F1404 MIDTERM 2

ANSWER KEY

1) In the synthesis of ammonia, $N_2(g) + 3H_2(g) \rightarrow 2 NH_3(g)$ if $-\Delta[H_2] / \Delta t = 4.5 \times 10^{-4}$ mol/L-min, what is $\Delta [NH_3] / \Delta t$? **(5 points)**

$$-\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} \quad (2)$$

$$-\frac{2}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[NH_3]}{\Delta t} \quad (1)$$

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\left[-4.5 \times 10^{-4}\ mol/L\text{-}min\right] = 3.0 \times 10^{-4}\frac{mol}{L\text{-}min} \quad (2)$$

-0.5 for units

2) Data for the reaction $2NO(g) + O_2(g) \rightarrow 2 NO_2(g)$ are given in the table

Experiment	Reactant Concentration (mol/L) [NO]	[O$_2$]	Initial rate mol/L-h
1	3.6×10^{-4}	5.2×10^{-3}	3.4×10^{-8}
2	3.6×10^{-4}	1.04×10^{-2}	6.8×10^{-8}
3	1.8×10^{-4}	1.04×10^{-2}	1.7×10^{-8}
4	1.8×10^{-4}	5.2×10^{-3}	???

2a) What is the rate law for this reaction? **(10 points)**

$$Rate = k[NO]^m[O_2]^n$$

Order with respect to NO - compare experiments 2 & 3

order with respect to O_2 - compare experiments 1&2

$$\frac{Rate_1}{Rate_2} = \frac{3.4 \times 10^{-8}\ mol/L\text{-}h}{6.8 \times 10^{-8}\ mol/L\text{-}h} = \left(\frac{5.2 \times 10^{-3}\ mol/L}{1.04 \times 10^{-2}\ mol/L}\right)^n \quad (4)$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n \quad n = 1 \quad \text{1st order in } O_2$$

$$\frac{Rate_2}{Rate_3} = \frac{6.8 \times 10^{-8}\ mol/L\text{-}h}{1.7 \times 10^{-8}\ mol/L\text{-}h} = \left(\frac{3.6 \times 10^{-4}\ mol/L}{1.8 \times 10^{-4}\ mol/L}\right)^m \quad (4)$$

$$4 = (2)^m \quad m = 2 \quad \text{2nd order in NO}$$

$$Rate = k[NO]^2[O_2] \quad (2)$$

2b) What is the rate constant for this reaction? **(5 points)**

$$\text{Rate} = k[NO]^2[O_2] \quad 2$$

$$3.4\times10^{-8}\ \frac{mol}{L\cdot h} = k\left(3.6\times10^{-4}\ \frac{mol}{L}\right)^2\left(5.2\times10^{-3}\ mol/L\right) \quad 1$$

$$k = 50.\ \frac{L^2}{mol^2\,h}$$

1

Units 1

2c) What is the initial rate of the reaction in Experiment 4? **(5 points)**

$$\text{Rate} = k[NO]^2[O_2] \quad 2$$

$$= 50\ \frac{L^2}{mol^2\,h}\left(1.8\times10^{-4}\ \frac{mol}{L}\right)^2\left(5.2\times10^{-3}\ \frac{mol}{L}\right) \quad 1$$

$$= 8.4\times10^{-9}\ \frac{mol}{L\cdot h}$$

1

Units 1

3) Identify which of the following statements are incorrect. If the statement is incorrect, in a maximum of TWO sentences, explain why.

3a) Reactions are faster at a higher temperature because activation energies are lower. **(4 points)**

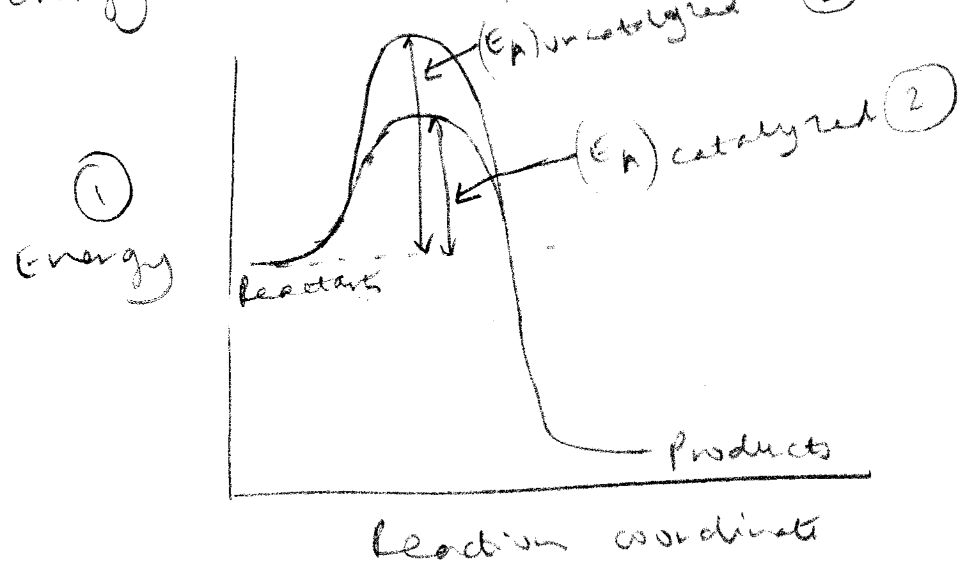
1 FALSE. Activation energy does not change with temperature. As temperature increases, fraction of molecules with energy greater than the activation energy increases, resulting in faster rates. 3

