



AP Computer Science A 2000 Student Samples

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6. Consider the reaction represented above.

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

	$\text{O}_3(g)$	$\text{NO}(g)$	$\text{NO}_2(g)$
Standard enthalpy of formation, ΔH_f° , at 25°C (kJ mol ⁻¹)	143	90.	33

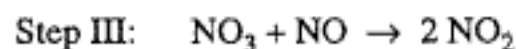
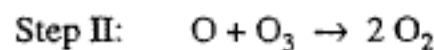
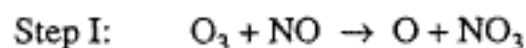
(b) Make a qualitative prediction about the magnitude of the standard entropy change, ΔS° , for the reaction at 25°C. Justify your answer.

(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, ΔG° , 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 $[\text{O}_3]$ (mol L ⁻¹)	Initial $[\text{NO}]$ (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.



a.) $\Delta H^\circ = [0 + 33] - [143 + 90] = 33 - 233 = -200 \text{ kJ/mol}$

b.) The entropy would remain about constant. This is because the moles of gas aren't increasing (increase in entropy) or decreasing. (decrease in entropy) Also, the degrees of freedom and states the molecules can exist in remain fairly constant

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c) $\Delta G = \Delta H - T\Delta S$ ΔH is negative
 ΔS is insignificant
 T is 25°C or 298K

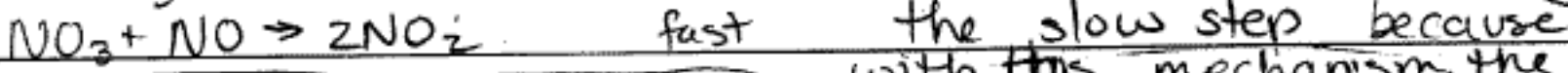
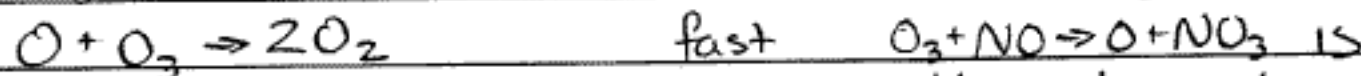
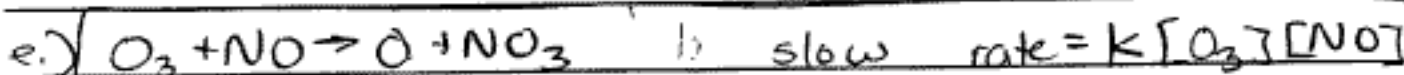
Based on this, $\Delta G = \Delta H - T\Delta S = \text{negative} - \text{positive}$. This makes ΔG negative, meaning the reaction is spontaneous.

d.) $\text{rate} = k [\text{O}_3]^x [\text{NO}]^y$

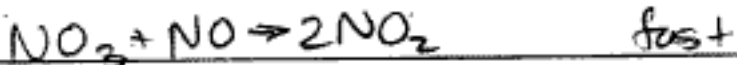
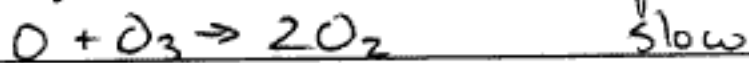
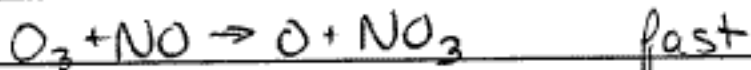
$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[\text{NO}_2]}{[\text{NO}_1]}\right)^y \quad \frac{2x}{x} = \left(\frac{.002}{.001}\right)^y \quad 2 = 2^y \quad y = 1$

$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[\text{O}_3]_2}{[\text{O}_3]_1}\right)^x \quad \frac{4x}{2x} = \left(\frac{.002}{.001}\right)^x \quad 2 = 2^x \quad x = 1$

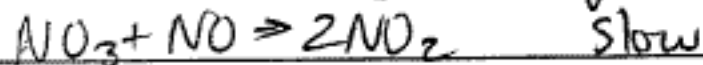
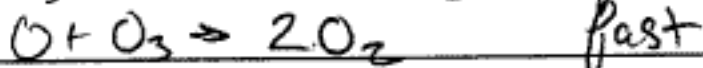
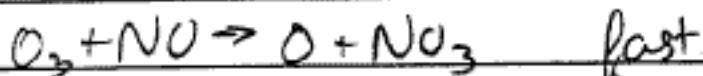
$\text{rate} = k [\text{O}_3][\text{NO}]$



with this mechanism, the rate is the same as by experiment

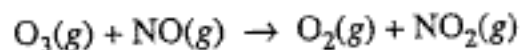


$\text{rate} = k [\text{O}][\text{O}_3] = k [\text{O}_3][\text{NO}][\text{O}_3]$
 $= k [\text{O}_3]^2 [\text{NO}]$



