 kJ (c) 200 kJ (d) 150 kJ (e) -50 kJ (f) -50 kJ (g) 50 kJ (h) 50 kJ

(8) (a) 300 kJ (b) 200 kJ (c) 150 kJ (d) 50 kJ (e) 150 kJ (f) 150 kJ (g) -150 kJ (h) -150 kJ

(9) overall: $2NO + Br_2 \rightarrow 2NOBr$
reaction intermediate: N_2O_2
$rate = k[NO]^2[Br_2]$



(10) Step 3: $OH + HO_2 \rightarrow H_2O + O_2$
reaction intermediates: HO_2, OH
$rate = k[H_2O_2]$