3b) The rates of reactions increase with increasing concentration of reactants because there are more collisions between reactant molecules. **(4 points)**

TRUE 4

4) Explain briefly why the rate of a catalyzed reaction is faster than the rate of an uncatalyzed reaction. Draw a reaction coordinate diagram for a one-step reaction mechanism illustrating the difference(s) between a catalyzed and uncatalyzed reaction. **(9 points)**

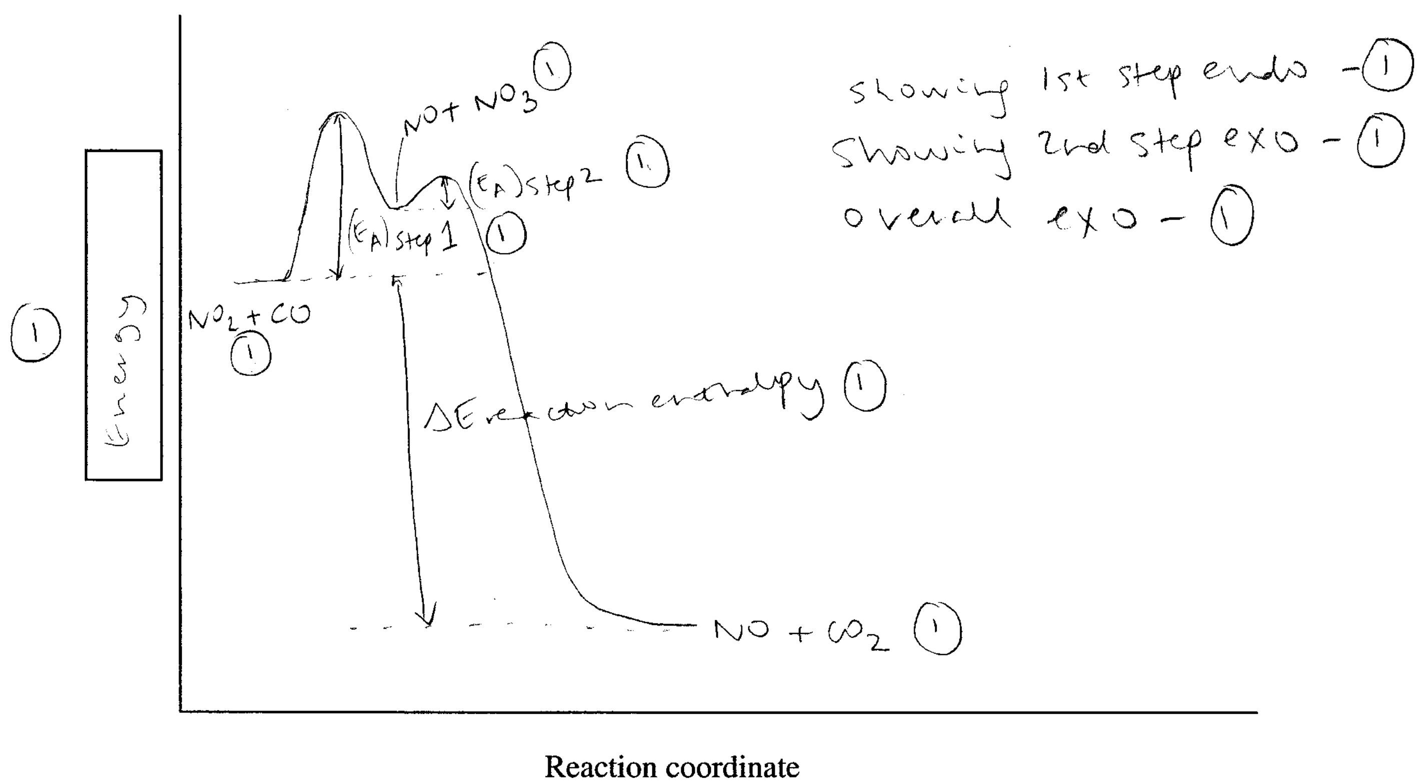
The reaction pathway of a catalyzed reaction has lower activation energy than reaction pathway of an uncatalyzed reaction. Since rate depends exponentially on activation energy, lower activation energy result in faster rate 4 2