$\text{rate} = k [\text{NO}_3][\text{NO}] = k [\text{O}_3][\text{NO}][\text{NO}]$
 $= k [\text{O}_3][\text{NO}]^2$

The $\text{O}_3 + \text{NO} \rightarrow \text{O} + \text{NO}_3$ is the rate determining step. The order of the reaction with this mechanism is 2 (as in the experiment)



6. Consider the reaction represented above.

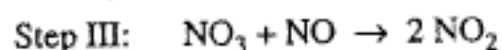
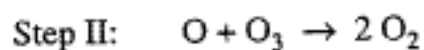
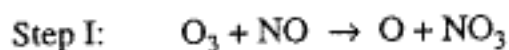
- (a) Referring to the data in the table below, calculate the standard enthalpy change, ΔH° , for the reaction at 25°C. Be sure to show your work.

	$\text{O}_3(g)$	$\text{NO}(g)$	$\text{NO}_2(g)$
Standard enthalpy of formation, ΔH_f° , at 25°C (kJ mol ⁻¹)	143	90	33

- (b) Make a qualitative prediction about the magnitude of the standard entropy change, ΔS° , 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, ΔG° , 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.

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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.



(a) $\Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) = \Delta H$
 $33 - (90 + 143)$
 $33 - 233 = -200 \text{ kJ mol}^{-1}$

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ADDITIONAL PAGE FOR ANSWERING QUESTION 6.

b) The entropy will not change considerably because both the products and the reactants are gases and there are 2 moles on either side of the equation.

c) Because $\Delta G = \Delta H - T\Delta S$ and ΔS is very small, I would predict ΔG to be + positive.

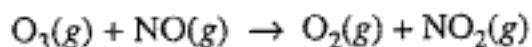
d) $\text{rate} = k [\text{O}_3]^1 [\text{NO}]^1$
because the reaction rate increases along with the concentration of EITHER of the reactants, and it increase as a power of 1 (not exponentially).

e) step 1 must be the rate defining step (the slowest) because it is the only step that has both ozone (O_3) and nitrogen monoxide (NO) in it and we already determined that the concentration of both is directly proportional to the rate of the reaction.

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6. Consider the reaction represented above.

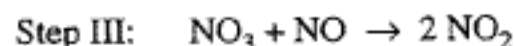
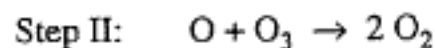
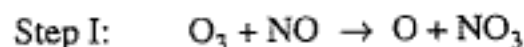
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- (c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, ΔG° , for the reaction at 25°C. Explain your reasoning.
- (d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

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- (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.



a) $\Delta H^\circ = \Delta H_{\text{prod}} - \Delta H_{\text{react}}$

$\Delta H^\circ = (33)(1) - (90)(1) - (143)(1)$

$= (-90)(1) - (143)$

$= -1287 \text{ kJ mol}^{-1}$

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ADDITIONAL PAGE FOR ANSWERING QUESTION 6.

b) ΔS° will tend towards zero or be non-spontaneous because each of the enthalpies of formation are positive and endothermic, and the products minus reactants tends toward zero because of less spontaneity.

c) The sign of ΔG° will be negative because ΔH is extremely negative and ΔS is not large enough that the magnitude will shift the sign when using the equation $\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T$.

d) Rate = $k[O_3]^x [NO]^y$

$$\frac{k[.0010]^x [.0020]^y}{k[.0010]^x [.0010]^y} = \frac{2x}{x} \quad 2 = \frac{(.0020)^y}{(.0010)^y} \quad y = 1$$

$$\frac{k[.0020]^x [.0010]^y}{k[.0010]^x [.0010]^y} = \frac{2x}{2x} \quad 1 = \frac{(.0020)^x}{(.0010)^x} \quad x = 0$$

rate = $k[O_3]^0 [NO]^1$

The rate may be determined by using the ratio $\frac{rate_1}{rate_2} = \frac{k[O_3]^x [NO]^y}{k[O_3]^x [NO]^y}$ and holding one rate constant so that part of the equation cancels to form 1. Thus, the equation may be solved simply for y , solving for the exponent.

e) Rate I must be the slowest reaction because the rate of O_3 is a zero power equation and thus, negligible in the rate expression. Step I is determinant on the rate of NO and not on the dissociation of O_3 .