5) A proposed mechanism for the reaction: NO_2 (g) + CO(g) → NO(g) + CO_2 (g) is

Step1: Slow, endothermic	2 NO_2 (g) → NO(g) + NO_3(g)
Step 2: Fast, exothermic	NO_3(g) + CO(g) → NO_2 (g) + CO_2 (g)
Overall: Exothermic	NO_2 (g) + CO(g) → NO(g) + CO_2 (g)

5a) Draw a reaction coordinate diagram for this reaction. Indicate on this drawing the activation energy for each step, the overall reaction enthalpy, and where the reactants (NO_2 + CO) and products (NO + CO_2) of the overall reaction are located. Indicate where the products from step 1 (NO + NO_3) are located. Label the y-axis. **(10 points)**



5b) What rate law does the proposed mechanism predict for the overall reaction? In **ONE** sentence explain how you determined the rate law. **(5 points)**

Rate = $k [NO_2]^2$ 2

The slow elementary step is the rate determining step 3

6) The ozone in the earth's ozone layer decomposes according to the equation:

$$2\,O_3\,(g) \rightarrow 3\,O_2\,(g)$$

The experimentally determined rate law is found to be second order in O_3 and a –1 order in O_2.

6a) Write an expression for the rate law for this reaction. **(5 points)**

$$\text{Rate} = k\,[O_3]^2\,[O_2]^{-1}$$

2 2

overall 1

6b) A proposed mechanism for this reaction is

Step 1: Fast, equilibrium $\quad O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2\,(g) + O(g)$

Step 2 Slow $\quad O_3\,(g) + O(g) \xrightarrow{k_2} 2\,O_2\,(g)$

Is this a plausible mechanism for the above reaction? Show all work to justify your answer **(10 points)**

Slow step is rate determining

$$\text{Rate} = k_2\,[O_3]\,[O]$$ 2)

O is an intermediate, need to eliminate this term.

From first step, fast, equilibrium

$$\Rightarrow k_1\,[O_3] = k_{-1}\,[O_2][O]$$ 3

$$[O] = \frac{k_1\,[O_3]}{k_{-1}\,[O_2]}$$ 1

$$\text{Rate} = k_2\,[O_3]\,\frac{k_1\,[O_3]}{k_{-1}\,[O_2]} = \frac{k_2 k_1}{k_{-1}}\,\frac{[O_3]^2}{[O_2]}$$

$$= k\,[O_3]^2\,[O_2]^{-1}$$ → same as experimentally determined rate law 3

This is a plausible mechanism 1

7) The work function for sodium is 3.60 x 10^{-19} J. What wavelength of radiation, in **nanometers (nm),** must be supplied to metallic sodium to release an electron with a velocity of 2.89 x 10^{5} m/s?

(10 points)

$\frac{1}{2} m_e v^2 = h\nu - \phi$

$h\nu = \frac{1}{2} m_e v^2 + \phi$ 2

$h\nu = \frac{1}{2}(9.109\times10^{-31}\,kg)(2.89\times10^{5}\,m/s)^2 + 3.60\times10^{-19}\,J$

$= 3.80\times10^{-20}\,J + 3.60\times10^{-19}\,J$

$h\nu = 3.98\times10^{-19}\,J$

$\nu = \frac{3.98\times10^{-19}\,J}{6.626\times10^{-34}\,J\text{-}s} = 6.00\times10^{14}\,s^{-1}$ 3

$\lambda = \frac{2.99792\times10^{8}\,m/s}{6.00\times10^{14}\,s^{-1}} = 4.99\times10^{-7}\,m$ 3

$\boxed{\lambda = 499\,nm}$ 2

8a) When light of a certain wavelength falls on a metal surface, causing electrons to be expelled, as the intensity of this light increases does the kinetic energy of the ejected electrons increase, decrease, or stay the same? In one sentence explain your answer.

(4 points)

2 STAY THE SAME. Kinetic energy of the ejected electron depends on the energy of the photon incident on the surface not on the intensity of the light. 2

8b) Does the kinetic energy of the emitted electrons increase, decrease, or stay the same as the frequency of the light is increased? In one sentence explain your answer.

(4 points)

2 INCREASE. As frequency of light increases, energy of photon increases, resulting in an increase in the energy of the electron ejected 2

9) Calculate the energy difference in **kJ/mol** between two different states of an atom known to absorb at 340.2 nm and 259.7 nm. **(10 points)**

$$\Delta E = E_1 - E_2$$

$$= \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$ 4

$$\Delta E = 6.2608\times10^{-34}\ Js \times 2.99792\times10^{8}\ \frac{m}{s}\left(\frac{1}{259.7\times10^{-9}m} - \frac{1}{340.2\times10^{-9}m}\right)$$ 3

$$\Delta E = 1.810\times10^{-19}\ J$$

$$\Delta E \text{ in } kJ/mole = 1.810\times10^{-22}\ kJ \times 6.023\times10^{23}/mole$$ 3

$$= 109.0\ kJ/mole$$